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As forms of gasification and combustion grow in the area of renewable energy in Minnesota the question arises regarding the utilization/application of the ash co product produced from these processes. Currently there are four facilities in Minnesota producing an ash coproduct (three ethanol facilities and one combusting biomass to produce energy).

These ash wastes are generated from using ethanol by-products as a fuel or heating source for fermentation. Other ash wastes from agricultural sources include turkey litter ash. When applied to agricultural fields, ash wastes can be a source of nutrients for agricultural crops. Chemical analyses of ash wastes vary, but 200 to 300 lb of P_2O_5 and K_2O per ton of ash is typical. The value of ash wastes as a fertilizer has increased because commercial fertilizer prices have increased significantly over the last few years. Specifically:

Compaction/Agglomeration research- Research included development of an appropriate product for use in current delivery systems by densifying the ash into the form of pellets or briquettes which may reduce fertilizer input cost to farmers. The initiative addresses the use of phosphorus and potassium from co-firing or gasification processes as a fertilizer source.

This report is a task-level final technical report.

No Intellectual Property or limitations

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Utilizing Ash Wastes as a Nutrient Source for Corn
2008 Annual Report (Feb. 2009)

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Introduction

Land application of industrial wastes and bi-products has been common for decades. Recent expansion of the biofuel industry has resulted in significantly large quantities of these bi-products, like dried distillers grains (DDG) and solubles. Utilizing these bi-products is critical to the future success, profitability, and sustainability of the biofuel industry.

Three biofuel, bi-product/waste sources were used in this study. A “co-fire” ash waste was obtained from Fibrominn, a power plant in Benson, Minnesota. This plant burns turkey manure as fuel to generate electricity and the resultant ash waste is land applied as a fertilizer source for crop production. A second ash waste from a fluidized bed reactor was obtained from Corn Plus an ethanol plant in Winnebago, Minnesota. This ash waste comes from burning distiller solubles, which are used to generate heat for the plant. Both of these ash wastes were in their “raw” or unprocessed form. The third source was a biochar ash from Chippewa Valley Ethanol Company, an ethanol plant in Little Falls, Minnesota. They use pyrolysis, a form of incineration that chemically decomposes organic material by heat and pressure in the absence of oxygen, to gasify wood chips and corn cobs (1). The bi-products of this gasification process are syngas (similar to natural gas and is used as fuel for the plant) and biochar.

Biochar is a fine-grained charcoal high in organic carbon and largely resistant to decomposition. As a soil amendment biochar has potential agronomic and environmental benefits. From an agronomic perspective, it has been shown to reduce soil acidity and be a fertilizer (2). Environmentally, it may help combat

global climate change by being a stable carbon sink (3) and by reducing emissions of nitrous oxides on some highly weathered soils (4).

The objectives of this study were: (i) to determine the availability of phosphorus (P) and potassium (K) contained in ash wastes from the biofuel industry in Minnesota, by measuring their effects on corn growth, corn grain yield, nutrient concentrations in small corn plants and corn grain; and (ii) to measure changes in soil test parameters before and after waste application (preplant and post harvest).

Materials and Methods

An experiment was conducted at the University of Minnesota Southern Research and Outreach Center in 2008 to evaluate the performance of three ash wastes as fertilizer sources for corn. The research site had been managed with minimal commercial inputs for the last several years and was cropped to alfalfa from 2005 through 2007. Nine treatments were replicated four times in a randomized complete-block design on a pattern, tile-drained (75-foot spacing) Webster clay loam soil. Each plot measured 15 ft. wide (six, 30-inch rows) by 25 ft. long.

Treatments consisted of two ash waste sources [turkey manure (co-fire) and distillers solubles (fluidized bed)] compared with triple super phosphate (TSP) fertilizer at rates of 80 and 240 lb P_2O_5/A , one ash waste source (char ash) compared with potash fertilizer at 120 lb K_2O/A , and an unfertilized control. All treatments were broadcast-applied by hand on May 5 and incorporated with a disk. The plots were field cultivated on May 9, just prior to planting corn (Pioneer brand 35F44) at 32,000 seeds/A. Pre-emergence herbicides (Harness at 1.5 pt/A, Callisto at 5 oz/A, and Roundup WeatherMax at 12 oz./A) were applied with 10 gal/A of UAN as a carrier on May 14. Significant grassy weed pressure required applications of Roundup WeatherMax (24 oz/A) with AMS on May 28 and again on June 14. Supplemental N (30 lb/A as UAN) was injected on all plots on June 23. No other fertilizer N was applied as the previous crop was alfalfa.

Experimental measurements included soil, plant, and grain samples. Soil samples (9 cores/plot, 0-6 inch depth) were taken from all plots prior to treatment application on April 30 and post harvest on October 30. These samples were analyzed for pH, Bray P1, Exch. K, and Zn (Zn on select treatments). Small corn plants (8 plants/plot) were harvested at V7 on June 23. These samples were dried at 150 F., weighed when dry, ground, and submitted for elemental analysis. Total dry matter yields from the small plants were

calculated along with nutrient concentration in the whole plants and nutrient uptake. Corn grain yields and grain moisture were determined by combine harvesting the center four rows with a small plot combine on October 29. Grain samples were dried, ground, and analyzed for P and K concentration in the grain.

Results and Discussion

Nutrient content (total elemental) in the ash wastes was determined by chemical analyses of two samples from each waste source by the University of Minnesota, Research Analytical Laboratory (Table 1). All ash wastes were strongly basic and ranged in pH from 11.5 to 12.3. Generally, char ash contained very low levels of essential crop nutrients compared with co-fire (CF) and fluidized bed (FB) sources. Total N–P₂O₅–K₂O–S content was 0–13.5–6.6–1.6 and 0–17.6–16.2–5.7 for CF and FB ash, respectively. The ash wastes used in this study contained detectable levels of the heavy metals: Cr, Cu, Ni, and Pb (except Pb in FB ash). Cadmium was not detected (detection limit <0.88 ppm) in any of the sources. Nutrient application rates in pounds of nutrient per acre for each treatment are listed in Table 1.

Early growth of corn as measured by plant height was significantly greater with FB ash compared with TSP fertilizer and CF ash (Table 2). Plant heights were increased with the high rate of P/ash (240 lb P₂O₅) compared with the low rate (80 lb P₂O₅). A significant source by rate interaction was not found. Statistical analysis of all nine treatments showed: (i) plant heights were increased above the control by all treatments except for the low P rate of TSP, (ii) char ash increased plant heights above the control, (iii) K fertilization (treatment #9) increased plant height, and (iv) tallest plant heights were obtained with the FB ash treatments.

Total dry matter yields from whole corn plants taken at V7 were affected by the main effect of source, but not by rate of application (Table 2). Total dry matter yields were greatest with FB ash, intermediate with TSP fertilizer, and least with CF ash. Dry matter yields were not affected by P/ash rate and a significant source by rate interaction was not found. Statistical analysis of all nine treatments showed total dry matter yields were increased above the control by both rates of TSP fertilizer and FB ash and by the high rate of CF ash, but yields were not increased by the low rate of CF ash, char ash, and potash (K) fertilizer. Greater variability, as evidenced by a 12.5% coefficient of variation (CV) for total dry matter yield vs. a CV of 4.2% for plant height, explained why char ash and K fertilizer significantly increased plant heights, but not dry matter yield.

Although significant differences in nutrient concentrations were found for treatment main effects, concentrations of all nutrients were greater than critical values reported in the literature (2). Phosphorus concentration in small corn plants was greater with TSP fertilizer compared with ash wastes, but was not affected by P rate (Table 2). A significant P source by rate interaction was not found. Potassium concentration was greatest with FB ash, intermediate with CF ash, and least with TSP fertilizer. Greater K concentration was found with the high rate of P application compared with lower rate. A significant source by rate interaction was shown by K concentration not being affected by TSP, but K concentration increased with the high rate of ash wastes. Statistical analysis of all nine treatments showed K concentration was increased above the control by char ash and that potash fertilization increased K in small plants more than char ash and similar to the high rate of FB ash. Sulfur concentration in whole plants was greater with FB ash compared with CF ash and TSP fertilizer. Sulfur concentration in small plants did not respond to rate of application and no significant interaction between source and rate was found. Zinc concentration in whole plants was greater with CF ash compared with other sources and was reduced slightly with the high rate of P. Other researchers have shown high rates of P fertilization can reduce Zn availability in corn plants. These data support those findings, however all Zn concentrations reported in this study were greater than critical values. Boron concentration in whole plants was greater with TSP fertilizer compared with ash waste sources and concentration was greater with the high P/ash rate. A significant source by rate interaction is shown by ash waste application rate having no effect on B concentration in V7 corn plants, while B concentration increased with increasing rates of TSP fertilizer.

Concentration of heavy metals in small corn plants was measured for Cd, Cr, Ni, and Pb (data not shown). Lead was below detectable limits in all of the plant samples, while Cd and Ni were above detectable limits in 6% of samples. Chromium was detected in all plant samples and the average concentration was 0.86 ppm. Metal concentrations in small corn plants were not affected by the treatments.

Phosphorus uptake in small corn plants was greater with FB ash and TSP fertilizer compared with CF ash waste and was increased by increasing P rate (Table 2). A significant P source by rate interaction was not found. Potassium uptake was greater with FB ash compared with CF ash and TSP fertilizer and greater with the high rate of application. A significant source by rate interaction was shown by K uptake being increased by the higher rate of ash wastes, while the high rate of TSP did not increase K uptake over the low TSP rate. Statistical analysis of all nine treatments showed K uptake was increased above the control by K fertilization (treatment # 9), but was not affected by char ash or the low rate of CF ash. Sulfur

uptake in whole plants was greatest with FB ash, intermediate with TSP fertilizer, and least with CF ash. The difference in S uptake between TSP and CF sources was primarily due to increased dry matter with TSP fertilization as S concentrations were not different. Sulfur uptake was not affected by P/ash rate and no significant interaction between main effects was found. Zinc uptake was greater with FB ash compared with other sources, which again was primarily due to increased dry matter in the FB ash treatments. Zinc uptake was not affected by P/ash rate and no significant interaction between main effects was found. Boron uptake in whole corn plants at V7 was greatest with TSP fertilizer, intermediate with FB ash, least with CF ash, and was greater at the high fertilizer P rate. A significant source by rate interaction was explained by increased B uptake at the high application rate of TSP, while CF and FB application rates did not affect B uptake. Char ash and K fertilizer did not affect B uptake in whole plants.

Corn grain moisture and yield were affected by the main effects of source and rate (Table 3). Corn grain moisture was reduced with TSP and FB ash compared with CF ash. Moisture was also reduced by the high P/ash rate compared with the low rate. These data along with greater grain moisture with char ash, which contained very little P, and potash fertilizer treatments, which contained no P, showed how P fertilization reduced grain moisture content. Grain yields were greater with TSP and FB ash compared with CF ash, and yields were greater with the high P/ash rate compared with the low rate. Statistical analysis of all nine treatments showed corn yields were increased above the control by potash (K) fertilizer, but not by the char ash treatment. These yield data show: (i) some of the corn yield response to treatments was due to K fertilization, not just P fertilization and (ii) char ash did not increase corn yields equal to K fertilizer, which suggests the K in char ash was not as available to plants as K fertilizer. A significant source by rate interaction was shown by corn yields being increased 28 bu./A with the high rate of CF ash, whereas corn yields increased only 8-9 bu./A with increasing rate of TSP and FB ash. These data suggest greater first-year P availability with FB ash compared with CF ash.

Grain P and K concentration and uptake were affected by the main effects of ash/fertilizer source and rate (Table 3). Concentration and uptake of P and K were greater with TSP fertilizer and FB ash compared with the CF ash, and were increased with increasing rate of application. Significant interactions between main effects were not found. These data showed K concentration and uptake in grain increased when P concentration and uptake increased. Moreover, an analysis of all nine treatments showed K fertilization (treatment # 9) did not increase K concentration in corn grain, but treatment 9 did increase K uptake in

grain due to greater grain yield. These data emphasize the importance of adequate P fertility for corn in Southern Minnesota.

Soil test results for pH, Bray P1, exchangeable K, and DTPA Zn for samples taken prior to treatment application (initial) and post harvest are presented in Table 4. Prior to treatment application water pH ranged from 6.3 to 6.7 and averaged 6.4, whereas after harvest pH ranged from 6.7 to 7.1 and averaged 6.9. Although pH increased about 0.4 units from spring to fall sampling no significant differences were found among treatments in fall sampling. Ash wastes may provide some liming effect when applied, but none was found in these fall data.

Soil test P (Bray P1) from spring samples ranged from 4.5 (very low) to 9.3 ppm (low) among treatments and averaged 6.5 ppm (low). Bray P after harvest ranged from a low 6.8 ppm in the potash treatment (# 9) to a high of 28.8 ppm in the 240 lb P_2O_5/A TSP treatment (# 3). Post harvest soil test P was affected by ash and fertilizer treatments, however considerable variability in the data ($CV = 51\%$) resulted in a large LSD value (7.4 ppm) at the 0.10 level of significance. Thus, the author has chosen to use a 0.20 level of significance for these data ($LSD = 5.7$ ppm). At this level of significance soil test P was increased above the control by P fertilizer and CF and FB ashes at the 240 lb P_2O_5/A rate, but soil test P was not increased at the 80 lb P_2O_5/A rate by any source.

Soil test K (exchangeable K) from spring samples ranged from 119 (medium) to 138 ppm (high) among treatments and averaged 129 ppm (high). After harvest, soil K ranged from 159 to 197 ppm and averaged 183 ppm across treatments. Post harvest soil test K was affected by ash and fertilizer treatments; however these treatment differences were over-shadowed by the large difference in soil test K observed between spring and post harvest samples. Soil test K averaged 45 ppm more in post harvest sampling compared with spring sampling. This phenomenon has been reported in the literature and is usually associated with soil moisture at the time of sampling.

Soil test Zn was slightly greater in post harvest samples compared with spring samples. However, no significant differences among treatments were found for the post harvest sampling.

Summary

Nutrient content (total elemental) of ash wastes varied dramatically. Char ash contained very low levels ($\leq 1\%$) of essential crop nutrients while co-fire (CF, Fibrominn) and fluidized bed (FB, Corn Plus) sources contained 0–13.5–6.6–1.6 and 0–17.6–16.2–5.7 percent of N–P₂O₅–K₂O–S, respectively. Corn plant height at V7 was significantly greater with FB ash compared with TSP fertilizer and CF ash and increased with increasing P/ash rate. Plant heights were increased above the control by all treatments except for the low P rate of TSP, and tallest plant heights were obtained with FB ash treatments. Total dry matter yields from whole corn plants taken at V7 were greatest with FB ash, intermediate with TSP fertilizer, and least with CF ash. Dry matter yields were not significantly affected by P/ash rate. Generally, significant differences in P, K, S, Zn, and B concentration in whole corn plants were found for treatment main effects, however, concentrations of these nutrients were greater than critical values reported in the literature. Uptake of P, K, S, Zn, and B in corn plants was affected by the main effect of source, whereas uptake of only B and K was affected by the main effect of P/ash rate.

Corn grain yields were increased with P fertilization from fertilizer and ash sources, while grain moisture was reduced with fertilization from these sources. Corn yields were greater with fertilizer P and FB ash compared with CF ash. Yields increased with the high P/ash rate compared with the low rate. Yields increased above the control with potash (K) fertilizer but not with the char ash treatment. These data showed: (i) most of the corn yield response at this site was a result of P fertilization from TSP and/or ash waste sources, (ii) some of the yield response was due to K (potash) fertilization, (iii) char ash did not produce corn yields equal to K fertilizer at equivalent rates of total K, (iv) this research site which had an initial soil test P of 6.5 (low) required a rate greater than 80 lb P₂O₅ per acre to maximize yield, and (v) P fertilization with TSP or ash resulted in increased P and K concentration and uptake in corn grain.

Soil test P from spring samples, prior to application, averaged 6.5 ppm (low), whereas after harvest it ranged from a low 6.8 ppm in the potash treatment (# 9) to a high of 28.8 ppm in the 240 lb P₂O₅/A TSP treatment (# 3). Soil test P was increased above the control by P fertilizer and CF and FB ashes at the 240 lb P₂O₅/A rate, but soil test P was not increased at the 80 lb P₂O₅/A rate. Soil test K from spring samples averaged 129 ppm (high) and increased about 45 ppm after harvest. Treatment effects on soil test K were small in comparison to the large difference in soil test K observed between spring and post harvest samples. Thus, no effect on soil test K could be attributed to the treatments.

Conclusions

Corn response to the FB ash was very similar to what was found with TSP fertilizer. This suggests that the first year availability of P between sources was similar; however soil test P did not increase to the same level with FB ash as with TSP fertilizer. This could be explained by the Bray P soil test not effectively representing the available P in the soil after harvest. A more likely explanation is the assumption that P was the only limiting nutrient was wrong and K and S in the FB ash were also contributing to the yield response of corn in this study. This hypothesis can be supported by K and S concentration and uptake in small plants increasing when FB ash was applied compared with TSP fertilizer. In this study the FB ash provided the greatest agronomic benefit to corn of any of the ash wastes used.

The lower rate of CF ash did not significantly affect the crop production parameters measured in this study. This suggests the “first-year” availability of the nutrients in the CF ash is somewhat lower than the total nutrient concentrations reported earlier in this report. The current fertilizer label for this product (personal contact) lists available P_2O_5 and K_2O at 8 and 5%, respectively, which is about 60% of the total. The higher rate of CF ash produced similar crop response to TSP and FB ash, while soil test P was slightly lower than with FB ash.

No measureable agronomic benefit to the char ash was found in this study. This could be a result of: (i) the short term nature of this experiment (spring applied for corn a crop that generally shows response to nutrients early in its development); (ii) the K and other nutrients in the char ash are not readily available to corn plants; or (iii) that many of the benefits of biochar have been found on highly weathered low organic matter soils, which this soil clearly is not.

Acknowledgement

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References

- 1) Morrison, E.M., 2008, Biomass bridge: Gasified wood chips and corn cobs are replacing natural gas at Benson ethanol plant. Ag Innovation News. Vol. 17, No. 1. [available online] http://www.auri.org/news/ainjan08/biomass_bridge.htm
- 2) Glaser, B., Lehmann, J. and Zech, W., 2002, Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal --- a review, *Biology and Fertility of Soils*, 35: 219-230.
- 3) Lehmann, J., Gaunt, J., and Rondon, M., 2006, Bio-char sequestration in terrestrial ecosystems – a review. *Mitigation and Adaptation Strategies for Global Change*, 11:403-427.
- 4) Yanai et al., 2007, Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments, *Soil Science and Plant Nutrition*, 53:181-188.
- 5) AESL Plant Analysis Handbook – Agronomic Crops – Corn. Univ. of Georgia, College of Agriculture and Environmental Sciences, Cooperative Extension Service. [available online] <http://aesi.ces.uga.edu/publications/plant/CornWhole.htm>

Table 1. Nutrient content of ash wastes and nutrient application rates by treatment.

Nutrient content of ash	Trt.	pH	P	P ₂ O ₅	K	K ₂ O	S	Zn	B	Mg	Mn	Fe	Ca	Cd	Cr	Cu	Ni	Pb
	#		%	%	%	%	%	ppm	ppm	%	ppm	%	%	ppm	ppm	ppm	ppm	ppm
Co-fire (Fibrominn)	4&5	12.3	5.92	13.5	5.5	6.6	1.55	670	140	2.01	923	0.45	14.5	<0.88	16.0	1167	32.1	19.8
Fluidized bed (Corn Plu 6&7	6&7	12.3	7.67	17.6	13.5	16.2	5.71	490	80	4.14	384	0.17	16.7	<0.88	15.1	20	27.3	<14.1
Char ash (CVEC)	8	11.5	0.06	0.1	0.9	1.0	0.03	111	39	0.29	440	0.55	4.5	<0.88	19.0	55	8.5	34.2
Rate of nutrient applied		----- lb per acre -----																
Co-fire (Fibrominn)	4		35	80	33	39	9	0.4	0.1	12	0.5	3	86	ND	0.01	0.69	0.02	0.01
Co-fire (Fibrominn)	5		105	240	98	118	27	1.2	0.2	36	1.6	8	257	ND	0.03	2.07	0.06	0.04
Fluidized bed (Corn Plu 6	6		35	80	61	74	26	0.2	0.0	19	0.2	1	76	ND	0.01	0.01	0.01	ND
Fluidized bed (Corn Plu 7	7		105	240	184	221	78	0.7	0.1	56	0.5	2	228	ND	0.02	0.03	0.04	ND
Char ash (CVEC)	8		7	15	101	121	3	1.3	0.5	34	5.1	64	518	ND	0.22	0.64	0.10	0.40

Table 2. Plant height, total dry matter yield, nutrient concentration, and nutrient uptake of whole corn plants at V7.

Trt	Ash & Fertilizer Treatments				Whole plant samples at V7										
	Source	P rate	K rate	Plant Height	DM	Concentrations					Uptake				
					Yield	P	K	S	Zn	B	P	K	S	Zn	B
#				inch	ton/A	%	%	%	ppm	ppm	lb/A				
1	Control	0	0	32.6	0.236	0.412	2.68	0.241	36.1	9.2	1.94	12.7	1.13	0.344	0.086
2	TSP (0-44-0)	80	0	34.2	0.313	0.461	2.73	0.235	33.7	10.0	2.90	17.2	1.47	0.424	0.126
3	TSP (0-44-0)	240	0	35.4	0.302	0.450	2.74	0.240	28.5	16.6	2.72	16.6	1.45	0.345	0.202
4	Co-fire (Fibrominn)	80	39	34.5	0.248	0.396	2.71	0.250	37.4	9.1	1.95	13.4	1.23	0.369	0.090
5	Co-fire (Fibrominn)	240	118	35.8	0.295	0.417	3.27	0.233	34.0	8.9	2.47	19.3	1.38	0.403	0.105
6	Fl. bed (Corn Plus)	80	74	37.3	0.343	0.417	3.18	0.259	32.5	9.1	2.87	21.8	1.78	0.447	0.124
7	Fl. bed (Corn Plus)	240	221	37.9	0.345	0.437	3.44	0.254	33.6	8.7	3.01	23.9	1.75	0.456	0.121
8	Char ash (CVEC)	15	121	34.5	0.263	0.415	2.91	0.252	39.2	9.5	2.20	15.4	1.32	0.412	0.100
9	Potash (0-0-60)	0	120	35.2	0.252	0.427	3.41	0.242	39.1	9.5	2.19	17.2	1.22	0.389	0.096
Mean:				35.3	0.289	0.426	3.01	0.245	34.9	10.1	2.47	17.5	1.42	0.399	0.117

Statistical analysis of main effects (factorial arrangement) for treatments 2 through 7.

Source

TSP	34.8	0.308	0.456	2.73	0.237	31.1	13.3	2.81	16.9	1.46	0.384	0.164
Co-fire (Fibrominn)	35.1	0.271	0.407	2.99	0.242	35.7	9.0	2.21	16.4	1.31	0.386	0.098
Fluidized bed (Corn Plus)	37.6	0.344	0.427	3.31	0.257	33.0	8.9	2.94	22.8	1.77	0.451	0.123
LSD (0.10):	0.8	0.024	0.024	0.18	0.012	2.7	1.4	0.30	1.7	0.15	0.058	0.022

Rate lb P₂O₅/A

80	35.3	0.301	0.425	2.87	0.248	34.5	9.4	2.57	17.5	1.49	0.413	0.113
240	36.3	0.314	0.435	3.15	0.243	32.0	11.4	2.73	19.9	1.53	0.401	0.143
P > F:	0.016	0.265	0.376	0.004	0.341	0.072	0.008	0.280	0.008	0.619	0.660	0.013

Interactions (P > F)

Source × rate	0.657	0.111	0.448	0.051	0.293	0.156	0.001	0.163	0.015	0.526	0.232	0.018
CV (%):	2.5	8.9	6.4	6.6	5.5	9.4	15.5	13.0	10.4	11.2	16.2	20.0

Statistical analysis of treatment effects for all nine treatments.

Treatment

P > F:	0.001	0.001	0.073	<0.001	0.082	0.001	<0.001	0.002	<0.001	<0.001	0.267	<0.001
LSD (0.10):	1.8	0.044	0.034	0.21	0.015	3.5	1.6	0.48	2.8	0.23	NS	0.029
CV (%):	4.2	12.5	6.5	5.7	5.2	8.4	13.2	16.2	13.2	13.3	17.6	20.2

Table 3. Corn grain yield, moisture, and nutrient uptake in corn grain.

Trt #	Ash & Fertilizer Treatments			Grain	Grain	Grain	Grain	Grain	Grain
	Source	P rate	K rate	H ₂ O	Yield	[P]	[K]	P up	K up
				%	bu/A	%	%	lb/A	lb/A
1	Control	0	0	23.7	192	0.21	0.31	19.2	28.4
2	TSP (0-44-0)	80	0	23.7	210	0.25	0.35	24.6	34.6
3	TSP (0-44-0)	240	0	22.9	219	0.29	0.38	30.1	39.7
4	Co-fire (Fibrominn)	80	39	24.5	190	0.20	0.31	17.8	27.7
5	Co-fire (Fibrominn)	240	118	23.9	218	0.24	0.34	25.2	35.1
6	Fl. bed (Corn Plus)	80	74	23.8	213	0.25	0.35	25.5	35.4
7	Fl. bed (Corn Plus)	240	221	23.2	221	0.27	0.37	28.4	38.6
8	Char ash (CVEC)	15	121	24.3	194	0.22	0.32	20.7	29.6
9	Potash (0-0-60)	0	120	24.5	208	0.23	0.33	23.2	33.0
Mean:				23.8	207	0.24	0.34	23.9	33.5

Statistical analysis of main effects (factorial arrangement) for treatments 2 through 7.

Source

TSP	23.3	215	0.27	0.37	27.4	37.1
Co-fire (Fibrominn)	24.2	204	0.22	0.32	21.5	31.4
Fluidized bed (Corn Plus)	23.5	217	0.26	0.36	26.9	37.0
LSD (0.10):	0.6	8	0.02	0.02	2.2	2.2

Rate lb P₂O₅/A

80	24.0	204	0.25	0.35	24.7	34.0
240	23.3	219	0.22	0.33	21.2	31.1
P > F:	0.029	0.001	0.001	0.004	<0.001	<0.001

Interactions (P > F)

Source × rate	0.969	0.092	0.458	0.706	0.220	0.287
CV (%):	2.7	4.5	8.9	6.2	9.8	7.3

Statistical analysis of treatment effects for all nine treatments.

Treatment

P > F:	0.008	0.005	0.003	0.006	0.001	<0.001
LSD (0.10):	0.7	15	0.04	0.03	4.2	4.3
CV (%):	2.4	6.0	12.2	8.0	14.6	10.6

Table 4. Soil test pH, Bray P, exchangeable K, and DTPA Zn as affected by nutrient sources and date of sampling.

Trt.	Ash and fertilizer sources and rates			Initial soil tests				Post harvest soil tests			
	Source	P ₂ O ₅	K ₂ O	pH	Bray P	K	Zn	pH	Bray P	K	Zn
#		lb/A	lb/A		----- ppm -----				----- ppm -----		
1	None	0	0	6.4	6.8	130	1.3	6.8	7.0	189	1.4
2	TSP	80	0	6.5	5.3	119		6.8	8.8	159	
3	TSP	240	0	6.3	7.0	133		6.7	28.8	172	
4	Co-fire (Fibrominn)	80	39	6.7	4.5	129		7.1	8.3	197	
5	Co-fire (Fibrominn)	240	118	6.4	7.3	131	1.4	6.9	13.8	189	1.5
6	Fluidized bed (Corn Plus)	80	74	6.4	7.3	130		6.9	10.3	189	
7	Fluidized bed (Corn Plus)	240	221	6.6	5.8	121	1.3	6.9	14.8	190	1.6
8	Char ash (CVEC)	15	121	6.3	9.3	131		6.8	9.3	174	
9	0-0-60	0	120	6.5	5.3	138		6.9	6.8	191	
	Mean:			6.4	6.5	129	1.3	6.9	11.9	183	1.5

Statistical analysis of treatment effects

Treatment

P > F:	0.605	0.564	0.609	0.866	0.296	0.001	0.106	0.790
LSD (0.10):	NS	NS	NS	NS	NS	7.4	NS	NS
LSD (0.20):	NS	NS	NS	NS	NS	5.7	17	NS
CV (%):	4	48	10	14	3	51	10	25



Use of Glycerol as a Corn Replacement in Calf Starter Diets

Project number: AIC044

Project date: July 7, 2010

Acknowledgement

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Summary Report 07/06/10

Project Number: 9-244 and 9-245

Title: Use of Glycerol as a replacement for corn in starter diets for individually fed dairy calves up to 9 weeks of age and in grain mixes during group feeding from 9 to 25 weeks of age.

Location(s): University of Minnesota, Calf and Heifer Research Facility,
Southern Research and Outreach Center (SROC), Waseca, MN.

Co-investigators Hugh Chester-Jones, Dairy/Beef Animal Scientist, SROC, Waseca
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Al Doering, Agricultural Utilization Research Institute (AURI)
Denny Timmerman, AURI

Collaborators Greg Golombeski, Graduate Student, Animal Science, St. Paul
Mary Raeth-Knight, Research Fellow, U of MN Animal Science, St. Paul

Background & Justification: Glycerol is a sugar alcohol by-product of bio-diesel production. About 1 gallon of glycerin is produced for every 10 gallons of bio-diesel of which the glycerol content may vary between 63 and almost 100%. There is some uncertainty of the exact energy value of glycerol as an ingredient for animal feed but it has been successfully used as a replacement for corn up to 10% of the diet dry matter for lactating dairy cows. There is a lack of information on incorporating glycerol into diets for pre- and post weaned dairy heifer calves which has the potential to expand the market for this by product. Preliminary work at SROC indicates that there are no palatability problems using glycerol up to 6% of the mix in post weaning pellets for group fed dairy heifers.

Objectives: To evaluate the use of glycerol as a replacement for corn in diets on performance and health of dairy calves individually fed from 2 days up to 9 weeks of age and group fed from 9 to 25 week of age.

Study Overview

Animals and Methods

Phase 1 to 56 day study:- One hundred-twenty calves housed in individual pens from 3 commercial dairy farms were assigned to one of four 18% crude protein (CP) calf starters (25 calves/treatment) upon arrival at SROC at 2-4 days of age. Isocaloric and isonitrogenous starter diets included: 1), Complete texturized control; 2), Complete pellet control; 3), Complete pellet with 3% glycerol replacing corn; 4), Complete pellet with 6% glycerol replacing corn. All diets were full fed with access to fresh water. All calves were fed a 20% protein:20% fat medicated milk replacer at 0.625 lbs in 4.4 lbs of water twice daily for 35 days and once daily from day 36 to weaning at 42 days. Calves continued to be full-fed their respective diets post weaning from day 43 to the end of the study at 56 days. Bodyweights were taken

initially and on days 14, 28, 42, and 56. Hip heights will be taken initially and at day 56. Daily feed intake and health records were documented for each calf.

Phase 2 – 112 day study:- 105 calves from phase 1 were re-assigned to one of three grain mixes. Calves were fed the control 18% CP starter from phase 1 for 7 days after moving calves from individual to group pens of 7 calves/pen. Calves were then be transitioned to one of 3 corn/pellet grain mixes with 5 replicated group pens/treatment. Treatments included: 1), 16% CP corn and pellet grain mix control fed at 6 lbs/day for 84 days with free choice hay; 2), 16% CP corn and pellet grain mix with 3% glycerol fed as for treatment 1 for 56 days then 5 lbs/day from day 57 to 84; 3), 16% CP corn and pellet grain mix with 6% glycerol fed as for treatment 2. From days 85-112 all group pens will be fed a common diet of a 16% CP grain mix fed at 5 lbs/day with free choice hay. Bodyweights were taken initially and on days 28, 56, 84 and 112. Hip heights were taken initially, days 84 and 112. Daily feed intake and health records were documented for each group pen.

Statistical analyses: Data were analyzed using the PROC MIXED procedure of SAS and repeated measures analyses applied where appropriate. Contrasts were used to differentiate treatment combination effects.

Results and Discussion

Phase 1 nursery phase - The nutrient composition of the diets fed during the nursery phase are summarized in Table 1. The complete pellet consisted of the same ingredient composition to the complete texturized starter. The quality of pellet was very good and the addition of 3 or 6% glycerin maintained the quality. The crude protein content of the respective starters were within the specifications expected. Performance of calves are summarized in Tables 2 and 3 with health data summarized in Table 4.

There were no treatment differences in pre- and post weaning growth during the nursery phase. Optimal performance goals during the nursery phase are for calves to double their initial body weight with a frame growth of 4 inches by 2 months of age. Calves averaged 1.84 times their initial body weight with 3.85 inches of frame growth (Table 2). There were no treatment differences in calf starter and total dry matter intake although there was a numerical trend towards lower intakes in calves fed the pellet with 6% glycerin (Table 3). Pre- and post weaning feed efficiencies were not affected by treatment and were very similar to previous studies. There were no treatment differences in pre- and post weaning fecal scores or pre-weaning scouring days. Post weaning scouring days tended to be higher for calves fed the texturized calf starter vs. those fed the pellet diets. Pre-weaning and overall treatment costs/calf were highest for calves fed the pellet with 6% glycerin.

Conclusions for the nursery phase – Under the conditions of this study formulating a calf starter pellet with the same nutrient specifications of a texturized calf starter was very successful. Partially replacing corn with 3 or 6% glycerin in a calf starter pellet was acceptable. There were indications that 6% glycerin may affect health costs.

Phase 2 group feeding phase - Post weaning calf performance in group pens are summarized in Table 5, 6 and 7. Mixing 3 or 6% glycerin in a grain mix worked well for the 84 day period when treatments were applied. There were no treatment differences in calf growth within each of the 28 day weigh periods (Table 5). Body weight gain overall for the 112 days study was also similar across all calf groups. As expected grain intake was similar across calf groups during the 84 day treatment period and

overall, days 1 to 112 (Table 6). Numerically hay intake tended to be lower for calves fed the glycerin diets. This was reflected in overall hay and total dry matter intake which was higher for the control calf groups vs. those fed the glycerin diets which were not different. However, feed efficiencies were not affected by glycerin treatments days 1 to 84 or when all calves were fed a common diet from days 85 to 112. There were no treatment differences in changes in body condition score or hip height gain (Table 7).

Conclusions for the group feeding phase – Under the conditions of this study partially replacing corn in grain mixes with 3 or 6% glycerin did not affect calf performance when fed in group pens with free choice hay from 9 to 25 weeks of age,

Study conclusions overall - Glycerol can be used as an alternative energy source as a partial replacement for corn in starter diets at 3 or 6% of the total formulation for individually fed dairy calves up to 9 weeks of age and similarly in grain mixes during group feeding from 9 to 25 weeks of age. The current study confirmed a previous study with post weaned heifer calves in group pens which indicated up to 6% glycerin can effectively replace corn in grain mixes. Contrary to the current study, the previous study found that heifer calves fed a 16% crude protein grain mix pellet containing 6% glycerin for 84 days had improved daily gain compared to heifers fed pellets with no or 3% glycerin. Heifers fed the grain mix pellet containing 3 or 6% glycerin for 84 days with free choice hay also had improved feed efficiency compared to heifers fed pellets without glycerin included. These differences were not maintained when all heifers were fed a common whole corn and pellet mix from days 85 to 112. However, daily gains and feed intake during the current study tended to be better than in the previous study.

Acknowledgements:

The financial support of AURI was much appreciated. Thanks to the SROC dairy staff for excellent care and management of the calves during the study

Table 1. Nutrient composition of milk replacer and calf starters (CS)¹

Item	Milk replacer	CS1	CS2	CS3	CS4
DM, %	98.36	87.79	89.02	88.43	88.51
CP, %	19.94	21.18	20.70	22.12	21.30
Fat, %	19.81	3.58	1.52	2.34	2.31
NDF, %	----	13.88	17.72	16.00	15.93
ADF, %	----	6.09	9.25	8.80	9.45
Ash, %	9.25	6.32	7.50	7.48	7.66
Ca, %	0.89	1.18	1.25	1.23	1.15
P, %	0.82	0.59	0.57	0.57	0.58
K, %	2.62	1.36	1.24	1.25	1.15
Mg, %	0.16	0.31	0.32	0.31	0.32
Na, %	1.13	0.22	0.25	0.31	0.38
Cu, ppm	13.4	30.2	27.8	17.0	21.9
Fe, ppm	24.4	138.2	235.4	237.2	263.5
Mn, ppm	31.0	104.0	105.5	79.8	93.7
Zn, ppm	29.6	137.7	137.9	96.8	117.8

¹ CS1 = complete texturized; CS2 = complete pellet; CS3 = complete pellet with 3% glycerin; CS4 = complete pellet with 6% glycerin.

Table 2 . Growth parameters day 1 to 56 of study.

	Treatments ¹					Contrasts		
	Control	2	3	4	SEM	1 vs 2, 3, 4	2 vs. 3, 4	1 vs 3, 4
No calves	30	30	30	30				
BW, lb								
Initial²	88.5	88.6	88.7	88.5	1.7			
d 14	96.5	96.6	95.9	96.1	0.63			
d 28	114.6	114.7	113.7	113.6	0.95			
d 42	134.5	135.1	135.7	133.2	1.36			
d 56	164.0	164.1	163.3	160.5	1.93			
Total BW gain, lb								
d 1 to d 42	46.1	46.4	47.4	44.5	1.35	0.99	0.76	0.93
d 1 to d 56	75.6	75.6	75.0	72.2	1.68	0.50	0.35	0.34
ADG, lb/d								
d 1 to 14	0.55	0.55	0.51	0.54	0.05			
d 15 to 28	1.31	1.30	1.29	1.25	0.05			
d 29 to 42	1.43	1.47	1.59	1.40	0.06			
d 1 to 42	1.10	1.10	1.13	1.06	0.03	0.99	0.76	0.93
d 43 to 56	2.12	2.08	1.98	1.95	0.07			
d 1 to 56	1.35	1.35	1.34	1.29	0.03	0.50	0.35	0.34
HH, inches								
Initial³	31.5	31.6	31.6	31.7	0.17			
d 56	35.5	35.5	35.4	35.2	0.13	0.46	0.26	0.28
HH gain, inches								
d 1 to 56	3.94	3.94	3.87	3.67	0.13	0.46	0.26	0.28

¹Treatments:

²Initial body weight (BW) utilized as a covariate for body weight, ADG and intake data when significant.

³Initial hip height (HH) utilized as a covariate for hip height (d 56) and hh gain.

^{a,b}Means within a row without common superscripts are different at P < 0.05.

Table 3. Milk replacer, starter and total DM intake and feed efficiency.

	Treatments					Contrasts		
	Control	2	3	4	SEM	1 vs 2, 3, 4	2 vs. 3, 4	1 vs 3, 4
Milk Replacer Intake, lb/d	-----% DM basis-----							
d 1 to 14	1.21	1.23	1.22	1.22	0.004			
d 15 to 28	1.24	1.24	1.24	1.24	0.004			
d 29 to 42	0.92	0.92	0.92	0.92	0.004			
d 1 to 42	1.12	1.13	1.13	1.13	0.002	0.12	0.48	0.22
Total MR intake, lb								
d 1 to 42	47.2	47.4	47.3	47.3	0.1	0.12	0.48	0.22
Starter intake, by period, lb/d								
d 1 to 14	0.11	0.10	0.10	0.08	0.02			
d 15 to 28	0.71	0.67	0.71	0.63	0.06			
d 29 to 42	1.64	1.69	1.82	1.51	0.09			
d 43 to 56	4.23	4.19	4.16	3.91	0.12			
Total Starter intake, lb								
d 1 to d 42 ¹	34.5	34.5	37.3	31.0	1.86	0.91	0.89	0.88
d 1 to d 56	93.5	93.2	95.2	85.7	3.64	0.62	0.54	0.50
Total DM intake by period, lb/d								
d 1 to 14	1.32	1.33	1.33	1.30	0.02			
d 15 to 28	1.94	1.91	1.95	1.86	0.06			
d 29 to 42	2.56	2.61	2.74	2.43	0.09			
d 43 to 56	4.24	4.26	4.16	3.92	0.12			
Total DM intake, lb								
d 1 to d 42 ²	81.7	81.9	84.6	78.3	1.87	0.96	0.86	0.92
d 1 to d 56	140.8	140.8	142.8	133.2	3.52	0.72	0.64	0.63
Feed per Gain								
d 1 to 42	1.79	1.78	1.80	1.77	0.03	0.79	0.83	0.86
d 43 to 56	2.11	2.07	2.17	2.04	0.07	0.86	0.65	0.99
d 1 to 56	1.88	1.87	1.92	1.86	0.03	0.99	0.69	0.89

¹Treatment P = 0.13

²Treatment P = 0.12

Table 4. Serum protein and health data

	Treatments					Contrasts		
	Control	2	3	4	SEM	1 vs 2, 3, 4	2 vs. 3, 4	1 vs 3, 4
Serum Protein	5.40	5.47	5.31	5.44	0.10	0.96	0.43	
Fecal Score¹								
Period								
d 1 to 14	1.64	1.51	1.49	1.55	0.06			
d 15 to 28	1.32	1.32	1.27	1.36	0.04			
d 29 to 42	1.13	1.16	1.15	1.14	0.03			
d 43 to 56	1.23	1.15	1.17	1.27	0.04			
d 1 to 42	1.35	1.31	1.30	1.34	0.02	0.28	0.81	0.35
d 1 to 56	1.33	1.28	1.27	1.33	0.02	0.21	0.60	0.31
Scouring days²								
# Days $\geq$ 3								
1 to 42 ³	2.10	1.39	1.65	2.32	0.30	0.37	0.11	0.75
43 to 56	0.28	0.05	0.14	0.18	0.08	0.08	0.23	0.22
# Days = 4								
1 to 42	0.00	0.03	0.00	0.001	0.02	0.61	0.13	0.97
Treatment cost, \$								
1 to 42	0.52 ^a	0.44 ^a	0.30 ^a	1.21 ^b	0.21	0.57	0.21	0.34
43 to 56 ³	0.10	0.00	0.00	0.42	0.17	0.99	0.21	0.67
1 to 56	0.61 ^a	0.37 ^a	0.24 ^a	1.64 ^b	0.26	0.65	0.07	0.30

¹Fecal score = 1 to 4; 1 = normal, $\geq$ 3 = scours

²Scouring day = any day with a fecal score $\geq$ 3.

³Treatment P = 0.13

^{a,b}Means within a row without common superscripts are different at $P < 0.05$.

Table 5 . Growth parameters d 1 to 112 of grower period.

	Treatments ¹				Contrasts	
	Control	2	3	SEM	1 vs. 2, 3	2 vs. 3
No. pens (7 hfrs/pen)	5	5	5			
BW², lb						
Initial	185.8	186.6	186.7	1.55		
d 28	247.1	248.7	248.8	1.85		
d 56	310.7	314.2	315.6	1.77		
d 84	375.8	374.7	378.4	2.23		
d 112	443.2	440.8	442.2	2.93		
d 1 to 112	344.2	344.6	346.3	1.88	0.59	0.52
ADG², lb/d						
d 1 to 28	2.18	2.22	2.22	0.07		
d 29 to 56	2.27	2.34	2.38	0.07		
d 57 to 84	2.33	2.15	2.24	0.07		
d 85 to 112	2.41	2.36	2.29	0.07		
d 1 to 112	2.30	2.27	2.28	0.03	0.32	0.58
BWG², lb						
d 1 to 28	61.0	62.2	62.2	1.96		
d 29 to 56	63.6	65.5	66.6	1.96		
d 57 to 84	65.2	60.2	62.7	1.96		
d 85 to 112	67.5	66.1	64.1	1.96		
Total gain, lb						
d 1 to 112	257.6	254.2	255.4	3.36		

¹Treatments

²Initial body weight (BW) during the starter period (study 8-242) utilized as a covariate for body weight and ADG when significant.

^{a,b}Means within a row without common superscripts are different at P < 0.05.

Table 6. Grain and hay intake day 1 to 112 of grower period.

	Treatments ¹			SEM	Contrasts	
	Control	2	3		1 vs. 2, 3	2 vs. 3
No. pens (7 hfrs/pen)	5	5	5			
Grain Intake, lb/d	-----% DM basis-----					
d 1 to 28	5.28	5.32	5.35	0.02		
d 29 to 56	5.35	5.32	5.34	0.02		
d 57 to 84	4.50	4.47	4.47	0.02		
d 84 to 112	4.49	4.49	4.45	0.02		
d 1 to 112	4.90	4.90	4.90	0.01	0.86	0.87
Hay Intake, lb/d						
d 1 to 28	1.39	1.38	1.27	0.06		
d 29 to 56	4.39	4.12	4.10	0.13		
d 57 to 84	6.87	6.54	6.50	0.12		
d 84 to 112	8.48	8.34	8.08	0.12		
d 1 to 112	5.28	5.10	4.99	0.08	0.02	0.32
Total Intake, lb/d						
d 1 to 28	6.67	6.70	6.61	0.07		
d 29 to 56	9.75	9.44	9.44	0.14		
d 57 to 84	11.4	11.0	11.0	0.12		
d 84 to 112	13.0	12.8	12.5	0.13		
d 1 to 112	10.2	10.0	9.89	0.08	0.02	0.37
Feed to Gain, DM/lb						
d 1 to 28	3.08	3.02	2.99	0.08		
d 29 to 56	4.30	4.06	3.96	0.12		
d 57 to 84	4.91	5.11	4.91	0.14		
d 84 to 112	5.41	5.45	5.49	0.13		
d 1 to 112	4.43	4.41	4.34	0.05	0.38	0.28

^{a,b}Means within a row without common superscripts are different at P < 0.05.

Table 7 . Body condition score and hip height day 1 to 112 of grower period.

	Treatments				Contrasts	
	Control	2	3	SEM	1 vs. 2, 3	2 vs. 3
No. pens (7 hfrs/pen)	5	5	5			
BCS						
Initial	2.98	3.00	2.98	0.03		
d 56	3.44	3.41	3.36	0.07		
d 112	3.76	3.84	3.77	0.04		
d 1 to 112	3.60	3.62	3.57	0.05	0.83	0.57
BCS Change						
d 1 to 112	0.78	0.84	0.79	0.04	0.53	0.47
HH, inches¹						
d 1	36.3	36.5	36.4	0.13		
d 56	40.8	41.1	41.3	0.21		
d 112	44.3	44.4	44.4	0.16		
1 to 112	40.5	40.7	40.7	0.12	0.16	0.98
HH gain¹, in. d 1 to 112	7.93	7.98	8.00	0.16	0.79	0.95

¹Initial hip height during the starter period (study 8-242) utilized as a covariate.

^{a,b}Means within a row without common superscripts are different at P < 0.05.

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SSTI Product Title: **Intervention Strategies for Reduction of Foodborne Pathogens in Cattle fed Ethanol Byproducts**

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Keywords: **E. Coli 0157:H7; Distillers Grains; Glycerin; Ethanol byproduct**

Description/Abstract:

Ethanol plants and cattle producers create a symbiotic relationship: The use of wet and dry distiller's grains in beef cattle rations provides significant improvement in overall feedlot performance for many producers in Minnesota and the Upper Midwest. Distiller's grain is the coproduct that remains following the distillation of ethanol. It may be dehydrated to produce dried distiller's grain (DDG) which is then commonly used as livestock feed. The use of distiller's grains in livestock rations has been the subject of numerous research projects over the past ten years. Recently published research data conducted at Kansas State University (K-State) has created controversy over the feeding of distiller's grains in beef cattle rations. The research indicates that cattle fed distiller's grain may have an increased probability of *Escherichia coli* O157 in their hindgut. Specifically:

This research assessment was a two part project consisting of feeding trials conducted at the University of Minnesota and an intervention study conducted at Kansas State University. This report is the Kansas State University portion. This report is a task-level final technical report.

PROJECT OBJECTIVES

Cattle are important reservoir of two major food-borne pathogens: *Escherichia coli* O157:H7 and *Salmonella*. Both organisms colonize the lower gastrointestinal tract of cattle and are shed in the feces. Characterization of factors affecting *E. coli* O157 and *Salmonella* persistence and shedding patterns in cattle is important to develop intervention strategies and improve the safety of food. The role of diet on fecal shedding of *E. coli* O157 in cattle has been studied (Buchko et al., 2000; Callaway et al., 2003; Berg et al., 2004; Van Baale et al., 2004). Distiller's grains, a byproduct derived during the production of ethanol from grains, particularly

corn, are commonly used in ruminant diets (Ham et al., 1994; Lodge et al., 1997; Kleinschmidt et al., 2006). The byproduct is comprised principally of the bran (fiber), protein, and germ (lipid) fractions of the corn and is an excellent source of energy and protein for feedlot and dairy cattle (Spiehs et al., 2002). We have conducted preliminary studies in the past year that indicated a surprising association between distiller's feed and prevalence of *E. coli* O157 and *Salmonella*.

We conducted studies aimed at identifying possible intervention strategies to reduce pathogen shedding in cattle fed distiller's grains. Specifically, our objectives were to:

1. Evaluate the effects of grain processing (steam flaking versus dry rolling) on prevalence of *E. coli* O157 in cattle fed distiller's grains.
2. Feed crude glycerin as a possible method for reducing prevalence of *E. coli* O157.
3. Utilize common feed additives as a possible means of reducing pathogen levels shed in feces of cattle fed distiller's grains.

No Intellectual Property or limitations

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Intervention Strategies for Reduction of Food-borne Pathogens in Cattle Fed Ethanol Byproducts

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1. Evaluate the effects of grain processing (steam flaking versus dry rolling) on prevalence of *E. coli* O157 in cattle fed distiller's grains.
2. Feed crude glycerin as a possible method for reducing prevalence of *E. coli* O157.
3. Utilize common feed additives as a possible means of reducing pathogen levels shed in feces of cattle fed distiller's grains.

BRIEF DESCRIPTION OF RESEARCH

Trial 1: Grain processing as a preharvest intervention strategy.

We previously conducted studies that revealed large differences in prevalence of *E. coli* O157 shedding due to the method of grain processing. Essentially, less rigorously processed grain, such as dry-rolled grain, appeared to afford some protection against *E. coli* shedding compared to more extensively processed grain (i.e., steam flaked). We have speculated that these differences may be attributable to differences in energy substrate that appears in the hind gut. Flaked grains are extensively

digested within the rumen, whereas rolled grains result in far greater starch supply to the hindgut. Increasing starch in the hindgut presumably creates an environment that is conducive to growth of bacteria that can effectively outcompete *E. coli* O157. We hoped to exploit this by substituting a portion of flaked corn with dry-rolled corn in an effort to increase starch supply to the hindgut.

Trial 2. Glycerin as an intervention strategy to control *E. coli* O157.

We have completed a series of experiments with crude glycerin, a co-product derived from the biodiesel industry, to assess its value as a feed for cattle. In our early laboratory experiments, we observed that low levels of glycerin can have a profound effect on fermentation by rumen bacteria. Furthermore, these changes in fermentation manifested as rather large improvements in efficiency of feedlot cattle, particularly when glycerin was included in the diet at a low level (2%). We have hypothesized that this is the result of changes in the microbial population within the gut. Furthermore, we are aware of at least one laboratory experiment in which glycerin inhibited growth of *Salmonella*, which is another gram negative bacteria (like *E. coli*) that colonizes the gastrointestinal tract. Consequently, we believed it might be useful to evaluate the effects of feeding glycerin on populations of pathogenic *E. coli* in cattle.

Trial 3. Reducing *E. coli* O157 shedding in cattle with feed additive compounds

The gut ecosystem is highly complex, consisting of a myriad of bacterial species that compete for space and nutrients. The various species of microbes that exist within the gut are in a continuous state of flux. As one population proliferates, there must be a compensatory decline in another competing population. Conditions within the gut that favor the proliferation of one species logically will reduce the prevalence of another organism. Feed additives that alter populations of gut bacteria can have both positive and negative consequences for colonization by pathogenic, food-borne pathogens. This study was aimed at examining three feed additive products that are known to influence fermentation, and thus bacterial populations: Urea, Ractopamine, and Monensin.

EXPERIMENTAL PROCEDURES

Trial 1:

qThirty nine Holstein steer calves were used for this study. The average initial body weight was 213 ± 20 kg. During the pre-inoculation phase, cattle were assigned randomly to 4 outdoor pens. Each pen received one of the four experimental diets consisting of a steam-flaked corn (SFC) base diet with 0 or 25% of dry-rolled corn (DRC) and 0 or 25% dried distiller's grains with soluble (DDGS, dry basis). Gradual transition, from high roughage diets to high concentrate diets, was accomplished by feeding a series of step-up diets over a 3-week period; after which, the calves received final diets containing approximately 6% alfalfa hay, as a roughage source, for 52 days. The detailed composition for the four final diets is given in Table 1.

At the end of the pre-inoculation phase, fecal sampling was achieved by rectal palpation to determine the prevalence of the wild-type of *E. coli* O157:H7. One gram of the fecal sample was enriched in 9 mL of Gram Negative broth (Difco, BD, Sparks, MD) with cefixime (0.05 mg/L), cefsulodin (10 mg/L), and vancomycin (8 mg/L; GNccv) for 6 h at 37°C. Immunomagnetic separation (IMS; Dynal, Inc., New Hyde Park, NY) was performed and samples were plated onto sorbitol-MacConkey agar (Difco, BD, Sparks, MD) with cefixime (0.05 mg/L) and potassium tellurite (2.5 mg/L; ct-SMAC). Sorbitol-negative colonies were picked and tested for indole production and O157 antigen latex agglutination. Five of the steers

were found positive for wild-type *E. coli* O157 and were excluded from the study. The repartition of the 31 animals, identified as negative carrier of *E. coli* O157, was as follows: 7 steers from the 25% DRC and 0% DDGS treatment and 8 animals from each of the other treatments. Selected calves were transferred to individual pens in a biosafety level-2 facility. Pens were separated by solid walls to prevent any physical contact between adjacent animals and were equipped with their own water supply and feed bunk. Calves were fed *ad libitum* once daily around 9:30am.

Composition of diets for Trial 1, dry matter basis

Ingredient, % dry matter	0% Dry-rolled Corn		25% Dry-rolled Corn	
	0% DDGS	25% DDGS	0% DDGS	25% DDGS
Steam-flaked corn	82.1	58.2	56.8	33.1
Dried distiller's grains	-	25.4	-	25.3
Dry-rolled corn	-	-	25.5	25.3
Alfalfa hay	5.9	5.9	5.9	5.8
Corn steep liquor	6.5	6.4	6.4	6.4
Supplement ¹	5.5	4.2	5.5	4.1

¹Formulated to provide 0.1 mg Co, 10 mg of Cu, 0.5 mg of I, 50 mg of Mn, 0.25 mg of Se, 50 mg of Zn and 2200 IU vitamin A per kg of diet DM, and provided 30 g/ton monensin and 9 g/ton tylosin.

Five strains of *E. coli* O157:H7 were grown on Blood agar (BAP; Remel, Lenexa, KS) overnight at 37°C. A single colony was selected from each strain, inoculated into 10 mL of tryptic soy broth (TSB; Difco, BD, Sparks, MD) and incubated overnight at 37°C. Then, 1 mL of the resulting culture was transferred to 100 mL of TSB and again incubated at 37°C. After 7 hours, all strains were pooled together. The mixture was diluted ten-fold with buffered peptone water and spread onto sorbitol-MacConkey agar (Difco, BD, Sparks, MD) plates with cefixime (0.05 mg/L), potassium tellurite (2.5 mg/L) and nalidixic acid (50 µg/L; ctn-SMAC).

Three days after relocation, the calves were orally inoculated, via a gastric tube, with 5 mL of the 5-strain mixture of Shiga-toxin producing Nal^R *E. coli* O157:H7 mixed with 200 mL of 1% sterile skim milk. The final concentration of the inoculate was 3.2 x 10⁹ colony-forming units (CFU) of Nal^R *E. coli* O157:H7.

After the oral challenge with Nal^R *E. coli* O157:H7, fecal samples were collected three times a week (Monday, Wednesday and Friday) over a 40-day period. To prevent cross contamination gloves were changed between pens and foot baths with bleach were used. Feces were collected in sterile bags, by rectal palpation, and transported immediately to the laboratory. Approximately 1 g of fecal sample was added to a 9 mL of GNccv. One milliliter of the culture was then diluted ten-fold in buffered peptone water. A 100-µL aliquot of the resulting dilution was directly plated, in triplicate, onto ctn-SMAC and incubated overnight at 37°C. The remaining of the GNccv broth was enriched for 6 h at 37°C, subsequently; 1 mL was removed and reinoculated into a fresh 9 mL of GNccv for a second enrichment. After 16 to 18 h of

incubation at 37°C, 100 µL was plated on ctn-SMAC and incubated overnight at 37°C. Sorbitol negative colonies from the direct and enriched ctn-SMAC plates were counted and colonies were tested for indole production and O157 antigen.

At the end of the 40-day period, all calves were euthanized and submitted for post mortem examination. Animals were euthanized on a 3-day period by group with homogenous repartition of the treatments. Contents from the rumen, cecum, colon, and rectum were collected and the concentrations of Nal^R *E. coli* O157 were determined as described above. The rectum was, additionally, excised and the mucosa rinsed with water to remove visible fecal material. The proximal area (3 to 5 cm from the recto-anal junction) was swabbed with a foam-tipped applicator (RAMS; VWR International, Buffalo Grove, IL, USA). Swabs were immediately placed in 3 mL of GNccv broth, transported to the laboratory, vortexed and processed for detection of Nal^R *E. coli* O157 by direct plating or enrichment technique, as previously described. Swabs were only used for a positive (direct plating or enrichment) or negative type response.

Fecal concentrations of Nal^R *E. coli* O157:H7 were log₁₀ transformed for the need of the analysis. Lowest detectable concentration per gram of wet feces was considered (approximately 10¹ CFU/g), when only direct plating was positive for Nal^R *E. coli* O157:H7.

Effects of treatments, sampling days and the interaction treatment × sampling day, on the concentrations of Nal^R *E. coli* O157:H7 in the serial fecal collections (days 2 through 40), were analyzed using the Proc MIXED procedure in SAS (Version 9.1, SAS Institute, Cary, NC, USA). The model included DDGS level, DRC level, sampling day, and all possible interactions as fixed effects and animal as a random effect.

The generalized linear models procedure was used to assess differences in Nal^R *E. coli* O157:H7 concentration in gut contents collected at necropsy. The model included DDGS level, DRC level and the interaction between DDGS and DRC.

The prevalence of Nal^R *E. coli* O157:H7 (positive by direct plating or by enrichment) in recto-anal mucosal swab samples (RAMS) and gastrointestinal tract samples were analyzed using the GLIMMIX procedure of SAS, whereas the prevalence of Nal^R *E. coli* O157:H7 in fecal samples was analyzed by using a GENMOD procedure of SAS.

TRIAL 2:

We added three levels of crude glycerin, 0, 4 or 8%, to growing diets containing dry-rolled corn, corn silage, alfalfa hay, and corn steep liquor. We formulated the diets to be isonitrogenous.

Composition of diets for Trial 2.

Ingredients, % of DM	0% Glycerin	4% Glycerin	8% Glycerin
Corn silage	60	60	60
Wet corn gluten feed	35	30.2	25.4
Crude Glycerin	-	4	8
Soybean meal	-	0.8	1.6
Limestone	1.6	1.6	1.6
Urea	0.4	0.4	0.4
Vitamin/mineral premix ¹	0.3	0.3	0.3
Feed additive premix ²	2.7	2.7	2.7

Dry matter	43.3	43.7	44.2
Organic matter	93.4	93.2	93.7
Crude protein	13.0	12.5	12.1
NDF	36.2	34.7	33.2
Calcium	0.9	0.9	0.9

¹Formulated to provide 0.1 mg Co, 10 mg of Cu, 0.5 mg of I, 50 mg of Mn, 0.25 mg of Se, 50 mg of Zn and 2200 IU vitamin A, per kg of diet DM.

²Provided 300 mg of monensin per animal daily in a ground corn carrier.

Each treatment was represented by 16 pens, each containing 7 to 8 heifers. We obtained fecal samples by fecal grab at the chute, once each week for 6 weeks. Fecal samples were kept on ice until analysis. We weighed approximately 1g of feces and placed it in 9 mL Gram Negative broth (Difco) with cefixime (0.05 mg/L), cefsulodin (10 mg/L), and vancomycin (8mg/L; GNccv) for a 6-hour incubation at 104F. We added 1 mL of GNccv to a sterile tube containing 20 µL of *E. coli* O157 specific beads and subjected it to immunomagnetic separation. We then resuspended the resulting *E. coli* O157 beads in 100 µL of phosphate buffer and plated them onto a selective agar for *E. coli* O157:H7 for an overnight incubation at 98F. After incubation, we picked up to 6 non-sorbitol fermenting colonies and tested them for indole production. We further analyzed indole positive colonies using a O157 antigen agglutination kit. We considered colonies positive for agglutination and indole production as *E. coli* O157:H7. We confirmed our results by a gram staining and API 20E kit.

TRIAL 3:

Seven hundred and twenty crossbred beef steers (initial BW = 433 ± 23.1 kg) were used in a randomized complete block design with a 2 x 3 x 2 factorial treatment arrangement. Factors were monensin level (33 or 44 mg/kg DM), level of supplemental urea (0, 0.35, or 0.70% of DM), and ractopamine (0 or 200 mg/steer daily, fed during the last 42 d before harvest). The basal diet consisted of steam-flaked corn with 30% wet sorghum DG. Steers were allowed *ad libitum* access to alfalfa hay and water from arrival until processing at the start of the adaptation phase. On day 0 of the adaptation period, steers were weighed, vaccinated, stratified by weight into two blocks and then randomly assigned to pens. Forty-eight dirt-floor pens (10.4 x 26.8 m) containing 15 steers each were randomly assigned to 1 of 12 treatment combinations. Two transition diets and a final diet were fed over a 21 day step-up period. The amount of feed offered to the pen was determined at approximately 7:00 a.m., and the daily rations for each pen was delivered at approximately 8:00 a.m. and 2:00 p.m. each day. Cattle were fed amounts sufficient to result in traces of residual feed at the next feeding and fresh water was available at all times.

The three feed additive manipulations were not started at the same time point of the study, and therefore, not all sample events occurred in steers fed diets with all treatments. Monensin was included in the transition and final diets, while urea supplementation was initiated at the end of the adaptation phase and after the first sampling event. Ractopamine administration began after five sampling events, and therefore, the last four samples were from steers fed diets that included all three treatments.

Ingredient and chemical composition of the diets for Trial 3.

Item	Percentage, DM basis
<i>Ingredient</i>	
Steam-flaked corn	58.1, 57.7, or 57.3
Wet sorghum distiller's grain	30.0
Wheat straw	7.0
Premix ¹	2.38
Limestone	1.80
Urea	0, 0.35, or 0.70
Supplement ²	0.71
<i>Nutrient Composition</i>	
Dry matter, %	57.5
CP, % DM	14.2, 15.4, or 16.5
NDF, % DM	19.2

¹Feed additive premix provided 33 or 44 mg of monensin sodium (Elanco Animal Health, Greenfield, IN) and 11 mg tylosin (Elanco Animal Health, Greenfield, IN) per kg of feed.

²Supplement contained 2,650 IU vitamin A; 10 mg Cu; 0.5 mg I; 0.15 mg Co; 0.25 mg Se; 50 mg Zn; and 50 mg Mn per kg of diet DM; Ractopamine hydrochloride (Elanco Animal Health, Greenfield, IN) included in the diet at 0 or 200 mg per animal daily the last 42 d before harvest.

Fecal samples (10/pen) were collected, July through November, from the surface of each pen approximately every 2 wk for 14 wk (n = 9). Samples (approximately 100 g) were collected from freshly defecated fecal pats using a plastic spoon, and care was taken to avoid ground contamination or repeat sampling from the same steer on the same sampling. The spoon with feces was placed into a Whirl-pack bag (Nasco, Ft. Atkinson, WI), and once samples were collected, they were placed in a cooler with ice packs and delivered to the Kansas State University College of Veterinary Medicine Pre-harvest Food Safety Laboratory for processing.

Fecal samples were cultured for *E. coli* O157:H7 as previously described (Greenquist et al., 2005). Briefly, samples were kneaded for 30 sec and approximately 1 g of feces was placed in tubes containing 9 mL Gram-negative (**GN**) broth (Becton Dickinson, Franklin Lakes, NJ) with cefixime (0.05 mg/L), cefsoludin (10 mg/L), and vancomycin (8 mg/L; **GNccv**). The GNccv broth was then incubated for 6 h at 37°C. After enrichment, immunomagnetic bead separation (**IMS**) was performed, followed by plating onto sorbitol-MacConkey agar with cefixime (0.5 mg/L) and potassium tellurite (2.5 mg/L; **CT-SMAC**). Plates were incubated overnight at 37°C, and up to six sorbitol negative colonies were streaked onto blood agar plates. Colonies were tested for indole production and latex agglutination for the O157 antigen, and further characterized by multiplex PCR to identify *eae* (intimin), *stx1* (Shiga toxin 1), *stx2* (Shiga toxin 2), *hly* (hemolysin), *rfbE* (O157 antigen) and *fliC* (flagella) genes (Bai et al., 2010). Personnel conducting sampling and laboratory analyses were blinded to the treatment assignments.

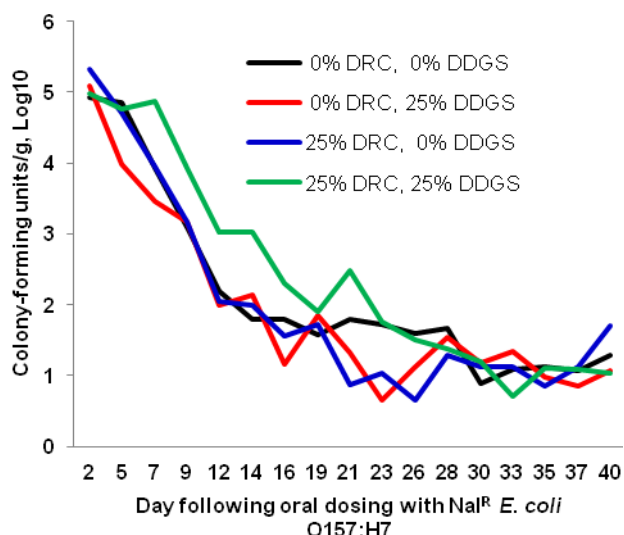
Descriptive statistics on prevalence outcomes were assessed prior to multivariable analysis. A repeated measures negative binomial generalized linear model (PROC GENMOD, SAS v. 9.2, Cary, NC) with a log links was used to analyze data. The negative binomial function was chosen, as it best represented data having a high number of zero prevalence samples and few samples with very high prevalence. It was verified to be the correct function by examining the dispersion parameter point estimate (α). Because the 95% confidence interval did not include 0, the negative binomial model was deemed appropriate (Heeringa et al., 2010). Pen was considered the experimental unit with the count of positive samples as the outcome. This was offset by the natural log of the number of samples processed for each pen. Pen over time was included as a repeated (random) effect to account for the lack of independence among samples from the same pen over sampling days. Score statistics for the generalized estimating equations were used to assess significance of sampling day, monensin, urea, ractopamine, and their interactions. Because urea and ractopamine were not fed throughout the trial, the data were analyzed in three phases. Results were considered significant at $P < 0.05$ and manual backward selection was used to remove variables that were not significant.

RESULTS and DISCUSSION

Trial 1:

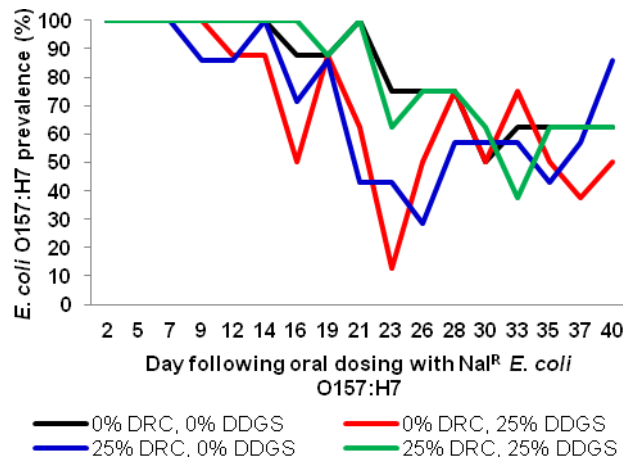
Figure 1 represents the concentration of Nal^R *E. coli* O157:H7 in feces of steers fed diet with 0 or 25% DDGS and 0 or 25% DRC following oral dosing with 3.2×10^9 CFU of the 5-strain mixture. Two days after inoculation, the concentration of Nal^R *E. coli* O157:H7 for all treatments was approximately 1×10^5 CFU/g of feces. Over the 40-day period, the concentration of Nal^R *E. coli* O157:H7 gradually decreased. The last measures fell between 1 and 2 log CFU/g of feces. There were no significant differences between diets ($P > 0.2$), however a day of sampling effect was observed ($P < 0.01$).

Figure 1: Concentration of Nal^R *E. coli* O157:H7 in fecal samples of steers, fed finishing diets with 0 or 25% dried distiller's grains with solubles and 0 or 25% dry-rolled corn, following oral dosing with 3.2×10^9 colony-forming units of a 5-strain mix of Nal^R *E. coli* O157:H7. Diet effect, $P > 0.20$; Sampling day effect, $P < 0.01$; SEM=0.29.



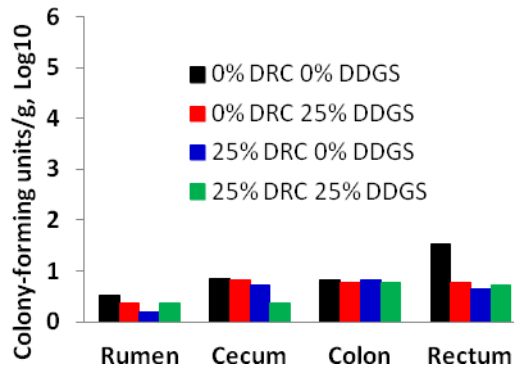
A comparison of the prevalence of culture positive for Nal^R *E. coli* O157:H7 in fecal samples among the different diets over the whole period of the experiment (Figure 2) revealed an effect of sampling day ($P<0.0001$), a treatment interaction DRC*DDGS ($P<0.01$), and a sampling day*DRC*DDG interaction ($P=0.05$). The individual analysis of every sampling day revealed no DRC or DDG effect, but an interaction DRC*DDG on days 16, 21, 23 and, 26 ($P<0.05$). The prevalence of culture positive samples was lower in steers receiving 25% DRC - 0% DDG and 0% DRG - 25% DDG.

Figure 2: Prevalence of culture positive for Nal^R *E. coli* O157:H7 in fecal samples from steers fed finishing diets with 0 or 25% dried distiller's grains with soluble and 0 or 25% dry-rolled corn following oral dosing with 3.2×10^9 colony-forming units of a 5-strain mix of Nal^R *E. coli* O157:H7. Sampling day effect, $P<0.0001$; DRC effect, $P>0.90$; DDGS effect, $P>0.70$; Diet interaction DRC*DDGS, $P<0.01$ (Interaction DRC*DDG, $P<0.05$ for sampling days 16, 19, 21, 23 and 26); Sampling day*DRC*DDG interaction, $P=0.05$.



Forty days after the inoculation of the steers with 3.2×10^9 CFU of a 5-strain mixture of Nal^R *E. coli* O157:H7, the experiment was terminated. The concentration of *E. coli* O157:H7 at the various locations in the gastrointestinal tract of the steers (Figure 3) did not differ significantly ($P > 0.3$). DDG, DRC, or the interaction of both did not have an effect on the shedding of *E. coli* O157:H7 in the rumen, cecum, colon, and rectum of the steers.

Figure 3: Concentration of Nal^R *E. coli* O157:H7, at necropsy, in various locations of the gastrointestinal tract of steers fed finishing diets with 0 or 25% dried distiller's grains with soluble and 0 or 25% dry-rolled corn following oral dosing with 3.2×10^9 colony-forming units of a 5-strain mix of Nal^R *E. coli* O157:H7. Location effect, $P>0.3$; DRC effect, $P>0.10$; DDGS effect, $P > 0.10$; interaction DRC*DDGS, $P > 0.10$; and location*DRC*DDGS interaction, $P > 0.10$.



The analysis of the prevalence of culture positive samples for *E. coli* O157:H7 at the various location of the gastrointestinal tract (Table 1) did not show any significant difference among treatments.

Table 1: Prevalence of Nal^R *E. coli* O157:H7 positive samples, at necropsy, in various location of the gastrointestinal tract of steers fed finishing diets with 0 or 25% dried distiller's grains with soluble and 0 or 25% dry-rolled corn following oral dosing with 3.2×10^9 colony-forming units of a 5-strain mix of Nal^R *E. coli* O157:H7

	0% Dry-rolled Corn		25% Dry-rolled Corn		SEM
	0% DDGS	25% DDGS	0% DDGS	25% DDGS	
Cecum (%)	37.5	37.5	42.9	25.0	0.82
Colon (%)	37.5	37.5	42.9	50.0	0.71
RAMS (%)	37.5	25.0	42.9	62.5	0.73
Rectum (%)	62.5	37.5	28.6	50.0	0.71
Rumen (%)	37.5	25.0	14.3	25.0	0.82

*Effect of DDGS, $P > 0.90$; Effect of Dry-rolled Corn (DRC); $P > 0.97$; Interaction, DDG*DRC, $P > 0.504$.

E. coli is naturally present in the gastrointestinal tract and feces of cattle, but at low prevalence and concentration. After the dosing of the animal with Nal^R *E. coli* O157:H7, we observed a decrease of the *E. coli* concentration throughout the experiment which was not influenced by any of the diets. Our results correlate with previous findings showing that, following dosing, *E. coli* O157:H7 transit through the intestinal tract and is excreted by the animals allowing only low doses to persist over time in the gastrointestinal tract.

Our first objective was to compare fecal shedding and gastrointestinal tract colonization by *E. coli* O157:H7 in cattle fed steam-flaked corn (SFC) with or without DDGS. Based on previous publications, we hypothesized that feeding DDGS would increase the *E. coli* O157:H7

shedding in feces, as well as its colonization within the intestinal tract. By the end of the 40-day experimental period, there were no significant differences in the concentration of *E. coli* O157:H7 between animals receiving DDGS and the one receiving only SFC. Neither the prevalence of *E. coli* O157:H7 positive samples, nor the concentration of the bacteria in the positive samples, were affected by the presence or absence of DDGS in the diets. These observations concur with the absence of statistical differences in the colonization rate and prevalence of *E. coli* O157:H7 in the gastrointestinal tract between the two groups of animals. There was no relationship between the use of DDGS in the diet and the level of *E. coli* O157:H7 shedding in cattle in this study. Our second objective was to evaluate the addition of dry-rolled corn in the diet, as a pre-harvest strategy. Previous studies showed that change in grain processing can influence the shedding of *E. coli* O157:H7 in cattle (9, 16). By dry-rolling the corn, we thought that the starch content reaching the hindgut will be increased, inducing an increase of fermentative activity and acid production, producing less favorable condition of growth and shedding for *E. coli* O157:H7. However, our results revealed no significant differences in the prevalence of *E. coli* O157:H7 in feces or in the gastrointestinal tract between animals receiving, or not, DRC. The concentrations of *E. coli* O157:H7 in positive samples were not different either. Once again, our results were in opposition with previous findings and our hypothesis.

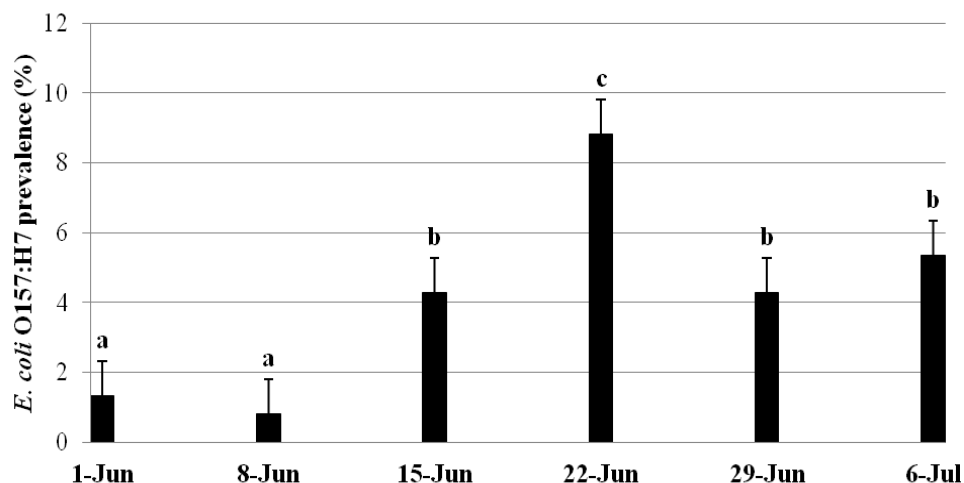
The influence of diet type and diet processing on *E. coli* O157:H7 shedding has been broadly studied and results have not always been consistent. The transient occurrence of *E. coli* O157:H7 and its low prevalence are possible explanations for this inconsistency, as well as many other factors, such as age, seasons and, animal stress. With so many variation sources, accurate results are challenging to obtain and require a large number of replications and animals.

In conclusion, shedding of *E. coli* O157:H7, under the conditions of our Trial 1, was not influenced by the presence of DDGS in the diet. The use of DRC as a preharvest intervention to reduce the carriage of *E. coli* O157:H7 in cattle was not effective.

Trial 2.

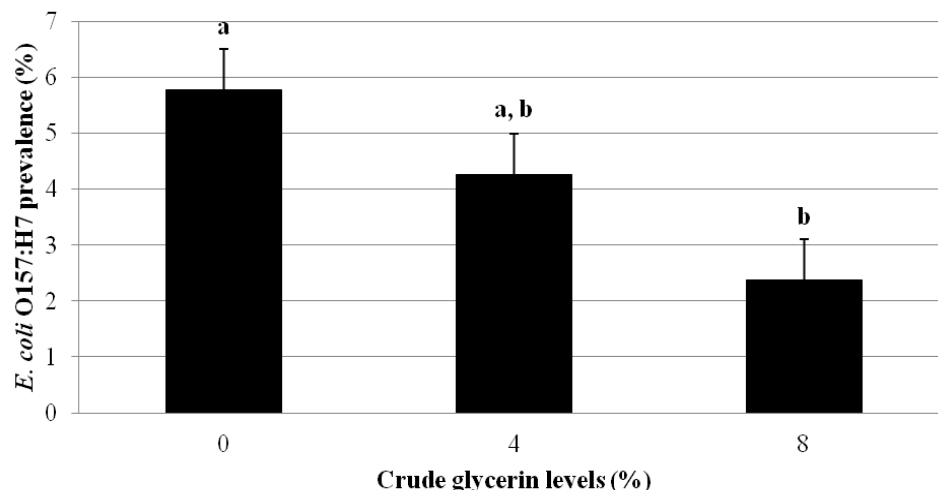
The crude glycerin used in this experiment contained 81.5% glycerol. After statistical analysis, we concluded that there was no interaction between sampling date and the levels of crude glycerin ($P>0.2$). There was, however, an effect of sampling date ($P<0.01$), as shown in Figure 4. For the two first weeks, percentages of samples that tested positive for *E. coli* O157:H7 were 1.3 and 0.8% respectively. Prevalence increased to peak of 8.8% during the 4th week, and then stabilized at around 4.3-5.8% in the last two weeks of the experiment.

Figure 4: *E. coli* O157:H7 prevalence in growing cattle fed crude glycerin



We also observed an effect of glycerin inclusion levels ($P < 0.01$, Figure 5). Fecal incidence rates of *E. coli* O157:H7 were 5.8, 4.3, and 2.4% for heifers fed 0, 4, and 8% glycerin, respectively. The prevalence we observed in heifers fed 0% glycerin was different from that of cattle fed 8% glycerin ($P < 0.05$), and tended to be different from cattle fed 4% glycerin ($P = 0.06$). Glycerin previously has been shown to inhibit the activity of cellulolytic bacteria in the rumen. Consequently, changes in fecal prevalence of *E. coli* O157:H7 observed in this study might be explained by alterations in gastrointestinal flora, with higher levels of glycerin producing a less favorable environment for the proliferation of pathogenic *E. coli* O157:H7.

Figure 5: Effect of crude glycerin levels fed to growing cattle on *E. coli* O157:H7 prevalence



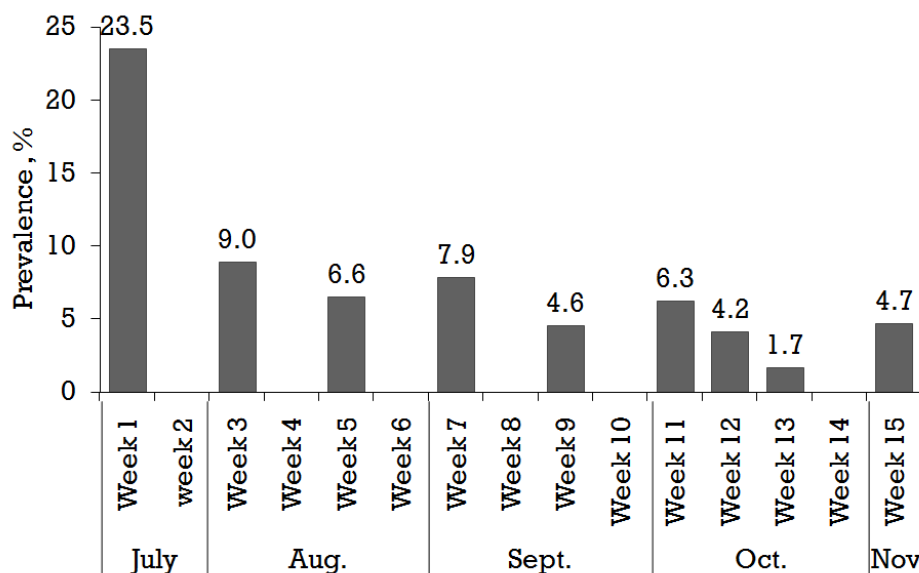
Our goal in this study was to determine whether or not glycerin could be added to cattle diets to decrease shedding of food-borne pathogens. Our results demonstrated that with increasing levels of crude glycerin the prevalence decreased. We find this observation to be of

interest, as glycerin is a secondary metabolite of yeast and normally is found in significant quantities in distiller's grain. This suggests that that glycerin is not the component within DDGS responsible for the increase in *E. coli* O157:H7, and that glycerin may actually be used as a means to decrease fecal prevalence of this pathogen in cattle.

TRIAL 3:

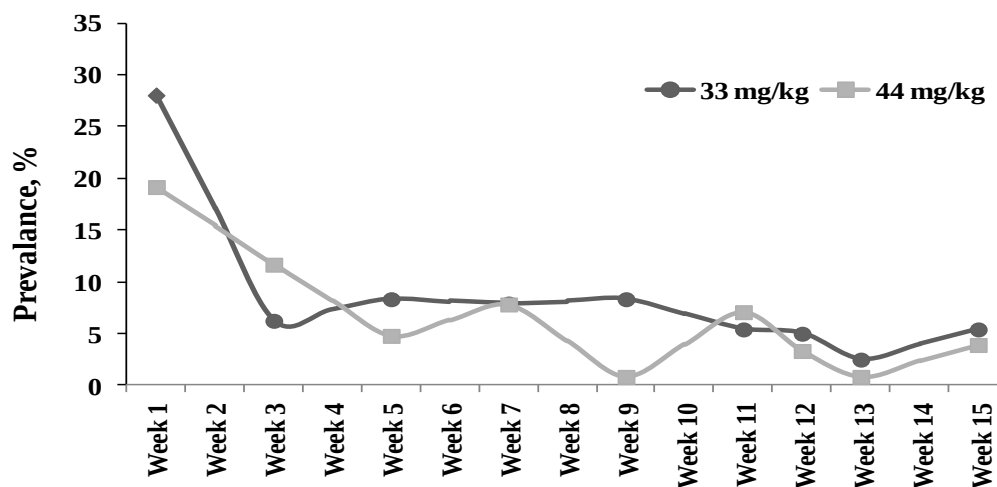
Overall, fecal prevalence of *E. coli* O157:H7 was 7.6% (327 of 4,300 fecal samples), ranging from 23.6% on the first collection (July) to 1.6 % on the eighth collection day (October; Figure 6). The multiplex PCR analyses revealed that all isolates (N=327) were positive for *eae*, *stx2*, *hly*, *rfbE* and *fliC*, and only 14% of the isolates (47/327) were positive for *stx1*. There were no two- or three-way interactions observed between monensin, urea and ractopamine treatment; however, there was a tendency for interaction between monensin and sampling week ($P = 0.06$), indicating that *E. coli* O157:H7 prevalence between monensin treatments tended to vary by sampling week. Fecal shedding of *E. coli* O157:H7 in cattle is influenced by a number of factors, including diets and dietary additives fed to the animal (Callaway et al., 2009; Jacob et al., 2009). It is believed that dietary ingredients that flow into the hindgut and alter the microbial population and fermentation products are likely to have an impact persistence and fecal shedding of *E. coli* O157:H7 (Jacob et al., 2009).

Figure 6. Overall fecal prevalence of *Escherichia coli* O157:H7 in cattle fed steam-flaked corn grain based diet supplemented with 30% wet distiller's grains (n = 48 pens; SEM = 0.7)



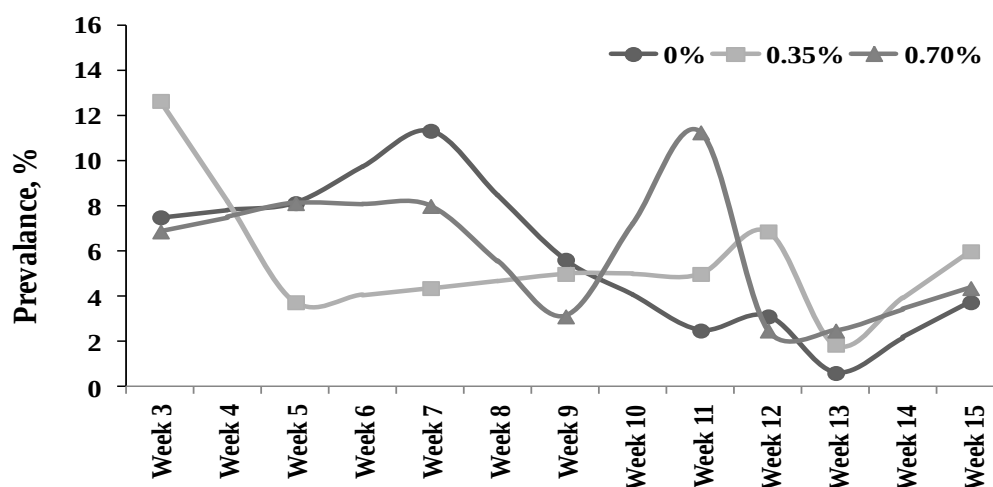
Cattle fed monensin at 44 mg/kg of feed had lower ($P = 0.05$) *E. coli* O157:H7 prevalence than cattle fed 33 mg/kg (4.3 vs 6.8%, Figure 7). Previous studies generally examined monensin at 33 mg/kg and compared it to a control group that lacked monensin in the diet. Van Baale et al., (2004) in a challenge study ($n = 12$) fed at a slightly higher dose of 39.6 mg/kg, found no difference in fecal *E. coli* O157 over a 63-d study period, but observed an initial decrease (first 5 d) in fecal concentration of *E. coli* O157 in monensin-fed cattle on a grain diet, but not in forage-fed animals. McAllister et al. (2006) observed no difference in fecal shedding of *E. coli* O157 (66 vs. 71%) when cattle ($n = 32$) were fed monensin at 0 or 33 mg/kg in the diet. Jacob et al., (2008) in a natural prevalence study found no differences ($P = 0.8$) in fecal *E. coli* O157:H7 between cattle fed diets with 0 and 33 mg/kg monensin. Although monensin is not generally inhibitory to gram negative bacteria, some are susceptible to high concentrations (Nagaraja and Taylor, 1987). *In vitro* studies have shown that monensin at concentrations equal to (Bach et al., 2002) or higher (Van Baale et al., 2004) than concentrations expected in the rumen when 33 mg/kg of monensin is fed did not affect the growth of *E. coli* O157:H7. Because a substantial proportion of monensin passes through the intestinal tract intact, it is likely that the reduction in fecal shedding of *E. coli* O157:H7 observed with the higher dose of monensin is because of changes in the microbial populations and fermentation products in the hindgut. The effects of monensin on hindgut fermentation, such as increased propionic acid, are similar to that described in the rumen (Yokoyama et al., 1985; Marounek et al., 1990).

Figure 7. Fecal prevalence of *Escherichia coli* O157:H7 in steers fed steam-flaked corn grain-based diet with 30% wet sorghum distiller's grains and supplemented with monensin at 33 or 44 mg/kg of feed ($n = 24$ pens/treatment; $SEM = 1.2$).



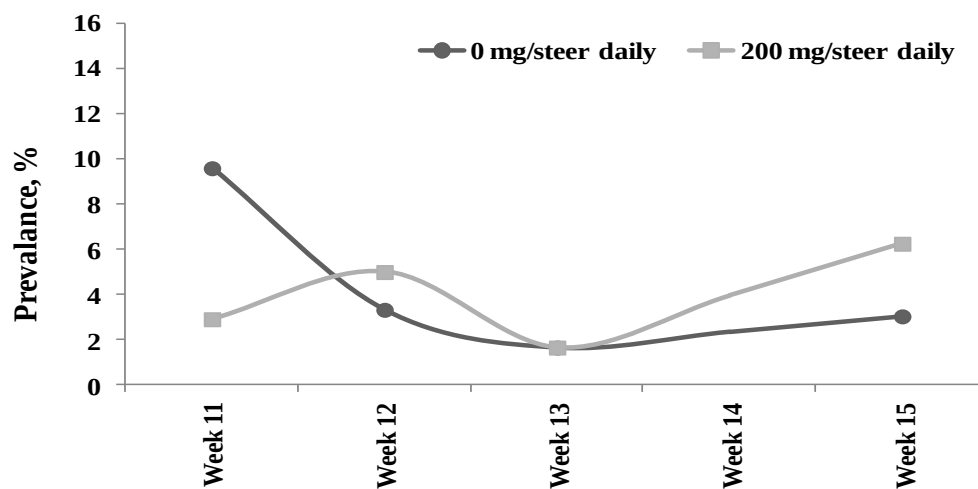
Supplemental urea at 0.35 or 0.7 % had no effect ($P = 0.87$) on fecal shedding of *E. coli* O157:H7. Fecal prevalence of *E. coli* O157:H7 were 5.3, 5.7, and 5.9 % for groups fed 0, 0.35 and 0.7% urea, respectively (Figure 8). Distillers grains, which contain little starch (< 5% in DG vs. >70% in corn, Belyea et al., 2004) and approximately three times higher lipid, protein, and fiber contents than corn grain (Spiehs et al., 2002), have been shown to increase *E. coli* O157:H7 prevalence in cattle (Jacob et al., 2008; Wells et al., 2009). Increased flow of lipid, protein and fiber to the hindgut are likely to alter ecology of the hindgut, which may have an impact on persistence of *E. coli* O157:H7. Increased flow of lipid into the hindgut may have a negative effect on *E. coli* O157:H7 because of the antibacterial effects of the released free fatty acids (Annamalai et al., 2004). It is possible that lipid may get digested and absorbed from the small intestine and not flow in sufficient amounts into the hindgut to have a negative effect. Dietary fiber is known to alter the physiology and stimulate bacterial growth in the human colon (Cummings and Stephan, 1980). Possibly, increased flow of fiber into the hindgut stimulates mucus production, which may be stimulatory to *E. coli* O157:H7 growth (Fox et al., 2009). Because DG contain less degradable protein (Klopfenstein et al., 2008), ruminal availability of nitrogen may be limiting, which may hinder fiber (Firkins et al., 1986) or starch (Fron et al., 1996) digestion in the rumen. Provision of supplemental ruminal ammonia as urea may enhance ruminal fermentation and decrease flow of fiber to the hindgut. Firkins et al. (1986) demonstrated that diets containing DG had less ruminal NDF digestion compared to a diet containing dry corn gluten feed, but the total tract NDF digestion was greater for DG diet suggesting greater hindgut fermentation. Based on *in vitro* and *in vivo* studies, Fron et al. (1996) demonstrated that inclusion of condensed distiller's byproducts altered microbial activities (increased ruminal populations of starch and lactate utilizing bacteria) and increased the rate of fermentation of lactic acid, however, ruminal pH was unaffected. Varying levels of urea, which could potentially improve ruminal fiber digestion, did not affect fecal prevalence of *E. coli* O157:H7 in this study. It is possible that ammonia was not a limiting factor, hence urea supplementation did not have an effect fecal shedding of *E. coli* O157:H7. Increased availability and degradation of protein in the hindgut and therefore, increased ammonia production and elevated pH may favor persistence of *E. coli* O157:H7.

Figure 8. Fecal prevalence of *Escherichia coli* O157:H7 in steers fed steam-flaked corn grain-based diet with 30% wet sorghum distiller's grains and supplemented with urea at 0, 0.35, or 0.70 % of the diet (n = 16 pens/treatment SEM = 1.2).



The inclusion of ractopamine at 0 or 200 mg/head/d had no effect ($P = 0.89$) on fecal prevalence of *E. coli* O157:H7 (4.4 vs 4.0 %; Figure 9). However, the power to detect an effect was low due to low *E. coli* O157:H7 prevalence in the final phase of the study. The mean fecal prevalence in the last four samples (collected in the month of October) was 4.2% compared to a mean of 10.3% in the first five samples (collected in July, August, and September). The reduction in prevalence in October is likely because of seasonal influence on fecal shedding of *E. coli* O157:H7 (Edrington et al., 2006a; Fernández et al., 2009). Ractopamine, a beta-agonist, is used to accelerate gain and improve efficiency in cattle during the final 4 to 6 wk of the finishing phase (Schroeder et al., 2003; Laudert et al., 2004). Ractopamine may potentially interact with the bacterial quorum-sensing systems (Sperandio et al., 2003) to affect *E. coli* O157:H7 prevalence. Studies have shown that the neuroendocrine environment of the gastrointestinal tract, particularly norepinephrine released by the enteric nervous system, has influence on bacterial growth, and in certain pathogens, including *E. coli* O157:H7, expression of virulence factors (Lyte et al., 1997). Edrington et al. (2006b) conducted a study with a small number of cattle ($n=20$) that were administered 0 or 20 mg of ractopamine daily for 28 d and observed a reduction in fecal shedding ($P = 0.006$) with ractopamine (51.2 vs 41.8%, for 0 and 20 mg ractopamine, respectively). In another study (Edrington et al., 2006b) with 1,800 feedlot heifers, in three replicates, ractopamine fed at 200 mg/animal daily for 28 d lowered ($P = 0.05$) *E. coli* O157:H7 prevalence (8.5 vs 13.8%) in feces compared to control heifers fed no ractopamine. However, there were no significant differences in two of the three replicates. Recently, Edrington et al., (2009) used 504 feedlot heifers in a 2 x 3 factorial design, with ractopamine included at 0 or 200 mg/heifer daily for 14, 28, or 42 d. Fecal samples were obtained at day 0 and then at days 14, 28, or 42 corresponding to each treatment period. There were no significant differences in prevalence among treatments.

Figure 9. Fecal prevalence of *Escherichia coli* O157:H7 in steers fed steam-flaked corn grain-based diet with 30% wet sorghum distiller's grains and supplemented daily with ractopamine at 0 or 200 mg/steer ($n = 24$ pens/treatment; SEM = 1.2).



In conclusion, results of trial 3 suggest inclusion of supplemental urea in the diet had no effect on fecal shedding of *E. coli* O157:H7 in cattle. Our premise in testing the effect of supplemental urea was the potential effects of altered ruminal and possibly hindgut fermentation on *E. coli* O157:H7. Because we did not monitor ruminal or hindgut fermentation changes, we have no evidence that fermentation was altered by feeding supplemental urea. Similarly, the low prevalence of *E. coli* O157:H7 during ractopamine feeding precluded us from assessing the impact of ractopamine. The reduction in fecal shedding of *E. coli* O157:H7 associated with feeding the high dose of monensin is interesting and somewhat surprising considering that prior studies (although with lower doses) had shown no effect. Therefore, additional research is needed to confirm the reduction in fecal shedding of *E. coli* O157:H7 in cattle fed 44 mg/kg monensin.

LITERATURE CITED

- Annamalai, T., M. K. M. Nair, P. Marek, P. Vasudevan, D. Schreiber, R. Knight, T. Hoagland, and K. Venkitanarayanan. 2004. *In vitro* inactivation of *Escherichia coli* O157:H7 in bovine rumen fluid by caprylic acid. *J. Food Prot.*, 67:884-888.
- Bach, S. J., T. McAllister, D. Veria, and R. Holley. 2002. Effect of monensin on survival and growth of *Escherichia coli* O157:H7 *in vitro*. *Can. Vet. J.* 43:718-719.
- Bai, J., X. Shi, and T. G. Nagaraja. 2010. A multiplex PCR procedure for the detection of six major virulence genes in *Escherichia coli* O157:H7. *J. Microbiol. Meth.* 82:85-89.
- Belyea, R. L., K. D. Rausch, and M. E. Tumbleson. 2004. Composition of corn and distillers dried grains with solubles from dry grind ethanol processing. *Bioresource Technol.* 94:293-298.
- Berg, J., T. McAllister, S. Bach, R. Stilborn, D. Hancock, and J. LeJune. 2004. *Escherichia coli* O157:H7 Excretion by Commercial Feedlot Cattle Fed Either Barley- or Corn-Based Finishing Diets. *J. Food Prot.* 67:666-671.
- Buchko, S. J., R. A. Holley, W. O. Olson, V. P. J. Gannon, and D. M. Veira. 2000. The Effect of Different Grain Diets on Fecal Shedding of *Escherichia coli* O157:H7 by Steers. *J. Food Prot.* 63:1467-1474.
- Callaway, T. R., M. A. Carr, T. S. Edrington, R. Anderson, and D. Nisbet. 2009. Diet, *Escherichia coli* O157:H7, and cattle: A review after 10 years. *Curr. Iss. Mol. Biol.* 11:67-79.
- Callaway, T. R., R. O. Elder, J. E. Keen, R. C. Anderson, and D. J. Nisbet. 2003. Forage Feeding to Reduce Preharvest *Escherichia coli* Populations in Cattle, a Review. *J. Dairy Sci.* 86:852-860.
- Cummings, J. H., and A. M. Stephen. 1980. The role of dietary fibre in the human colon. *Can. Med. Assoc. J.* 123:1109-1114.
- Dewell, G. A., J. R. Ransom, R. D. Dewell, K. McCurdy, I. A. Gardner, A. E. Hill, J. N. Sofos, K. E. Belk, G. C. Smith, and M. D. Salman. 2005. Prevalence of and Risk Factors for *Escherichia coli* O157 in Market-Ready Beef Cattle from 12 U.S. Feedlots. *Foodborne Pathog Dis.* 2:70-76.
- Edrington, T. S., T. R. Callaway, S. E. Ives, M. J. Engler, M. L. Looper, R. C. Anderson, and D. J. Nisbet. 2006a. Seasonal shedding of *Escherichia coli* O157:H7 in ruminants: A new hypothesis. *Foodborne Path. Dis.* 3:413-421.
- Edrington, T.S., T. R. Callaway, S. E. Ives, M. J. Engler, T. Welsh, D. Hallford, K. Genovese, R. A. Anderson, and D. J. Nisbet. 2006b. Effect of ractopamine HCL supplementation on fecal shedding of *Escherichia coli* O157:H7 and salmonella in feedlot cattle. *Curr. Microbiol.* 53:340-345.
- Edrington, T. S., R. L. Farrow, G. H. Loneragan, S. E. Ives, M. J. Engler, J. J. Wagner, M. J. Corbin, W. J. Platter, D. Yates, J. P. Hutcheson, R. A. Zinn, T. R. Callaway, R. C. Anderson, and D. J. Nisbet. 2009. Influence of -agonists (ractopamine HCl and zilpaterol HCl) on fecal shedding of *Escherichia coli* O157:H7 in feedlot cattle. *J. Food Prot.* 72:2587-2591.
- Fernández, D., E. M. Rodríguez, G. H. Arroyo, N. L. Padola, and A. E. Parma. 2009. Seasonal variation of Shiga toxin-encoding genes (*stx*) and detection of *E. coli* O157 in dairy cattle from Argentina. *J. Appl. Microbiol.* 106:1260-1267.
- Firkins, J. L., L. L. Berger, N. R. Merchen, and G. C. Fahey, Jr. 1986. Effects of forage particle size, level of feed intake and supplemental protein degradability on microbial protein synthesis and site of nutrient digestion in steers. *J. Anim. Sci.* 62:1081-1094.

- Fox, J. T., J. S. Drouillard, X. Shi and T. G. Nagaraja. 2009. Effects of mucin and its carbohydrate constituents on *Escherichia coli* O157 growth in batch culture fermentations with ruminal or fecal microbial inoculums. J. Anim. Sci. 87:1304-1313.
- Fron, M., H. Madeira, C. Richards, and M. Morrison. 1996. The impact of feeding condensed distillers byproducts on rumen microbiology and metabolism. Anim. Feed Sci. Technol. 61:235-245.
- Greenquist, M. A., J. S. Drouillard, J. M. Sargeant, B. E. Depenbusch, X. Shi, K. F. Lechtenberg, and T. G. Nagaraja. 2005. Comparison of Rectoanal Mucosal Swab Cultures and Fecal Cultures for Determining Prevalence of *Escherichia coli* O157:H7 in Feedlot Cattle. Appl. Environ. Microbiol. 71:6431-6433.
- Ham, G. A., R. A. Stock, T. J. Klopfenstein, E. M. Larson, D. H. Shain, and R. P. Huffman. 1994. Wet Corn Distillers Byproducts Compared with Dried Corn Distillers Grains with Solubles as a Source of Protein and Energy for Ruminants. J. Anim. Sci. 72:3246-3257.
- Heeringa, S., B. West, and P. Berglund. 2010. Applied survey data analysis. Chapman & Hall/CRC., Boca Raton, FL.
- Jacob, M. E., T. R. Callaway, and T. G. Nagaraja. 2009. Dietary interactions and interventions affecting *Escherichia coli* O157 colonization and shedding in cattle. Foodborne Path. Dis. 6:785-792.
- Jacob, M. E., J. T. Fox, S. K. Narayanan, J. S. Drouillard, D. G. Renter, and T. G. Nagaraja. 2008. Effects of feeding wet corn distillers grains with solubles with or without monensin and tylosin on the prevalence and antimicrobial susceptibilities of fecal foodborne pathogenic and commensal bacteria in feedlot cattle. J. Anim. Sci. 86:1182-1190.
- Kleinschmit, D. H., D. J. Schingoethe, K. F. Kalscheur, and A. R. Hippen. 2006. Evaluation of various sources of corn dried grains plus solubles for lactating dairy cattle. J. Dairy Sci., 89:4784-4794.
- Klopfenstein T. J., G. E. Erickson, and V. R. Bremer. 2008. Board-invited review: use of distillers by-products in the beef cattle feeding industry. J. Anim. Sci. 86:1223-1231.
- Laudert, S. B., G. L. Vogel, A. L. Schroeder, W. J. Platter, and M. T. Van Koevinger. 2004. The Effect of Optaflexx on growth performance and carcass traits of steers. Optaflexx Exchange No. 4. Elanco Animal Health, Greenfield, IN.
- Lodge, S. L., R. A. Stock, T. J. Klopfenstein, D. H. Shain, and D. W. Herold. 1997. Evaluation of corn and sorghum distillers byproducts. J. Anim. Sci., 75:37-43.
- Lyte, M., A. K. Erickson, B. P. Arulanandam, C. D. Frank, M. A. Crawford, and D. H. Francis. 1997. Norepinephrine induced growth and expression of virulence associated factors in enterotoxigenic and enterohemorrhagic strains of *Escherichia coli*. Adv. Exp. Med. Biol., 412:331-339.
- Marounek, M., O. Petr, and L. Machanova. 1990. Effect of monensin on *in vitro* fermentation of maize starch by hindgut contents of cattle. J. Agric. Sci. Camb. 115:389-92.
- McAllister, T. A., S. J. Bach, K. Stanford, and T. R. Callaway. 2006. Shedding of *Escherichia coli* O157:H7 by cattle fed diets containing monensin or tylosin. J. Food Prot. 69:2075-2083.
- NADA 095-735, Freedom of Information Summary, Supplemental New Animal Drug Applications. 2006. <http://www.fda.gov/downloads/AnimalVeterinary/Products/ApprovedAnimalDrugProducts/FOIADrugSummaries/ucm064848.pdf> Accessed on 12/16/2009.
- Nagaraja, T. G. and M. B. Taylor. 1987. Susceptibility and resistance of ruminal bacteria to antimicrobial feed additives. Appl. Environ. Microbiol. 53:1620-1625

- Naylor, S. W., J. C. Low, T. E. Besser, A. Mahajan, G. J. Gunn, M. C. Pearce, I. J. McKendrick, D. G. E. Smith, and D. L. Gally. 2003. Lymphoid follicle-dense mucosa at the terminal rectum is the principal site of colonization of enterohemorrhagic *Escherichia coli* O157:H7 in the bovine host. *Infect. Immun.* 71:1505-1512.
- Rangel, J. M., P. H. Sparling, C. Crowe, P. M. Griffin, and D. L. Swerdlow. 2005. Epidemiology of *Escherichia coli* O157:H7 outbreaks, United States, 1982-2002. *Emerg. Infect. Dis.* 11:603-609.
- Schroeder, A. L., D. M. Polser, S. B. Laudert, and G. J. Vogel. 2003. The effect of Optaflexx on growth performance and carcass traits of steers. Optaflexx Exchange No. 1. Elanco Anim. Health, Greenfield, IN.
- Sperandio, V., A. G. Torres, B. Jarvis, J. P. Nataro, and J. B. Kaper. 2003. Bacteria-host communication: The language of hormones. *Proc. Nat. Acad. Sci. U. S. A.* 100:8951-8956.
- Spiehs, M. J., M. H. Whitney, and G. C. Shurson. 2002. Nutrient database from distiller's dried grains with solubles produced from new ethanol plants in Minnesota and South Dakota. *J. Anim. Sci.* 80:2639-2645.
- Van Baale, M. J., J. M. Sargeant, D. P. Gnad, B. M. DeBey, K. F. Lechtenberg, and T. G. Nagaraja. 2004. Effect of forage or grain diets with or without monensin on ruminal persistence and fecal *Escherichia coli* O157:H7 in cattle. *Appl. Environ. Microbiol.* 70:5336-5342.
- Walker, C., X. Shi, M. Sanderson, J. Sargeant, and T. G. Nagaraja. 2010. Prevalence of *Escherichia coli* O157:H7 in gut contents of beef cattle at slaughter. *Foodborne Path. Dis.* 7:249-255.
- Wells, J. E., S. D. Shackelford, E. D. Berry, N. Kalchayanand, M. N. Guerini, V. H. Varel, T. M. Arthur, J. M. Bosilevac, H. C. Freetly, T. L. Wheeler, C. L. Ferrell, and M. Koohmaraie. 2009. Prevalence and level of *Escherichia coli* O157:H7 in feces and on hides of feedlot steers fed diets with or without wet distillers grains with solubles. *J. Food Prot.* 72:1624-1633.
- Yokoyama, M. T., K. A. Johnson, P. S. Dickerson, and W. G. Bergen. 1985. Effect of dietary monensin on the cecal fermentation of steers. *J. Anim. Sci.* 61:469 (Abstr.).

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Agricultural Utilization Research Institute / University of Minnesota

SSTI Product Title: **Impact of Distiller Grains and Glycerin on E. Coli 0157:H7**

Author: Jaderborg, J.P.; . Paulus, D.M; Fink, R.; Diez-Gonzalez, F.; Crawford, G.I.; DiCostanzo, A.

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STI Product Type: Technical Report

Publication Issue Date: 06/30/2012

STI Technical Reporting Period: 07/01/2008 – 6/30/2012

Sponsoring DOE Program Office: EERE

Subject Categories: 09 Biomass Fuels; 99 General and Miscellaneous

Keywords: E. Coli 0157:H7; Distillers Grains; Glycerin; Ethanol byproduct

Description/Abstract:

Ethanol plants and cattle producers create a symbiotic relationship: The use of wet and dry distiller's grains in beef cattle rations provides significant improvement in overall feedlot performance for many producers in Minnesota and the Upper Midwest. Distiller's grain is the coproduct that remains following the distillation of ethanol. It may be dehydrated to produce dried distiller's grain (DDG) which is then commonly used as livestock feed. The use of distiller's grains in livestock rations has been the subject of numerous research projects over the past ten years. Recently published research data conducted at Kansas State University (K-State) has created controversy over the feeding of distiller's grains in beef cattle rations. The research indicates that cattle fed distiller's grain may have an increased probability of *Escherichia coli* O157 in their hindgut. Specifically:

This research assessment was a two part project consisting of feeding trials conducted at the University of Minnesota and an intervention study conducted at Kansas State University. This report is the University of Minnesota portion. This report is a task-level final technical report.

Summary

Two experiments were designed to determine the effect of feeding distillers' grains (DGS) and glycerin on the fecal shedding, colonization and prevalence of *Escherichia coli* O157:H7 (ECO157) in cattle. The specific objectives of this study were to: 1) Assess the impact of feeding dry rolled corn (DRC) or steam flaked corn (SFC) and glycerin (GLY) in the presence of DGS on the fecal shedding and colonization of artificially inoculated calves (Experiment 1); 2) Determine the effects of feeding DGS on the ECO157 prevalence in naturally infected beef cattle (Experiment 2) fed SFC; 3) Assess the impact of feeding glycerin with or without DGS on ECO157 prevalence in naturally infected beef cattle (Experiment 2). In experiment 1, 28 Holstein steer calves (initial BW 353 ± 40 lb) were assigned randomly to one of four

dietary treatment resulting from a 2 x 2 factorial arrangement (DRC vs SFC and GLY vs no GLY) of treatments in a completely randomized design. Diets contained (DM basis): 35% modified distillers grains with solubles, 8% grass hay, 9% supplement, and either 0 or 10% soy glycerin, with the balance of the diet made up of either SFC or DRC. Soy glycerin replaced corn in the 10% GLY treatments. Cattle were inoculated with a dose of 10^{11} CFU per calf with a cocktail of four ECO157 strains resistant to two specific antibiotics (nalidixic acid and rifampin) at the start of the 20-d experiment. Individual fecal samples from each animal were collected three times weekly over the course of the experiment. No significant differences ($P \geq 0.05$) in ECO157 concentrations were found between treatments. Results from this experiment indicate that neither soy glycerin inclusion nor corn processing method stimulated the shedding of artificially inoculated ECO157. In Experiment 2, 48 crossbred yearling cattle (21 steers and 27 heifers) averaging 838 lb initial BW were blocked by sex and allotted to one of 48 individual feed bunks. Nine animals were removed from the study; one for health reasons, and the others were confirmed outliers resulting from feed stealing. Cattle were fed one of four dietary treatments resulting from the 2 x 2 factorial arrangement of DGS at 0% or 35% of diet DM (resulting DGS concentrations were 40% of diet DM) and GLY at 0% or 10% of diet DM in SFC (36.5 lb/bu flake density) and grass hay (10% of diet DM) diets: 1) DGS and no GLY, 2) no DGS and no GLY, 3) DGS and GLY, 4) no DGS and GLY. Cattle for this study were selected from a larger population so the number of ECO157 positive for each dietary treatment group was 50%. After 14 d on feed, number of cattle testing ECO157 shedding ceased. Dry matter intake was greater ($P < 0.003$) for cattle fed diets containing DGS than for those fed diets without DGS (22.0 vs. 18.6 lb/d). Carcass-adjusted ADG (3.11 ± 0.53 lb) was not affected ($P > 0.10$) by feeding either co-product. A tendency ($P = 0.06$) for greater carcass-adjusted F:G (6.15 vs. 7.25) was observed for cattle consuming diets without DGS (analyzed as gain-to-feed). Carcass-adjusted F:G was similar ($P > 0.10$) for cattle fed GLY and those fed no GLY (6.84 vs. 6.57). Hot carcass weight (816 ± 62 lb), ribeye area (12.8 ± 1.0 sq in), 12th rib fat depth (0.551 ± 0.146 in), yield grade (2.74 ± 0.64) and marbling score (430 ± 60) were not ($P > 0.10$) affected by dietary treatment. However, KPH was greater ($P < 0.01$) for cattle fed DGS diets than for those fed diets without DGS (2.71% vs. 2.42%). Iterated ME values of diets containing DGS were 13% lower ($P < 0.05$) than those without DGS. Neither corn distillers grains, nor soy glycerin, in steam-flaked corn-based diets supported shedding of *E. coli* O157:H7. At the inclusion levels in this study, soy glycerin had a similar energy value and DGS a lesser energy value than SFC.

No Intellectual Property or limitations

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Impact of Distillers' Grains and Glycerin on Cattle Fecal Shedding of *Escherichia coli* O157:H7

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Summary

Two experiments were designed to determine the effect of feeding distillers' grains (DGS) and glycerin on the fecal shedding, colonization and prevalence of *Escherichia coli* O157:H7 (ECO157) in cattle. The specific objectives of this study were to: 1) Assess the impact of feeding dry rolled corn (DRC) or steam flaked corn (SFC) and glycerin (GLY) in the presence of DGS on the fecal shedding and colonization of artificially inoculated calves (Experiment 1); 2) Determine the effects of feeding DGS on the ECO157 prevalence in naturally infected beef cattle (Experiment 2) fed SFC; 3) Assess the impact of feeding glycerin with or without DGS on ECO157 prevalence in naturally infected beef cattle (Experiment 2). In experiment 1, 28 Holstein steer calves (initial BW 353 ± 40 lb) were assigned randomly to one of four dietary treatment resulting from a 2 x 2 factorial arrangement (DRC vs SFC and GLY vs no GLY) of treatments in a completely randomized design. Diets contained (DM basis): 35% modified distillers grains with solubles, 8% grass hay, 9% supplement, and either 0 or 10% soy glycerin, with the balance of the diet made up of either SFC or DRC. Soy glycerin replaced corn in the 10% GLY treatments. Cattle were inoculated with a dose of 10^{11} CFU per calf with a cocktail of four ECO157 strains resistant to two specific antibiotics (nalidixic acid and rifampin) at the start of the 20-d experiment. Individual fecal samples from each animal were collected three times weekly over the course of the experiment. No significant differences ($P \geq 0.05$) in ECO157 concentrations were found between treatments. Results from this experiment indicate that neither soy glycerin inclusion nor corn processing method stimulated the shedding of artificially inoculated of ECO157. In Experiment 2, 48 crossbred yearling cattle (21 steers and 27 heifers) averaging 838 lb initial BW were blocked by sex and allotted to one of 48 individual feed bunks. Nine animals were removed from the study; one for health reasons, and the others were confirmed outliers resulting from feed stealing. Cattle were fed one of four dietary treatments resulting from the 2×2 factorial arrangement of DGS at 0% or 35% of diet DM (resulting DGS concentrations were 40% of diet DM) and GLY at 0% or 10% of diet DM in SFC (36.5 lb/bu flake density) and grass hay (10% of diet DM) diets: 1) DGS and no GLY, 2) no DGS and no GLY, 3) DGS and GLY, 4) no DGS and GLY. Cattle for this study were selected from a larger population so the number of ECO157 positive for each dietary treatment group was 50%. After 14 d on feed, number of cattle testing ECO157 shedding ceased. Dry matter intake was greater ($P < 0.003$) for cattle fed diets containing DGS than for those fed diets without DGS (22.0 vs. 18.6 lb/d). Carcass-adjusted ADG (3.11 ± 0.53 lb) was not affected ($P > 0.10$) by feeding either co-product. A tendency ($P = 0.06$) for greater carcass-adjusted F:G (6.15 vs. 7.25) was observed for cattle consuming diets without DGS (analyzed as gain-to-feed). Carcass-

adjusted F:G was similar ($P > 0.10$) for cattle fed GLY and those fed no GLY (6.84 vs. 6.57). Hot carcass weight (816 ± 62 lb), ribeye area (12.8 ± 1.0 sq in), 12th rib fat depth (0.551 ± 0.146 in), yield grade (2.74 ± 0.64) and marbling score (430 ± 60) were not ($P > 0.10$) affected by dietary treatment. However, KPH was greater ($P < 0.01$) for cattle fed DGS diets than for those fed diets without DGS (2.71% vs. 2.42%). Iterated ME values of diets containing DGS were 13% lower ($P < 0.05$) than those without DGS. Neither corn distillers grains, nor soy glycerin, in steam-flaked corn-based diets supported shedding of *E. coli* O157:H7. At the inclusion levels in this study, soy glycerin had a similar energy value and DGS a lesser energy value than SFC.

Introduction

Escherichia coli O157:H7 (**ECO157**) is common foodborne pathogen that is naturally present in the digestive tract of cattle. It can contaminate beef during cattle harvest. Concern with ECO157 has led to a great deal of investigation into what causes an increase or decrease in ECO157 prevalence in cattle. Diet, environment, and production practices have all been considered and examined for their effect on ECO157 prevalence in cattle.

Results from previous studies indicate that there is a link between corn processing method and ECO157 prevalence in a beef cattle herd. Feeding steam flaked corn (**SFC**) resulted in a greater amount of ECO157 fecal shedding by beef cattle than when feeding dry rolled corn (**DRC**) (Depenbusch et al., 2008). Scientists have discovered that the hindgut of cattle is hospitable for ECO157. Thus, changes to the hindgut environment will have a greater impact on ECO157 prevalence than changes to the rumen environment. More processed corn, such as SFC, is mostly digested in the rumen; thereby, limiting concentration of starch reaching the small intestine. Lower starch concentrations in the small and large intestine are thought to lead to greater pH and lower VFA concentrations; conditions that support ECO157 growth. This theory appears to apply to corn distillers grains (**DGS**) also. Percentage of cattle positive for ECO157 in fecal or hide samples was greater for those fed 40% wet DGS than those fed 0% wet DGS (Wells et al., 2009). Whether soy glycerin (**GLY**), a co-product that is mainly digested in the rumen, impacts ECO157 shedding is not known.

Increased production of both DGS and GLY over the last ten years coupled with recent spikes in corn grain prices led to greater incorporation of these co-products in finishing diets. U.S. biodiesel production has grown rapidly to over 750 million gallons in 2008. This led to production of 564 million pounds of GLY allowing feedlot owners access to a potentially inexpensive feedstuff that is needed during times when corn prices increase. Glycerin's liquid form gives versatility to this co-product while helping maintain diet integrity. In a recent experiment, feeding glycerin at 2% DM of diet improved gain and feed efficiency in feedlot heifers (Parsons et al., 2009). In a similar study Van Cleef et al. (2011) reported no effect on ADG from feeding GLY up to 15% diet DM, but a linear decrease in DMI with a concomitant improvement in gain efficiency was observed. However, while glycerin inclusion has been studied in SFC diets; there have been no studies evaluating this co-product when fed in DGS.

Therefore, our objectives were to: 1) Assess the impact of feeding dry rolled corn DRC or steam flaked corn SFC and glycerin GLY in the presence of DGS on the fecal shedding and colonization of artificially inoculated calves (Experiment 1); 2) Determine the effects of feeding DGS on the ECO157 prevalence in naturally infected beef cattle (Experiment 2) fed SFC; 3) Assess the impact of feeding glycerin with or without DGS on ECO157 prevalence in naturally infected beef cattle (Experiment 2).

Materials and Methods

Experiment 1. This experiment was conducted at the University of Minnesota Rosemount Research and Outreach Center feedlot at UMore Park in Rosemount, MN. Twenty-four Holstein steers (initial BW 353 ± 40 lb) were arranged randomly into one of four treatments with a 2 x 2 factorial arrangement of treatments. Cattle were housed in groups in an isolation facility with no physical contact between cattle groups and no contact with the outside environment.

Treatment diets contained (DM basis): 35% modified distillers grains with solubles (47% moisture; Western Wisconsin Energy, Boyceville, WI), 8% grass hay, 9% supplement, and either 0 or 10% soy glycerin, with the balance of the diet made up of either SFC (36.5 lb/bu) or DRC. Soy glycerin replaced corn in the 10% soy glycerin treatments. Cattle were fed *ad libitum* once daily at 0900 and were acclimated to the treatments diets prior to the start of the experiment.

On d 0 of the experiment cattle were fecal sampled. Following fecal sampling, the cattle were inoculated orally with a dose of 10^{11} CFU/calf cocktail of four *E. coli* O157:H7 strains resistant to two specific antibiotics (nalidixic acid and rifampin). Cattle were fecal sampled three times weekly beginning on d 1 of the experiment. In total the experiment lasted 20 d. Fecal samples were examined for concentrations of *E. coli* O157:H7 determined through enumeration on selective medium and reported in log CFU/g. Testing was sensitive for samples with *E. coli* O157:H7 concentrations greater than 1.0 log CFU/g.

Data were analyzed with the Proc Mixed procedure of SAS 9.2 with an autoregressive covariance structure. Fixed effects included treatment and day. Statistical significance was declared with *P*-values < 0.05, and trends were discussed with *P*-values between 0.05 and 0.10. Samples with *E. coli* O157:H7 concentrations less than 1.0 log CFU/g were reported as 1.0 log CFU/g for analytical procedures.

Experiment 2. This experiment was conducted at the University of Minnesota Rosemount Research and Outreach Center feedlot at UMore Park in Rosemount, MN. Forty-eight Charolais-cross, 21 steer and 27 heifer calves (initial BW 838 lb) were blocked by sex and assigned randomly to bunks in a Calan gate individual feeding system. The Calan gate system consisted of 48 bunks (22 linear in bunk space per animal) in four pens (12 bunks/pen). Nine animals were removed from the study; one for health reasons, and the others were confirmed outliers resulting

from feed stealing. Dietary treatments were formulated to contain either modified DGS (Western Wisconsin Energy, Boyceville, WI) at 0% or 35% of dietary DM and glycerin at 0% or 10% of diet DM in SFC (36.5 lb/bu flake density) and grass hay (10% of diet DM) diets: 1) DGS and no glycerin, 2) no DGS and no glycerin, 3) DGS and glycerin, 4) no DGS and glycerin. Diets contained 16.5% CP, 0.67 Mcal/lb NEg DM, 0.75% Ca, 0.47% P, and from 0.17% to 0.25% S (Table 1). Resulting DGS inclusion averaged 40% as its DM content was greater than anticipated. Treatments were assigned randomly within pen, for a total of 12 replications per treatment. Cattle were fed ad-libitum once daily at 0800 and feed refusals were collected daily prior to feeding. A bunk score of 0 (scale 0, slick, to 4, full) for two consecutive days elicited a 0.5-lb DM increase. Dry matter intake was calculated from DM offered and refusal collections.

Cattle were implanted on d 56 with a Revalor 200 (200 mg of trenbolone acetate and 20 mg of estradiol). Cattle were weighed every 28 d, and initial body weight was taken after a 16-h period without access to feed and water. Cattle were harvested in two harvest groups on d 124 and d 173 when determined to have 0.5 in of backfat at the 12th rib. All cattle were harvested at PM Beef in Windom, MN and carcass data were collected by University and USDA personnel. Carcass data collection included dressing percentage, HCW, marbling score, 12th rib fat thickness, ribeye area, kidney, pelvic, and heart fat (KPH), USDA yield grade, and USDA quality grade. Dressing percentage was calculated as the sum of the HCW from each block divided by the cumulative live BW of each block as measured at the packing plant prior to harvest.

Based on visual behavior observation after feed was delivered, the presence of outlier DMI data generated by cattle that stole or had feed stolen was tested using the Regression procedure of SAS. The Regression procedure led to the discovery of eight outliers which removed from the study. Data were then analyzed using Mixed procedure of SAS with animal being experimental unit. Fixed effects included DGS and soy glycerin concentrations, with interaction affect between the two. Individual animal was the random effect. Effects were considered significant when *P* values were less than or equal to 0.05 and were considered trends when *P* values were between 0.05 and 0.10. Iterated ME values of the diet were calculated using iterative procedures of the NRC (2000) using DMI and ADG.

Results and Discussion

Experiment 1. Results are displayed in Figure 1. Initial *E. coli* O157:H7 concentrations were less than 1.0 log CFU/g for all treatments. After inoculation, *E. coli* O157:H7 concentrations spiked to 3.6 log CFU/g or higher for all treatments. After d 1 *E. coli* O157:H7 concentrations decreased for the rest of the study. On the final d of the experiment *E. coli* O157:H7 concentrations were less than 1.0 log CFU/g for all treatments. No significant differences (*P* = 0.998) were observed between treatments throughout the entire experiment. However, *E. coli*

O157:H7 concentrations varied ($P \leq 0.005$) significantly between days with the highest *E. coli* O157:H7 concentrations occurring on d 1 for all treatments.

Based on the results of this study, it is clear that the dietary inclusion of processed corn or soy glycerin in feedlot diets has no effect on the shedding of *E. coli* O157:H7 in steers. Additionally, it is clear that the dietary ingredients utilized in this experiment do not contribute to the survival of *E. coli* O157:H7 in the gastrointestinal tract of feedlot steers. In fact, the ingredients utilized in this study may in fact lead to a reduction in *E. coli* O157:H7 concentrations in the gastrointestinal tract of feedlot steers.

Overall the results presented in this study are contradictory to previous studies that have found that specific forms of processed corn can have an impact on the survival of *E. coli* O157:H7 in the gastrointestinal tract of feedlot steers. This suggests that environmental factors may play a larger role in *E. coli* O157:H7 survival than diet. However, more research is needed to determine what other factors contribute to *E. coli* O157:H7 survival in cattle.

Experiment 2. Treatment means for initial and final BW, ADG, DMI, and feed:gain are shown in (Table 2). Feed-to-gain ratio was analyzed as G:F. The interactive effect between DGS and soy glycerin was not significant ($P > 0.10$). Dry matter intake was greater ($P < 0.003$) for cattle fed diets containing DGS than for those fed diets without DGS (22.0 vs. 18.6 lb/d; Table 2). Final BW was not significant ($P < 0.10$) among treatments. Carcass-adjusted ADG (3.11 ± 0.53 lb) was not affected ($P > 0.10$) by feeding either co-product. A tendency ($P = 0.07$) for greater carcass-adjusted F:G (6.15 vs. 7.25) was observed for cattle consuming diets without DGS. Carcass-adjusted F:G was similar ($P > 0.10$) for cattle fed glycerin and those fed no glycerin (6.84 vs. 6.57).

Hot carcass weight (816 ± 62 lb), ribeye area (12.8 ± 1.0 sq in), 12th rib fat depth (0.551 ± 0.146 in), yield grade (2.74 ± 0.64) and marbling score (430 ± 60) were not ($P > 0.10$) affected by dietary treatment (Table 3). However, KPH was greater ($P < 0.01$) for cattle fed DGS diets than for those fed diets without DGS (2.71% vs. 2.42%).

Iterated ME values of diets containing DGS were 13% lower ($P < 0.05$) than those without DGS (Figure 1). At the inclusion levels in this study, soy glycerin had a similar energy value and DGS a lesser energy value than SFC. With these results the economics of what purchasing soy glycerin compared to SFC in your area should be considered.

Literature Cited

- Depenbusch, B. E., T. G. Nagaraja, J. M. Sargeant, J. S. Drouillard, E. R. Loe, and M. E. Corrigan. 2008. Influence of processed grains on fecal pH, starch concentration, and shedding of *Escherichia coli* O157 in feedlot cattle. *J. Anim. Sci.* 86:632-639.
- Fox, J.T., B. E. Depenbusch, J. S. Drouillard and T. G. Nagaraja. 2007. Dry-rolled or steam-flaked grain-based diets and fecal shedding of *Escherichia coli* O157 in feedlot cattle. *J. Anim. Sci.* 85:1207-1212.
- NRC. 2000. Nutrient Requirements of Beef Cattle (7th Rev. Ed.). National Academy Press. Washington, D.C.
- Parsons, G. L., M. K. Shelor, and J. S. Drouillard. 2009. Performance and carcass traits of finishing heifers fed crude glycerin. *J. Anim. Sci.* 87:653-657.
- van Cleef, E. H. C. B., S. Uwituze, C. L. Van Bibber, K. A. Miller, C. C. Aperce, K. L. Blaine, J. J. Higgins, and J. S. Drouillard. 2011. Effects of crude glycerin in byproducts diets on performance and carcass characteristics of feedlot cattle. *J. Anim. Sci.* 89(E-Suppl. 1): 124(Abstr.).
- Wells, J. E. S. D. Shackelford, E. D. Berry, N. Kalchayanand, M. N. Guerini, V. H. Varel, T. M. Arthur, J. M. Bosilevac, H. C. Freetly, T. L. Wheeler, C. L. Ferrell, And M. Koohmaraie. 2009. Prevalence and level of *Escherichia coli* O157:H7 in feces and on hides of feedlot steers fed diets with or without wet distillers grains with solubles. *J. Food Prot.* 72:1624-1633.

Table 1. Ingredient composition and nutrient analysis (% DM-basis) of finishing diets.

	Treatment ¹			
	DGS Y GLY N	DGS N GLY N	DGS Y GLY Y	DGS N GLY Y
Steam Flaked Corn ²	44.5	78.8	35.3	67.1
Modified DGS ³	41.0	0.0	40.7	0.0
Soy Glycerin	0.0	0.0	9.9	11.0
Geass Hay	10.6	11.7	10.3	11.6
Liquid mineral	3.6	4.0	3.6	3.9
Liquid protein	0.0	5.3	0.0	6.1
Myco CURB ⁴	0.2	0.2	0.2	0.2
DM, %	69.8	80.7	71.4	78.1
CP, %	17.6	13.8	16.4	13.7
ADF, %	15.2	9.4	11.8	11.7
Ca, %	0.74	0.77	0.89	0.82
P, %	0.47	0.35	0.48	0.39
S, %	0.25	0.13	0.22	0.17

¹ Treatment diets included: DGS Y GLY N, containing 40% distillers grains and 0% soy glycerin, DGS N GLY N, containing 0% distillers grains and 0% soy glycerin, DGS Y GLY Y, containing 40% distillers grains and 10% soy glycerin, DGS N GLY Y, containing 0% distillers grains and 10% soy glycerin.

² Flake density = 36.5 lb/bu.

³ Modified distillers grains with solubles (48% DM; Western Wisconsin Energy, Boyceville, WI).

⁴ Mold inhibitor (Kemin Industries, Inc., Des Moines, IA).

Table 2. Main effects of feeding distillers grains or glycerin on feedlot performance

	DGS¹				Glycerin²			
	No	Yes	SEM³	P-Value	No	Yes	SEM³	P-Value
Initial BW, lb	851	817	18	0.21	831	838	18	0.77
DMI, lb/d	18.6	22.0	0.7	< 0.01	21.0	19.6	0.7	0.16
ADG, lb	3.13	3.07	0.11	0.73	3.19	3.01	0.11	0.28
Feed:Gain	6.15	7.25	0.33	0.07	6.57	6.84	0.33	0.28
Final BW, lb	1,293	1,268	14	0.42	1,286	1,275	21	0.74

¹ DGS treatment diets included: No, containing 0% distillers grains, Yes, containing 40% distillers grains.

² Glycerin treatment diets included: No, containing 0% soy glycerin, and Yes, containing 10% soy glycerin.

³ Standard error of least square means.

Table 3. Main effects of feeding distillers grains or glycerin on carcass traits

	DGS¹		SEM³	P-Value	Glycerin²		SEM³	P-Value
	No	Yes			No	Yes		
HCW, lb	822	807	13	0.43	818	812	14	0.74
12th rib back fat, in	0.54	0.56	0.03	0.63	0.56	0.55	0.03	0.87
Ribeye area, sq. in	12.89	12.73	0.24	0.62	12.76	12.86	0.23	0.75
KPH ⁴	2.4	3.0	0.1	0.01	2.5	2.6	0.1	0.42
YG ⁵	2.6	2.8	0.1	0.22	2.7	2.6	0.1	0.57
Marbling score ⁶	424	434	14	0.63	435	424	20	0.62

¹ DGS treatment diets included: No, containing 0% distillers grains, Yes, containing 40% wet distillers grains.

² Glycerin treatment diets included: No, containing 0% soy glycerin, and Yes, containing 10% soy glycerin.

³ Standard error of least square means.

⁴ Kidney, pelvic, and heart fat.

⁵ USDA yield grade.

⁶ where 400 = small⁰⁰, 500 = modest⁰⁰.

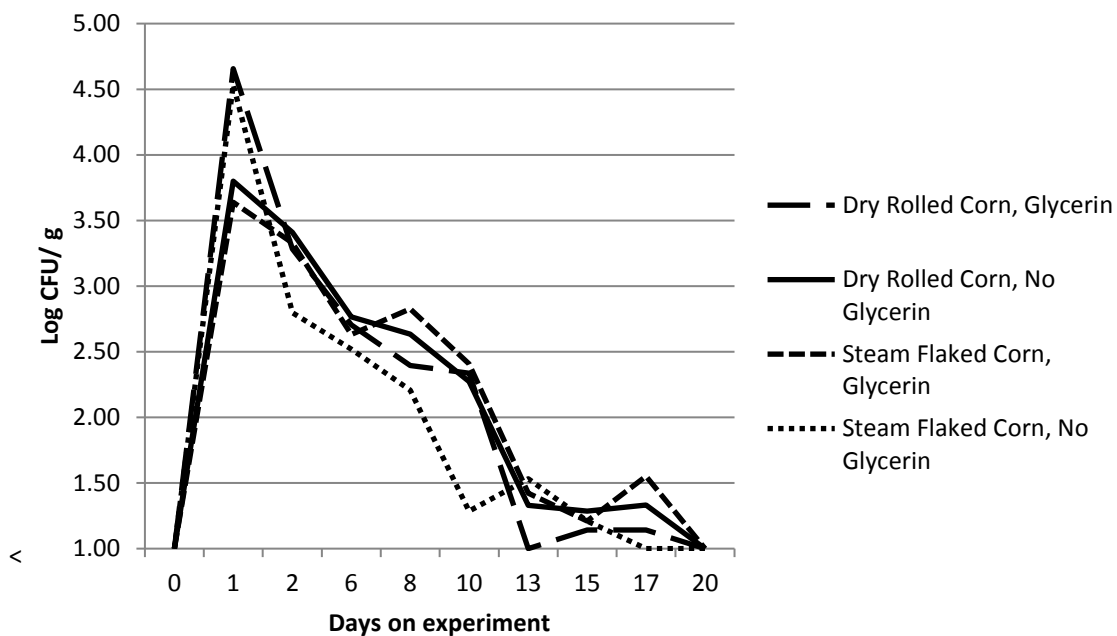


Figure 1. Effect of soy glycerin, steam flaked corn, and dry rolled corn on *Escherichia coli* 0157:H7 concentrations in fecal samples.

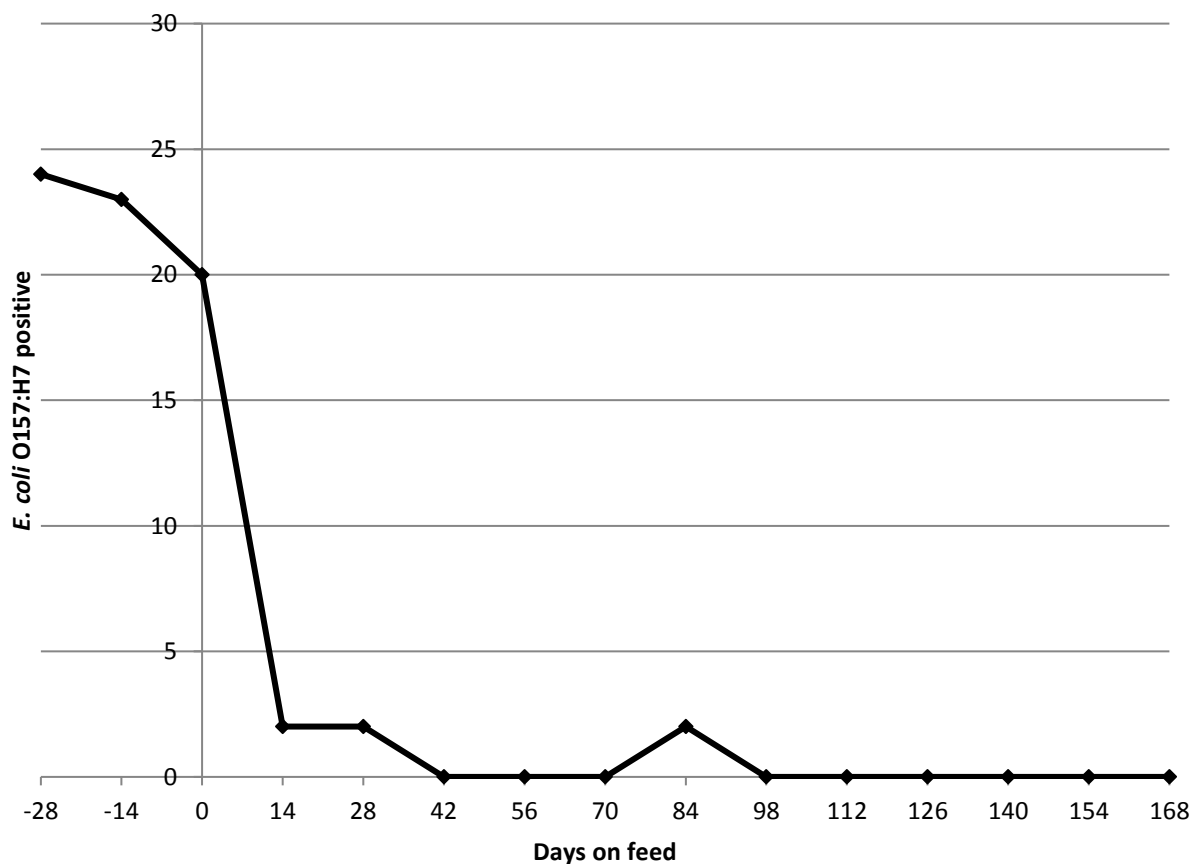


Figure 2. Prevalence of *Escherichia coli* 0157:H7 in fecal samples of all steers in Experiment 2 (treatment effects were not significant $P > 0.05$).

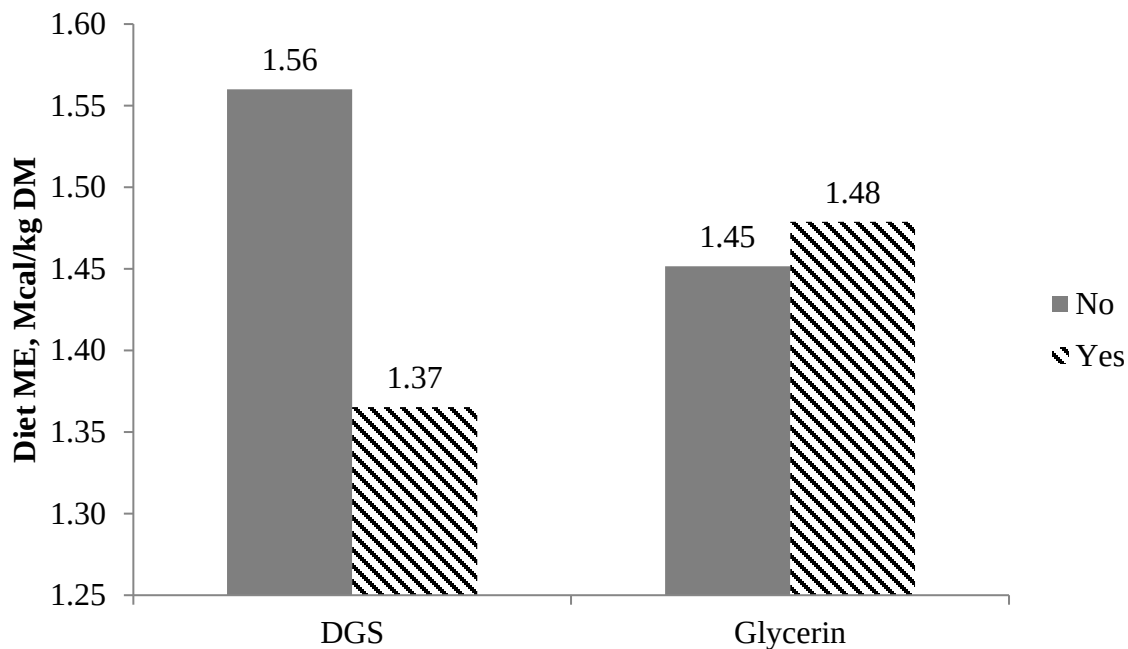


Figure 3. Iterated ME values of diets containing DGS were 13% lower ($P < 0.05$) than those without DGS. At the inclusion levels in this study, soy glycerin had a similar energy value and DGS a lesser energy value than SFC. DGS treatment diets included: No, containing 0% modified distillers grains, Yes, containing 40% modified distillers grains. Glycerin treatment diets included: No, containing 0% soy glycerin, and Yes, containing 10% soy glycerin.

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Description/Abstract:

This research project focused on the identification the next generation of technologies in renewable energy value-added agricultural processing. The research was designed to add value to agricultural commodities employing emerging new innovations for renewable energy processes and identification new processes, products and technologies utilizing agricultural commodities.

This report is a task-level final technical report.

Summary:

Based on demand/market potential, economic feasibility, stage of development and strength of institutional support, Informa Economics, Inc. ("Informa") narrowed down a list of more than 100 emerging soybean products and to 8 of the most promising for soybean, considered to have the greatest potential to add significant value to Minnesota's soybean commodity production. However, as with the potential of any biobased product or technology, the development of these emerging soybean products and technologies will be heavily reliant on future market price environments (especially for petroleum) and government policies. This report identifies what the contractor believes are the top 8 products and technologies for soybeans at the time of publishing.

No Intellectual Property or limitations

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Organization: Agricultural Utilization Research Institute

A Study Assessing the Opportunities and Potential of Soybean Based Products and Technologies

Developed by



For

The Agricultural Utilization Research Institute

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Disclaimer

This report was produced for Agricultural Utilization Research Institute (AURI). Informa Economics, Inc. ("Informa") has used the best and most accurate information available to complete this study. Informa is not in the business of soliciting or recommending specific investments. The reader of this report should consider the market risks inherent in any financial investment opportunity. Furthermore, while Informa has extended its best professional efforts in completing this analysis, the liability of Informa to the extent permitted by law, is limited to the professional fees received in connection with this project.

I. Executive Summary

Based on demand/market potential, economic feasibility, stage of development and strength of institutional support, Informa Economics, Inc. ("Informa") narrowed down a list of more than 100 emerging soybean products and technologies to 8 of the most promising, considered to have the greatest potential to add significant value to Minnesota's soybean commodity production. However, as with the potential of any biobased product or technology, the development of these emerging products and technologies will be heavily reliant on future market prices (especially for petroleum) and government policies. The following are what Informa considers to be the top 8 products and technologies for soybeans at this point in time.

A. Renewable Diesel

Renewable diesel is a diesel substitute derived from any triglyceride feedstock (such as soybean oil) based on conventional hydroprocessing technology. Unlike biodiesel, renewable diesel replicates the chemical structure of its diesel counterpart, therefore working seamlessly with existing distribution infrastructures, storage systems, and engines. Renewable diesel also has better cold-flow properties than biodiesel.

One significant advantage of this process is its ability to utilize a wide array of input; as free fatty acids (FFAs) can be completely converted to biofuel. The process' energy balance, however, is reportedly less favorable than conventional transesterification, implying higher processing costs. Still, the processing cost difference with transesterification is expected to be relatively low and is more than offset by the compatibility with existing distribution infrastructures. Renewable diesel can be pipelined, whereas biodiesel is generally either trucked or railed.

Three companies have developed standalone hydrotreating processes: Neste Oil, Syntroleum, and UOP/Eni. The first standalone U.S. renewable diesel plant, Dynamic Fuels LLC, a joint venture between Syntroleum and Tyson Foods, is expected to become operational in 2010.

B. Enzymatic Transesterification

Enzymatic transesterification is a novel approach to the conventional chemical transesterification process used to produce biodiesel. Although still under development, the process holds considerable potential considering its advantages over its chemical counterpart:

- Compatibility with feedstocks of various quality (the process converts FFAs);
- Fewer process steps;
- Higher quality of glycerin;
- Improved phase separation (no emulsification from soap); and
- Reduced energy consumption and wastewater volumes.

Still, a number of hurdles need to be overcome before enzymatic transesterification becomes commercially available. Currently the two biggest problems researchers are examining deal with the reaction speed and enzyme durability. Furthermore, the cost of the enzyme needs to be lowered in order to make the process cost competitive.

Overall, progress is being made and it is expected that the process could become cost competitive relative to chemical transesterification within three years. Other than some efforts done by the USDA Agricultural Research Service (“ARS”), most of the research is being conducted abroad, especially in Europe and Asia. Currently, the largest private company involved in enzymatic transesterification is Novozymes.

C. Soy-Based Polyols

Polyols are chemical building blocks used primarily as reactants to make polymers, polyurethanes in particular. These chemical compounds have historically been produced using petroleum-based feedstocks but are now increasingly made from vegetable oils. Natural oil polyols (NOPs) offer multiple advantages over their petroleum-based counterparts. Specifically, their use results in significant reductions in greenhouse gas (GHG) and volatile organic compounds (VOCs) emissions.

Since their initial development, NOP technologies have overcome the problems of consistency and odor that plagued the first generations and now offer products with performance that rivals petroleum-based polyols. NOPs are now used in a number of polyurethane foam applications including furniture, bedding and flooring products.

The United Soybean Board estimates the annual North American product demand for polyols represents 3.4 billion pounds, with a conservative estimate of the potential for soy-oil-based polyols of about 600 to 800 million pounds (2006 estimates). The market for NOPs has great growth potential if prices for petroleum rise as the economy rebounds, and as manufacturers become more eco-friendly.

Several companies including Cargill, The Dow Chemical Company, Urethane Soy Systems Co. are already involved in the manufacturing of these compounds.

D. Epichlorohydrin

Epichlorohydrin is an epoxy raw material, increasingly used in applications in the electronics, automotive, aerospace and windmill sectors. It is traditionally derived indirectly by reacting propylene with chlorine. The process, however, is somewhat inefficient due to the formation of unwanted chlorinated organics that are expensive to dispose of. New glycerin-to-epichlorohydrin technologies, however, reduce energy consumption by about one-third, generate less than 1/10th of the wastewater and considerably less salt and chlorinated organics, when compared to traditional production processes. Until recently, however, this pathway was uneconomical due to the high price of glycerin.

According to information released by Solvay and Dow in 2007, the demand for epichlorohydrin has significantly outpaced production and there is significant growth potential, especially in regions with large biodiesel/glycerin production like Europe or the U.S. It is important to stress, however, that since 2008 a number of chemical firms that had unveiled plans to use glycerin as a feedstock for the production of chemicals have either shelved or delayed projects. Indeed, although glycerin production has increased in recent years, glycerin has proven to be very volatile with large price swings, and there are concerns in picking suppliers as a number of biodiesel facilities in the U.S. have shut down. Dow Chemical, Solvay SA and Spolchemie have announced plans to produce epichlorohydrin from glycerin.

E. Soy-Based Wood Adhesive

The use of soy-based adhesives is not *per se* new to the chemical industry, as they were first studied in the 1920s and 1930s. Nevertheless, poor functional properties and price competitiveness at the time relative to petroleum-based adhesives limited their use.

Today, phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins enjoy a dominant place in the wood adhesive market. Nevertheless, environmental and health concerns along with rising costs for resins have prompted a resurgence of interest in developing new soy-based products. An additional factor supporting the growing adoption of soy-based adhesives has been the passage in California of a law limiting the level of formaldehyde that can be emitted from interior panel products. Since companies manufacturing wood adhesives often cannot modify their products solely for California, the California rule is rapidly becoming a national standard, supporting the growth of soy-based adhesives.

Companies like Hexion Specialty Chemicals, Ashland/Heartland, and Eka Chemicals have commercialized several soy-based glues. These glues generally perform at least as well as their petroleum-based counterparts.

Out of the 3.72 billion lbs of wood adhesives estimated to have been used in the U.S. in 2006, 40-50 million pounds of soy-based glue systems are estimated to be in use. In the next few years, the United Soybean Board expects that soy-based wood adhesives could account for as much as 20% of the U.S. market.

F. High-Oil Soybeans

New high-oil soybean varieties have the potential to provide a significant increase in vegetable oil production and to help processors meet the growing demand for vegetable oil for food and bio-fuel. The prospect of increasing the oil content in soybeans is especially appealing since it has the potential to add value to soybean production considering that most new soybean applications are focused on the oil part as opposed to the protein.

Monsanto's Renessen joint venture with Cargill is currently researching a high-oil soybean variety that could increase oil content by 3% to 5%, without a loss in protein or grain yield. The first generation of the new variety is projected to be commercialized within 2-4 years and is thought to have an acreage potential of 15-40 million acres. The second generation is in a much earlier phase of development but could be released within 10 years.

G. High Stability Oil Soybeans

The phasing out of partial hydrogenation by food processors following the move away from *trans* fatty acids in food has generated a strong demand for highly stable vegetable oils. One solution brought forward by seed developers has been to develop oilseeds with a low content in polyunsaturated fatty acids that are prone to oxidation and that adversely impact the shelf-life of the oil.

The first improved trait brought to the marketplace was low-linolenic varieties. Asoyia, Monsanto and Pioneer all have released such value-added soybean varieties. Nevertheless, although more stable than conventional soybean oil, the oil from low-linolenic soybeans is still prone to rancidity and is not well suited for deep frying applications. As a result, seed companies have developed mid- and high-oleic varieties that have superior oxidative and flavor stability. Asoyia was the first seed company to release a mid-oleic/low-linolenic soybean variety in 2008, followed in July 2009 by Pioneer, which released Plenish, a brand of high oleic soybean oil. Monsanto is expected to commercialize Vistive III, a line of mid-oleic/low-linolenic/low saturates in the next few years.

With reported premiums as high as \$0.60/bu, these soybeans offer farmers a great way to diversify and earn extra profit.

There were approximately 1.6 million acres of low-linolenic soybeans grown in the U.S. in 2007/08. Although 2008/09 acreage was disappointing due mainly to the limited performance of low-linolenic oil, the recent release of mid- and high-oleic soybean varieties is expected to significantly increase the demand for high-stability soybean oil. For instance, Monsanto estimates the acreage potential in the U.S. for its Vistive III soybean variety at 10-20 million acres.

H. Aquaculture Feed

The global aquaculture industry is expanding steadily, averaging 6.6% growth over the past 10 years (1998-2007). As aquaculture keeps growing, so does the demand for protein meal. Fishmeal is the major protein source for aquaculture, but as aquaculture production outpaces fishmeal production, some are concerned fishmeal availability will constrain the expansion of the industry. As a result, researchers, aquaculture producers and feed manufacturers have been looking at alternative protein sources to replace fishmeal in diets.

Soybean meal can be used in aquaculture feed but anti-nutritional factors that reduce fish performance, particularly at higher inclusion levels, and in carnivorous fish species have limited its adoption. Contrary to soybean meal, however, soy protein concentrates (SPC) do not contain these high levels of anti-nutritional factors and can be utilized at higher inclusion rates. Consequently, SPC have the potential to play a major role in the aquafeed market

It is estimated that 3.1 million tonnes of fishmeal are currently consumed by the aquaculture market in the world. The current consensus is that SPC could account for 10-30% of the protein meal used in aquaculture feed. The U.S. Soybean Export Council estimates that, conservatively, the inclusion rate of SPC in aquafeed could reach 1 million tonnes.

There are currently only a few SPC producers in the U.S.: Cargill, ADM and Solae, with an additional player, Hamlet Protein, considering establishing a plant in Iowa.

II. Introduction

The Agricultural Utilization Research Institute (“AURI”) commissioned Informa Economics, Inc. (“Informa”) to assess and identify those existing and emerging products and technologies (both domestic and international) associated with the biobased economy that will boost economic opportunities for the corn and soybean agricultural sectors in the United States and the State of Minnesota. The overarching objective of the project was to specify eight products or technologies for each commodity which would likely add value to the corn and soybean complexes over the next ten years. This project has been achieved by conducting a blend of desk research (review of the literature) and targeted interviews, by phone and in-person, with the companies that are producing the biobased products and the scientists and technology leaders that are conducting ground-breaking research in the ever-evolving biobased economy. In the end, this study provides AURI with recommendations regarding which products and technologies show the most promise, thereby laying the foundation as a roadmap which will serve as valuable input to AURI in their strategic planning processes.

A. Report Layout

This introductory section precedes two distinct reports that have been prepared for AURI. The two distinct reports are the analyses, findings and recommendations for the biobased products and technologies for the respective commodities of corn and soybeans. The “corn report” and “soybean report” are distinct and stand alone from each other. The role of this introductory section is to “set the stage” for each of the reports by discussing the project methodology and process flow and presenting a general overview of the biobased and energy economies. This overview should provide the reader a framework from which to better appreciate the opportunities and complexities of the technologies and products that are discussed in the corn and soybean reports.

B. Project Methodology and Process Flow

The biobased economy is a rapidly changing environment where government policies combined with volatile commodity prices can dramatically affect the returns to the participants in said markets. Given this ever-changing context, it was important to provide solid fundamental research with both quantitative (when available) and qualitative analyses to ascertain the top promising corn and soybean products and technologies. It should be noted that the final so called “top eight winners” for each commodity should not be viewed as a list that is “set in stone” because of the uncertain nature of the markets surrounding energy and agricultural commodities. The products and technologies that have been identified as the top eight in both reports actually have the potential to move up or down in relative importance as policies change and technological breakthroughs occur over time. The study team took into consideration the issues of market and political uncertainty

when conducting the research. In the end, the goal was to provide recommendations to AURI regarding those products and technologies that have the highest probability of market success and can impact the State of Minnesota's economy.

The project could be characterized as being a continual flow process where feedback loops were put into place in order to test and retest the justification for including a product or technology in the study. Ultimately, the study was carried out in three Phases, which are summarized in Figure 1. The flow diagram highlights the use of multiple check points or "Phases" in order to "funnel" the products and technologies down to the two top eight lists. In Phase I, Informa conducted desk research that was extremely broad, identifying over 100 products and technologies each for corn and soybeans. Each product or technology was catalogued in a large matrix in which there was with a brief description of said product or technology, identification of the companies or institutions that are engaged in the respective "space," and also special notes.¹ In order to further refine the list in Phase I, four criteria were used by the research team in order to select a limited number of products and technologies that were deemed worthy for moving on to Phase II for more in-depth evaluation. The four criteria are based on those factors that are key characteristics for determining potential success in the marketplace. The four criteria were as follows:

1. Demand/Market Potential:

This addresses the potential size (in value and volume) of the marketplace for a respective product or technology. Some biobased products or technologies, for example, may show significant promise regarding market penetration into existing markets or market adoption; however, the overall market may be extremely small and highly specialized. This means that the introduction of the product or technology would have very little impact to the economy at large. The economic returns or benefits would be confined to a very narrow sector of the economy because of the small market size. The ambition of the study team was to identify those products and technologies which are associated with bigger demand markets and thus potentially larger economic impacts.

2. Economic Feasibility:

Just because a product can be produced or a technology can be used says nothing regarding the cost of producing the product or utilizing the technology. Some products or technologies have highly desirable results or characteristics; however, the cost associated with the product or technology is beyond what the marketplace will likely bear. It should be noted that economic feasibility can be accomplished by either public support (e.g., the 45 cent per gallon tax credit for ethanol production) or the ability of the product or technology to be produced in

¹ Note: Appendices at the end of each report display the large product and technology lists developed in Phase I.

such a manner that real economic returns are achieved without the aid of government support (or a blend of both the marketplace and government support as is the case for ethanol and biodiesel). The study team focused on specifying those products or technologies that would likely become commercially and economically viable over the next ten years.

3. Development Stage:

The development stage is important in the context of the expected planning time horizon of AURI. AURI has established the objective for Informa to identify those products or technologies that will likely have a material economic impact over the next ten years. This means that some products or technologies that might have been identified as being very promising would not be considered for inclusion in the final list because they are too early in the development cycle. Many products or technologies display significant promise from a technical perspective, meaning the mechanical or chemical execution of said technology or product can be achieved in the laboratory or at the pilot scale of operation. Success at the pilot scale level is desirable; however, the more significant hurdle, is the ability to transfer the technology or product to a commercial scale such that they can be introduced into the marketplace and expected to compete with other more traditional products or technologies.

4. Strength of Institutional Support:

The level of institutional support is critical for influencing the success or failure of launching a new product or technology. Institutional support can come in the form of either public or private support or a blend of both. Launching a new product on a “shoe string” budget out of someone’s garage is the exception rather than the rule regarding the probability of success. Those products or technologies which have deep funding sources and access to production and distribution infrastructure and systems generally have a higher likelihood of achieving market penetration and the necessary traction to remain economically viable in the long-run. Large corporations such as DuPont or Cargill are generally advantaged relative to much smaller capitalized companies regarding the ability to invest in the development of new products and technologies and bring them to market on a significant scale. U.S. Federal agencies such as the U.S. Department of Energy (DOE) have also played a vital role in the discovery process of new products and technologies. The DOE has spent billions of dollars helping to fund the discovery of new products and technologies playing the role of a basic research benefactor and even a venture capital firm, investing in emerging products and technologies where often the private sector has deemed the initiatives as being too early-stage or risky to fund completely on their own. The study team evaluated all of the products and technologies in light of the

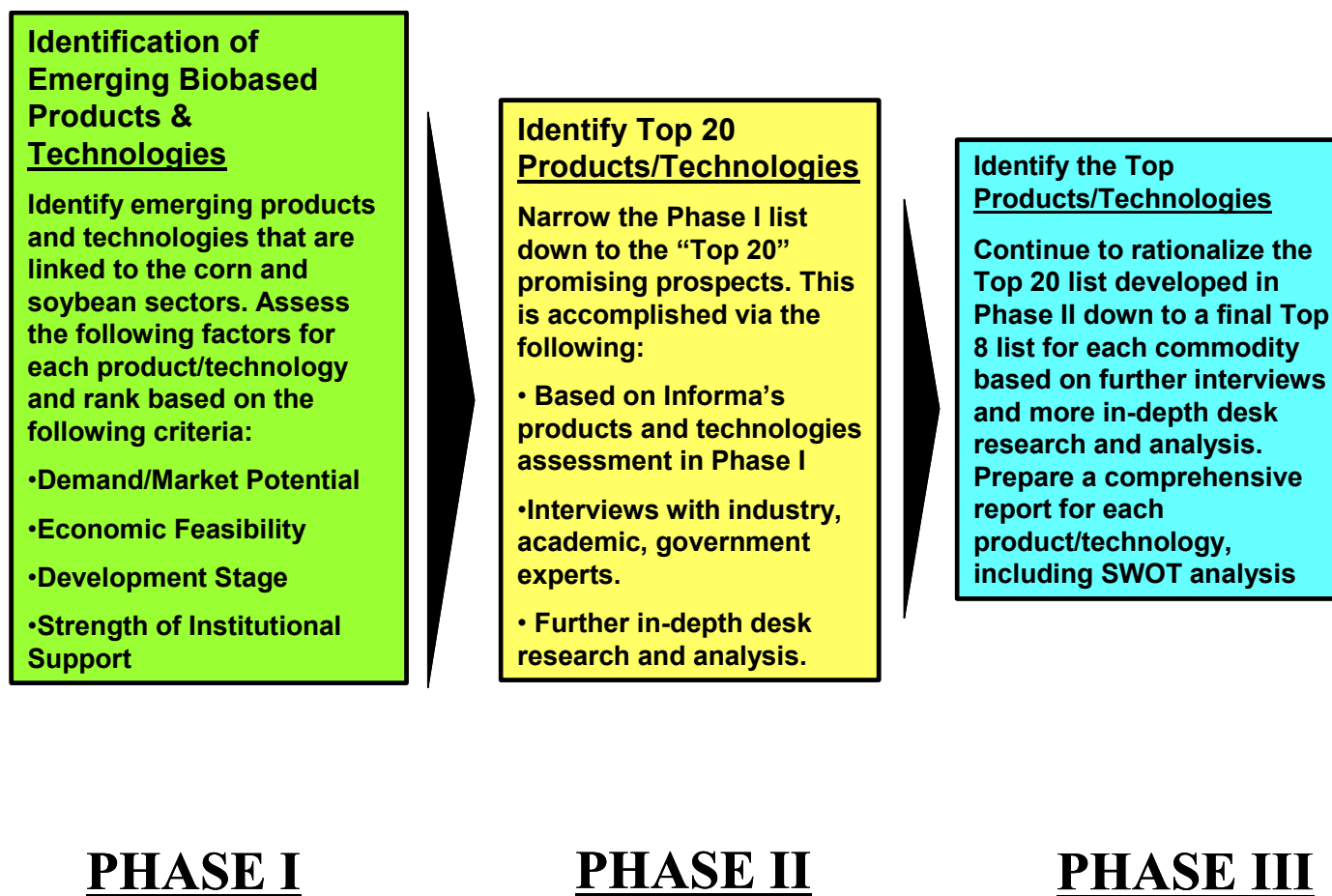
perceived extent of public and private support for the respective product or technology.

In Phase I quantitative scores were generated for each of the 100 products and technologies for corn and approximately 140 products and technologies for soybeans, where they were awarded a score of 10 (being the lowest), 20, 30 or 40 (being the highest) for each of the four criteria. Each of the four criteria was given different “weights” of importance, as follows: Demand/Market Potential 40%, Economic Feasibility 15%, Stage of Development 20% and Institutional Support 25%.² The combination of the criteria weights multiplied by the scores awarded each of the criteria generated a “weighted score” for each of the respective products or technologies. The Informa team independently scored and then ranked the products and technologies for corn and then soybeans. The scoring process was further refined to reflect an enhanced consensus of the team. The ranked scores led to a “Top 30” list for corn and a “Top 30 list” for soybeans. This concluded Phase I of the project.

Phase II began the process of refining the “Top 30” down to a “Top 20 list,” each for corn and soybeans. The study team then began to strategically engage a broad cross section of academic and industry experts with interviews (site visits and telephone interviews) in order to reduce the top 30 list down to top 20. Examples of interviews and trips are as follows: trip to the National Renewable Energy Laboratory (NREL), trip to the National Corn to Ethanol Research Center (NCERC), trip to the USDA Agricultural Research Service Laboratory in Peoria, IL, phone interviews with Oak Ridge National Laboratory, MBI International (Michigan Biotechnology Institute), and numerous other private sector researchers. The experts were asked to comment on the top 30 list to identify a number of key points, (1) specify if there were any omissions from the list, and if so, what products/technologies should be included, (2) identify what products or technologies should be removed from the list, (3) provide an opinion on what product/technologies should be included in the top 20, and (4) distinguish what their preferred top ten products/technologies were and explain in depth why. The Informa research team analyzed the findings from the interviews and constructed a product/technology top 20 list for each of the commodities.

² It is acknowledged that the reader of this report might perceive the weights given to each of the criteria should be changed depending on their point of reference. Informa, however, spent a significant amount of time developing this quantitative framework in order to remain sensitive to AURI's expectations and needs as an organization.

Figure 1: AURI Corn and Soybean Project Flowchart



The Informa research team then conducted more detailed desk research based on a consensus of the expert interviews and prepared brief position papers for each of the top 20 product/technologies for each commodity. The findings in Phase II formed the foundation for the final Phase III and the selection of the two “Top 8” lists. In Phase III highly targeted interviews were conducted for specific products/technologies. For example, succinic acid (a corn-based chemical) was a product that received significant attention and interest in the early stages of the project and was a logical product to move through Phase I and to Phase II and then into Phase III. Moving into Phase III, the team sought those individuals or firms that had special knowledge of succinic acid, such as MBI International and Bioamber (a firm that is dedicated to making succinic acid competitive with maleic anhydride). The highly targeted interviews and desk research in Phase III ultimately yielded the identification and selection of the “Top 8” products/technologies for corn and soybeans.

The selected top 8 products/technologies for corn and soybeans were then given detailed write-ups (more detailed than the top 20 write ups). Each of the detailed product/technology write ups includes an overview of the product/technology, an analysis of its market potential, profiles of the companies and research institutions that are involved in the space and SWOT analyses (Figure 2). SWOT analysis is a widely used and versatile paradigm for strategic planning where the acronym stands for Strengths, Weakness, Opportunities and Threats. The application of the SWOT model provided the framework to distill the key findings of research and analysis into a summary matrix which is easily understood and identifies the key aspects and issues for each products/technologies. Figure 2 displays the SWOT and how each of the product/technology was filtered through the grid structure. In the end, the key decision and policy makers at AURI have an authoritative reference tool to guide them in their strategic planning processes.

Figure 2: SWOT Grid

	Strengths	Weaknesses	Threats	Opportunities
Social				
Technology				
Economic				
Environment				
Political				

C. Energy Markets: A Foundation for Biobased Products and Technologies

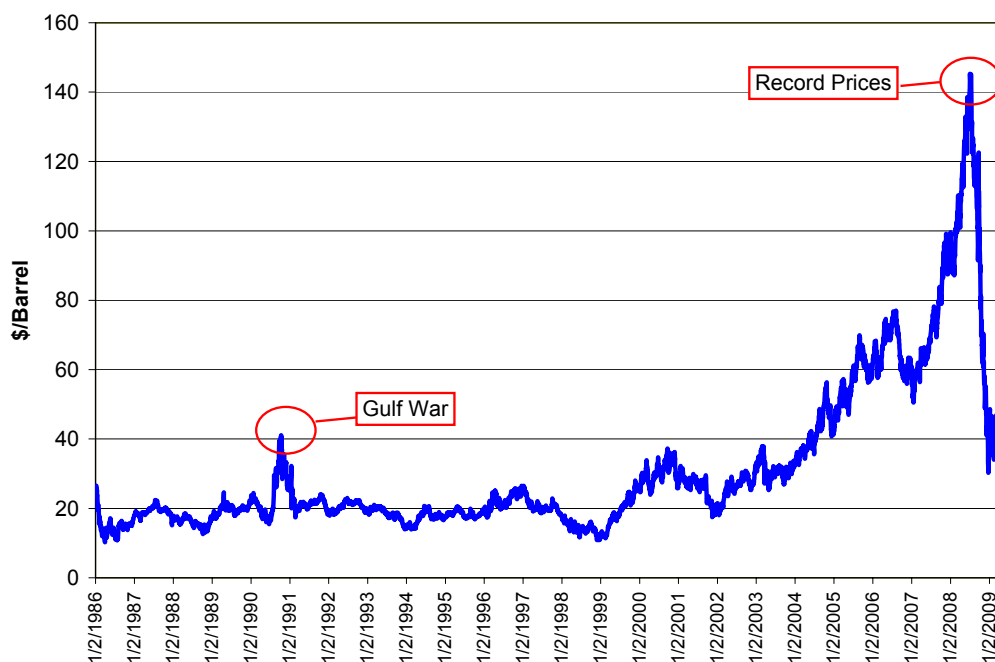
Petroleum is defined in Greek as being "rock oil" or more commonly known as crude oil. Crude oil or crude petroleum oil is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of hydrocarbons of various molecular weights, plus other organic compounds. Crude oil has always been a substance in plentiful supply; the demand for oil, however, has changed dramatically over time given the advent of the combustion engine and the rise of geopolitical tensions surrounding who owns the oil and where is the oil located. Initially, oil wasn't used as a fuel, in the 1860's oil was in fact hailed as a disinfectant, a vermin killer, hair oil, boot grease, and a cure for kidney stones. In 1933, the U.S. paid \$275,000 to Saudi Arabia's King Ibn Saud for an oil concession. The King actually thought he'd sold the Americans sand, since the British didn't think there was oil there. After five years of disappointment, the Americans struck oil in Saudi Arabia. One expert at the time described Saudi Arabia's oil as "the single greatest prize in all history," a prophetic statement for the ages.

The true importance of oil worldwide wasn't understood until World War I and especially, World War II. World War II brought to light the notion of national security and the importance of the U.S. government having a safe supply of oil. After World War II, and the beginning of widespread economic recovery, it became clear that the world was going to need a lot more oil than the companies of Socal and Texaco in Saudi Arabia could provide. Since World II, the global landscape of the supply and demand for oil has become even more complex as synchronistic global expansion of developing countries coupled with continued Middle East conflicts has placed a new premium on petroleum.

Interest in the area of biofuels and biobased products (based on renewable carbohydrate feedstocks such as corn) has increased dramatically over the last ten years as energy prices, primarily crude oil, reached record highs. As described in this section, consumption of crude oil and refined products is on a very large scale, and as a result the potential market for biofuels and certain biobased replacements for petrochemicals is large.

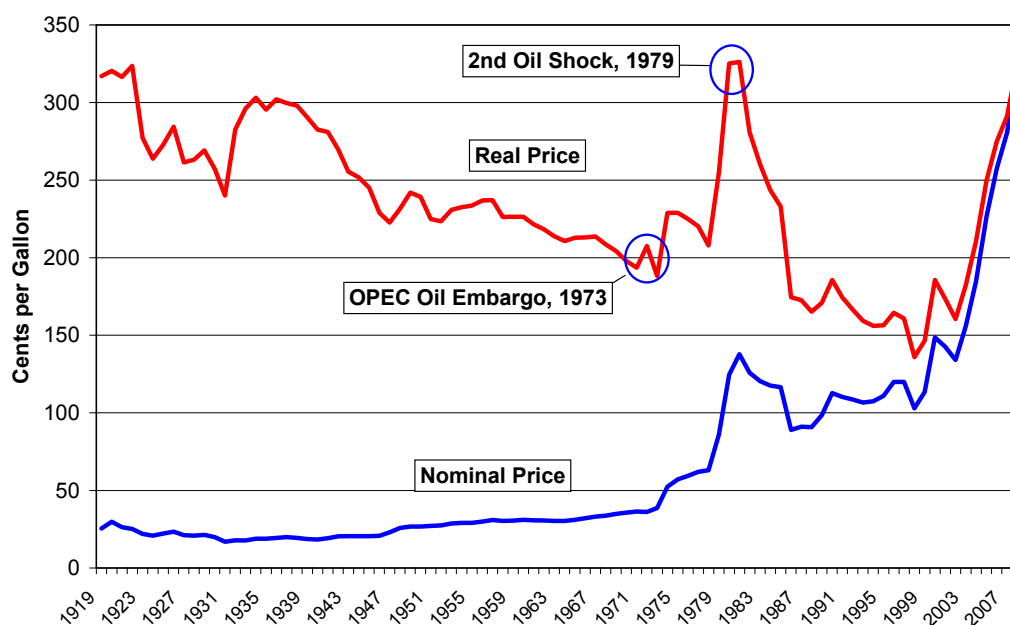
The recent price shock of 2008, quickly reminded U.S. consumers of their vulnerability and dependence on foreign sources of oil. Crude oil prices, as benchmarked by West Texas Intermediate (WTI) averaged only \$19.09/barrel from 1986 to 1999, ranging from a low of \$10.25/barrel to a high of \$41.07 during this period of time. As global economies rapidly expanded and the infrastructure to supply oil increased at a much slower pace, nominal oil prices for the WTI crude reached record high levels on July 3, 2008, at \$145.31/barrel (Figure 3). Adjusted for inflation, oil prices were actually in a long run decline since 1919 (Figure 4), with only brief price spikes. The 2008 jump in oil prices, however, elevated real prices to levels not experienced since the oil shock experienced in the late 1970's and early 1980's.

Figure 3: Crude Oil Price, West Texas Intermediate: January 02, 1986 to June 16, 2009 (daily prices, nominal dollars)



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

Figure 4: U.S. Real Gasoline Pump Price: Annual Average 1919-2008 (consumers price index-urban, 1982-84=1.00)



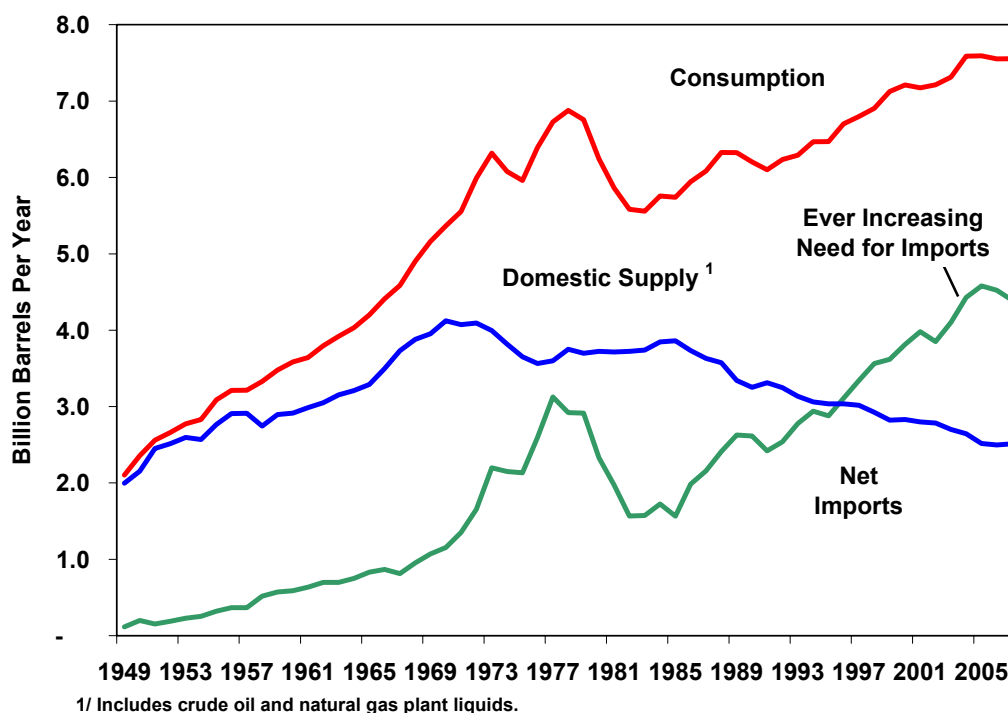
Source: U.S. Department of Energy, Energy Information Administration.

The higher real petroleum prices, concern over a slowdown in the development of new supplies of oil and the September 11, 2001, terrorist attacks and subsequent wars in Afghanistan and Iraq have renewed interest of the American public in finding ways to reduce this country's dependence on foreign imports of petroleum and develop new technologies that consume less gasoline, such as the upcoming Chevy Volt, with claims of achieving 230 miles per gallon (mpg). In 2006, the Bush administration acknowledged the need to find alternative, and preferably renewable, sources of energy. President Bush outlined in his 2006 State of the Union Address, the announcement of The Advanced Energy Initiative, which is designed to "help break America's dependence on foreign sources of energy." Former President Bush set as a national goal the replacement of more than 75% of the oil imports from the Middle East by 2025. The Advanced Energy Initiative provided for a 22% increase in clean-energy research at the U.S. Department of Energy (DOE). The intent of the funding increase was to accelerate breakthroughs in two critical areas, how we power our homes and businesses, and how we power our automobiles, thus stimulating a reduction in our country's demand for fossil based energy sources. The new Obama administration has followed through with a clear mandate to continue the country's need to address the energy predicament with new solutions. President Obama's comprehensive energy plan calls for some of the following initiatives:

- Help create five million new "green" jobs by strategically investing \$150 billion over the next ten years to catalyze private efforts to build a clean energy future.
- Within 10 years, save more oil than we currently import from the Middle East and Venezuela combined.
- Put 1 million plug-in hybrid cars (cars that can get up to 150 mpg) on the road by 2015; cars that will be built in America.
- Ensure 10% of our electricity comes from renewable sources by 2012, and 25% by 2025.
- Implement an economy wide cap and trade program to reduce greenhouse gas emissions 80% by 2050.

Statistics are very clear and impartial regarding the trends of oil consumption and production in the U.S. Since the mid-1950s, the U.S. has imported more energy than it has exported. Consumption of petroleum, the most prominent U.S. energy resource, has expanded from 6.2 million barrels/day in 1950 to almost 20 million barrels/day in 2007, or an annual total of 7.5 billion barrels (Figure 5). During this period, petroleum imports have grown from being insignificant to surpassing U.S. domestic supplies. Most oil imports have been met by North American countries, with Canada and Mexico providing over 29.2% of U.S. petroleum needs in 2008 (Table 1). The U.S. is faced with the continual concern of consistent supplies in the future from politically sensitive regions such as the Middle East. In 2008, OPEC countries accounted for over 46% of U.S. oil imports. Saudi Arabia represented 11.9%, Venezuela 9.2% and Nigeria 7.7% of total U.S. oil imports in 2008.

Figure 5: U.S. Petroleum Situation: 1949-2007



Source: U.S. Department of Energy, Energy Information Administration.

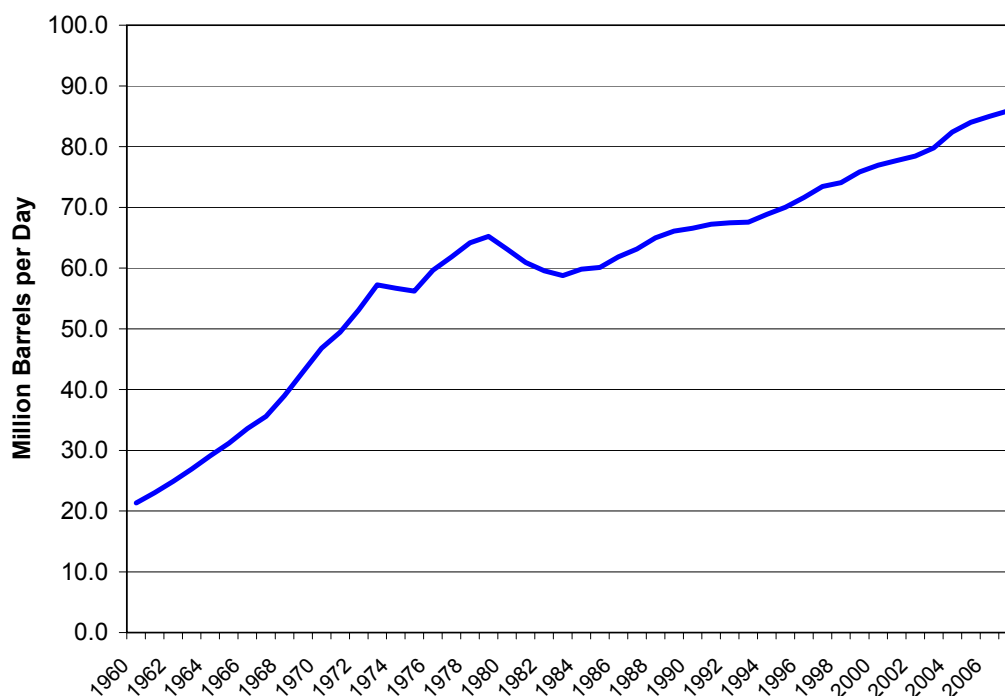
Table 1: U.S. Imports of Crude Oil, by Country of Origin for 2008

	Country of Origin	Thousand Barrels	Percent Total
1	Canada	899,935	19.1%
2	Saudi Arabia	560,705	11.9%
3	Mexico	475,545	10.1%
4	Venezuela	435,769	9.2%
5	Nigeria	362,263	7.7%
6	Iraq	229,300	4.9%
7	Algeria	200,192	4.2%
8	Angola	187,761	4.0%
9	Russia	169,415	3.6%
10	Virgin Islands (U.S.)	117,191	2.5%
	Rest of World		22.8%
Total		4,711,238	100.0%
Non OPEC Countries		2,530,488	53.7%
Persian Gulf		868,516	18.4%
Total OPEC Countries		2,180,750	46.3%

Source: U.S. Department of Energy, Energy Information Administration.

The global supply of and demand for energy is being challenged not just by the level of U.S. consumption and political instability in certain oil-producing countries, but also by growing demand in emerging economies such as China and India. World consumption of petroleum rose from just over 20 million barrels/day in 1960 to 85.9 million barrels/day in 2007, a compound annual growth rate of 3.12% (Figure 6).

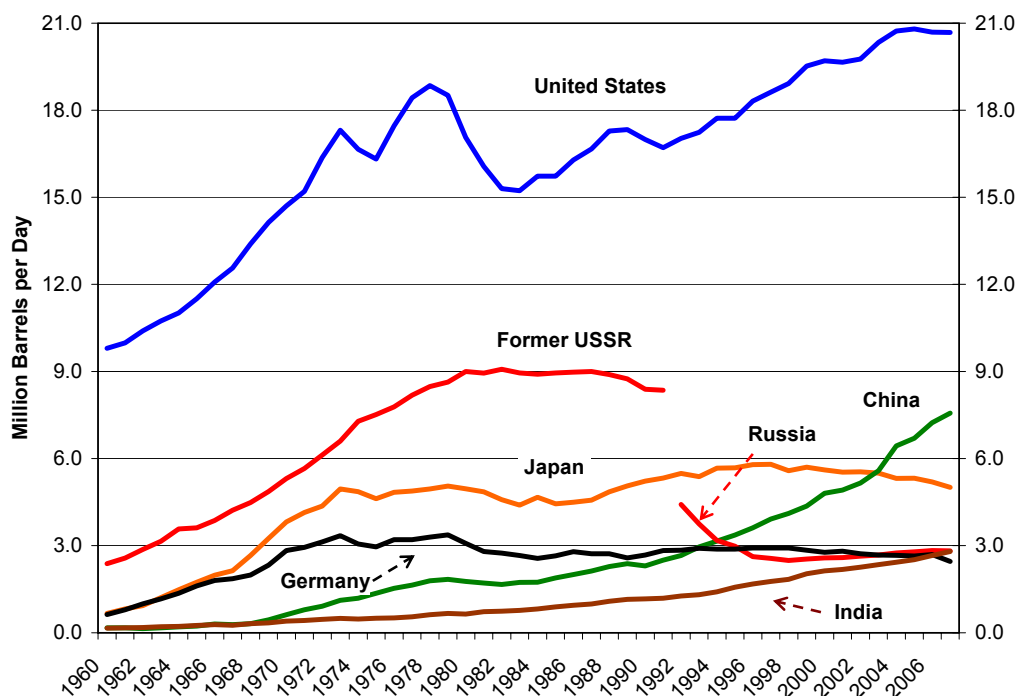
Figure 6: World Daily Consumption of Petroleum, 1960-2007



Source: U.S. Department of Energy, Energy Information Administration.

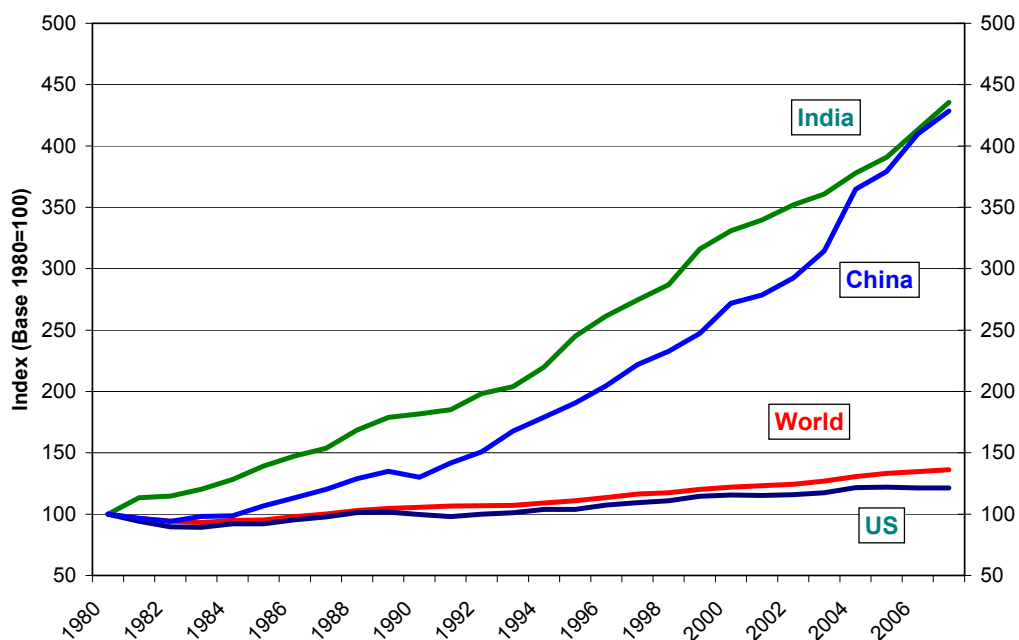
The U.S. is the most significant petroleum-consuming economy in the world (Figure 7). The former Soviet Union was second in importance until its breakup in the early 1990s; now China is the second-largest petroleum consuming economy. Since 1960, China has increased its consumption of petroleum faster than any country (over 3,000%), while India has increased consumption by almost 1,500% (Figure 8). More mature economies such as the U.S. and Canada actually exhibit growth rates that are below the world trend, this is also true for most of the major and mature economies in the European Union.

Figure 7: Leading Petroleum Consuming Countries, Average Daily Consumption, 1960-2007



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

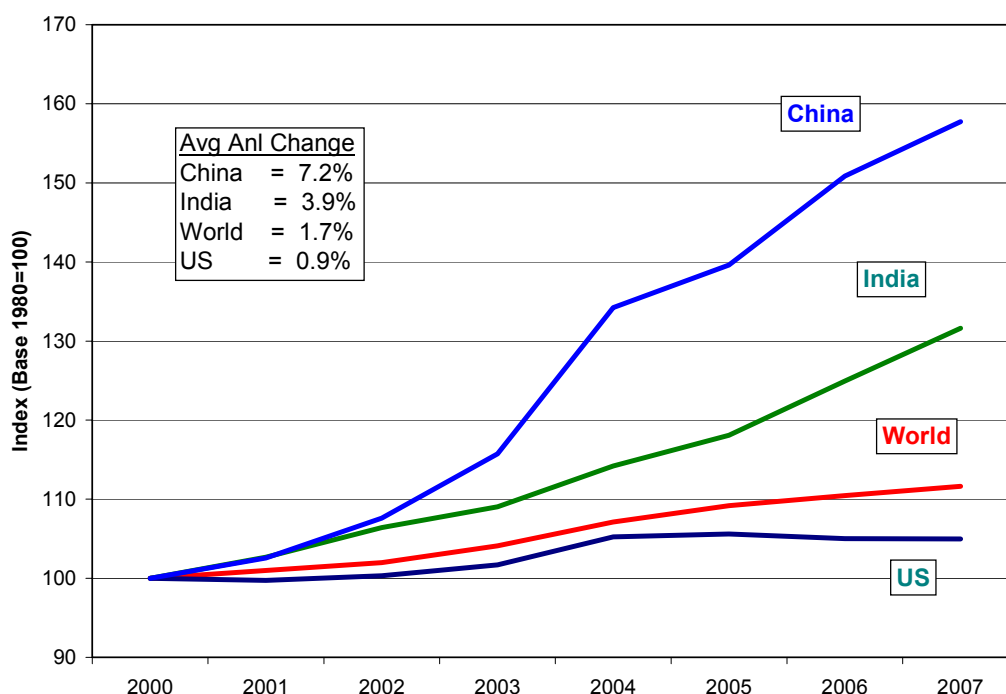
Figure 8: Indexed Growth of Petroleum Consumption for Key Countries, 1980-2007 (Barrels of Oil Consumed Daily)



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

In recent years, the rate of growth for China, for example, has increased significantly (Figure 9). From 2000 to 2007, China's consumption of oil increased at an average annual rate of 7.2%; this was almost twice as fast as India's annual growth rate and significantly ahead of the U.S. annual growth rate of only 0.9%.

Figure 9: Indexed Growth of Petroleum Consumption for Key Countries, 2000-2007 (barrels of oil consumed daily)



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

As previously mentioned, many European Union countries have generally fallen in their level of consumption of petroleum globally as emerging economies have rapidly increased their share of total petroleum demand (Table 2). From 1960 to 1969, the U.S. consumed, on average, 37.6% of the total global use of petroleum; the next largest oil consumer was the Former Soviet Union (FSU) at 11.6% (Table 3). Now the FSU has been dissolved and numerous developing countries have significantly expanded their economies, while the U.S. share of global oil consumption has actually declined to 25.7%, still extremely large; however, the impact of growing foreign economies is palpable. For example, often overshadowed by China and India, Brazil has also experienced rapid consumption in petroleum over the last 20 years (Table 4). Spain and Russia have also exhibited strong recent relative growth in oil consumption from 2000 to 2008.

Table 2: Petroleum Consumption, Daily Average Barrels Consumed, Key Countries, 1960-2008 (million barrels)

	1960-69	Rank	1970-79	Rank	1980-89	Rank	1990-99	Rank	2000-08	Rank
WORLD	30.74		57.03		61.84		70.26		81.62	
Total OECD	22.47		40.41		39.11		44.66		48.65	
Total Non-OECD	8.27		16.62		22.72		25.60		32.97	
United States	11.56	(1)	16.98	(1)	16.27	(1)	17.878	(1)	20.17	(1)
China	0.24	(12)	1.28	(9)	1.93	(5)	3.294	(3)	6.25	(2)
Japan	1.69	(3)	4.65	(3)	4.69	(3)	5.564	(2)	5.26	(3)
Russia							3.068	(4)	2.73	(4)
Germany	1.45	(4)	3.13	(4)	2.73	(4)	2.862	(5)	2.67	(5)
India	0.24	(13)	0.51	(13)	0.88	(13)	1.524	(13)	2.47	(6)
Brazil	0.36	(9)	0.86	(10)	1.15	(11)	1.767	(12)	2.23	(7)
Canada	1.10	(6)	1.76	(8)	1.63	(9)	1.829	(9)	2.21	(8)
South Korea	0.05	(14)	0.33	(14)	0.61	(14)	1.772	(11)	2.17	(9)
Mexico	0.35	(10)	0.75	(12)	1.48	(10)	1.858	(8)	2.04	(10)
France	1.05	(7)	2.33	(5)	1.87	(6)	1.935	(6)	2.00	(11)
Italy	0.97	(8)	1.93	(7)	1.80	(7)	1.900	(7)	1.78	(12)
United Kingdom	1.42	(5)	2.07	(6)	1.66	(8)	1.810	(10)	1.76	(13)
Spain	0.25	(11)	0.83	(11)	0.94	(12)	1.177	(14)	1.55	(14)
Former USSR	3.56	(2)	7.16	(2)	8.94	(2)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

Table 3: Percent Share of World Petroleum Consumed by Key Countries, 1960-2008

	1960-69	Rank	1970-79	Rank	1980-89	Rank	1990-04	Rank	2000-08	Rank
WORLD	100%		100%		100%		100%		100%	
Total OECD	73.1%		70.9%		63.3%		63.6%		59.6%	
Total Non-OECD	26.9%		29.1%		36.7%		36.4%		40.4%	
United States	37.6%	(1)	29.8%	(1)	26.3%	(1)	25.4%	(1)	24.7%	(1)
China	0.8%	(12)	2.2%	(9)	3.1%	(5)	4.7%	(3)	7.7%	(2)
Japan	5.5%	(3)	8.1%	(3)	7.6%	(3)	7.9%	(2)	6.4%	(3)
Russia							4.4%	(4)	3.3%	(4)
Germany	4.7%	(4)	5.5%	(4)	4.4%	(4)	4.1%	(5)	3.3%	(5)
France	0.8%	(7)	0.9%	(5)	1.4%	(6)	2.2%	(6)	3.0%	(6)
Canada	1.2%	(6)	1.5%	(8)	1.9%	(9)	2.5%	(7)	2.7%	(7)
South Korea	3.6%	(14)	3.1%	(14)	2.6%	(14)	2.6%	(8)	2.7%	(8)
Mexico	0.2%	(10)	0.6%	(12)	1.0%	(10)	2.5%	(9)	2.7%	(9)
Brazil	1.1%	(9)	1.3%	(10)	2.4%	(11)	2.6%	(10)	2.5%	(10)
Italy	3.4%	(8)	4.1%	(7)	3.0%	(7)	2.8%	(11)	2.4%	(11)
United Kingdom	3.1%	(5)	3.4%	(6)	2.9%	(8)	2.7%	(12)	2.2%	(12)
India	4.6%	(13)	3.6%	(13)	2.7%	(13)	2.6%	(13)	2.2%	(13)
Spain	0.8%	(11)	1.5%	(11)	1.5%	(12)	1.7%	(14)	1.9%	(14)
Former USSR	11.6%	(2)	12.5%	(2)	14.5%	(2)				

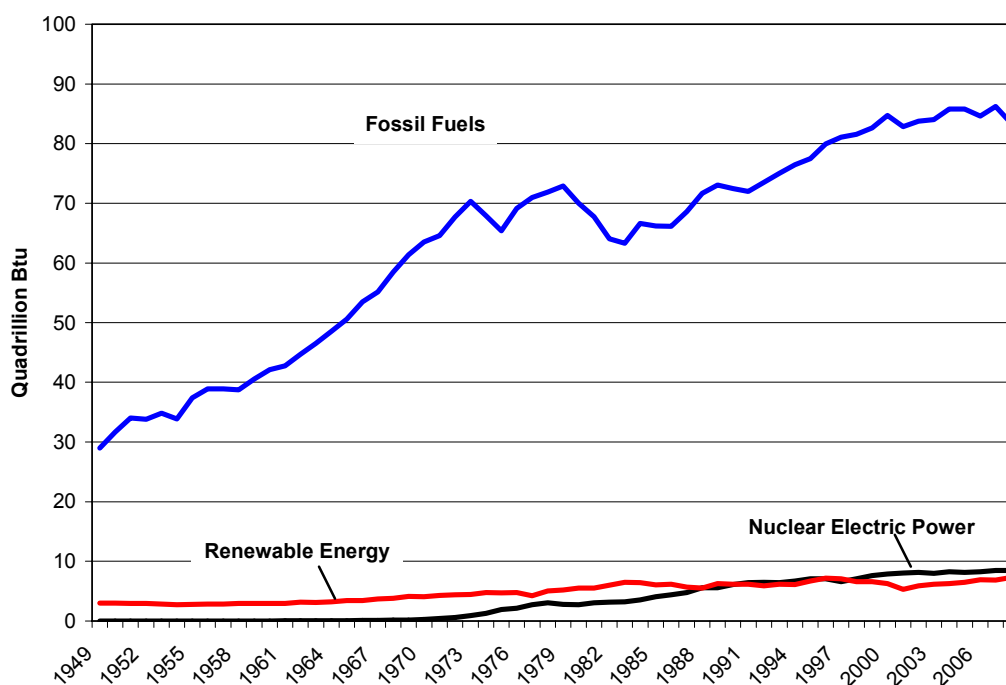
Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

Table 4: Annual Growth Rate of Petroleum Consumption in Key Countries, 1960-2008

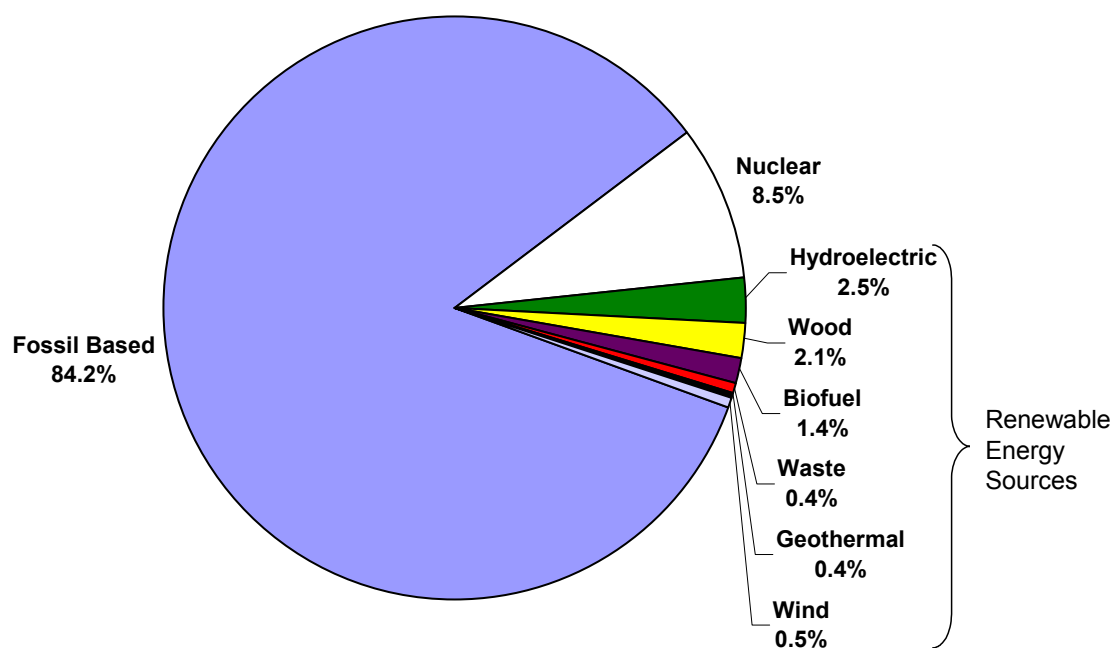
	Anl Rate 1960-69	Rank	Anl Rate 1970-79	Rank	Anl Rate 1980-89	Rank	Anl Rate 1990-99	Rank	Anl Rate 2000-08	Rank
WORLD	7.5%		3.4%		0.8%		1.5%		1.5%	
Total OECD	7.6%		2.4%		0.3%		1.6%		0.2%	
Total Non-OECD	7.4%		5.9%		1.7%		1.3%		3.5%	
China	11.4%	(7)	10.9%	(1)	4.0%	(3)	7.0%	(1)	6.8%	(1)
India	8.3%	(8)	5.1%	(7)	6.2%	(1)	6.4%	(3)	4.1%	(2)
Brazil	6.1%	(11)	8.5%	(4)	2.5%	(5)	4.8%	(4)	1.8%	(3)
Canada	6.0%	(12)	2.6%	(8)	-0.5%	(12)	2.0%	(6)	1.7%	(4)
Russia							-8.4%	(14)	1.5%	(5)
Spain	18.6%	(2)	6.0%	(5)	-0.5%	(11)	3.6%	(5)	1.2%	(6)
Mexico	4.9%	(13)	8.6%	(3)	2.7%	(4)	0.8%	(10)	1.0%	(7)
South Korea	26.1%	(1)	10.8%	(2)	4.9%	(2)	6.5%	(2)	0.4%	(8)
United States	4.1%	(14)	2.5%	(9)	0.8%	(6)	1.7%	(7)	0.4%	(9)
United Kingdom	7.9%	(9)	-1.8%	(14)	0.3%	(7)	0.0%	(13)	0.0%	(10)
France	11.5%	(6)	1.5%	(11)	-2.0%	(14)	0.9%	(9)	-0.3%	(11)
Germany	12.6%	(5)	1.4%	(12)	-1.0%	(13)	0.5%	(11)	-1.2%	(12)
Italy	13.1%	(4)	1.0%	(13)	-0.1%	(9)	0.4%	(12)	-1.6%	(13)
Japan	16.1%	(3)	2.4%	(10)	0.1%	(8)	1.0%	(8)	-1.7%	(14)
Former USSR	7.6%	(10)	5.4%	(6)	-0.2%	(10)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

Since 1949, fossil fuel as a percentage share of total U.S. energy consumption has risen considerably relative to nuclear electric power and renewable energy sources (Figure 10). The U.S. consumed almost 30 quadrillion Btu of fossil fuels in 1949; this has increased significantly to approximately 85 quadrillion Btu of fossil fuels in 2008. Just as the U.S. relies heavily on petroleum as a primary source of energy, other sources play a significant role in the intricate energy balance (Figure 11). The U.S. uses an extensive amount of natural gas, coal, and nuclear electric power, with renewable energy growing more popular. In 2008, fossil fuel-based energy sources (coal, natural gas and petroleum) accounted for 84.2% of total U.S. energy consumed, with the remainder being nuclear electric power (8.5%) and renewable energy (7.3%).

Figure 10: Energy Consumption by Source, 1949-2008

Source: U.S. Department of Energy, Energy Information Administration

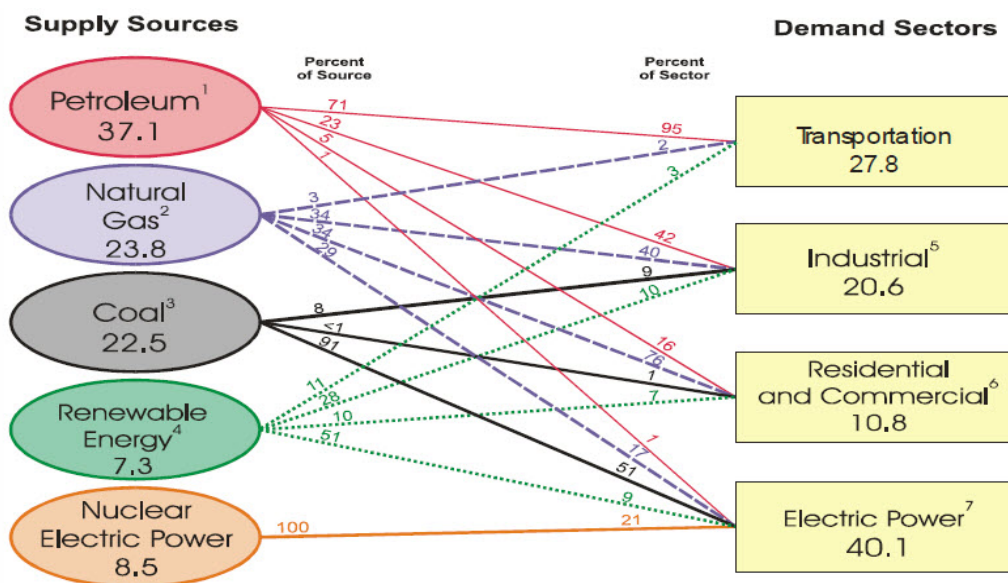
Figure 11: Percent Energy Consumption by Source, 2008

Source: U.S. Department of Energy, Energy Information Administration

There are four primary energy consuming sectors in the U.S. The four sectors are: residential, which accounts for 21.9% of the total energy consumption; commercial, which accounts for 17.9% of the total energy consumption; industrial, which accounts for 32.1% of the total energy consumption; and transportation, which accounts for 28.1% of the total energy consumption (Figure 12). Highlights of the supply/demand balance flow diagram are as follows:

- Transportation uses the largest share of petroleum at 71%, while the industrial sector uses 23% of petroleum and the remaining 6% goes to residential/commercial and electric power.
- The consumption of natural gas is evenly distributed between three sectors, with industry using 34%, residential/commercial using 34% and electric power using 29%; the remainder is consumed by transportation at only 3%.
- The consumption of coal primarily linked to two sectors, the generation of electricity at 91% and industrial consumption at 8%.
- Nuclear electric power is used exclusively, at 100% consumption, by the electric power demand sector.
- The use of renewable energy is divided across all four demand sectors with electric power using the most at 51% and industrial demand the second largest sector using 28%.

**Figure 12: U.S. Primary Energy Consumption by Source and Sector, 2007
(Quadrillion Btu)**



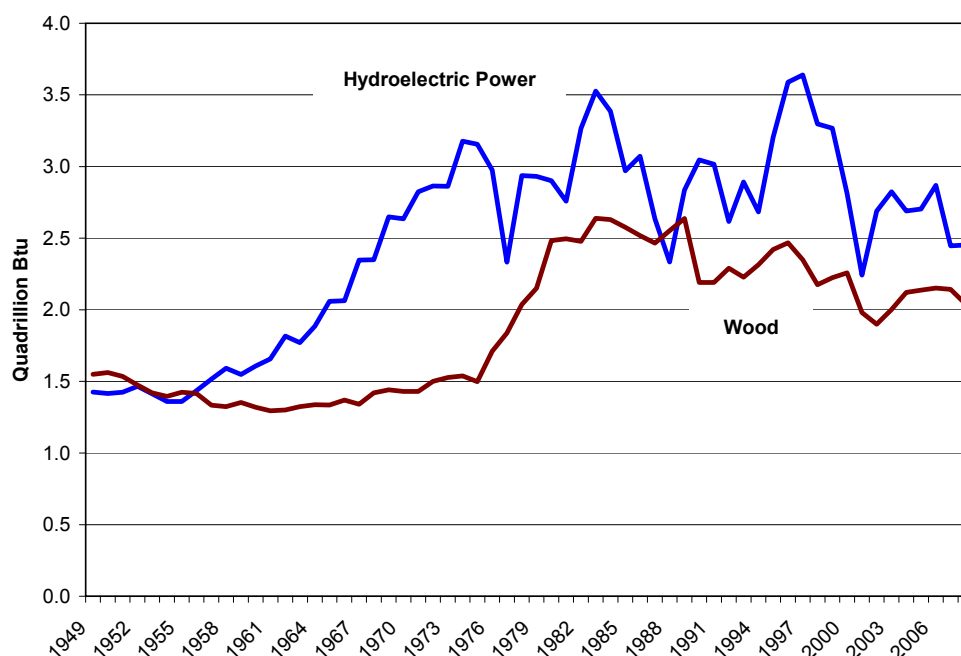
Source: USDOE, Energy Information Administration, Annual Energy Review 2007.

- 1 Excludes 0.6 quadrillion Btu of ethanol, which is included in "Renewable Energy."
- 2 Excludes supplemental gaseous fuels.
- 3 Includes 0.1 quadrillion Btu of coal coke net imports.
- 4 Conventional hydroelectric power, geothermal, solar/PV, wind, and biomass.
- 5 Includes industrial combined-heat-and-power (CHP) and industrial electricity-only plants.
- 6 Includes commercial combined-heat-and-power (CHP) and commercial electricity-only plants.
- 7 Electricity-only and combined-heat-and-power (CHP) plants whose primary business is to sell electricity, or electricity and heat, to the public.

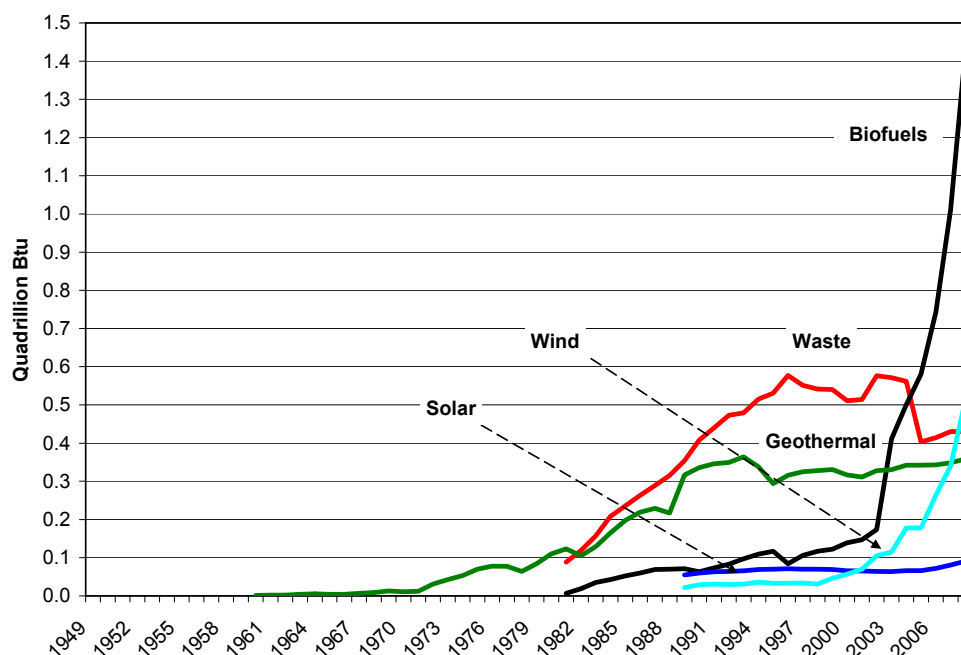
Briefly, the renewable energy sources can be segmented into the following general categories:

- Hydroelectric: Renewable energy from hydroelectricity.
- Wood: Wood, black liquor, and other wood waste.
- Waste: Municipal solid waste, landfill gas, sludge waste, tires, and agricultural byproducts, including animal waste, and other biomass (plant material and residue)
- Biofuels: Ethanol blended into motor gasoline and biodiesel.
- Geothermal: Geothermal electricity net generation, heat pump, and direct use energy.
- Solar: Solar thermal and photovoltaic electricity net generation, and solar thermal direct use energy.

Hydroelectric power and wood-based power contribute the largest amount of renewable energy by a wide margin (Figure 13). However, their growth has remained flat since the 1980s. In general, other renewable energy sources have shown greater increases in their rate of adoption. Alcohol (ethanol) and wind based renewables have grown the most significantly from 1990 to the present (Figure 14).

Figure 13: U.S. Renewable Energy Consumption by Source - Part I, 1949-2008

Source: U.S. Department of Energy, Energy Information Administration, Monthly Energy Review.

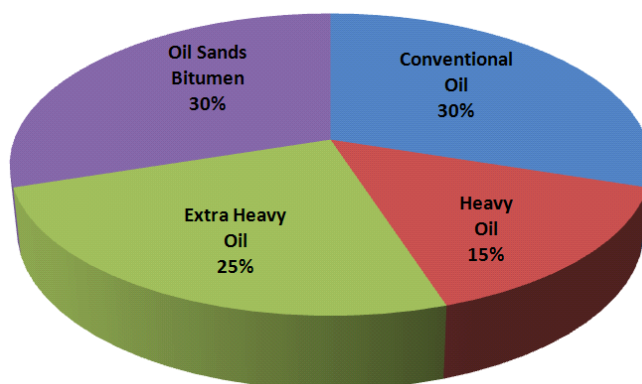
Figure 14: U.S. Renewable Energy Consumption by Source - Part II, 1949-2008

Source: U.S. Department of Energy, Energy Information Administration, Monthly Energy Review.

Today's marketplace is making a concerted effort to find larger supplies of renewable energy feedstocks and substitutes in order to replace the traditional fossil

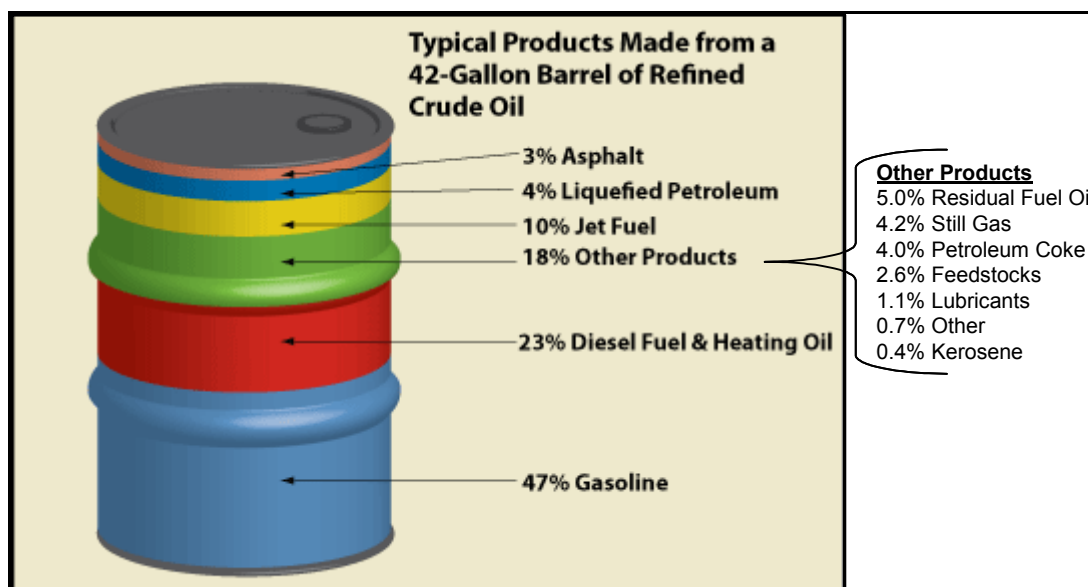
fuel (hydrocarbon based) sources of energy, as evidenced by such strong growth in the biofuels and wind sectors. Global economies are concerned that the supplies of conventional oil are declining rapidly and that the supplies of conventional oil might have passed what is called “peak oil.” Peak oil is defined as the point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline. The concept is based on the observed production rates of individual oil wells, and the combined production rate of a field of related oil wells. The aggregate production rate from an oil field over time usually grows exponentially until the rate peaks and then declines, sometimes rapidly, until the field is depleted. Given the recent record prices for crude oil, the peak oil debate has gained significant attention with strong arguments both for and against the concept. Some experts have now estimated that total world reserves of *conventional* oil are now less than 30% of total oil supplies which include heavy oil, oil sands and extra heavy oil (Figure 15). The heavier oils are not easy to use (require special refining procedures) and are more expensive to extract compared to conventional oil. In addition to concerns over peak oil, energy security and mitigation of climate change are important reasons for the move toward biofuels and wind energy.

Figure 15: Total World Oil Reserves



Source: Alboudwarej, Husswin, Highlighting Heavy Oil, Oilfield Review, Summer 2006.

One of the reasons that conventional oil has become such a vital link and input in global economies is because of its chemical versatility which provides a plethora of uses. When refined, one barrel of crude oil yields about 19 gallons of finished motor gasoline, 9 gallons of diesel fuel, as well as other petroleum based derivatives used in products such as ink, crayons, bubble gum, dishwashing liquids, deodorant, eyeglasses, records, tires, ammonia, and heart valves, etc. (Figure 16).

Figure 16: Products Made from a Barrel of Crude Oil³

Source: USDOE, Energy Information Administration and American Petroleum Institute.

In general, each barrel of oil in the U.S. is fractionated into fairly consistent components as described below.⁴

- **Gasoline:** Of all the crude oil refined for use in the United States, almost half (47%) becomes gasoline for automobiles, boats and other gasoline-driven motors.
- **Jet Fuel:** Airplanes utilize approximately 10% of a refined barrel of oil in the form of jet fuel.
- **Diesel Fuel and Home Heating Oil:** 23% becomes distillate, two-thirds of which is refined for diesel fuel for trucks, buses and other diesel engines, while the remaining one-third is used as home heating oil.
- **Boiler Oil:** Boiler oil, or residual fuel oil, makes up 5% of refined crude oil and is used on ships, in industrial boilers and in power plants to produce electricity.
- **Asphalt and Road Oil:** Asphalt and road oil accounts for 3% of crude oil consumption.

³ Note: Percentages total 105% because of “processing gain.” A 42 gallon barrel of oil actually yields 44 gallons of products.

⁴ It should be noted that this crude oil fractionation recipe does vary by country, where a different economies require different input streams depending on the structure of their economies.

- **Other:** Approximately 9.4% of the crude oil is refined into non-energy related feedstocks for manufacturing products such as lubricants, wax, coke for steel making, and naphthas that are used in the drycleaning process.
- **Petrochemical Feedstocks:** Petrochemical feedstocks, products of the refining process, make up the remaining 2.6% of all refined crude oil. Half of this is used to make plastics (approximately 1.3% of the total) for thousands of items such as tableware, furniture, aircraft and automobile parts, luggage, surfboards, helmets, medical supplies and packaging. The remaining 1.3% is used to make products such as solvents, synthetic fibers for wearing apparel, synthetic rubber, paints and coatings.

From a scientific and chemical perspective these refined crude oil products can be described as follows:

- **Petroleum gas** - used for heating, cooking, making plastics small alkanes (1 to 4 carbon atoms) commonly known by the names methane, ethane, propane, and butane, which is often liquified under pressure to create LPG (liquified petroleum gas).
- **Naphtha or Ligroin** - intermediate that will be further processed to make gasoline mix of 5 to 9 carbon atom alkanes, and a motor fuel liquid mix of alkanes and cycloalkanes (5 to 12 carbon atoms).
- **Kerosene** - fuel for jet engines and tractors; starting material for making other products as a liquid mix of alkanes (10 to 18 carbons) and aromatics.
- **Gas oil or Diesel distillate** - used for diesel fuel and heating oil; starting material for making other products liquid alkanes containing 12 or more carbon atoms.
- **Lubricating oil** - used for motor oil, grease, other lubricants; consists of liquid long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, and aromatics.
- **Heavy gas or Fuel oil** - used for industrial fuel; starting material for making other products liquid long chain (20 to 70 carbon atoms) alkanes, cycloalkanes, and aromatics.
- **Residuals** - coke, asphalt, tar, waxes; starting material for making other products solid multiple-ringed compounds with 70 or more carbon atoms.

Consistent with the nomenclature or breakdown of how a barrel of oil is used in the U.S. as previously discussed, the DOE's, Energy Information Agency (EIA) estimated the volume of oil consumption per respective product category in 2007, as shown in Table 5. The average daily oil consumption for all refined oil products in

the U.S. was approximately 20.5 million barrels in 2007. Annually, total oil consumption in the U.S. is a staggering 7.5 billion barrels of oil. Keep in mind that volumetrically a barrel of oil is approximately 42 gallons. Finished motor gasoline consumption was approximately 3.4 billion barrels in 2007; multiplying a barrel of oil times 42 gallons makes the volume of finished motor gasoline consumed in the U.S. even more imposing at an estimated level of 143 billion gallons. Even with this comprehensive list of petroleum products, a barrel of crude oil can be reduced into more specialized products; that is why the term feedstock is used to explain the potential to further add value to the crude stream.

Table 5: Volume of U.S. Petroleum Products Consumed in 2007

	Annual (Thousand Barrels Per Day)	Annual (Thousand Barrels Total)
Finished Motor Gasoline	9,286	3,389,390
Distillate Fuel Oil	4,196	1,531,540
Liquefied Refinery/Petroleum Gases	2,085	761,025
Kero-Type Jet Fuel	1,622	592,030
Petroleum Coke	490	178,850
Still Gas	697	254,405
Residual Fuel Oil	723	263,895
Asphalt and Road Oil	494	180,310
Other Oils for Feedstocks	350	127,750
Naptha for Feedstocks	294	107,310
Lubricants	142	51,830
Miscellaneous Products	63	22,995
Kerosene	32	11,680
Special Napthas	41	14,965
Finished Aviation Gasoline	17	6,205
Waxes	11	4,015
Total	20,543	7,498,195

Source: U.S. Department of Energy, Energy Information Administration.

The final markets for value-added refined crude oil product streams are extremely large and diverse in the U.S. Table 6 highlights the estimated value of the major markets that use both petroleum and biobased feedstocks (i.e., corn and soybeans). The markets range in value from the largest market; that is gasoline at \$298 billion in 2006, down to the high emerging growth market for wood substitutes at \$3.4 billion. All of these markets use hydrocarbon based petroleum feedstocks as an input to their manufacturing activities. The petroleum content level varies significantly across markets. Gasoline and diesel are exclusively petroleum based; however, the petroleum input stream is much smaller as a percent share of the total product volume for cosmetics and personal care products.

Biobased feedstocks continue to make inroads into these different markets at a significant rate. Many companies are espousing the virtues of being green and not

using petroleum based feedstock; rather, they are focused on increasing their use of renewable sources of inputs. It is unclear just how far renewable feedstocks from corn and soybeans have penetrated these markets. The easiest markets to estimate are the gasoline and diesel markets where ethanol and biodiesel production volumes are closely tracked by the industries. Less clear is an adequate understanding, for example, of the actual percent share of the sanitary cleaning products market that is biobased. Many market estimates are bantered about with little clear empirical supporting evidence, compared to such reliable surveys as the U.S. Census of Manufacturing.

Table 6: Major U.S. Markets for Petroleum and Biobased Feedstocks, 2006

Sector	Value of Shipments/Markets (\$1,000)
Gasoline	298,589,184
Diesel (on highway)	87,703,231
Pharmaceuticals	163,005,621
Textiles (clothing, carpets, bedding linens, auto)	38,028,266
Lubricants (motor oil, transformer fluid, hydraulic fluids, etc.)	11,308,102
Solvents	5,500,000
Sanitary Cleaning Products (hand cleaners, janitorial cleaners, household, food service, laundry)	34,267,288
Cosmetics and Personal Care Products	5,900,000
Adhesives/binders	9,230,331
Paints and Coatings (inks, paints, etc.)	22,558,703
Plastics (films, containers, polymers, insulations, foams)	203,496,075
Resins and Synthetic Rubber Manufacturing	93,499,662
Fertilizers	12,652,957
Sorbents	3,280,000
Wood Substitutes Composite Panels	3,380,000

Source: U.S. Department of Commerce: 2006 Census of Manufacturing, Freedonia Group, DOE: EIA, Informa Economics.

1. Conclusion

The biobased corn and soybean products and technologies will ultimately be challenged by two basic obstacles relative to petroleum; the first is economic and second is performance (attributes). The first challenge relates to the simple question: is the biobased product or technology cost competitive with traditional petro based feedstocks or related technological processes? In general, as petroleum prices rise, the easier it is to justify substituting a crude oil feedstock with a biobased corn or soybean feedstock. As petroleum prices fall the inverse is true, biobased feedstocks face inflection points in pricing where they become more costly

relative to petroleum. The record high prices of crude above \$100/barrel in 2008 provided significant opportunities for biobased products to gain interest from those manufactures that were looking to replace their high cost oil feedstocks.

The second question relates to how well the respective biobased product or technology performs relative to traditional petroleum manufacturing platforms. For example, in the world of lubricants, specifically motor oil, a significant amount of research has been conducted regarding the use of soybean oil as a potential replacement for motor oil. The challenge for soybean researchers has been to try and replicate the same qualities and characteristics of petroleum based motor oil regarding its ability to withstand high temperatures without experiencing any loss in lubricity. It is within this context that the Informa research team “set out” to indentify those corn and soybean based products and technologies that could successfully compete in terms of their relative economics and attributes compared to traditional hydrocarbon based petroleum products and technologies. It should be noted that petroleum markets have certainly played a major role in the recent interest and developments in biobased products and technologies; the growth however, has not been confined to only the large fuel markets. Significant advancements have occurred in numerous other markets because of the desirable environmental properties of renewability and biodegradability. These attractive properties are creating new and exciting opportunities for feedstocks that are based on corn or soybeans. Beyond biobased products/technologies, significant advances are also emerging in other fields like health with soy isoflavones or in more traditional ones like animal feed. Results and recommendations of this endeavor can be found in the individual commodity reports (i.e., for corn and soybeans).

III. Phase II – Overview of Top 20 Soybean Products/Technologies

After assessing the products/technologies listed in the Appendix section based on the criteria previously discussed (i.e., demand/market potential, economic feasibility, development stage and strength of institutional support), the top 20 products/technologies were identified. These products/technologies are briefly reviewed within this section and are listed in Table 7. Upon further analysis and interviews (see appendix), this list was then further refined down to the top 8, which are each presented in more detail within the next section (IV).

Table 7: List of Top 20 Soybean Products/Technologies

Product/Technology Name	Soybean Origin	Product	Technology	Product/Technology Timeframe
Renewable Fuel				
Biodiesel Additives	NA	✓	✓	Short Term
Enzymatic Transesterification	Soybean Oil		✓	Short Term
Renewable Diesel	Soybean Oil	✓	✓	Short Term
Solid Transesterification Catalyst	Soybean Oil		✓	Short Term
Green Chemicals				
Epichlorohydrin	Glycerin	✓		Medium Term
Epoxidized Soybean Oil	Soybean Oil	✓		Short Term
Lubricant	Soybean Oil	✓		Short Term
Polyols	Soybean Oil or Glycerin	✓	✓	Short Term
Propylene Glycol	Glycerin	✓	✓	Short Term
Soy Methyl Ester (non-fuel applications)	Soybean Oil	✓		Short Term
Wood Adhesive	Soybean Protein	✓		Short Term
Soybean Crushing				
Enzymatic Degumming	Soybean Oil		✓	Short Term
Supercritical Carbon Dioxide Extraction of Oil	Soybean		✓	Short Term
Value-Added Soybean Varieties				
High Oil Soybeans	Soybean		✓	Medium Term
High Stability Oil Soybeans	Soybean		✓	Short Term
Omega-3 Fortified Soybeans	Soybean		✓	Medium Term
Other				
Aquaculture Feed	Soybean Protein	✓		Short Term
Animal Feed	Glycerin	✓		Short Term
Olefin Metathesis	Soybean Oil		✓	Short Term
Soy Isoflavones	Soybean	✓		Short Term

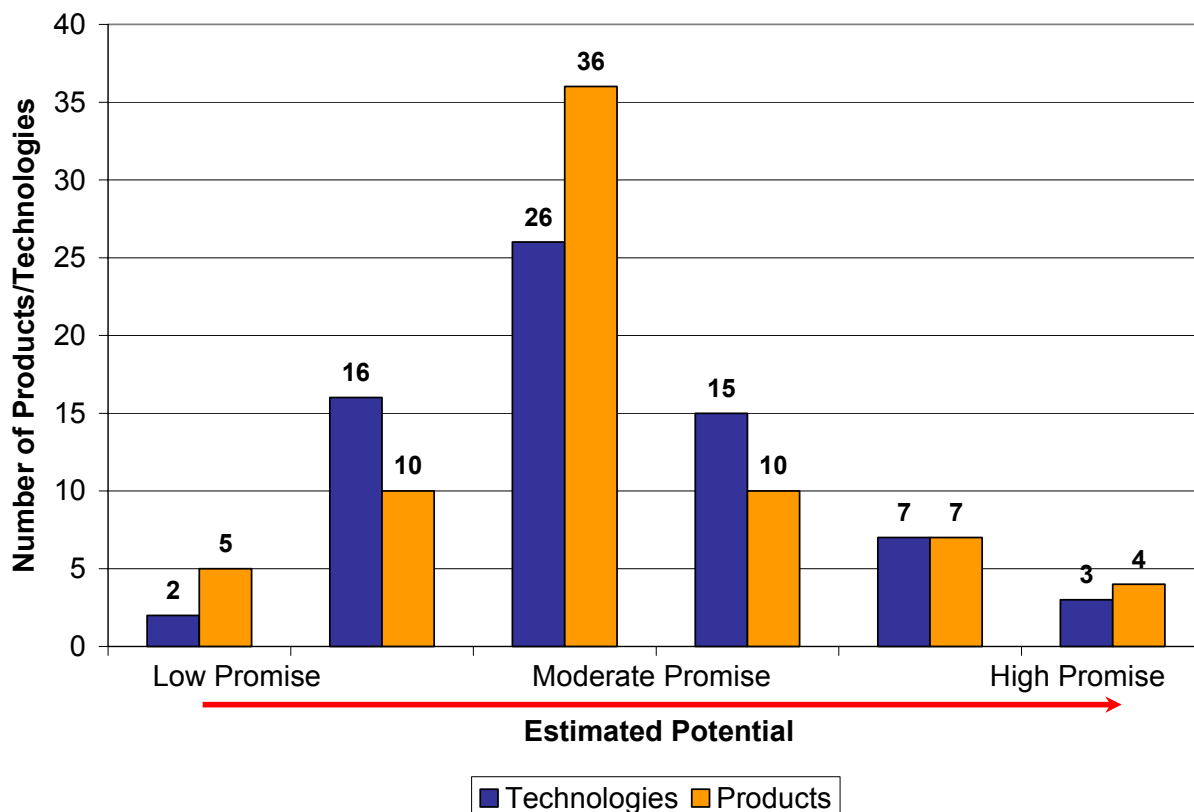
Short term: 0-3 years
Medium term: 3-5 years
Long term: > 5 years

It is important to keep in mind that this list is ever changing, as new developments are brought forth and as new information about these technologies becomes available. These products and technologies have the potential to move in either direction, up or down the list of top prospects.

Each of the 100+ products and technologies were assessed based on their demand/market potential, their economic feasibility, their stage of development, and their strength of institutional support. The distribution of the assessed potential for the reviewed products and technologies is presented within Figure 17. In order to

facilitate the identification of the most promising emerging products/technologies, Informa also conducted interviews with industry specialists to provide confirmation and insight into the finalization of the top 20 list.

Figure 17: Distribution of Soybean Products/Technologies Based on their Estimated Potential



A. Renewable Fuel

The advent of the biodiesel industry has created a large new outlet for soybean oil. Nevertheless, despite strong government support, the industry is struggling, as biodiesel production generally remains unprofitable. Overall production capacity utilization currently does not exceed 20%, and although biodiesel consumption is expected to increase at least in line with the Renewable Fuel Standard (1 billion gallons of biomass-based diesel by 2012), there is a possibility the RFS will favor animal fats and recycled grease over soybean oil because of lower greenhouse gas emissions. Still, new process technologies have the potential to improve the quality and/or the cost competitiveness of biofuels and could contribute to a larger use of biofuels.

1. Biodiesel Additives

In the early 20th century, Rudolph Diesel, the inventor of the diesel engine, experimented with fuels ranging from powdered coal, peanut oil and soybean oil. Ultimately, the most prevalent and cheap form of diesel feedstock emerged in the form of petroleum distillate (made from oil). As petroleum prices rose dramatically in the late 70's and reached an all-time high peaking at over \$145/barrel for West Texas Intermediate in the summer of 2008, new and creative feedstocks have once again emerged for the production of biodiesel. Biodiesel companies are using vegetable oils (e.g., palm oil, corn oil, canola and especially soybean oil) as a potential feedstock as well as different types of animal fats from renderers and even spent greases from restaurants have been used to produce biodiesel. Even these various biodiesels can be blended into different formulations ranging from B100 (100% biodiesel) down to B2 (2% biodiesel blended with 98% diesel fuel).

Since the industry began expanding in the late 1990s, soybean oil has clearly been the most prevalent source for making biodiesel in the U.S. Despite all of the numerous benefits of using and making soy-diesel, such as lubricity, ability to auto-ignite and high cetane levels there are a number of significant challenges faced by the users of soy-diesel. Chemically speaking, soy-diesel is a fuel comprised of mono-alkyl esters of long-chain fatty acids. These fatty acids have several unique characteristics which may cause operational difficulties for the user. The most significant issues facing the marketers and end users of biodiesel fuel are: low-temperature fluidity (known as cold flow) and thermal and oxidation stability.

- Cold flow is the problem where biodiesel performs significantly worse than traditional diesel fuel under cold conditions. When biodiesel begins to form wax crystals (called the cloud point) it can clog fuel lines and filters in a vehicle's fuel system. At even more extreme temperatures, biodiesel fuel can become a gel that cannot even be pumped; this is called the pour point (the temperature at which the biodiesel cannot flow). This is of course a major concern for the use of biodiesel in regions of the U.S. with colder climates.
- The use of vegetable oils and their high levels of unsaturates are well-known as root causes of fuel instability. Vegetable oils contain polyunsaturated fatty acids that are susceptible to oxidation, polymerization and gum formations.

These challenges have led to the investigation and development of various additives in hopes of alleviating the performance concerns of biodiesel under certain conditions. A number of companies have recently claimed to have made progress in the development of new additives. A list of some of these new biodiesel additive products is as follows:

- **Eastman Chemical, BioExtend 30HP:** this is a product that is designed to provide oxidative stability of biodiesel and blends up to B10. The company

claims that their blend of antioxidants plus a chelating agent will offer protection against the detrimental effect of oxidative stability on metals contamination.

- The German company **BASF** has built a new plant to produce a number of products under the name of **Keroflux**. The Keroflux products are chemicals which improve the flow of fuel and diesel in the winter by dispersing wax crystals, even at low temperatures.
- **Amsoil, Diesel Concentrate Plus Cold Flow** Improver (DFC); the product combines a detergent and cold flow anti-gelling agent. The detergent helps to keep injectors, rings and piston crowns lubricated and free of soot. More importantly, is the inclusion of the Cold Flow Improver additive, which is claimed to reduce the cold filter plugging point by as much as 34°F in ultra-low sulfur diesel fuel (ULSD).
- **Afton Chemical Corp**; Announced this summer (June 2nd) the launch of a new product line to address the cold flow problem. The company states that their research team, “have developed a new line of additives that represent a significant leap forward in performance and reliability for the end user.”

2. Enzymatic Transesterification

The conventional transesterification process to produce biodiesel involves the reaction of triglycerides with methanol in the presence of a catalyst (mainly NaOH or KOH). This approach offers high yields and short reaction times but it is also associated with several problems:

- High energy consumption;
- Difficulty in glycerin recovery (the co-product of biodiesel production);
- High amount of alkaline waste water (as a result of the catalyst use); and
- Interference of free fatty acids with the catalyst⁵.

Enzymatic reactions involving lipases can be an excellent alternative to produce biodiesel through a process referred to as alcoholysis, a form of transesterification reaction, or through an interesterification (ester interchange) reaction. By contrast, to conventional transesterification, the reaction temperature is much lower, recovery of the glycerin is simpler and there is no spent catalyst to remove or waste water to treat. Moreover, the free fatty acids in the feedstock can be completely converted to biodiesel. At this point, enzymatic transesterification is still being researched but it has the potential to significantly decrease production costs. Still, a number of shortcomings need to be addressed, including the high price of lipase and its short operational life.

⁵ Conventional biodiesel technologies generally use feedstock with a FFA no higher than 0.2%, as FFAs neutralize the catalyst and form soaps that (i) complicate phase separation and (ii) form sediments that may plug pipes and filters. As a result, unless refined vegetable oil is used (i.e., max FFA ≤0.1%), conventional processes generally require a pre-treatment step to remove the FFAs in the feedstock.

Novozymes has already developed an operational enzyme but is still working on it so as to bring its cost down. The company has reportedly partnered with Piedmont Biofuels from North Carolina to improve the process. The project was awarded a \$197,000 grant in 2009 by the Chatham County Economic Development Corporation in North Carolina. In addition to Novozymes, several research units including the USDA ARS are currently investigating the matter.

3. Renewable Diesel

Mono-alkyl esters of vegetable oil or animal fats (i.e., biodiesel) has, until now, been the sole source of “biomass-based diesel” in the U.S.. This situation, however, could soon change as Dynamic Fuels LLC⁶ is expected to open the first renewable diesel facility in the U.S. early 2010.

Renewable diesel, sometimes also referred to as “green diesel” or “second-generation biodiesel”⁷, is a diesel-like fuel derived from any triglyceride feedstock (like vegetable oil or animal fats). Unlike biodiesel, renewable diesel replicates the chemical structure of its diesel counterpart, therefore working seamlessly with existing distribution infrastructures, storage systems, and engines.

One major advantage of renewable diesel technologies over transesterification is that the product’s cloud point (from +50°F to -4°F) can be tailored to the application, with yields increasing at higher cloud points. A key attribute of renewable diesel technologies is also their ability to utilize a wide array of inputs as free fatty acids can be completely converted to biofuel. Furthermore, contrary to biodiesel whose production is associated with the production of glycerin that currently has little value and can be hard to dispose of, the production of renewable diesel is associated with the formation of propane and other naphtha products that are much more valuable.

Technologies also provide flexibility in the type of biofuel produced. One excellent avenue is jet fuel as conventional biodiesel does not meet the cold-flow properties and high energy densities associated with jet fuel.

One weakness of renewable diesel over biodiesel is the higher conversion cost as the reaction requires a greater amount of energy. Moreover, renewable diesel has greater particulate emissions than biodiesel.

Several companies like Petrobras, UOP, Neste, Syntroleum, and Nippon Oil Corporation have developed renewable diesel technologies.

⁶ A 50:50 venture between Tyson and Syntroleum.

⁷ Note that many consider the use of the terms “green diesel” or “second-generation biodiesel” incorrect since renewable diesel, like conventional diesel fuel, is not easily biodegradable (green refers to the origin of the fuel) and it does not meet the definition of biodiesel in terms of fuel composition.

One should note that Petrobras and Nippon Oil Corporation technologies are based on a commingled hydrotreating process. Renewable diesel made using a commingled hydrotreating process (i.e., co-processing) is only eligible for a \$0.50/gal tax credit compared to a standalone hydrotreating process.

4. Solid Transesterification Catalysts

The conventional transesterification reaction to produce biodiesel consists in reacting a triglyceride feedstock with methanol in the presence of a liquid catalyst, generally sodium hydroxide, potassium hydroxide or sodium methylate. These homogeneous catalysts (i.e., they completely dissolve in the medium) are relatively effective and inexpensive. Nevertheless, they also suffer from several drawbacks:

- They require catalyst recovery and aqueous treatment steps.
- They cannot be recovered and lead to waste products, decreasing efficiency and increasing costs.
- Base catalysts react with free fatty acids (FFAs) to form soaps that (i) complicate phase separation and (ii) form sediments that may plug pipes and filters.
- Sodium methylate is highly explosive.
- The catalyst contaminates the glycerin co-product.

In order to circumvent these problems, it is possible to use heterogeneous catalysts, a solid whose surface is catalyzing reaction of liquids and/or gases. Heterogeneous catalysts are generally made from mixed metal oxide. A common approach is to have a reactor packed with catalyst particles, with the reactants flowing past.

Their use requires neither catalyst recovery nor aqueous treatment steps, thereby simplifying downstream separation steps and enabling the production of salt-free glycerin at purities exceeding 98%. Furthermore, the process can handle low-quality feedstocks with high levels of FFAs without the need for costly pre-processing steps. Also, the catalyst can be recovered and reused, which can cut biodiesel catalysis costs by up to two-thirds.

Several companies including Axens, Better Biodiesel, New Century Lubricants, and Süd-Chemie Group have already developed several variants of heterogeneous catalysts.

B. Green Chemicals

The utilization of renewable resources as raw materials for green chemicals is gaining momentum in a context of high energy prices⁸ and increasing efforts to decrease greenhouse gas emissions. Vegetable oils, and soybean oil in particular, bear an especially large potential for the substitution of currently used chemicals,

⁸ \$60+/bbl for crude petroleum oil is high by historical standards.

since monomers, fine chemicals and polymers can be derived from these resources in a straightforward fashion.

1. Epichlorohydrin

Epichlorohydrin is a high volume commodity chemical used largely in epoxy resins to produce plastics and elastomers. In 2003, the US production capacity was estimated at 960 million lbs. Most of the production is made from propylene and chloride as primary raw materials in a multi-step process. This process, however, suffers from some undesirable features, especially low yields. Moreover, inefficiencies in some of the reactions lead to the formation of unwanted chlorinated organics that are expensive to dispose of. Such factors have prompted the search for alternative routes to produce epichlorohydrin that are more efficient and environmentally friendly.

It has been known for decades that glycerin can be made to react with hydrochloric acid to form an intermediate dichlorohydrin that can then be converted to epichlorohydrin. This chemical path, however, traditionally was not used commercially to any significant extent because of the high cost of glycerin compared to propylene. The advent of the biodiesel industry that generates large amounts of glycerin, and the tight propylene market, have now reversed this situation.

Several companies, including Dow Chemical, Solvay SA and Spolchemie, have announced plans to commercialize epichlorohydrin from glycerin.

The production of epichlorohydrin from glycerin holds great potential but the volatility of glycerin prices along with the uncertainty surrounding the future of the biodiesel industry (tight economics and emergence of renewable diesel technologies that are not associated with any glycerin production) could act as major barriers.

2. Epoxidized Soybean Oil

The term “epoxide” indicates the presence of a three membered cyclic ether (also called oxirane or alkylene oxide) in which an oxygen atom is joined to each of two carbon atoms that are already bonded with each other. Chemically speaking, epoxides undergo reactions such as C-O bond cleavage, nucleophilic addition, hydrolysis and reduction under mild conditions and more rapidly than other ethers. Epoxides are formed by some oxidation reactions of alkenes with peracids. Epoxidized soybean oil (ESO) is the most prevalent epoxidized oleochemical (glycerol fatty ester). Soybean oil offers numerous advantages as a feedstock, such as low toxicity and inherent biodegradability. In general ESO shows excellent potential as a renewable material for industrial applications.

In recent years, extensive work has been conducted to develop polymers for epoxidized triglycerides or fatty acids. These renewable resource-based polymers can form a platform to replace/substitute for petroleum-based polymers through innovative design this biobased platform can compete and sometimes even surpass

petroleum-based materials on a cost-performance basis with the added advantage of being eco-friendly. As a result, there is interest, for example, in the development of new biobased thermosetting polymers.

The current difficulties with some of the biobased polymers in commercial applications are mainly due to their inferior mechanical and thermophysical properties in comparison with conventional petroleum-based polymers. Therefore, it is currently difficult to completely replace petroleum-based polymer materials for nothing more than the necessary mechanical and thermophysical physical properties. It is not necessary, however, to completely replace petroleum-based polymer material with a biobased material. As a result, an excellent solution combines different features and benefits of both synthetic and biobased materials to reduce the dependence on petroleum. Consequently, biobased materials can be used to partly replace thermosetting resins, such as epoxy resin and unsaturated polyester.

The largest category of industrial ESO oil use includes plastics and resins. ESO is primarily used as a plasticizer or stabilizer to modify the properties of plastic resins such as polyvinyl chloride (PVC), and ESO can also be used as a reactive modifier or diluent⁹ of other systems. For example, numerous studies of ESO and epoxy resin blends have been performed to obtain modified networks. More recently, researchers have begun to explore the feasibility of manufacturing composites from ESO. Up to now, the widespread structural application of ESO has been limited because of its low crosslinking density and mechanical performance. The development of soybean oil-based resins for structural applications is still a challenge for the polymer and composite industries.

Dow Chemical Company (Dow) used to be a major producer of ESO. In 2006, however, Dow announced their departure from ESO manufacturing. The primary firms in the ESO manufacturing market are Arkema, Chemtura and Ferro. Since 2006, these remaining firms have been faced with a challenging economic environment given the extreme price volatility and record high price levels of soybean oil. The rapid growth of the U.S. biodiesel industry and the demand for soybean oil as a feedstock is a key contributor to the difficult situation.

3. Lubricant

Biobased lubricants and especially soy-based lubricants can be considered a fairly mature area of research, where the pros and cons are well understood by the scientific community compared to mineral oil lubricants. This does not mean however, that soy-based lubricants do not have a significant opportunity for gaining market share from traditional petroleum based lubricants (mineral oils). In the end, the ultimate challenge of soy-based lubricants will be the ability to measure up to the technical and economic characteristics of mineral-oil (hydrocarbon based) lubricants while providing the desired benefit of being biodegradable.

⁹ A diluent decreases the viscosity of a fluid.

The market potential for soy-based lubricants, both domestically and internationally, is quite large and diverse. This diversity is exemplified in the fact that many of the lubricant market studies exhibit a lack of consistency in the categories that they highlight. In general, the primary lubricant product categories are as follows: hydraulic fluid, two-cycle engines, bar/chain (chainsaws), crankcase (engines), drip oil, rail and flange, wire rope, metal cutting, dedusting.

Estimates by the Freedonia Group in 2007, identified the world market for lubricants as being approximately 11.8 billion gallons per year (41.8 million metric tons) and the market being segmented by the following categories:

- Engines 48%
- Process oils 15.3%
- Hydraulic oils 10.2%
- All other 26.5%

An estimate of the U.S. market for lubricants was conducted by the National Petroleum Refiners Association (NPRA) in 2006. The NPA estimated that the U.S. lubricant market is approximately a 2.5 billion gallon a year industry. Based on the NPRA study, the U.S. market is segmented into the following categories;

- Automotive 56.1%
- Industrial 21.2%
- Process oils 18.1%
- Metal working 2.1%
- Greases 2.4%

Two of the biggest hurdles facing the use of soybean oil (and most vegetable oils in general) as a lubricant are performance issues related to thermal oxidative and hydrolytic stability (note: traditional mineral oil lubricants do not have these problems). These issues are being addressed by the industry on a number of important fronts, they are as follows:

- The use of biotechnology (by such firms as Monsanto and DuPont) to produce soybeans that are high in oleic acid (18:1), with monosaturated levels that are better than canola/rapeseed.
- Non-transgenic modification of soybeans in order to develop new varieties with high levels of oleic acid (18:1) and lower levels of unsaturates.
- ADM and others are working on the development of low-cost soybean oil modification processes to produce high-temperature stability attributes.
- Researchers at such companies as Valvoline have been working on the blending of chemical additives in order to improve soybean oil stability. This pathway has proven to have a much lower cost of development compared to the other advancements.

Future demand for conventional lubricants will likely be consistent with the overall economic growth (based on Gross Domestic Product, GDP) of a respective country. This means that areas with faster anticipated economic growth such as China and India will probably experience much stronger demand for conventional lubricants versus slower growth economies such as the U.S. and Europe. A caveat is in order however, these faster growth regions will also be difficult to penetrate with soy-based lubricants unless favorable policies are enacted in those countries to promote the use of bio-based lubricants. Countries such the U.S. and regions like the European Union have been encouraging policies where biobased products such as soy-based lubricants are valued for their environmental benefits. Further policy progress in these “environmentally friendly” countries will be necessary along with significant technological advancements in order for soy-based lubricants to gain notable market share away from traditional mineral oil applications/markets.¹⁰

4. Polyols

Polyols are chemical compounds whose main use is as reactants to make polymers, polyurethanes in particular. Although polyols traditionally originate from the petrochemical industry, a class of “renewable” polyols has recently emerged. These renewable materials, that qualify as “biobased products” under the Farm Security and Rural Investment Act of 2002, are made from vegetable oil and help reduce the carbon footprint of the various downstream applications. The United Soybean Board estimates the annual North American product demand for polyols represents 3.4 billion pounds, with a conservative estimate of the potential for soy-oil-based polyols of about 600 to 800 million pounds (2006 estimates). NOP or (natural-oil polyols)¹¹ made from such seed oils as soybean oil, are making inroads as a polyurethane precursor. In 2006, the US production of polyurethane was estimated at 6.3 billion lbs.

Dow Chemical (Dow) is one of the primary leaders in the utilization of soy-based polyols in the production of their trademarked product named RENUVA. Dow has high expectations for its RENUVA™ process since it creates polyols with a reduced impact on the environment.¹² Dow has gone to great lengths to conduct life-cycle analysis, the results show that the RENUVA™ technology is in fact greenhouse gas neutral and uses 60% fewer fossil fuels versus conventional polyols. The primary target markets for RENUVA™ are transportation, bedding, furniture, carpet, and CASE (coatings, adhesives, sealants, and elastomers) markets, with applications

¹⁰ For example, the United States Department of Agriculture’s BioPreferredSM program, which “aims to increase the purchase and use of renewable, environmentally friendly biobased products while providing “green” jobs and new markets for farmers, manufacturers, and vendors.”

¹¹ Polyols are alcohols containing multiple hydroxyl groups with typical applications in food science and polymer chemistry.

¹² RENUVA is created by a four step process of methanolysis, hydroformulation, hydrogenation and polymerization. Interestingly, where the soybeans are grown (hotness or dryness of the season) impacts the fatty acid levels in the oil, the hydroformulation process is used to address the irregularity in the oil, thus providing a more uniform and predictable feedstock.

including seating, arm, headrest and headliner foams in vehicles; viscoelastic “memory” foam for bedding; carpet backing; and coatings, spray elastomers and one and two-component adhesives and sealants. Dow scientists believe that in some applications RENUVA™ has performance benefits over petroleum-derived foams, citing an improved compression set and enhanced hardness for greater durability. It should be noted that Dow is also looking at the use of other vegetable oils besides soybean oil (such as sunflower and canola) so that they are not vulnerable to sourcing only one feedstock for their process.

Cargill has also been active in the soy-based polyol market since 2005. Their branded product is called BiOH™ and they are initially targeting North America, European and Latin American markets. They will eventually expand their offerings in Asia. Cargill broke ground on a \$22-million BiOH™ brand polyols manufacturing plant in Chicago in July 2008; the plant was expected to be fully operational in November 2009. The new production facility is claimed to be the first world-scale biobased polyols plant. Cargill estimates that the global market for polyols in polyurethane production stands at over 10 billion pounds and is expanding at 3-4% per year. Cargill is expected to compete in the same markets as Dow Chemical and their product RENUVA.

5. Propylene Glycol

Propylene glycol (PG) is also known by the systematic name of propane-1,2-diol. PG is an organic compound (diol alcohol) that is usually a faintly sweet and colorless clear viscous liquid that is hygroscopic (the ability of a substance to attract water molecules) and miscible (can be mixed in all proportions) with water, acetone and chloroform. Interest in PG relates to the production of biodiesel and the coproduction of glycerin. Glycerin can be used as a feedstock to produce PG which has created a great deal of interest in many large companies such as Dow Chemical, ADM and Cargill. These companies are interested in taking crude glycerin which has had limited value (has actually been used as boiler fuel and land filled) and converting it to a higher value product, i.e., PG to use in numerous applications.

Propylene glycol is a highly versatile product and is used in many value-added functions. A sampling of the uses of PG is as follows (note this is not an exhaustive list);

- Unsaturated polyester resins (UPRs) can be made from PG which is consumed primarily in the construction, marine and transportation industries (UPRs is the largest market for PG). Nearly three-quarters of UPR is reinforced with fiber glass or mineral fillers to form fiber glass reinforced plastics (FRPs), these are tough, lightweight composites.
- As a solvent in many pharmaceuticals, including oral, injectable and topical formulations.
- As a moisturizer in medicines, cosmetics, food, toothpaste, mouth wash and tobacco products.

- As a solvent for food colors and flavorings.
- As an ingredient, along with wax and gelatin, in the production of paintballs.
- As a less-toxic antifreeze.
- In hand sanitizers, antibacterial lotions and saline solutions.
- As a coolant in liquid cooling systems.
- To treat livestock ketosis, propylene glycol acts as a glucose precursor and may be effective as ketosis therapy, especially in mild cases or in combination with other therapies.¹³
- As the main ingredient in deodorant sticks.
- As an aircraft de-icer.

In the U.S., domestic consumption of PG has grown modestly over the last five years, led primarily by the production of UPR. The other market showing strong growth is in the area of personal care products. Going forward demand growth for PG will be heavily influenced by the status of the U.S. economy. ICB (ICIS Chemical Business) forecasts that the UPR market will expand at 1.5% per year and the personal care segment will grow at a slightly faster rate of 2.5% per year. While PG growth in the U.S. and Europe is predicted at GDP rates, Asia is expected to experience much stronger growth at approximately 7.0% per year.

Future expansion in the production of PG will depend heavily on two factors, the ready supply of glycerin from biodiesel production and the level of economic activity in a respective country/region. For example, Dow Chemical is currently in the process of “mulling” over its long-term strategy to produce what they are calling “green” propylene glycol (PGR or PG renewable) using glycerin from biodiesel as a feedstock. Mandy Bricco, global product director with Dow stated that, “we have sensed some customer interest on the green aspects of PGR/PG renewable, as well as a hedge against rising propylene feedstock prices. However, we must weigh factors such as the price of glycerin, the production of biodiesel and price of hydrocarbons in this decision.”¹⁴ If Dow did decide to build a new PGR facility, Bricco said, “it would be world scale in size” equating to 50,000-100,000 tonnes/year. ADM is constructing a 100,000 tonne/year PG and ethylene glycol facility in Decatur, IL, using glycerin and sorbitol as starting materials. Startup of the plant is expected to begin in the third quarter of 2009. Cargill has recently announced that they have suspended their joint venture with Ashland Chemical to construct a 65,000 tonne/year plant in Europe due to uncertainties in the economy and the volatility in commodity prices.

6. Methyl Soyate / Soy Methyl Ester (non-fuel applications)

Methyl soyate is also known as fatty acid methyl esters, soybean oil methyl esters and soy methyl ester. It is best known as biodiesel, but it also has other applications, which are discussed in this section. Methyl soyate is manufactured by the esterification of soybean oil. Soy oil is heated and reacted with methanol in the

¹³ The Merck Veterinary Manual.

¹⁴ Statement was made March 2009, press release.

presence of a catalyst. The reaction causes the separation of soy oil into methyl ester and glycerin. Following the separation, the crude glycerin goes to storage for further refining or other applications such as animal feed. The methyl ester goes through a number of finishing steps to derive the final product. Methyl soyate fits neatly in the category of being a versatile “green chemical” with numerous applications. As a chemical, methyl soyate is highly competitive in terms of its cost relative to petroleum chemicals, is low in toxicity, has a high flash point, has low VOCs (volatile organic compounds), is readily biodegradable and can be easily substituted for traditional hydrocarbon based chemicals such as solvents. Methyl soyate is ideally situated as a chemical to take advantage of the ever increasing regulatory pressure on ozone-depleting chemicals (ODCs), hazardous air pollutants (HAPs) and VOCs.

To date, most of the uses on methyl soyate have been in the following markets;

- **Solvents:** Methyl soyate has been used as a specialty chemical (versus a bulk commodity chemical) in the dissolving, suspending, carrying or removal of other materials. In 2007, the U.S. solvent market was approximately 11.9 billion pounds. Methyl soyate products participated in approximately 12% of the total market representing a 1.4 billion pound market. The estimated market share of the 1.4 billion pounds for methyl soyate is approximately 40 million pounds, or 2.8%.
- **Cleaning Products:** It is estimated that this market is the largest user of methyl soyate. Methyl soyate can be found in a broad array of both institutional and residential applications, such as hard surface cleaners, household cleaners, glass cleaners, flood cleaners, hand cleaners, bathroom cleaners, stainless steel cleaners and graffiti removers. Major consumer companies such as SC Johnson and Procter and Gamble have taken significant steps to assess their impact on the environment regarding the formulation of their products. This has to the introduction of many new greener products, especially in the area of cleaning products.
- **Coatings, Inks and Adhesives:** This is a fairly well established and mature market. Methyl soyate has been formulated into inks, for example, since the late 70's when the Newspaper Association of America was looking for different ways to make ink substitutes in order to replace the high cost of petroleum based ink. As previously mentioned, SC Johnson is very active in the area of sustainability and the use of renewable resources. For example, they limit the number of printed editions of its Public Report and encourages distribution via the Internet at www.scjohnson.com. Also, the report is printed with soy ink, which is naturally low in VOCs.
- **Paint Strippers:** This is a fairly small market, however it is gaining more interest because of the large number traditional stripping products that use methylene chloride (MeCL). MeCL is facing regulatory pressure because of worker safety

and its ozone-depletion properties. Methyl soyate can be easily formulated with other organic cosolvents and surfactants, thus replacing the need for MeCL based strippers.

- **Parts Cleaners and Degreasers:** This is a large yet fragmented market that relies heavily on the use of mineral spirits for cold parts cleaning and trichloroethylene (TCE) for vapor degreasing. These chemicals are highly flammable and are also high in VOCs. Methyl esters can be easily combined with other biocosolvents to replace traditionally formulated parts cleaners and degreasers.
- **Other Removers - Adhesives, Mastics, Resins, Inks, Asphalt and Rust:** Methyl soyate can be used to replace numerous traditional solvents such as toluene, mineral spirits, MeCL and methyl ethyl ketone (MEK). Methyl soyate can be formulated to clean and remove many types of polymeric and petroleum based materials. One interesting application is the use in remediating the environment when there has been an oil or fuel spill. It is actually listed by the U.S. EPA on the National Contingency Plan product schedule for oil spills, and it is the only shoreline cleaner licensed by the State of California.

Environmental regulations will play an important factor in the further adoption and expansion of methyl soyate as a chemical in replacing hydrocarbon based petroleum products. The pricing of methyl soyate remains fairly competitive with other traditional chemicals, however, petroleum prices have fallen significantly from their record highs, meaning methyl soyate will likely need to rely more heavily on the advancement of green policies in the U.S. in the short-run.

7. Wood Adhesive

Wood adhesives are used in a number of applications including plywood, wood flooring, particleboard, oriented strand board (OSB), and medium-density fiberboard. Traditionally, urea formaldehyde, phenol formaldehyde, and phenol-resorcinol-formaldehyde resins have been the preferred adhesives.

Soy-based adhesives have been utilized to manufacture wood products for over 70 years, but until recently, their use was primarily limited to niche applications as a result of their lower performance and high cost relative to petrochemical-based resins. Nevertheless, environmental and health concerns along with rising costs for resins have prompted a resurgence of interest in developing new soy-based products.

Soy hydrolyzate, for instance, can be used with a phenolic resin in plywood, OSB and engineered wood product applications to reduce the use of the phenol component by up to 40%, while providing similar properties. Soy flour can also be used as a foaming agent for phenol formaldehyde resins in lieu of blood meal in order to reduce resin usage.

Companies like Hexion Specialty Chemicals, Hercules/Heartland, LCB Worldwide and USM Corporation have all developed their own soy-based adhesive.

In 2006, it is estimated that 3.72 billion lbs of wood adhesives were used in the U.S.. A weak housing market and the current economic recession are expected to adversely impact the demand for wood products, but a study released by the United Soybean Board in 2007 estimates that soy-based wood adhesives could account for as much as 20% of the U.S. market by 2011.

C. Soybean Crushing

Crushing is the common process used to add value to soybean production. In 2007/08, 1.8 billion bu. of soybeans were crushed in the U.S. Because of the predominance of this process, it is critical to monitor new technological developments that can help improve the efficiency of this process.

1. Enzymatic Degumming

In vegetable oil refining, it is necessary to remove the impurities that affect the taste, smell, visual appearance and storage stability of the oil. The degumming step in the refining process consists of removing phosphatides that are not desirable because they settle out of the oil during shipping and storage and have adverse effects on the color and flavor of oil. Degumming is traditionally accomplished through chemical or physical processes. However, Danisco, Novozymes and Verenium have recently started to market an alternative to these processes with enzymatic degumming.

The principle of enzymatic degumming is to convert non-hydratable phosphatides into hydratable ones in a reaction catalyzed by a phospholipase. Both the phosphatides and enzymes are collected in the water phase and can be easily removed with a one-step centrifugation process.

Enzymatic degumming is an important new development in the oil refining industry as it provides a number of benefits over chemical and physical refining methods:

- Higher yields: Very little oil is lost in the process, due to little water usage, resulting in a 1-2% yield increase compared to the other methods, depending on the phosphatide content of the crude vegetable oil.
- Significant cost saving: The process is conducted at a lower temperature than conventional approaches and uses less water. Combined with the yield gain, these savings can add up to \$1-11 per tonne (up to ½ cent per lb) depending on the process (chemical degumming tends to be more expensive), the yield increase, and vegetable oil prices.
- Environmentally friendly handling: No chemicals are used.

Enzymatic degumming can also be implemented by biodiesel producers that use crude vegetable oil as a feedstock. Additionally, the method does not generally increase free fatty acids as do other processes.

2. Supercritical Carbon Dioxide Extraction of Oil

Conceptually Supercritical Fluid Extraction (SFE) or in this case Supercritical CO₂ extraction (SC) has been around for a significant period of time. The applications and type of products produced using this extraction process, however, have been fairly limited because of the sophisticated and expensive high-pressure equipment that is required. As new equipment and analytical techniques have evolved, the SC process is finding numerous new uses and applications in the industrial and food grade processing areas. The increased demand for SC is being heavily influenced by the need for greater information on processing, quality control, contamination, environmental and food regulations, and the need for faster, more powerful, cleaner and cheaper analytical procedures required by chemists, regulatory agencies and regulatory agencies and quality control laboratories. The SC method of extraction can be characterized as being fast, reliable, clean, and advanced enough for numerous food and industrially related applications.

A supercritical fluid, which is a function of the SFE or SC process, is any substance at a temperature and pressure above its critical point. The fluid can diffuse through solids like a gas, and dissolve materials like a liquid. Additionally, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of the feedstock to be "tuned". Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids, being used for decaffeination and power generation respectively.

Most soybean crushing facilities in the U.S. utilize hexane as a solvent in their oil extraction processes. Hexane is a highly flammable and volatile chemical in that can also experience significant price swings. The hexane extraction process also yields crude soybean oil that must be degummed. The SC extraction process produces soybean oil which does not contain any phospholipids, thus eliminating the degumming step. Two issues are critical drivers in the future adoption levels of this process/technology in soybean crushing (1) capital costs and the continued advancement of the biodiesel industry and (2) environmental regulations.

- The SC extraction process has factual benefits compared to traditional hexane extraction. The biggest barrier to entry is the additional capital costs that are necessary for adoption of the technology. Two variables are important for overcoming the cost (1) continued expansion of the biodiesel industry and (2) the potential inclusion of the process in an integrated biodiesel facility (both crushing and biodiesel production). Syracuse University (SU) and The New York State Energy Research and Development Authority have been exploring the technical performance and economics of the integrated biodiesel model. In August 2006,

they authored a report entitled “Integrated Multistage Supercritical Technology to Produce High Quality Vegetable Oil and Biofuels.” The initial findings of the report have been highly favorable regarding the concept. Additional research continues at these institutions concerning the feasibility of the integrated model. Another economic consideration will also be required for advancing the SC method, a financial improvement of the biodiesel industry; over the last two years returns to the industry have been very weak which has caused new growth in capacity to stall.

- The SC process could gain greater interest if the government (EPA) imposes tighter regulations on the soybean crushing industry regarding the use of hexane.
- There is also a segment of the population that is willing to pay a premium for non hexane extracted soybean oil because of the environmental and toxicity concerns.

D. Value-Added Soybean Varieties

Over the years, improvements in breeding tools and seed varieties have played a major role in improving farm performance and revenue. Seed developers are currently working on several promising new value-added soybean varieties that have the potential to increase farmers’ revenues.

1. High Oil Soybeans

With all the new molecular breeding tools now available to seed developers, important gains in productivity and changes in product attributes are expected in the coming years. High-oil traits, in particular, have the potential to provide a significant increase in vegetable oil production and to help processors meet the growing demand for vegetable oil for food and bio-fuel. The prospect of increasing the oil content in soybeans is especially appealing since it has the potential to add value to soybean production considering that most new soybean applications are focused on the oil part as opposed to the protein.

Monsanto's Renessen joint venture with Cargill is currently researching a high-oil soybean variety that could increase oil content by 3% to 5%, without a loss in protein or grain yield. The first generation of the new variety is projected to be commercialized within 2-4 years and is thought to have an acreage potential of 15-40 million acres. The second generation is in a much earlier phase of development but could be released within 10 years.

2. High Stability Oil Soybeans

Since vegetable oils rich in polyunsaturated fatty acids (e.g., linolenic and linoleic fatty acids) are prone to oxidation and shelf-life issues, hydrogenation has been widely applied to convert unsaturated fatty acids (“FA”) into saturated ones.

However, the controversy over trans fats and the subsequent emphasis on trans fat reduction has generated a strong demand for alternatives to partial hydrogenation. One solution brought forward by seed developers has been to develop through breeding and genetic modifications oilseeds with a low content in polyunsaturated FA.

The release of low linolenic varieties by Monsanto, Pioneer and Asoyia has been the first step in improving the oxidative stability of soybean oil. Nevertheless, the resulting oils still lack oxidative stability, due to a relatively high polyunsaturated fatty acid content, and have had limited success as a result.

The second step in improving stability has been to develop oils rich in oleic FA, a monounsaturated FA. Asoyia was the first player in this market by releasing a mid-oleic low-linolenic soybean variety in 2008, followed in July 2009 by Pioneer, which released Plenish, a brand of high oleic soybean oil. The high levels of oleic acid significantly increase the stability of the oil when used in frying and food processing applications. Additionally, there are numerous bio-based industrial applications for high oleic soy oil, including lubricants, foam products, liners and other oleo-chemical applications.

Additional modified oilseeds are at various stages of development. For instance, soybeans with increased levels of stearic acid are being developed as an alternative to partially hydrogenated fats and high saturate fats which are required to provide solidity and structure to certain foods. Monsanto expects to release this new variety within 4-8 years.

One particularity of these new seed varieties is that seed companies tend to utilize traditional breeding and marker assisted breeding by opposition to genetic modifications, which have a bad connotation for a segment of consumers.

These oilseeds are grown on a contract basis and sold at a premium. As a result, these new varieties have the potential to bring significant value-added for soybean producers.

3. Omega-3 Fortified Soybeans

Since the FDA has recognized the importance of omega-3 fatty acids for reducing the risk of coronary heart disease, a growing number of food companies have enriched their products in omega-3. According to Datamonitor, more than 1,200 products containing omega-3 were launched worldwide in 2006, with the biggest sectors coming from dairy, bakery and processed meats and fish. In fact, a recent study released by *Frost & Sullivan* predicts that the omega-3 ingredients market will grow at a rate of 24.3% annually, and will be worth \$1.6 billion by 2014.

The omega-3 market has traditionally been dominated by fish oil but the animal-origin of the oil, its high price, and concerns over the sustainability of fish stocks

have had the industry looking for alternatives. One of these alternatives has been to genetically modify soybeans to provide oil enriched in the omega-3 fatty acid called stearidonic acid (SDA).

SDA is an intermediate omega-3 fatty acid in the conversion of alpha-linolenic acid (ALA), an omega-3 found in plants, into eicosapentaenoic acid (EPA), the long-chain omega-3 found in fish. SDA is not as readily used by the body as EPA but it is much more stable and does not impart a fishy taste. As a result, oil rich in SDA can be incorporated into many existing foods without losing consumer acceptance.

In 2007, Monsanto and Solae announced a collaboration over the development of omega-3 from genetically-modified soybeans. Monsanto is expected to release the new soybean variety within 2-4 years.

E. Other Soybean Products/Technologies

In addition to the aforementioned sectors of developments, there are numerous other initiatives that could help increase the demand for soybeans.

1. Aquaculture Feed

The global aquaculture industry is expanding steadily, averaging 6.6% over the past 10 years (1998-2007). Nevertheless, as aquaculture keeps growing, so does the demand for protein meal. Fishmeal, with 3.1 million tonnes currently consumed by the aquaculture market, is the major protein source for aquaculture, but as aquaculture production outpaces fishmeal production, some are concerned fishmeal availability will constrain the expansion of the industry, leading many producers to look for ways to lessen their dependence on fishmeal. As a result, researchers, aquaculture producers and feed manufacturers have been looking at alternative protein sources to replace fishmeal in diets.

It has been known for a long time that soybean meal can be used in aquaculture feed but anti-nutritional factors that reduce fish performance, particularly at higher inclusion levels and within carnivorous fish specie diets, have limited its adoption. In general, herbivorous fish species tend to be somewhat tolerant to plant proteins and can more easily substitute for fishmeal in the diet. Nevertheless, carnivorous species cannot tolerate plant proteins as well and have had less success in reducing their dependence on fishmeal.

Contrary to soybean meal, however, soy protein concentrates (SPC) do not contain these high levels of anti-nutritional factors and can be utilized at higher inclusion rates as well as within carnivorous fish specie diets. Consequently, SPC have the potential to play a major role in the aquafeed market

Only a few companies, ADM, Cargill and Solae, currently produce SPC in the U.S. but their production is food-grade and high prices have prevented their use in

aquaculture. A few other companies, however, including Danish manufacturer Hamlet Protein, have developed processes to produce feed-grade SPC. This feed-grade SPC, with 56-60% protein compared to 65-67% for food grade applications, is far more competitive and is expected to play a role in the U.S. aquafeed market in the future. Already, Hamlet Protein has bought land in Iowa and intends to break ground on a new feed-grade SPC production facility in 2010.

2. Animal Feed

The production of biodiesel and ethanol generates co-products in the form of glycerin and distillers dried grains (DDGS) respectively. The renewable energy industry is faced with the opportunity/challenge of finding a home for these co-products in order to add meaningful revenue to their bottom line. In the production of biodiesel for example, a gallon of biodiesel from soybeans yields approximately two-thirds of a pound of crude glycerin.

For many years, U.S. crude glycerin production remained relatively flat (averaging between 300 to 350 million pounds per year), until 2003 when the biodiesel industry began to dramatically expand capacity. In 2008, Informa estimates that the U.S. biodiesel industry produced a total of 784 million pounds of crude glycerin. An additional amount of crude glycerin, approximately 14 million pounds, was produced from other processes such as the manufacture of soap.

The rapid rise in glycerin levels has far exceeded the demand for glycerin and caused the need to look for new/creative ways of utilizing glycerin. Typically, crude glycerin is refined for value-added applications, spread as a dust suppressant, burned as fuel or in some cases land filled. Recent research however, has explored the use of crude glycerin as a feed supplement. The USDA Agricultural Research Service, Iowa State University and Auburn University have been very active in the development of feeding trials using glycerin for poultry (layers and broilers) and swine at various stages of their lifecycle. Crude glycerin is approximately 85 percent glycerin with 10 percent water and 5 percent salts. The goal of the researchers has been to, “use glycerin as an energy source for swine and poultry. You have to have energy for pigs and chickens to grow, as well as amino acids and other items, and glycerin is used for growth and productive purposes.”¹⁵ Most of the research shows that crude glycerin provides energy to the swine and poultry diets with a caloric energy level that is similar to corn. Most of the swine rations had crude glycerin inclusion rates of 5 to 10 percent (replacement corn). At these inclusion levels studies have shown that there were, “no effects on weight, carcass composition, and meat quality in the pigs”, from weaning to market weight. The layers and broilers experienced similar performance successes using lower glycerin inclusion rates in the 6 percent range.

Three important factors still remain concerning the use of glycerin, (1) logistics, (2) more consistent and better quality of glycerin and (3) price.

¹⁵ Brian Kerr, USDA, Agricultural Research Service, Ames Iowa.

- Glycerin is highly liquid and the handling and storing of the co-product as an alternative feedstuff for swine and poultry in an integrated feed mill setting will require additional investigation. Another similar logistical issue is the need to limit the distance that the glycerin would have to be moved from the biodiesel plant and ultimately to the end user. Liquids are typically more difficult to handle and more costly to transport relative to solids (like corn).
- The biodiesel industry as with the corn to ethanol industry is challenged by providing consistent high quality co-products. The ethanol industry has made significant strides in providing more uniform DDGS to the feed industry. The biodiesel industry however, is not as consistent as the ethanol industry in the quality and consistency of glycerin production. Animal livestock nutritionists are very particular in the way that they formulate their rations, if the quality of a feedstock is not consistent overtime from a feed provider they will not include the product in their rations.
- Since crude glycerin is being considered a supplement to corn in the diets of livestock, the price of glycerin relative to corn will play a significant role in the usage of glycerin over time. Corn and glycerin prices can be very volatile and do not necessarily move together in the same manner. In the future, if glycerin is cheaper relative to corn on a pound to pound basis, then livestock nutritionists will be more likely to include crude glycerin in the animals' diets. If however, corn is cheaper relative to glycerin, it will be difficult to encourage the use of glycerin in the animals' diets.

3. Olefin Metathesis

In 2005, three scientists, Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock shared the Nobel Prize in Chemistry for "the development of the metathesis method in organic synthesis," also known as the Grubbs reaction. Technically speaking, the process is defined as an organic reaction that entails the redistribution of alkylene fragments by the scission of carbon - carbon double bonds in olefins. Described in layman terms, "Metathesis is a reaction in which chemists selectively strip out certain atoms from one carbon compound and swap them with atoms from another compound. The end result is a custom-built molecule that has specialized properties"¹⁶

The process as defined by Robert Grubbs in his Nobel Laureate lecture as one that is based on "green chemistry" with the following characteristics;

- Starting material
 - Utilizes a renewable feedstock (such as soybean oil)
 - The starting material has simple structures

¹⁶ Rhonda Hillbery, Caltech News.

- Processing
 - Few/no by products
 - No/little solvents (Water)
 - Low energy input
- Products
 - Replace polluting materials
 - Replace petroleum based material

As acknowledged in the lecture, a codevelopment program for the conversion of seed oils to value added chemicals was formed between Cargill, Materia¹⁷ (www.materia-inc.com), California Institute of Technology and the Department of Energy (DOE) with the stated goal to replace petroleum based products with those from renewable resources. The renewable resources to concentrate development efforts are soybean and corn oils which are highly unsaturated (many double bonds) and can be modified by olefin metathesis to value added functional molecules. Total funding for the effort reached \$3.8 million.

Cargill has the option to acquire an exclusive license from Materia to commercialize discoveries made in the field of the agreement.

In 2008, Materia announced the creation and independent financing of a new company built on the technology developed by the Materia and Cargill relationship. The new firm that emerged was Elevance Renewable Sciences (www.elevance.com). Elevance has moved aggressively to expand operations by recently securing more than \$40 million in venture capital led by investments from TPG STAR, L.P. and TPG Biotechnology Partners II, L.P. Elevance has a stated goal of generating \$1 billion in sales by 2016 by participating in the \$500 billion a year global specialty chemicals market. K'Lynne Johnson, CEO of Elevance stated the following, "Elevance was founded to create a next generation specialty chemical company that can leverage multiple feedstocks such as soy, canola and corn." The company's first highly visible product was the Cargill branded NatureWax, natural soy wax. Elevance promotes NatureWax as "a premium natural soy wax that allows candle makers to create superior soy wax candles with outstanding manufacturing performance, excellent fragrance holding and improved pour. Soy candles made with Cargill's NatureWax burn slower and last longer than paraffin wax candles giving candle lovers more value and satisfaction." Because all of these companies are privately held, there is no sales data (value or volume) regarding initial success of NatureWax.

¹⁷ Materia, Inc. was founded in 1998 to commercialize olefin metathesis catalyst technology. Materia is a privately held corporation headquartered in Pasadena, California with additional manufacturing facilities in Huntsville, Texas with a total of 60 employees.

4. Soy Isoflavones

Soy isoflavones are a class of phytoestrogens—plant-derived compounds with estrogenic activity. They have been studied for their role in cancer prevention and slowing down the ageing process in peri-menopausal women, and have proved to be a popular alternative to hormone replacement therapy for those wishing to control menopause symptoms without resorting to drugs. However some critics claim that isoflavones can increase the incidence of epithelial hyperplasia and cause goitre and hyperthyroidism.

Isoflavones are present in relatively large amounts in virtually all soy products, with the exception of soy-protein concentrate. Soy isoflavone are also available in the form of dietary supplements, extracts and supplements are available as dietary supplements without a prescription in the U.S.

ADM is the primary producer of isoflavones in the U.S. Acatris, a Dutch company with its American regional office in Minneapolis, is another large producer of isoflavones. There are several processes reported for isoflavone purification, but ADM reportedly extracts isoflavones from soy molasses while Acatris uses soy germ.

Although conflicting studies regarding the health effects of isoflavones have slowed down the growth of this market, the aging of the U.S. population present some growth prospects.

IV. Phase III Top 8 Soybean Products/Technologies

Upon further analysis of the top 20, which was based on information gathered from more in-depth desk research and interviews with general experts within the field of biobased product and technologies and with product/technology specific representatives, the top 20 list was refined down to the top 8 considered to have the greatest potential to add significant value to Minnesota's soybean production.

This section reviews the top 8 products and technologies, which are listed in Table 8, in more detail than was presented in the previous section.

Table 8: Top 8 Soybean Products and Technologies

Product/Technology Name	Soybean Origin	Product	Technology	Product/Technology Timeframe
Enzymatic Transesterification	Soybean Oil		✓	Short Term
Renewable Diesel	Soybean Oil	✓	✓	Short Term
Epichlorohydrin	Glycerin	✓		Medium Term
Polyols	Soybean Oil or Glycerin	✓	✓	Short Term
Wood Adhesive	Soybean Protein	✓		Short Term
High Oil Soybeans	Soybean		✓	Medium Term
High Stability Oil Soybeans	Soybean		✓	Short Term
Aquaculture Feed	Soybean Protein	✓		Short Term

Short term: 0-3 years

Medium term: 3-5 years

Long term: > 5 years

A. Renewable Diesel

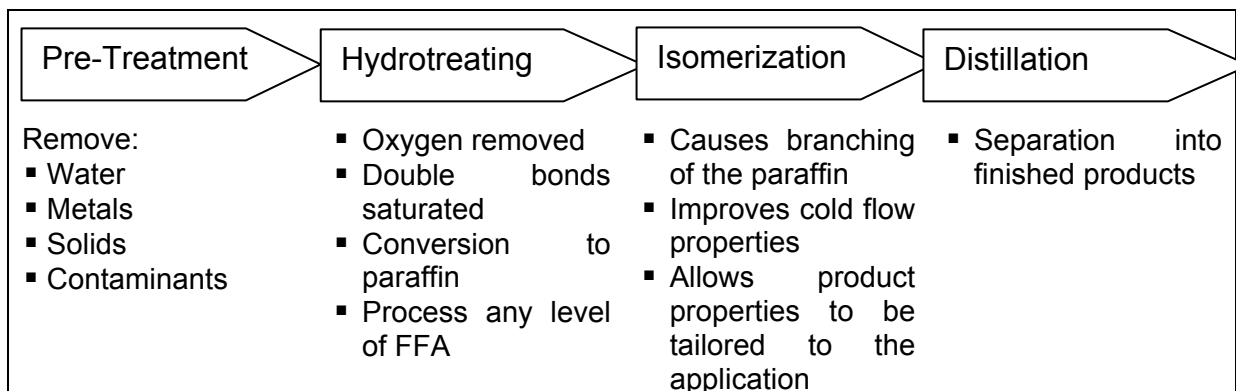
1. Product/Technology Overview

Existing technology for producing diesel-like fuel from animal fats and vegetable oils has largely centered on transesterification of fats and oils with methanol in the presence of a catalyst to produce fatty acid methyl esters, commonly referred to as biodiesel. While biodiesel has many desirable qualities such as low particle emissions, a good cetane number and lubricity, it also suffers from poor storage stability, marginal cold flow properties, excessive solvency, and engine compatibility issues. Renewable diesel, on the other hand, is a diesel substitute derived from any triglyceride feedstock based on conventional hydroprocessing technology that is already widely deployed in refineries. Unlike biodiesel, renewable diesel replicates the chemical structure of its diesel counterpart, therefore working seamlessly with existing distribution infrastructures, storage systems, and engines. Additionally, the cold flow properties of the fuel can be adjusted in the process, with yields increasing at higher cloud points. Finally, contrary to biodiesel whose co-product is glycerin (that currently has very little value), renewable diesel has several valuable co-products that include propane and naphtha.

Renewable diesel is produced by hydrotreating the triglyceride feedstock with a metal catalyst. The reaction pathway involves hydrogenation of the C=C bonds of the feedstock followed by alkane production by three different pathways:

decarbonylation, decarboxylation and hydrodeoxygenation. The straight chain alkanes can then undergo isomerization and cracking to produce lighter and isomerized alkanes. In some cases, pretreatment may be required to remove contaminants such as solids or salts. A significant advantage of this process is its ability to utilize a wide array of inputs as free fatty acids (FFA) which can be completely converted to biofuel. Conversion of feed and the volumetric yield of hydrocarbon products is 100%. A simplified flow diagram of the process is shown in Figure 18.

Figure 18: Simplified Process Flow of Renewable Diesel Production



Source: Syntroleum

The process requires significant amounts of hydrogen in the hydrotreating phase. Nevertheless, feedstocks rich in saturated fats such as palm oil and animal fats require substantially less hydrogen than feedstocks higher in olefin (i.e., unsaturation) content such as soybean oil. For that reason, palm oil and animal fats are favored to soybean oil from an energy balance standpoint. It should be noted, however, that the yield obtained with soybean oil has been reported higher than with animal fats.

One advantage of renewable diesel technologies is that they provide flexibility in the type of biofuel produced. For example, jet fuel can be produced, which represents an excellent new market for the industry considering biodiesel does not meet the cold-flow properties and high energy densities associated with jet fuel.

No information on the energy balance of renewable diesel is available, but considering the reaction conditions, it would appear that it is less favorable than with transesterification. This fact would explain the higher processing costs associated with renewable diesel, even though no specific costs are publicly reported for renewable diesel. Still, the processing cost difference with transesterification is expected to be relatively low and is more than offset by the compatibility with existing distribution infrastructures, which includes pipeline. Hence, renewable diesel can be pipelined whereas biodiesel is generally either trucked or railed. Capital cost requirements are reportedly similar to transesterification. For instance, UOP reports

that the capital costs associated with a 92 million gallon a year (mmgy) plant is \$60-80 million.

One should note that renewable diesel made using a commingled hydrotreating process (i.e., co-processing) is only eligible for a \$0.50/gal tax credit compared to a standalone hydrotreating process which receives a \$1.00/gal. credit.

2. Market Potential

U.S. diesel consumption in 2008 was approximately 60.6 billion gallons. Although renewable diesel could, in theory, replace all this volume, its high price relative to regular diesel fuel and the limited availability of fats and oils (U.S. production of fats and oils was 35.8 billion lbs in 2008, or approximately 4.6 billion gallons) will limit its market to a fraction of the total diesel market.

In 2007, the Energy Independence and Security Act mandated the use of one billion gallons of biomass-based diesel by 2012. Hence, the maximum market potential for renewable diesel is one billion gallons¹⁸. More conservatively, however, renewable diesel will, in all likelihood, only account for part of this volume, with biodiesel accounting for the remainder.

There is currently no renewable diesel production in the U.S. but Dynamic Fuels LLC is expected to start operating a 75 mmgy plant in 2010.

3. Profiles - Companies & Research Institutions

Three companies have developed standalone hydrotreating processes: Neste Oil, Syntroleum, and UOP/Eni.

Neste Oil

Neste Oil is a Finnish refiner with a regional office in Houston, TX. Its technology, NExBTL™, is a standalone renewable diesel process.

Neste Oil currently operates a renewable diesel unit at its Porvoo oil refinery in Finland, with a production capacity of 170,000 tonnes per annum (about 54 mmgy). A second NExBTL plant is under construction at Porvoo (170,000 t/a) and a third unit in Singapore (800,000 t/a). Neste has also recently broken ground on an 800,000 t/a plant in Rotterdam. NExBTL's raw materials include palm oil, rapeseed oil, and animal fats.

Syntroleum

Syntroleum Corporation is a U.S. company based in Tulsa, OK, and engaged in development and commercialization of proprietary fuel technologies. The company

¹⁸ Note that renewable diesel derived from co-processing biomass with a petroleum feedstock does not qualify as biomass-based diesel.

owns the Biofining™ technology that can convert animal fat and vegetable oil feedstocks into middle distillate products such as renewable diesel and jet fuel.

In 2007, Syntroleum teamed with Tyson Foods to form a 50/50 joint venture called Dynamic Fuels LLC, which aims to produce synthetic fuels at multiple standalone commercial facilities. Syntroleum is to supply the technology for the plants, while Tyson is to supply the animal fats, greases and vegetable oil feedstocks.

Dynamic Fuels LLC is currently building a 75 mmgy plant in Geismar, LA. The facility cost estimate is \$138 million. The project is being funded by cash investments from Tyson Foods and Syntroleum, plus the GO Zone bond proceeds. The facility is expected to become operational in 2010.

UOP/Eni

UOP LLC, headquartered in Des Plaines, IL, is a supplier and licensor of process technology, catalysts, adsorbents, process plants to the petroleum refining, petrochemical, and gas processing industries.

Together with Eni S.p.a., an Italian integrated energy company, UOP has developed the Ecofining process. The process uses conventional hydroprocessing technology to convert vegetable oil and animal fats to renewable diesel.

Two Ecofining processes are currently in development. The first license was to Italian refiner Eni for a 6,500 bbl/day (96 mmgy) facility to be located in Livorno, Italy. The second license is to Portugal's largest refiner, Galp Energia, for a 6,500 bbl/day facility to be located in Sines, Portugal. The two projects are planned to be completed in 2010.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to renewable diesel.

Table 9: SWOT – Renewable Diesel

<u>Strengths</u> ▪ Good cold flow properties. ▪ Compatible with current diesel storage and distribution systems. Renewable diesel can be pipelined, which confers a significant cost advantage over biodiesel. ▪ Better specifications than biodiesel. ▪ Renewable diesel produced in standalone plants can be used to comply with the biomass-based diesel mandate. ▪ Large market potential.	<u>Weaknesses</u> ▪ Renewable diesel technologies are more adapted to animal fats as a feedstock than soybean oil. ▪ Late entrant in the U.S. biomass-based diesel market. The U.S. already has over 2 billion gallons in biodiesel production capacity. ▪ Higher processing costs than biodiesel. ▪ Currently not economically competitive with diesel fuel without government incentives. ▪ Renewable diesel from co-processing does not qualify as a biomass-based diesel and is only eligible for a \$0.50/gal tax credit.
<u>Opportunities</u> ▪ The Renewable Fuel Standard (RFS) mandates the use of one billion gallons of biomass-based diesel by 2012. ▪ Renewable diesel technologies can be used to produce renewable jet fuel. ▪ High petroleum prices could bolster the demand for renewable fuels.	<u>Threats</u> ▪ Low crude petroleum oil prices. ▪ The EPA has not yet released its final rule regarding the implementation of the RFS. In an initial draft, soybean oil-based biofuel did not comply as biomass-based diesel. There is a risk soybean oil-based biofuels will not comply as biomass-based diesel in the future. ▪ The indirect land use change controversy might be solved by grandfathering biodiesel plants built or under construction before the passage of EISA in December 2007, which would favor existing trans-esterification technologies already in place over renewable diesel ones. ▪ Development of biomass-to-liquid (BTL) technologies that would replace fats and oils by cellulosic material. ▪ Tight capital markets. ▪ Tight economics of biofuel production could prevent new investments.

B. Enzymatic Transesterification

1. Product/Technology Overview

Essentially, all biodiesel is produced using chemical transesterification. However, this multi-step process, which involves the reaction of triglycerides with methanol in the presence of a catalyst (mainly NaOH or KOH) and which may require extra process steps to eliminate the free fatty acids, suffers from multiple shortcomings:

- High energy consumption;
- Difficulty in glycerin recovery (the co-product of biodiesel production);
- High amount of alkaline waste water (as a result of the catalyst use); and
- Interference of FFAs with the catalyst¹⁹.

Enzymatic transesterification, on the other hand, holds considerable potential considering its advantages over its chemical counterpart:

- Compatibility with feedstock of various quality (the process converts FFAs);
- Fewer process steps;
- Higher quality of glycerin;
- Improved phase separation (no emulsification from soap); and
- Reduced energy consumption and wastewater volumes.

As a result of these benefits, research efforts to develop the process have increased significantly over the last few years. However, a number of hurdles still need to be overcome before it becomes commercially available and the consensus is that the cost of the enzyme needs to be lowered in order to make the process cost competitive.

Currently the two biggest problems researchers are examining deal with the reaction speed and enzyme durability.

- Academic studies report long reaction times, meaning total tank volume needs to be larger resulting in higher capital costs.
- Enzymes are far more expensive than the chemical catalysts used for biodiesel production. Therefore, for the process to be cost effective, enzymes need to be recovered. This has led to the use of immobilized enzymes. Nevertheless, the carrier itself, as well as the immobilization process, adds significantly to the cost of the process. Furthermore, the addition of a solid phase to the reaction system generally results in slower reaction times. However, the development of new immobilization technologies may improve the cost competitiveness of the process.

¹⁹ Conventional biodiesel technologies generally use feedstock with a FFA no higher than 0.2%, as FFAs neutralize the catalyst and form soaps that (i) complicate phase separation and (ii) form sediments that may plug pipes and filters. As a result, unless refined vegetable oil is used (i.e., max FFA $\leq 0.1\%$), conventional processes generally require a pre-treatment step to remove the FFAs in the feedstock.

- Methanol and phospholipids have been reported to inactivate the enzyme. This is a very serious problem as it results in frequent replacement of the enzyme, hence increasing costs. Nevertheless, it appears that decreasing the methanol concentration and using degummed oil can overcome the problems.

Overall, good progress is being made and it is expected that the process could become cost competitive relative to chemical transesterification within three years. However, it is important to emphasize that many consider one of the main advantages of enzymatic transesterification to be its ability to utilize low-cost, low quality feedstocks with high FFA content, which favors animal fats and recycled grease over soybean oil, even though the availability of those is extremely limited relative to virgin vegetable oils.

2. Market Potential

The potential for enzymatic transesterification is to replace chemical processes currently being used. Just in the U.S., there are over 300 biodiesel plants with nearly 3 billion gallons in production capacity. Over the last few years, the biodiesel industry has been plagued with poor production margins and, if costs come down, enzymatic transesterification could significantly improve the bottom line for producers, hence increasing demand for soybean oil.

In 2007, the Energy Independence and Security Act mandated the use of one billion gallons of biomass-based diesel by 2012, and enzymatic transesterification processes could account for a large share of this volume.

3. Profiles - Companies & Research Institutions

Several institutions are currently engaged in enzymatic transesterification research. Nevertheless, other than some efforts by the USDA ARS, most of the research is being conducted abroad, especially in Europe and Asia. Currently, the largest private company involved in enzymatic transesterification is Novozymes.

Novozymes

Novozymes, headquartered in Denmark is a leader in the development and sale of enzymes for industrial uses. Novozymes has already developed an operational enzyme for enzymatic transesterification but is still working on improving reaction times and enzyme lifetime.

In Europe, Novozymes is part of a consortium of Danish companies and academic groups including Emmelev – a Danish biodiesel producer – the University of Aarhus, and the Technical University of Denmark, to establish a world-leading enzyme technology for the next generation of biodiesel production. The consortium received a EUR 2.4 million grant from the Danish National Advanced Technology Foundation (HTF) late 2008. The project will take place over the next three years and the goal is

to develop and document a biodiesel process that is cost-effective and environmentally superior to chemical transesterification.

The company has also reportedly partnered with Piedmont Biofuels from North Carolina to improve its process. The project was awarded a \$197,000 grant in 2009 by the Chatham County Economic Development Corporation in North Carolina.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to enzymatic transesterification technologies for the production of biodiesel.

Table 10: SWOT – Enzymatic Transesterification

<u>Strengths</u> ▪ Feedstock flexibility. ▪ Few processing steps. ▪ High quality glycerin. ▪ Low energy consumption.	<u>Weaknesses</u> ▪ High enzyme cost. ▪ Late entrant in the U.S. biomass-based diesel market. The U.S. already has over 2 billion gallons in biodiesel production capacity. ▪ Not proved at a commercial scale. ▪ Still at an early stage of development
<u>Opportunities</u> ▪ Ongoing research to decrease process costs. ▪ High petroleum prices could bolster the demand for renewable fuels. ▪ The RFS as mandated in 2007 requires fuel to meet greenhouse gas emission standards. The lower energy consumption associated with enzymatic transesterification may favor this technology.	<u>Threats</u> ▪ Low crude petroleum oil prices. ▪ Renewable diesel. ▪ The indirect land use change controversy might be solved by grandfathering biodiesel plants built or under construction before the passage of EISA in December 2007, which would favor existing transesterification technologies already in place. ▪ Development of biomass-to-liquid (BTL) technologies that would replace fats and oils by cellulosic material. ▪ Tight capital markets. ▪ Tight economics of renewable fuel production could prevent new investments.

C. Soy Polyols

1. Product/Technology Overview

With the trend in eco-friendly products gaining momentum, manufacturers are looking for solutions to reduce their environmental footprint and offer finished products that are both high quality and environmentally sound.

Polyols are chemical building blocks used primarily as reactants to make polymers, polyurethanes in particular. These chemical compounds have historically been produced using petroleum-based feedstocks but are now increasingly made from vegetable oils. Chemical pathways to produce these natural oil polyols (NOPs) are multiple, but overall, their use results in significant greenhouse gas (GHG) emission reductions. For instance, Cargill reports that its BiOH polyols generate 36% fewer GHG emissions than petroleum-based polyols. Another advantage of NOPs is that with more regulations and concerns over volatile organic compounds (VOCs), they offer an environmentally friendly option for many manufacturers as they can help reduce VOCs by up to 2/3.

Since their initial development, NOP technologies have overcome the problems of consistency and odor that plagued the first generations and now offer products with performance that rivals petroleum-based polyols. NOP are now used in a number of polyurethane foam applications including furniture, bedding and flooring products. Additionally, several producers report a significant improvement in the energy balance (e.g., -1 Cargill reports a -23% in total energy balance).

2. Market Potential

The United Soybean Board estimates the annual North American product demand for polyols represents 3.4 billion pounds, with a conservative estimate of the market potential for soy-oil-based polyols at about 600 to 800 million pounds (2006 estimates). NOPs made by such seed oils as soybean oil, are making inroads as a polyurethane precursor. In 2006, the U.S. production of polyurethane was estimated at 6.3 billion lbs.

The market for NOPs has great growth potential as prices for petroleum rise and manufacturers become more eco-friendly.

3. Profiles - Companies & Research Institutions

Several manufacturers have created soy polyols that are used in a wide range of applications including carpet-backing agents, spray-foam insulations, furniture, bedding products, body panels, etc. The main players in the NOP field are: Arkema Inc., Battelle Memorial Institute, BioBased Technologies, LLC, Cargill, The Dow Chemical Company and Urethane Soy Systems Co.

Arkema Inc.

Arkema Inc. is a diversified chemicals manufacturer headquartered in Pennsylvania and with a facility in Blooming Prairie, MN. The company launched its Vikol line of soy polyols for polyurethane foams and coatings in 2006.

Battelle Memorial Institute

Battelle is a large non-profit independent research and development organization headquartered in Columbus, Ohio. Battelle has developed several novel biobased polyols derived from soybean oil, other vegetable oils and glycerin. According to the non-profit organization, the cost of the polyols is expected to be significantly less than polyols derived from petroleum sources. Furthermore, coatings prepared from Battelle polyols would significantly out-perform coatings prepared from competing biobased polyols and would have comparable characteristics as coatings prepared from petroleum-based polyols.

Generally, Battelle's business strategy is to license technology to interested companies.

BioBased Technologies, LLC

Biobased Technologies, headquartered in Rogers, AR, began its operations in 2003, specializing in the research and development of NOPs for the polyurethane industry. The company has launched Agrol®, a line of biobased polyols for flexible (slabstock and molded) and rigid (insulation) commercial and industrial polyurethane applications for coatings, adhesives, sealants, elastomers, etc.

Cargill

Cargill has been active in the soy-based polyol market since 2005. Their branded product is called BiOH™. Cargill broke ground on a \$22 million polyols manufacturing plant in Chicago in July 2008, expecting to be fully operational in the November 2009. The new production facility will be the first world-scale biobased polyols plant. Cargill is also producing polyols at one of its existing vegetable oil processing sites in Sao Paulo state, Brazil. Cargill estimates that the global market for polyols in polyurethane production stands at over 10 billion pounds for BiOH and is expanding at 3-4% per year.

The Dow Chemical Company

Dow Chemical (Dow) is one of the primary leaders in the utilization of soy-based polyols in the production of their trademarked product named RENUVA. The primary target markets for RENUVA™ are transportation, bedding, furniture, carpet, and CASE (coatings, adhesives, sealants, and elastomers) markets, with applications including seating, arm, headrest, and headliner foams in vehicles;

viscoelastic “memory” foam for bedding; carpet backing; and coatings, spray elastomers, and one and two-component adhesives and sealants. Dow scientists believe that in some applications RENUVA™ has performance benefits over petroleum-derived foams, citing an improved compression set and enhanced hardness for greater durability. It should be noted that Dow is also looking at the use of other vegetable oils besides soybean oil (such as sunflower and canola) so that they are not vulnerable to sourcing only one feedstock for their process.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to soy polyols.

Table 11: SWOT – Soy Polyols

<u>Strengths</u> ▪ Biobased product. ▪ Comparable characteristics relative to petroleum-based polyols. ▪ Reduction of VOCs emissions. ▪ Large market potential. ▪ Strong institutional support.	<u>Weaknesses</u> ▪ Not always economically competitive with petroleum-based polyols. ▪ Ability to substitute other vegetable oils for soybean oil as the primary raw material.
<u>Opportunities</u> ▪ Evolution of environmental regulations. ▪ Growing population and world demand for plastics. ▪ High crude petroleum prices. ▪ Marketability of green products (government biobased program, LEED). ▪ Ongoing development of new soy-based polyols.	<u>Threats</u> ▪ Low crude petroleum prices. ▪ Declining use of foams and plastics for environmental reasons in the U.S.. ▪ Tight capital markets.

D. Epichlorohydrin

1. Product/Technology Overview

Epichlorohydrin is an epoxy raw material, increasingly used in applications in the electronics, automotive, aerospace and windmill sectors. It is traditionally derived indirectly by reacting propylene with chlorine. The process, however, is somewhat inefficient due to the formation of unwanted chlorinated organics that are expensive to dispose of.

New glycerin-to-epichlorohydrin (GTE) technologies, however, reduce energy consumption by about one-third, generate less than 1/10th of the wastewater and considerably less salt, chlorinated organics, etc., when compared to traditional production processes. Until recently, however, this pathway was uneconomical due to the high price of glycerin. The advent of the biodiesel industry that generates large amounts of glycerin has now reversed this situation.

2. Market Potential

According to information released by Solvay and Dow in 2007, the demand for epichlorohydrin has significantly outpaced production. Although the current economic crisis may have somewhat impacted demand, there is significant growth potential, especially in regions with large biodiesel/glycerin production like Europe or the U.S.. Most of the growth is now being experienced in Asia, with Solvay reporting that demand has been expanding by more than 20% per year in China. One should note, however, that in recent years, U.S. exports to Asia have decreased as local production capacity has increased. In 2003, the U.S. production capacity was estimated at 960 million lbs.

It is important to stress that since 2008, a number of chemical firms had previously unveiled plans to use glycerin as a feedstock for the production of chemicals have either shelved or delayed projects. Indeed, although glycerin production has increased in recent years, glycerin has proven to be very volatile with large price swings. Some companies, also, have questioned the long term sustainability of glycerin given poor margins in the biodiesel industry, although the European and U.S. mandates should guarantee that large supplies of glycerin are available in the future.

3. Profiles - Companies & Research Institutions

Several companies, including Dow Chemical, Solvay SA and Spolchemie, have announced plans to commercialize epichlorohydrin from glycerin.

The Dow Chemical Company

Dow is one of the largest epoxy resins and intermediates manufacturers. With its subsidiary Dow Epoxy, it has a large epoxy resin supply capability in Texas USA and a strong production capacity in Germany. Epoxy resins are usually imported from these two countries to meet the supply needs in Asia.

Dow is currently developing a new 150,000 metric tons/year epichlorohydrin production facility in Shanghai. The plant, slated to start up in 2010, will be the first to use Dow's proprietary glycerin-to-epichlorohydrin technology.

Solvay SA

Solvay SA is an international chemical and pharmaceutical group with headquarters in Brussels, Belgium. The company has developed Epicerol[®], a process to convert glycerin to epichlorohydrin. After the successful completion of a first plant in France, Solvay is currently working on a new 100,000 tonnes/year epichlorohydrin production facility in Thailand. Solvay is to have invested \$184 million in the new facility.

Spolchemie

Spolchemie is a large European manufacturer of synthetic resins based in the Czech Republic. The company is expected to start building an \$80 million glycerin-to-epichlorohydrin facility in Malaysia in 2009.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to epichlorohydrin.

Table 12: SWOT – Epichlorohydrin

<u>Strengths</u> ▪ Compared to traditional production processes, glycerin-to-epichlorohydrin processes are more environmentally friendly. ▪ Epichlorohydrin produced from glycerin is similar to product made from traditional manufacturing processes. ▪ Biobased product. ▪ Depending on glycerin prices, processes may also be more competitive than conventional petroleum-based processes. ▪ Creates a new outlet for glycerin, as production has increased greatly with the advent of the biodiesel industry. ▪ Strong institutional support.	<u>Weaknesses</u> ▪ Glycerin price volatility ▪ Feedstock production dependent on biodiesel production.
<u>Opportunities</u> ▪ Biofuel mandates in the U.S. and Europe could lead to large glycerin production. ▪ Evolution of environmental regulations. ▪ Growing world plastic (and epoxy resins) consumption. ▪ High energy prices. ▪ Marketability of green products (government biobased program, LEED).	<u>Threats</u> ▪ Phasing out of transesterification technologies for new technologies like renewable diesel that do not produce glycerin. ▪ Use of large glycerin volumes for other chemical applications. ▪ Low energy prices. ▪ Tight capital markets.

E. Wood Adhesives

1. Product/Technology Overview

Soybean oil has emerged as a growing “green” feedstock to replace petroleum-based chemicals in various industrial applications. Soybean meal, on the other hand, has found little industrial uses. Since soybean meal accounts for 80% of the throughput volume in the soybean crushing industry, it is critical to develop “new” uses as it is meal demand that primarily drives soybean production.

One such emerging use for soybean meal is wood adhesives. The use of soy-based adhesives is not *per se* new to the chemical industry, as they were first studied in the

1920s and 1930s, but poor functional properties and price competitiveness at the time relative to petroleum-based adhesives limited their use. Today, phenol-formaldehyde (PF) resins enjoy a dominant place in the resin market for exterior wood composites, whereas urea-formaldehyde (UF) resins dominate the interior wood composites market. Nevertheless, increases in petroleum prices, concerns with formaldehyde emissions, along with greater interest in biobased products have led to an interest in replacing some phenol and urea formaldehyde in wood adhesives with soybean flour.

There is currently an opportunity to develop the market for soy-based adhesive:

- In 2004, the International Agency for Cancer Research announced that formaldehyde was a known carcinogen and many composite wood panel manufacturers looked for alternatives to current UF resin systems.
- In 2007, the California Air Resources Board (CARB) approved regulations to reduce the levels of formaldehyde that can be emitted from interior panel products. The CARB rule sets thresholds for emissions of formaldehyde from various panel products that take effect in two phases between 2009 and 2011. Since companies manufacturing wood adhesives cannot modify their products solely for California, the CARB rule is rapidly becoming a national standard.
- The rising prices of phenol resins have stimulated interest in replacing phenol in PF glues with soy.

It should be stressed that in formaldehyde-based resins, the interpenetration and covalent bonding (cross-linking) of polymer chains produce adhesives with high bond strength and moisture resistance. In proteins, however, chain interpenetration is hindered by protein molecular folding, which is the reason why denatured proteins are better adhesives. The proteins are denatured, with minimal hydrolysis, to maximize their incorporation into the final polymerized structure.

Companies like Hexion Specialty Chemicals, Ashland/Heartland, and Eka Chemicals have commercialized several soy-based glues. These glues generally perform at least as well as their petroleum-based counterparts.

However, the high viscosity and limited durability of soy-based glues still prevent their use in some applications and there is ongoing research to expand the number of products available. Some of the research is currently focused on the development of heat resistant adhesives and enzymatic processing for new soy hydrolyzates. The other challenge is to develop these soy-based glues at a cost advantage to conventional petroleum-based resins.

2. Market Potential

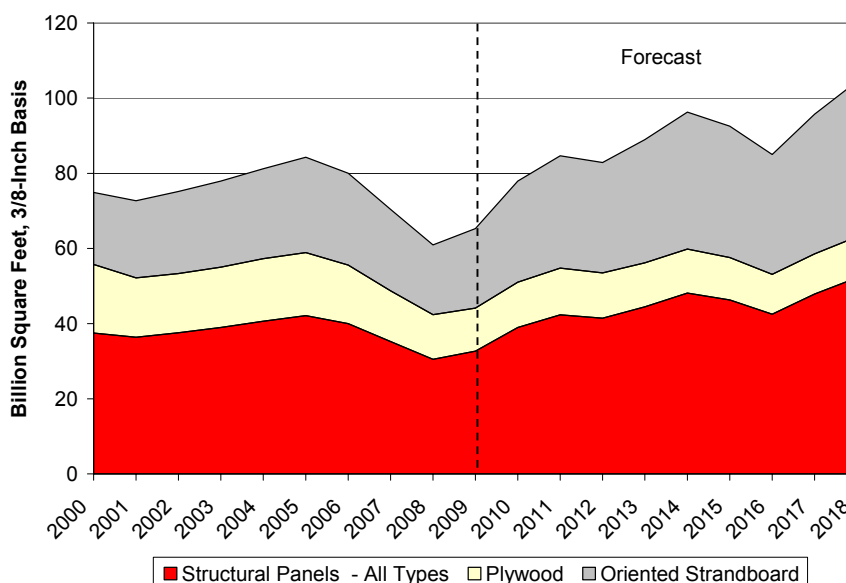
Out of the 3.72 billion lbs of wood adhesives estimated to have been used in the U.S. in 2006, 40-50 million pounds of soy-based glue systems are estimated to be in

use today. In the next few years, the United Soybean Board expects that soy-based wood adhesives could account for as much as 20% of the U.S. market. Still, a weak housing market and the current economic recession are projected to adversely impact the demand for wood products and could slow-down the demand for soy-based adhesives.

Over the long term, however, demand for wood products is projected to resume its growth (Figure 19). Indeed, the fundamentals underlying consumptions have not changed. The population is growing, implying an increase in the number of households and, as a result, housing units.

The market for soy-based adhesives holds tremendous potential for soybeans considering some glues contain up to 90% soy flour.

Figure 19: U.S. Structural Wood Panel Consumption by End-Use



Source: RISI

3. Profiles - Companies & Research Institutions

A number of companies/institutions are currently involved in the development of soy-based wood adhesives.

Ashland

On November 13, 2008, Hercules Incorporated was acquired by Ashland Inc.

Hercules was involved early in the development of soy-based wood adhesives. The company owns the license for SOYAD®, a soy-based adhesive technology developed cooperatively with Columbia Forest Products, and Oregon State

University. The three organizations were awarded a 2007 Presidential Green Chemistry Challenge Award for their roles in developing and commercializing the technology.

Hercules also formed with Heartland Resource Technologies LLC a joint venture named H2H Innovations. The new company focuses on developing cost-competitive formaldehyde-free resins for decorative plywood, wood flooring, particleboard and medium-density fiberboard markets. The joint venture will also offer technologies for oriented strand board manufacturers that allow traditional phenolic resins to be extended, resulting in lower-cost adhesives with reduced formaldehyde content.

Battelle Memorial Institute

Battelle is a large non-profit independent research and development organization headquartered in Columbus, Ohio. Battelle is currently researching wood adhesives derived from wood flour. The process is undergoing further tests in several lumber mills throughout the Pacific Northwest and the Southeast.

Battelle has developed the PRF/Soy 2000 wood finger joint adhesive, a mixture of monomer (phenol formaldehyde), resorcinol, and soy protein.

Generally, Battelle's business strategy is to license the technology to interested companies.

Heartland Resource Technologies

Heartland was created in 2000 to develop green building products for the construction industry. Its business model is based on straight licensing and royalties.

Since July 2007, Heartland works with Hercules/Ashland to develop further SOYAD®.

Columbia Forest Products

One of the three institutions at the origin of SOYAD®, Columbia Forest Products is the exclusive seller of the product in North America.

Hexion Specialty Chemicals

Hexion Specialty Chemicals is the world's largest producer of binder, adhesive, coating and ink resins for industrial applications. As part of EcoBind™, a family of ultra-low emitting resin technologies for wood product manufacturers, Hexion has developed a soy/PVA wood adhesive that is formaldehyde-free.

Eka Chemicals

Eka Chemicals is a manufacturer of bleaching and performance chemicals for the pulp and paper industry. The company has developed a wood adhesive formulated to bond green lumber during finger-jointing applications that uses a two-part system consisting of a soy-based adhesive and a phenol-resorcinol-formaldehyde resin.

Oregon State University

Dr. Kaichang Li, an Associate Professor at Oregon State University, received a 2007 Presidential Green Chemistry Challenge Award for a non-toxic adhesive used in the production of wood composite panels. The adhesive was developed jointly with Hercules (now Ashland Chemicals) and Columbia Specialty Chemicals.

Li has also been receiving soybean checkoff support for his project that uses soy adhesive to bond oriented strand board (OSB).

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to soy-based wood adhesives.

Table 13: SWOT – Soy-Based Wood Adhesives

<u>Strengths</u> ▪ Low formaldehyde emissions. ▪ Meet LEED certification requirements. ▪ Can help meet the new California formaldehyde emission requirements. ▪ Less expensive than petroleum-based adhesives in some applications. ▪ Large market potential.	<u>Weaknesses</u> ▪ High viscosity and durability problems may limit the use of soy-based adhesives in some applications.
<u>Opportunities</u> ▪ Environmental policy. ▪ Development of heat resistant adhesives and enzymatic processing for new soy hydrolyzates. ▪ The housing market is projected to resume its growth in the coming years as the economy improves. ▪ High energy prices. ▪ Marketability of green products (government biobased program,	<u>Threats</u> ▪ Low energy prices. ▪ Soybean flour price. ▪ Currently weak housing market.

LEED).	

F. High-Oil Soybeans

1. Product/Technology Overview

With all the new molecular breeding tools now available to seed developers, important gains in productivity are expected in the coming years. High-oil traits, in particular, are likely to provide significant increase in vegetable oil production and will help processors meet the growing demand for vegetable oil for food and bio-fuel. The prospect of increasing the oil content in soybeans is especially appealing since it has the potential to add value to soybean production, especially considering that most new soybean applications are focused on the oil part by opposition to the proteins.

Monsanto's Renessen joint venture with Cargill is currently researching a high-oil soybean variety that could increase oil content by 3% to 5%, without a loss in protein or grain yield. The first generation of the new variety, that would increase oil yield by 1-3%, is projected to be commercialized within 2-4 years. The second generation, that could increase oil yield by an additional 1-3%, is in a much earlier phase of development but could be released within 10 years. By 2019, soybean oil yields could therefore reach 25% compared to about 19% currently, hence effectively increasing oil production by nearly 26%. Based on conversations with Monsanto's representatives, the high-oil trait could ultimately be combined with some of the agronomic traits already available like Roundup Ready.

It is important to stress that this new variety will not require the soybeans to be identity preserved since there is no change in the composition of the oil or the proteins. However, it will require that grain elevators measure the oil content to determine the payment to the farmers, which is not currently done.

2. Market Potential

Monsanto currently estimates the acreage potential in the U.S. for the first generation high-oil soybean variety at 15-40 million acres, which represents 20-53% of the estimated 2008/09 planted soybean acreage (75.7 million acres). Assuming the five-year yield average experienced between 2003/04 and 2007/08, 40.7 bu/acre, these 15-40 million acres would represent a 10-26% increase in U.S. soybean oil production.

3. Profiles - Companies & Research Institutions

Renessen is a joint venture between Cargill and Monsanto, bringing together Monsanto's expertise in biotechnology and plant breeding with Cargill's capabilities in animal nutrition, grain processing, and logistics. To date, Renessen is the only major company that has been reported developing high-oil soybean varieties.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to high-oil soybeans.

Table 14: SWOT – High-Oil Soybeans

<u>Strengths</u> ▪ 3-5% increase in oil content. ▪ No loss in protein or grain yield. ▪ No need for identity preservation. ▪ Large market potential. ▪ Strong institutional support.	<u>Weaknesses</u> ▪ Grain elevators will have to start measuring the oil content of soybean shipments in order to determine the price received by farmers.
<u>Opportunities</u> ▪ Combine the high-oil traits with other agronomic traits. ▪ Growth in vegetable oil demand for food and industrial activities ▪ High vegetable oil prices, soybean oil in particular. ▪ The indirect land use change controversy might be solved by grandfathering biodiesel plants built or under construction before the passage of EISA in December 2007, which would favor existing transesterification technologies already in place. ▪ Concerns over the level of saturated fat in food products may limit the use of palm oil in the future and favor other alternative vegetable oils like soy.	<u>Threats</u> ▪ Low vegetable oil prices, soybean oil in particular. ▪ Growth of oil palm and canola that yield more oil per acre of production. ▪ Soybean oil-based biodiesel does not meet the greenhouse gas emission threshold as set by the Notice of Proposed Rulemaking released by the EPA with regard to the implementation of the RFS as amended in 2007.

G. High Stability Oil Soybeans

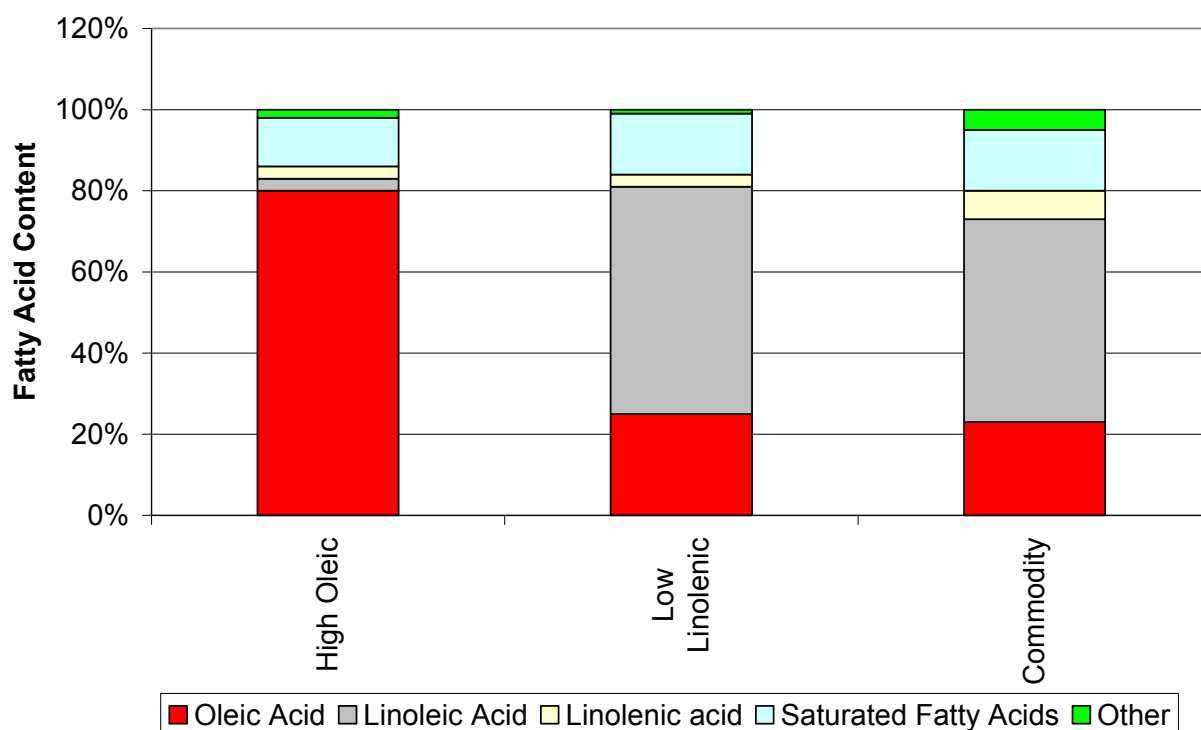
1. Product/Technology Overview

The phasing out of partial hydrogenation by food processors following the move away from *trans* fatty acids in food has generated a strong demand for highly stable vegetable oils. One solution brought forward by seed developers has been to develop oilseeds with a low content in polyunsaturated fatty acids. Polyunsaturated fatty acids (e.g., linolenic and linoleic fatty acids) are indeed prone to oxidation and decreasing the oil content in these fatty acids (FA) enables extended shelf-life.

The first step in improving the stability of vegetable oils has been to limit the content of linolenic FA, a FA with three unsaturations. Such oils are commonly referred to as low-linolenic oils (Figure 20). These oils, however, are generally still rich in linoleic FA, a FA with two unsaturations, which prevents their use in heavy frying applications. Asoya, Monsanto and Pioneer all have, to date, released low-linolenic oils.

The second step in improving the stability of vegetable oils is to limit the content of linoleic FA. Such oils are rich in oleic FA, a monounsaturated FA, and are commonly referred to as high- or mid-oleic oils. These oils are very stable and have numerous food and industrial applications.

Figure 20: Fatty Acid Content of High Stability Soybean Varieties



Source: Pioneer

It is important to stress, however, that the taste commonly associated with fried food is due to the presence of linoleic FA. As a result, mid-oleic/low-linolenic oils are perfectly adapted to frying applications whereas high-oleic oils are ill-suited. High-oleic oils, in contrast are better adapted to oleo-chemical applications, which include lubricants, coatings, paintings, foam products, and green chemicals.

Asoya was the first seed company to release a mid-oleic/low-linolenic soybean variety in 2008, followed in July 2009 by Pioneer that released Plenish, a brand of high oleic soybean oil. Monsanto is expected to commercialize Visitive III, a line of

mid-oleic/low-linolenic/ low saturates in the next few years (Table 15). Vistive III is an advanced version of Vistive (low-linolenic), which is currently commercialized.

Table 15: Mid- and High-Oleic Soybean Varieties Overview

Company	Product	Description	Availability
Asoyia	Asoyia Mid Oleic Ultra Low Lin	Min. 50% oleic acid Max. 1% linolenic acid	Now
Monsanto	Vistive III	Min. 50% oleic acid Max. 3% linolenic acid Low saturated fat	2-5 years
Pioneer	Pioneer High-Oleic	80-90% oleic acid Max. 3% linolenic acid 12% saturated fat	Now

Source: Qualisoy

With reported premiums as high as \$0.60/bu, these soybeans offer farmers a way to diversify and earn extra profit, although it is important to stress that yields and identity preservation may complicate matters for farmers.

2. Market Potential

There were approximately 1.6 million acres of low-linolenic soybeans grown in the U.S. in 2007/08. Acreage was initially anticipated to reach 3-3.5 million acres in 2008/09 but lower than expected demand for low-linolenic oil forced seed companies to revise estimates downward to less than 1 million acres. The main reason for this disappointing result is the limited improvement in oxidative stability that prevented the use of the oil in deep-frying applications, especially considering the high premiums asked for the oil. Food manufacturers favored blends of oils (which could include canola oil, palm oil, and even limited amounts of partially-hydrogenated oil) and/or the use of antioxidants to prevent rancidity and extend shelf-life (low-linolenic soybean oil). Nevertheless, the recent release of mid- and high-oleic soybean varieties is expected to significantly increase the demand for high-stability soybean oil. For instance, Monsanto estimates the acreage potential in the U.S. for its Vistive III soybean variety at 10-20 million acres.

3. Profiles - Companies & Research Institutions

Three companies, Asoyia, Monsanto and Pioneer Hi-Bred, market the new high-stability oil soybean varieties. Qualisoy is also an important player as the group was founded to develop and commercialize varieties with enhanced compositional traits that add value to U.S. soybeans and soy products.

Asoyia

Asoyia is a farmer and employee-owned seed company based in Iowa City, IA. Asoyia markets the soybean varieties developed at Iowa State University.

In September 2008, Asoyia received a \$300,000 from the USDA under the Value-Added Producer Grant program in connection with the release of their ULTRA Low Linolenic Soybeans.

Monsanto

Monsanto, based in St. Louis, MO, is a major international seed developer. Monsanto is currently distributing Vistive I, a low-linolenic soybean variety, and is expected to release Vistive III, a mid-oleic/low-linolenic/ low saturates variety within the next few years. A high stearate variety, that would be used in margarine and spreads, is in an early stage of development.

Pioneer Hi-Bred

Pioneer Hi-Bred, a DuPont business, has developed Treus, a line of high stability soybeans. Low-linolenic and high-oleic varieties are currently available. The soybean varieties were developed in cooperation with Bunge.

Qualisoy

Qualisoy™ is a collaborative effort between farmers and all levels of the soybean industry to develop and commercialize varieties with enhanced compositional traits that add value to U.S. soybeans and soy products. The group originated from a soybean checkoff-funded initiative and was introduced in 2004.

The Qualisoy Board consists of 22 individuals representing all components of the U.S. soybean industry. The Qualisoy Board includes seven USB farmer-leaders, three representatives from multinational technology corporations, two representatives from regional technology corporations, four individuals representing various soybean processors and end users, one farmer-leader from the American Soybean Association, two farmer-leaders from Qualified State Soybean Boards, one academic and one scientist from USDA's Agricultural Research Service (ARS).

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to high stability oil soybeans.

Table 16: SWOT – High Stability Oil Soybeans

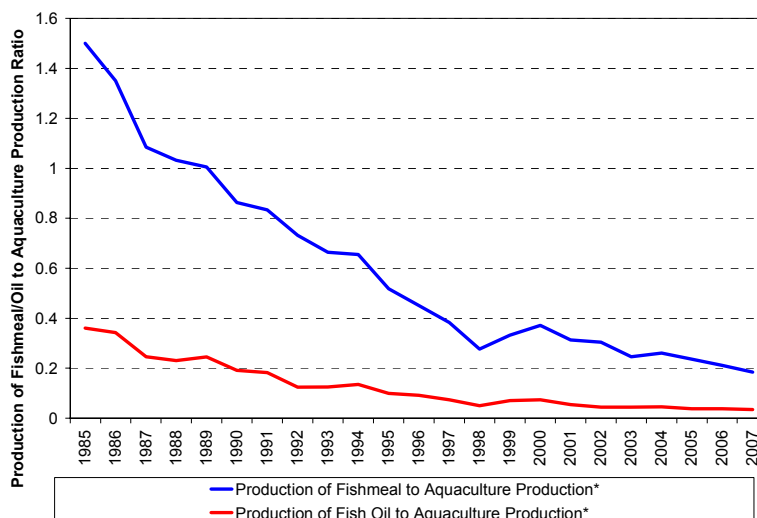
<u>Strengths</u> ▪ No trans fats. ▪ Only food products that have less than 0.5g of trans fats can claim 0g of trans fats on their nutritional label. ▪ High- and mid-oleic soybean oils are extremely stable. ▪ High-oleic varieties open many new industrial applications. ▪ Premium paid to farmers growing high-stability soybeans. ▪ In the U.S., consumers are used to the taste of soybean oil in frying applications. ▪ Strong institutional support.	<u>Weaknesses</u> ▪ Low-linolenic soybean oil is not stable enough for frying applications. ▪ Some farmers have reported a yield drag for low- linolenic soybeans over conventional varieties. ▪ Identity preservation is necessary for high-stability soybeans. ▪ High cost of high stability soybean oil relative to conventional soybean oil.
<u>Opportunities</u> ▪ Mid-oleic and high-oleic soybean varieties offer a significant improvement over low-linolenic varieties in terms of oxidative stability. ▪ Concerns over the level of saturated fat in food products may limit the use of palm oil in the future and favor other alternative vegetable oils like soy.	<u>Threats</u> ▪ Low soybean oil prices. ▪ Canola, corn and sunflower oils are far more stable than conventional soybean oil and can be used in lieu of high-stability soybeans. ▪ Interesterification technologies offer an alternative to high stearate soybean varieties for spread and margarine applications. ▪ The use of antioxidants can prevent the need for high stability oils. ▪ Despite being high in saturated fats, palm oil usage increased as a way for food companies to avoid trans fats and associated labeling.

H. Aquaculture Feed

1. Product/Technology Overview

The global aquaculture industry is growing steadily, averaging 6.6% over the past 10 years (1998-2007), while fishmeal supplies have remained relatively stagnant (Figure 21). This supply and demand imbalance has driven up the premium for fishmeal over other protein meals including soybean meal (Figure 22), and while this premium has receded from the peaks seen in 2006 and 2007, it remains high relative to historical averages. Yet, over time fishmeal prices are expected to keep increasing, as supplies continue to tighten and demand continues to grow. This has led many aquaculture producers to look for ways to lessen their dependence on fishmeal.

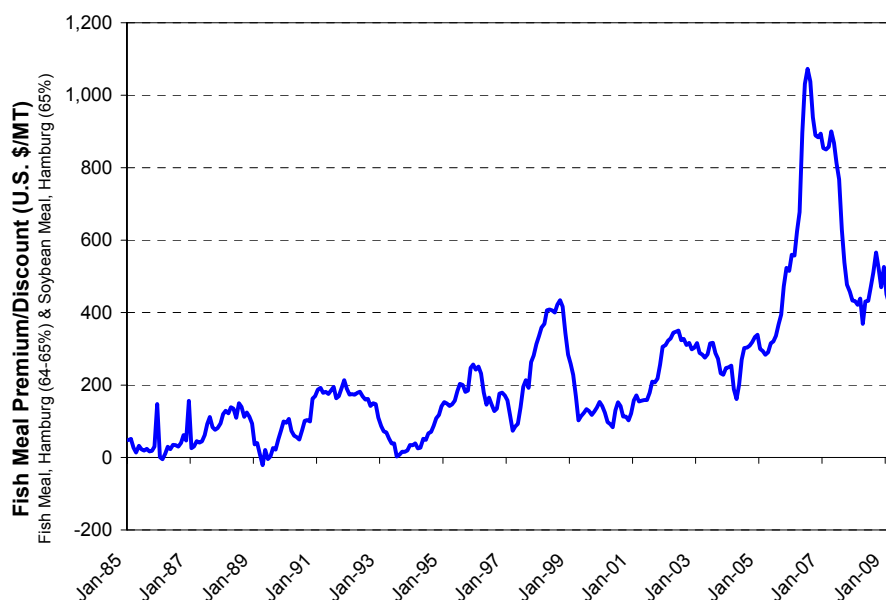
Figure 21: Fishmeal and Fish Oil Supply and Demand Imbalance



Source: FAO, FIGIS & Oil World

*World aquaculture production – top 5 global fishmeal/oil consuming species: salmon, trout, carp, shrimp, and marine fish.

Figure 22: Fishmeal Premium/Discount to Soybean Meal



Source: Oil World

It has been known for a long time that soybean meal can be used in aquaculture feed but anti-nutritional factors that reduce fish performance, particularly at higher inclusion levels, and in carnivorous fish specie diets have limited its adoption. In general, herbivorous fish species tend to be somewhat tolerant to plant proteins and can more easily substitute for fishmeal in the diet. Nevertheless, carnivorous species are more affected by anti-nutritional factors and cannot tolerate plant proteins as well.

Contrary to soybean meal, however, soy protein concentrates (SPC) do not contain these high levels of anti-nutritional factors and can be utilized at higher inclusion rates as well as in carnivorous fish specie diets. Consequently, SPC have the potential to play a major role in the aquafeed market

SPC is made by removing a portion of the carbohydrates from the high protein soybean meal. There are different SPC production methods. The most frequent method used for producing SPC is alcohol extraction. This results in a product that is higher in protein and lower in anti-nutritional factors. SPC generally has 65-67% protein.

By most industry accounts, SPC has not commonly been used within the aquaculture industry, despite being a relatively good fishmeal substitute, because it has been priced too high for that market. Most SPC sales are focused on the more lucrative food market (by opposition to feed) where it is used as a functional or nutritional ingredient in products such as baked goods and cereals, as well as meats.

Some companies, like Hamlet Protein, have recently started to target the feed market. Hamlet uses a biological enzyme process that yields a product with a protein content of 56% which is slightly less than that of standard SPC. Production costs, however, are reportedly lower, which enable the product to be competitive in the feed market.

Price is the primary factor limiting current SPC utilization within the aquaculture industry. In order to increase SPC utilization within the aquaculture market by any significant degree, SPC is going to have to be priced at a sustained discount to fishmeal. Nevertheless, even priced competitively, it will take some time for the industry to become familiar with SPC and to gain trust in its performance.

2. Market Potential

It is estimated that 3.1 million tonnes of fishmeal are currently consumed by the aquaculture market in the world. By comparison, world SPC production was estimated to be 575 thousand tonnes in 2005, with less than 150 thousand tonnes used in aquafeed.

The current consensus is that SPC could account for 10-30% of the protein meal used in aquaculture feed. The U.S. Soybean Export Council estimates that, conservatively, the inclusion rate of SPC in aquafeed could reach 1 million tonnes. This represents a significant increase over current uses and indicates that SPC production could nearly triple in the future.

3. Profiles - Companies & Research Institutions

There are currently only a few SPC producers in the U.S., ADM, Cargill and Solae, with an additional player, Hamlet Protein, considering establishing a plant in Iowa.

One should note that Imcopa, a Brazilian soybean processor, also produces SPC.

ADM

Archer Daniels Midland Company (ADM) produces a wide range of functional soy protein concentrates under its NutriSoy® product line. All the soy protein products are targeted to the food market. ADM has reportedly no interest in the aquaculture market at this point.

Hamlet Protein

Hamlet Protein, headquartered in Denmark, manufactures an enhanced soy protein product that is similar to SPC. Hamlet uses a biological enzyme process that yields a product with a protein content of 56% which is slightly less than that of SPC and which has reduced anti-nutritional factors. The company currently operates one plant in Horsens, Denmark and has recently bought land in Iowa with the intention of breaking ground in the spring of 2010 on a feed grade SPC (enhanced soy protein) manufacturing facility.

Solae

The Solae Company is an alliance between DuPont and Bunge Limited to bring more soy protein and other soy products on the market. Solae produces a range of soy protein concentrates but, like ADM, it has reportedly no interest in the aquaculture market at this point.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities, and threats relative to soy protein concentrates as an aquaculture feed.

Table 17: SWOT – Aquaculture Feed

<u>Strengths</u> ▪ SPC can be used in carnivorous fish feed. ▪ SPC can replace 10-30% of the protein meal used in aquaculture feed.	<u>Weaknesses</u> ▪ Food markets can add much more value to SPC than feed markets. ▪ SPC cannot completely replace fish meal in diets. ▪ Current production costs are high.
<u>Opportunities</u> ▪ Declining fishmeal stock. ▪ Increasing fishmeal prices relative to other proteins. ▪ Growing aquaculture industry.	<u>Threats</u> ▪ All the SPC for the feed market is currently coming from Europe and Brazil. ▪ Tight capital cost markets. ▪ High soybean meal prices.

V. Appendices

A. Soybean Products/Technologies

All through the process to complete this study, Informa Economics reviewed a large array of emerging soy-based products and technologies. Over 100 products and technologies were evaluated based on their market potential, economic feasibility, stage of development and strength of institutional support. This appendix lists the products/technologies that were reviewed. While Informa attempted to be as complete and as accurate as possible in its evaluation of each of these products/technologies, it is acknowledged that given the lack of perfect information about all four assessment criteria for all 100+ products and technologies, the potential of some products and/or technologies may have been under/over estimated. Furthermore, this list is by no means exhaustive as, for example, many new products/technologies are under development and are kept confidential.

Note that the stage of development was divided into four distinct phases as shown in Table 18.

Table 18: Development Stage

Well Established	Initial Commercialization	Early Development Stage	Research/ Conceptual Stage
			

1. Soybean Technologies

a) Soy-based Chemicals

Table 19: List of Emerging Technologies to Produce Soy-Based Chemicals

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Olefin Metathesis	Soybean Oil	The technology allows carbon atoms in natural oils to "swap" places, enabling new chemical compounds and manufacturing processes.	- Adhesives - Agricultural fungicides - Candles - Diesel (improves biodiesel fuel properties) - Lubricants - Personal care and cosmetics - Plastics - Textiles	Davy Process Technology Elevance Renewable Sciences	
Soy-Based Polyols	Soybean Oil or Glycerin	Polyols are utilized extensively for polyurethane coatings, foams and adhesives. Most polyols in use today are derived from petroleum refining. Several companies have introduced technologies to produce biobased polyols derived from vegetable oil (glycerin might also be used).	- Adhesives - Carpet-backing agents - Coatings - Elastomers - Flexible foam cushioning for furniture, bedding and automotive products - Paints and varnish - Plastics - Sealants	Archer Daniels Midland Battelle Memorial Institute BioBased Technologies, LLC Cargill Chevron Phillips Chemical Dow Chemical Ferro Corporation Merquinsa Textile Rubber & Chemical Co. Urethane Soy Systems Co.	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Sophorolipid Production	Soybean Oil or Glycerin	Glycerin and/or soybean oil used as a fermentative substrate for the microbial synthesis of sophorolipids, which are glycolipids with multiple pharmaceutical applications.	- Cosmetics and personal care products - Detergent - Emulsifier - Pharmaceuticals - Skin care	Saraya Co., Ltd Soliance USDA	
Rhamnolipid Production	Soybean Oil	Soybean oil can be used as a fermentative substrate for the microbial synthesis of rhamnolipids, which are glycolipids with various surfactant properties.	- Cosmetics and personal care products - Enhanced oil recovery (petroleum industry) - Food additives - Pharmaceuticals - Sanitary cleaning products	Cargill Rhamnolipid, Inc.	
Hydrolytic Product of Polymerized Epoxidized Soybean Oil (Hydrogel)	Soybean Oil	Epoxidized soybean oil is cross-linked into a polymer by thermal polymerization with triethylene glycol diamine.	- Pharmaceuticals (e.g., drug delivery, wound care, breast implant materials, tissue engineering)	USDA ARS	
Modified Soy Proteins for Polymer Applications	Soy Proteins (meal, flour, concentrate or isolate)	Isolated soybean protein are chemically treated in various reactive processes to modify the protein chain to impart desired functional properties. These chemical processes are used to modify the functional nature of the soy polymer and optimize the properties for use in industrial applications.	- Adhesives - Paints and coatings - Pharmaceuticals	DuPont University of Missouri	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Triglyceride-Based Polymers	Soybean Oil	Broad range of chemical routes to use oils to make polymers. Some routes consist in functionalizing the triglyceride with polymerizable chemical groups, while others consist in converting the triglyceride to monoglycerides through glycerolysis.	- Adhesives - Automotive - Coatings - Cosmetics and personal care - Paper - Pharmaceuticals - Plastics - Rubber - Textiles/clothing	Ashland Chemical Co Degen Oil & Chemical Co. Hexion Specialty Chemicals New Century Coatings PPG Reichhold Rust-Oleum Sherwin-Williams University of Delaware University of Southern Mississippi	
Epoxidized Soyate Allyl	Soybean Oil	The resin is prepared through a two-step chemical process involving transesterification and epoxidation	- Coating - Manufacturing of composite materials - Plastics	University of Missouri	
Acrylated Epoxidized Soybean Oil	Soybean Oil	Acrylated epoxidized soybean oil is synthesized from the reaction of acrylic acid with epoxidized triglycerides.	- Coating - Plastics	Cytac Industries University of Delaware	
Maleinized Soy Oil Monoglyceride	Soybean Oil	Soybean oil monoglycerides, obtained by the glycerolysis of soybean oil, are reacted with maleic anhydride to produce maleinized soy oil monoglyceride.	- Composite material with glass fibers	University of Delaware	
Maleinized Hydroxylated Oil	Soybean Oil	Various chemical pathways to synthesize maleinized hydroxylated oil from oil.	- Composite material	University of Delaware	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Plasticizers Derived from Vegetable Oils	Soybean Oil	These vegetable oil-based plasticizers are made by method which includes the basic steps of (i) creating ester linkages by attaching fatty acids derived from vegetable oils to monoalcohols (monools) or polyalcohols (polyols) by means of direct esterification; and (ii) epoxidizing the esterified products. Alternative reaction steps exist. Unlike other bio-based products, the invention provides plasticizers that can be used as a primary plasticizer in PVC applications.	- Plasticizers in PVC resins	Battelle Memorial Institute / PolyOne	
Methanol	Glycerin	New method to produce methanol directly from glycerin. The process uses direct catalytic hydrogenolysis of glycerol under mild conditions	- Methanol production	Oxford University	
Lactic Acid Production	Glycerin	Process to convert glycerin into lactic acid for use in making polylactic acid, a type of biodegradable plastic.	- Biodegradable plastics	Tohoku Electric power Co. / Zosen Corp.	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Polyhydroxyalkanoate (PHA)	Glycerin	Bacterial production of polyhydroxyalkanoates from glycerin	- Biodegradable plastics	Danimer Scientific LLC National Institute of Advanced Industrial Science and Technology State University of New York USDA	
Propylene Glycol	Glycerin	There are several routes to produce propylene glycol using glycerin. Generally, glycerin is hydrogenated in the presence of metallic catalysts and hydrogen under different reaction conditions.	- Antifreeze - Coolant - Emulsifier - Heat transfer fluid - Humectant - Moisturizer - Polyester resin - Solvent - Unsaturated polyester resins (e.g., boat hull)	Archer Daniels Midland Cargill / Ashland Chemical Davy Process Technology Dow Chemical Huntsman Corporation Michigan State University Senergy Chemical	
		Microbial conversion of glycerol to propylene glycol (1,2-propanediol) has also been evaluated.		University of Wisconsin	
Epichlorohydrin Production	Glycerin	It has been known for decades that glycerin can be converted to epichlorohydrin. But this chemistry has not been used commercially to any significant extent because of the high cost of glycerin compared to propylene (traditional route). The availability of bio-based glycerin and the tight	- Epoxy resins - Paper reinforcement - Pharmaceuticals - Surfactant - Water purification	Aser SRL Dow Chemical Solvay Spolchemie	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
		propylene market has reversed this situation. Several companies have also disclosed technologies that claim improvements to the conventional pathway.			
1,3-Propanediol Production	Glycerin	Microbial conversion of glycerol to 1,3-propanediol	- Antifreeze - Building block in the production of polymers (polyester fabric) - Solvent - Wood paint	Institut für Agrartechnologie und Biosystemtechnik (Germany) Dupont Ecole National Supérieure des Industries Chimiques (France) Iowa State University Michigan State University Shanghai Academy of Agricultural Sciences Universidad Complutense de Madrid Universidade Católica Portuguesa University of Georgia University of Wisconsin	
Dihydroxyacetone	Glycerin	There are several routes to produce dihydroxyacetone using glycerin. Generally, glycerin is converted in the presence of metallic catalysts under different reaction conditions.	- Food additive - Pharmaceutical - Tanning lotion	Forschungszentrum Jülich GmbH, Institut für Biotechnologie (Germany) Munich University of Technology (Germany) Purdue University	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Acetol	Glycerin	Process that couples copper-chromite catalyst with reactive distillation to convert glycerin to acetol.	- Polyols	University of Missouri	
Succinic Acid	Glycerin	Biobased fermentation processes have been developed to produce succinic using glycerol as a carbon source.	- Cosmetics and personal care products - Chemicals - Food additive (flavoring agent) - Plastics - Pharmaceuticals	Korea Advanced Institute of Science and Technology Rice University	
Glyceric Acid	Glycerin	Bacterial conversion of glycerin to glyceric acid.	- Cosmetics and personal care products - Chemicals - Pharmaceuticals	National Institute of Advanced Industrial Science (Japan)	
Acrolein	Glycerin	Production of acrolein through the dehydration of glycerin.	- Chemicals - Detergent - Plastics	Arkema Chinese Academy of Sciences Tohoku University (Japan)	
Propionic Acid	Glycerin	Biobased fermentation using a strain of Propionibacterium acidipropionici bacteria to produce propionic acid from glycerin to convert glycerin into ethanol.	- Grain and seed preservative - Pharmaceuticals	INRA (France) Ohio State University	

Not an exhaustive list

b) Biodiesel Technologies

Table 20: Biodiesel Technologies

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Supercritical Methanol Transesterification	Soybean Oil	Transesterification of soybean oil in supercritical methanol has been shown to increase the chemical reaction speed and yield, while preventing the need for a catalyst.	- Biodiesel production	Beijing University of Chemical Technology Kyoto University Texas A&M University The University of Iowa	
In Situ Transesterification	Soybean	It is possible to have an in situ transesterification, the transesterification occurring directly in the raw soy flakes containing the oil. This method skips the conventional oil-extraction step, hence eliminating the need for hexane.	- Biodiesel production - Oil Extraction	USDA ARS	
Ultrasonic Cavitation	Soybean Oil	Ultrasonic cavitation mixing helps achieve a better mixing in commercial biodiesel processing. It increases the chemical reaction speed and yield of the transesterification of vegetable oils into biodiesel.	- Biodiesel production	Hielscher Ultrasonics GmbH (Germany) Mississippi State University	
Magnetic Pulse Cavitation	Soybean Oil	Magnetic pulse cavitation mixing helps achieve a better mixing in commercial biodiesel processing. It increases the chemical reaction speed and yield of the transesterification of vegetable oils into biodiesel.	- Biodiesel production	W2 Energy Inc.	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Hydrodynamic Cavitation	Soybean Oil	Micro bubbles generated by pressure pulses help achieve a better mixing in commercial biodiesel processing. It increases the chemical reaction speed and yield of biodiesel production.	- Biodiesel production	Arisdyne Systems	
Solid Transesterification Catalyst	Soybean Oil	The solid catalyst process enables a significant reduction in waste streams compared to other processes and leads to the direct production of a very high quality glycerin (98% purity). The catalyst can be reused.	- Biodiesel production	Axens Better Biodiesel New Century Lubricants Süd-Chemie Group	
Enzymatic Transesterification	Soybean Oil	Lipase-catalyzed transesterification of soybean oil and methanol for biodiesel production is more efficient, highly selective, involves less energy consumption (reactions can be carried out in mild conditions), and produces less side products or waste (environmentally favorable).	- Biodiesel production	Donghua University (China) Hongik University (Korea) Indian Institute of Chemical Technology National Chung Hsing University (Taiwan) Seoul National University Songjiang University (China) University of Georgia	
Peroxidation Process	Soybean Oil	A peroxidation technique can be combined to conventional transesterification in order to improve fuel properties (e.g., fuel consumption rate) and reduce the emission pollution (i.e., CO ₂ , CO and NO _x) of biodiesel.	- Biodiesel production	National Taiwan Ocean University	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Mcgyan Process	Soybean Oil	Novel transesterification process using a continuous fixed-bed reactor filled with a sulfated metal oxide catalyst. The process increases the reaction speed and eliminates unwanted side reactions with free fatty acids, thereby reducing the amount of waste. The process also uses no water and only produces traces of glycerin.	- Biodiesel production	Augsburg College / StarTec Corporation	
PermaFlow	Soybean Oil	The PermaFlow process incorporates urea into the traditional transesterification process, which enables the separation of the saturated and unsaturated biodiesel molecules via the mechanism of urea-biodiesel clathration. By separating (fractionating) the saturated and unsaturated oil molecules from each other, the remaining unsaturated oil molecules have much lower cloud points than traditional biodiesel.	- Biodiesel and cold flow properties	Indiana Soybean Alliance Purdue University	
Farm-Scale Biodiesel Production	Soybean Oil	The microreactor consists of a series of parallel channels through which vegetable oil and alcohol are pumped simultaneously. The process is efficient, fast, and portable, and could enable farmers to produce	- Transesterification microreactor	MTEK Energy Solutions / Oregon Nanoscience and Microtechnologies Institute	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
		biodiesel on their farms using seed crops they grow.			
Modified Transesterification with Glycerin Conversion into Biodiesel Additive	Soybean Oil	Continuous transesterification process in which the glycerin is converted into glycerol acetal suitable for inclusion in biodiesel as a fuel additive. The acetal additive reduces particulate emissions, particularly from diesel engines and functions like an oxygenate.	- Biodiesel - Biodiesel additive	Michigan State University	
Biodiesel Additives	NA	Important barriers for the expansion of biodiesel use include its poor cold flow properties, low oxidation stability, and high NOx emissions. Numerous additives have been developed to improve biodiesel properties.	- Cold flow improver - Antioxidant - Particulate matter emission reduction	Afton Chemical ARCO Chemical Technology Dawn Chemical Corp. Eastman Chemical Co. Enertch Labs Innospec Institut Francais du Petrole Lubrizol Midcontinental Power Service Schaeffer Manufacturing SVO Specialty Products University of Bologna (Italy) University of Nebraska	

Not an exhaustive list

c) Fuel / Energy Technologies (other than biodiesel)

Table 21: Fuel / Energy Technologies (other than biodiesel)

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Hydroprocessing	Soybean Oil	Catalytic hydrogenation of fats and oil into renewable diesel. The glycerin chain is hydrogenated to produce propane. There is no glycerin sidestream. The resulting renewable diesel is identical to conventional diesel.	- Renewable diesel production	BP ConcoPhillips/Tyson Dynamic Fuels Neste Oil Petrobras Syntroleum Renewable Diesel	
Renewable Diesel Fuel Production Technology	Soybean Oil	Small reactor able to produce renewable diesel from vegetable oil without the need for external inputs other than the feedstock (i.e., no need for methanol or hydrogen).	- Renewable diesel production	Renewable Fuel Products, Inc.	
Emulsification for Fuel Production	Soybean Oil	The process consists of an additive blending process in an emulsion to manage the properties of vegetable oil at the point of combustion.	- Renewable diesel production	New Generation Biofuels	
Soy Oil Biofuel Cell	Soybean Oil or Glycerin	Biofuel Cells create electricity using a wide variety of fuels for power generation such as alcohol, sugar, soybean oil, and glycerol.	- Electricity generation	St. Louis University	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
GlyClene	Glycerin	Technology capable of converting glycerin into a fuel suitable for use in turbine engines. In this process, the glycerin is cracked and then treated with a chemical and thermal heat process to create the fuel.	- Energy production	XcelPlus Global Holdings Inc.	
Glycerin Burner	Glycerin	The system uses a novel spray atomization swirl burner architecture that overcomes technical and safety issues usual with glycerin burners.	- Energy production	Diversified Energy Corporation North Carolina State University	
GlyCoal	Glycerin	Technology capable of converting glycerin into a sulfur-free supplement for large industrial applications. GlyCoal reduces coal emissions and byproducts when used as a replacement fuel.	- Energy production in coal plants	XcelPlus Global Holdings Inc.	
BioForming	Glycerin	The technology combines Virent Energy Systems' Aqueous Phase Reforming (APR) process that converts glycerin directly into hydrogen and natural gas with catalytic processing to produce renewable gasoline, diesel, jet fuel, and hydrogen from a wide range of biomass feedstock, including glycerin.	- Hydrogen generation - Renewable fuel generation	Virent Energy Systems Inc.	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Centia	Soybean Oil	Technology design to convert oils derived from any triglyceride feedstock to high value biofuels. The technology integrates a sequence of four steps to produce biogasoline, jet fuel, and renewable diesel.	- Renewable fuel generation	Diversified Energy Corporation / North Carolina State University	
Hydrogen Generation	Glycerin	Technology uses a bi-functional monolith autothermal reforming catalyst to generate hydrogen from liquid such as glycerin.	- Hydrogen generation	Eden Energy Ltd. / Hythane Company	
Glycerin to Renewable Diesel Conversion	Glycerin	The process, IUCT-S50, converts glycerin into biodiesel.	- Renewable diesel production	Institut Universitari de Ciència i Tecnologia (Barcelona, Spain)	
Fuel Oxygenates Production	Glycerin	Solid transesterification catalyst technology that convert glycerin into fuel oxygenates, primarily di- and tri-ethers of glycerin.	- Fuel oxygenates	New Century Lubricants	
Ethanol	Glycerin	Biobased fermentation using a strain of E. coli to convert glycerin into ethanol.	Ethanol production	Rice University / Glycol Biotechnologies	
Butanol	Glycerin	Biobased fermentation using Clostridium pasteurianum bacteria to produce butanol from crude.	- Fuel - Solvent - Coatings: paint, varnish, and inks - Agricultural chemicals: insecticides, pesticides and herbicides - Synthetic resin and adhesives - Textiles (scatter rugs, sets...) - Sealants	German Research Center for Biotechnology University of Alabama	

Not an exhaustive list

d) Oilseed Crushing and Processing

Table 22: Oilseed Crushing and Processing

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Supercritical Carbon Dioxide Extraction of Oil	Soybean	Mechanical screw press modified to inject liquid or gases into the internals of the press cage. Currently, liquid CO ₂ is used in the press, resulting in more efficient removal of oil from the seed and a higher quality press cake.	- Oil extraction process	Crown Iron Works	
Enzymatic Degumming	Soybean Oil	Novel enzymatic degumming process designed to increase the oil yield and reduce low-value byproducts by removing oil phospholipids in the oil refining process. The phospholipase enzyme increases total oil yield by reducing heavy phase entrainment and converting phospholipids into diacylglycerol oil.	- Oil degumming process	Bunge North America Danisco Novozymes Verenium	

Not an exhaustive list

e) Food Technologies

Table 23: Food Technologies

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Flatulence-Free Soybean Products	Soybean	The indigestibility of oligosaccharides is blamed as the causing factor for flatulence associated with the human consumption of soy products. Germinating black soybeans under stress from fungus may reduce flatulence-causing carbohydrates.	- Soy dairy products	National University of Singapore	
Frozen Tofu	Soy Proteins (meal, flour, concentrate or isolate)	Generally, by freezing tofu, the large ice crystals that develop within the tofu results in the formation of large cavities. Furthermore, the tofu takes on a yellowish hue. A new technology was developed to allow the soy-based product to be frozen while maintaining all of its characteristics. Using a patented flash-freezing process, frozen tofu can be stored for up to a year (compared to no more than seven to ten days for the fresh product).	- Food	Battelle Memorial Institute / Ohio Soybean Council	
Enzymatic Interesterification	Soybean Oil	Interesterification rearranges fatty acids, resulting in a product with a higher melting point without forming trans fatty acids as is the case with partial hydrogenation.	- Margarine - Shortening for baking	De Smet/Novozymes Bunge	

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Soy Protein Isolation Method	Soy Proteins (meal, flour, concentrate or isolate)	Upfront has developed a new concept for isolating fractions of soluble soy protein. This enables the industry to add a new high value product category to the traditional insoluble soy protein product.	- Food ingredients - Pharmaceuticals	Upfront Chromatography A/S	
Omega-3 Fatty Acids	Glycerin	Glycerin is used as a carbon source to grow microalgae that produce omega-3 fatty acids.	- Food - Animal feed	Battelle Memorial Institute / Ohio Soybean Council Virginia Tech	
Soybean Protein Concentrate Preparation	Soy Proteins (meal, flour, concentrate or isolate)	New process for the preparation of soybean protein concentrate by directly extracting full-fat soy flour with a mixture of hexane and aqueous ethanol. The process saves energy and reduces protein denaturation caused by heat action during solvent recovery.	- Food - Aquaculture Feed	Wuhan Polytechnic University (China)	

Not an exhaustive list

f) Value-Added Soybean Varieties

Table 24: Value-Added Soybean Varieties

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
High Stability Oil Soybeans	Soybean	Biotech soybean varieties with a low polyunsaturated fatty acid content. New varieties include low linolenic, high- and mid-oleic, and high stearate soybean.	- Functional food - Frying applications - Industrial applications - Margarine - Shortening for baking	Monsanto Asoya Pioneer Syngenta	
Omega-3 Fortified Soybeans	Soybean	Biotech soybean variety that provides oil enriched in the omega-3 fatty acid called stearidonic acid (SDA).	- Functional food - Frying applications - Industrial applications	Monsanto Solae (with its majority owner DuPont)	
High Oil Soybeans	Soybean	Biotech soybean variety with a high oil content (19-25% depending on development stage). Protein quality would not be impacted.	- Soybean oil production	Monsanto Pioneer University of Guelph	
Improved Feed Soybeans	Soybean	Pioneer Hi-Bred is working to develop soybean varieties that improve the meal quality and digestible energy in animal feeds.	- Feed	Pioneer	
Soybean with Increased Tocopherol Content	Soybean	Development of soybean varieties with increased tocopherol (vitamin) content through genetic modification or conventional crossing.	- Food	University of Guelph University of Kentucky	

Not an exhaustive list

g) Other Technologies/Processes

Table 25: Other Technologies/Processes

Technology Name / Product	Soybean Product Used	Description of Technology	Applications	Institutions/Companies Involved (Technology Name)	Stage of Development
Powder Coating	Soybean Oil	Innovative technology that combines resin composites derived from soybeans to produce a powder coating that has the ability to operate at 130°C (compared to 175°C typically), increasing the range of applications, and lowering energy consumption compared to conventional powder coating.	- Powder coating (e.g., refrigerators, tractor panels...)	Battelle Memorial Institute / Ohio Soybean Council	
Bowman-Birk Inhibitor Extract from Soybeans	Soy Proteins (meal, flour, concentrate or isolate)	The new method includes taking defatted soybean material, removing its fiber, and then using a special ultra filtration process to produce Bowman-Birk inhibitor extract that has chemopreventive activity.	- Pharmaceutical (cancer treatment)	Lolae, LLC	
Candle Making	Soybean Oil	The properties of partially hydrogenated soybean oil in wax applications can be improved through the combination of epoxidation, ring-opening reaction, and esterification.	- Candles - Coating	Iowa State University	
Ambersep BD50 Glycerin purification process	Glycerin	Chromatographic separation process to purify crude glycerin and produce a purified glycerin product with 99.5% purity. The system has low energy requirements and only consumes small quantities of water.	- Glycerin refining	Rohm and Haas / Novasep Process	

Not an exhaustive list

2. Soybean Products

a) Soy-Based Chemicals

Table 26: Soy-Based Chemicals

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Soy Methyl Ester (non-fuel applications)	Soybean Oil	- Methyl ester sulfonate - Epoxidized methyl soyate	- Paints and coatings - Solvent		ADM Biospan Technologies Cargill Citrus Oleo Cognis Corporation Columbus Foods Cortec Corporation Diversified Chemical Technologies Eco Safety Products Florida Chemical Gemtek Products, LLC Green Products Inc. IMET Corp. Lambent Technologies Corp. Lubrizol New Century Coatings Soy Technologies, LLC Stepan Company Sun Products Corp. Vertec BioSolvents, Inc. REG

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Polyols	Soybean Oil or Glycerin	- Alkyd resins - Polyurethanes	- Adhesives - Carpet-backing agents - Coatings - Elastomers - Flexible foam cushioning for furniture, bedding and automotive products - Paints and varnish - Plastics - Sealants		Arkema Inc. Battelle Memorial Institute BioBased Technologies, LLC Cargill The Dow Chemical Company Urethane Soy Systems Co.
Epoxidized Soybean Oil	Soybean Oil	- Acrylated epoxidized soybean oil - Alcohols (industrial) - Alkanolamines - Carbonyl compounds - Epoxy resins - Maleinized hydroxylated oil - Olefinic compounds - Polyol - Polyvinyl chloride (PVC) - Polyester resins	- Adhesives - Agricultural and pharmaceutical molecules - Coatings - Fiberglass manufacturing - Flexible foam cushioning for furniture, bedding and automotive products - Pharmaceutical - Plastics - Rubbers - Sealant - Sheet molding composite panels (e.g., covers for tractors) - Surfactants		Chemtura Corporation Cognis Corporation Cytec Industries ICC Chemical Corporation The Dow Chemical Company University of Delaware USDA ARS
Epoxidized Allyl Soyate	Soybean Oil	- Epoxy resin	- Coating (especially metal, plastic or glass surfaces) - Manufacturing of composite materials - Plastics		University of Missouri

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Maleinized Soy Oil Monoglyceride	Soybean Oil	- Resin	- Composite material with glass fibers		University of Delaware
Maleinized Hydroxylated Oil	Soybean Oil	- Resin	- Composite material with glass fibers		University of Delaware
Epoxidized Pentaerythritol Tetrasoyate	Soybean Oil	- PVC resin	- Plastics		Battelle Memorial Institute / PolyOne
Epoxidized Propylene Glycol Disoyate	Soybean Oil	- PVC resin	- Plastics		Battelle Memorial Institute / PolyOne
Epoxidized Ethylene Glycol Disoyate	Soybean Oil	- PVC resin	- Plastics		Battelle Memorial Institute / PolyOne
Epoxidized Sucrose Octasoyate	Soybean Oil	- PVC resin	- Plastics		Battelle Memorial Institute / PolyOne
Epoxidized Methyl Soyate	Soybean Oil	- Carbonated methyl soyates - Epoxy resin - PVC resin	- Composite material with glass fibers - Lubricant - Plastics		Battelle Memorial Institute / PolyOne University of Missouri ASDA ARS
Epoxidized Product of Soybean Oil Interesterified with Linseed Oil	Soybean Oil	- PVC resin	- Plastics		Battelle Memorial Institute / PolyOne
Polyethiol	Soybean Oil		- Crosslinking / curing agents in epoxy resins (adhesives, coatings)		Chevron Phillips Chemical Co.
Ethoxylated Soybean Oil	Soybean Oil		- Surfactant (e.g., fungicide, herbicide)		

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Acetol	Glycerin	- Polyols	- Adhesives - Carpet-backing agents - Coatings - Elastomers - Flexible foam cushioning for furniture, bedding and automotive products - Paints and varnish - Plastics - Sealants		University of Missouri
Acrolein	Glycerin	- Acrylic acid - Acrylonitrile - Polyester resin - Polyurethane - 1,3-propanediol - Propylene glycol	- Antifreeze - Chemical intermediate - Herbicides - Plastics		Arkema Chinese Academy of Sciences Tohoku University (Japan) University of Tennessee
Propylene Glycol	Glycerin	NA	- Antifreeze - Coolant - Emulsifier - Heat transfer fluid - Humectant - Moisturizer - Polyester resin - Solvent - Unsaturated polyester resins (e.g., boat hull)		Archer Daniels Midland Cargill / Ashland Chemical Davy Process Technology Huntsman Corporation Michigan State University Senergy Chemical The Dow Chemical Company University of Wisconsin
Epichlorohydrin	Glycerin	- Epoxy resins	- Paper reinforcement - Plastics - Pharmaceuticals - Surfactant - Water purification		Solvay Spolchemie The Dow Chemical Company

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
1,3-Propanediol	Glycerin	- Polyester fibers - Polyurethanes	- Adhesives, - Antifreeze - Composites, - Moldings - Paints and coatings		Institut für Agrartechnologie und Biosystemtechnik (Germany) Dupont Ecole National Supérieure des Industries Chimiques (France) Iowa State University Michigan State University Shanghai Academy of Agricultural Sciences Universidad Complutense de Madrid Universidade Católica Portuguesa University of Georgia University of Wisconsin
Rhamnolipids	Soybean Oil or Glycerin	NA	- Cosmetics and personal care products - Enhanced oil recovery (petroleum industry) - Food additives - Pharmaceuticals - Sanitary cleaning products		Cargill Rhamnolipid, Inc.
Sophorolipids	Soybean Oil or Glycerin	NA	- Cosmetics and personal care products - Pharmaceuticals - Sanitary cleaning products		Saraya Co., Ltd Soliance USDA
Glyceryl soyate	Soybean Oil or Glycerin	NA	- Cosmetics and personal care products		Lubrizol

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Dihydroxyacetone	Glycerin	- Methotrexate (chemotherapie)	- Cosmetics and personal care products - Food additive - Pharmaceutical		Forschungszentrum Jülich GmbH, Institut für Biotechnologie (Germany) Munich University of Technology (Germany) Purdue University
Methanol	Glycerin	- Denaturing agent - Feedstock in the fabrication of various chemicals	- Chemical industry - Fuel		Oxford University
Lactic Acid	Glycerin	- Lactide - Polylactic acid	- Food additive - Plastic		Tohoku Electric power Co. / Zosen Corp.
Polyhydroxyalkanoate (PHA)	Glycerin	NA	- Plastic		Danimer Scientific LLC Meredian National Institute of Advanced Industrial Science and Technology State University of New York USDA

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Succinic Acid	Glycerin	- 1,4-Butanediol (BDO) - Tetrahydrofuran (THF) - γ-Butyrolactone (GBL) - 2-Pyrrolidinone - N-Methyl Pyrrolidone (NMP) - Succindiamide - 1,4-Diaminobutane - Succinonitrile - DBE - 4,4-Bionolle	- Cosmetics and personal care products - Chemicals - Food additive (flavoring agent) - Plastics - Pharmaceuticals		Korea Advanced Institute of Science and Technology Rice University
Glyceric Acid	Glycerin	NA	Building block for several chemical compounds		National Institute of Advanced Industrial Science (Japan)
Butanol	Glycerin	- Butyl Acrylate - Methacrylate - Glycol Ethers - Butyl Acetate	- Fuel (gasoline substitute) - Solvent - Coatings: paint, varnish, and inks - Agricultural chemicals - insecticides, pesticides and herbicides - Synthetic resin and adhesives - Textiles: scatter rugs, bathmats, and sets - Sealants		German Research Center for Biotechnology University of Alabama
Propionic Acid	Glycerin	NA	- Grain and seed preservative - Pharmaceuticals		INRA (France) Ohio State University

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Glycerol Ethers	Glycerin	NA	- Biodiesel / diesel additive (improves cold flow properties and particulate matter emissions)		ARCO Chemical Technology University of Nebraska
Glycerin Acetate Carbonates	Glycerin	NA	- Biodiesel / diesel additive (reduces particulate matter emissions)		Institut du Petrole University of Bologna (Italy)
Glycerin Acetals	Glycerin	NA	- Biodiesel / diesel additive (improves cold flow properties and particulate matter emissions)		Institut Francais du Petrole
Triacetin	Glycerin	NA	- Fuel Additive (improves cold flow properties when added to diesel or antiknocking properties when added to gasoline)		Rey Juan Carlos UniVersity (Spain)
Abietoyl Hydrolyzed Soy Polypeptide	Soy Proteins (meal, flour, concentrate or isolate)	NA	- Cosmetics and personal care products		Arch Chemicals Rita Corporation Sinerga S.p.A. (Italy)
Cocodimonium Hydroxypropyl Hydrolyzed Soy Protein	Soy Proteins (meal, flour, concentrate or isolate)	NA	- Cosmetics and personal care products		Arch Chemicals Rita Corporation Sinerga S.p.A. (Italy)
Hydroxypropyltrimonium Hydrolyzed Soy Protein	Soy Proteins (meal, flour, concentrate or isolate)	NA	- Cosmetics and personal care products		Arch Chemicals Rita Corporation Sinerga S.p.A. (Italy)

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Socoyl Hydrolyzed Soy Protein	Soy Proteins (meal, flour, concentrate or isolate)	NA	- Cosmetics and personal care products		Arch Chemicals Rita Corporation Sinerga S.p.A. (Italy)
Soy Stearyl Polypeptide	Soy Proteins (meal, flour, concentrate or isolate)	NA	- Cosmetics and personal care products		Arch Chemicals Rita Corporation Sinerga S.p.A. (Italy)
Undecylenoyl Polypeptide	Soy Proteins (meal, flour, concentrate or isolate)	NA	- Cosmetics and personal care products		Arch Chemicals Rita Corporation Sinerga S.p.A. (Italy)
Soy Isoflavones	Soybeans	NA	- Nutraceutical		ADM Acatris
Soy Saponins	Soybeans	NA	- Nutraceutical		ADM
Citric Acid	Glycerin	NA	- Preservative - Flavoring		Andhra University (India) Wroclaw University (Poland)

Not an exhaustive list

b) Soy-Based Fuels

Table 27: Soy-Based Fuels

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Renewable Diesel	Soybean Oil	NA	- Fuel (diesel substitute)		BP ConcoPhillips/Tyson Diversified Energy Corporation / North Carolina State University Dynamic Fuels Neste Oil Petrobras Syntroleum Renewable Diesel
Direct Soybean Oil Use as Fuel	Soybean Oil	NA	- Diesel (biofuel)		
Turbine Engine Fuel	Glycerin	NA	- Fuel		Diversified Energy Corporation North Carolina State University XcelPlus Global Holdings Inc.
Renewable Diesel	Glycerin	NA	- Fuel (diesel substitute)		Institut Universitari de Ciència i Tecnologia (Barcelona, Spain) Virent Energy Systems Inc.
Renewable Gasoline	Glycerin	NA	- Fuel (gasoline substitute)		Virent Energy Systems Inc.
Hydrogen	Glycerin	NA	- Chemical industry - Fuel		Eden Energy Ltd. / Hythane Company Virent Energy Systems Inc.

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Jet Fuel Substitute	Glycerin	NA	- Fuel (jet fuel)		Virent Energy Systems Inc.
Fuel oxygenate	Glycerin	NA	- Fuel		New Century Lubricants
Ethanol	Glycerin	NA	- Gasoline		Rice University / Glycol Biotechnologies

Not an exhaustive list

c) Other Emerging Soy-Based Applications

Table 28: Other Emerging Soy-Based Applications

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Lubricant	Soybean Oil	NA	- Bar and chain oil - Crankcase oi - 2-cycle oil - Drip oil - Hydraulic fluid - Metalworking fluid - Transformer oil - Wire rope oil		ABB Alcoa Bunge/AgriTech Cargill/Cooper Power Systems Chevron ELM Environmental Lubricants Manufacturing, Inc. Exxon Mobil Fuchs Houghton TribSys Inc. Valvoline

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Soy Wax	Soybean Oil	NA	- Candles - Coating		Bitter Creek Candle Supply, Inc. Bubbles 'N Lights Cargill Elevance Renewable Sciences Gelluminations Nature's Gifts International, LLC Peter Cremer North America Soyawax SoyLights
Drying oil	Soybean Oil	- Polyol	- Intermediate for polyols - Paints, coatings and inks		Cargill Degen Oil & Chemical Co. Georgia-Pacific Resins, Inc.
Soyscreen	Soybean Oil		- Cosmetics and personal care products (hair care, sunscreen) - Pharmaceutical (drug delivery)		iSoy Technologies USDA ARS
Adhesives	Soybean Oil		- Adhesive		Kansas State University University of Delaware W.F. Taylor Co., Inc.
Animal Feed	Glycerin	NA	- Animal feed		Iowa State University Kansas State University Oklahoma State University Purdue University University of Arkansas University of Missouri University of Wyoming USDA ARS

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Soybean Hulls in Polyurethane Applications	Soybean Hull	- Polyurethane	- Rigid and flexible polyurethane foams		University of Missouri
Soybean Hulls in Food Applications	Soybean Hulls	NA	- Doughnuts		Korea Food Research Institute Korea University
Carboxylated Proteins	Soy Proteins (isolate or flour)	NA	- Plastics		Dupont University of Missouri
Hydrolyzed Proteins	Soy Proteins (isolate or flour)	NA	- Plastics		Dupont University of Missouri
Wood Adhesive	Soy Proteins (meal, flour, concentrate or isolate)	Alternatives to: - Urea formaldehyde resins - Phenol formaldehyde resins - Phenol-resorcinol-formaldehyde - Blood meal in adhesives	- Oriented strand board - Plywood - Fiberboard - Particleboard - Structural engineered wood products (e.g., finger joints)		Ashland Chemicals Battelle Memorial Institute Columbia Forest Products Eka Chemicals Heartland Resource Technologies Hexion Specialty Chemicals Oregon State University
Soy Protein Fiber	Soy Proteins (meal)	NA	- Textile		Soy silk is currently made in China and is available in the US under the SOYSILK® brand.
Hydrogel	Soy Proteins (isolate)	NA	- Personal care products - Pharmaceuticals		University of Toronto University of Wisconsin US Agricultural Research Service

Biobased Products / Chemicals	Soybean Origin	Derivatives / Utilization	Applications / End Uses (Product and Derivatives)	Lifecycle Stage	Companies/Institutions Involved
Aquaculture	Soy Proteins (meal and concentrate)	NA	- Feed		Archer Daniels Midland Company United Soybean Board
Charcoal Briquette	Soybean Stalk	NA	- Food (grill use)		USDA ARS
Fiberboard	Soybean Stalk	NA	- Furniture		USDA ARS
TerraMat (soy-based cork)	NA	NA	- Corkboards - Floor mat		Purdue / Indiana Soybean Alliance
Melt-A-Way Cupcake Liners	NA	NA	- Cupcake liner that disappears after cooking		Purdue / Indiana Soybean Alliance
Omega-3 Fatty Acids	Glycerin	NA	- Food additive		Battelle Memorial Institute / Ohio Soybean Council Virginia Tech
Bypass Protein Soybean Meal	Soy Proteins (flour)	NA	- Feed for dairy cows		AGP Cargill Grain States Soya West Central Soy

Not an exhaustive list

B. Interview List

Table 29: Interview List

Name	Area of expertise	Company/Institution	Position
Bernard Tao	Soybean utilization	Purdue University	Professor of Agricultural & Biological Engineering and Food Sciences
Susan Couch	Renewable diesel	UOP	Sales Representative
Gerhard Knothe	Biofuel	USDA ARS	Research Chemist
Kathleen Warner	Veg oil in food applications	USDA ARS	Research Food Technologist
Kenneth Doll	Soybean utilization	USDA ARS	Research Chemist
Shailesh N. Shah	Biofuel and glycerol utilization	USDA ARS	Research Chemist
Nicole R. Brown	Adhesives and Forest Products	Pennsylvania State University	Assistant Professor of Wood Chemistry
Michael Haas	Enzymatic transesterification	USDA ARS	Acting Research Leader
Don Lindsey	Soy Protein Concentrates	Solae	
Tony Shepherd	Soy Protein Concentrates	Hamlet Protein	Vice president of Sales
Kaichang Li	Wood Adhesives	Oregon State University	Associate Professor
Catalina Valencia	Soy Protein Concentrates	US Soybean Export Council	Marketing Manager
Charles Frihart	Wood Adhesives	US Forest Service	Research Chemist
Adam Bratis	General	NREL	Biochemical Program Manager
James McMillan	General	NREL	Principal Chemical Engineer
Randy Powell	General	Independent	Chemical Consultant
Michael Cotta	General	USDA ARS	Supervisory Microbiologist
Joseph Rich	General	USDA ARS	Research Leader
Cletus Kurtzman	General	USDA ARS	Supervisory Microbiologist
Julious Willett	General	USDA ARS	Supervisory Chemical Engineer
Mark Berhow	General	USDA ARS	Research Chemist
Sean Liu	General	USDA ARS	Research Leader
Brian H. Davison	General	Oak Ridge National Laboratory	Chief Scientist for Systems Biology and Biotechnology

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Description/Abstract:

This research project focused on the identification the next generation of technologies in renewable energy value-added agricultural processing. The research was designed to add value to agricultural commodities employing emerging new innovations for renewable energy processes and identification new processes, products and technologies utilizing agricultural commodities.

This report is a task-level final technical report.

Summary:

Based on demand/market potential, economic feasibility, stage of development and strength of institutional support, Informa Economics, Inc. ("Informa") narrowed down a list of more than 100 emerging corn products and technologies to 8 of the most promising for corn, considered to have the greatest potential to add significant value to Minnesota's corn commodity production. However, as with the potential of any biobased product or technology, the development of these emerging corn products and technologies will be heavily reliant on future market price environments (especially for petroleum) and government policies. This report identifies what the contractor believes are the top 8 products and technologies for corn at the time of publishing.

No Intellectual Property or limitations

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A Study Assessing the Opportunities and Potential of Corn-Based Products and Technologies

Developed by:



Prepared For:

The Agricultural Utilization Research Institute

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Acronyms

3-HPA – 3-Hydroxypropionic Acid
ARS – Agricultural Research Service
BBL – Barrel (of crude oil or other fuel)
BDO – Butanediol
BTU - British thermal units
BTX – Benzene, Teluene and Xylene
C5 – 5 carbon
C6 – 6 carbon
CDS – Condensed distillers solubles
DDG – Dried distillers grains
DDGS – Dried distillers grains with solubles
DOE – Department of Energy
GBL – γ -butyrolactone
ME-THF – Methyl-Tetrahydrofuran
Mmgy – Million gallons per year
MSU – Michigan State University
MBI – Michigan Biotechnology Institute
NCERC – National Corn-to-Ethanol Center
NREL – National Renewable Energy Laboratory
ORNL – Oak Ridge National Laboratory
PDO – 1,3- Propanediol
PET – Polyethylene terephthalate
PLA – Polylactic acid
PNNL – Pacific Northwest National Laboratory
PSI – Pounds per square inch
PTT – Polytrimethylene terephthalate
THF – Tetrahydrofuran
USDA – United State Department of Agriculture
WDG – Wet distillers grains
WDGS – Wet distillers grain with solubles

Disclaimer

This report was produced for the Agricultural Utilization Research Institute ("AURI"). Informa Economics, Inc. ("Informa") has used the best and most accurate information available to complete this study. Informa is not in the business of soliciting or recommending specific investments. The reader of this report should consider the market risks inherent in any financial investment opportunity. Furthermore, while Informa has extended its best professional efforts in completing this analysis, the liability of Informa to the extent permitted by law, is limited to the professional fees received in connection with this project.

I. Executive Summary

Based on demand/market potential, economic feasibility, stage of development and strength of institutional support, Informa Economics, Inc. (“Informa”) narrowed down a list of more than 100 emerging corn products and technologies to 8 of the most promising, considered to have the greatest potential to add significant value to Minnesota’s corn commodity production. However, as with the potential of any biobased product or technology, the development of these emerging corn products and technologies will be heavily reliant on future market price environments (especially for petroleum) and government policies. The following are what Informa considers to be the top 8 products and technologies for corn at this point in time, listed in alphabetical order.

1. Anaerobic Digestion

Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-80%), CO₂ (20-50%), and trace amounts of H₂, NH₃, and H₂S, which can be burned for energy as a substitute for natural gas. This process reduces energy costs and greenhouse gas emissions and helps to conserve water relative to traditional corn-to-ethanol production. Furthermore, if collected, the struvite, a sludge that builds up in the digester, could be sold as a valuable fertilizer or a livestock feed additive.

It is estimated that anaerobic digestion using thin stillage can reduce the energy needs of an ethanol facility by 43-66%, and if using whole stillage, energy needs could be entirely met by the biogas. However, currently, it is not widely used by the ethanol industry at any significant scale, as current capital costs are significant.

2. Butanol

Butanol is currently produced mainly via petrochemical feedstocks and is used primarily as an industrial solvent. However, fermentation processes are currently being developed to produce “biobutanol”, and if cost competitive, it can also be used as a renewable fuel, greatly expanding its market potential. Butanol offers several key advantages over ethanol, including a higher energy content, the ability to transport it via pipeline, a lower reid vapor pressure which makes it safer to use and means that it generates fewer volatile organic compound emissions, and the ability to be blended with gasoline at higher levels. Additionally, several researchers are going one step further and are looking at ways to make higher valued products from butanol that can serve as gasoline, diesel and jet fuel replacements (not blends).

There have been many advancements made to the biobutanol production process over the last several decades and many of the challenges previously preventing butanol production from being economically viable have largely been resolved. The technology appears to be currently cost competitive with petrochemical based butanol (said to be economical at \$60/bbl crude oil) and also competitive or nearly competitive with ethanol. Of those companies currently pursuing its development,

the earliest stated year for expected commercial production is 2010, but many do not expect to see commercial scale production until 2011/2012.

3. Cellulosic Ethanol – Biochemical Platform

Over the past few years, there has been significant research and development effort given toward improving the high production cost areas of biochemical cellulosic ethanol production: pretreatment, hydrolysis, and fermentation. There are essentially three key challenges involved in these processing steps. The first is the development of cost efficient pretreatments, which are necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis. Once the sugars are hydrolyzed, broken down into 5-carbon and 6-carbon sugars, they can then be fermented using biological agents (e.g., microorganisms, yeast) to produce ethanol. However, it is far more difficult, and thus more costly, to hydrolyze cellulosic biomass than it is to hydrolyze the starch from the traditional corn-to-ethanol process, and while hemicellulose is relatively easy to hydrolyze compared to cellulose (fractions of the lignocellulosic biomass), it is more difficult to ferment. Therein lie challenges two and three: hydrolyzing the cellulose and fermenting the xylose sugars released from the hemicellulose.

There are numerous companies and research institutions developing their own approaches and unique technologies to improve upon current pretreatment, hydrolysis and fermentation processes. However, the bottom line is that a cost efficient process has yet to be commercialized. There are several companies that are expecting to reach commercialization by 2011/2012. Yet, the tight capital market is inhibiting many from obtaining the capital needed to go forth with their commercialization efforts.

4. Ethanol Distillation

Energy costs currently account for about 12% of overall operating costs of traditional corn-to-ethanol production, the second largest operating cost expenditure next to feedstock costs. Of the overall energy consumption, distillation and dehydration consume about 50% (McAloon et al., 2004; Kim and Dale, 2005 – cited by Vaperma). It is also one of the key cost components in the biochemical cellulosic ethanol platform. However, several alternative ethanol distillation technology developers claim to achieve a 40% reduction in energy costs over traditional distillation methods; this would equate to an approximate 6 ¢/gal cost savings, or \$3 million per year for a 50 million-gallon-per-year (mmgy) ethanol facility (using current natural gas prices). Additionally, according to one technology developer, Vaperma, overall fuel production could also be increased by 20% using their process.

Traditionally, the separation of ethanol and water is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also reducing greenhouse gas emissions. Alternative ethanol distillation technologies currently being developed include: vacuum stripping, gas stripping, membrane separation, solvent (liquid)

extraction, and supercritical CO₂. While each of these methods has its own pros and cons, the leading technology at this time appears to be membrane separation. This technology uses membranes, which are vapor phase separation units, to allow the preferred permeation of water over other vapor components in a gas mixture. The removed ethanol is then distilled and the remaining fermentation broth is recycled.

These technologies are largely in the late development/early commercialization stage, and are expected to reach commercial status within 3-5 years, if not sooner.

5. Front-End Fractionation

There are several front-end fractionation processes that separate the corn entering into the dry-mill ethanol facility into three fractions: pericarp (bran/fiber), germ (the oil-bearing portion of the kernel) and endosperm. Revenue streams generated from this process include corn oil; high protein, low fat and fiber distillers grains; fiber and ethanol. Additionally, according to some technology developer claims, front-end fractionation can reduce energy consumption and lower volatile organic compound emissions. Another benefit of fractionation comes in the form of risk mitigation, as producers are not relying solely on the revenues from two product markets and they have increased flexibility.

Front-end fractionation technologies can generally be classified as either wet fractionation processes or dry fractionation processes. In general, wet fractionation technologies tend to be more costly. However, they also produce higher-valued co-products and have less starch loss than dry fractionation technologies. In a new twist, the company MOR Technology claims to have developed a unique fractionation process known as MOR FRAC+ with costs similar to those generally associated with dry fractionation technologies but with the higher valued co-products and the lower starch loss generally associated with wet fractionation technologies. However, this technology is not yet proven at commercial scale.

6. 3-Hydroxypropionic Acid

3-Hydroxypropionic acid (3-HPA) is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications including solvents, plastics and moldings, fibers and resins, composites, adhesives, coatings, aliphatic polyesters and copolyesters and disinfectants. One of the most promising aspects of this building block chemical is not only the current petrochemical products which it could potentially replace, but also the new and unique chemical properties it would bring to the market. Given its potential, it was identified by the U.S. Department of Energy (DOE) in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

Cargill, along with Codexis and the Pacific Northwest National Laboratory, have already developed a bioprocess to produce 3-HPA which converts glucose or other carbohydrate sources into 3-HPA. 3-HPA can then be converted into a variety of high-value chemicals, including acrylic acid, 1,3-propanediol, malonic acid, and

acrylamide. In early 2008, Cargill announced a joint agreement with Novozymes to develop a technology enabling the production of the derivative acrylic acid. At the time of the announcement, the companies said they expected their technology to be ready in 5 years. However, through personal communication, Cargill has revealed that they no longer plan to pursue the development of 3-HPA, as they do not feel that the product has the ability to “bring profitability in a reasonable time.” This would indicate that this product/technology is more likely a long-term prospect, as the market potential still exists despite recent developments.

7. Succinic Acid

Succinic acid is a building block chemical produced by converting the glucose and/or five carbon sugars from a variety of possible feedstocks, including corn, using a specific succinic acid fermenting microorganism and CO₂. This building block chemical can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics. In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO₂, leading to what some claim to be a carbon negative process.

Its potential has been recognized by many countries and was identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas. Furthermore, this chemical can be used to produce other top 12 chemicals. If a technology is developed to produce biobased succinic acid that is cost competitive with similarly functioning petrochemicals, the potential world market is in excess of \$1 billion per year. And, according to one technology developer, Bioamber, commercial biobased succinic acid production is expected by 2011/2012.

8. Zein Extraction

Various processes have been developed to extract zein protein from corn and corn by-products (e.g., distillers grains). Zein is a high-value protein which can be used in a wide range of applications. Zein is not used extensively in human food products, despite being edible, due to its negative nitrogen balance and poor water solubility. However, this insolubility is what makes zein and its resins form tough, glossy, hydrophobic grease proof coatings that are resistant to microorganisms, heat and humidity. Zein applications include: specialty coatings for pharmaceutical tablets, candies, nuts, and paper products, chewing gum, adhesives and binders, ink, cosmetics, fibers and textiles, resins and biodegradable plastics and high-value biomedical applications.

Currently, zein can be extracted from corn gluten meal, a by-product of the wet milling process. However, current extraction and purification technologies are such that the price of zein limits current market applications. Yet, there are several technology companies/institutions currently working to develop an economically viable extraction and/or purification process.

II. Introduction

The Agricultural Utilization Research Institute (“AURI”) commissioned Informa Economics, Inc. (“Informa”) to assess and identify those existing and emerging products and technologies (both domestic and international) associated with the biobased economy that will boost economic opportunities for the corn and soybean agricultural sectors in the United States and the State of Minnesota. The overarching objective of the project was to specify eight products or technologies for each commodity which would likely add value to the corn and soybean complexes over the next ten years. This project has been achieved by conducting a blend of desk research (review of the literature) and targeted interviews, by phone and in-person, with the companies that are producing the biobased products and the scientists and technology leaders that are conducting ground-breaking research in the ever-evolving biobased economy. In the end, this study provides AURI with recommendations regarding which products and technologies show the most promise, thereby laying the foundation as a roadmap which will serve as valuable input to AURI in their strategic planning processes.

A. Report Layout

This introductory section precedes two distinct reports that have been prepared for AURI. The two distinct reports are the analyses, findings and recommendations for the biobased products and technologies for the respective commodities of corn and soybeans. The “corn report” and “soybean report” are distinct and stand alone from each other. The role of this introductory section is to “set the stage” for each of the reports by discussing the project methodology and process flow and presenting a general overview of the biobased and energy economies. This overview should provide the reader a framework from which to better appreciate the opportunities and complexities of the technologies and products that are discussed in the corn and soybean reports.

B. Project Methodology and Process Flow

The biobased economy is a rapidly changing environment where government policies combined with volatile commodity prices can dramatically affect the returns to the participants in said markets. Given this ever-changing context, it was important to provide solid fundamental research with both quantitative (when available) and qualitative analyses to ascertain the top promising corn and soybean products and technologies. It should be noted that the final so called “top eight winners” for each commodity should not be viewed as a list that is “set in stone” because of the uncertain nature of the markets surrounding energy and agricultural commodities. The products and technologies that have been identified as the top eight in both reports actually have the potential to move up or down in relative importance as policies change and technological breakthroughs occur over time. The study team took into consideration the issues of market and political uncertainty

when conducting the research. In the end, the goal was to provide recommendations to AURI regarding those products and technologies that have the highest probability of market success and can impact the State of Minnesota's economy.

The project could be characterized as being a continual flow process where feedback loops were put into place in order to test and retest the justification for including a product or technology in the study. Ultimately, the study was carried out in three Phases, which are summarized in Figure 1. The flow diagram highlights the use of multiple check points or "Phases" in order to "funnel" the products and technologies down to the two top eight lists. In Phase I, Informa conducted desk research that was extremely broad, identifying over 100 products and technologies each for corn and soybeans. Each product or technology was catalogued in a large matrix in which there was with a brief description of said product or technology, identification of the companies or institutions that are engaged in the respective "space," and also special notes.¹ In order to further refine the list in Phase I, four criteria were used by the research team in order to select a limited number of products and technologies that were deemed worthy for moving on to Phase II for more in-depth evaluation. The four criteria are based on those factors that are key characteristics for determining potential success in the marketplace. The four criteria were as follows:

1. Demand/Market Potential:

This addresses the potential size (in value and volume) of the marketplace for a respective product or technology. Some biobased products or technologies, for example, may show significant promise regarding market penetration into existing markets or market adoption; however, the overall market may be extremely small and highly specialized. This means that the introduction of the product or technology would have very little impact to the economy at large. The economic returns or benefits would be confined to a very narrow sector of the economy because of the small market size. The ambition of the study team was to identify those products and technologies which are associated with bigger demand markets and thus potentially larger economic impacts.

2. Economic Feasibility:

Just because a product can be produced or a technology can be used says nothing regarding the cost of producing the product or utilizing the technology. Some products or technologies have highly desirable results or characteristics; however, the cost associated with the product or technology is beyond what the marketplace will likely bear. It should be noted that economic feasibility can be accomplished by either public support (e.g., the 45 cent per gallon tax credit for ethanol production) or the ability of the product or technology to be produced in

¹ Note: Appendices at the end of each report display the large product and technology lists developed in Phase I.

such a manner that real economic returns are achieved without the aid of government support (or a blend of both the marketplace and government support as is the case for ethanol and biodiesel). The study team focused on specifying those products or technologies that would likely become commercially and economically viable over the next ten years.

3. Development Stage:

The development stage is important in the context of the expected planning time horizon of AURI. AURI has established the objective for Informa to identify those products or technologies that will likely have a material economic impact over the next ten years. This means that some products or technologies that might have been identified as being very promising would not be considered for inclusion in the final list because they are too early in the development cycle. Many products or technologies display significant promise from a technical perspective, meaning the mechanical or chemical execution of said technology or product can be achieved in the laboratory or at the pilot scale of operation. Success at the pilot scale level is desirable; however, the more significant hurdle, is the ability to transfer the technology or product to a commercial scale such that they can be introduced into the marketplace and expected to compete with other more traditional products or technologies.

4. Strength of Institutional Support:

The level of institutional support is critical for influencing the success or failure of launching a new product or technology. Institutional support can come in the form of either public or private support or a blend of both. Launching a new product on a “shoe string” budget out of someone’s garage is the exception rather than the rule regarding the probability of success. Those products or technologies which have deep funding sources and access to production and distribution infrastructure and systems generally have a higher likelihood of achieving market penetration and the necessary traction to remain economically viable in the long-run. Large corporations such as DuPont or Cargill are generally advantaged relative to much smaller capitalized companies regarding the ability to invest in the development of new products and technologies and bring them to market on a significant scale. U.S. Federal agencies such as the U.S. Department of Energy (DOE) have also played a vital role in the discovery process of new products and technologies. The DOE has spent billions of dollars helping to fund the discovery of new products and technologies playing the role of a basic research benefactor and even a venture capital firm, investing in emerging products and technologies where often the private sector has deemed the initiatives as being too early-stage or risky to fund completely on their own. The study team evaluated all of the products and technologies in light of the

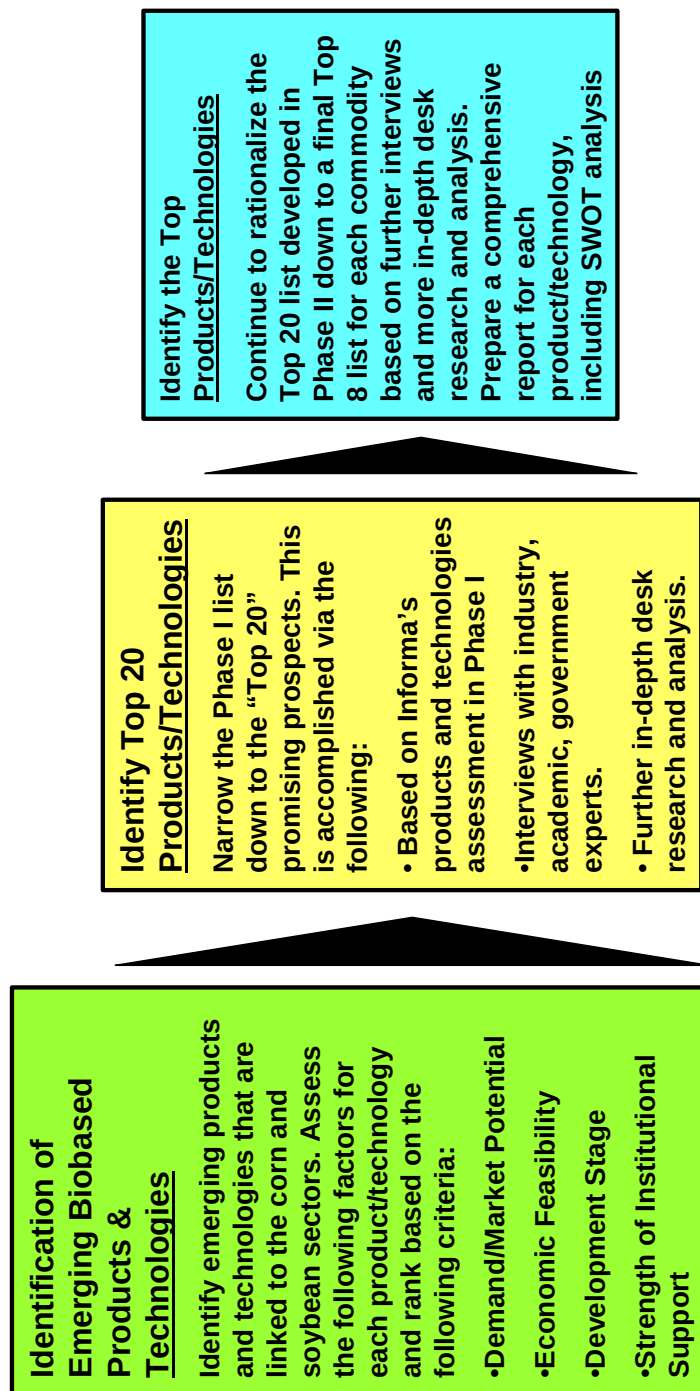
perceived extent of public and private support for the respective product or technology.

In Phase I quantitative scores were generated for each of the 100 products and technologies for corn and approximately 140 products and technologies for soybeans, where they were awarded a score of 10 (being the lowest), 20, 30 or 40 (being the highest) for each of the four criteria. Each of the four criteria was given different “weights” of importance, as follows: Demand/Market Potential 40%, Economic Feasibility 15%, Stage of Development 20% and Institutional Support 25%.² The combination of the criteria weights multiplied by the scores awarded each of the criteria generated a “weighted score” for each of the respective products or technologies. The Informa team independently scored and then ranked the products and technologies for corn and then soybeans. The scoring process was further refined to reflect an enhanced consensus of the team. The ranked scores led to a “Top 30” list for corn and a “Top 30 list” for soybeans. This concluded Phase I of the project.

Phase II began the process of refining the “Top 30” down to a “Top 20 list,” each for corn and soybeans. The study team then began to strategically engage a broad cross section of academic and industry experts with interviews (site visits and telephone interviews) in order to reduce the top 30 list down to top 20. Examples of interviews and trips are as follows: trip to the National Renewable Energy Laboratory (NREL), trip to the National Corn to Ethanol Research Center (NCERC), trip to the USDA Agricultural Research Service Laboratory in Peoria, IL, phone interviews with Oak Ridge National Laboratory, MBI International (Michigan Biotechnology Institute), and numerous other private sector researchers. The experts were asked to comment on the top 30 list to identify a number of key points, (1) specify if there were any omissions from the list, and if so, what products/technologies should be included, (2) identify what products or technologies should be removed from the list, (3) provide an opinion on what product/technologies should be included in the top 20, and (4) distinguish what their preferred top ten products/technologies were and explain in depth why. The Informa research team analyzed the findings from the interviews and constructed a product/technology top 20 list for each of the commodities.

² It is acknowledged that the reader of this report might perceive the weights given to each of the criteria should be changed depending on their point of reference. Informa, however, spent a significant amount of time developing this quantitative framework in order to remain sensitive to AURI’s expectations and needs as an organization.

Figure 1: AURI Corn and Soybean Project Flowchart



PHASE I

PHASE II

PHASE III

The Informa research team then conducted more detailed desk research based on a consensus of the expert interviews and prepared brief position papers for each of the top 20 product/technologies for each commodity. The findings in Phase II formed the foundation for the final Phase III and the selection of the two “Top 8” lists. In Phase III highly targeted interviews were conducted for specific products/technologies. For example, succinic acid (a corn-based chemical) was a product that received significant attention and interest in the early stages of the project and was a logical product to move through Phase I and to Phase II and then into Phase III. Moving into Phase III, the team sought those individuals or firms that had special knowledge of succinic acid, such as MBI International and Bioamber (a firm that is dedicated to making succinic acid competitive with maleic anhydride). The highly targeted interviews and desk research in Phase III ultimately yielded the identification and selection of the “Top 8” products/technologies for corn and soybeans.

The selected top 8 products/technologies for corn and soybeans were then given detailed write-ups (more detailed than the top 20 write ups). Each of the detailed product/technology write ups includes an overview of the product/technology, an analysis of its market potential, profiles of the companies and research institutions that are involved in the space and SWOT analyses (Figure 2). SWOT analysis is a widely used and versatile paradigm for strategic planning where the acronym stands for Strengths, Weakness, Opportunities and Threats. The application of the SWOT model provided the framework to distill the key findings of research and analysis into a summary matrix which is easily understood and identifies the key aspects and issues for each products/technologies. Figure 2 displays the SWOT and how each product/technology was filtered through the grid structure. In the end, the key decision and policy makers at AURI have an authoritative reference tool to guide them in their strategic planning processes.

Figure 2: SWOT Grid

	Strengths	Weaknesses	Threats	Opportunities
Social				
Technology				
Economic				
Environment				
Political				

C. Energy Markets: A Foundation for Biobased Products and Technologies

Petroleum is defined in Greek as being "rock oil" or more commonly known as crude oil. Crude oil or crude petroleum oil is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of hydrocarbons of various molecular weights, plus other organic compounds. Crude oil has always been a substance in plentiful supply; the demand for oil, however, has changed dramatically over time given the advent of the combustion engine and the rise of geopolitical tensions surrounding who owns the oil and where is the oil located. Initially, oil was not used as a fuel; in the 1860's oil was in fact hailed as a disinfectant, a vermin killer, hair oil, boot grease, and a cure for kidney stones. In 1933, the U.S. paid \$275,000 to Saudi Arabia's King Ibn Saud for an oil concession. The King actually thought he had sold the Americans sand, since the British did not think there was oil there. After five years of disappointment, the Americans struck oil in Saudi Arabia. One expert at the time described Saudi Arabia's oil as "the single greatest prize in all history," a prophetic statement for the ages.

The true importance of oil worldwide was not understood until World War I and especially, World War II. World War II brought to light the notion of national security and the importance of the U.S. government having a safe supply of oil. After World War II, and the beginning of widespread economic recovery, it became clear that the world was going to need a lot more oil than the companies of Socal and Texaco in Saudi Arabia could provide. Since World II, the global landscape of the supply and demand for oil has become even more complex as synchronistic global expansion of developing countries coupled with continued Middle East conflicts has placed a new premium on petroleum.

Interest in the area of biofuels and biobased products (based on renewable carbohydrate feedstocks such as corn) has increased dramatically over the last ten years as energy prices, primarily crude oil, reached record highs. As described in this section, consumption of crude oil and refined products is on a very large scale, and as a result the potential market for biofuels and certain biobased replacements for petrochemicals is large.

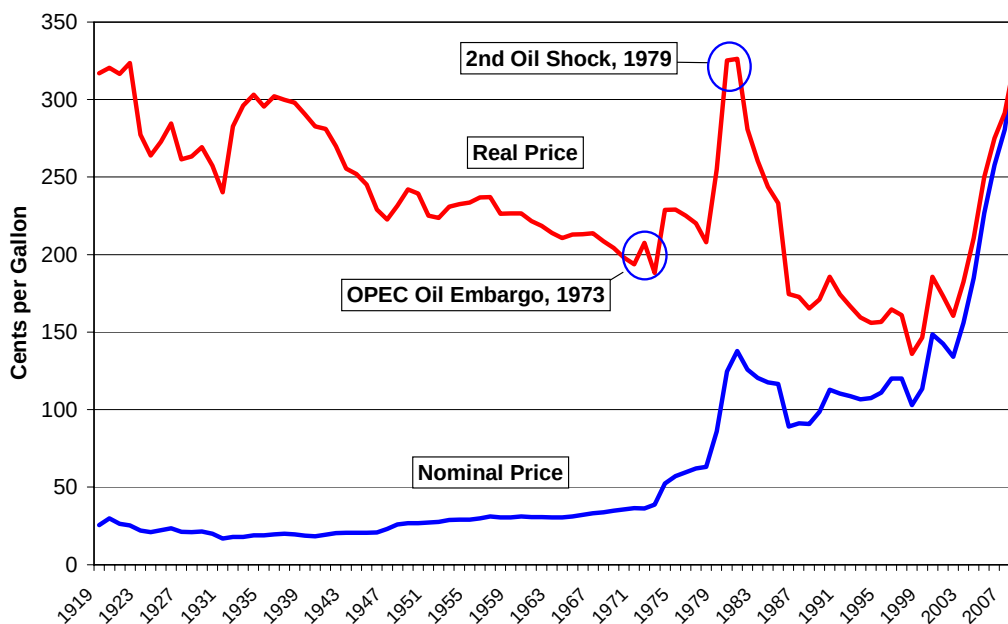
The recent price shock of 2008, quickly reminded U.S. consumers of their vulnerability and dependence on foreign sources of oil. Crude oil prices, as benchmarked by West Texas Intermediate (WTI) averaged only \$19.09/barrel from 1986 to 1999, ranging from a low of \$10.25/barrel to a high of \$41.07 during this period of time. As global economies rapidly expanded and the infrastructure to supply oil increased at a much slower pace, nominal oil prices for the WTI crude reached record high levels on July 3, 2008, at \$145.31/barrel (Figure 3). Adjusted for inflation, oil prices were actually in a long run decline since 1919 (Figure 4), with only brief price spikes. The 2008 jump in oil prices, however, elevated real prices to levels not experienced since the oil shock experienced in the late 1970's and early 1980's.

Figure 3: Crude Oil Price, West Texas Intermediate: January 02, 1986 to June 16, 2009 (daily prices, nominal dollars)



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

Figure 4: U.S. Real Gasoline Pump Price: Annual Average 1919-2008 (consumers price index-urban, 1982-84=1.00)

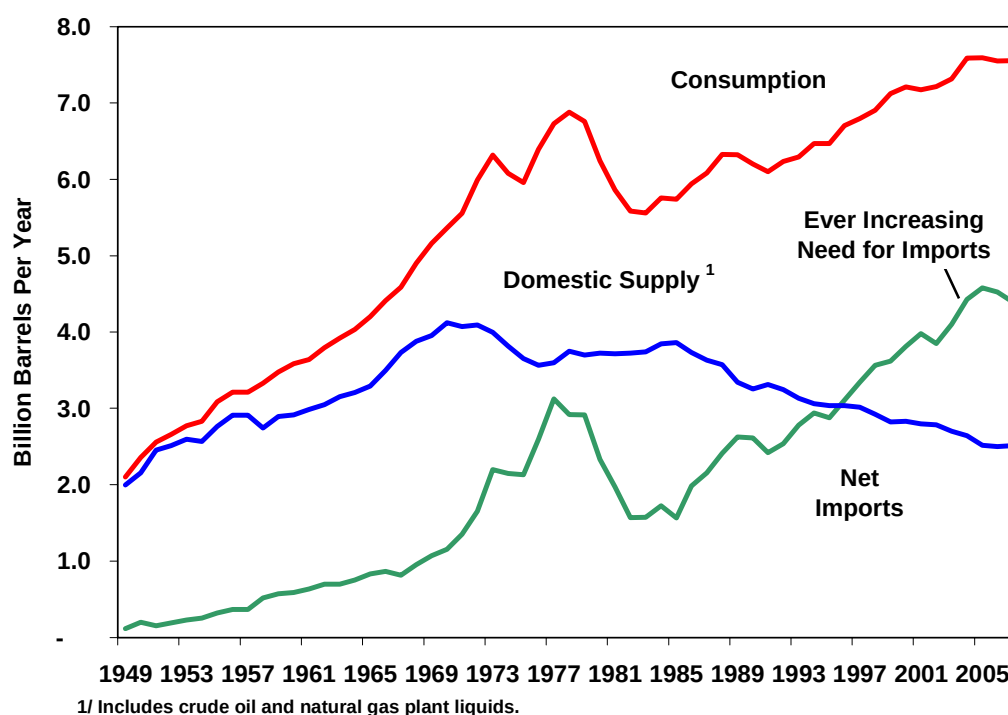


Source: U.S. Department of Energy, Energy Information Administration.

The higher real petroleum prices, concern over a slowdown in the development of new supplies of oil and the September 11, 2001, terrorist attacks and subsequent wars in Afghanistan and Iraq have renewed an interest of the American public in finding ways to reduce this country's dependence on foreign imports of petroleum and develop new technologies that consume less gasoline, such as the upcoming Chevy Volt, with claims of achieving 230 miles per gallon (mpg.). In 2006, the Bush administration acknowledged the need to find alternative, and preferably renewable, sources of energy. President Bush outlined in his 2006 State of the Union Address, the announcement of The Advanced Energy Initiative, which is designed to "help break America's dependence on foreign sources of energy." Former President Bush set as a national goal the replacement of more than 75% of the oil imports from the Middle East by 2025. The Advanced Energy Initiative provided for a 22% increase in clean-energy research at the U.S. Department of Energy. The intent of the funding increase was to accelerate breakthroughs in two critical areas, how we power our homes and businesses, and how we power our automobiles, thus stimulating a reduction in our country's demand for fossil based energy sources. The new Obama administration has followed through with a clear mandate to continue the country's need to address the energy predicament with new solutions. President Obama's comprehensive energy plan calls for some of the following initiatives:

- Help create five million new "green" jobs by strategically investing \$150 billion over the next ten years to catalyze private efforts to build a clean energy future.
- Within 10 years save more oil than we currently import from the Middle East and Venezuela combined.
- Put 1 million plug-in hybrid cars (cars that can get up to 150 miles per gallon) on the road by 2015; cars that will be built in America.
- Ensure 10% of our electricity comes from renewable sources by 2012, and 25% by 2025.
- Implement an economy wide cap and trade program to reduce greenhouse gas emissions 80% by 2050.

Statistics are very clear and impartial regarding the trends of oil consumption and production in the U.S. Since the mid-1950s, the U.S. has imported more energy than it has exported. Consumption of petroleum, the most prominent U.S. energy resource, has expanded from 6.2 million barrels/day in 1950 to almost 20 million barrels/day in 2007, or an annual total of 7.5 billion barrels (Figure 5). During this period, petroleum imports have grown from being insignificant to surpassing U.S. domestic supplies. Most oil imports have been met by North American countries, with Canada and Mexico providing over 29.2% of U.S. petroleum needs in 2008 (Table 1). The U.S. is faced with the continual concern of consistent supplies in the future from politically sensitive regions such as the Middle East. In 2008, OPEC countries accounted for over 46% of U.S. oil imports. Saudi Arabia represented 11.9%, Venezuela 9.2% and Nigeria 7.7% of total U.S. oil imports in 2008.

Figure 5: US Petroleum Situation: 1949-2007

Source: U.S. Department of Energy, Energy Information Administration.

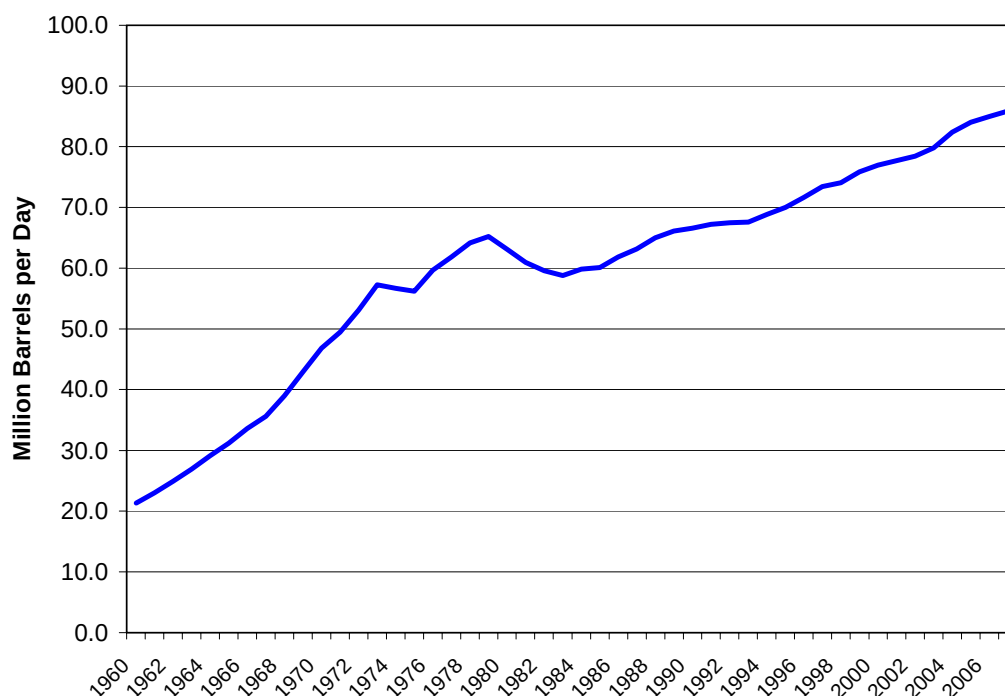
Table 1: U.S. Imports of Crude Oil, by Country of Origin for 2008

	Country of Origin	Thousand Barrels	Percent Total
1	Canada	899,935	19.1%
2	Saudi Arabia	560,705	11.9%
3	Mexico	475,545	10.1%
4	Venezuela	435,769	9.2%
5	Nigeria	362,263	7.7%
6	Iraq	229,300	4.9%
7	Algeria	200,192	4.2%
8	Angola	187,761	4.0%
9	Russia	169,415	3.6%
10	Virgin Islands (U.S.)	117,191	2.5%
	Rest of World		22.8%
Total		4,711,238	100.0%
Non OPEC Countries		2,530,488	53.7%
Persian Gulf		868,516	18.4%
Total OPEC Countries		2,180,750	46.3%

Source: U.S. Department of Energy, Energy Information Administration.

The global supply of and demand for energy is being challenged not just by the level of U.S. consumption and political instability in certain oil-producing countries, but also by growing demand in emerging economies such as China and India. World consumption of petroleum rose from just over 20 million barrels/day in 1960 to 85.9 million barrels/day in 2007, a compound annual growth rate of 3.12% (Figure 6).

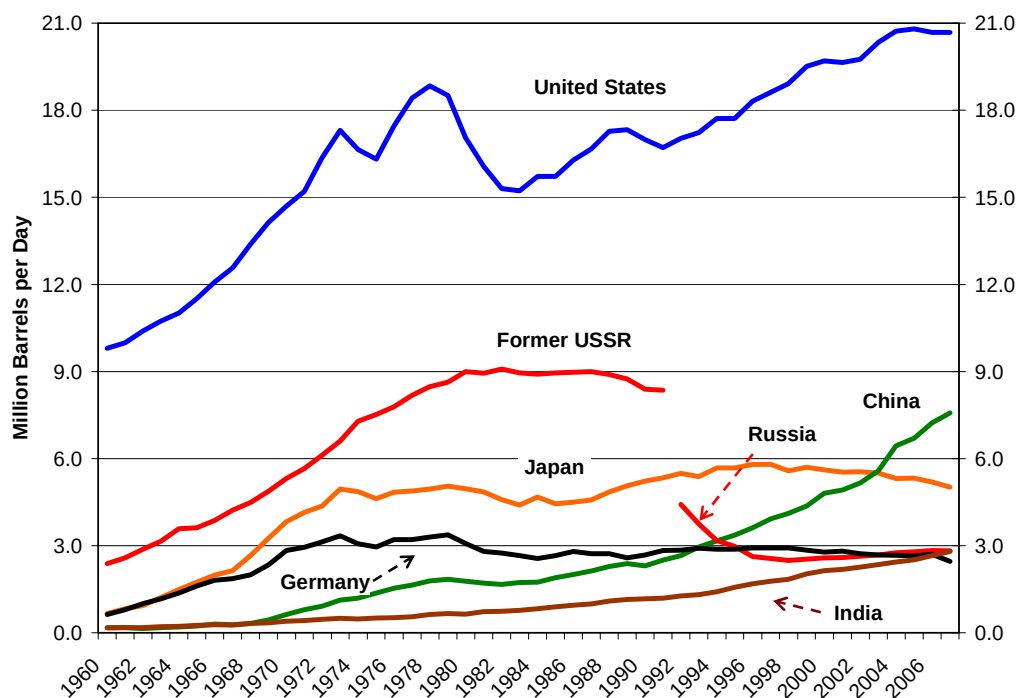
Figure 6: World Daily Consumption of Petroleum, 1960-2007



Source: U.S. Department of Energy, Energy Information Administration.

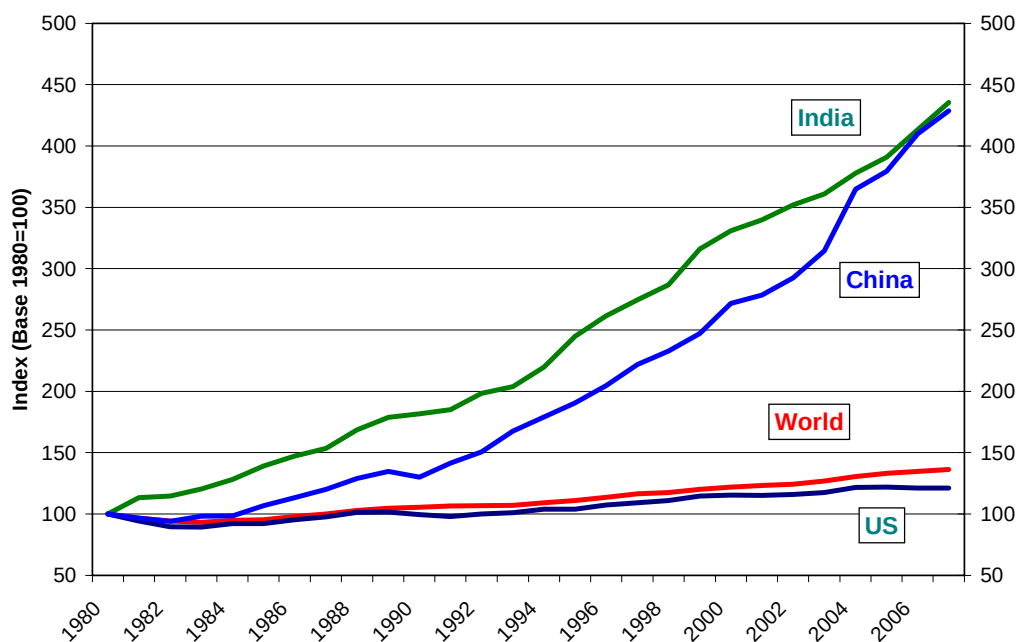
The U.S. is the most significant petroleum-consuming economy in the world (Figure 7). The former Soviet Union was second in importance until its breakup in the early 1990s; now China is the second-largest petroleum consuming economy. Since 1960, China has increased its consumption of petroleum faster than any country (over 3,000%), while India has increased consumption by almost 1,500% (Figure 8). More mature economies such as the U.S. and Canada actually exhibit growth rates that are below the world trend, this is also true for most of the major and mature economies in the European Union.

Figure 7: Leading Petroleum Consuming Countries, Average Daily Consumption, 1960-2007



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

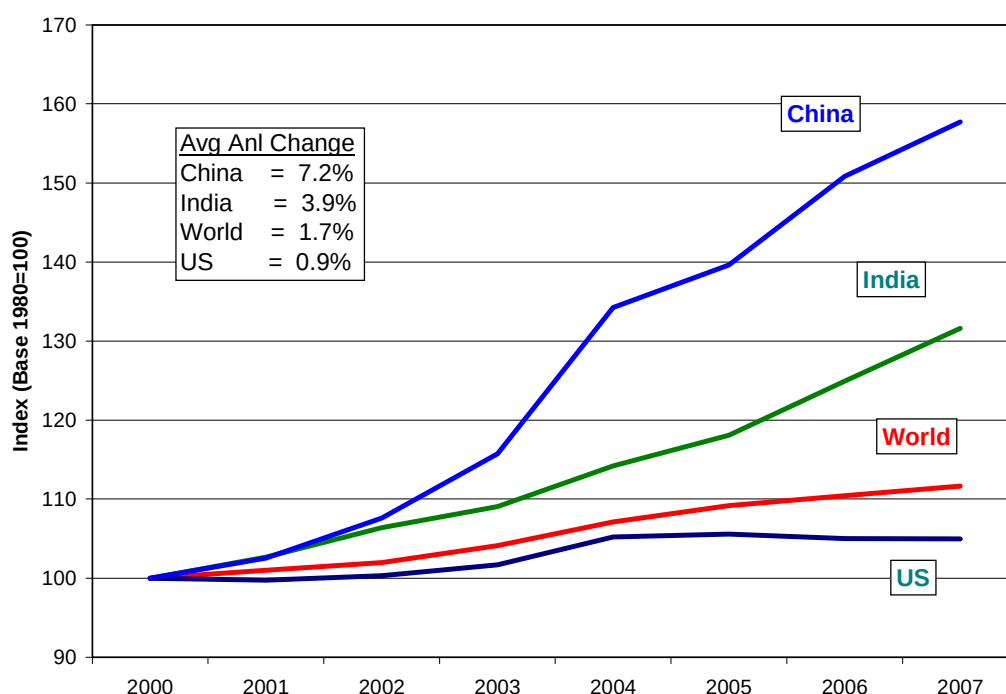
Figure 8: Indexed Growth of Petroleum Consumption for Key Countries, 1980-2007 (Barrels of Oil Consumed Daily)



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

In recent years, the rate of growth for China, for example, has increased significantly (Figure 9). From 2000 to 2007, China's consumption of oil increased at an average annual rate of 7.2%; this was almost twice as fast as India's annual growth rate and significantly ahead of the U.S. annual growth rate of only 0.9%.

Figure 9: Indexed Growth of Petroleum Consumption for Key Countries, 2000-2007 (barrels of oil consumed daily)



Source: U.S. Department of Energy, Energy Information Administration and Informa Economics.

As previously mentioned, many European Union countries have generally fallen in their level of consumption of petroleum globally as emerging economies have rapidly increased their share of total petroleum demand (Table 2). From 1960 to 1969, the U.S. consumed, on average, 37.6% of the total global use of petroleum; the next largest oil consumer was the Former Soviet Union (FSU) at 11.6% (Table 3). Now the FSU has been dissolved and numerous developing countries have significantly expanded their economies, while the U.S. share of global oil consumption has actually declined to 25.7%, still extremely large; however, the impact of growing foreign economies is palpable. For example, often overshadowed by China and India, Brazil has also experienced rapid consumption in petroleum over the last 20 years (Table 4). Spain and Russia have also exhibited strong recent relative growth in oil consumption from 2000 to 2008.

Table 2: Petroleum Consumption, Daily Average Barrels Consumed, Key Countries, 1960-2008 (million barrels)

	1960-69	Rank	1970-79	Rank	1980-89	Rank	1990-99	Rank	2000-08	Rank
WORLD	30.74		57.03		61.84		70.26		81.62	
Total OECD	22.47		40.41		39.11		44.66		48.65	
Total Non-OECD	8.27		16.62		22.72		25.60		32.97	
United States	11.56	(1)	16.98	(1)	16.27	(1)	17.878	(1)	20.17	(1)
China	0.24	(12)	1.28	(9)	1.93	(5)	3.294	(3)	6.25	(2)
Japan	1.69	(3)	4.65	(3)	4.69	(3)	5.564	(2)	5.26	(3)
Russia							3.068	(4)	2.73	(4)
Germany	1.45	(4)	3.13	(4)	2.73	(4)	2.862	(5)	2.67	(5)
India	0.24	(13)	0.51	(13)	0.88	(13)	1.524	(13)	2.47	(6)
Brazil	0.36	(9)	0.86	(10)	1.15	(11)	1.767	(12)	2.23	(7)
Canada	1.10	(6)	1.76	(8)	1.63	(9)	1.829	(9)	2.21	(8)
South Korea	0.05	(14)	0.33	(14)	0.61	(14)	1.772	(11)	2.17	(9)
Mexico	0.35	(10)	0.75	(12)	1.48	(10)	1.858	(8)	2.04	(10)
France	1.05	(7)	2.33	(5)	1.87	(6)	1.935	(6)	2.00	(11)
Italy	0.97	(8)	1.93	(7)	1.80	(7)	1.900	(7)	1.78	(12)
United Kingdom	1.42	(5)	2.07	(6)	1.66	(8)	1.810	(10)	1.76	(13)
Spain	0.25	(11)	0.83	(11)	0.94	(12)	1.177	(14)	1.55	(14)
Former USSR	3.56	(2)	7.16	(2)	8.94	(2)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

Table 3: Percent Share of World Petroleum Consumed by Key Countries, 1960-2008

	1960-69	Rank	1970-79	Rank	1980-89	Rank	1990-04	Rank	2000-08	Rank
WORLD	100%		100%		100%		100%		100%	
Total OECD	73.1%		70.9%		63.3%		63.6%		59.6%	
Total Non-OECD	26.9%		29.1%		36.7%		36.4%		40.4%	
United States	37.6%	(1)	29.8%	(1)	26.3%	(1)	25.4%	(1)	24.7%	(1)
China	0.8%	(12)	2.2%	(9)	3.1%	(5)	4.7%	(3)	7.7%	(2)
Japan	5.5%	(3)	8.1%	(3)	7.6%	(3)	7.9%	(2)	6.4%	(3)
Russia							4.4%	(4)	3.3%	(4)
Germany	4.7%	(4)	5.5%	(4)	4.4%	(4)	4.1%	(5)	3.3%	(5)
France	0.8%	(7)	0.9%	(5)	1.4%	(6)	2.2%	(6)	3.0%	(6)
Canada	1.2%	(6)	1.5%	(8)	1.9%	(9)	2.5%	(7)	2.7%	(7)
South Korea	3.6%	(14)	3.1%	(14)	2.6%	(14)	2.6%	(8)	2.7%	(8)
Mexico	0.2%	(10)	0.6%	(12)	1.0%	(10)	2.5%	(9)	2.7%	(9)
Brazil	1.1%	(9)	1.3%	(10)	2.4%	(11)	2.6%	(10)	2.5%	(10)
Italy	3.4%	(8)	4.1%	(7)	3.0%	(7)	2.8%	(11)	2.4%	(11)
United Kingdom	3.1%	(5)	3.4%	(6)	2.9%	(8)	2.7%	(12)	2.2%	(12)
India	4.6%	(13)	3.6%	(13)	2.7%	(13)	2.6%	(13)	2.2%	(13)
Spain	0.8%	(11)	1.5%	(11)	1.5%	(12)	1.7%	(14)	1.9%	(14)
Former USSR	11.6%	(2)	12.5%	(2)	14.5%	(2)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

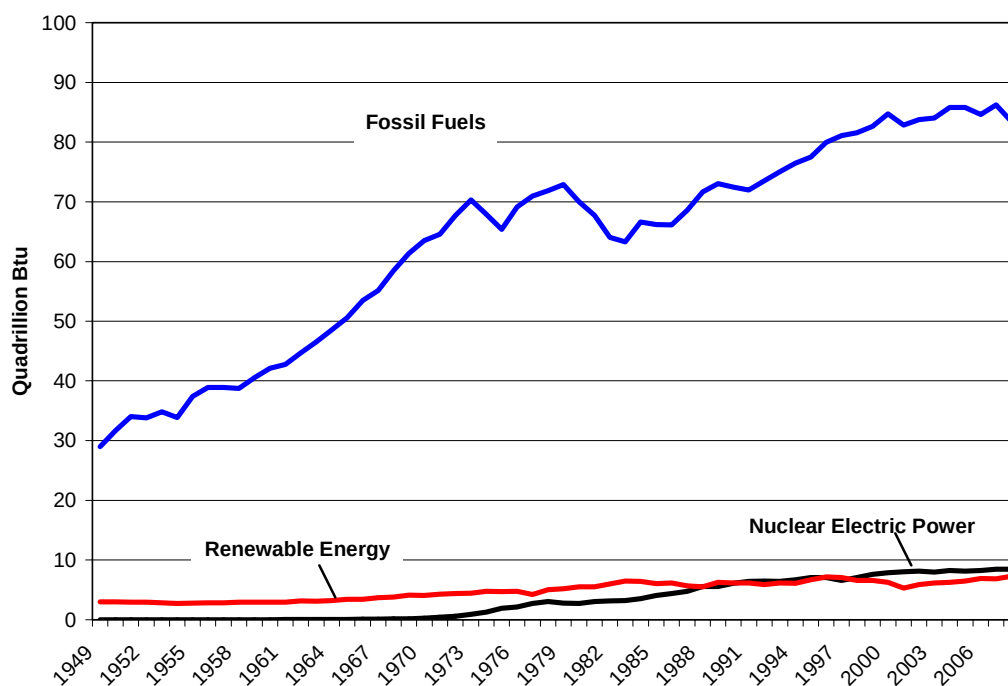
Table 4: Annual Growth Rate of Petroleum Consumption in Key Countries, 1960-2008

	Anl Rate 1960-69		Anl Rate 1970-79		Anl Rate 1980-89		Anl Rate 1990-99		Anl Rate 2000-08	
		Rank		Rank		Rank		Rank		Rank
WORLD	7.5%		3.4%		0.8%		1.5%		1.5%	
Total OECD	7.6%		2.4%		0.3%		1.6%		0.2%	
Total Non-OECD	7.4%		5.9%		1.7%		1.3%		3.5%	
China	11.4%	(7)	10.9%	(1)	4.0%	(3)	7.0%	(1)	6.8%	(1)
India	8.3%	(8)	5.1%	(7)	6.2%	(1)	6.4%	(3)	4.1%	(2)
Brazil	6.1%	(11)	8.5%	(4)	2.5%	(5)	4.8%	(4)	1.8%	(3)
Canada	6.0%	(12)	2.6%	(8)	-0.5%	(12)	2.0%	(6)	1.7%	(4)
Russia							-8.4%	(14)	1.5%	(5)
Spain	18.6%	(2)	6.0%	(5)	-0.5%	(11)	3.6%	(5)	1.2%	(6)
Mexico	4.9%	(13)	8.6%	(3)	2.7%	(4)	0.8%	(10)	1.0%	(7)
South Korea	26.1%	(1)	10.8%	(2)	4.9%	(2)	6.5%	(2)	0.4%	(8)
United States	4.1%	(14)	2.5%	(9)	0.8%	(6)	1.7%	(7)	0.4%	(9)
United Kingdom	7.9%	(9)	-1.8%	(14)	0.3%	(7)	0.0%	(13)	0.0%	(10)
France	11.5%	(6)	1.5%	(11)	-2.0%	(14)	0.9%	(9)	-0.3%	(11)
Germany	12.6%	(5)	1.4%	(12)	-1.0%	(13)	0.5%	(11)	-1.2%	(12)
Italy	13.1%	(4)	1.0%	(13)	-0.1%	(9)	0.4%	(12)	-1.6%	(13)
Japan	16.1%	(3)	2.4%	(10)	0.1%	(8)	1.0%	(8)	-1.7%	(14)
Former USSR	7.6%	(10)	5.4%	(6)	-0.2%	(10)				

Source: U.S. Department of Energy, Energy Information Administration, and Informa Economics.

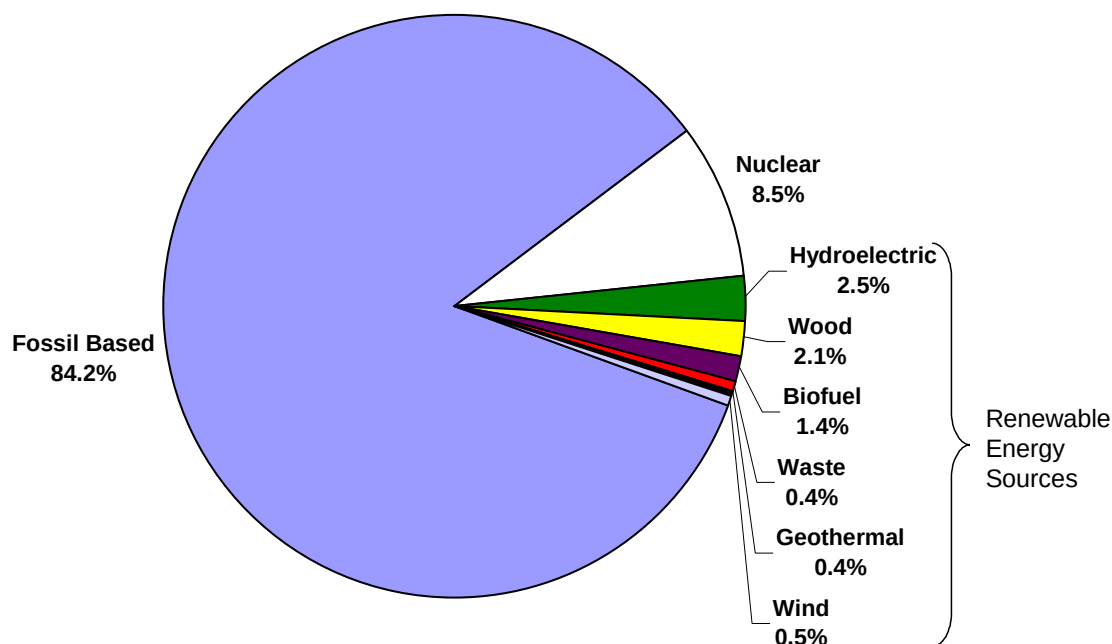
Since 1949, fossil fuel as a percentage of total U.S. energy consumption has risen considerably relative to nuclear electric power and renewable energy sources (Figure 10). The U.S. consumed almost 30 quadrillion Btu of fossil fuels in 1949; this has increased significantly to approximately 85 quadrillion Btu of fossil fuels in 2008. Just as the U.S. relies heavily on petroleum as a primary source of energy, other sources play a significant role in the intricate energy balance (Figure 11). The U.S. uses an extensive amount of natural gas, coal, and nuclear electric power, with renewable energy growing more popular. In 2008, fossil fuel-based energy sources (coal, natural gas and petroleum) accounted for 84.2% of total U.S. energy consumed, with the remainder being nuclear electric power (8.5%) and renewable energy (7.3%).

Figure 10: Energy Consumption by Source, 1949-2008



Source: U.S. Department of Energy, Energy Information Administration

Figure 11: Percent Energy Consumption by Source, 2008

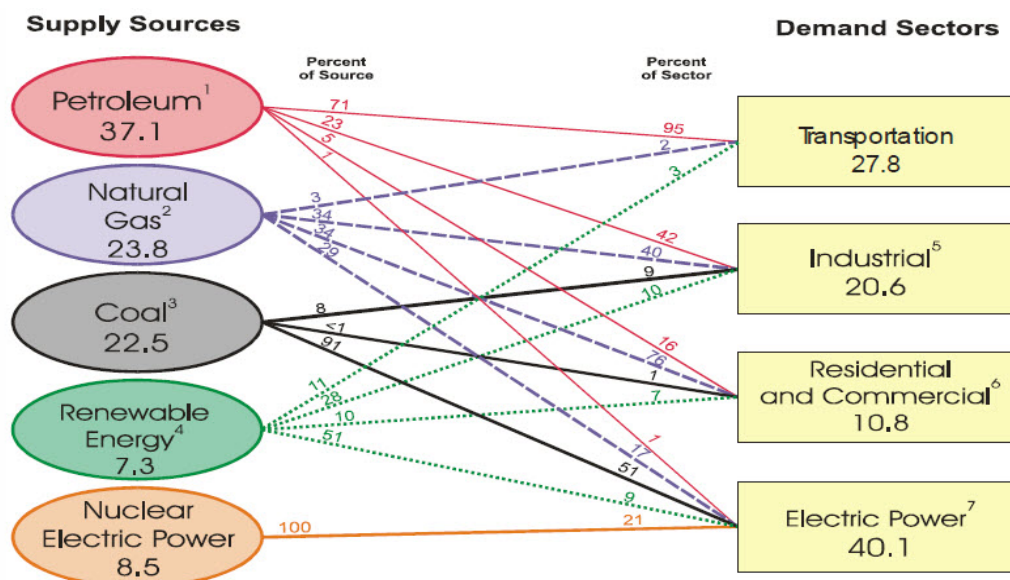


Source: U.S. Department of Energy, Energy Information Administration

There are four primary energy consuming sectors in the U.S. The four sectors are: residential, which accounts for 21.9% of the total energy consumption; commercial, which accounts for 17.9% of the total energy consumption; industrial, which accounts for 32.1% of the total energy consumption; and transportation, which accounts for 28.1% of the total energy consumption (Figure 12). Highlights of the supply/demand balance flow diagram are as follows:

- Transportation uses the largest share of petroleum at 71%, while the industrial sector uses 23% of petroleum and the remaining 6% goes to residential/commercial and electric power.
- The consumption of natural gas is evenly distributed between three sectors, with industry using 34%, residential/commercial using 34% and electric power using 29%; the remainder is consumed by transportation at only 3%.
- The consumption of coal primarily linked to two sectors, the generation of electricity at 91% and industrial consumption at 8%.
- Nuclear electric power is used exclusively, at 100% consumption, by the electric power demand sector.
- The use of renewable energy is divided across all four demand sectors with electric power using the most at 51% and industrial demand the second largest sector using 28%.

Figure 12: U.S. Primary Energy Consumption by Source and Sector, 2007 (Quadrillion Btu)



Source: USDOE, Energy Information Administration, Annual Energy Review 2007.

- 1 Excludes 0.6 quadrillion Btu of ethanol, which is included in "Renewable Energy."
- 2 Excludes supplemental gaseous fuels.
- 3 Includes 0.1 quadrillion Btu of coal coke net imports.
- 4 Conventional hydroelectric power, geothermal, solar/PV, wind, and biomass.
- 5 Includes industrial combined-heat-and-power (CHP) and industrial electricity-only plants.
- 6 Includes commercial combined-heat-and-power (CHP) and commercial electricity-only plants.
- 7 Electricity-only and combined-heat-and-power (CHP) plants whose primary business is to sell electricity, or electricity and heat, to the public.

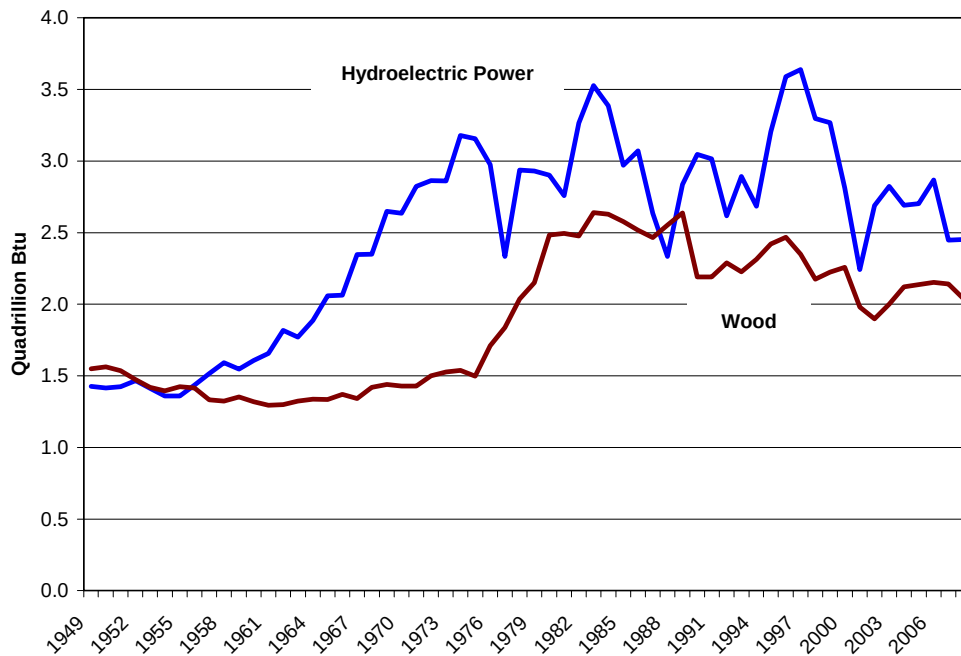
Briefly, the renewable energy sources can be segmented into the following general categories:

- Hydroelectric: Renewable energy from hydroelectricity.
- Wood: Wood, black liquor, and other wood waste.
- Waste: Municipal solid waste, landfill gas, sludge waste, tires, and agricultural byproducts, including animal waste, and other biomass (plant material and residue)
- Biofuels: Ethanol blended into motor gasoline and biodiesel.

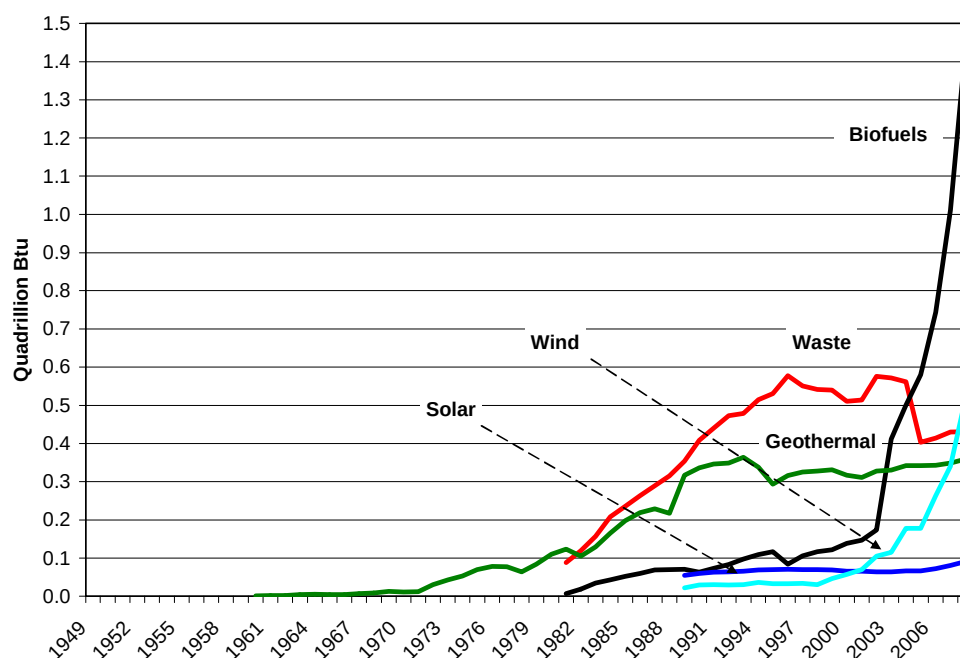
- Geothermal: Geothermal electricity net generation, heat pump, and direct use energy.
- Solar: Solar thermal and photovoltaic electricity net generation, and solar thermal direct use energy.

Hydroelectric power and wood-based power contribute the largest amount of renewable energy by a wide margin (Figure 13). However, their growth has remained flat since the 1980s. In general, other renewable energy sources have shown greater increases in their rate of adoption. Alcohol (ethanol) and wind based renewables have grown the most significantly from 1990 to the present (Figure 14).

Figure 13: U.S. Renewable Energy Consumption by Source - Part I, 1949-2008



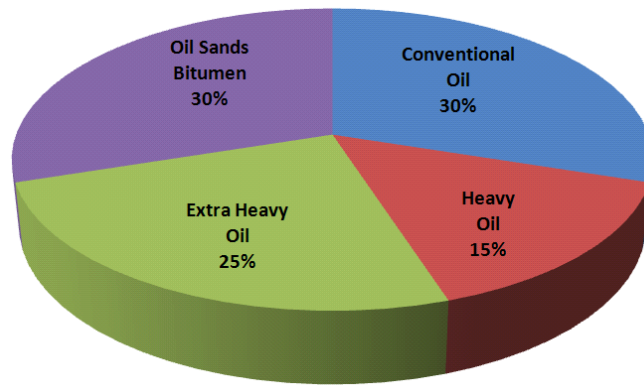
Source: U.S. Department of Energy, Energy Information Administration, Monthly Energy Review.

Figure 14: U.S. Renewable Energy Consumption by Source - Part II, 1949-2008

Source: U.S. Department of Energy, Energy Information Administration, Monthly Energy Review.

Today's marketplace is making a concerted effort to find larger supplies of renewable energy feedstocks and substitutes in order to replace the traditional fossil fuel (hydrocarbon based) sources of energy, as evidenced by such strong growth in the biofuels and wind sectors. Global economies are concerned that the supplies of conventional oil are declining rapidly and that the supplies of conventional oil might have passed what is called "peak oil." Peak oil is defined as the point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline. The concept is based on the observed production rates of individual oil wells, and the combined production rate of a field of related oil wells. The aggregate production rate from an oil field over time usually grows exponentially until the rate peaks and then declines, sometimes rapidly, until the field is depleted. Given the recent record prices for crude oil, the peak oil debate has gained significant attention with strong arguments both for and against the concept. Some experts have now estimated that total world reserves of *conventional* oil are now less than 30% of total oil supplies which include heavy oil, oil sands and extra heavy oil (Figure 15). The heavier oils are not easy to use (require special refining procedures) and are more expensive to extract compared to conventional oil. In addition to concerns over peak oil, energy security and mitigation of climate change are important reasons for the move toward biofuels and wind energy.

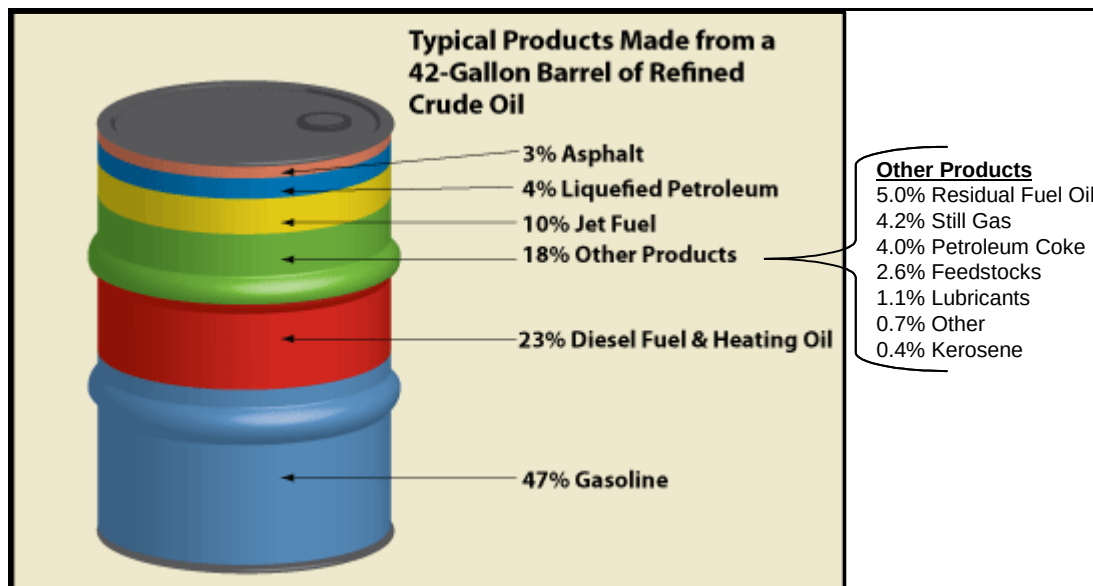
Figure 15: Total World Oil Reserves



Source: Alboudwarej, Husswin, Highlighting Heavy Oil, Oilfield Review, Summer 2006.

One of the reasons that conventional oil has become such a vital link and input in global economies is because of its chemical versatility which provides a plethora of uses. When refined, one barrel of crude oil yields about 19 gallons of finished motor gasoline, 9 gallons of diesel fuel, as well as other petroleum based derivatives used in products such as ink, crayons, bubble gum, dishwashing liquids, deodorant, eyeglasses, records, tires, ammonia, and heart valves, etc. (Figure 16).

Figure 16: Products Made from a Barrel of Crude Oil³



Source: USDOE, Energy Information Administration and American Petroleum Institute.

³ Note: Percentages total 105% because of “processing gain.” A 42 gallon barrel of oil actually yields 44 gallons of products.

In general, each barrel of oil in the U.S. is fractionated into fairly consistent components as described below.⁴

- **Gasoline:** Of all the crude oil refined for use in the United States, almost half (47%) becomes gasoline for automobiles, boats and other gasoline-driven motors.
- **Jet Fuel:** Airplanes utilize approximately 10% of a refined barrel of oil in the form of jet fuel.
- **Diesel Fuel and Home Heating Oil:** 23% becomes distillate, two-thirds of which is refined for diesel fuel for trucks, buses and other diesel engines, while the remaining one-third is used as home heating oil.
- **Boiler Oil:** Boiler oil, or residual fuel oil, makes up 5% of refined crude oil and is used on ships, in industrial boilers and in power plants to produce electricity.
- **Asphalt and Road Oil:** Asphalt and road oil accounts for 3% of crude oil consumption.
- **Other:** Approximately 9.4% of the crude oil is refined into non-energy related feedstocks for manufacturing products such as lubricants, wax, coke for steel making, and naphthas that are used in the drycleaning process.
- **Petrochemical Feedstocks:** Petrochemical feedstocks, products of the refining process, make up the remaining 2.6% of all refined crude oil. Half of this is used to make plastics (approximately 1.3% of the total) for thousands of items such as tableware, furniture, aircraft and automobile parts, luggage, surfboards, helmets, medical supplies and packaging. The remaining 1.3% is used to make products such as solvents, synthetic fibers for wearing apparel, synthetic rubber, paints and coatings.

From a scientific and chemical perspective these refined crude oil products can be described as follows:

- **Petroleum gas** - used for heating, cooking, making plastics small alkanes (1 to 4 carbon atoms) commonly known by the names methane, ethane, propane, and butane, which is often liquified under pressure to create LPG (liquified petroleum gas).

⁴ It should be noted that this crude oil fractionation recipe does vary by country, where differing economies require different input streams depending on the structure of their economies.

- **Naphtha or Ligroin** - intermediate that will be further processed to make gasoline mix of 5 to 9 carbon atom alkanes, and a motor fuel liquid mix of alkanes and cycloalkanes (5 to 12 carbon atoms).
- **Kerosene** - fuel for jet engines and tractors; starting material for making other products as a liquid mix of alkanes (10 to 18 carbons) and aromatics.
- **Gas oil or Diesel distillate** - used for diesel fuel and heating oil; starting material for making other products liquid alkanes containing 12 or more carbon atoms.
- **Lubricating oil** - used for motor oil, grease, other lubricants; consists of liquid long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, and aromatics.
- **Heavy gas or Fuel oil** - used for industrial fuel; starting material for making other products liquid long chain (20 to 70 carbon atoms) alkanes, cycloalkanes, and aromatics.
- **Residuals** - coke, asphalt, tar, waxes; starting material for making other products solid multiple-ringed compounds with 70 or more carbon atoms.

Consistent with the nomenclature or breakdown of how a barrel of oil is used in the U.S. as previously discussed, the DOE's, Energy Information Agency (EIA) estimated the volume of oil consumption per respective product category in 2007, as shown in Table 5. The average daily oil consumption for all refined oil products in the U.S. was approximately 20.5 million barrels in 2007. Annually, total oil consumption in the U.S. is a staggering 7.5 billion barrels of oil. Keep in mind that volumetrically a barrel of oil is approximately 42 gallons. Finished motor gasoline consumption was approximately 3.4 billion barrels in 2007; multiplying a barrel of oil times 42 gallons makes the volume of finished motor gasoline consumed in the U.S. even more imposing at an estimated level of 143 billion gallons. Even with this comprehensive list of petroleum products, a barrel of crude oil can be reduced into more specialized products; that is why the term feedstock is used to explain the potential to further add value to the crude stream.

Table 5: Volume of U.S. Petroleum Products Consumed in 2007

	Annual (Thousand Barrels Per Day)	Annual (Thousand Barrels Total)
Finished Motor Gasoline	9,286	3,389,390
Distillate Fuel Oil	4,196	1,531,540
Liquefied Refinery/Petroleum Gases	2,085	761,025
Kero-Type Jet Fuel	1,622	592,030
Petroleum Coke	490	178,850
Still Gas	697	254,405
Residual Fuel Oil	723	263,895
Asphalt and Road Oil	494	180,310
Other Oils for Feedstocks	350	127,750
Naptha for Feedstocks	294	107,310
Lubricants	142	51,830
Miscellaneous Products	63	22,995
Kerosene	32	11,680
Special Napthas	41	14,965
Finished Aviation Gasoline	17	6,205
Waxes	11	4,015
Total	20,543	7,498,195

Source: U.S. Department of Energy, Energy Information Administration.

The final markets for value-added refined crude oil product streams are extremely large and diverse in the U.S. Table 6 highlights the estimated value of the major markets that use both petroleum and biobased feedstocks (i.e., corn and soybeans). The markets range in value from the largest market; that is gasoline at \$298 billion in 2006, down to the high emerging growth market for wood substitutes at \$3.4 billion. All of these markets use hydrocarbon based petroleum feedstocks as an input to their manufacturing activities. The petroleum content level varies significantly across markets. Gasoline and diesel are exclusively petroleum based; however, the petroleum input stream is much smaller as a percent share of the total product volume for cosmetics and personal care products.

Biobased feedstocks continue to make inroads into these different markets at a significant rate. Many companies are espousing the virtues of being green and not using petroleum based feedstock; rather, they are focused on increasing their use of renewable sources of inputs. It is unclear just how far renewable feedstocks from corn and soybeans have penetrated these markets. The easiest markets to estimate are the gasoline and diesel markets where ethanol and biodiesel production volumes are closely tracked by the industries. Less clear is an adequate understanding, for example, of the actual percent share of the sanitary cleaning products market that is biobased. Many market estimates are bantered about with little clear empirical supporting evidence, compared to such reliable surveys as the U.S. Census of Manufacturing.

Table 6: Major U.S. Markets for Petroleum and Biobased Feedstocks, 2006

Sector	Value of Shipments/Markets (\$1,000)
Gasoline	298,589,184
Diesel (on highway)	87,703,231
Pharmaceuticals	163,005,621
Textiles (clothing, carpets, bedding linens, auto)	38,028,266
Lubricants (motor oil, transformer fluid, hydraulic fluids, etc.)	11,308,102
Solvents	5,500,000
Sanitary Cleaning Products (hand cleaners, janitorial cleaners, household, food service, laundry)	34,267,288
Cosmetics and Personal Care Products	5,900,000
Adhesives/binders	9,230,331
Paints and Coatings (inks, paints, etc.)	22,558,703
Plastics (films, containers, polymers, insulations, foams)	203,496,075
Resins and Synthetic Rubber Manufacturing	93,499,662
Fertilizers	12,652,957
Sorbents	3,280,000
Wood Substitutes Composite Panels	3,380,000

Source: U.S. Department of Commerce: 2006 Census of Manufacturing, Freedonia Group, DOE: EIA, Informa Economics.

1. Conclusion

The biobased corn and soybean products and technologies will ultimately be challenged by two basic obstacles relative to petroleum; the first is economic and second is performance (attributes). The first challenge relates to the simple question: is the biobased product or technology cost competitive with traditional petro based feedstocks or related technological processes? In general, as petroleum prices rise, the easier it is to justify substituting a crude oil feedstock with a biobased corn or soybean feedstock. As petroleum prices fall the inverse is true; biobased feedstocks face inflection points in pricing where they become more costly relative to petroleum. The record high prices of crude above \$100/barrel in 2008 provided significant opportunities for biobased products to gain interest from those manufactures that were looking to replace their high cost oil feedstocks.

The second question relates to how well the respective biobased product or technology performs relative to traditional petroleum manufacturing platforms. For example, in the world of lubricants, specifically motor oil, a significant amount of

research has been conducted regarding the use of soybean oil as a potential replacement for motor oil. The challenge for soybean researchers has been to try and replicate the same qualities and characteristics of petroleum based motor oil regarding its ability to withstand high temperatures without experiencing any loss in lubricity. It is within this context that the Informa research team “set out” to indentify those corn and soybean based products and technologies that could successfully compete in terms of their relative economics and attributes compared to traditional hydrocarbon based petroleum products and technologies. It should be noted that petroleum markets have certainly played a major role in the recent interest and developments in biobased products and technologies; the growth however, has not been confined to only the large fuel markets. Significant advancements have occurred in numerous other markets because of the desirable environmental properties of renewability and biodegradability. These attractive properties are creating new and exciting opportunities for feedstocks that are based on corn or soybeans. Beyond biobased products/technologies, significant advances are also emerging in other fields like health with soy isoflavones or in more traditional ones like animal feed. Results and recommendations of this endeavor can be found in the individual commodity reports (i.e., for corn and soybeans).

III. Overview of Top 20 Corn Products and Technologies

After assessing the products/technologies listed in Appendix A: Phase I – Corn Products/Technologies based on the criteria previously discussed (i.e., demand/market potential, economic feasibility, development stage and strength of institutional support), the top 20 products/technologies were identified. These products/technologies are briefly reviewed within this section and are listed in Table 7. Upon further analysis and interviews, this list was then further refined down to the top 8, which are each presented in more detail within the next section (IV. Top 8 Corn Products/Technologies).

Table 7: Top 20 Corn Products and Technologies

Product/Technology Name	Product/Technology Timeframe
<u>Ethanol Process Improvements and Co-Product Utilization</u>	
Anaerobic Digestion	Medium
Back-End Corn Oil Extraction	Short
CO ₂ in Algae Production	Long
Ethanol Distillation	Medium
Front-End Fractionation	Short
Microwave Drying of Distillers Grains	Short
Reactive Distillation	Short
Supercritical Carbon Dioxide Corn Oil Extraction	Medium
Zein Extraction	Medium
<u>Second Generation Biofuels</u>	
Butanol	Medium
Cellulosic Ethanol - Biochemical Platform	Medium-Long
Cellulosic Ethanol - Thermochemical Platform	Medium-Long
<u>Value Added Chemicals</u>	
3-Hydroxypropionic Acid	Long
Itaconic Acid	Long
Levulinic Acid	Long
Lignin - Aromatics	Long
Polylactic Acid	Short
1,3-Propanediol	Short
Sorbitol/Isosorbide	Short-Long*
Succinic Acid	Medium

*The commercial production of sorbitol is well established . However, technology developments to improve the sorbitol production process and to produce derivative chemicals such as isosorbide are under development.

Short term: 0-3 years

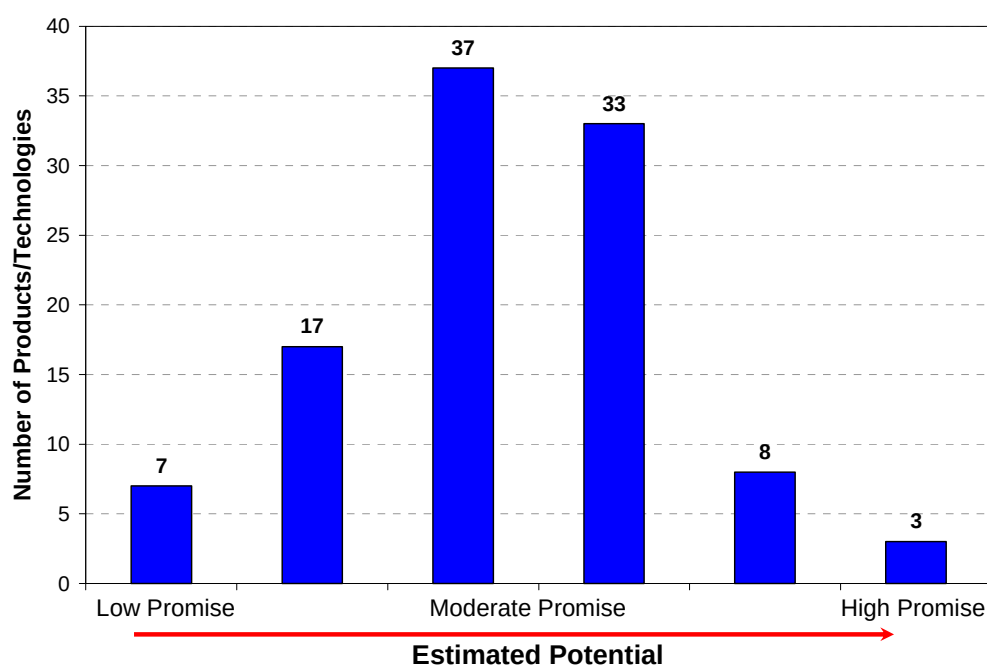
Medium term: 3-5 years

Long term: > 5 years

It is important to keep in mind that this list is ever changing, as new developments are brought forth and as new information about these technologies is realized. These products and technologies have the potential to move in either direction, up or down the list of top prospects.

Each of the 100+ products and technologies were assessed based on their demand/market potential, their economic feasibility, their stage of development, and their strength of institutional support. The distribution of the assessed potential for the reviewed products and technologies is presented within Figure 17. As illustrated, 11 of the top 20 were assessed as having a high degree of promise; however, the decision regarding which of the other 9 to include in the top 20 was more subjective. This is where the value in the interviews with generalists in the field of biobased products and technologies was truly realized. These interviews helped to provide confirmation and insight into the finalization of the top 20 list.

Figure 17: Distribution of Corn Products/Technologies Based on their Estimated Potential



While the process utilized to reach the top 20 was designed to identify those products and/or technologies which are considered to have the greatest potential to add significant value to Minnesota's corn commodity production, the value in many of the remaining products and technologies (listed in that Appendix A: Phase I – Corn Products/Technologies) should not be entirely overlooked. For instance, there is often a trade-off between “big bang” technologies – those with potentially large demand effects - and those products and technologies that may not have the “big bang” effect but are less capital intensive. Based on the review process and the scoring weights that were placed on products and technologies considered to have

potentially large demand effects, many of the products and technologies deemed to have a smaller demand impacts did not make the top 20 list. Yet, many of these smaller demand impact products and technologies are less capital intensive and they may be more obtainable/suitable for certain companies or institutions, particularly in the short-term.

Many of the identified top 20 products and technologies are energy related products/technologies. These could constitute either technologies that improve upon the economics of existing corn-to-ethanol production processes (these are presented in Appendix B: Traditional Corn-to-Ethanol Production Processes) or “new” energy products such as butanol and cellulosic ethanol. Energy markets are large and energy prices have been high. These high prices, along with environmental concerns have driven governments around the world, and the U.S. in particular, to push for the development of renewable fuels. This push has come in the form of mandates as well as increased funding for research and development.

One additional thing to keep in mind when reviewing the products and technologies identified throughout all phases of this report is that many are centered around the utilization of the sugar components within corn. Depending on the individual technology, this sugar can be from the 6-carbon sugar glucose that is produced from starch found within the corn kernel; the glucose and 5-carbon sugars, such as xylose, that are found in the lignocellulosic biomass of corn (e.g., corn fiber, corn stover and corn cobs); or from other sugars such as sucrose or fructose. The caveat that should be kept in mind throughout all of this is that corn is not the only source of sugar, and many of the reviewed technologies can also utilize sugar from other feedstocks. Which feedstock is utilized by the given technology will come down to regional economics - which is the cheapest sugar source within a given area.

A. Ethanol Process Improvements and Co-Product Utilization

Given the large and growing ethanol market and its impact on corn demand, as well as the existing infrastructure already established within the state of Minnesota, products/technologies designed to improve the production economics of traditional corn-to-ethanol processes were generally weighted favorably throughout the review of emerging products and technologies in phase I. Throughout the remainder of this report, when discussing the benefits of these new technologies, references are often made in relation to how said technology differs or improves upon the traditional corn-to-ethanol production process. This being the case, Appendix B: Traditional Corn-to-Ethanol Production Processes provides an overview of current ethanol production processes.

1. Anaerobic Digestion

Anaerobic digestion uses bacteria to convert the thin⁵ or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-80%), CO₂ (20-50%), and trace amounts of H₂, NH₃, and H₂S, which can be burned for energy as a substitute for natural gas. This process reduces energy costs and greenhouse gas emissions and helps to conserve water relative to traditional corn-to-ethanol production. Furthermore, if collected, the struvite, a sludge that builds up in the digester, could be sold as a valuable fertilizer or a livestock feed additive, as it is composed of magnesium, phosphate, and ammonia. Additionally, if the final rulemaking for the Renewable Fuel Standard established under the Energy Independence and Security Act of 2007 (only the proposed rulemaking has been issued as of the writing of this report), anaerobic digestion will provide a mechanism for an ethanol facility to reduce the greenhouse gas “score” associated with its ethanol output. However, these benefits should be weighed against a possible reduction in revenues from the co-product sales of distillers grains, depending on whether whole or thin stillage is utilized.

It is estimated that anaerobic digestion using thin stillage can reduce the energy needs of an ethanol facility by 43-66%, and if using whole stillage, energy needs could be entirely met by the biogas.

According to an August, 2008 article in *Technology Review*, University of Minnesota research fellow Douglas Tiffany says that the challenge with anaerobic digesters is the expertise required to maintain a stable bacterial community at high temperatures and avoid system crashes. Additionally, according to Otter Tail Ag Enterprises’ CEO Kelly Longin, the up-front costs of the technology would be at least \$20 million for their 55 mmgy dry-mill ethanol facility (2008). Yet, despite its drawbacks, its potential has spurred the interest of several large companies and research universities, and research and development efforts to improve the anaerobic digestion process of corn ethanol thin and whole stillage are ongoing.

POET recently began using an anaerobic digester at its cellulosic ethanol pilot plant in Scotland, SD, which uses corn cobs as its primary feedstock. The anaerobic digester is being used to power the cellulosic plant and offset natural gas usage at its attached grain ethanol plant. Another cellulosic ethanol company looking to incorporate an anaerobic digester is BioGasol; Canadian ethanol producer Kawartha Ethanol is doing so as well.

⁵ Thin stillage is the solubles portion of whole stillage (the liquid fraction that remains after the ethanol has been removed), which is generally evaporated to produce condensed distillers solubles and is often added back to the distillers grains to become distillers grains with solubles.

2. Back-End Corn Oil Extraction

The basic corn oil extraction technology involves a centrifuge process to separate the oils from the corn stillage. By removing the oil from the distillers grains, the ethanol facility not only captures an additional revenue stream from the extracted corn oil, but also reduces their distillers grains drying costs and associated greenhouse gas emissions, while still producing a marketable co-product in the form of low fat distillers grains⁶. However, in comparison to front-end oil extraction processes (see Section III.A.5 “Front-End Fractionation”), the oil extracted from the back-end is a lower-value product, as it cannot be used in food applications. The trade-off is that the technology is ready now and is already being used in several commercial ethanol facilities and the capital cost requirements are much lower.

GreenShift and Primafuel are two companies currently offering back-end corn oil extraction technologies to ethanol facilities. Both companies are offering packages where they supply the capital for building the process in return for an oil buy back agreement. Greenshift prices the oil off of an index which is based on the price of diesel fuel. They then use the oil they purchase to supply their biodiesel refinery in Adrian, Michigan.

A recent analysis conducted by the U.S. Environmental Protection Agency showed that the process increased the yields of biofuel from corn by 7% (e.g., when oil is used for biodiesel production) and reduces the amount of fossil fuel used in the ethanol production process by 10%. Based on USDA economic analysis, the capital cost to install the GreenShift corn oil extraction system in a 50 mmgy facility would be \$6 million.

While this technology is already commercialized, process developments are ongoing. For example, Iowa State University is researching ways to increase the quantity of oil removed via centrifugation, and Primafuel Solutions announced in an August 2008 *Ethanol Producer* article that they were planning on introducing additional bio-separation innovations in 2009.

3. CO₂ in Algae Production

CO₂ is a current by-product of ethanol production that only a limited number of ethanol facilities are able to sell it due to the geographic concentration and size of the ethanol industry relative to the gas industry's needs. In some cases, it is used by the soft drink industry as a source of carbonation, or by other food processors (e.g., quick freeze applications), but in many cases ethanol facilities simply release it into the atmosphere. Any further value that could be received from this product stream would improve the economics of ethanol production, if the value were to justify the costs associated with its capture. Additionally, with legislation under

⁶ Yet, while low fat, high protein distillers grains may be desirable for some markets, it is not desirable for all (e.g., it is more beneficial for beef, dairy and possibly swine than for poultry).

consideration for cap-and-trade implementation, there may be even greater economic incentive in the future for ethanol producers to reduce the amount of CO₂ that is released into the atmosphere.

One potential use of CO₂ is in the production of algae. The CO₂ emitted from the ethanol production process can be captured and used as a key input (via photosynthesis) in the production of algae, which is in turn used to produce oil. , Many algae technology developers are targeting the production of “biocrude”, which is essentially algae oil that can be cracked or refined just like crude oil into traditional petroleum products such as gasoline, diesel, jet fuel, heating oil, or other chemicals.

Today, there are many companies/institutions developing algae production systems and there is strong financial backing from both the public and private sectors. There is also a wide array of distinct process technologies being developed. Furthermore, according to the National Renewable Energy Laboratory (NREL) representatives, off-take of CO₂ from an ethanol facility would be of a quantity complimentary to the needs of a commercial scale algae operation. However, algae production is not yet commercially viable, and is not likely to be commercialized within the next 5 years.

4. Ethanol Distillation

Energy costs currently account for about 12% of overall operating costs of traditional corn-to-ethanol production, the second largest operating cost next to feedstock costs. Of the overall energy consumption, distillation and dehydration consume about 50% (McAloon et al., 2004; Kim and Dale, 2005 – cited by Vaperma). It is also one of the key cost components in the biochemical cellulosic ethanol platform. However, several alternative ethanol distillation technology developers claim to achieve a 40% reduction in energy costs over traditional distillation methods, this would equate to an approximate 6¢ per gallon cost savings or \$3 million per year for a 50 mmgy ethanol facility (using current natural gas prices). Additionally, according to one technology developer, Vaperma, if using their process, overall fuel production could also be increased by 20% through reductions in process bottlenecks that increase plant throughput/capacity.

Traditionally, the separation of ethanol and water is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also reducing greenhouse gas emissions. Alternative ethanol distillation technologies currently being developed include: vacuum stripping, gas stripping, membrane separation, solvent (liquid) extraction, and supercritical CO₂.

While each of these methods has its own pros and cons, the leading technology at this time appears to be membrane separation, currently being pursued by Vaperma (Siftek) and Whitefox Technologies. This technology uses membranes, which are

vapor phase separation units, to allow the preferred permeation of water over other vapor components in a gas mixture. The removed ethanol is then distilled and the remaining fermentation broth is recycled.

Another ethanol dewatering technology is MOR Supercritical's supercritical CO₂ process, which has the added benefit of CO₂ utilization. The company claims that their process is economically competitive with proposed membrane technologies.

These technologies are largely in the late development/early commercialization stage, and are expected to reach commercial status within 3-5 years, if not sooner.

5. Front-End Fractionation

There are several front-end fractionation processes that separate the corn entering into the dry-mill ethanol facility into three fractions: pericarp (bran/fiber), germ (the oil-bearing portion of the kernel) and endosperm. Revenue streams generated from this process include corn oil; high protein, low fat and fiber distillers grains; bran/fiber and ethanol. Additionally, according to some technology developer claims, front-end fractionation can reduce energy consumption and lower volatile organic compound emissions. And while there are also back-end fiber and oil extraction technologies that are either currently available or being developed that are less expensive, these processes do not produce the high value co-products that are generated from front-end fractionation. Additionally, there are ethanol production efficiencies that are gained when the starch fraction is separated out at the beginning of the process.

Front-end fractionation technologies can generally be classified as either wet fractionation processes (e.g., Quick Germ Quick Fiber, Enzymatic Milling, CVP's HydroMill) or dry fractionation processes (Cereal Process Technologies, Delta-T/Ocrim Milling, Crown Fractionation System, Renessen-Extrax Processing System, POET's BFRAC system). While there are numerous companies, each with slightly different technologies, there are a few basic pros and cons that can be identified between the wet and dry fractionation technologies for modified dry-mill ethanol plants. In general, wet fractionation technologies tend to be more costly. However, they also produce higher-valued co-products and have less starch loss than dry fractionation technologies. The germ extracted by wet fractionation technologies has an oil content of approximately 40+% compared to 20-25% from typical dry fractionation technologies. This low oil germ produced by dry fractionation is sometimes referred to as "dirty germ," and often oilseed processing facilities or wet mills are not geared to take germ with this low of an oil content. Yet, because corn oil extraction equipment is currently considered cost prohibitive and many companies do not want to handle hexane, ethanol producers typically do not want to extract the oil themselves. Additionally, the higher starch loss associated with the dry fractionation technologies is a revenue factor for the ethanol producer, as ethanol yields are compromised. Nonetheless, dry fractionation technologies are more prevalent in current plant installations, primarily due to cost differences.

The company MOR Technology claims to have developed a unique fractionation process known as MOR FRAC+, with costs similar to those generally associated with dry fractionation technologies, but with the higher valued co-products and the lower starch loss generally associated with wet fractionation technologies. MOR is currently working with a number of customers, design-build firms and financing institutions to install the technology in corn-based ethanol plants. While unproven at a commercial scale, this process appears to have promise.

6. Microwave Drying of Distillers Grains

Microwave drying technology is an alternative to conventional rotary drum gas dryers used to dry the ethanol by-product, distillers grains. There are several companies currently pursuing the development and commercialization of this technology. The most commonly reported company supplying this microwave drying technology is Cellencor. Yet, based on an interview with John Caupert, director of the National Corn-to-Ethanol Research Center (NCERC), there have been multiple other companies interested in pursuing the development of this technology. However, the names of these companies were withheld due to non-disclosure agreements with NCERC.

Microwave drying technology works by vibrating the water molecules within the distillers grains, creating friction which converts radio energy to heat energy and vaporizing the water molecules; because the protein and fiber in distillers grains do not readily absorb microwave energy, they do not heat up as much and the product is kept cooler. Additionally, according to technology developer Cellencor, microwave dryers typically have a 90% energy efficiency compared to about 50% for gas rotary dryers.

Cellencor claims that their microwave drying system significantly reduces process energy consumption, enhances the value of animal feed co-products, reduces air emissions, potentially reduces water usage, and is safer and more reliable than current drying systems. Animal feed co-product value is enhanced as microwave drying systems avoid the protein and amino acid damage that results from the high temperatures of conventional gas dryers. The company also has a patented enzyme enhancement process whereby the activity of enzyme additives is enhanced when the structure of the cellular walls is broken down by the microwave energy, resulting in an animal feed with higher available energy. Additionally, the system is electrically powered and uses one-half to one-third of the BTUs per pound of water removed than conventional gas dryers. An added benefit of electric powered drying systems is that they avoid the price volatility of natural gas. The company claims that the system could save ethanol producers 20% or more in operating costs and that the payback period for installation would be 2-5 years.

The Cellencor system has been field tested in both wet and dry mill ethanol facilities, including at Corn Plus in Minnesota in the spring of 2008. Additionally, according to a May, 2009 article in "Biofuels Canada", Kawartha Ethanol, Inc, plans to use a microwave drying process in their 80 mmgy plant in Havelock, Ontario.

7. Reactive Distillation

While inorganic catalysts have long been known as a method to produce valuable chemicals in the petroleum industry, their application on corn-based feed streams has up until now been cost prohibitive due to challenges associated with separating the mixture of chemicals that are derived from such a feed stream with multiple compounds. However, the reactive distillation process can successfully separate a mixed stream of different chemicals by treating that stream with a reactive chemical in the presence of a catalyst, resulting in a mixture of chemicals that can be easily separated.

One of the challenges facing both corn starch-based ethanol and cellulosic ethanol producers is that while the fermenting agent is producing ethanol, other unwanted acid by-products are also being produced. These by-products are often difficult to separate out of the mixture. And while many current research efforts are focused on minimizing the production of these acids, this technology is designed to separate out these acids from the ethanol in such a way that would allow an ethanol or cellulosic ethanol facility to produce a valuable co-product. For example, Michigan State University (MSU) researchers are currently focusing on the production of ethyl lactate from lactic acid and ethanol. Ethyl lactate is a general, all-purpose solvent as well as a common input in pharmaceuticals, food additives, and fragrances. Today, ethyl lactate is not commonly used due to its high production costs. In 2007, the cost of producing ethyl lactate was \$1.30-1.60 per pound (Carl Lira, MSU). However, researchers claim that they have cut this cost in half using reactive distillation. The National Corn Growers Association is currently seeking ethanol companies interested in purchasing a license for this technology to be retrofitted into an existing dry-grind ethanol plant.

8. Supercritical CO₂ Corn Oil Extraction

Rather than using hexane, MOR Supercritical's technology uses carbon dioxide as the only solvent in their process to extract corn oil from germ and vegetable oil from oilseeds. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products

including undegraded meal with high protein digestibility; and can be paired with an accompanying refining technology to extract and refine the oil in one step.

This system can be coupled with MOR Technology's fractionation system (MOR-FRAC Plus+) to provide added value for ethanol facilities or installed as a stand alone facility to produce high quality specialty oils, bioactive ingredients, or nutraceuticals. It can also be used to extract oil from algae. Additionally, the technology can be applied to ethanol dehydration. While the success of separating alcohol and water via supercritical fluids has been demonstrated for many years, these previous demonstrations have not been able to compete with the economics of traditional steam distillation methods or other methods such as membrane separation. However, MOR Supercritical claims their process is scalable and cost-efficient relative to other proposed dehydration technologies.

MOR Supercritical is currently building a 15 ton/day oil extraction plant in Pennsylvania that is expected to be completed by the 3rd quarter of 2009. Afterward, they plan to offer their technology to commercial plants at initial volumes of up to 300 tons/day. Meanwhile, MOR is also working with a number of customers, design-build firms and financing institutions to install their fractionation technology (which can be coupled with the CO₂ oil extraction technology) in corn-based ethanol plants around the country.

9. Zein Extraction

Various processes have been developed to extract zein protein from corn and corn by-products (e.g., DDGS). Zein is a high-value protein which can be used in a wide range of applications. Zein is not used extensively in human food products, despite being edible, due to its negative nitrogen balance and poor water solubility. However, this insolubility is what makes zein and its resins form tough, glossy, hydrophobic grease proof coatings that are resistant to microorganisms, heat and humidity. Zein applications include: specialty coatings for pharmaceutical tablets, candies, nuts, and paper products; chewing gum; adhesives and binders; inks; cosmetics; fibers and textiles; resins and biodegradable plastics and high-value biomedical applications.

Currently, zein can be extracted from corn gluten meal, a by-product of the wet milling process. However, current extraction and purification technologies are such that the price of zein limits current market applications. Zein is currently a high value product. According to various sources, purified zein prices range from \$4.54-\$32 per lb, depending on the level of purification and quality. With a cited yield of 0.8 lbs of zein per bushel of corn, zein revenues could potentially exceed that of ethanol if implemented into a corn-to-ethanol facility. However, the big question is cost. While a December 2008 article in *Ethanol Producer Magazine* stated that there is currently no cost-effective way to recover and purify zein protein, there are several companies and research institutions currently working to develop technologies to bring these

extraction and purification costs down, including the University of Nebraska, Lincoln; Purdue University; University of Illinois; Iowa State University; Prairie Gold; USDA, Agricultural Research Service (ARS); Global Protein Products, Zea Fuels and Bio Process Innovations.

B. Second Generation Biofuels

The demand for cellulosic ethanol is in part supported by the Renewable Fuel Standard established by the Energy Independence and Security Act of 2007, which contained a 21 billion gallon mandate for advanced biofuels by 2022, including 16 billion gallons of cellulosic biofuel. Some cellulosic biofuel companies are focused on feedstocks other than corn which offer greater environmental benefits and less impact on prices of major agricultural commodities; yet, corn biomass (e.g., corn stover, corn cobs, and corn fiber) will likely have a place in the mix of future feedstocks. Given the volume of ethanol that can be produced from corn starch and the interest in corn biomass as a cellulosic feedstock, this emerging technology has the potential to have a large demand impact on the corn industry.

Butanol is another second generation biofuel that is currently being developed which could potentially be used as an ethanol replacement, an ethanol substitute, or in the manufacture of traditional petrochemically based fuels, such as gasoline, diesel, and jet fuel.

1. Butanol

Butanol is a 4 carbon alcohol currently produced via petrochemical feedstocks and used primarily as an industrial solvent. In 2007, the worldwide butanol market was estimated at about 350 mmgy, with the U.S. accounting for 220 mmgy (*Ethanol Today*, March 2007). Yet, if cost competitive, butanol could also be produced via fermentation of sugars (including sugars derived from corn starch) and could function as an alternative renewable fuel, expanding the market to several billion gallons. Butanol has several key advantages over ethanol, including its higher energy content, its ability to be transported via pipeline, its lower Reid vapor pressure which makes it safer to use and means that it generates fewer volatile organic compound emissions, and higher allowable blend levels with gasoline.

While there are several different butanol production processes being developed, essentially the process is very similar to the ethanol production process, as any ethanol facility can be retrofitted to produce biobutanol, and cellulosic ethanol technology developments currently underway can also be applied to butanol production. Rather than using the ethanol producing yeast, a butanol producing microorganism is used to ferment the sugars from corn (or any sugar feed source, including cellulosic biomass) to produce butanol. However, more recent challenges facing developers have been largely in the area of reducing distillation costs and

there will likely have to be alterations made to an ethanol facility's distillation process in order to produce butanol. There have been many advancements made to the biobutanol production process over the last several decades and many of the challenges previously preventing biobutanol production from being economically viable have largely been resolved. The technology appears to be currently cost competitive with petrochemical based butanol (said to be economical at \$60/bbl crude oil) and also competitive or nearly competitive with ethanol.

There are many companies and research institutions working on the development of commercial biobutanol production, including BP and DuPont. Of those companies currently pursuing its development, the earliest stated year for expected commercial biobutanol production is 2010, but many do not expect to see commercial scale production until 2011/2012.

2. Cellulosic Ethanol – Biochemical Platform (Pretreatment, Hydrolysis, and Fermentation)

There are two main technology pathways currently being developed for the production of cellulosic ethanol from lignocellulosic feedstocks: biochemical and thermochemical. There have been significant investments made in the development of both of these production routes, and commercial scale facilities have been proposed and are beginning to be built

Over the past few years, there has been significant research and development efforts given toward improving the high production cost areas of biochemical cellulosic ethanol production: pretreatment⁷, hydrolysis, and fermentation⁸. There are essentially three key challenges involved in these processing steps. The first is the development of cost efficient pretreatments, which are necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis. Once the sugars are hydrolyzed, broken down into 5-carbon and 6-carbon sugars, they can then be fermented using biological agents (e.g., microorganisms, yeast) to produce ethanol. However, it is far more difficult, and thus more costly, to hydrolyze cellulosic biomass than it is to hydrolyze the starch from the traditional corn-to-ethanol process, and that while hemicellulose is relatively easy to hydrolyze compared to cellulose (fractions of the lignocellulosic biomass⁹), it is more difficult to ferment. Therein lies challenges two and three: hydrolyzing the cellulose and fermenting the xylose sugars released from the hemicellulose.

⁷ The pretreatment of biomass is currently one of the single largest cost components in the overall cellulosic ethanol production process via the biochemical platform, accounting for 19% of the overall cost, second only to raw material costs (NREL, May 2007 presentation).

⁸ Distillation costs are another large cost component to the overall process, and distillation and dehydration technology developments being made for the traditional corn-to-ethanol process will also apply to cellulosic ethanol processes. See section III.A.4 "Ethanol Distillation" for more details.

⁹ Corn stover is composed of approximately 36.0% cellulose, 23.4% hemicellulose, and 18.6% lignin (Dien et al., 2006).

There are numerous companies and research institutions developing their own approaches and unique technologies to improve upon current pretreatment, hydrolysis and fermentation processes. However, the bottom line is that a cost efficient process has yet to be commercialized. There are several companies that are expecting to reach commercialization by 2011/2012. Yet, the tight capital market is inhibiting many from obtaining the capital needed to go forth with their commercialization efforts.

3. Cellulosic Ethanol – Thermochemical Platform

Pyrolysis/gasification technologies are used to produce pyrolysis oil/syngas, from which a wide range of long carbon chain biofuels and chemicals can be reformed. In contrast to the biochemical platform, the thermochemical platform is largely based on existing technologies used within the petroleum industry and there appears to be fewer technical hurdles. Although, being a more mature technology, there may also be fewer opportunities for cost reductions.

Gasification is the process of heating biomass by partial oxidation or in the presence of steam to produce a mixture of carbon monoxide and hydrogen called synthesis gas or syngas. The syngas is then cleaned before being passed through the Fischer-Tropsch process to create fuels or chemicals. Research and development efforts are focusing on perfecting the gasification of biomass so that it is more reliable and cost efficient. One of the major technical challenges is that much of the syngas produced from biomass tends to be more heterogeneous than petroleum-based syngas, leading to variations in product quality. Also, the number of inhibitory substances vary by biomass feedstock and gasifier design. This variation in syngas composition creates problems for the Fischer-Tropsch process, including low product selectivity and unavoidable co-products, as well as contaminants which can inhibit the catalytic reaction. Additionally, the large quantity of biomass required to reach a scale where the process is economical remains a concern. Larger scale requires feedstocks to be brought in from greater distances, which erodes economic competitiveness.

Pyrolysis is the process of heating biomass in the absence of added oxygen to decompose the biomass and produce a liquid called pyrolysis oil. This oil is generally quite unstable to viscosity changes and oxidation, which makes its use as a chemical or a fuel problematic. Therefore, it must first be pre-treated and stabilized prior to its incorporation into petroleum refinery processes. Research efforts focus on preconditioning the oil before stabilization, catalyst and process developments to stabilize the pyrolysis oil, and validation of the compatibility of the stabilized oil with current petroleum conversion catalysts and processes.

Both gasification and pyrolysis could be incorporated into a thermochemical biorefinery or a biochemical biorefinery. There are several companies currently

pursuing the commercial development of cellulosic ethanol via the thermochemical platform; however, commercial viability is yet to be proven.

C. Value-Added Chemicals

There are many chemicals that can be produced from corn and other sugar sources. These chemicals can then be used in the production of a wide array of biobased products. In general, the biobased product industry is growing as more and more consumers are showing preference for non-petroleum based products and as the general product markets grow, driven by the steadily increasing world population and rising income levels. Additionally, programs such as LEED¹⁰ and USDA BioPreferred¹¹ also help stimulate biobased product demand.

However, in order for a biobased chemical to gain any significant share of the petroleum based chemical market, it must also be cost competitive with similarly functioning petroleum based chemicals. There are currently significant research and development efforts underway to find biobased production routes that are economically competitive with traditional petrochemicals.

In 2004, a U.S. Department of Energy (DOE) report identified 12 of the top value added chemicals that can be produced from sugars and synthesis gas, beginning from a list of more than 300 candidates. These 12 were identified by examining the potential markets of the chemicals and their derivatives, as well as the technical complexity of their synthesis pathways. The value added chemicals presented in this top 20 list were in part identified based on further analysis of these top 12 chemicals. However, other chemicals were also included based on information gathered from desk research and interviews with industry experts, as it related to the previously established evaluation criteria.

1. 3-Hydroxypropionic Acid

3-Hydroxypropionic acid (3-HPA) is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, plastics and moldings, fibers and resins, composites, adhesives, coatings, aliphatic polyesters and copolyesters, and disinfectants. One of the most promising aspects of this building block chemical is not only the current petrochemical products which it could potentially replace, but also the new and unique chemical properties it would bring to the market. Given its

¹⁰ LEED (Leadership in Energy and Environmental Design) is third-party certification program for the design, construction and operation of high performance green buildings. Qualifying for LEED credits can qualify a company for tax rebates, zoning allowances and other financial incentives.

¹¹ USDA's BioPreferred program includes a preferred procurement program for Federal agencies and their contractors, and a voluntary labeling program for the broad scale consumer marketing of biobased products.

potential, it was identified by the U.S. DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

There is currently no commercially viable production route for 3-HPA using petrochemical feedstocks. However, many of the derivative chemicals that can be produced from 3-HPA are commercially produced from fossil fuel feedstocks. Cargill, along with Codexis and the Pacific Northwest National Laboratory (PNNL), have already developed a bioprocess to produce 3-HPA which converts glucose or other carbohydrate sources into 3-HPA using a multi-step enzymatic reaction within the cells of a microorganism. 3-HPA can then be converted into a variety of high-value chemicals, including acrylic acid, 1,3-propanediol, malonic acid, and acrylamide. In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HPA, supported by a \$1.5 million matching cooperative agreement from the DOE. At the time of the announcement, the companies said that they expected their technology to produce 3-HPA and its derivatives, such as acrylic acid, to be ready in 5 years. According to a 2005 DOE presentation, acrylic acid production via this biochemical route could result in an advantage of more than 5 ¢/lb over propylene oxidation for a Midwest plant (West Texas Intermediate crude oil 2005 average = \$56.5/bbl).

However, through personal communication, Cargill has revealed that they no longer plan to pursue the development of 3-HPA, as they do not feel that they have the expertise required to “bring profitability in a reasonable time.” This would indicate that this product/technology is more likely a long-term prospect.

2. Itaconic Acid

Itaconic acid is a building block chemical that can be produced by sugar fermentation and used to derive many other high-value chemicals. Itaconic acid derivatives include 3- & 4-Methyl- γ -Butyrolactone, 3-Methyl Tetrahydrofuran, and 2-Methyl-1,4-Butanediol, among others. These derivatives yield new properties for the butanediol (BDO), γ -butyrolactone (GBL), and tetrahydrofuran (THF) family of polymers. Applications of itaconic acid include paper coatings, carpet backings, medicines, cosmetics, lubricants, herbicides, solvents, acrylic fibers and rubbers, reinforced glass fiber, artificial diamonds and lenses, and as a potential component of P-series fuels¹². Itaconic acid was also identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

The base technology for the fermentation of itaconic acid is commercialized, but research efforts on efficient, low cost methods for the production of itaconic acid and its derivatives are ongoing. According to a 2001 study, the itaconic acid market was 15,000 tons/year and the selling price was \$4/kg. According to a Netherlands company, TNO Quality of Life, the production potential of itaconic acid has been

¹² According to the DOE a “P-Series fuel is a blend of natural gas liquids (pentanes plus), ethanol, and the biomass-derived co-solvent methyltetrahydrofuran

inhibited by the fact that the genes involved in the biosynthesis of itaconic acid have not been well-known. However, the company claims to have identified three genes crucial to the microbial production of itaconic acid. Additionally, in a USDA, ARS project aimed at finding new microbial processes for using glycerol and the effect of various reaction parameters to produce new compounds, a new fungal strain was incidentally found that can use glucose or maltose sugars (but not glycerol) to produce itaconic acid. This process has since been patented.

3. Levulinic Acid

Levulinic acid is another building block chemical from which many other high-value chemicals can be derived, and was also identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas. Potential applications from levulinic acid and its derivative chemicals include, but are not limited to, food/beverage acidulants, synthetic rubbers and plastics, pharmaceuticals, solvents, coatings, herbicides and pesticides. In addition to being a building block chemical for many other high-value chemicals, levulinate esters (85%) mixed with other alcohols (e.g., ethanol, methanol, butanol) produce a desirable fuel product. Levulinate esters produce a clean burning fuel (burns cleaner than pure hydrocarbon products) that can be transported via pipeline, has a low cloud point in diesel blends (lower than biodiesel), has a higher fuel efficiency than ethanol, reduces soot, and exceeds ASTM D-975 standards.

Maine BioProducts' Biofine process is a thermochemical process using acid hydrolysis to produce levulinic acid and other co-products (e.g., furfural, formic acid, and char) from cellulose. The company intends to focus on the fuel market, stating that the high value, low volume chemicals do not yield the profit needed to justify the construction of a full sized plant. For this reason, the strategy of Maine BioProducts is to co-locate their Biofine process along with existing/future bio-alcohol supplies (e.g. ethanol, cellulosic ethanol, butanol). The company claims that even with co-location, the initial investment will be in excess of \$120 million.

Processes are still being developed to produce derivatives from levulinic acid, and some of these processes are further along than others. The PNNL and NREL have developed and patented a process ready for licensing to produce methyl tetrahydrofuran (ME-THF) from levulinic acid. ME-THF is a potential component of P-series fuels¹² and has been demonstrated to be a useful replacement for the solvent tetrahydrofuran. They are also developing, although at a less advanced stage, a process to produce delta-amino levulinic acid, an active chemical in a new group of herbicides and pesticides.

4. Lignin - Aromatics

Lignin accounts for 18.6% of corn stover biomass (Dien et al., 2006), and currently, the proposed value of lignin in a cellulosic biorefinery is largely limited to its value as a boiler fuel to supply power for the plant. However, conceptual and early stage research is exploring cost efficient methods to produce high-value chemicals from lignin, which would help increase the overall revenues of the cellulosic biorefinery. According to the PNNL, "lignin is the only renewable source of an important and high-volume class of compounds - the aromatics." U.S. demand for three of the largest aromatics; BTX (benzene, toluene, and xylene), phenol, and terephthalic acid, is approximately 27.9 million metric tons per year. This class of chemicals can be found in a wide range of consumer products, including pharmaceuticals, synthetic rubbers, upholstery, clothing, plastics, various car parts (e.g., body, bumpers, lighting, dashboard, seats, upholstery, fuel systems, under-the-bonnet components) and CDs/DVDs. Yet, despite its demand potential, this long-term technology has some significant technical barriers it must first overcome and is not likely to be commercialized within the next 5 years.

5. Polylactic Acid

Polylactic Acid (PLA) is a thermoplastic derived from lactic acid, a fermentation product produced from biomass sugars. PLA is currently commercially produced from corn feedstocks at Cargill's 140,000 MT/yr facility in Blair, Nebraska. However, full market penetration has not been reached and Cargill projects a possible market of 3.6 million metric tons by 2020. Yet, they are not the only ones that are optimistic. A recent (August 2008) study by the Freedonia Group estimated that PLA demand will expand by nearly 20% between 2008-2012.

Cargill markets their PLA as Ingeo™ through the company NatureWorks. Ingeo biopolymers and biofibers have many market applications, including packaging (e.g., high-value films, rigid thermoformed food and beverage containers, and coated papers and boards), apparel, carpet, furnishings (e.g., drapery, panel and wall covering, and bedding), non-wovens (e.g., diapers, baby and facial wipes and feminine products), and industrial textiles (e.g., geotextiles, agrotexiles and specialist filtration media).

Cargill claims that their PLA production technology is cost competitive with conventional polymers, and that the PLA produced has many performance properties equal to or greater than conventional polymers such as polyethylene terephthalate (PET) and nylon. Additionally, PLA is biodegradable. Since its commercial launch in 2002, the company has made improvements to its process that have further reduced CO₂ emissions and reduced process energy requirements. According to the Institute for Energy and Environmental Research in Heidelberg, Germany, the new Ingeo resin emits 77 percent less CO₂ than PET. The company

is also looking to develop fermentation organisms to convert 5-carbon sugars as well as glucose into PLA.

6. 1,3-Propanediol

1,3-propanediol (PDO) is a commercially produced building block chemical commonly used in the production of polymers. DuPont Tate&Lyle BioProducts is the primary producer of this bio-chemical, producing Zemea™ propanediol and Susterra™ propanediol from corn glucose. Their Bio-PDO plant is located in Loudon, TN, and has an annual production capacity of 100 million pounds. However, the market potential for Bio-PDO is estimated to be quite a bit higher. Currently, PDO is primarily produced from chemical feedstocks (e.g., ethylene oxide or propylene) and is a chemical precursor to polytrimethylene terephthalate (PTT). PTT is a replacement chemical for PET and nylon, two common polymers used to make a wide range of consumer products, with several enhanced properties.

According to DuPont Tate&Lyle's website, "Susterra™ propanediol provides low toxicity and biodegradability to applications such as deicing fluids, anti-freeze and heat transfer fluids. In deicing applications, it significantly reduces energy use and emissions over other propylene glycol formulations. Susterra™ propanediol is also a key ingredient for DuPont™ Sorona® polymer and DuPont™ Cerenol™ polyols." Sorona® is a polymer used in apparel, built-in stain protection carpet, and thermoplastic elastomers used in an array of functional applications for the automotive industry. Cerenol™ is used in a variety of market applications, including personal care products, functional fluids, and specialty polymers. Examples of applications for Zemea™ propanediol include cosmetics and personal care products, as well as liquid detergents.

DuPont Tate&Lyle also claim that their Bio-PDO process consumes 40% less energy and reduces greenhouse gas emissions by 20% compared to petroleum based PDO.

7. Sorbitol / Isosorbide

Producing sorbitol from corn syrup is a well established industry, and at times the industry has been characterized as having excess capacity. In 2006, the production of sorbitol was dominated by four companies, producing approximately 1.2 billion pounds per year (CRADA 223 Report). Major sorbitol players include Roquette, ADM, Cerestar/Cargill, and SPI Polyol. Yet, while the production of sorbitol is well established, new production technologies are emerging to produce new chemical derivatives from sorbitol, such as isosorbide. Isosorbide is a new biochemical intermediate which can be used to produce new polymers, solvents, and plasticizers with unique properties. When isosorbide is added to PET, it makes the co-polymer stronger and more rigid. This would allow manufacturers to use less material to

manufacture their products while maintaining product strength and durability. Another unique property that isosorbide can add to the traditional PET market is increased heat tolerance, making it uniquely positioned for use in hot-fill container applications.

Several companies and research institutions, including Roquette (the world's leading producer of sorbitol) and a consortium comprising of PNNL, the Iowa Corn Promotions Board, the New Jersey Institute of Technology, and General Electric Global Research, have been developing cost effective ways to produce isosorbide from sorbitol. In June of 2008, Roquette launched their 100 MT/yr demonstration plant for the production of isosorbide diesters (POLYSORB ID®) in Lestrem, France.

Additionally, PNNL is trying to develop a more environmentally benign sorbitol production process that would not use mineral acid catalysts, which create separation and waste disposal issues. On another front, PNNL is working to develop a cost efficient production process to produce propylene glycol from sorbitol. Propylene glycol is a commonly used chemical with a wide range of product applications. Yet, it can also be derived from glycerin, a relatively low value by-product of biodiesel production.

8. Succinic Acid

Succinic acid is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics. In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO₂, leading to what some claim to be as a carbon negative process. Its potential has been recognized by many countries and was identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas. Furthermore, this chemical can be used to produce other top 12 chemicals.

While succinic acid is currently commercially produced via petrochemical production routes in small quantities (15,000 MT/yr – 50,000 MT/yr), commercially viable biobased production routes are currently being pursued by numerous companies and research institutions. The three leading companies/partnerships currently pursuing the commercialization of succinic acid are Bioamber (DNP Green Technology and Agro Industrie Recherches et Développments), Roquette and DSM, and BioEnergy International (now Myriant Technologies).

Biobased succinic acid is produced by converting the glucose and/or five carbon sugars from a variety of possible feedstocks, including corn, using a specific succinic acid fermenting microorganism and CO₂. If a technology is developed and proven at commercial scale to produce biobased succinic acid that is cost competitive with similarly functioning petrochemicals, the potential world market for this four carbon

dicarboxylic acid is in excess of \$1 billion per year. And, by one account, Bioamber expects to see commercial biobased succinic acid production being reached in 2011/2012.

IV. Top 8 Corn Products/Technologies

Upon further analysis, the top 20 list was refined down to the top 8 considered to have the greatest potential to add significant value to Minnesota's corn commodity production. This analysis was based on information gathered from more in-depth desk research and interviews with general experts within the field of biobased product and technologies and with product/technology specific representatives.

This section reviews the top 8 products and technologies, which are listed in Table 8, in more detail than was presented in the previous section.

Table 8: Top 8 Corn Products and Technologies

Product/Technology Name	Product/Technology Timeframe
Anaerobic Digestion	Medium
Butanol	Medium
Cellulosic Ethanol - Biochemical Platform	Medium-Long
Ethanol Distillation	Medium
Front-End Fractionation	Short
3-Hydroxypropionic Acid	Long
Succinic Acid	Medium
Zein Extraction	Medium

Short term: 0-3 years

Medium term: 3-5 years

Long term: > 5 years

A. Anaerobic Digestion

1. Product/Technology Overview

Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-80%), CO₂ (20-50%), and trace amounts of H₂, NH₃, and H₂S, which can be burned for energy as a substitute for natural gas. This process reduces energy costs and greenhouse gas emissions and helps to conserve water relative to traditional corn-to-ethanol production. Furthermore, if collected, the struvite, a sludge that builds up in the digester, could be sold as a valuable fertilizer or a livestock feed additive, as it is composed of magnesium, phosphate, and ammonia. Additionally, if the final rulemaking for the Renewable Fuel Standard established under the Energy Independence and Security Act of 2007 (only the proposed rulemaking has been issued as of the writing of this report) continues to conclude that the greenhouse gas savings from ethanol relative to gasoline is less than the 20% threshold that the Act requires for new facilities, anaerobic digestion will provide a mechanism for an ethanol facility to reduce the greenhouse gas “score” associated with its ethanol output. However, these benefits

should be weighed against a possible reduction in revenues from the co-product sales of distillers grains, depending on whether whole or thin stillage is utilized.

There are essentially three ways in which an ethanol plant can turn their distillers grains into fuel: direct burning, gasification, or anaerobic digestion. Direct burning of the distillers grains is the simplest of these three options, but in this case, the ethanol facility sacrifices the value of the distillers grains and net energy benefits are weakened by the fact that energy is used in the process. The second, gasification, is a rather promising technology receiving a lot of recent attention; however, this technology is the least developed of the three. The third, anaerobic digestion, can use either thin or whole stillage to generate energy, requires relatively little energy to operate, and the base technology is ready now (i.e., it is already used in other industries).

Anaerobic digestion is considered an “off-the-shelf” technology because it has been around for awhile. It is currently used in many food and ag-processing industries, such as the brewery industry and for municipal wastewater treatment. However, currently, it is not widely used by the ethanol industry at any significant scale.

Anaerobic digestion refers to a decomposition process that occurs regularly in nature and that can be recreated using “digesters” or airtight tanks/ponds, where a variety of microorganisms are utilized to turn the organic material into biogas. One set of microorganisms converts the organic material to a form that another set of microorganisms can utilize in order to form organic acids that can then be utilized to produce biogas using anaerobic bacteria in an environment absent of oxygen. For every percent of methane in the resulting biogas, 10 BTUs of heat energy can be produced when the biogas is burned. One of the key factors that impacts productivity rates is temperature. While anaerobic bacteria can endure temperatures below freezing to above 135°F, they thrive best under mesophilic (98°F) and thermophilic (130°F) conditions, preferring the thermophilic range. However, processes operated in the mesophilic range are less sensitive to changes in feed materials or temperatures. Yet, due to longer decomposition time requirements, these processes also require larger digesters.

According to an August 2008 article in *Technology Review*, University of Minnesota research fellow Douglas Tiffany says that the challenge with anaerobic digesters is the expertise required to maintain a stable bacterial community at high temperatures and avoid system crashes. Additionally, capital cost requirements are not insignificant. Yet, despite its drawbacks, its potential has spurred the interest of several large companies and research universities, and research and development efforts to improve the anaerobic digestion process of corn ethanol thin and whole stillage are ongoing.

2. Market Potential

It is estimated that anaerobic digestion using thin stillage can reduce the energy needs of an ethanol facility by 43-66%, and if using whole stillage, energy needs could be entirely met by the biogas.

According to a study conducted by Rein and Associates, funded by AURI, anaerobic digestion could add as much as \$10 million to the bottom line of a 50 mmgy ethanol plant (2008). The study reported that if whole stillage is used, the digester could generate enough biogas to replace all the plant's natural gas needs, but that using thin stillage may be more attractive to ethanol producers because it allows for the maintained production of distillers grains (minus the solubles). According to the study, if using thin stillage, a 50 mmgy ethanol plant could produce enough biogas to displace approximately 2/3 of the plant's natural gas needs. The economics of this trade-off between using thin and whole stillage will depend on the value of distillers grains versus the cost of natural gas.

Dr. Largus Angenent and his team at Washington University¹³ have developed an anaerobic digestion system, and he estimates that if the production rates were scaled up to industrial levels, the process could reduce the power needs of an ethanol plant by 50%.

In a February 2008 article published in the journal *Water Environment Research*, the results of a study evaluating anaerobic digestion of corn ethanol thin stillage at thermophilic temperatures in stirred tank reactors were published. The results indicated that anaerobic digestion could reduce an ethanol facility's natural gas consumption by 43-59%.

According to Otter Tail Ag Enterprises' CEO Kelly Longin, the up-front costs of the technology would be at least \$20 million for their 55 mmgy dry-mill ethanol facility (2008 AURI article).

3. Profiles - Companies & Research Institutions

- ♦ **POET** - POET recently began using an anaerobic digester at its cellulosic ethanol pilot plant in Scotland, SD, which uses corn cobs as its primary feedstock, producing approximately 20,000 gallons per year. The anaerobic digester is being used to power the cellulosic plant and offset natural gas usage at its attached grain ethanol plant. The intention is that once this process has been refined, it will be installed in their 25 mmgy cellulosic ethanol demonstration facility (Project LIBERTY) at Emmetsburg, IA, which is on schedule to begin production in 2011 (6/17/09, Poet press release).

¹³ Dr. Angenent has recently become an assistant professor of Biological and Environmental Engineering at Cornell University.

- ♦ **BioGasol** - Denmark based BioGasol is a cellulosic ethanol developer that is incorporating the use of an anaerobic digester. According to a March 2009 article in *Ethanol Producer Magazine*, BioGasol has received \$13.4 million from the Danish Energy Agency's Energy Technology Development and Demonstration Program to fund the \$45 million project of building a 1.3 mmgy cellulosic ethanol demonstration facility in Aakirkeby, Denmark. Additionally, in the U.S., the company is collaborating with Pacific Ethanol and the Joint BioEnergy Institute to build a demonstration scale plant in Boardman, OR, for which it received \$24 million from the DOE in January of 2008. According to this March 2009 article, the company intends to have this U.S. plant completed by the fourth quarter of 2009.
- ♦ **Washington University** - Dr. Largus Angenent and his team at Washington University have developed an anaerobic digestion technology that uses bacteria and cobalt to break down the thin stillage. Their research found that adding cobalt increased process yields. Dr. Angenent estimates that if the production rates were scaled up to industrial levels, the process could reduce the power needs of an ethanol plant by 50%.
- ♦ **Richard Kohn** - A patent application is currently filed for the "Process for rapid anaerobic digestion of biomass using microbes and the production of biofuels therefrom", with Richard Allen Kohn listed as the inventor. According to the patent application, it is claimed that this process is at least twice as fast as conventional anaerobic digestion processes.
- ♦ **Eisenmann AG**. – Eisenmann AG has a patent-pending anaerobic digestion process called EtOH-TS that can produce biogas and a clean effluent that can be recycled back into the fermentation process from thin stillage. According to a June 2009 article in *Biomass Magazine*, the process can produce as much as 24 million BTU/hr of biogas in a 50 mmgy ethanol facility producing 80 gal/min. Eisenmann has developed a specialized ammonia adapted microorganism to be used in an anaerobic digester so that ammonia, a product ethanol producers already have on hand, can be used as a pH neutralizer. The ammonia can then be recycled and reused to provide nutrition for the yeast during fermentation.
- ♦ **Kawartha Ethanol** – Canadian ethanol producer Kawartha Ethanol has announced plans to install an anaerobic digester in their recently completed 21 mmgy ethanol facility in Ontario, Canada.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to anaerobic digestion technology development for the Minnesota corn industry.

Table 9: SWOT – Anaerobic Digestion

<u>Strengths</u> ▪ Large market potential - o Size of ethanol industry - o Strong potential impact on ethanol margins ▪ Well established technology ▪ Moderate institutional support ▪ Can reduce the energy needs of an ethanol facility by 43-66% ▪ Reduces greenhouse gas emissions ▪ Under the RFS, as amended in 2007, this technology would help new or expanding ethanol facilities meet greenhouse gas reduction requirements.	<u>Weaknesses</u> ▪ High capital costs ▪ Well established technology leaves marginal room for process improvement. ▪ Potential reduction in distillers grains revenues ▪ Cost advantage is reliant on natural gas prices. ▪ Not yet proven at commercial scale - currently being tested in several commercial and demonstration scale facilities. ▪ Expertise is required to maintain a stable bacterial community at high temperatures and avoid system crashes.
<u>Opportunities</u> ▪ High energy prices ▪ A cap and trade system would further improve process economics relative to the traditional ethanol facility. ▪ Technology offers a potential advantage for existing ethanol producers – helps keep already existing infrastructure investments profitable. ▪ Could help ethanol utilization in California relative to other traditional Midwestern ethanol plants once the Low Carbon Fuel Standard goes into effect in 2011. ▪ Could help provide an alternative use of distillers grains, particularly as distillers grains markets become saturated. ▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this will facilitate an increase in ethanol production.	<u>Threats</u> ▪ Low energy prices ▪ High distillers grains prices ▪ Tight capital markets ▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall”

B. Butanol

1. Product/Technology Overview

Butanol is a 4 carbon alcohol. Other chemical compounds in the alcohol family include methanol (1 carbon), ethanol (2 carbon), and propanol (3 carbon). It is currently produced mainly via petrochemical feedstocks and is used primarily as an industrial solvent. Yet, if proven commercially cost competitive, butanol could also be produced via sugar fermentation and could function as an alternative renewable fuel. Table 10 lists the derivative chemicals that can be produced from butanol, their applications, and the institutions/companies involved in its development.

Table 10: Butanol – Derivatives, Applications, and Institutions/Companies Involved

Derivatives ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/Companies Involved ¹
- Butyl Acrylate - Methacrylate - Glycol Ethers - Butyl Acetate	- -Fuel - Solvents - Coatings - paint, varnish, and inks - Agricultural chemicals insecticides and herbicides - Synthetic resins and adhesives - Textiles (e.g., scatter rugs, bathmats) - Sealants	- BP and DuPont - ButylFuel LLC - TetraVita BioScience - Gevo - Cobalt Biofuels - Green Biologics - Syntec - METabolic Explorer - University of Illinois - University of California - Caltech - Ohio State University Research Foundation - Joint BioEnergy Institute - USDA, ARS

Source: Informa Economics

1/ Not an exhaustive list

While butanol has traditionally been produced via petrochemical routes, the technology to produce biobutanol from non-petrochemical feedstocks such as corn has been around for several decades. It has just not been cost competitive. The most common process for producing biobutanol in the past has been acetone-butanol-ethanol (ABE) fermentation, using *Clostridium acetobutylicum* as the fermenting bacterium. This process was common during World War II, but was phased out as petrochemical routes became more economical. Then, as the interest in renewable fuel production gained momentum, biobutanol once again entered into the discussion. Yet, despite its many benefits over ethanol, which include a higher energy content and the ability to transport it in existing pipelines, low yield and low concentrations prevented it from being economically competitive, and the ethanol market took off.

“Traditional” ABE fermentation yielded butanol, acetone, and ethanol at a ratio of 6:3:1. One bushel of corn would produce 1.3 gallons of butanol, 0.7 gallons of acetone and 0.13 gallons of ethanol. This 1.3 gallons per bushel was much lower than the ethanol production process that then produced 2.5 gallons per bushel. According to David Ramey of ButylFuel, other limitations of the “traditional” ABE fermentation process include:

- ♦ Toxicity - At alcohol concentrations of 1-2%, the fermenting bacteria are killed.
- ♦ Low final concentration - 1-2%, relative to 10-15% for ethanol.
- ♦ A high boiling point of 117°C, and at the 1-2% final batch concentration, there is a lot of water to boil off.

However, over the past 20 years, research and development efforts have focused on improving various aspects of the ABE process. Molecular biology research has focused on developing various microbial strains with improved tolerance to butanol toxicity, which has resulted in significant yield increases. In 1990, the bacterium *Clostridium beijerinckii* was developed by Hans Blaschek from the University of Illinois, doubling butanol production over its parent strain, *Clostridium acetobutylicum*. Additionally, the development and application of in-situ gas stripping to remove the solvent from the fermenter, which minimizes product inhibition (the problem whereby the butanol becomes toxic to the fermenting agent), has enabled much higher feed concentrations. With this process, butanol, acetone, and ethanol production in a fed-batch mode reached a ratio of 65:35:1 (Argonne National Laboratory), a drastic improvement over the 6:3:1 ratio yielded via “traditional” ABE fermentation methods. A yield of 2.5 gallons of butanol and little to no acetone and ethanol per bushel of corn is now commonly reported.

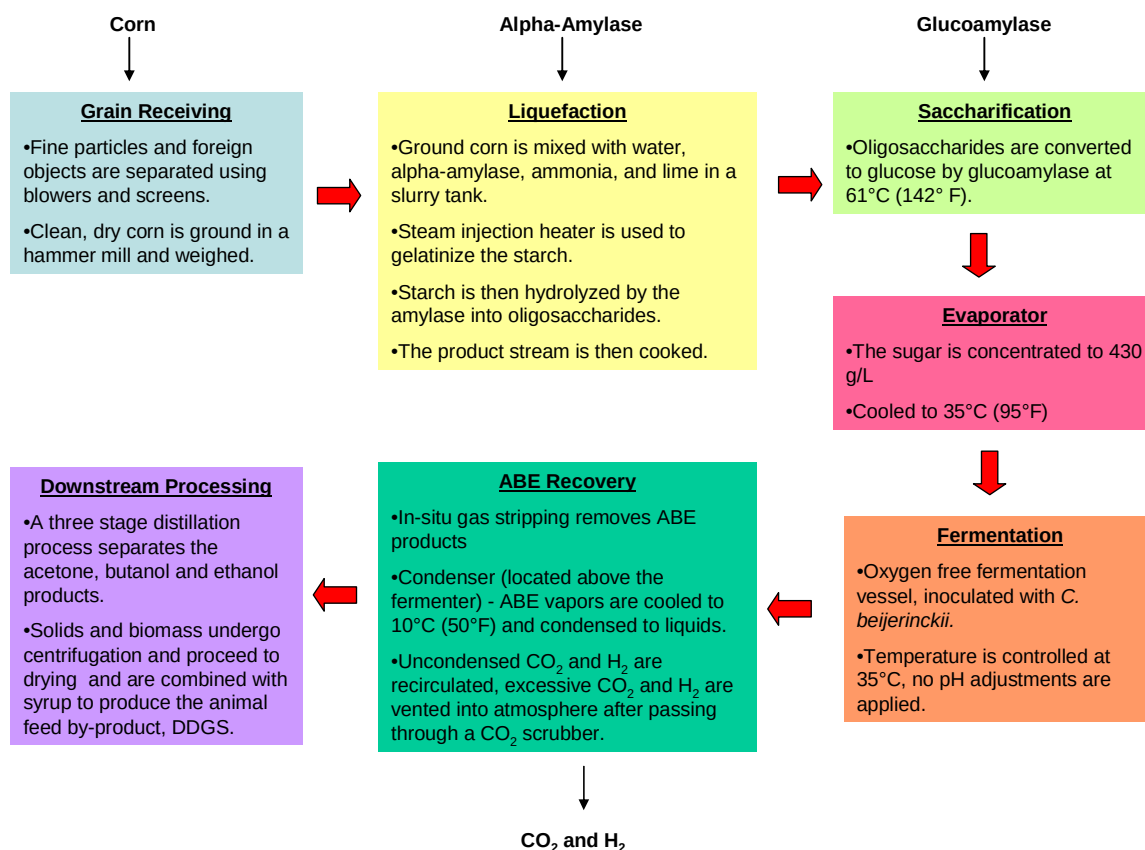
The following is a description of the ABE fermentation process developed by Qureshi and Blaschek (from 1999 and 2001 studies) and reported within the Argonne National Laboratory November 2007 report, “The Life-Cycle Assessment of Corn-Based Butanol as a Potential Transportation Fuel”. In this process, acetone, butanol and ethanol are produced from the bacterium *Clostridium beijerinckii*. The description and visual illustration (Figure 18) below serve as a basis for understanding the biobutanol production process. However, there are many variations on this theme and other production technologies are being developed by various companies and research institutions, many of which will be profiled in section IV.B.3, “Profiles - Companies & Research Institutions”.

“Corn is fed into a conventional corn dry mill for conversion to glucose through liquefaction and saccharification. The glucose is fermented to ABE through a fed-batch system. After fermentation, the ABE compounds are removed by means of in-situ gas stripping. ABE products are recovered through molecular sieve adsorption and a three-stage distillation that separates the acetone, butanol, and ethanol. Solids and biomass that are removed from grain processing and fermentation undergo centrifugation and proceed to drying,

along with syrup from distillation; DDGS generated from drying is used as animal feed."

(Argonne National Laboratories)

Figure 18: ABE Fermentation Process



Source: Argonne National Laboratory and Informa Economics

It was noted in the text of the Argonne National Laboratory report that condensing the sugars to 430g/L (refer to the evaporator step in Figure 18) is a concentration eight times higher than that required in ethanol production, and that while there are alternative technologies available, this step requires a large amount of heat and additional capital for the necessary equipment.

2. Market Potential

In 2007, the worldwide butanol market was estimated at about 350 mmgy, with the U.S. accounting for 220 mmgy (*Ethanol Today*, March 2007). According to a September 2008 presentation by Cobalt Biofuels, the worldwide chemical butanol market is estimated at \$864 million. By February 2009, the price of butanol had reached \$3.64-\$3.92 per gallon (ICIS).

If butanol were to become cost competitive in the fuel market, the market potential becomes much larger, likely several billion gallons. Butanol possesses many positive properties that make it worthy of consideration as a potential biofuel. Benefits include:

- ♦ High energy content – the energy content of butanol is 99,840 BTU per gallon – 86% of gasoline and 30% higher than ethanol. (Argonne National Laboratory, Nov. 2007)
- ♦ Low water solubility (not as hydroscopic as ethanol) – reduces corrosion in fuel tanks and pipelines, enabling butanol to be stored and transported via traditional petroleum infrastructure, as opposed to ethanol which cannot be transported through existing pipelines.
- ♦ Less evaporative than both gasoline and ethanol – it is safer to use and generates fewer volatile organic compound emissions.
 - Low Reid Vapor Pressure (RVP) - the RVP of butanol is 0.33 pounds per square inch (psi) versus ethanol's 2 psi and gasoline's 4.5 psi. This makes butanol 6 times less evaporative than ethanol and 13.5 times less than gasoline.
- ♦ Can be blended at higher concentrations.
 - Currently, biobutanol can be blended up to 10% by volume in European gasoline and 11.5% in U.S.
 - With the results of recent trials, there is potential to increase this to 15-16%.
 - Some studies have shown that butanol can even be used between 85-100% without the need for any engine modification. However, at this level, fuel mileage is compromised relative to gasoline.
- ♦ Can be produced from the same feedstocks as ethanol (e.g., corn, wheat, sugar beet and sugar cane).
- ♦ The production process is similar to ethanol, allowing for the possibility of retrofitting existing ethanol facilities.
- ♦ Can be upgraded to higher valued molecules for use in a wide array of industrial applications. This four carbon building block chemical can be used to make gasoline, diesel, or jet fuel using traditional refinery reactions.
- ♦ Can benefit from many of the same technologies as those being developed for cellulosic ethanol.
- ♦ Blending butanol with ethanol allows for higher ethanol usage.
- ♦ Relatively low carbon footprint – A 2007 study, "Life-Cycle Assessment of Corn-Based Butanol as a Potential Transportation Fuel", conducted by Argonne National Laboratory concluded that the production of corn-based butanol achieves energy benefits and reduces greenhouse gas emissions, but that the results varied depending on the method used to treat the co-product acetone¹⁴.

¹⁴ According to a February 2008 press release, BP and DuPont have commissioned a full environmental life cycle analysis of their proposed biobutanol process.

3. Profiles - Companies & Research Institutions

Many of the companies currently pursuing biobutanol production are planning on first marketing their product to the chemical solvent market and later into the fuel market. As biobutanol production grows, the current premium price will be reduced to commodity levels. While these industrial applications of butanol give new biobutanol market entrants a high-valued product outlet, its growth potential in this market is limited. In order for biobutanol to grow beyond the current market estimate of 350 mmgy, it must eventually be competitive in the fuel market.

The discussion thus far has focused on the general term butanol (or biobutanol if specifically noting that it was produced from non-petrochemical feedstocks), which typically refers to the straight chain butanol isomer, n-butanol. However, there are companies pursuing the development of other butanol isomers, which include sec-butanol, iso-butanol, and terc-butanol. According to Gevo, a company currently pursuing the development of isobutanol, the key production process difference between the various isomers is the fermenting agent itself. As a fuel, Gevo states that isobutanol has a higher octane level than n-butanol but is similar to n-butanol in other performance characteristics such as RVP and water solubility. Additionally, the company states that since you are starting out with a longer chain alcohol, it is “easier/simpler” to then derive higher valued fuel products that target jet and diesel fuel markets.

In general, it is assumed that unless otherwise stated, the companies/institutions profiled below are referring to the standard, straight chain isomer, n-butanol. However, many companies do not specify and could be using the generic term “butanol” to refer to any of the four isomers, as the terminology is not consistent within the industry.

BP and DuPont (also working with British Sugar)

- ♦ DuPont scientists have genetically modified *E.coli* to make butanol. The company is now looking to extend the technology to make the butanol isomers 2-butanol and 2-methylpropanol (isobutanol). These other butanol isomers differ from butanol in their chemical structures and they have somewhat different melting and boiling points. Nonetheless, they are all less hydroscopic than ethanol and more so than longer carbon chain alcohols.
- ♦ A \$400 million demonstration facility in the UK is expected to begin producing 5 mmgy in 2010. They are then expecting to have their first commercial plant operational by 2013.
- ♦ BP and DuPont have commissioned a full environmental life cycle analysis of their proposed biobutanol process, according to a February 2008 BP press release.
- ♦ Recently (July 2009), BP and DuPont announced the commencement of their butanol commercialization venture, Butamax Advanced Biofuels. Butamax, based out of Wilmington, Delaware, will complete the ongoing biobutanol research and development program and eventually expects to license the

technology to other biofuel producers as well as work with fuel blenders and distributors to bring biobutanol to the global fuel market.

ButylFuel LLC

- ♦ ButylFuel, LLC (formerly Environmental Energy Inc.) has developed a patented process which it claims makes butanol production more economically viable and competitive with current petrochemical processes and with the production of ethanol.
- ♦ Process improvements made under a federal Department of Energy Small Business Technology Transfer (DOE/STTR) grant include:
 - o A recovery process whereby the solvents are continuously removed. This essentially prevents alcohol accumulation to levels that are lethal to the fermenting microbe.
 - o A gravity driven process, whereby the costly recovery problem associated with the high boiling point is resolved.
 - o A continuous process which eliminates the need to clean up every 4-5 days and having to restart the fermentation, thus reducing associated costs.
- ♦ The process produces 2.5 gallons of butanol per bushel of corn with no acetone or ethanol. Also, it produces hydrogen as a by-product.
- ♦ Preliminary cost estimates suggest that their biobutanol production process produces butanol at costs much lower than that of petro-butanol and slightly less than ethanol.
 - o Cost estimates suggest that they can produce biobutanol at \$1.20 per gallon (not including a credit for the hydrogen), compared to \$1.28/gal for ethanol with gasoline at \$1.35/gal and corn at \$2.50/bu. Another way to view this is the energy that is produced per dollar - 105,000 BTU/\$ for butanol versus 84,000 BTU/\$ for ethanol.
 - o While these prices are somewhat dated given commodity market developments over the last few years, they may still be indicative of relative prices among commodities.
- ♦ ButylFuel is currently completing testing at their 50 gal/week pilot plant, and is working on designs of a 1,000 gal/week demonstration plant.
- ♦ ButylFuel expects commercialization to be reached in one year.
- ♦ According to an interview with a ButylFuel founder and technical director, David Ramey, their competitive advantage relative to their competition is that “we have a higher yield ~2x with about 42% more energy out with Bu100 (100% biobutanol) production, we are less expensive to produce and recover and we are continuous.” Additionally, the representative pointed out that some of its competitors will have “to overcome the stigma of genetically modified organisms such as e-coli...”
- ♦ In terms of current barriers/hurdles/threats to their commercialization process and to butanol in general, Ramey responded that the company had resolved all problems associated with the production and recovery of biobutanol, but that acceptance, governmental testing, and funding were current barriers.

TetraVitae BioScience

- ♦ TetraVitae BioScience has patented a mutant strain of *Clostridium beijerinckii*, developed by company co-founder Hans Blaschek from the University of Illinois that produces higher butanol yields. TetraVitae BioScience claims that their bacterium is more genetically stable, robust, and responsive to genetic modification and improvement, than previous strains.
- ♦ The process results in high final product concentration and reduced product inhibition.
- ♦ The company is currently enhancing strains, developing more efficient process engineering, and looking for the ability to use low-cost feedstocks.
- ♦ TetraVitae is currently working on scaling up their biobutanol production process. They are currently producing biobutanol in a 300 liter reactor.

University of Illinois, Hans Blaschek

- ♦ Recent research has focused on producing a second generation of the strain.
- ♦ Dr. Blaschek's work has funding from the Department of Energy, Illinois Corn Marketing Board, Illinois-Missouri Biotechnology Alliance, Council for Food and Agricultural Research, Mitsubishi Chemical and the USDA Value-Added Non-Foods program.
- ♦ According to Dr. Blaschek, distillation is one of the largest differences between ethanol and butanol production, as it is currently a very energy intensive process. However, Blaschek points out that there are a lot of people working on this issue and believes the issue can be solved within the next two years.
- ♦ Dr. Blaschek says that sensitivity analysis suggests that biobutanol will be economically competitive at crude oil prices around \$60/bbl.
- ♦ Dr. Blaschek believes that TetraVitae's biobutanol production process will be commercialized within the next two years.
- ♦ Current barriers to commercialization include scaling up the production process and all the "unique issues" that that entails.

Gevo

- ♦ Gevo has developed a process known as "Gevo's Integrated Fermentation Technology" (GIFT). GIFT enables the production of isobutanol and hydrocarbons from retrofitted ethanol plants. No acetone or ethanol is produced. They are planning to focus initially on isobutanol development and then later add on a hydrocarbon component and cellulosic, fractionation and biorefinery concepts.
- ♦ The company was founded in 2005 by Drs. Frances Arnold, Matthew Peters and Peter Meinhold of the California Institute of Technology.
- ♦ In December 2007, Gevo acquired an exclusive license for the method developed by Dr. James Liao at the University of California, Los Angeles (UCLA) for modifying the metabolic pathway of *E.coli* bacteria for the non-fermentative synthesis of higher alcohols.
 - o Liao was quoted in January of 2008 as saying, "We should be in the initial stages of commercial scale biobutanol production in two to three years."

- ♦ In May 2008, it closed a \$17 million third round of financing to add to the \$30 million it had already raised since January, 2007.
 - o Gevo is backed by venture capitalists Richard Branson (Virgin Green Fund), Vinod Khosla (Khosla Ventures), Burrill and Company, the Malaysian Life Sciences Capital Fund and Total.
- ♦ In November of 2008, Gevo entered into an exclusive partnership with the engineering and construction firm ICM to commercialize the technology.
- ♦ Gevo also has a joint agreement with Bye Energy to explore opportunities for the marketing and distribution of renewable aviation fuels to small and medium sized airports.
- ♦ Gevo claims that GIFT yields economic concentrations and a simple, inexpensive way to separate butanol from water, a current challenge to biobutanol production technology development.
- ♦ The isobutanol process unit would cost about \$30 million to retrofit an existing 100 mmgy ethanol facility. Then, to add on the hydrocarbon unit it would cost an additional \$18 million.
- ♦ Production costs are expected to be 50% of the cost of petrochemical based butanol production processes (assuming February 2009 oil prices).
- ♦ Gevo is now operating a 10,000 gal/yr pilot plant.
- ♦ The company expects to be operating at 1 mmgy by the end of August 2009 at ICM's St. Joseph, MO, biofuels research center, by retrofitting an existing ethanol facility.
- ♦ Gevo then expects to have its first commercial scale plant on-line, producing 20-50 mmgy of isobutanol and other hydrocarbons by 2011.

Caltech, Frances Arnold

- ♦ Frances Arnold, co-founder of Gevo and professor at Caltech, is currently working on developing cellulases (an array of enzymes) that can metabolize cellulose and create fuel in one step.

Cobalt Biofuels

- ♦ Cobalt Biofuels has made advances in microbial strain fermentation reaction management and separation technology.
 - o This fermentation reaction management technology allows their continuous fermentation process to operate at peak production rates for extended periods of time.
 - o They have patented a vapor compression distillation (VCD) fluid separation technology that removes alcohol from the fermentation vessel using 25-50% of the energy required by typical separation techniques. The water used by the VCD process is then recycled.
 - o The company is now developing and patenting a high-throughput process to identify the optimal microbe for any selected feedstock. They are also engineering a bioreactor where biomass enters the bioreactor, the bacteria processes this biomass, and butanol and water flow out.
- ♦ Cobalt had raised a total of \$38 million to accelerate the commercialization of their biobutanol production process as of September 2008. Investors include

Pinnacle Ventures LLC, Vantage Point Venture Partners, The Malaysian Life Sciences Capital Fund, @Ventures, LSP, and Harris and Harris.

- ♦ They expect to build a 35,000 gal/yr pilot plant in 2009, a 2.5 mmgy demonstration scale plant in 2010, and a commercial scale facility producing 25 mmgy in 2012.
- ♦ Pamela Contag, company founder and CEO, says, "Our models tell us it is a very low-cost process that can be competitive with anything on the market today" (October 2008).

Green Biologics / EKB Technology

- ♦ Green Biologics is based in Oxfordshire, UK, and is working with EKB Technology.
- ♦ The company has developed their own heat-tolerant thermophilic bacteria and thermostable enzymes for producing biobutanol from biomass.
- ♦ Their technology can be used to retrofit existing commercial scale ethanol facilities.
- ♦ Their process produces higher yields and is tolerant to butanol concentrations up to 4%.
- ♦ The goal is to achieve a two-to-three fold increase in butanol yield and a two-to-three fold decrease in cost.
- ♦ In 2008, they installed a 300 liter/yr lab scale operation at their Milton Park headquarters.
- ♦ The company is currently working with existing biobutanol producers to incorporate their technology into existing facilities. They have signed a letter of intent for a strategic partnership with a Chinese biobutanol producer and plan to build a 1,000 metric ton/yr demonstration scale facility in India with biochemical partner, Laxmi Organic Industries. The goal is to have the plant fully operational in 2010. This particular plant will run on molasses produced from the sugarcane industry.

METabolic EXplorer

- ♦ METabolic Explorer is based in Clermont-Ferrand, France.
- ♦ The company is using their expertise in molecular biology, metabolic engineering and bioinformatics to design high-performance microorganisms to transform plant material to existing bulk chemicals, including butanol.

Agriculture Research Service (ARS), USDA

- ♦ The ARS is in the process of refining an integrated method for producing cellulosic biobutanol that could make biobutanol more competitive with ethanol and gasoline.
- ♦ Key researchers include: Nasib Qureshi, Bruce Dien, Michael Cotta, and Badal Saha.
- ♦ They have consolidated three of the four steps into a simultaneous saccharification, fermentation and recovery process using wheat straw as a feedstock. After the wheat straw has been pretreated with dilute sulfuric acid or other chemicals, the material is fermented in a bioreactor containing different

types of enzymes and the *C.beijerinckii* bacteria. These enzymes and bacteria do their jobs simultaneously. Throughout this process, gas stripping is used to remove the acetone, butanol and ethanol as they are produced.

- ♦ Early trials showed a two fold increase in productivity above traditional glucose-based fermentation, but the pace of fermentation outran the pace of hydrolysis and they changed to fed batch system.
- ♦ The process, if scaled up, could produce 99 gallons of alcohol per ton of wheat straw. In comparison, Dr. Richard Bain at NREL says the current expected yields for cellulosic ethanol from a biochemical process is about 90 gal/ton of biomass. Dry-mill corn ethanol yields about 102 gal/ton of grain.
- ♦ Currently, they are using a strain of *C.beijerinckii* which produces acetone butanol and ethanol, but efforts are underway to develop a bacterium to produce only butanol.

Joint BioEnergy Institute (JBEI)

- ♦ The JBEI has “engineered the common industrial yeast *Saccharomyces cerevisiae* with an n-butanol biosynthetic pathway, resulting in a ten-fold improvement in n-butanol production from one of the strains to 2.5 mg/L.” (Steen et al., December 2008).
- ♦ Steen et al. point out that while *Clostridia* strains are commonly used as the fermenting agent in butanol production, *Clostridia* has several drawbacks:
 - o Relative lack of genetic tools to manipulate their metabolism
 - o Slow growth
 - o Intolerance to n-butanol above 1-2%, and
 - o Production of butyrate, acetone, and ethanol as by-products.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to butanol technology development for the Minnesota corn industry.

Table 11: SWOT – Butanol

<u>Strengths</u> ▪ Very large market potential ▪ Several advantages over ethanol, including: - o Higher energy content - o Can be transported via traditional infrastructure. - o Can be blended with gasoline at higher blend levels. - o Less evaporative than both gasoline and ethanol – it is safer to use and generates fewer volatile organic compound emissions. ▪ Its development is further along than many other advanced biofuel technologies and its implementation requires less capital investment. ▪ Appears to be cost competitive with current petrochemically produced butanol, and based on some company claims, it may be close to being competitive with ethanol. ▪ Strong institutional support	<u>Weaknesses</u> ▪ Not yet proven at a commercial scale. ▪ Not yet cost competitive with ethanol. ▪ Moderate-high capital costs ▪ Lack of access of retrofitted ethanol plants to pipeline origins ▪ Marketing issues associated with penetrating a well established market. ▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.
<u>Opportunities</u> ▪ High crude oil prices ▪ Can benefit from cellulosic ethanol technology developments. ▪ Ability to utilize current ethanol infrastructure – current ethanol facilities can be retrofitted to produce butanol. ▪ First mover advantage – ability to capture higher prices initially from high value, non-fuel markets. ▪ “Green product” marketability for chemical product applications (e.g., solvents) – may command small premium in niche markets/products. ▪ Could be used to make any type of traditional fuel using traditional refinery reactions.	<u>Threats</u> ▪ Low crude oil prices ▪ High feedstock costs ▪ Tight capital markets ▪ Favorable economic competitiveness of non-corn based butanol. ▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this might moderately counteract the blending rate advantage for butanol.

C. Cellulosic Ethanol – Biochemical Platform

1. Product/Technology Overview

There are two main technology pathways being developed for the production of cellulosic ethanol from lignocellulosic feedstocks: biochemical and thermochemical. There have been significant investments made in the development of both of these production routes, and commercial scale facilities have been proposed and are beginning to be built. Yet, there are still significant research and development efforts needed for this technology to become commercially viable.

While the “winner” of these two routes is yet to be determined, Informa has chosen to focus on the biochemical platform based on information gathered from interviews and desk research. While the base technology for the thermochemical platform is more developed, its application in the world of cellulosic ethanol would reportedly require very large facilities in order to reach economies of scale. This larger scale requires feedstocks to be brought in from greater distances, which erodes economic competitiveness. Additionally, given that the biochemical approach is “newer”, there is more room for process improvements. Also, several interviewees expressed statements to the effect that the biochemical platform produces a product that can be used today, whereas the thermochemical platform produces a product that has to undergo additional processing to reach a usable product form. Furthermore, the biochemical platform allows for multiple value-added product streams to be carved out – sometimes referred to as a biorefinery concept.

In terms of the biochemical platform, research and development are focused on the high production cost areas of pretreatment, hydrolysis, and fermentation^{15,16}. Whereas the main carbohydrate in traditional corn-to-ethanol production is starch, lignocellulosic biomass is composed of cellulose (35-50%), hemicellulose (20-35%), and lignin (10-25%)¹⁷. The cellulose is composed of glucose (a 6 carbon or hexose sugar); while the hemicellulose contains primarily xylose (a 5 carbon or pentose sugar), yet it also contains a mixture of other 5 carbon sugars such as arabinose and small amounts of glucose. One of the key challenges presented by the biochemical platform over traditional corn-to-ethanol technology is that it is far more difficult, and thus more costly, to hydrolyze cellulosic biomass than it is to hydrolyze starch, and that while hemicellulose is relatively easy to hydrolyze compared to cellulose, it is more difficult to ferment.

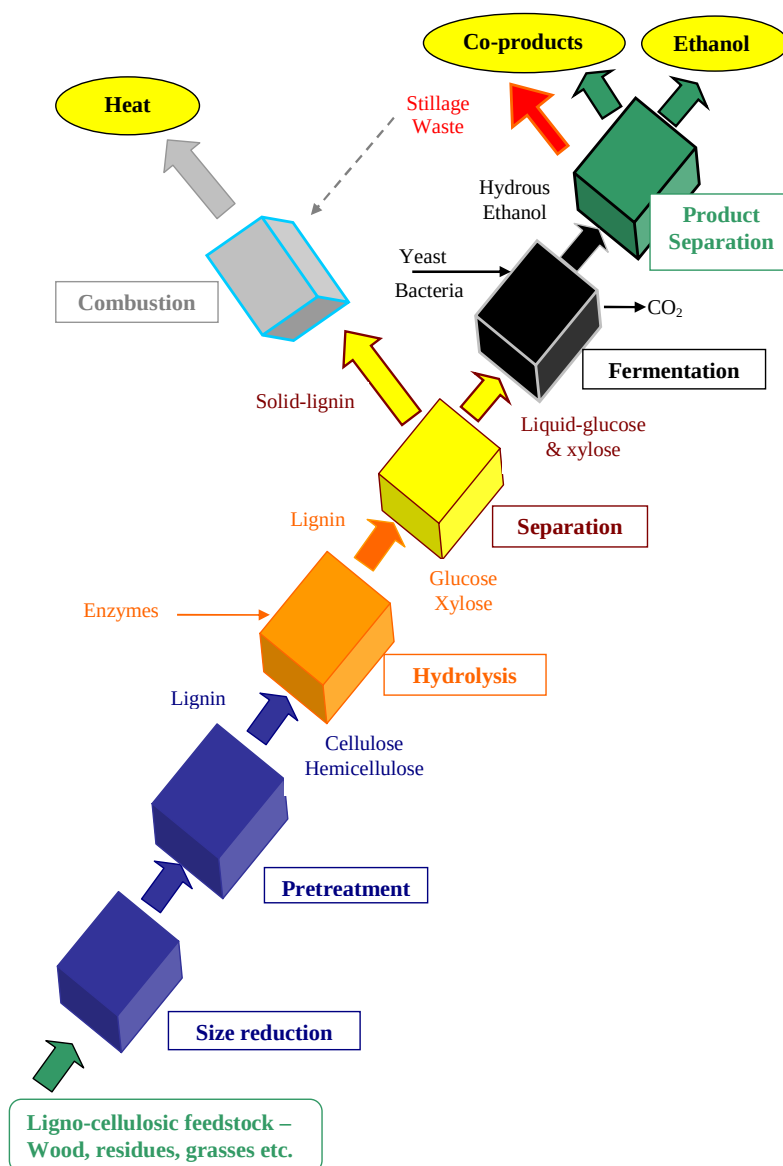
¹⁵ Distillation costs are another large cost component to the overall process, and distillation and dehydration technology developments being made traditional corn-to-ethanol production processes will also apply to cellulosic ethanol processes. See section III.A.4 “Ethanol Distillation” for more details.

¹⁶ Logistical costs and considerations are another large part of the overall economic viability of cellulosic ethanol production technologies. However, these issues and costs are not discussed within this study.

¹⁷ Corn stover is composed of approximately 36.0% cellulose, 23.4% hemicellulose, and 18.6% lignin (Dien et al., 2006).

The following discussion outlines the general cellulosic ethanol production process currently being developed for the biochemical platform. It is also illustrated in Figure 19. However, as discussed below, there are differences between individual processes, as some of these steps can be combined. Additionally, the order along the production chain in which the lignin is separated out differs between processes. In some processes, the lignin is removed during pretreatment, in others it is removed after hydrolysis, and in others it goes along with the sugars until the end and is removed after fermentation.

Figure 19: Cellulosic Ethanol – Biochemical Process Diagram



Source: International Energy Agency, "From 1st-to 2nd - Generation Biofuel Technologies"

Step 1 - Pretreatment

The pretreatment of biomass is currently one of the single largest cost components in the overall cellulosic ethanol production process via the biochemical platform, accounting for 19% of the overall cost, second only to raw material costs (NREL, May 2007 presentation). However, this step is necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis.

There are many pretreatment methods currently being developed by numerous companies and research institutions. At this time, there is not a clear front-runner in emerging pretreatment processes, as each process has its own benefits and disadvantages. There are physical pretreatment processes, generally involving some type of grinding, shredding or chopping, and there are chemical pretreatment processes. Chemical pretreatments can be alkalines¹⁸ (e.g. sodium hydroxide, ammonia, ammonium sulfite), acids (e.g., sulfuric acid, hydrochloric acid, phosphoric acid), or even water heated to high temperatures. In general, the stronger the acid the greater the hydrolysis yield and the more fermentation inhibitors created. Whereas, the more alkaline approaches tend to result in less effective hydrolysis but fewer inhibitors are produced. According to Dien and Bothast (2007), most pretreatments encompass multiple mechanisms. And according to personal communications with Bruce Dien¹⁹, the more common approaches currently being pursued are that of dilute acid and steam explosion, or a combination thereof.

A brief description of select chemical pretreatment processes is provided in Table 12, including, but not limited to, those identified by the Consortium for Applied Fundamentals Innovation (CAFI). CAFI was formed in early 2000 to compare leading pretreatment technologies (indicated by the red text).

¹⁸ Not a viable option for woody crops, more appropriate for herbaceous crops.

¹⁹ Bruce Dien is a chemical engineer in the Fermentation Biotechnology Research department of the USDA, ARS, at the National Center for Agricultural Utilization Research.

Table 12: Chemical Pretreatment Processes

Technology ¹	Description of Technology	Institutions / Companies Involved ¹
Dilute Acid (Sulfuric Acid)	A high pressure/temperature reactor mixes biomass and dilute acid, converting the hemicellulose to xylose and making the cellulose enzyme digestible without the need for explosive decompression. CAFI found the process to achieve a 91.1% conversion of corn stover at 72 hours for an enzyme loading of 15 filter paper unit (FPU) per gram of cellulose. This process released mostly xylose sugars. However, process limitations include: limitations in solids concentrations to about 30%, expensive construction materials due to the corrosive environment of the process, separation of the liquid hydrolyzate from the pretreated solids, acid neutralization costs, costs associated with the removal of product inhibitors produced from the process, energy costs associated with the high temperature/pressure, and yield losses during hydrolyzate conditioning. All of these limitations make this a relatively high cost process.	- NREL - Netherlands Organization for Applied Scientific Research, Techno Invent, and Wageningen University and Research Centre (BioSulfurol Process) - University of California, Riverside - Charles Wyman
Steam Explosion & Sulfur Dioxide	Steam explosion requires high pressure and high temperature, which is then suddenly reduced, causing the materials to undergo explosive decompression. Sulfur dioxide has been used in steam explosion to achieve similar yields to dilute sulfuric acid. One advantage over dilute sulfuric acid is the more rapid penetration of the sulfur dioxide and possible recyclability. However, there are safety concerns, and costs are projected to be similar to dilute sulfuric acid.	- Lund University, Sweden - Iogen (modified steam explosion process) - University of British Columbia - Budapest University of Technology and Economics - ENEA-National Agency for New Technology, Energy, and Environment (Italy)
Controlled pH	By monitoring and controlling the pH at near neutral conditions, hydrolytic reactions are minimized, while physical changes are maximized. This process helps to enhance the susceptibility of cellulose to enzymes and avoids formation of the inhibitory products which later interfere with cellulose hydrolysis or ethanol fermentation. It also helps maximize physical changes that improve enzymatic hydrolysis of cellulose, decrease cellulose crystallinity, and lowers the association of cellulose with lignin. CAFI found the process to achieve a 85.2% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose.	- Purdue University - M. R. Ladisch and N. Mosier - USDA, ARS - B. Dien

Technology ¹	Description of Technology	Institutions / Companies Involved ¹
Ammonia Fiber Expansion (AFEX)	A patented process whereby lignocellulosic material is treated with liquid ammonia under pressure and then by rapidly releasing that pressure cellulose and hemicellulose are converted to fermentable sugars at very low enzyme levels. CAFI found the process to achieve a 96.0% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose. An added advantage is that the ammonia is recyclable and there is no need to wash or detoxify the pretreated material, as is the case with acid pretreatments. Construction costs for the process are lower than for the dilute sulfuric acid, the hydrolyzate is compatible with fermentation organisms without conditioning, and the process does not produce inhibitory products. The AFEX process is more effective on biomass that does not contain high levels of lignin.	- Michigan State University - Bruce Dale
Fiber Extrusion (FIBEX)	Similar to AFEX, only it is a continuous process as opposed to a batch process. The added advantage is that this process reduces the time and ammonia levels required, while giving similar results.	
Ammonia Recycle Percolation (ARP)	An ammonia solution is passed through a reactor with biomass at 80°-180°C. Then, the ammonia is separated and recycled. This process fractionates the biomass into three components (pentose, cellulose, and lignin). At high temperatures, the ammonia breaks down the lignin. By removing the lignin, microbial activity and overall enzyme efficiency is increased, thus reducing enzyme requirements and costs. CAFI found the process to achieve a 90.1% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose. The disadvantage of this process is the challenge in reducing liquid loadings to keep energy costs low.	- Auburn University - Y.Y.Lee - Kyungwon University, Korea - Iowa State University— K. Tae Hyun
Soaking in Aqueous Ammonia (SAA)	A process being developed to reduce the liquid loading and energy costs of the ARP process.	- Auburn University - NREL - Iowa State University - K. Tae Hyun
Lime	Lime is a relatively low cost, safe to handle and available chemical that removes lignin and improves cellulose digestion by enzymes. Lime can then be recycled by using water and carbon dioxide. CAFI found the process to achieve a 93.0% conversion of corn stover at 72 hours for an enzyme loading of 15 FPU/g of cellulose. However, the process is slower than that of ammonia or other more expensive bases. Therefore, low cost pretreatment containment, such as treatment in piles, is needed in order to be cost effective.	- Texas A&M University - Mark Holtzaple
Organosolv	An organic or aqueous organic solvent is used to remove or breakdown the lignin and part of the hemicellulose, leaving reactive cellulose in the solid phase. An additional catalyst can also be used to reduce operating temperatures or to enhance the delignification process. This process does not produce inhibitory products and does not use corrosive acids which require washing/detoxing and high cost construction materials.	- Lignol Innovations, - Kendall Pye
Solvent-Based Clean Fractionation	This process uses a solvent-based pretreatment to separate/fractionate cellulose, hemicellulose, and lignin. This process allows the lignin and the hemicellulose to be used as a feedstock in higher-valued products, as opposed to other pretreatment technologies which use these products as fuel and fermentation feedstocks, respectively.	- NREL

Technology ¹	Description of Technology	Institutions / Companies Involved ¹
Cellulose Solvent-Based Lignocellulose Fractionation	Virginia Tech has developed a pretreatment process they claim to be cost effective. The process, licensed by Mascoma, uses a combination of three technologies: a cellulose solvent pretreatment, concentrated saccharification and organosolv. This process does not use corrosive chemicals, high pressure or high temperature. Products produced from this process include amorphous cellulose, hemicellulose sugars, lignin, and acetic acid. Amorphous cellulose is a form of cellulose that is more accessible to further hydrolysis and is hydrolyzed by adding a special enzyme developed by Genencor International. Results have shown a 97% conversion of corn stover cellulose after 24 hours at an enzyme loading level of 15 FPU/g of cellulose.	- Virginia Tech - Percival Zhang - Dartmouth College - Lee R. Lynd - Mascoma
Ionic Liquid	An ionic liquid solvent is used along with a co-solvent such as acetone and an anti-solvent such as ethanol and/or water to break apart the crystalline plant cell walls and loosen lignin and hemicellulose materials. Results have shown 95% cellulose recovery in less time relative to other processes and under reduced temperatures and pressures relative to dilute acid and ammonium explosion techniques, which reduces energy requirements/costs. Additionally, the solvent can be recycled at 94% efficiency and does not produce inhibitory products. However, some reports indicate that more cost effective recovery techniques are required.	- University of Toledo - Joint BioEnergy Institute
Carbon Dioxide Explosion	Supercritical carbon dioxide is used as an extraction solvent along with co-solvents such as ethanol-water or acetic acid-water to increase lignin removal. The process has the potential to reduce costs over ammonia explosion and since it is operated at lower temperatures, it does not cause degradation of sugars, such as those treated by steam explosion. However, another study concluded that despite its numerous advantages, it may be cost prohibitive for industrial applications.	- Purdue University - Seoul National University, Korea
IBUS Process – Continuous Hydrothermal Solution	At a high dry matter content, biomass is pretreated by steam and afterwards washed to remove potassium chloride, part of the hemicelluloses, and produced inhibitors with no additional chemicals which otherwise have to be recovered or neutralized. This reduces capital and operational costs as well as problems with corrosion.	- Inbicon (Denmark)
Wet Explosion	A combination of wet oxidation and steam explosion is used to pressure boil the biomass.	- BioGasol

* Red = Identified by the Consortium for Applied Fundamentals Innovation (CAFI)

1/ Not an exhaustive list

Step 2 – Hydrolysis

After the cellular structure has been opened up, enzymes or acids can then be used to break down the bonds and release fermentable sugars. The enzymatic hydrolysis of lignocellulosic biomass is far more challenging than that of the starch used in traditional corn-to-ethanol production. The hydrolysis of starch requires a single family of amylases, whereas, the hydrolysis of lignocellulosic material requires a number of different cellulases to deal with the interconnected matrix of cellulose, hemicellulose, and lignin. In this step, the hemicellulose is more easily hydrolyzed

than the cellulose, releasing mostly xylose sugars. However, the glucose sugars released from the cellulose are far easier to ferment (the next process step) than the xylose sugars.

Both acid hydrolysis and enzymatic hydrolysis methods are currently being developed. However, enzymatic hydrolysis is more suitable to homogeneous feedstock mixtures, whereas concentrated acid hydrolysis is more suitable for heterogeneous mixtures such as municipal solid wastes. Brief descriptions of a few of the hydrolysis processes currently being developed are provided below.

- *Dilute Acid Hydrolysis* - The dilute acid process is conducted under high temperatures and pressure and reaction time occurs in seconds to minutes, aiding in continuous processing. One drawback of this process is that despite process improvements, sugar degradation still occurs and yields are limited.
- *Concentrated Acid Hydrolysis*- Concentrated acid processes use lower temperatures and pressure, but reaction times are longer. There is little sugar degradation and the yield potential is higher than in the dilute acid hydrolysis process. However, in order to make this process more economical, sugar recovery and acid recycling must be optimized.
- *Enzyme Hydrolysis* - Enzymes, which are purchased or produced, are used to hydrolyze the pretreated biomass.
- *Direct Microbial Conversion (DMC)* -A hydrolysis process in which a single microorganism produces both ethanol and enzymes. DMC is further away from commercialization because researchers are still searching for a microorganism that produces sufficient ethanol and enzyme yields, but it has an advantage in that a dedicated process step for the production of cellulase enzymes is not needed, thus reducing overall process costs.

There have been significant advancements made over the past few years in regard to cellulase enzyme development, which has reduced the cost of these enzymes by a factor of 10-30, reducing overall costs down to 20-30 ¢/gal (figures cited from various sources within an EPA report²⁰). However, it is estimated that these costs need to be reduced even further. Some analyses have suggested that these costs need to get down to 3-4 ¢/gal. However, developing these enzymes for a single, homogeneous feedstock may be easier than developing one for multiple feedstocks. This factor favors the development and use of abundant cellulosic biomass materials such as corn stover, at least in the short-term.

Combined Pretreatment and Hydrolysis

Some of the more advanced pretreatments are done under conditions that would be amenable to enzyme stability and activity. This would enable the possibility of

²⁰ EPA, 2009, "Draft of Regulatory Impact Analysis: Changes to Renewable Fuel Standard Program"

incorporating hydrolyzing enzymes into pretreatment stages, thereby combining the pretreatment and hydrolysis stages of cellulosic ethanol production. One of the more commonly reported approaches to cellulosic ethanol production using corn stover or corn fiber is that of using an acid pretreatment, whereby some of the hemicellulose is hydrolyzed, and then later, enzymes are used to hydrolyze the cellulose fraction.

Step 3 – Fermentation

Once hydrolyzed, the glucose and xylose sugars can be co-fermented to ethanol. However, it is more difficult to effectively ferment the xylose sugars, and hence, there has been a great deal of effort directed toward the development of improved yeast strains/microorganisms that can efficiently co-ferment both xylose and glucose. While significant progress in this area has been achieved over the last few years, other issues such as microorganism sensitivity to inhibitors and the production of unwanted by-products continue to thwart the efficacy of these fermenting agents. Additionally, technology developers are also looking to lower the required dosage of the fermenting agent.

Combined Hydrolysis and Fermentation

There are efforts underway by technology developers to combine hydrolysis and fermentation into a single step. Such efforts could significantly reduce capital costs by requiring fewer reactors and less supporting equipment and piping. The process could also reduce processing costs.

Step 4 – Product Separation and Distillation

Once fermented, the ethanol is separated from the water and other by-products. Technology developments in this area are explored in more detail in Section III.G "Ethanol Distillation".

2. Market Potential

The demand for cellulosic ethanol is in part supported by the Renewable Fuel Standard expanded by the Energy Independence and Security Act of 2007, which contained a 21 billion gallon mandate for advanced biofuels by 2022, including 16 billion gallons of cellulosic biofuel. Some cellulosic biofuel companies are focused on feedstocks other than corn, which offer greater environmental benefits and less impact on prices of major agricultural commodities; yet, corn biomass (e.g., corn stover, corn cobs, and corn fiber) will likely have a place in the mix of future feedstocks. Given the volume of ethanol that can be produced from corn starch and the interest in corn biomass as a cellulosic feedstock, this emerging technology has the potential to have a large demand impact on the corn sector.

3. Profiles - Companies & Research Institutions

There are numerous companies and research institutions developing their own approaches and unique technologies to cellulosic ethanol production via the biochemical platform, each with their own advantages and disadvantages. However, the bottom line is that a cost efficient process has yet to be commercialized. There are several companies that are expecting to reach commercialization by 2011/2012. Yet, the tight capital market is inhibiting many from obtaining the capital needed to go forth with their commercialization efforts.

Table 13 lists operational, under construction, and planned biochemical cellulosic ethanol facilities, as reported within a May 2009 EPA report²¹. Brief comments on a few of these companies and their technologies, along with a few other technology developers are included below.

BioGasol

BioGasol, along with its international partner Tate & Lyle, is working on a demonstration plant in Denmark, demonstrating the conversion of a wide array of feedstocks, including wood chips, garden waste, wheat and barley straw, energy crops and grass clippings. According to a March 2009 article in *Ethanol Producer Magazine*, BioGasol received \$13.4 million from the Danish Energy Agency's Energy Technology Development and Demonstration Program to fund the \$45 million project of building a 1.3 mmgy cellulosic ethanol demonstration facility in Aakirkeby, Denmark. Additionally, in the U.S., the company is collaborating with Pacific Ethanol and the Joint BioEnergy Institute to build a demonstration scale plant in Boardman, OR, for which it received \$24 million from the DOE in January of 2008. According to this March 2009 article, the company intends to have this U.S. plant completed by the fourth quarter of 2009.

BioGasol's cellulosic ethanol technology process is said to improve ethanol yields by 7.5%. The pretreatment process uses wet explosion, a combination of wet oxidation and steam explosion, essentially pressure boiling the biomass. Then, in the first bioreactor, enzymes from Novozymes hydrolyze the cellulose and hemicellulose into glucose and xylose, where the glucose is simultaneously fermented using industrial yeast. The xylose then goes to a second bioreactor, while the lignin is separated and pelleted as a fuel. In the second reactor, their novel thermophilic bacterium converts the xylose to ethanol and hydrogen. Any remaining organic material goes through a second anaerobic digester and is converted to methane. The company then uses its proprietary desalination technology so that the process water can be reused, minimizing water requirements.

BlueFire

While the EPA reported wood chips, grass cuttings, and yard waste as the feedstocks for the BlueFire cellulosic ethanol process, the company's website expands this list to include other feedstock forms as well, including agricultural

²¹ EPA, 2009, "Draft of Regulatory Impact Analysis: Changes to Renewable Fuel Standard Program"

residues such as corn stalks and corn cobs, dedicated energy crops and paper. The company has been operating their pilot plant in California for roughly five years (not included in Table 13). According to the International Energy Agency, this pilot plant is at a 300 liter/day scale.

Their process uses a patented concentrated acid hydrolysis system and several other “improvements” that they claim make ethanol production more economical relative to older acid hydrolysis methods. According to the May 2009 EPA report, “Bluefire’s stated improvements include a more efficient acid recovery system; higher sugar purities and concentrations; use of more efficient microbes to ferment C6 (6 carbon) and C5 (5 carbon) sugars into ethanol; the processes ability to use biomass feedstocks containing silica.”

Mascoma

In February 2009, Mascoma began production at its 20,000 gal/year demonstration plant in Rome, NY. The facility can utilize numerous feedstocks, including woodchips, grasses, corn stover and sugarcane bagasse.

Mascoma announced in May 2009 that they had made a major breakthrough in their consolidated bioprocessing (CBP) system. They have engineered microorganisms to produce cellulases and ethanol at a high yield in a single step. The Vice President of Mascoma’s Development and Operations division said that “these advances enable the reduction in operating and capital costs required for cost effective commercial production of ethanol, bringing Macoma substantially closer to commercialization.”

POET

Poet, formerly Broin, has decided to use corn cobs as their primary cellulosic ethanol feedstock. Reasons for focusing on corn cobs over stover include: the collection will require minimal additional effort; it will not adversely affect soil quality, as the cob is only 15% of the above ground stover; it has higher carbohydrate content and it is a denser feedstock.

In January 2009, POET started-up operations at its 20,000 gal/year pilot scale plant in Scotland, S.D. The company now plans to expand production at its 50 mmgy grain-to-ethanol facility in Emetsburg, IA, to 125 mmgy, 25% of which is expected to be produced from corn fiber and corn cobs. This facility is expected to begin production in late 2011.

Vercipia (Verenium / BP)

Verenium is focusing on grasses, energy cane, and bagasse as their key feedstocks. The company’s proprietary technology is capable of fermenting both 5-carbon (C5) and 6-carbon (C6) sugars. Verenium uses dilute acid steam explosion to hydrolyze the hemicellulose to C5 sugars. The C5 sugars are then washed and separated from the cellulose and are sent to the C5 fermentation process while the C6 sugars are sent to the C6 fermentation process. Then, the C5 and C6 beers are

blended together and run through a three stage distillation process to produce fuel grade ethanol.

Verenium and its joint venture partner, BP, have announced plans to build a 36 mmgy plant in Highlands County, FL. The companies intend to break ground in 2010 and begin production in 2012. They are calling the joint venture “Vercipia.”

ZeaChem

ZeaChem uses a unique process that combines elements of biochemical and thermochemical cellulosic technologies. This hybrid process fractionates the biomass at the front-end, separating off the lignin. Glucose and xylose sugars are fermented into acetic acid (not ethanol), without releasing CO₂ as a by-product. Then, the acetic acid is converted to an ester and then reacted with hydrogen to get ethanol. This hydrogen stream comes from the gasification of the lignin separated out at the front-end, while the remaining syngas is burned to create steam and power for the system.

The company plans to begin construction of its 1.5 mmgy facility in Boardman, OR, this year, with an expected completion date in mid 2010.

Oteros

Oteros, formerly known as SunEthanol, has announced “unprecedented” lab results from its proprietary conversion technology known as “C3” (Complete Cellulosic Conversion). The company plans to open up a pilot plant in Springfield, MA, this year. Lab results have shown that its Q Microbe can produce 70 grams of ethanol per liter of industrially pretreated biomass in a single step (combining hydrolysis and fermentation steps into one). The company states that “these unprecedented yield results far surpass the 50 grams per liter considered to be the threshold for commercial production of cellulosic ethanol.

Table 13: Biochemical Cellulosic Ethanol Plants (Operational, Under Construction, & Planned)

Company / Plant Name	Location	Feedstocks	Prod Cap (MGY)	Est. Op. Date	Stage ^a	DOE Funding (for planned)
Abengoa Bioenergy Corporation	York, NE	Wheat straw, corn stover, energy crops	0.02	Sep-07	O	
Abengoa Bioenergy Corporation	Hugoton, KS	Corn stover, wheat straw, milo stubble, switchgrass	11.4	Early 2012	P	\$76 M
AE Biofuels	Butte, MT	Switchgrass, small-grain straw, corn stover	N/A	Aug-08	O	
Arkenol Technology Center	Orange, CA	Biomass	N/A	1994	O	
Auburn University / Masada Resources Group	Auburn, AL	Wood	N/A	1995	O	
BlueFire Ethanol, Inc.	Lancaster, CA	Woodchips, grass cuttings, yard waste	3.9	TBD	P	
BlueFire Mecca, LLC	El Sobrante, CA	Woodchips, grass cuttings, yard waste	17	TBD	P	\$40 M
BPI & Universal Entech	Phoenix, AZ	Paper waste (sorted MSW)	0.01	2004	O	
Cornell University's Biofuels Research Laboratory	Ithaca, NY	Perennial grasses, woody biomass	N/A	Jan-09	O	
DOE National Renewable Energy Laboratory	Golden, CO	Corn stover, other biomass	N/A	2001	O	
DuPont Danisco Cellulosic Ethanol	Vonore, TN	Corn cobs then switchgrass	0.25	Dec-09	C	
EcoFin / Alltech	Springfield, KY	Corn cobs	1.3	2010	P	\$30 M
ICM, Inc.	St. Joseph, MO	Corn fiber/stover, sorghum, switchgrass	1.5	2010	P	\$30 M
Macoma Corporation	Kinross, MI	Wood fiber	40	2012	P	\$26 M
Mascoma Corporation	Rome, NY	Wood chips	0.2	Feb-09	O	
Novozymes	Franklinton, NC	Corn stover	N/A	N/A	O	
Pacific Ethanol	Boardman, OR	Wheat straw, wood chips, corn stover	2.7	Early 2011	P	\$24 M
Pan Gen Global	Calusa County, CA	Rice straw and hulls	N/A	1995	O	
POET Project Bell	Scotland, SD	Corn cobs and fiber	0.02	Jan-09	O	
POET Project Liberty	Emmetsburg, IA	Corn cobs and fiber	25	End of 2011	P	\$80 M
POET Research Center	Scotland, SD	Corn cobs and fiber	N/A	N/A	O	
Pure Vision Technology, Inc	Fort Lupton, CO	Corn stover, wood, sugarcane bagasse	N/A	2003	O	
Pure Vision Technology, Inc	Fort Lupton, CO	Corn stover, wood, sugarcane bagasse	N/A	2009	O	
RSE Pulp and Chemical	Old Town, ME	Woody biomass	2.2	2010	P	\$30 M
Southeast Renewable Fuels LLC ^b	Clewiston, FL	Sweet sorghum, bagasse	20	End of 2010	P	
USDA Citrus & Subtropical Products Laboratory	Winter Haven, FL	Citrus residues	N/A	1990	O	
Verenium	Jennings, LA	Sugarcane bagasse	0.05	2006	O	
Verenium	Jennings, LA	Sugarcane bagasse, wood, energycane	1.5	Feb-09	O	
Verenium / BP	Lake Okeechobee, FL	Energycane, high-biomass sorghum	36	2011	P	\$ 10 M
Western Biomass Energy, LLC	Upton, WY	Wood waste (softwood)	1.5	2007	O	
ZeaChem	Boardman, OR	Wood chips, saw dust, logging debris	1.5	2010	P	

a/ O = Operational, C = Under Construction, P = Planned

b/ Biochemical or Thermochemical - process is unknown.

Source: EPA, 2009, "Draft of Regulatory Impact Analysis: Changes to Renewable Fuel Standard Program"

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to biochemical cellulosic ethanol technology development for the Minnesota corn industry.

Table 14: SWOT – Cellulosic Ethanol – Biochemical Platform

<u>Strengths</u> ▪ Very large market potential ▪ Able to utilize C5 and C6 sugars. ▪ Uses biomass - not limited to the corn kernel – averts food v. fuel debate. ▪ Very strong institutional support ▪ Relative to the thermochemical platform: - o Ability to carve out more value-added product streams – biorefinery concept. - o Less developed technology – more room from process improvements. - o Projected scale required is smaller. Larger scale requires feedstocks to be brought in from greater distances, which erodes economic competitiveness.	<u>Weaknesses</u> ▪ Depending on the biomass (e.g., corn cobs, corn stover) utilized, some argue that soil erosion and soil quality issues can result. ▪ Logistical cost issues associated with transporting the biomass. ▪ Currently high production costs. ▪ Not yet proven at a commercial scale. → Expected to approach commercial scale production in 2011/2012. ▪ Does not allow for the production of a suite of traditional fuel products as does the thermochemical platform. ▪ Very high capital costs relative to corn-based ethanol. ▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.
<u>Opportunities</u> ▪ High crude oil prices ▪ Green funding – favorable policy environment ▪ “Green product” marketability for chemical products produced from cellulosic ethanol biorefinery.	<u>Threats</u> ▪ Low crude oil prices ▪ Economic competitiveness of alternative feedstocks ▪ Tight capital markets ▪ Over time, an EPA allowance for mid-level ethanol blending rates above the current 10%, or low costs for cellulosic ethanol production sufficient to allow high-level blends (e.g., E85), is necessary for cellulosic ethanol volumes to reach levels envisioned in the Renewable Fuel Standard.

D. Ethanol Distillation

1. Product/Technology Overview

The separation of alcohol and water is typically a costly, energy intensive process, representing a significant portion of the overall energy required by an ethanol facility. It is also one of the key cost components in the biochemical cellulosic ethanol platform. Traditionally, this separation is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also reducing greenhouse gas emissions. Alternative ethanol distillation technologies currently being developed include: vacuum stripping, gas stripping, membrane separation, solvent (liquid) extraction and supercritical CO₂. These technologies are largely in the late development/early commercialization stage, and are expected to reach commercial status within 3-5 years, if not sooner.

Vacuum Stripping - The fermenting vessel is coupled with a vacuum chamber which extracts, in-situ, the more volatile ethanol and allows for partial product removal.

Gas Stripping - The fermenting broth overflowing from one stage to the next is contacted with a CO₂ stream that entraps the ethanol. The ethanol is then removed when this gas stream passes across a reactor and through an absorption tower where it is contacted with water. The CO₂ is then re-circulated. By using this process, the concentration of sugar in the product stream entering the fermenter is increased.

Membrane Separation - Membranes are used to filter the water/ethanol mixture during fermentation. The membranes are vapor phase separation units that allow the preferred permeation of water over other vapor components in a gas mixture.

Solvent (Liquid) Extraction - This approach removes the product that causes inhibition through an extractive biocompatible solvent that favors the migration of ethanol to solvent phase, a process known as extractive fermentation. However, it has been noted in one publication that this approach lowers solubility and results in a poisonous effect on yeast, thus restricting the development of this method.

Supercritical Fluids - While the success of separating alcohol and water via supercritical fluids has been demonstrated for many years, these previous demonstrations have not been able to compete with the economics of traditional steam distillation methods or other proposed methods such as membrane separation. However, MOR Supercritical has applied their supercritical extraction technology to ethanol dehydration, and claims a process that is scalable and cost-efficient relative to other proposed dehydration technologies.

2. Market Potential

Approximately 9.3 billion gallons of corn-based ethanol were produced in 2008, and given the current Renewable Fuel Standard, this production volume is expected to continue to grow along with that of cellulosic ethanol production. Yet, one of the areas in which technology can help improve the economic viability of this industry is in reduced energy consumption. In reducing the ethanol facility's energy consumption, not only are cost savings realized but greenhouse gas emissions are also reduced. And, while the outcome of a potential cap and trade system is uncertain, future economic incentives favoring lower carbon footprint facilities could further improve the economics of facilities implementing energy saving technologies.

Energy costs currently account for about 12% of overall operating costs, the second largest operating cost next to feedstock costs. Of the overall energy consumption, distillation and dehydration consume about 50% (McAloon et al., 2004; Kim and Dale, 2005 – cited by Vaperma). If an alternative ethanol technology reduced energy consumption of the distillation process by 40%, as several of the current technology developers claim to achieve, this would equate to an approximate 6¢ per gallon cost savings or \$3 million per year for a 50 mmgy ethanol facility (using current natural gas prices). If a royalty fee of 2 ¢/gal is assessed, as is the case with one technology developer, the cost savings for the 50 mmgy facility is still \$2 million per year. These are broad generalizations; the economics of advanced ethanol distillation will vary by individual technology.

3. Profiles - Companies & Research Institutions

While each of these methods has its own pros and cons, the leading technology at this time appears to be membrane separation, currently being pursued by Vaperma (Siftek) and Whitefox Technologies. Other technologies briefly reviewed below include Trans Ionics Corporation's extraction technology (ESep) and MOR Supercritical's supercritical CO₂ extraction technology. However, it is to be noted that there are also developments being made on gas and vacuum stripping technologies, as well as other solvent extraction methods.

Vaperma

Vaperma is a Quebec based company that specializes in the development, manufacturing and commercialization of advanced gas separation systems. Their Siftek™ membrane separation technology can be integrated into new or existing ethanol plants to reduce energy costs and increase plant throughput. The Siftek™ membrane is a hydrophilic polymer membrane that can be used to dry ethanol in the vapor phase in a continuous process. The membrane system can replace both the rectification column and the molecular sieve unit in a conventional process. The feed gas flows into the membrane modules, which contain multiple hollow fibers packed

in a shell and tube configuration. The water vapor then permeates through the walls of the membrane and is vacuum pumped out (see Figure 20).

Figure 20: Vaperma Siftek Distillation Technology Concept



Source: Vaperma

Vaperma claims that their technology can increase overall fuel production by 15-20% and reduce energy consumption by up to 50% compared to traditional distillation and molecular sieves. By reducing the energy consumption, costs are reduced along with CO₂ emissions. For example, the company estimates that for a 40 mmgy ethanol facility, implementing the Siftek™ membrane system could reduce CO₂ production by 21,000 tons/yr. The company also claims that the technology has proven to be low maintenance, predicting that the membrane cartridge would not need replacing until after three years of continuous operation. Their technology was recognized by *Frost and Sullivan*, receiving the 2008 North America Technology Innovation of the Year Award.

The company has completed tests of its patented membrane separation technology, Siftek™, on a pilot scale (100K gal/yr) at a Greenfield Ethanol facility in Canada. Additionally, demonstration scale testing was just completed at a Greenfield Ethanol facility in Chatham, Ontario. According to a company representative, this demonstration was 8,000 liters per day (740K gal/yr).

Christian Roy, Vice President of Business Development for Vaperma, said that their membrane technology has immediate potential in ethanol market applications whereby the membrane is used as a replacement for molecular sieves for boosting or de-bottlenecking the current production process. Roy said that they had been in serious discussions to implement this technology in several commercial applications prior to the economic downturn, but that these companies have currently put this on hold given economic conditions. Several potential market applications for molecular sieve replacement by membrane technology are listed below.

- (1) Existing ethanol plants could use the membrane at the front end of current molecular sieve units (MSU) to boost the production capacity of a plant by roughly 16%, at half the expense of a new MSU. In this case, the payback period is estimated to be between 6 months and a year.
- (2) A new plant could use membranes in replacement of molecular sieves altogether. In this case, the payback period is less than 6 months.

- (3) Industrial ethanol production facilities could use membranes to help restore the 30% capacity that is lost when trying to increase the quality. Again, the payback period is estimated at less than 6 months.

As for replacing the rectification column, Roy estimated that it would be 2-4 years before the technology was commercially feasible, stating that while it is currently technically feasible it is not yet economically feasible. Roy explained that while it would be ideal to use membranes at the top of the beer column to separate the ethanol and water, you need a certain pressure differential to achieve efficient separation and beer columns are typically kept at low pressures to keep the temperature low (temperatures are kept low for a variety of reasons). And while there are ways to get around this problem, such as using a mechanical vapor compressor, these are expensive, and given current membrane costs, this route was said to be uneconomical at this point in time.

Whitefox Technologies Limited

Whitefox Technologies Limited, a London based company, has also developed an ethanol dehydration process using membrane separation. The company claims their continuous process is capable of dehydrating aqueous ethanol with a water content of 50-99.95% at atmospheric or elevated pressures without membrane saturation. The company says that they do not plan to commercialize their technology until it has been demonstrated in full-scale operations for four years. Currently, the company is testing their core technology in retrofitted and newly built plants, producing a combined total of 520 mmgy of ethanol.

Trans Ionics Corporation

Trans Ionics has developed a process they call ESep, which uses “proprietary extraction technology” to remove the ethanol from the water. The beer produced from the fermentation step, containing 3-15% alcohol, is fed to the ESep unit where an extraction process selectively removes the ethanol, producing a product stream that is typically 97+% ethanol. While a 60% reduction in energy consumption is estimated when incorporating the system into new ethanol and cellulosic ethanol plants, a 28% energy reduction and a 16 month payback period is estimated when retrofitting an existing ethanol plant. Additionally, the process is expected to reduce capital costs by eliminating the need for costly stainless steel distillation components. The company’s goals are to reduce capital costs and operating costs by 30% each versus their “next best competitor.” Trans Ionics’ business model for their ESep technology includes an estimated selling price of skid-mounted units for a 20 mmgy facility of \$1.25 million, plus a 2¢ per gal processing fee.

MOR Supercritical CO₂

Another ethanol dewatering technology is MOR Supercritical’s supercritical CO₂ process, which has the added benefit of CO₂ utilization. The company claims that their process is economically competitive with proposed membrane technologies. According to MOR’s website, the company is currently seeking technology and

project development partners. They have already tested their technology in a small pilot unit are currently seeking a partner to install a large demonstration scale unit.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to ethanol distillation technology development for the Minnesota corn industry.

Table 15: SWOT – Ethanol Distillation

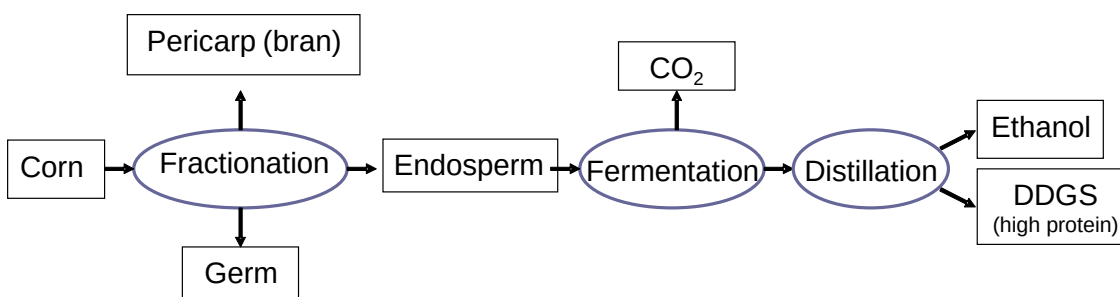
<u>Strengths</u> ▪ Large market potential - o Size of ethanol industry - o Strong potential impact on ethanol margins ▪ Moderate/strong institutional support ▪ Moderate capital investment requirements ▪ Increases plant throughput capacity ▪ Reduces greenhouse gas emissions ▪ Under the RFS as amended in 2007, this technology would help new or expanding ethanol facilities meet greenhouse gas reduction requirements. ▪ Application as a molecular sieve replacement is deemed economical now – with a payback period of 6 months to a year for an existing ethanol facility.	<u>Weaknesses</u> ▪ Not yet proven at a commercial scale. ▪ Cost advantage is heavily reliant on volatile natural gas prices. ▪ Unknown economic viability as a complete distillation and dehydration system – company claims vary.
<u>Opportunities</u> ▪ High energy prices ▪ Technology offers a potential advantage for existing ethanol producers – helps keep already existing infrastructure investments profitable. ▪ Technology is at an early stage of commercialization with opportunities for process improvements. ▪ A cap and trade system would further improve process economics relative to the traditional ethanol facility. ▪ Could help ethanol utilization in California relative to other traditional Midwestern ethanol plants once the Low Carbon Fuel Standard goes into effect in 2011. ▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this will facilitate an increase in ethanol production.	<u>Threats</u> ▪ Low energy prices – reduces cost advantage ▪ Tight capital markets ▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall.”

E. Front-End Fractionation

1. Product/Technology Overview

Front-end fractionation separates the corn into three fractions including pericarp (bran/fiber), germ (the oil-bearing portion of the kernel) and endosperm prior to ethanol fermentation (see Figure 21). Currently, in dry mill ethanol production facilities, these other fractions go along with the starch into the fermentation vessel, taking up space and reducing production efficiency. A consequence of decreasing the unfermentable fraction of the corn during fractionation is to improve the fermentation efficiency and increase the ethanol yield (up to 12% according to some industry sources). Additionally, in the traditional ethanol process, the oil and the fiber end up in the distillers grains (DDGS) and are sold at feed ingredient prices of roughly 6.1¢/lb (March 2009). Whereas, their combined value if sold as separate co-products could be significantly greater. Another benefit of fractionation comes in the form of risk mitigation, as producers are not relying solely on the revenues from two product markets (i.e. ethanol and DDGS) and they have increased flexibility. Additionally, some technology developers claim, front-end fractionation can also reduce energy and water consumption, thus also reducing volatile organic compound emissions.

Figure 21: Front-End Corn Fractionation



Source: Informa Economics

As a result of removing the pericarp and germ from the front-end of the ethanol production process, the resulting DDGS are lower in fiber and oil and higher in protein. The high-protein DDGS obtained through fractionation can become a differentiated higher-value product. Yet, high-protein DDGS is a relatively new product and will require the development of a market. For that reason and since the lower oil content should in theory result in a lower energy value, it is expected that high-protein DDGS will trade at a price close to that of DDGS until such a market is developed and the value of the higher protein is proven.

Although the wet-mill industry benefits from large co-product value recovery, the dry-mill industry has tended to believe that these benefits could not be achieved without unacceptable increases in capital costs. However, over the years, there have been

numerous technological advancements that are moving front-end fractionation technologies for a dry-mill toward economical viability. Examples of companies currently using fractionation include:

- Lifeline Foods in St. Joseph, MO (50 mmgy)
- Poet in Coon Rapids, IA, (54 mmgy)
- Poet in Albert Lea, MN, (45 mmgy),
- Poet in Laddonia, MO, (50 mmgy), and
- Renew Energy in Jefferson, WI (130 mmgy).

There are several modified dry-mill fractionation processes, each with their own unique advantages and disadvantages. However, there are a few generalizations that can be made. These processes can generally be classified as either wet fractionation or dry fractionation processes.

In general, wet fractionation technologies tend to be more costly to implement. However, they also produce higher-valued co-products and there is less starch loss. The germ extracted by wet fractionation technologies has an oil content of approximately 40+% compared to 20-25% from typical dry fractionation technologies. This low oil germ produced by dry fractionation is sometimes referred to as “dirty germ,” and often wet mills and other oil extraction facilities are not geared to take germ with this low of an oil content. Yet, because corn oil extraction equipment is expensive and many companies do not want to handle hexane, most ethanol producers do not wish to extract the oil themselves. Additionally, the higher starch loss associated with the dry fractionation technologies is a revenue factor for the ethanol producer, as ethanol yields are compromised. Nonetheless, dry fractionation technologies are more prevalent in current plant installations, primarily due to cost differences.

The company MOR Technology claims to have developed a fractionation process, MOR FRAC+, with the costs generally associated with dry fractionation technologies but the higher valued co-products and the lower starch loss generally associated with wet fractionation technologies. While unproven at a commercial scale, this process appears to have promise.

2. Market Potential

Front-end fractionation offers the ethanol producer several ways in which to increase ethanol margins and reduce risk. Estimates of net income increases range from 9-28 ¢/gallon, while estimates of capital costs range from 17-70 ¢/gallon of capacity. These estimates range across the various technologies and depend on input cost and co-product value assumptions²². Given these company-provided estimates, the payback period for front-end fractionation is generally less than 2 years.

²² Most of the underlying value assumptions for the high protein DDGS behind the income estimates are significantly higher than traditional DDGS. However, as discussed previously, high-protein DDGS is a relatively new product and will require market development, and for that reason, it is expected

While there are also back-end fiber and oil extraction technologies that are either currently available or being developed that are less expensive, these processes do not produce the high revenue co-products that are generated from front-end fractionation. For example, the oil that is extracted at the back end of the process typically cannot be used in food products and is thereby a lower valued product. Additionally, there are ethanol production efficiencies that are gained when the starch fraction is separated out at the beginning of the process.

The following section profiles a few of the front-end fractionation technologies currently available, detailing where information is available, production parameters, net income impacts, and capital cost requirements.

3. Profiles - Companies & Research Institutions

As much quantifiable data as could be uncovered via desk research and personal interviews at the time of this report are provided in the profiles below. Many of the following companies/institutions make claims on their websites or within press releases that are similar in nature; examples include:

- lower capital cost requirements
- reduced operational costs
- increased protein and reduced fiber and oil content of DDGS
- reduced energy and/or water consumption
- reduced fermentation time
- increased capacity
- increased co-product value

However, this information was only included in the profiles below if quantifiable claims were made.

Modified Dry-Mill Wet Fractionation Technologies

Wet fractionation technologies typically involve soaking/steeping the corn prior to fractionation. In general, the capital costs are higher than that of dry fractionation technologies, but the starch loss is lower and the quality/value of co-products is higher.

- ♦ **Corn Value Products (CVP) / Quality Technology International Inc.** – Quality Technology is heading the marketing efforts of CVP's wet fractionation system, HydroMilling. The system produces a suite of co-products marketed under the brands "Prairie Sky" and "Solaris".

that high-protein DDGS will trade at a price close to that of DDGS until such a market is developed and the value of the higher protein is proven.

- ♦ **Maize Processing Innovators (MPI) / FCStone Carbon** – The Quick Germ (QG) wet fractionation technology was originally developed by the University of Illinois. This process was later enhanced to fractionate both the germ and the pericarp fiber, and is known as the Quick Germ Quick Fiber (QGQF) process. The license for the technology is now held by MPI which has an agreement with FCStone Carbon LLC to lead commercialization efforts. According to an online presentation on MPI's website, quantifiable claims include:
 - The process yields approximately 3.1-3.7 lbs/bu of germ; 3.3-4.0 lbs /bu of fiber; and 10.3-11.6 lbs/bu of low fat, low fiber DDGS
 - Minimum oil content of germ is 38%
 - Maximum 3% starch loss
 - Crude protein content of DDGS = 49.31%, fat content ~3.85%; ash = 3.24%; and ADF = 6.80%; compared to 28.5%, 12.7%, 5.32% and 10.80%, respectively, with traditional dry grind technology (no fractionation)
- ♦ **University of Illinois** – The University of Illinois has since made process improvements to the QGQF process, developing what they call enzymatic milling, also known as E-Mill. In addition to recovering the germ and the pericarp fiber, the E-Mill process also recovers the endosperm fiber; this further reduces the quantity of DDGS produced to 65-70% of the conventional dry-grind process. However, the E-Mill process also adds an additional enzyme to the process. Whereas the QGQF only requires amylase, the E-Mill process requires both amylase and protease.
 - According to data from University of Illinois professor Vijay Singh: crude protein content of DDGS = 58.5%, fat content =4.5%; ash = 3.2%; and ADF = 2%
 - In an Agriculture Research Service (ARS) study comparing the E-Mill process to conventional dry grind, the E-Mill process:
 - increased fermentation capacity by 27%,
 - reduced fiber content of DDGS by 81%, and
 - increased the protein content of DDGS by 105%.

Modified Dry-Mill Dry Fractionation Technologies

Dry fractionation technologies typically separate the germ and fiber from the corn kernel mechanically without the need for soaking. In general, capital costs are lower than that of wet fractionation technologies, but starch loss is higher and the quality/value of co-products is lower.

- ♦ **Renessen LLC.** – Renessen is a joint venture between Cargill and Monsanto. Renessen is currently operating a pilot facility using their Extrax Processing System at Cargill's BioProcessing Center in Eddyville, IA, processing 10,000 bushels of corn per day. Meanwhile, Monsanto is in the fourth and final stage prior to product launch of their high oil corn (7% compared to 3.5%) for use in Renessen's Extrax corn fractionation system. They are focusing on higher oil content as this is the most valuable fraction of the corn. According to a 1st quarter

2009 issue of *Distillers Grains Quarterly*, company vice president Michael Morgan expects their first commercial facility to be in place within two years.

- ♦ **Cereal Process Technologies** – Cereal Process Technologies has installed its patented dry fractionation technology in several dry-grind corn mills, including Renew Energy LLC's 130 mmgy facility in Jefferson, WI. Quantifiable company claims include:
 - 35% reduction in drying costs – reducing energy consumption to 21,000-22,000 BTU/gal.
 - Water consumption is reduced to 2.7 gallons per gallon of ethanol (33% savings).
 - Each module processes 650-800 bu. of corn per hour, but 650 is the “sweet spot”.
 - The use of their new “MarketFlex” enables producers to adjust the amount of oil versus starch they want in order to better respond to market price fluctuations.
 - Resulting DDGS contain about 40% crude protein.
 - Capital costs will vary, but are estimated at \$30 million for a nine-module system such as the one installed at Renew Energy. The estimated payback for this system was two years.
 - The technology can add more than 20 ¢/gal to the producer's net income.
 - Yield: germ = 12.5%; bran = 7.5%; and endosperm = 80%
- ♦ **Delta-T Corp. / Ocrim Milling** – Delta-T and Ocrim Milling have developed a dry fractionation technology known as “Dry Separation Technology.” The process works by using a degerminator to separate the germ from the corn kernel by forcing the kernel against a stationary screen, which contains holes large enough to push the germ fraction through but small enough to prevent the endosperm from passing through. Then, the fiber and the endosperm are fractionated by using a series of roller mills and vibrating screens. Quantifiable company claims include:
 - Guaranteed maximum starch loss of 4%
 - Guaranteed minimum increase in throughput capacity of 10% for an existing Delta-T designed facility
 - 6,000 BTU/gal reduction in energy use
 - Neal Jakel, Fractionation Program Manager for Delta-T Corp, believes fractionation can reduce operational costs by 8-15 ¢/gal.
- ♦ **Crown Iron Works Co.** – This Minnesota based company has developed a dry fractionation and corn oil extraction system (Crown solvent extraction and oil refining system). The fractionation system is a combination of de-germinators, aspirators, screeners and roller mills in sequence to refine a germ and starch stream from whole corn. ICM has recently agreed to have Crown Iron Works as their preferred technology provider.

- ♦ **Poet-BFRAC / Satake Corp.** – There are several ethanol facilities currently using Poet’s Bfrac system. The resulting DDGS created from this system are marketed as Dakota Gold HP.
- ♦ **FWS Technologies** – FWS Technologies is a Canadian based company that has developed and patented a dry fractionation system they call “FWS Fractionation System”.
 - Yields: germ = 4.4 lbs/bu (8%); bran = 3.4 lbs/bu (6%); endosperm = 48.2 lbs/bu (86%); DDGS = 12.5-13 lbs/bu
 - Crude protein content of DDGS = 35-37%, fat content = 6.5%; ash = 3.8%; and NDF = 21%
 - Starch loss = 5%; ethanol yield 2.66 gal/bu
 - Capacity increase = 12%
 - Capital cost ~ \$10 million for a 57 mmgy ethanol facility
 - Increased net income is estimated to be ~25¢/gal

MOR Technology’s MOR Frac+

MOR Frac+ is promoted as a "second generation fractionation" process with the product separation and co-product quality advantages of wet fractionation technologies and the lower capital and operating costs typical of dry fractionation technologies. The process utilizes parts of MOR’s original dry separation technology at the front of the process and then uses various wet milling steps to further refine and separate the products. In this way the original MOR technology is combined with Corn Value Products’ wet separation technology, HydroMilling.

The company claims that rather than having to sell the “dirty germ” into the animal feed market and receive lower than typical DDGS prices, as is the concern with dry fractionation systems, their system produces a high quality germ that exceeds wet milling germ specifications (germ oil yield is 40-45%), which can be sold as food-grade. Additionally, the company claims that compared to the dry fractionation systems, their technology results in lower starch loss (less than 2%), near zero sugar loss, does not require additional water use, and requires fewer additional nutrients. The DDGS produced also has a higher protein content (58+ %) than that produced from dry fractionation and even some wet fractionation systems. In comparison to wet fractionation systems, the company claims that their process produces a higher quality germ, uses less energy and water and requires less capital.

The MOR system is 20-40% more expensive than the average fractionation system, at a cost of about \$35 million for a 50 mmgy ethanol facility, but MOR claims that the payback period is shorter.

“In a recent analysis of a typical 55 mmgy plant operating over the past year, MOR’s fractionation design could have generated an additional \$14 million in net income over this span or an average of \$0.28 per nameplate

gallon²³. Put another way, when ethanol sells for \$1.60/gal, a producer's breakeven price for corn may be close to \$3.70/bu. With MOR's system, however, the breakeven price is increased to \$5.00/bu." (*Trade and Industry Development*)

MOR also offers an additional technology package whereby the CO₂ produced from the ethanol facility is captured and converted to supercritical CO₂, a solvent which is then used to remove the corn oil from the germ. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products including un-degraded meal with high protein digestibility; and has an accompanying refining technology to extract and refine the oil in one step.

MOR states that the \$0.28/gal increase in profit generated from using MOR's fractionation system could be increased by an additional \$0.10/gal as food markets are maximized and the CO₂ oil extraction process is added.

According to an April 2009 article in *Ethanol Producer Magazine*, "MOR Technology doesn't have its patent-pending system installed in any ethanol plants yet, but the company has a pilot fractionation plant in the SEMO Mill in Scott City, MO.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to front-end fractionation technology development for the Minnesota corn industry.

²³ MOR claims that this 28 cent/gallon estimate is based off of fairly conservative values for co-products, "recognizing that some are newer and it may take time to establish values (*Ethanol Producer Magazine*, April 2009).

Table 16: SWOT – Front-End Fractionation

<u>Strengths</u> ▪ Large market potential - o Size of ethanol industry - o Potential impact on ethanol margins ▪ Strong institutional support ▪ Certain individual technologies have already been proven at commercial scale. ▪ Increases plant throughput/capacity ▪ Reduces greenhouse gas emissions ▪ Under the RFS as amended in 2007, this technology would help new or expanding ethanol facilities meet greenhouse gas reduction requirements. ▪ Risk mitigation - o More than two revenue sources - o Increased flexibility ▪ Corn oil is favored relative to other oils in certain foods as it does not require partial hydrogenation which results in trans fats.	<u>Weaknesses</u> ▪ Depending on the individual technology, capital costs could be 17-70 ¢/gal. ▪ Reduced yield due to starch loss – more so with dry than wet fractionation technologies ▪ With dry fractionation – “dirty germ” may become a problem – extraction facilities don’t want it and on-site extraction costs can be uneconomical. ▪ Need to find an oil extraction facility to extract the oil. ▪ If oil is extracted on site - oil marketing issues may arise. ▪ Greater marketing capabilities are required to handle multiple product streams – weakness for facilities lacking such skills or opportunities.
<u>Opportunities</u> ▪ High vegetable oil prices ▪ There is still room for process improvements ▪ There are several developments being made regarding new uses for fiber. ▪ A cap and trade system would further improve process economics. ▪ If EPA grants an allowance for an ethanol blending up to 15%, ethanol production has room to increase. ▪ Growing vegetable oil demand stemming from population growth and biodiesel industry. ▪ Benefit for facilities with the greater marketing capabilities required to handle multiple product streams. ▪ Technology offers a potential advantage for existing ethanol producers – helps keep existing infrastructure investments profitable.	<u>Threats</u> ▪ Low vegetable oil prices ▪ Tight capital markets ▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall.” ▪ If all ethanol facilities incorporated the technology, co-product values will be depressed. ▪ High protein, low fiber, low fat DDGS may not be valued at a premium to traditional DDGS, particularly in monogastrics.

F. 3-Hydroxypropionic Acid (3-HPA)

1. Product/Technology Overview

3-Hydroxypropionic acid (3-HPA) is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, plastics and moldings, fibers and resins, composites, adhesives, coatings, aliphatic polyesters and copolyesters and disinfectants. One of the most promising aspects of this building block chemical is not only the current petrochemical markets which it could potentially replace, but also the new and unique chemical properties it would bring to the market. Given its potential, it was identified by the U.S. DOE in 2004 as one of the top 12 chemicals from biomass sugars and syngas.

Unlike some of the other building block chemicals, there are no petrochemical production routes to 3-HPA. However, many of the derivative chemicals that can be produced from 3-HPA are now commercially produced from fossil fuel feedstocks. 3-HPA can be converted into a variety of high-value chemicals, including acrylic acid, 1,3-propanediol, malonic acid, acrylamide, methyl acrylate, acrylonitrile, propiolactone, and ethyl 3-HPA. Table 17 provides an overview of potential derivatives and applications of 3-HPA, as well as the companies/institutions involved in its development.

Table 17: 3-HPA – Derivatives, Applications, and Institutions/Companies Involved

Derivatives ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/Companies Involved ¹
- 1,3-Propanediol - Acrylic Acid - Methyl Acrylate - Acrylamide - Malonic Acid - Ethyl 3-HP - Propiolactone - Acrylonitrile	- Solvents - Plastics and moldings - Fibers and resins - Composites - Adhesives - Laminates, floor polishes, paints and coatings - Aliphatic polyesters and copolyesters - Wastewater treatment, gel electrophoresis, papermaking, ore processing, and the manufacture of permanent press fabrics. - Vitamins - Disinfectant; has been used to sterilize blood plasma, vaccines, tissue grafts, surgical instruments, and enzymes.	- Cargill² - Codexis - Pacific Northwest National Laboratory - Novozymes - U.S. Department of Energy - Qingdao Institute of Biomass Energy and Bioprocess Technology (China) - Perstorp

Source: Informa Economics

1/ Not an exhaustive list

2/ Recently, Cargill has said that they have decided not to further pursue the development of 3-HPA

2. Market Potential

The market potential for 3-HPA lies in the numerous applications for which its derivatives can be used. Acrylic acid is the derivative that is currently receiving the most attention, as it is a high value, high volume chemical used in a wide array of products, such as plastics, fibers, coatings, adhesives, paints, and superabsorbent polymers²⁴. Currently, acrylic acid is primarily produced by oxidation of propylene, a petrochemical feedstock. The acrylic acid market is approximately 3 million metric tons²⁵, with almost half of this going toward the production of glacial acrylic acid for superabsorbents, which is largely used to produce personal care items such as diapers (more than 1 million tons annually)²⁶. Additionally, the acrylic acid market grows approximately 4% per year²⁶. According to ICIS Pricing, the August 2008 acrylic acid price was \$1.10-1.15/lb.

According to an August 2008 ICIS market report, the acrylic acid market is growing at an average annual rate of 3.4% (2002-2007). The report also stated that 55% of the acrylic acid is used to produce acrylate esters, which are used primarily in architectural and industrial coatings, but also in adhesives, paper and leather coatings, polishes, carpet backing compounds, and tablet coatings. Forty-two percent of the acrylic acid produced is used to make polyacrylic acid and salts, with approximately 83% of this being used to make superabsorbents (ICIS). However, according to their market report, this market is now saturated. Yet, they identified “soaker pads” used in food packaging for poultry, meat, fish, fruits and vegetables as a new market application.

Acrylamide is another derivative that can be produced from 3-HPA. Acrylamide, which is classified as a resin, is used to synthesize polyacrylamides which are used as water-soluble thickeners. Applications include: wastewater treatment, gel electrophoresis, papermaking, ore processing, and the manufacture of permanent press fabrics. According to a 2003 report by the DOE, cited on the Wisconsin Biorefining Development Initiative’s website, the market for acrylamide derivatives (e.g., polyacrylamide, styrenebutadiene latex, acrylic resins, and other comonomers) is 206 million pounds per year, at a market price of \$1.76-1.86/lb.

3. Profiles - Companies & Research Institutions

Cargill, Codexis, Pacific Northwest National Laboratory and Novozymes

Cargill, along with Codexis and the Pacific Northwest National Laboratory (PNNL), have developed a bioprocess to produce 3-HPA which converts glucose or other carbohydrate sources into 3-HPA using a multi-step enzymatic reaction within the

²⁴ Superabsorbent polymers were mentioned as a large potential market for starch derived products during an interview with USDA, Agricultural Research Service.

²⁵ 2005 acrylic acid market estimates ranged from 2.99 million MT (DOE) to 3.1 million MT (Cargill).

²⁶ Source: Cargill. January 14, 2008 press release

cells of a microorganism. Cargill already has patents related to its biobased 3-HPA production process.

In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HPA, supported by a \$1.5 million matching cooperative agreement from the DOE. At the time of the announcement, the companies said they expected their technology to produce 3-HPA and its derivatives, such as acrylic acid, to be ready in 5 years (2013).

According to a 2005 DOE presentation, acrylic acid production via this biochemical route could result in an advantage of more than 5 ¢/lb over propylene oxidation for a Midwest plant (West Texas Intermediate crude oil 2005 average = \$56.5/bbl).

However, according to an interview with Bill Brady, director of media relations for Cargill, the company has recently decided not to further pursue the development of 3-HPA. According to Brady, this decision was not a result of recent economic conditions, nor a reflection on 3-HPA's market potential, but rather, they did not feel that given their core area of expertise that they would be able to bring the technology to commercialization within a reasonable time frame. Such a response may indicate that this product/technology may be more of long term prospect.

Perstorp

According to *Chemical and Engineering News*, Perstorp, a Swedish based specialty chemical firm, has a five year project to study the manufacture of natural raw-materials based 3-HPA.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to 3-HPA technology development for the Minnesota corn industry.

Table 18: SWOT – 3-Hydroxypropionic Acid

<u>Strengths</u>	<u>Weaknesses</u>
▪ Large market potential ▪ Technology to develop 3-HPA already exists. ▪ Green process that provides an alternative to petrochemicals	▪ The largest source of institutional support behind 3-HPA has recently decided not to further pursue its development. There is no word yet if their partners, Novozymes or PNNL, will continue. ▪ Technology to develop derivatives from 3-HPA is still being developed. ▪ Not yet proven at a commercial scale. ▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.
<u>Opportunities</u>	<u>Threats</u>
▪ High crude oil prices ▪ Might be an opportunity for a company/institution to further build upon the intellectual foundation already established by Cargill. ▪ In addition to acrylic acid, other high value, high volume chemical derivatives could also be developed. ▪ First mover advantage allows early market entrants the opportunity to capture premium prices in higher value-added markets. ▪ “Green product” marketability for chemical product applications (e.g., solvents) – may command small premium in niche markets/products. ▪ Biobased products could help meet LEED certification requirements. ▪ Growing world demand for plastics and other biobased products. ▪ Biobased products may qualify for the USDA BioPreferred program.	▪ Low crude oil prices ▪ High feedstock costs ▪ Biobased 1,3-propanediol is already produced at a commercial scale. It is unclear as to whether its production via 3-HPA could be economically viable in the future. ▪ Tight capital markets ▪ Cargill may be unwilling to share intellectual property – outside company/institution would have to “reinvent the wheel.” ▪ Favorable economic competitiveness of non-corn based 3-HPA.

G. Succinic Acid

1. Product/Technology Overview

Succinic acid is a building block chemical that can be used to produce many other commodity and specialty chemicals used in a wide array of product applications, including solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics (see Table 19). While succinic acid is currently commercially produced via petrochemical production routes in small quantities, biobased production routes are currently being developed by numerous companies and research institutions. If a technology is developed and proven at commercial scale to produce biobased succinic acid that is cost competitive with similarly functioning petrochemicals, the potential world market for this four carbon dicarboxylic acid is in excess of \$1 billion per year.

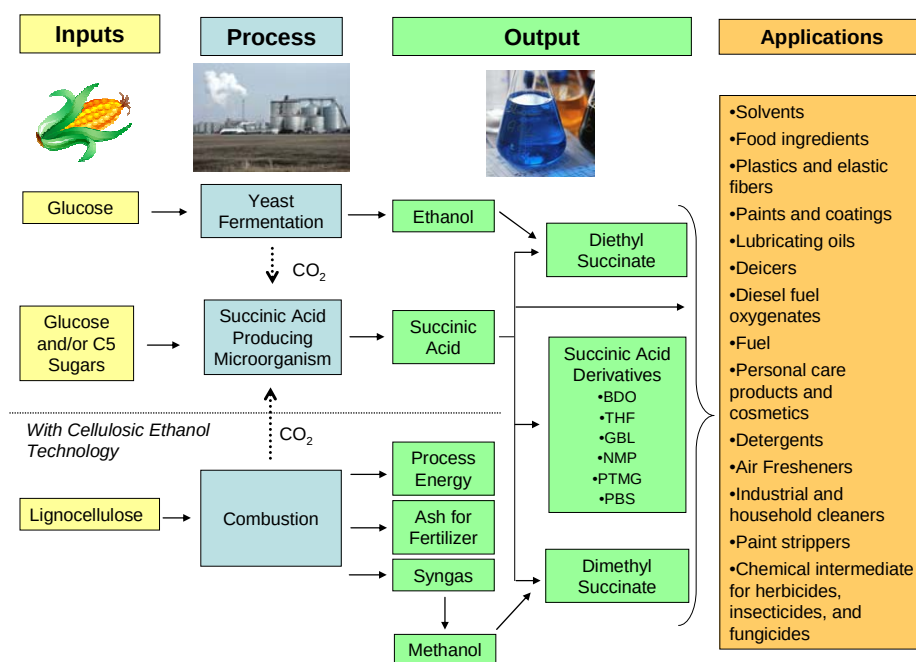
In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO₂, leading to what some claim to be as a carbon negative process. While there are various renditions of possible succinic acid biorefinery concepts, Figure 22 illustrates one such concept. Biobased succinic acid is produced by converting the glucose and/or five carbon sugars from a variety of possible feedstocks, including corn, using a specific succinic acid fermenting microorganism and CO₂. Once succinic acid is produced, a variety of other chemicals can then be derived, each with their own list of potential market applications.

Table 19: Succinic Acid – Derivatives, Applications, and Institutions/Companies Involved

Derivatives ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/Companies Involved ¹
- 1,4-Butanediol (BDO) - Tetrahydrofuran (THF) - γ-Butyrolactone (GBL) - 2-Pyrrolidinone - N-Methyl Pyrrolidone (NMP) - Polytetra-methylene Glycol (PTMG) - Poly-Butylene Succinate (PBS) - Diethyl and Dimethyl Succinate (Succinic Acid + Ethanol/Methanol)	- Solvents - Food ingredients, flavors - Plastics and elastic fibers, including Nylon-4,6; films, sheets, filaments, laminates, molded foam products, and injection-molded products - Paints and coatings, including as a resin solvent in wood stains and varnishes - Lubricating oils, engine coolants and deicers - Diesel fuel oxygenates - Personal care products and cosmetics - Detergents, air fresheners and household cleaners - Automotive and industrial cleaners - Paint strippers and graffiti removers - Chemical intermediate for herbicides, insecticides and fungicides	- Agro Industrie Recherches et Développments (ARD), France - DNP Green Technology - Bioamber (JV: DNP and ARD) - US Department of Energy - National Research Council of Canada Biotechnology Research Institute - Rice University - Roquette and DSM - University of Georgia - Toyota Tsusho Company, Japan (shareholder of Bioamber) - Michigan State University, Michigan Biotechnology Institute - BioEnergy International (Myriant Technologies) - Mitsubishi Chemical Corporation

Source: Informa Economics

1/ Not an exhaustive list

Figure 22: Succinic Acid Biorefinery Concept

Source: Informa Economics

2. Market Potential

The potential of succinic acid has been recognized by many countries and was identified by the DOE in 2004 as one of the top 12 chemicals from biomass sugars. Furthermore, this chemical can be used to produce other top 12 chemicals.

Succinic acid is currently commercially produced via petrochemical feedstocks (e.g., n-butane via maleic anhydride). Worldwide market estimates for the current succinic acid market vary widely, from 15,000 MT/yr to 50,000 MT/year. Yet, while estimates of the current market size vary from one source to another, industry representatives consistently agree that the potential for this market is much larger.

- In a 2007 article in *Biomass Magazine*, Susanne Kleff, a senior scientist for MBI International, stated that the market potential for biobased succinic acid was well over 100 times its current market of 15,000 MT/year.
- A 2008 USDA report, "U.S. Biobased Products Market Potential and Projections Through 2025," which Informa and MBI International were involved in writing, stated that the succinic acid market could "easily exceed \$1 billion per year by 2015."
- Dilum Dunuwila, vice president for business development at Bioamber, a biobased succinic acid technology developer, believes that succinic acid could potentially become a \$50-70 billion market in 10-20 years.
- According to the website of BioEnergy International, another biobased succinic acid technology developer (which has recently formed Myriant Technologies to develop biobased products), the total immediate addressable market for succinic acid is in excess of \$7.2 billion.

Current petrochemical production processes for succinic acid and its derivatives are not cost competitive with other petrochemicals, and thus, succinic acid is currently a high cost chemical that serves only in niche market applications. However, if a cost competitive biobased production route for succinic acid were developed, succinic acid could potentially serve as a replacement or partial replacement for many petrochemicals currently on the market. One such chemical in which succinic acid could potentially serve as a partial replacement is maleic anhydride, a chemical with a current global market of about 1.65 million tons (Kleff, 2007). However, succinic acid is not suitable for all maleic anhydride applications. Succinic acid could also serve as a potential replacement for other petrochemicals, including 1,4-butanediol (BDO), a chemical with a 1.2 -1.4 million MT/yr market, as well as adipic acid, a 2.4-2.8 million MT/yr market (Dunuwila, personal communication). Other derivative markets include tetrahydrofuran (THF), γ -butyrolactone (GBL), 2-pyrrolidinone, N-methyl pyrrolidone (NMP), polytetramethylene glycol (PTMG), poly-butylene succinate (PBS), and diethyl and dimethyl succinate (succinic acid + ethanol/methanol). Potential market applications for these chemicals include, but are not limited to, solvents, coatings, adhesives, plastics, fibers, lubricating oils, diesel fuel oxygenates, personal care products and cosmetics (see Table 19).

3. Profiles - Companies & Research Institutions

There are several companies and research institutions currently developing biobased production routes to produce succinic acid and its derivatives from a variety of renewable feedstocks containing sugar (see Table 19). The majority of the research focus has been concentrated on developing higher yielding microorganisms. Yet, there has also been significant effort directed toward reducing downstream processing costs. Many of the succinic acid producing microorganisms produce at least some quantity of by-products (e.g., acetic acid, formic acid, lactic acid and pyruvic acid) that must be removed/separated from the succinic acid. In a 2008 literature review of succinic acid, Bechthold et al. stated that the “downstream purification cost for fermentation-based processes normally amounts to more than 60% of the total production costs.”

DNP Green Technology and ARD - Bioamber

DNP Green Technology has partnered with Agro Industrie Recherches et Développments (ARD) to form Bioamber, with Toyota Tsusho Corporation as a strategic shareholder. The company also has ongoing relationships with the DOE, Oak Ridge National Laboratories, Michigan State University, and Biotechnology Research Institute of Montreal. Bioamber is using a strain of *E. coli* developed by the DOE in the mid 1990s and has developed a technology for the separation and purification of succinic acid. The current strain of *E. coli* can be used to produce succinic acid from glucose and 5-carbon sugars. Additionally, if cellulosic ethanol technologies are developed to where 6-carbon sugars from wood chips can be economically produced, the *E. coli* strain will be able to use this sugar form as well. However, sucrose must first be hydrolyzed before it can be utilized.

Bioamber claims to be the “first company to successfully develop a commercially viable technology for the production of succinic acid by fermentation of various renewable feedstocks,” claiming to be 2-3 years ahead of their competition. According to Dunuwila, Bioamber’s succinic acid technology is cost competitive with petrochemically produced succinic acid, and is close to being competitive with petrochemical alternatives at \$65/barrel crude oil, at the demonstration scale. The company currently has a pilot facility in France and construction of its 2,000 MT/yr, \$27 million demonstration facility is already underway. The facility will be integrated with a wheat refinery for glucose, utilities, and waste handling and can utilize CO₂ from the 90 mmgy ethanol plant and hydrolyzed sucrose from the sugar beet plant from the existing biorefinery in Pomacle, France. Production from this facility is expected to come online in the fall of 2009. Bioamber intends to license out its 1st turn-key solution packages in 2010 and claims that commercial-scale biobased succinic acid production will be reached in 2011/2012. In terms of what feedstock will be used – whichever sugar source is most economical – the company is taking a regional approach.

The company's development efforts are currently focusing on improving their current technology through yield improvements and through purification improvements, as well as developing direct fermentation routes to succinic acid derivatives. Recently, as of May of 2009, DNP announced a scientific agreement with the National Research Council of Canada Biotechnology Research Institute (NRC-BRI) to develop a second-generation microorganism for biobased succinic acid production.

Roquette and DSM – SUCCINIUM Project

Roquette and its partner DSM are also focused on commercializing a biobased succinic acid production process. Roquette and DSM have announced the SUCCINIUM project under the BioHub program. BioHub, which is subsidized by OSEO Innovation, is a development program of new cereal bio-refineries led by Roquette and seven other industrial partners: Arkema Chemists (France), DSM (Netherlands), Solvay (Belgium), Cognis (Germany), the road designer Eurovia (Vinci group), the company Sidel (specializes in bottling systems of polymers), and Tergal Industries (producer of polyethylene terephthalate). The SUCCINIUM project is related to the production of biosourced succinic acid by fermentation. Roquette has obtained rights to an E. coli strain developed by Rice University which claims a succinic acid yield close to maximum theoretical yields. Additionally, the company has licensed a succinic acid production technology using microorganisms from the University of Georgia. The company plans to have a demonstration plant in France of several hundred MT/yr operational by the end of 2009, and expects to reach large scale production by 2011/2012.

BioEnergy International

BioEnergy International, which has recently announced the formation of Myriant Technologies to house their biobased chemicals business and related intellectual property, has developed a biocatalyst to manufacture succinic acid. The company claims that its proprietary technology enables the derivation of five other DOE top 12 chemicals. According to the company's website, the company plans to begin commercial scale production of succinic acid in early 2010. However, according to 2008 company presentations, the technology appears to be 3-6 years away from commercialization. More detailed information was unavailable.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to succinic acid technology development for the Minnesota corn industry.

Table 20: SWOT – Succinic Acid

<u>Strengths</u>	<u>Weaknesses</u>
▪ Very large market potential ▪ The process consumes CO₂ ▪ Green process that provides an alternative to petrochemicals ▪ Economics are such that biobased succinic acid is close to being competitive with petrochemical alternatives when crude oil is ~\$65/barrel. ▪ Fermenting microorganisms can utilize 5 carbon sugars as well as glucose.	▪ Not yet proven at a commercial scale → expected to approach commercial scale production in 2011/2012. ▪ High downstream processing costs – purification and separation of succinic acid and process by-products. ▪ Not all of the derivatives can be produced from succinic acid at a cost that is competitive with petrochemical alternatives ▪ High capital cost requirements ▪ Distance from traditional chemical industry – infrastructure, knowledgeable personnel, and potential investors. ▪ Benefits from this technology are not limited to corn; other sugar feedstocks can also be utilized – will depend on regional economics.

<u>Opportunities</u>	<u>Threats</u>
▪ High crude oil prices ▪ Ability to co-locate with current corn processing facilities, including ethanol plants. ▪ First mover-advantage allows early market entrants the opportunity to capture premium prices in higher value-added markets. ▪ Technology is at an early stage of commercialization with opportunities for process improvements. ▪ A cap-and-trade system would improve process economics. ▪ “Green product” marketability – may command small premium in niche markets ▪ The development of cellulosic ethanol technologies can provide additional sugar streams for succinic acid production. ▪ Biobased products could help meet LEED certification requirements. ▪ Growing world demand for plastics and other biobased products. ▪ Biobased products may qualify for the USDA BioPreferred program.	▪ Low crude oil prices ▪ High feedstock costs ▪ Tight capital markets ▪ Favorable economic competitiveness of non-corn based succinic acid.

H. Zein Extraction

1. Product/Technology Overview

Various processes have been developed to extract zein protein from corn and corn by-products (e.g., DDGS). Zein is a high-value protein which can be used in a wide range of applications. Zein is not used extensively in human food products, despite being edible, due to its negative nitrogen balance and poor water solubility. However, this insolubility is what makes zein and its resins form tough, glossy, hydrophobic grease proof coatings that are resistant to microorganisms, heat and humidity.

Applications include:

- Specialty coatings for pharmaceutical tablets, candies, nuts, and paper products (e.g., glossy magazines) – serves as a water barrier
- Chewing gum
- Adhesives and binders
- Printing ink
- Cosmetics
- Fibers and textiles
- Paints and varnishes
- Resins and biodegradable plastics
- Edible moisture barrier on fruits and vegetables to extend shelf life
- Food coatings that reduce fat absorption
- Edible hay bale wrappers
- Used to mimic fat to replace 50-100% of the fat in mayonnaise, ice cream, and spreads.
- High-value bio-medical applications (e.g. tissue scaffolding used for skin regeneration). Because it is of plant origin and not animal, there is less concern of disease or virus issues. Only the high purity zein can be used for these applications.

Currently, zein can be extracted from corn gluten meal, a by-product of the wet milling process. However, current extraction and purification technologies are such that the price of zein limits current market applications. However, there are several technology companies/institutions currently working to lower extraction and purification costs.

Approximately 75% of the proteins in corn are found within the endosperm (portion of the corn kernel that contains the starch used to make ethanol), and zein is the main protein within corn, accounting for 40-50% of the total corn protein. The zein protein can be extracted from the corn prior to fermentation or from the resulting DDGS co-product. The different companies/institutions pursuing the development of zein extraction technologies have varying approaches as to whether it is more economical for the dry grind ethanol facility to extract the zein prior to fermentation

or from the DDGS at the back-end of the process. Each of their technologies and approaches are profiled in section IV.H.3.

In addition to zein extraction, most of these processes also extract corn oil, and some processes are integrated fractionation technologies which combine the zein extraction technology with other corn fractionation technologies, thus producing a whole suite of co-products, including corn oil, bran/fiber, zein proteins, and ethanol. The combined value of these products is higher than the value of the DDGS produced from a typical dry grind ethanol facility.

2. Market Potential

Zein is currently a high value product. According to zein extraction technology developer, Cheryan Munir of the University of Illinois, the current cost of purified zein is \$9-32/lb. Another technology developer based in the Netherlands quoted zein prices in a June 2009 presentation at \$4.54-18.14/lb, and a U.S. technology developer (Bio Process Innovations) is using a price of \$7/lb in its own economic analysis. All sources note that this price range depends largely on the purity of the zein protein, and that at these current prices, it is uneconomical for the use in many market applications, such as biodegradable plastics. Prices would likely come down toward the bottom end of the range if large-scale zein extraction at dry-mill began to take place.

However, current zein prices, even at the low end, provide significant economic incentive for technology developers to create an economically viable process that corn-to-ethanol facilities can use to extract zein from corn or from DDGS. According to Bio Process Innovations, the yield of zein proteins from their process is 0.8 lbs/bu. At a zein price of \$7/lb, an ethanol price of \$1.55/gal, and a ethanol yield of 2.7 gal/bu, the revenues from zein exceed that of ethanol, and most certainly compensate for any loss in DDGS revenue (see Table 21).

Table 21: Comparison of Potential Zein, Ethanol, and DDGS Revenues

Product	Price	Yield	Gross Revenue
Zein Protein*	7 \$/lb	0.8 lbs/bu	\$ 5.60
Ethanol	1.55 \$/gal	2.7 gal/bu	\$ 4.19
DDG	125 \$/ton	17 lbs/bu	\$ 1.06

*Yield and price - Bio Process Innovations

The big question is cost. While a December 2008 article in *Ethanol Producer Magazine* stated that there is currently no cost-effective way to recover and purify zein protein, there are several companies and research institutions working to develop technologies to bring these extraction and purification costs down.

3. Profiles - Companies & Research Institutions

University of Nebraska, Lincoln

University of Nebraska, Lincoln has patented a process to extract and isolate zein and oil (if desired) from DDGS or corn using an acidic extraction solution. While either cereal grains or cereal grain by-products can be utilized, technology developers argue that using by-products is a less expensive production method. The zein obtained from this process is said to be suitable for fibers, films, and binders in paints. They also claim that their new acidic extraction technique improves the quality of the zein product.

Purdue University

Purdue University has patented a technology which uses alcohol to extract the zein and oil from the corn prior to fermentation. Then, the insoluble bran fiber and gluten meal are separated out before the remaining solution of starch and sugars is fermented into ethanol. Developers claim that the process uses 1/3 less water than traditional dry grind ethanol plants and produces no wastewater streams, while increasing ethanol yields and reducing throughput time. They also claim that the process reduces operational costs compared to a traditional ethanol plant.

Prairie Gold / University of Illinois

Prairie Gold is the developing and commercializing company for a corn oil and protein extraction process (COPE) developed by the University of Illinois which uses ethanol to extract oil and zein from corn prior to fermentation and then membrane technology to separate, isolate, and purify the zein. This membrane technology also allows for the recycling of the ethanol solvent without substantial evaporation losses, which currently limit other zein extraction processes. According to the extraction technology developer, Cheryan Munir, preliminary economic analysis shows a \$2-4/bu net income increase without any additional materials required (process requires corn and recyclable ethanol).

Prairie Gold claims that because the zein has not been exposed to the steeping chemicals and processing steps used in wet corn milling, where it can be extracted from corn gluten meal, it is in a more “natural” state and has better functionality for certain applications. The process can produce several grades of zein ranging from 50-90% protein (dry basis) and with varying amounts of color.

The company has formed collaborations with KATZEN, an ethanol plant technology and design company, to integrate the process into dry grind ethanol plants.

According to Munir, the insolubility of zein proteins limit their functionality in human food products. However, the University of Illinois has developed a unique two phase process involving an organic phase enzyme reaction followed by an aqueous phase enzyme reaction to improve the water solubility of zein proteins from 0-99%.

USDA, ARS / Global Protein Products

The USDA, ARS is also working to develop cost efficient methods to extract and purify zein from corn and corn by-products, as well as investigating new uses for zein. Recently, ARS researcher, David Sessa, has developed a cost effective method to purify zein. Global Protein Products, which currently sells zein protein products, plans to use this process, taking it from pilot to commercial scale. The company notes that there is industrial demand for the product.

Prior to this ARS process, activated carbons were used to bind and trap the compounds causing zein's color and odor (limiting its use in a variety of products, including biomedicines). However, this process results in a 37% to 95% loss in zein, thereby making purified zein very costly. ARS's process uses zeolites, silicate, or clay-based particles to act as molecular sieves, reducing loss to 25%.

Iowa State University

Iowa State University has evaluated aqueous ethanol, alkaline-ethanol, and aqueous enzyme treatment methods for extracting oil and protein from distillers grains. Study results indicated that enzymatic and alkaline-ethanol extraction methods were equally effective, while the basic alcohol extraction method was less effective.

Zea Fuels

Netherlands based Zea Fuels is working to improve small scale bioenergy solutions with their ethanol and biogas system that isolates zein proteins using a proprietary process. Lab studies indicate that their process can reduce the price of zein more than 400%, going from €5-45/kg to €1-5/kg.

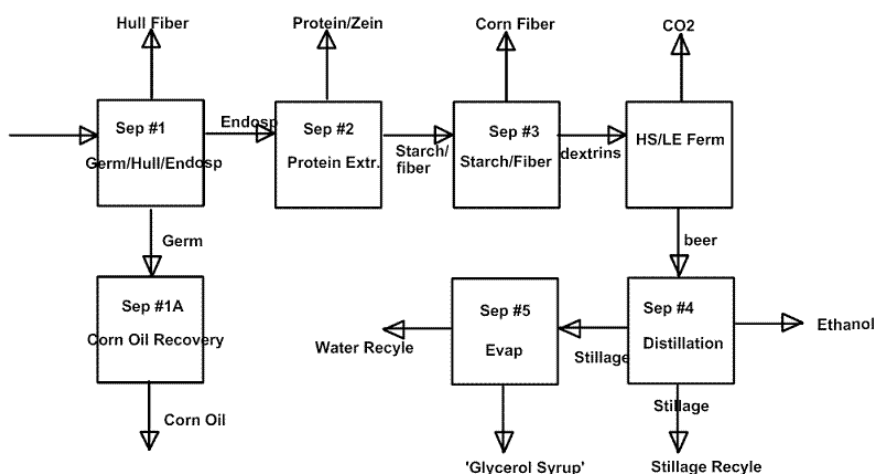
Bio Process Innovation, Inc

Bio Process Innovation, Inc (BPI) is marketing a technology they refer to as "High Value Corn" (HV Corn), whereby the corn germ is separated out using Cereal Process Technologies' front-end fractionation system and then extracted using a proprietary recovery system. Then, proprietary processes are to used extract the zein from the endosperm. In the end, their process produces six products: corn germ/oil, corn bran, zein proteins, nutritional proteins²⁷, corn fiber, and ethanol. According to the company's website the HV Corn process increases gross sales by a factor of nearly 3.

BPI is currently working on two projects, one in Iowa and the other in Indiana. However, both are still in the capital raising stages.

Figure 23 illustrates the concept of the HV Corn process, integrated with other proprietary processes.

²⁷ The residual non-soluble proteins that remain after extraction of zeins.

Figure 23: Bio Processing Innovation's HV Corn Process

Source: Bio Processing Innovations, Inc.

4. SWOT

The following is a summary of the strengths, weaknesses, opportunities and threats to zein extraction technology development for the Minnesota corn industry.

Table 22: SWOT – Zein Extraction

<u>Strengths</u> ▪ Moderate market potential - o Strong potential impact on ethanol margins, particularly for 1st movers ▪ Moderate institutional support ▪ High zein prices ▪ Some claim that the process reduces wastewater ▪ Some claim that the process increases ethanol yields and reduces throughput time	<u>Weaknesses</u> ▪ Loss of distillers grains revenues ▪ High purification costs ▪ Current economic feasibility is questionable. ▪ Not yet proven at a commercial scale
<u>Opportunities</u> ▪ Technology offers a potential advantage for existing ethanol producers – helps keep already existing infrastructure investments profitable. ▪ First mover-advantage allows early market entrants the opportunity to capture premium prices in higher value-added markets. ▪ Technology is at an early stage of commercialization with opportunities for process improvements ▪ Risk mitigation - o More than two revenue sources - o Increased flexibility ▪ Development of front-end fractionation technology. ▪ Could help provide an alternative use of distillers grains, particularly as distillers grains markets become saturated. ▪ “Green product” marketability ▪ Biobased products could help meet LEED certification requirements. ▪ Growing world demand for plastics and other biobased products. ▪ Biobased products may qualify for the USDA BioPreferred program. ▪ If the EPA grants an allowance for an ethanol blending rate of up to 15%, this will facilitate an increase in ethanol production.	<u>Threats</u> ▪ Tight capital markets ▪ If the EPA does not grant an allowance for an ethanol blending rate of up to 15%, ethanol production volumes will be constrained by the current 10% “blend wall.” ▪ If a number of ethanol facilities incorporated the technology, zein values will decrease.

Appendix A: Phase I – Corn Products/Technologies

Initially, more than 100 “emerging” corn products and/or technologies were identified. This appendix lists the products/technologies which were each reviewed based on their demand/market potential, economic feasibility, stage of development, and strength of institutional support. While Informa attempted to be as complete and as accurate as possible in its evaluation of each of these products/technologies, it is acknowledged that given the lack of perfect information about all four assessment criteria for all 100+ products and technologies, some products and/or technologies may have been under/over estimated. However, through interviews with industry experts, confirmation was given to final selections.

Products/technologies presented within this section are grouped into the following categories:

- Improving Current Ethanol Production Economics
- Second Generation Biofuels
- Value-Added Chemicals from Sugars
- New Uses of Corn Cobs
- New Uses of Distillers Grains
- New Uses of CO₂
- Lignin Derived Products
- Other New Corn Uses/Products
- New Corn Varieties Designed for Non-Fuel Applications

It is noted that some products/technologies may apply to more than one category, yet they are only listed once. For example, some of the technologies listed under “Improving Current Ethanol Production Economics” may also be applied to cellulosic ethanol production processes; new uses of distillers grains and new uses of CO₂ can also be considered technologies under “Improving Current Ethanol Production Economics”; lignin derived products could also be classified as cellulosic ethanol technologies; and butanol is listed under second generation biofuels, but is also a “Value-Added Chemical from Sugar”.

Note that the stage of development was divided into four distinct phases as shown in Table 23.

Table 23: Development Stage

Well Established	Initial Commercialization	Early Development Stage	Research/ Conceptual Stage
			

Table 24: Improving Current Ethanol Production Economics

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Feed Stock Preparation Technologies (Milling, Liquefaction, and Saccharification)			
Static, Hydrodynamic Cavitation	A patented process designed to improve ethanol processing efficiency and yield. The goal is to improve starch recovery by 2-5%. Grain and liquid medium flows through a controlled flow cavitation apparatus at a velocity capable of generating a hydrodynamic cavitation zone where the grain size can be reduced. Powerful cavitation forces fracture the particles, resulting in high surface area dispersions. This high surface area causes faster hydrolysis from starch to sugar. This is a continuous flow process which any ethanol facility can be retrofitted to include. Company claims include: high throughput, accelerated reaction times; high capacity, small footprint system and simplicity of design; scalable system; energy-savings; high conversion efficiency; and lower capital, maintenance, and spare part costs.	- Arisdyne Systems, Inc. (Controlled Flow Cavitation™) - Delta-T	
Ethanol Reactor Tower	The ethanol reactor tower (ERT) is positioned next to the liquefaction tank so that the slurry passes through the ERT prior to liquefaction. Highly atomized steam is used to cause cell disruption and to activate more starch. This decreases liquefaction time and heat, reduces amylase requirements by 20-50%, and ultimately produces a reported 10% higher ethanol yield. The company claims that the technology could amount to a \$500,000 a year savings.	- Pursuit Dynamics	
Ultrasonic Process	The ultrasonic technology is applied to the cooked corn slurry, resulting in a more efficient breakdown of starch and ultimately higher ethanol yields.	- FCStone Carbon LLC - Iowa State University	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Enzyme Development	Research is ongoing to find and develop enzymes for liquefaction and saccharification with similar optimal temperature and pH requirements, so as to reduce the cost and time currently associated with having to make temperature and pH adjustments between the liquefaction step and the saccharification step, where optimal pH and temperatures differ between amylase and glucoamylase.	- National Research Laboratory for Functional Food Carbohydrate and Center for Agricultural Biomaterials - Seoul National University	
Granular Starch Hydrolyzing Enzymes (GSHE)	GSHEs help ferment starch even when it is still crystalline in nature and reduces the use of heat in the dry grind process. Converts the starch without the "cooking" step, thus reducing energy consumption. May also result in higher ethanol yields, reduces microbial contamination, and lowers enzyme requirements.	- University of Illinois - POET (BPX™ Process) - Genencor (Stargen) - Novozymes	
Fermentation Technologies			
High Speed/Low Effluent Process	A patented process that allows near complete fermentation of 18-25% glucose to ethanol in 4-10 hours in continuous cascade or consecutive batch mode over extended periods of several to many months. Bio Process Innovation claims that the process increases the productivity of fermenters by a factor of 6-10 times without resorting to centrifugal cell recycling, it decreases effluent stillage by using a high degree of backset, decreases nutrient needs/costs, produces a clean 'beer' to take to the distillation column, produces a clean, high density yeast paste by-product with no need for centrifuges, reduces waste water/cleaning chemicals by eliminating the need for "cleaning in place" (CIP) of fermenters between batches, reduces operator/lab labor as the process is easily automated, and eliminates the need for yeast purchase/propagation.	- Bio Process Innovation, Inc	
High Gravity Fermentation	An experimental technology that would allow for higher ethanol concentrations during the fermentation process by using a highly concentrated mash. This process would lower the water required in the ethanol production process (up to 59%), which in turn reduces energy costs by 4% (Belcher, 2005), as there is less fluid to heat, cool and distill. Additionally the process would increase plant throughput. Tests have shown increased fermentation yields, but challenges still exist in overcoming tolerance issues.	- University, Tirupati, India - University of Sheffield, UK - Technical University of Denmark - Novozymes - University of Saskatchewan	
Yeast/Bacteria Developments			
More Tolerant Yeast	Research is ongoing to find or develop yeast strains with improved tolerance to higher temperatures, ethanol, and osmotic pressure. This would allow for faster throughput via faster reaction times and higher ethanol concentrations (limiting the toxicity issue). It would also reduce contamination issues. However, higher temperatures mean increased energy use and increased ethanol vaporization.	- Massachusetts Institute of Technology - Berlin University of Technology - Whitehead Institute for Biomedical Research	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Arabinose Yeast	NREL is working on designing unique biocatalysts to ferment arabinose, a major component in the available sugars from corn fiber, a residue of the corn-to-ethanol process, into ethanol. Research is ongoing to find a thermophilic (heat loving) bacteria to ferment the sugars rather than a yeast. This would allow for fermentation to occur at higher temperatures which would increase plant throughput through faster reaction time. One benefit of bacteria over yeast is that it is easier to genetically manipulate. However, there are several drawbacks of using bacteria, including increased by-product production, higher pH requirements, limited range of acceptable feed sugars, and low ethanol concentrations. There are several bacteria strains that have been considered, each with their own advantages and disadvantages.	- NREL - NCGA - Corn Refiners Association	
Thermophilic Bacteria	Low temperature fermentation results in lower energy usage and lower ethanol evaporation; however, with the lower temperatures, reaction times are slower and there is increased bacterial contamination. While these pros and cons must be weighed against one another, there are research efforts ongoing to develop "cold loving" yeast strains with improved performance in cold conditions over traditionally used yeast strains.	- Dartmouth College	
Lower Temperature Fermentation - Yeast	Rather than using freely suspended yeast cells, "yeast immobilization" refers to the use of immobilized cell reactors to constrain the volume of yeast to a defined volume, typically imbedded or bound to a solid support structure. These immobilized cell structures eliminate cell washout and the need for cell recycle, increases productivity as there is no constraint on feed flow rates, and allows for better overall control over the microbial environment. However, there are still several disadvantages, including mass transfer limitations which may slow cell metabolisms and reaction kinetics, and damage to the support structure can occur over time.	- Universitat Rovira i Virgili (Spain)	
Yeast Immobilization	One of the challenges facing both corn-based ethanol and cellulosic ethanol producers is that while the fermenting agent is producing ethanol, other unwanted acid by-products are also being produced which are difficult to separate out of the mixture. These contaminants also compete with the yeast for vital nutrients and decrease ethanol production efficiency. Traditionally, antibiotics are used to control contaminating bacteria; however, there is rising concern over the use of antibiotics and the resulting presence of residual material in distillers grains, not to mention the cost of these antibiotics. However, there are several novel alternatives to dealing with this contaminating bacteria issue.	- University of Melbourne (Australia) - Chinese Academy of Sciences - Universiti Sains Malaysia	
Contaminant Bacteria Reduction		(see below)	(see below)

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Inhibitory Organisms Detection Kit	This detection kit is designed to detect the presence of the acid-producing bacteria and yeast within the ethanol production process that produce acids such as lactic acid and acetic acid. These acids compete with the ethanol producing yeast <i>Saccharomyces cerevisiae</i> for vital nutrients, which in turn inhibit ethanol yields. This technology is different from the standard detection technology often used in the industry which only detects the acids themselves. This detection technology allows ethanol producers to take proactive measures to prevent the formation of these harmful acids.	- ETS Laboratories (Scorpions)	
Reactive Distillation	While inorganic catalysts have long been known as a method to produce valuable chemicals in the petroleum industry, its application on corn-based feed streams has been cost prohibitive due to challenges associated with separating the mixture of chemicals that are derived from a feed stream with multiple compounds. However, the "reactive distillation" process separates a mixed stream of different chemicals by treating that stream with a reactive chemical in the presence of a catalyst. This technology is designed to separate out these acids from the ethanol. This would allow an ethanol or cellulosic ethanol facility to be a biorefinery, producing more than just ethanol. For example, MSU researchers are currently focusing on the production of ethyl lactate from lactic acid.	- Michigan State University - National Corn Growers Association	
Hops (Contaminating Bacteria Reduction)	Recently, it has been shown that the natural acids of hops will stop the growth of certain contaminating bacteria well enough to avoid the use of antibiotics.	- BetaTec Hop Products - Universität Hohenheim Institut for Food Technology	
Distillation Technologies			
Alternative Ethanol Distillation Technologies	The separation of alcohol and water is typically a costly, energy intensive process, representing a significant portion of the overall energy use required by an ethanol facility. Traditionally, this separation is performed through a combination of steam distillation and a molecular sieve. However, there are various processes being developed whereby ethanol is removed during fermentation, reducing product inhibition and energy costs, and thereby also decreasing greenhouse gas emissions.	(see below)	
Vacuum Stripping	The fermenting vessel is coupled with a vacuum chamber which extracts, in-situ, the more volatile ethanol and allows for partial product removal.	- University of Illinois	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Gas Stripping	The fermenting broth overflowing from one stage to the next is contacted with a CO ₂ stream that entraps the ethanol. The ethanol is then removed when this gas stream passes across a reactor and through an absorption tower where it is contacted with water. The CO ₂ is then re-circulated. By using this process, the concentration of sugar in the product stream entering the fermenter is increased.	- Bio-Process Innovation, Inc	
Solvent (Liquid) Extraction	This approach removes the product that causes inhibition through an extractive biocompatible solvent that favors the migration of ethanol to solvent phase, a process known as extractive fermentation. However, it has been noted in one publication that this approach lowers solubility and results in a poisonous effect on yeast, thus restricting the development of this method.		
Membrane Separation	Membranes are used to filter the water/ethanol mixture during fermentation. The membranes are vapor phase separation units that allow the preferred permeation of water over other vapor components in a gas mixture.	- Vaperma (Siftek) - Whitefox Technologies Limited	
Esep	"ESeP is a modular, low-energy process for the recovery of ethanol from fermentation broth with an estimated reduction of up to 60% in both capital and operating costs versus conventional distillation. Use of non-stainless steel components also results in a substantial reduction in construction time". While a 60% reduction in energy consumption is estimated when incorporating the system into new ethanol and cellulosic ethanol plants, a 28% energy reduction and a 16 month payback period is estimated when retrofitting and existing ethanol plant.	- Trans Ionics Corp. (Esep)	
Supercritical Fluids	While the success of separating alcohol and water via supercritical fluids has been demonstrated for many years, these previous demonstrations have not been able to compete with the economics of traditional steam distillation methods or other proposed methods such as membrane separation. However, MOR Supercritical has applied their supercritical extraction technology ethanol dehydration, and claims a process that is scalable and cost-efficient relative to other proposed dehydration technologies.	- MOR Supercritical, LLC	
Low Energy Distillation Technology	A commercially demonstrated process whereby the concentration of 96% ethanol is allowed without the use of thermal energy, saving the facility in energy costs. The process uses "specially designed columns, packing, condensers, and reboilers to replace 12-15 lbs of steam required in distillation of a gallon of ethanol with 0.3 KW of electricity." The company claims that this process could save a 10 MMGY ethanol plant \$2-\$4 million a year.	- Liqua Ethanol	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Co-Product Technologies			
Enhancing Water Removal from Whole Stillage by Enzymes	The addition of cell-wall-degrading enzymes are added to the ethanol production process in order to reduce the amount of water bound within the wet grains. This allows for more water to be removed during centrifugation, reducing the time and energy required to dry the distillers grains.	- USDA, ARS - Washington University, St. Louis	
GlycosBio	GlycosBio has developed microorganisms that make high-value chemicals from lower valued co-product streams of existing industries, such as thin stillage from ethanol.	- GlycosBio - Rice University (original technology developer)	
Fungus Removal of Organic Material and Solids from Thin Stillage	Researchers have added a fungus to the thin stillage by-product of ethanol production. This fungus removes about 80% of the organic material and all of the solids, allowing the water and enzymes to be recycled. The remaining fungi can potentially be used as a high value feed supplement. Normally, because the solids can interfere with ethanol production, only about 50% of the thin stillage can be recycled back into the ethanol process, while the rest is evaporated and blended with the dried distillers grains. Researchers say that this process could reduce energy costs by as much as a third. It also reduces water consumption and saves producers enzyme costs.	- University of Hawaii - Iowa State University - Mycolnnovations Inc (MycMax)	
Anaerobic Digestion	Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas – a mixture of methane (50-70%), CO2 (30-50%), and trace amounts of H2, NH3, and H2S, which can then be used to reduce natural gas usage. This process reduces energy costs and greenhouse gas emissions and helps to conserve water.	- Washington University - University of Minnesota - USDA, ARS - Iowa State University - Rein & Associates (MN) - Biogasol - POET - University of Borås - Kwartha Ethanol	
Microwave Drying of Distillers Grains	Microwave drying technology is an alternative to conventional rotary drum gas dryers used to dry the animal feed co-product. This process uses industrial drying systems to dry and treat the feed co-product. While the microwave energy breaks down the structure of the cell walls, Cellencor's patented enzymes increase the value of the by-product feed, increasing the available energy of the feed. The process uses less energy than traditional dryers, reduces greenhouse gas emissions, improves water reclamations, and enhances the value of the animal feed co-product. This process has been field tested at both dry and wet mill ethanol facilities. The company claims that the process could save ethanol producers 20% or more in operating costs. The payback period for the technology was estimated to be 2-5 years (estimated in 2008).	- Cellencor- Corn Plus- Kwartha Ethanol	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Acetic Acid - Produced from Bottoms Fraction of Ethanol Distillation	A patented process designed to increase ethanol yield by taking the bottoms fraction from ethanol distillation, and through a combination of biochemical and synthetic conversion processes, produces acetic acid. Acetic acid can then be converted into ethanol using esterification and hydrogenation reactions.	- Zechem, Inc.	
Fractionation and Extraction Technologies			
Front-End Fractionation	There are several modified dry-mill front-end fractionation processes that separate the corn entering into the ethanol facility into three fractions: pericarp (bran/fiber), germ, and endosperm. The germ is the oil-bearing portion of the kernel. Revenue streams generated from this process include corn oil; high protein, low fat and fiber distillers grains; fiber and ethanol. Additionally, front-end fractionation allows for more efficient starch fermentation as non-fermentable products are no longer taking up valuable space in the fermenters, yet there is also some level of starch loss during fractionation. According to some technology developer claims, front-end fractionation can also reduce energy consumption and lower volatile organic compound emissions.	(see below)	(see below)
Modified Dry Grind Wet Fractionation	Wet fractionation technologies typically involve soaking/steeping the corn prior to fractionation. In general, the costs are higher than that of dry fractionation technologies, but the starch loss is lower and the quality of co-products is higher.	- Maize Processing Innovators & FCStone Carbon LLC (Quick Germ Quick Fiber) - Corn Value Products (HydroMilling™) - University of Illinois (E-Mill)	
Modified Dry Grind Dry Fractionation	Dry fractionation technologies typically separate the germ and fiber from the corn kernel mechanically without the need for soaking. In general, the costs are lower than that of wet fractionation technologies, but the starch loss is higher and the quality of co-products is lower	- University of Illinois (Dry Degerm Defiber Process) - Renessen LLC. (Extrax™ Processing System) - Delta-T/Ocrim (Dry Separation Technology™) - Poet / Satake Corp. (BFRAC™ Process) - Crown Iron Works (Crown Fractionation System) - Cereal Process Technologies	
MOR-Frac™ Plus ⁺ (Dry Fractionation, Wet-Mill Germ)	A "second generation fractionation" process with the product separation and co-product quality advantages of wet fractionation technologies (expected to generate less than 2% starch loss, germ oil yield is 40%-45% and crude protein of DDGS is > 58%) with lower capital and operating costs, closer to that of a dry fractionation technology.	- MOR Technologies (MOR-Frac™ Plus ⁺)	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Corn Oil Extraction/Separation (Front-End)	Processes whereby the corn oil is separated from the corn germ prior to fermentation.	(see below)	(see below)
Aqueous Enzymatic Extraction	An alternative oil extraction technology that does not use hexane or other hazardous solvents. This process uses an aqueous enzymatic oil extraction technology to separate the oil from enzymatically wet milled corn germ. Developers claim oil yields of 70-90%.	- USDA, ARS (Amazing Oil)	
Supercritical Carbon Dioxide Corn Oil Extraction	This system can also be coupled with MOR Technology's fractionation system (MOR-FRAC Plus+) to provide added value for ethanol facilities or as a stand alone facility to produce high quality, specialty oils, bioactive ingredients, or nutraceuticals. Rather than using hexane, MOR Supercritical's technology uses carbon dioxide as their only solvent in their corn oil and oilseed extraction system. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products including undegraded meal with high protein digestibility; and an accompanying refining technology to extract and refine the oil in one step.	- MOR Supercritical, LLC	
Zein Extraction	Various processes have been developed to extract zein protein from corn and corn by-products (DDGS). While most of these processes focus on extracting the zein prior to fermentation others concentrate on extracting the high-value protein from the back-end. In addition to zein extraction most of these processes also extract corn oil and some processes are further integrated fractionation technologies which separate out products such as bran and fiber. Zein is a high-value protein which can be used in a wide range of applications, including: specialty coatings for pharmaceutical tablets, candies, and paper products; chewing gum, adhesives and binders; resins and bio-plastics; printing ink; cosmetics; and high-value bio-medical applications. The purer the zein, the more high value food and pharmaceutical applications it can be used in.	- Prairie Gold (COPE) - University of Illinois - KATZEN - Purdue University - Bio Process Innovation, Inc - University of Nebraska - USDA, ARS - Global Protein Products - Iowa State University - Zea Fuels (Netherlands)	
Protein Separation - Chromatography	A method used to extract high-value protein from raw material, which can be used in the production of food additives and ingredients and in the healthcare industry. The process is already being used at industrial scale in the potato industry and at a large dairy cooperative in Australia that processes cheese whey. The company has been talking with corn processors and ethanol producers to explore the possibility of implementing this technology in these industries.	- Upfront Chromatography (Rhobust)	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Elusieve Process (back-end fiber recovery)	Process to recover the pericarp fiber at the back end of the dry grind process. Process involves elutriation and sieving, reducing the problem of using solely elutriation, a processes whereby non-fiber particles also get removed. This new process results in low fiber, high fat DDGS and a fiber co-product.	- University of Illinois (Elusieve Process) - USDA, ARS	
Corn Oil Extraction (back-end)	Basic corn oil extraction technology involves a centrifuge process to separate the oils from the corn stillage. By removing the oil from the distillers grains, the ethanol facility not only captures an additional revenue stream from the extracted corn oil, but also reduces their distillers grains drying costs and potentially greenhouse gas emissions. However, in comparison to front-end oil extraction processes, the oil extracted from the back-end is a lower-value product, as it cannot be used in food applications.	- GreenShift/Veridium (Corn Oil Extraction Systems) - Primafuel (SMAART Oil) - Iowa State University	
Corn Fiber Fractionation	This collaborative public/private partnership was formed to create high value products from corn fiber. They have developed a process by which a fiber stream is fractionated into its primary components: carbohydrates, oils, and proteins. The glucose within the carbohydrate fraction can be used to make ethanol/butanol and the other sugars can be catalytically converted to propylene glycol and ethylene glycol. In addition to capturing the 3% of the fiber fraction which is oil, the process also recovers the small oil fraction (5-25% of fiber oil) which is phyosterols. This small oil fraction has high value applications in the nutraceuticals markets and in the botanical oils market for personal care products. The remaining protein can then be used as a high value feed.	- National Corn Growers Association - Archer Daniels Midland Company - Pacific Northwest National Laboratory	Current status is unknown
New Corn Varieties Designed for Ethanol Applications			
High Amylase Corn	Using 3% amylase corn and 97% dent corn eliminates the need to add additional amylase to the ethanol production process. Syngenta estimates technology could cut production costs by 10%.	- Syngenta	
High Total Fermentable Ethanol Hybrid Corn	Corn that contains higher levels of fermentable starch, designed to improve ethanol yields. Many hybrids also contain Herculex® I insect protection which helps reduce the presence of mold and mycotoxins.	- Pioneer	
Extrax Corn	Monsanto is in the fourth and final stage prior to product launch of their high oil corn (7% compared to 3.5%) for use in Renessen's (JV between Monsanto and Cargill) Extrax corn fractionation system. They are focusing on higher oil content as this is the most valuable fraction of the corn.	- Monsanto	
High Available Energy	Hybrids with above average digestible energy for increased feeding value in swine and poultry diets. Helps to improve the value of the DDGS by-product.	- Pioneer	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Mavera™ High Value Corn with Lysine	Corn with higher levels of lysine. Reduces the need for lysine supplements in swine and poultry diets. Helps to improve the value of the DDGS by-product, which has a low lysine content compared to other protein sources such as soybean meal.	- Renessen LLC. (JV: Cargill and Monsanto)	

1/ Not an exhaustive list

Table 25: Second Generation Biofuels

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Cellulosic Ethanol – Biochemical Platform	Process to produce ethanol from corn biomass using biological agents to ferment the biomass, including corn kernel, corn stover, and/or corn cobs.		
Pretreatment, Hydrolysis, and Fermentation Process Developments	While there are many technologies and processes being developed to support economical cellulosic ethanol production, the base of the technology rests on pretreatment, hydrolysis, and fermentation.		
Pretreatments	The pretreatment of biomass is currently one of the single largest cost components in the overall cellulosic ethanol production process via the biochemical platform. Pretreatment is necessary in order to open up the structure of the biomass sufficiently to allow for effective hydrolysis. The protective sheath of lignin and hemicellulose must be removed or opened up so that the cellulose sugars are made accessible to be hydrolyzed, broken down into 5-carbon (C5) and 6-carbon (C6) sugars. There are many pretreatment methods currently being developed by numerous companies and research institutions, each with their own advantages and disadvantages. However, the bottom line is that a cost efficient process has yet to be commercialized.		 a
El Membrane Process	A process using DuPont's Nafion perfluorosulfonic membrane to recover the alkaline catalyst used in the cellulosic biofuel digesters during the pretreatment stage.	- Electrosep Inc.	
Combined Pretreatment and Hydrolysis Enzymes	Some of the more advanced pretreatments are done under conditions that would be amendable to enzyme stability and activity. This would enable the possibility of incorporating hydrolyzing enzymes into pretreatment stages, thereby combining the pretreatment and hydrolysis stages of cellulosic ethanol production.	- NREL	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Hydrolysis	Hydrolysis converts the cellulose and hemicellulose to C5 and C6 sugars so that they can subsequently undergo fermentation.		
Fermenting Yeast/ Microorganisms	Researchers and technology companies are aiming to develop fermenting yeast/microorganisms that can efficiently utilize both the C5 and C6 sugars, thus increasing overall ethanol yields. Developments in this area are also looking to lower the required dosage of the fermenting agent and to increase their tolerance to fermenting conditions.	- BP Energy Biosciences Institute - NREL - BioGasol - Mascoma - Dartmouth - DSM - Genencor - Novozymes - Verenum - Sandia National Laboratory - Abengoa Bioenergy New Technologies	
Combined Hydrolysis and Fermentation	Development of a "cocktail" of enzymes that can both break down the cellulose and hemicellulose into C5 and C6 sugars and ferment them in a single step. Such a process is often referred to as consolidated bioprocessing.	- Qteros - Mascoma	
Sequential Hydrolysis and Fermentation (SHF)	As opposed to the simultaneous saccharification and fermentation process whereby the cellulase enzymes and the fermenting microbes are combined in one vessel, this process separates the hydrolysis step from the fermenting step. This enables the hydrolyzing enzymes to operate under their optimal temperatures and the fermenting microbes to operate under their optimal temperatures, thus increasing the overall utilization of the sugars.		
Continuous Reactor Separator (CRS) System	A system designed for combined hydrolysis, fermentation and separation of ethanol. The technology company claims that the process increases conversion rates, lowers energy usage during distillation, and efficiently recycles nutrients, chemicals and enzymes.	- Liqua Ethanol	
Triple-Crop Sugar Corn	A hybrid corn variety with high sugar-filled stalks, low grain yields, but high biomass yields - yields that beat record switchgrass yields for the Midwest. Also, this variety requires less nitrogen than grain corn varieties. The hybrid is a cross between popular U.S. lines and a tropical line. It would be similar to sweet sorghum but Bt and Roundup Ready versions could be applied, whereas biotech traits have not yet been developed for sorghum.	- University of Illinois	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Altered Plant Genetics - Self Degrading Biomass	Novel varieties of corn whereby the cellulosic biomass begins to break down after harvest; reducing/eliminating the need for costly pretreatments.		
	A gene from the bacterium of a cow's stomach is inserted into a corn plant so that it can more easily convert the fiber in the corn stalks and leaves into simple sugars.	- Michigan State University (tech developer) - Edenspace Systems (holds license to tech) - (Energy Corn	
	Makes the plant's cell wall sugars more easily converted to biofuel. The company claims that the cell-wall sugars are more than twice as accessible to enzymatic digestion.	- Performance Plants (Efficient Conversion Trait)	
	Scientists have engineered novel "on/off" protein switches that are used to activate an enzyme within the plant cell wall that will begin to degrade cellulose into sugars after harvest. This enables the cellulosic biomass to be broken down at the cellulosic refinery using less severe pretreatments and without the addition of exogenous enzymes, resulting in a cost savings at the processing level.	- Agrivida (GreenGenes™) - Codon Devices (utilizes their BioLOGIC™ Engineering Platform) - University of Illinois	
Hydrocarbon Mixtures	Hydrocarbon mixtures can be used to produce a range of fuels and chemicals. Hydrocarbon fuels are virtually indistinguishable from gasoline, diesel, and jet fuel; can be distributed in existing pipeline infrastructure and can be used in any existing vehicle.		
Microbial Conversion of Sugars to Hydrocarbons	Custom deigned microbes convert sugars into hydrocarbon based fuels and chemicals.	- LS9 (DesignerBiofuels™) - Amyris - University of California, Los Angeles - University of California, Berkeley	 b

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Thermochemical Platform	Pyrolysis/gasification technologies are used to produce a pyrolysis oil/syngas, from which a wide range of long carbon chain biofuels and chemicals can be reformed. In contrast to the biochemical platform, the thermo chemical platform is largely based on existing technologies and there appears to be fewer technical hurdles; although being a more mature technology there may be less opportunity for cost reductions. Research and development efforts are focusing on perfecting the gasification of biomass so that it is more reliable and cost efficient. One of the major technical challenges is that much of the syngas produced from biomass tends to be more heterogeneous than gas-based syngas, leading to variations in product quality. Also, the number of inhibitory substances vary by biomass feedstock and gasifier design. This variation in syngas composition creates problems for the Fischer-Tropsch process which creates a variety of chemical and fuel products from the syngas. Problems include low product selectivity and unavoidable co-products, as well as contaminants that can inhibit the catalytic reaction. Additionally, the large quantity of biomass required to reach a scale where the process is economical remains a concern.	- ALICO - Range Fuels - Flambeau LLC - New Page Corp. - Neste Oil - Stora Enso	
Bioforming	The Bioforming™ process combines the utility of aqueous phase reforming with catalysts and reactor systems similar to those found in traditional petroleum refineries to convert plant sugars into hydrocarbon mixtures that can be used to make a variety of conventional fuels (e.g., gasoline, jet fuel, diesel). The system is a catalytic, low-temperature thermochemical route to biofuel production.	- Virent Energy Systems (BioForming) - Royal Dutch Shell - Cargill and Honda Motor (Virent Investors)	

Technology ¹	Description of Technology	Institutions/Companies Involved ¹ (Technology Name)	Stage of Development
Other	Butanol is currently produced via petrochemical feedstocks and has the potential to be used in a wide array of applications, including: fuel, solvents, coatings (e.g., paint, varnish, and inks), agricultural chemicals (e.g., insecticides and herbicides), synthetic resins and adhesives, textiles (e.g., scatter rugs, bathmats), and sealants. As a fuel, butanol holds several key advantages over ethanol, including a higher energy content as well as its ability to be transported via pipeline.	- BP and DuPont - Butyl Fuel LLC - TetraVita BioScience - Gevo - Cobalt Biofuels - Green Biologics - Syntec - METabolic Explorer - University of Illinois - University of California - Caltech - Ohio State University Research Foundation - Joint BioEnergy Institute - USDA, ARS	
Butanol	Over the past 20 years, research and development efforts have focused on improving various aspects of the acetone butanol, ethanol (ABE) production process. Molecular biology research has focused on developing various microbial strains with improved tolerance to butanol toxicity, which has resulted in significant yield increases. In 1990, the bacterium <i>Clostridium beijerinckii</i> was developed by Hans Blaschek from the University of Illinois, doubling butanol production over its parent strain, <i>Clostridium acetobutylicum</i> . Additionally, the development and application of in-situ gas stripping to remove the solvent from the fermenter, which minimizes product inhibition (the problem whereby the butanol becomes toxic to the fermenting agent), has enabled much higher feed concentrations.		

* Red = Identified by the Consortium for Applied Fundamentals Innovation (CAFI)

1/ Not an exhaustive list

a/ Different pretreatment processes are at different stages of development. However, while some are currently being used in pilot and demonstration scale facilities, the pretreatment process remains one of the more costly steps in the overall cellulosic ethanol production process.

b/ Both LS9 and Amyris have announced plans to reach commercial scale production by 2011. However, both are focusing on using sugarcane from Brazil.

Table 26: Value-Added Chemicals from Sugars

* Red = DOE Top 12 Value-Added Chemicals from Sugars and Syngas

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
1,4-Diacids (Succinic, Fumaric, and Malic)					
Succinic Acid (SA)	- 1,4-Butanediol (BDO) - Tetrahydrofuran (THF) - γ-Butyrolactone (GBL) - 2-Pyrrolidinone - N-Methyl Pyrrolidone (NMP) - Polytetramethylene Glycol (PTMG) - Poly-Butylene Succinate (PBS) - Diethyl and Dimethyl Succinate (Succinic Acid + Ethanol/Methanol)	- Solvents - Food ingredients, flavors - Plastics and elastic fibers - Paints and coatings - Lubricating oils, engine coolants and deicers - Diesel fuel oxygenates - Personal care products and cosmetics - Detergents, air fresheners and household cleaners - Automotive and industrial cleaners - Paint strippers and graffiti removers - Chemical intermediate for herbicides, insecticides, and fungicides	- Agro Industrie Recherches et Développments (ARD), France - DNP Green Technology - Bioamber (JV: DNP and ARD) - US Department of Energy - National Research Council of Canada - Biotechnology Research Institute - Rice University - Roquette and DSM - University of Georgia - Toyota Tsusho Company, Japan (shareholder of Bioamber) - Michigan State University, Michigan - Biotechnology Institute - BioEnergy International (Myriant Technologies) - Mitsubishi Chemical Corporation - Luleå University of Technology, Sweden	Current petrochemical production processes for succinic acid and its derivatives are not cost competitive with other petrochemical derived materials, and thus, succinic acid is currently a high cost chemical that serves only in niche market applications. However, biobased production routes are currently being developed by numerous companies and research institutions, and if a cost competitive biobased production route for succinic acid were developed, succinic acid could potentially serve as a replacement or partial replacement for many petrochemicals currently on the market. In addition to the many market applications for which succinic acid and its derivative chemicals can be applied, another promising attribute is that its production requires CO ₂ .	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Fumaric Acid	- Unsaturated succinate derivatives - Aspartic acid	- Food acidulant - Polyester resins - Sweetener - Fabric dye - Animal feed - Alkyd resins - widely used in adhesives and paint - Printing Inks - Paper sizing - Cleaning agent - Food and beverage - Soaps, mouthwashes, and toothpaste - Throat lozenges, cough syrups, and effervescent powdered preparations - Skin care products - Animal feed	- Delft University of Technology, Netherlands	Base technology is commercialized, but research efforts on efficient, low cost production methods for fumaric acid and its derivatives via fermentation are ongoing.	
Malic Acid	- Hydroxy succinate derivatives	- Potential replacement for terephthalic acid, a widely used component in various polyesters, such as polyethylene terephthalate (PET) and polybutyleneterephthalate (PBT) - New polyesters and nylons - Adhesives, coatings, inks, composites, binders, and/or foams - Pharmaceuticals - Agrochemicals - Antibacterial agents - Fragrances - (see above uses of succinic acid)	- Delft University of Technology, Netherlands	Base technology is commercialized, but research efforts on efficient, low cost production methods for malic acid and its derivatives via fermentation are ongoing.	
2,5-Furan Dicarboxylic Acid (FDCA)	- 2,5-Dihydroxymethylfuran - 2,5-Bis(hydroxymethyl) tetrahydrofuran - 2,5-Bis(aminomethyl) tetrahydrofuran - 2,5-Furandicarbaldehyde - Succinic Acid	- Potential replacement for terephthalic acid, a widely used component in various polyesters, such as polyethylene terephthalate (PET) and polybutyleneterephthalate (PBT) - New polyesters and nylons - Adhesives, coatings, inks, composites, binders, and/or foams - Pharmaceuticals - Agrochemicals - Antibacterial agents - Fragrances - (see above uses of succinic acid)	- Canon - Batelle, Memorial Institute - Technical University of Denmark - Danish National Advanced Technology Foundation - Institute of Technology, Federal Agricultural Research Centre, Germany	Base technology is still under investigation.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
3-Hydroxy-propionic Acid (3-HPA)	- 1,3-Propanediol - Acrylic Acid - Methyl Acrylate - Acrylamide - Malonic Acid - Ethyl 3-HP - Propiolactone - Acrylonitrile	- Solvents - Plastics and moldings - Fibers and resins - Composites - Adhesives - Laminates, floor polishes, paints and coatings - Aliphatic polyesters and copolyesters - Wastewater treatment - Gel electrophoresis - Papermaking - Ore processing - Permanent press fabrics. - Vitamins - Disinfectant; has been used to sterilize blood plasma, vaccines, tissue grafts, surgical instruments, and enzymes.	- Cargill - Codexis - Pacific Northwest National Laboratory - Novozymes - DOE - Qingdao Institute of Biomass Energy and Bioprocess Technology (China) - Perstorp (Sewden)	There is currently no commercially viable production route for 3-HPA using petrochemical feedstocks. Yet, many of the derivative chemicals that can be produced from 3-HPA are commercially produced from fossil fuel feedstocks. Cargill, along with Codexis and the Pacific Northwest National Laboratory, have developed a bioprocess to produce 3-HPA. In this process glucose or another carbohydrate source is converted into 3-HPA using a multi-step enzymatic reaction within the cells of a microorganism. 3-HPA can then be converted into a variety of high-value chemicals. In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HPA. At the time of the announcement, the companies said that they expected the technology to be ready in 5 years.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Aspartic Acid	- Amine Tetrahydrofuran - Amine Butyrolactone - Amine Butanediol - Aspartic Anhydride - Polyaspartic acid and Polyasparates - Amino-2-Pyrrolidone	- Salts for chelating agent - Sweeteners - Pharmaceuticals - Polyaspartic acid, synthetic resins, and cosmetics - Potential for polymer and solvent applications - Novel polyester - potential exists as a drug delivery biomaterial. - Novel polymers that could be substituted for polyacrylic acid and polycarboxylates. Potential applications include: a suspending and textile-sizing agent, adhesives, paints, hydraulic fluids, detergents, water treatment systems, corrosion inhibition, and super-absorbents.		Can be produced directly from sugar substrate or from fumaric acid and ammonia feedstocks. Currently, aspartic acid is commercially produced from fumaric acid for some high value market applications; therefore, reducing the cost of fumaric acid production would decrease the cost of aspartic acid, making it more competitive across a wider range of product applications. However, if the technical performance of producing aspartic acid directly from the sugar substrate could be improved, this route could be cheaper. A direct fermentation from sugar route is not yet economical.	
Glucaric Acid	- Glucaro-γ-Lactone - Glucaro-δ-Lactone - Glucarodilactone - Polyhydroxy-polyamides - α-Ketoglucarates - Esters and Salts	- Solvents - Nylons - Detergent surfactant - Dietary supplements (some evidence suggests that glucaric acid may reduce the risk of cancer development - not strongly supported). - Other potential uses range from human therapeutics to polymer synthesis.	- Massachusetts Institute of Technology	Two different pathways for the synthesis of glucaric acid from glucose are currently being researched by the Massachusetts Institute of Technology.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Glutamic Acid	- Glutaminol - Norvaline - 5-Amino-1-Butanol - 1,5-Pentandiol - Glutaric Acid - Pyroglutaminol - Proline - Prolinol - Pyroglutamic Acid	- Food flavoring agent - Pharmaceuticals - Surfactants - Fabric coatings - Moisturizer in cosmetics - Production of polymers such as polyester polyols and polyamides. - Potential uses similar to BDO, THF, GBL	- Pacific Northwest National Laboratory - Cerestar Holding B.V., Netherlands - University of Minnesota - Tufts University School of Medicine	Base technology is commercialized, but research efforts on efficient, low cost production methods for the production of glutamic acid and its derivatives are ongoing.	
Itaconic Acid	- 3- & 4- Methyl-GBL - 3-Methyl THF - 2-Methyl-1,4-BDO - 3- & 4- Methyl-NMP - 2-Methyl-1,4-Butanediamine - 3-Methylpyrrolidine - Itaconic Diamide	- New properties for the BDO, GBL, and THF family of polymers. - Acrylic fibers and rubbers, reinforced glass fiber, artificial diamonds and lens. - Paints, coatings, adhesives, thickeners, and binders - Water treatment systems - Detergent - Lubricant oil - Carpets - Pharmaceuticals - Potential as a component of P-series fuels^a	- TNO Quality of Life, Netherlands - National Science Council, Taiwan - USDA, ARS	Base technology is commercialized, but research efforts on efficient, low cost production methods for the production of itaconic acid and its derivatives are ongoing.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Levulinic Acid	- 2-Methyl-THF - g-Valerolactone - Angellactones - 1,4-Pentanediol - b-Acetylacrylic Acid - Diphenolic Acid - Levulinic Esters - d-Aminolevulinic Acid	- Food/beverage acidulant - Nylon, synthetic rubbers and plastics - Pharmaceuticals - Cigarettes - Potential as a component of P-series fuels - Solvent - Coatings - Perfume and flavor industries - Pesticides and herbicides - Copolymerization with other monomers for property enhancement - Polycarbonate synthesis	- Maine BioProducts (Biofine) - BioMetrics, Inc - Pacific Northwest National Laboratory and NREL	Maine BioProducts' Biofine process is a thermochemical process using acid hydrolysis to produce levulinic acid and other co-products (e.g., furfural, formic acid, and char) from cellulose. In addition to being a building block chemical for many other high-value chemicals, levulinic esters (85%) mixed with other alcohols (e.g., ethanol, methanol, butanol) produce a desirable fuel product; clean burning (burns cleaner than pure hydrocarbon products), can be transported via pipeline, low cloud point in diesel blends (lower than biodiesel), higher mpg than ethanol, soot reduction, and exceeds ASTM D-975 standards. For this reason, the strategy of Maine BioProducts is to co-locate their Biofine process along with existing/future bio-alcohol (e.g. ethanol, cellulosic ethanol, butanol) supplies. Processes are still being developed to produce derivatives from levulinic acid; some of these processes are further along than others.	
3-Hydroxy-butyrolactone	- 3-Hydroxy-tetrahydrofuran - 3-Amino-tetrahydrofuran - 2-Amino-3-Hydroxy-tetrahydrofuran - Acrylate-Lactone - Epoxy-Lactone - g-Butenyl-Lactone	- High value pharmaceutical applications - Solvents - Lycra fibers	- Michigan State University	While there are research efforts looking at developing efficient, low cost production methods for 3-hydroxybutyrolactone and its derivatives, there is relatively little incentive to develop this specialty chemical with high-value use into a commodity chemical.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Glycerol (glycerin)	- Glyceric Acid - 1,3-Propanediol (PDO) - Propylene Glycol (PG) - Branched polyesters and nylons - Glycidol - Propanol - Mono-, Di-, or Tri-Glycerate - Diglyceraldehyde - Glycerol Carbonate	- Cosmetic and personal/oral care products - Pharmaceuticals - Foods/beverages - Fuels - Polyether polyols (for polyurethane) and for polyol foams - Polyactic acid with better polymeric properties and polyester fibers with new properties - Adhesives, laminates, coatings, and moldings - Aliphatic polyesters and copolyesters. - Solvent - Antifreeze - Unsaturated polyurethane resins for use in insulation	- Current biodiesel manufacturers - University of Wisconsin (tech Glycerol to PG) Applications: - Diversified Energy Corporation - North Carolina State University - XcelPlus Global Holdings Inc. - Institut Universitari de Ciència i Tecnologia (Barcelona, Spain) - Virent Energy Systems Inc. - New Century Lubricants - Rice University / Glycol Biotechnologies	While glycerol can be produced from the sugars present in corn and corn biomass, current production of glycerol largely comes as a by-product of biodiesel production. There are several routes to produce PG using glycerin. Generally, glycerin is hydrogenated in the presence of metallic catalysts and hydrogen under different reaction conditions. Additionally, microbial conversion of glycerol to PG has also been evaluated. There are numerous companies currently developing technologies to produce fuel products from glycerol.	
Sorbitol / Isosorbide	- Isosorbide - 1,4-Sorbitan - 1,5-Anhydrosugars - Glycerol - Ethylene Glycol - Propylene Glycol - Lactic Acid	- Food; sugar substitute - Laxative - Pharmaceuticals - Cosmetics and personal care products - Adhesives - Paper products - Textiles	- Roquette - Archer Daniels Midland - Danisco - SPI Polyols - Cargill - BASF - Bayer AG - Pacific Northwest National Laboratory (PNNL)	Production of sorbitol is well developed; however, low cost technologies for the production of its derivatives, such as isosorbide, are currently being developed (see below). Additionally, Pacific Northwest National Laboratory is also trying to develop a more environmentally benign sorbitol production process that would not use mineral acid catalysis, which creates separation and waste disposal issues.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Isosorbide	<u>Derived from:</u> - Sorbitol <u>Derivatives:</u> - Isosorbide Diglycidyl Ether Resins - Dimethyl Isosorbide - Mono and Dinitrate Isosorbide - Isosorbide Diesters	- Increases the strength and rigidity, particularly under high temperatures, of polymers such as polyethylene terephthalate (PET), which are used widely to manufacture food and beverage containers. - Potential as a liner in food and beverage cans - CDs - Pharmaceuticals and fine chemical market - High performance fibers - Solvent - Skin-care products	- Roquette - Iowa Corn Promotion Board - Pacific Northwest National Laboratory - General Electric Global Research - New Jersey Institute of Technology - Monsanto EnviroChem	Various processes are actively being developed by a range of companies to economically produce isosorbide from commercially available sorbitol.	
Propylene Glycol (PG)	<u>Derived from:</u> - Lactic acid - Glycerin - Sorbitol	- Surface coatings - Glass fiber resins - Antifreeze - Solvents - Humectant - Manufacturing of plasticizers - Hydraulic brake fluids - Non-ionic detergents - Emulsifier - Heat transfer fluid - Moisturizer - Unsaturated polyester resins (e.g., boat hull)	- Pacific Northwest National Laboratory (PNNL) - Archer Daniels Midland - Cargill / Ashland Chemical - Davy Process Technology - Dow Chemical - Huntsman Corporation - Michigan State University - Senenergy Chemical - University of Wisconsin	PNNL is working to develop a cost efficient production process to produce PG from sorbitol. There are also several routes to produce PG using glycerin. Generally, glycerin is hydrogenated in the presence of metallic catalysts and hydrogen under different reaction conditions. Microbial conversion of glycerol to PG has also been evaluated.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Xylitol/ Arabinitol	- Xylaric Acid - Propylene Glycol - Ethylene Glycol - Lactic Acid - Glycerol - Mixture of Hydroxyfurans	- Foods - Oral hygiene products (mouthwash and toothpaste) - Pharmaceuticals - Dietetic products - Cosmetics	- Virginia Polytechnic Institute - DNP International - Federal University of Viçosa, Brazil - ARS - ZuChem - DFI (licensed tech from Purdue University)	Xylitol is currently commercially available; however, commercial-scale quantities are typically derived from birch-wood fibers that have been subjected to a combination of acids, high pressures and temperatures, chemical catalysts, and a series of separation and purification steps. Cost efficient production routes via corn fiber are being developed and improved. DFI has licensed a potentially breakthrough process for the production of xylitol from Purdue University.	
Methyl Ethyl Ketone (MEK)		- Solvents - Paints and coatings	- Genomatica	Genomatica has developed a process to produce MEK using existing ethanol manufacturing infrastructure. The process uses the same equipment, temperatures, and processes. The development comes in the form of a new organism that converts sugar and water into MEK.	
Furfural		- Fuel - Solvents	- Raven Biofuels - Lignol Innovations Ltd. - Avantium - University of California, Davis	- Steam Distillation: The 6-carbon sugars are processed into ethanol through a normal fermentation process and the 5-carbon sugars are removed and processed via steam distillation of the acidified hemicellulose into furfural. - Catalytic - Non-Fermentative: A production process whereby furfural is produced without fermentation, enzymes, or pretreatments, using hydrochloric acid.	
Hydroxy-methylfurfural (HMF)		- Fuel - Plastics	- Pacific Northwest National Laboratory	Researchers believe they have discovered a one step process to convert cellulose into HMF. Recyclable catalysts are used in tandem to break down the cellulose into glucose and then convert the glucose into HMF.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Methyl Halides		- Solvents - Propellants - Soil fumigants - Fuel - Aromatics	- University of California - San Francisco	An engineered bacterial/yeast duo have successfully converted sugarcane bagasse, corn stover, switchgrass and poplar into methyl halide, a chemical that is commonly used in the petrochemical industry. Using zeolite catalysts, the methyl halides can be manufactured into gasoline, olefins, aromatics, alcohols, ether, and other chemicals.	
1,4-Butanediol (BDO)	- Polybutylene succinate (PBS) - Polybutylene succinate adipate (PBSA) - Polybutylene succinate terephthalate - Polybutylene terephthalate (PBT) - Thermoplastic polyurethanes - Tetrahydrofuran (THF) - γ-Butyrolactone (GBL) - Polytetramethylene Glycol (PTMG)	- Solvents - Plastics and packaging - Paints and coatings - Elastic fibers - Hair and scalp conditioners - Automotive applications: hoses, belts, gaskets, grease boots, CV joints, wire and cable bushings - Many polyurethane and polyester applications	- Genomatica - BioAmber	BDO is most commonly produced via petrochemical feedstocks. In September of 2008, Genomatica announced its novel technology development to produce BDO directly from sugars, and has since continued to make improvements designed to make the process more cost effective and productive. Other companies developing biobased succinic acid are also working on cost efficient production of BDO via succinic acid.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
1,3-Propanediol (PDO)	- Polytrimethylene Terephthalate (PTT) - Polyurethane and polyesters	- Polymer with remarkable "stretch-recovery" properties - Textiles - clothing and upholstery - Adhesives - Antifreeze and lubricants - Pharmaceuticals - Fragrances - Fabric softener - Vitamin H - Composites - Moldings - Paints and coatings New Use: Scratch-resistant varnish	- DuPont Tate & Lyle BioProducts (Sorona) - Genencor International - Pacific Northwest National Laboratory - DOE	PDO was historically produced via petrochemical based feedstocks. More recently, biobased production routes have been developed. The bioprocessing of (PDO) developed by DuPont and Genencor is claimed to be economically competitive with petrochemical production routes.	
Polyhydroxyalkanoates (PHAs)	- Poly-beta-hydroxybutyrate - PHB - Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) - PHBV	- Thermoplastic or elastomeric plastics - Packaging - Pharmaceuticals - Medical devices and tissue engineering	- Hawaii Natural Energy Institute and the University of Hawaii - I-PHA BioPolymers, Hong Kong (licensed technology) - Metabolix - Monsanto (Biopol) - DOE - Biomer, Germany - Proctor & Gamble - Mitsubishi Gas, Japan - PHB Industrial, Brazil - Tianan Biologic Material Co, Ltd Ningbo, China - Bio-on	In June 2005, Metabolix received the US Presidential Green Chemistry Challenge Award (small business category) for their development and commercialization of a cost-effective method for manufacturing PHAs. While already commercially produced, a process is being developed to produce this class of bioplastics as a by-product of cellulosic ethanol production, a process that would reduce greenhouse gas emissions.	
Lysine	- Caprolactam	- Animal feed - Pharmaceutical New Use: "AlsoSalt" - a no sodium salt substitute	- ADM - Ajinomoto - CJ Corp - Degussa - BASF	New technology developments, such as the production of caprolactam from lysine could increase future market demand for lysine (see below).	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Caprolactam	- Polyamide-6 (Nylon-6) <u>Derived from:</u> -Lysine	- Fibers and textiles - Tires - Engineering plastics in structural material for applications in the automotive and electronics industries - Packaging - Film coating - Plasticizers and polyurethanes - Paint	- Michigan State University	New technologies are being developed to produce caprolactam from lysine.	
Lactic Acid	- Polylactic acid - Ethyl Lactate - Acrylic Acid - Propylene Glycol - Pyruvic Acid - 1-Amino-2-Propanol - Lactonitrile - Lactic Amide - Lactide - 2,5-Dimethyl-1,4-Dioxane	- Food/Beverage - acidulant - Electroplating bath additive - Mordant - Film and thermoformed packaging - Consumer electronics - Textiles - clothing, upholstery, and carpet - Personal care products - Solvents - Detergents - Super absorbent polymers - diapers - Coatings - Antifreeze, hydraulic brake fluids - Cleaning product	- Cargill (NatureWorks) - PURAC - NREL - Institute of Chemical Technology Prague	Research efforts have been directed toward developing ways to improve the yields of lactic acid via the fermenting microorganism Lactobacillus and various fungal strains, and to produce lactic acid using lignocellulosic feedstocks. Also, the production of polylactic acid via lactic acid has been recently commercialized and the process has been improved since its initial commercialization (see polylactic acid).	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Poly(lactic Acid (PLA))	Derived from: - Lactic acid	- Film and thermoformed packaging - Textiles - clothing, upholstery, carpet, and diapers - Personal care products	- Cargill (NatureWorks) - PURAC	Technology whereby polylactic acid is converted from lactic acid, a fermentation product of biomass sugars. This commercially produced product is cost competitive with conventional polymers and has many performance properties equal to or greater than conventional polymers such as polyethylene terephthalate (PET) and nylon. The company has made improvements to its process since its commercial debut that have further reduced CO ₂ emissions and reduced process energy requirements. Additionally, the company is looking to develop fermentation organisms to convert 5-carbon sugars as well as glucose into PLA.	 e
Acrylic Acid	Derived from: - Lactic Acid - 3-Hydroxypropionic Acid	- Coatings and adhesives - Super absorbent polymers (e.g. diapers) - Detergents - Plastics - Fibers	- Cargill - Novozymes	Acrylic acid is most commonly produced via petrochemical feedstocks (e.g. propylene). Commercially viable biobased production route is yet to be established. In early 2008, Cargill announced a joint agreement with Novozymes to develop technology enabling the production of acrylic acid via 3-HP. At the time of the announcement, the companies said that they expected the technology to be ready in 5 years.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ²	Description of Technology	Stage of Development
Ethyl Lactate	Derived from: - Lactic acid	- Solvents - Pharmaceuticals - Food - Fragrances	- DOE - Vertec Biosolvents Inc. - Argonne National Laboratory - Cargill - Ashland Specialty Chemical Company - University of Pennsylvania - Michigan State University	Although ethyl lactate has been around for years, the cost of producing it has been too high to allow it to compete economically with lower-priced chemical solvents. Advancements in lactic acid separation technologies using electro dialysis, advanced membrane, and reactive separations have decreased ethyl lactate costs, making it more competitive with other commercially available solvents. Argonne Laboratory has developed a process based on a selective membrane separation and purification process that permits low-cost synthesis of high-purity ethyl lactate from fermentation-derived lactic acid. The University of Pennsylvania has been developing an integrated semi-continuous distillation, reaction, and pervaporation process for the production of ethyl lactate from ethanol and lactic acid. Michigan State University researchers have demonstrated the effectiveness of applying their reactive distillation technology to the production of ethyl lactate from lactic acid and ethanol.	

* Red = DOE Top 12 Value-Added Chemicals from Sugars and Syngas

1/ Not an exhaustive list

2/ Not an exhaustive list. Some companies/institutions may no longer be involved, some may be working with one another, and some may only be financially involved.

a/ According to the DOE a "P-Series fuel is a blend of natural gas liquids (pentanes plus), ethanol, and the biomass-derived co-solvent methyltetrahydrofuran (MeTHF). P-Series fuels are clear, colorless, 89-93 octane, liquid blends that are formulated to be used in flexible fuel vehicles (FFVs)."

b/ Sorbitol is already commercially produced. However, technology developments to lower production costs and to produce derivatives such as isosorbide could expand this product's market demand.

c/ The production of PG via some technologies and base chemicals is already commercialized (e.g., traditional hydrogenation of glycerol), while production via other technologies and base chemicals (e.g., from sorbitol) are still being developed. Many of the companies listed are focusing on PG from glycerin, the by-product of biodiesel production.

d/ While already commercialized, other processes are still being developed.

e/ In a March 09 article, Cargill announced it was looking at prospective locations for a second plant. The company "anticipates continued advancements in the resin's performance, as well as an increase in the number of products and applications using Ingeo."

Table 27: New Uses of Corn Cobs

Biobased Products/ Chemicals ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
Anhydrous Ammonia	- Fuel - Fertilizer	- SynGest Inc.	SynGest Inc. is employing a gasification process which uses corn biomass, initially corn cobs, to produce anhydrous ammonia for fuel and fertilizer. The company plans to originally produce fertilizer, but in the long run, intends to produce fuel as well. The company claims to have a carbon negative process and low production costs that can undercut the cost of ammonia produced from natural gas.	
Energy (natural gas substitute)	- Energy	- Chippewa Valley Ethanol Company - Frontline BioEnergy Gasifiers - University of Minnesota	Chippewa Valley Ethanol Company (CVEC) plans to use corn cobs and other biomass to run its ethanol plant using Frontline BioEnergy's biomass gasification technology. CVEC's plant engineer says that the "cobs could cut the plant's energy cost by one fourth or more."	
Cellulosic Ethanol	- Fuel	- POET	Poet plans to begin producing 25 million gallons of cellulosic ethanol from corn cobs as early as 2011 at its Emmetsburg, IA biorefinery.	
Polishing Materials	- Polishing materials	- Andersons Inc.	N/A	
Animal Bedding	- Animal bedding	- Andersons Inc.	N/A	
Cat Litter	- Cat Litter	- Andersons Inc.	N/A	

1/ Not an exhaustive list

Table 28: New Uses of Distillers Grains

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
DDGS - Fillers in Plastics	- DDGS fillers in plastics	- Adhesives - Furniture - Architectural panels - Composite molding applications - Golf tees	- University of Minnesota - USDA, ARS - South Dakota State University - Northern Illinois University (NIU)	N/A	
DDGS - Zein	- Corn Protein	- Biodegradable plastics - Food and paper coatings - Chewing gum base - Biodegradable textile fiber - Medical applications - Printing ink - Antioxidants - Adhesives and binders	- USDA, ARS	Currently, unpurified zein is used in specialty coatings. However, a new, cost-effective process to purify the zein makes the protein suitable for cosmetic, food, and biomedical applications.	
DDGS - Fuel	- Corn Fiber	- Fuel (ethanol or butanol)	- University of Illinois - NREL - NCGA - Corn Refiners Association	The fiber portion of the DDGS is separated via the elusieve process. Then, after enzymatic hydrolysis the sugars can be fermented to produce butanol or ethanol. NREL is working on designing unique biocatalysts to ferment arabinose, a major component in the available sugars from corn fiber, a residue of the corn-to-ethanol process, into ethanol.	
DDGS - Energy	- DDGS	- Energy	- Washington University - University of Minnesota - USDA, ARS - Iowa State University - Rein & Associates (MN) - Biogasol - POET - University of Borås - Kwartha Ethanol	-Anaerobic Digestion: Anaerobic digestion uses bacteria to convert the thin or whole stillage by-product of ethanol production into biogas, which can then be used to reduce natural gas usage. This process reduces energy costs and greenhouse gas emissions and helps to conserve water. - Direct Burning - Gasification	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
DDGS - Fertilizer	- DDGS	- Organic fertilizer	- USDA, ARS - Summit Seed Inc.	Researchers are now looking at the effectiveness of this application when the fiber and germ portion of the DDGS are removed prior to fermentation.	
DDGS - Weed Control	- DDGS	- Weed control	- USDA, ARS - Summit Seed Inc.	Researchers are now looking at the effectiveness of this application when the fiber and germ portion of the DDGS are removed prior to fermentation.	
Corn Fiber Gum	- Corn Fiber	- Emulsifier - flavor stabilizer in soft drinks - a substitute to the costly "gum arabic" that is currently imported from African countries.	- USDA, ARS - University of Illinois - University of Missouri	ARS researchers are using their elusive fractionation process to recover the fiber from the distillers grains at the back-end of the ethanol production process or fiber extracted from the corn wet milling process.	
Astaxanthin	- Corn Fiber	- High value specialty product used in the diets of farm-raised fish in order to give the flesh of salmonids, shrimps, lobsters, and crayfish the pinkish-red hue.	- USDA, ARS - Clemson University	Astaxanthin would be produced from the fermentation of corn fiber. Several strains of fermenting yeast are currently being explored.	
DDGS - Flour	- DDGS Flour	- Cookies, breads, pastas (While DDGS flour is nutritious, the fermentation process used to make ethanol tends to give the food product a bitter off-flavor and odor that lacks consumer appeal.)	- USDA, ARS - South Dakota State University	N/A	
DDGS - Food Flavorant	- DDGS	- Food flavorant - sodium flavor replacement	- Kraft Foods Holdings, Inc.	Patented application - Rather than using DDGS in food applications as a filler and trying to find ways to disguise its bitter taste, this application would use smaller amounts of DDGS and use its distinct flavor as a flavor substitute (e.g. sodium).	

1/ Not an exhaustive list

Table 29: New Uses of CO₂

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
CO ₂ - Algae Production Systems	- Algae	- Biodiesel - Ethanol - Biocrude - renewable petroleum products: gasoline, diesel, and jet fuel	- Petrosun - Greenshift - Diversified Energy - Solazyme - Valcent - Green Star - Aurora Biofuels - XL Renewables - Others	The CO ₂ emitted from the ethanol production process can be captured and used as a key input in the production of algae, which is in turn used to produce oil. Among other uses, this oil can then be used to make a range of fuel products.	
CO ₂ - Biodegradable Plastics	- Biodegradable plastics	- Packaging - Insulating foam for buildings - Computer cases	- Novomer - Cornell University	This patented technology, which has been demonstrated on a small scale, mixes liquid metal with CO ₂ or CO in a reactor at low pressure. Depending on the feedstock and the catalyst, the end product can be adjusted to be more flexible or slower to decompose.	
CO ₂ - Oil Extraction	- Supercritical CO ₂	- Vegetable oil extraction from oilseeds - Potential also exists in algae oil extraction applications	- MOR Supercritical, LLC	Rather than using hexane, MOR Supercritical's technology uses carbon dioxide as their only solvent in their corn oil and oilseed extraction system. As opposed to conventional supercritical processes, MOR Supercritical claims that their technology greatly reduces operating costs which have prevented other supercritical systems from replacing petrochemical extraction using hexane, despite the numerous benefits. MOR Supercritical claims that their technology is energy efficient; automated, modular and scalable; has a small environmental footprint (1/6 of a typical solvent extraction plant); produces safe, solvent-free, non-degraded, high-quality products including undegraded meal with high protein digestibility; and an accompanying refining technology to extract and refine the oil in one step.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
CO ₂ - Medical Implants - Drug Delivery	- Supercritical CO ₂	- Used to push chemicals/medicines into a plastic that is often used in bone replacement	- Ohio State University	By using compressed CO ₂ , researchers at Ohio State University discovered that they could alter the internal structure of plastic and create voids that could be used to hold medicine. The idea is that medicines implanted in bone replacements could help prevent inflammation and infection following surgery or serve as a means to dispense anti-tumor agents in patients where bone has been replaced as part of a cancer treatment program. Currently implants are sterilized with heat, radiation, and chemicals that can make embedded medicines less effective.	
CO ₂ - Sand and Magnesium Carbonate	- Sand and Magnesium Carbonate	- Sand - Replacement for limestone in cement	- Pennsylvania State University - Los Alamos National Laboratory	Serpentine rock is mixed in a reactor with water and acid, in order to get magnesium and silica. Then, ammonia and CO ₂ are added to get magnesium carbonate. Previous technologies which have attempted to store CO ₂ in magnesium carbonate have been highly energy intensive due to high pressure requirements, while this proposed technology operates under ordinary pressures. However, serpentine, which is plentiful near the Atlantic and Pacific coasts, is expensive to transport inland.	
Carbon Sequestration	-N/A	- CO ₂ Storage	- Archer Daniels Midland	In an effort to decrease the carbon footprint of an ethanol facility, ADM is pursuing a project involving drilling an injection well 7,200 feet deep to store a total of 1 million metric tons of CO ₂ .	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
CO₂ - High Value Materials	- Formic Acid - Formate Salts - Oxalic Acid - Methanol	- A replacement for hydrochloric acid in the steel pickling process - Diesel fuel additive (ammonium formate) - Energy (hydrogen or methanol)	- Mantra Venture Group Ltd. - British Columbia's Clean Energy Research Center	The Mantra Venture Group is working to develop a technology to convert CO ₂ into formic acid and other high value materials by combining electricity with water, CO ₂ and an electrolyte in a process they call electro-reduction.	
CO₂ - Succinic Acid	- 1,4-Butanediol (BDO) - Tetrahydrofuran (THF) - γ-Butyrolactone (GBL) - 2-Pyrrolidinone - N-Methyl Pyrrolidone (NMP) - Polytetramethylene Glycol (PTMG) - Poly-Butylene Succinate (PBS) - Diethyl and Dimethyl Succinate (Succinic Acid + Ethanol/Methanol)	- Solvents - Food ingredients, flavors - Plastics and elastic fibers - Paints and coatings - Lubricating oils, engine coolants and deicers - Diesel fuel oxygenates - Personal care products and cosmetics - Detergents, air fresheners and household cleaners - Automotive and industrial cleaners - Paint strippers and graffiti removers - Chemical intermediate for herbicides, insecticides, and fungicides	- Agro Industrie Recherches et Développments (ARD), France - DNP Green Technology - Bioamber (JV: DNP and ARD) - US Department of Energy - National Research Council of Canada - Biotechnology Research Institute - Rice University - Roquette and DSM - University of Georgia - Toyota Tsusho Company, Japan - (shareholder of Bioamber) - Michigan State University, Michigan - Biotechnology Institute - BioEnergy International (Myriant Technologies) - Mitsubishi Chemical Corporation - Luleå University of Technology, Sweden	CO ₂ is used as input in the production process of succinic acid. Biobased production routes are currently being developed whereby succinic acid can be produced from a range of sugar feedstocks, including corn.	

1/ Not an exhaustive list

Table 30: Lignin Derived Products

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
Power, Fuel, & Syngas	- Ethanol - Process heat - Propanol - Butanol - Green fuels olefins - MeOH/DME - Fischer-Tropsch green fuels - Pyrolysis oil - Reformulated gasoline	- Fuel - Power - Solvents - Coatings - paint, varnish, and inks - Agricultural chemicals - insecticides, pesticides and herbicides - Synthetic resin and adhesives - Textiles (e.g., scatter rugs, bathmats) - Sealants	N/A	Various technologies, including lignin combustion, gasification, pyrolysis, and hydrolification can be used to produce these various products from lignin.	 a
Macro-molecules	- Carbon fiber - Polymer fillers - Thermoset resins - Formaldehyde-free resins - Adhesives and Binders	- Steel panels in automobiles (reduces weight and improves fuel economy) - High strength engineering plastics - Heat-resistant polymers - Antibacterial surfaces - High strength and formaldehyde-free adhesives - Light and ultraviolet resistant polymers - Adhesives and binders	N/A	Various technological developments have been made in this arena, and there are many more technical challenges still remaining to be solved.	

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Description of Technology (if applicable)	Stage of Development
Aromatics ^b - BTX (Benzene, Toluene, and Xylene) - Phenol - Terephthalic acid	- Benzene: Cyclo (hexane, hexanol, and hexanone), Caprolactam, Adipic Acid, 1,6-Diaminohexane, Cumene, and Styrene - Toluene: Dinitrotoluene, Diminotoluene, Toluene Disocyanate, Benzoic Acid - Xylene: Isophthalic Acid and Terephthalic Acid - Phenol: Bisphenol A, Nitrophenols, Aminophenols, Cyclohexanone, and Cyclohexanol	- Pharmaceuticals - Synthetic rubbers - Upholstery - Car parts: body, bumpers, lighting, dashboard, seats, upholstery, fuel systems, under-the-bonnet components - Clothing - Plastics - CDs, CD-ROMs and DVDs	N/A	Various technological developments have been made in this arena, and there are many more technical challenges still remaining to be solved.	

1/ Not an exhaustive list

a/ Different technologies are at varying stages of development.

b/ According to the Pacific Northwest National Laboratory, "lignin is the only renewable source of an important and high-volume class of compounds - the aromatics."

Table 31: Other New Corn Uses/Products

Biobased Products/ Chemicals ¹	Derivatives/ Utilization ¹	Applications/End Uses ¹ (Product and Derivatives)	Institutions/ Companies Involved ¹	Stage of Development
AlisoSalt	Produced from Lysine	- No sodium salt substitute (Product is being used in Heinz' no-salt added ketchup)	- Michigan State University - Diversified Natural Products, Inc.	
Scratch-Resistant Varnish	Produced from 1,3-Propanediol	- Scratch resistant furniture varnish	- Institute for Wood Research, Germany	
HOLDOUT	N/A	- A bio-based formulation to replace fluorinated compounds in paper-based food packaging products	- Cerealus - Maine Technology Institute	
TerraMat (cork)	N/A	- Corkboards - Floormats	- Purdue University	
Melt-A-Way Cupcake Liners	N/A	- Cupcake liner that is designed to become part of the cupcake during baking	- Purdue University	
Nature's Silk	N/A	- Biodegradable toilet paper	- Purdue University	

1/ Not an exhaustive list

Table 32: New Corn Varieties Designed for Food and Feed Applications

Technology ¹	Description of Technology	Institutions/Companies Involved (Technology Name)	Stage of Development
New Corn Varieties Designed for Food Applications			
Food-Grade White and Yellow Corn Hybrids	These hybrids are targeted toward the wants and needs of food processors, designed for characteristics such as kernel density, composition, size, and ear rot disease.	- Pioneer	
High Extractable Starch and Waxy Corn	These hybrids have above average levels of extractable starch, a characteristic that is beneficial for wet milling.	- Pioneer	
Extrax Corn	Monsanto is in the fourth and final stage prior to product launch of their high oil corn (7% compared to 3.5%) for use in Renessen's (JV between Monsanto and Cargill) Extrax corn fractionation system. They are focusing on higher oil content as this is the most valuable fraction of the corn.	- Monsanto	
New Corn Varieties Designed for Animal Feed Applications			
High Available Energy	Hybrids with above average digestible energy for increased feeding value for pork and poultry producers.	- Pioneer	
Mavera™ High Value Corn with Lysine	Corn with higher levels of lysine, reducing need for lysine supplements in swine and poultry diets.	- Renessen LLC. (JV: Cargill and Monsanto)	

*Some of these technologies can also be used to improve ethanol production economics and are dually listed above in Table 24.

Appendix B: Traditional Corn-to-Ethanol Production Processes

There are two production processes for grain-based ethanol production – wet milling and dry milling. The main difference between the two is in the initial preparation of the grain prior to fermentation, and as a result the dry milling process is less capital intensive and production costs are lower. However, whereby the wet milling process results in multiple co-product streams (e.g., corn oil, corn gluten meal, corn gluten feed, and ethanol/chemicals, starch, or corn syrup), the dry milling process results in two products (e.g. ethanol and distillers grains). In the U.S., dry mill facilities account for the overwhelming majority of ethanol production capacity (85-90%).

A. Traditional Dry Milling Ethanol Production Process

The process steps involved in traditional dry milling ethanol production are detailed below and illustrated within Figure 24.

In dry milling, the corn kernel is first removed from the husk and chaff. Then, the entire kernel is ground into a fine meal to expose the starch in what is often referred to as a hammer mill. Although processes vary, most dry mill facilities continue the process without separating out the various component parts of the kernel.

The meal is then sent to the “cooker” and mixed with water and amylase enzymes. Ammonia is also added for pH control and as a nutrient to the yeast (used in the next step of fermentation). Initially, the mixture is “jet cooked” for a brief period of time at 105-110°C. Then, the temperature is brought down to 70-95°C for about 1-2 hours. The heat is used to help rupture the cell walls and to reduce bacteria levels, as bacteria would otherwise compete with the yeast for the sugar feed. During this time, the amylase enzymes break down the exposed starch into dextrans (5 to 10 glucose molecule chains), which are water soluble. This water solubility is what causes the meal and water mixture to liquefy into what is referred to as a mash. For this reason, this particular process step is often referred to as “liquefaction”. After cooling the mash to 30-60°C and adjusting the pH, glucoamylase enzymes are added to further break down the dextrans into glucose molecules. This step is referred to as “saccharification”. The objective is to get the final solution to a point where the glucose or simple sugar concentration is between 20-24%.

The mash is then transferred to fermenters and mixed with yeast, typically of the genus *Saccharomyces*. The yeast then changes the sugar (glucose) into ethanol and carbon dioxide. It takes about 40-50 hours for the mash to ferment. During this time, the temperature, pH, and various nutrient concentrations must be controlled to maximize ethanol production. As the ethanol concentration of the

mixture increases, it becomes toxic to the yeast and the sugar fermentation process begins to slow down.

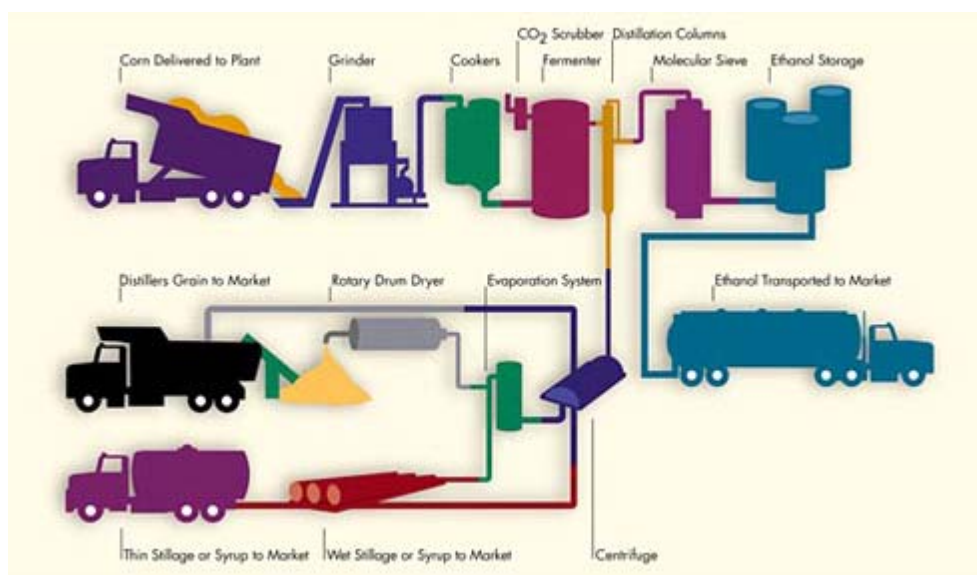
In the newer ethanol plants, the saccharification and the fermentation steps are often combined into one, referred to as Simultaneous Saccharification and Fermentation (SSF). In SSF, the glucoamylase enzymes and the yeast are added to the mash at the same time, allowing the yeast to metabolize the glucose at the same time it is produced. This limits the chances that undesired microbes/bacteria will consume the glucose before the yeast gets a chance.

The fermented mash, called "beer", contains about 10-15% ethanol by volume. The rest of the mixture is water and grain/yeast solids that could not be fermented. To separate the ethanol, the mixture is sent to the distillation column and heated once again - this time to a temperature at which ethanol vaporizes, but the remaining materials do not. The ethanol vapor is collected and cooled, where it condenses to its liquid form. At this stage, the ethanol is concentrated to 190 proof (95% alcohol).

To purify the ethanol and remove any remaining water, it's passed through a dehydration system (e.g., molecular sieve), creating anhydrous ethanol. After this step, the ethanol is approximately 200 proof (100%). All water must be removed because a water-alcohol mixture cannot dissolve in gasoline. The anhydrous ethanol is then blended with 1% (2-5% in the U.S.) denaturant such as gasoline to make the ethanol unfit for human consumption - a requirement for fuel-grade ethanol. It is then ready for shipment to gasoline terminals or retailers.

Meanwhile, the remaining product at the bottom of the distillation column, known as the stillage is sent through a centrifuge that separates the water/solubles (~90%) from the non-fermentable solids (~10%). The solubles are then concentrated to about 30% solids by evaporation, resulting in Condensed Distillers Solubles (CDS) or "syrup." The coarse grain or non-fermentable solids is then referred to as wet distillers grains (WDG) and can be marketed as such, or it can be mixed with the CDS and sold as wet distillers grains with solubles (WDGS). Alternatively the WDG can also be dried to form dried distillers grains (DDG) or mixed with CDS and dried to form dried distillers grains with solubles (DDGS). WDGS and DDGS are often used as a high protein feed source suitable for livestock. Generally, due to drying costs, distillers grains sold to nearby livestock operations, particularly dairy or beef cattle, are sold in the form of WDGS. However, swine, poultry and more distant beef or dairy operations typically receive DDGS.

Depending on local demand, the CO₂ produced during fermentation can either be released directly into the atmosphere or captured and sold for use in many food preparations and other industrial processes, such as carbonating beverages and the manufacture of dry ice.

Figure 24: Traditional Dry Milling Ethanol Production Process

Source: Renewable Fuels Association

B. Traditional Wet Milling Ethanol Production Process

The process steps involved in traditional wet milling ethanol production are detailed below and illustrated within Figure 25.

In wet milling, the grain is soaked or "steeped" in water and dilute sulfurous acid for 24 to 48 hours. This steeping facilitates the separation of the grain into its many component parts such as starch, protein, germ and fiber in an aqueous medium prior to fermentation.

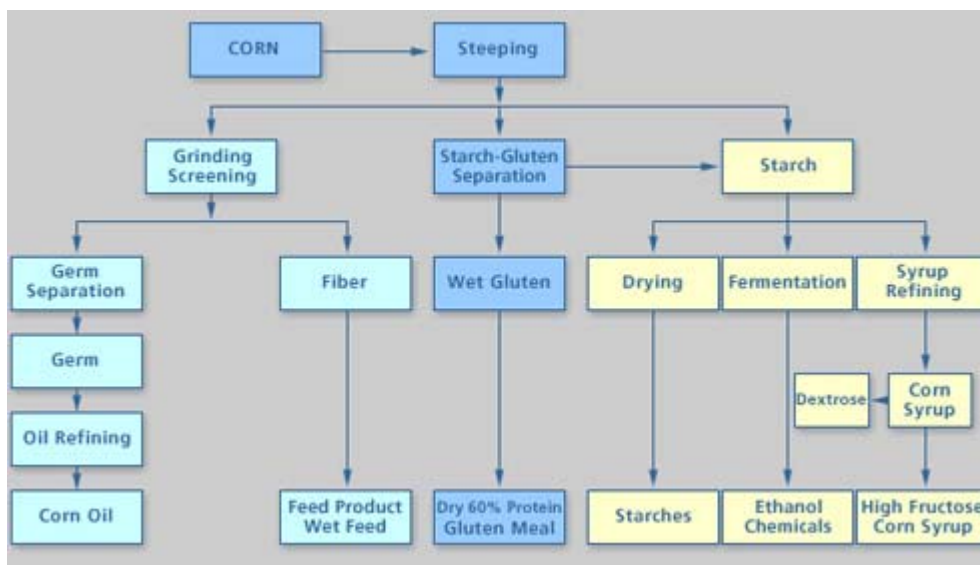
After steeping, the grain slurry is processed through a series of grinders to separate the germ portion of the kernel. In the case of corn, oil from the germ is either extracted on-site or sold to crushers who extract the corn oil. The remaining fiber, gluten and starch components are further segregated using centrifugal, screen and hydroclonic separators.

The steeping liquor is concentrated in an evaporator. This concentrated product, heavy steep water, is co-dried with the fiber component and is then sold as gluten feed to the livestock industry. Heavy steep water is also sold by itself as a feed ingredient or can be used in other applications such as a component in an environmentally friendly alternative to salt for removing ice from roads.

The gluten component (protein) is filtered and dried to produce the gluten meal co-product. This product is sought after as a feed ingredient in poultry broiler operations.

The starch and any remaining water from the mash can then be processed in one of three ways: fermented into ethanol, dried and sold as modified starch, or in the case of corn, processed into corn syrup. The fermentation process for ethanol is very similar to the dry mill process described above.

Figure 25: Traditional Wet Milling Ethanol Production Process



Source: Renewable Fuels Association

Appendix C: Interview List

Table 33: Interview List

Company	Product/ Technology	Contact	Position
ORNL	General	Brian Davidson	Chief Scientist for Systems Biology and Biotechnology
NREL	General	Adam Bratis	Biochemical Platform Program Manager
NREL	General	James McMillan	Principal Chemical Engineer; Manager, Biorefining Process R&D
NCERC	General	John Caupert	Director
NCERC	General	Gene Peters	Process Engineering
Memphis BioWorks & Powell Consulting, LLC*	General	Randy Powell	AgBio Co-Coordinator / President
USDA, ARS,	General	Joseph Rich	Bioproducts and Biocatalysis Research, Research Leader
USDA, ARS	General	Cletus Kurtzman	Microbial Genomics and Bioprocessing Research, Supervisory Microbiologist
USDA, ARS	General	Julious Willett	Plant Polymer Research, Supervisory Chemical Engineer
USDA, ARS	General	Mark Berhow	New Crops and Processing Technology Research, Research Chemist
USDA, ARS	General	Sean Liu	Cereal Products and Food Science Research, Research Leader
USDA, ARS	General & Cellulosic Ethanol Biochemical Platform	Michael Cotta	Fermentation Biotechnology Research, Supervisory Microbiologist
USDA, ARS	Cellulosic Ethanol Biochemical Platform	Bruce Dien	Fermentation Biotechnology Research, Chemical Engineer
ButylFuel	Butanol	David Ramey	CEO
Gevo	Butanol	Dave Munz	Manager - Business Development
University of Illinois & Tetravita	Butanol	Hans M. Blaschek	Professor
Bioamber	Succinic Acid	Dilum Dunuwila	Business Development
BioProcess Innovations	Zein Extraction	Clark Dale	President
Cargill	3-HPA	Bill Brady	Media Relations
Vaperma	Ethanol Distillation - Membrane	Christian Roy	Founder and VP of Business Development
University of Minnesota	Anaerobic Digestion	Bill Lazarus	Professor
Prairie Gold	Zein Extraction	Oncor Patel	Project Engineer
MBI	Succinic Acid	Bernie Steele	Director of Operations

*Previously served as the VP of Performance Chemicals Manufacturing for Eastman Chemical Company.

Distributed Power Generation Technology (Roseau Gasification)

Project Coordinator: Michael Sparby, Senior Project Strategist, (320) 760-1260

Recipient Organization: Agricultural Utilization Research Institute

The Agricultural Utilization Research Institute (AURI) is in the process of demonstrating a distributed power generation technology including electricity and synthetic diesel production. AURI is working with multiple partners to achieve the goals of this demonstration project. Collaborators include the City of Roseau, Roseau County, National Farmers Union, the Minnesota Barley Growers Association, Minnesota Turf Seed Council, Minnesota Wheat Research and Promotion Council, the Department of Energy, the Minnesota Department of Commerce, DEED and now the Northwest Minnesota Foundation. The project technical team includes AURI, The City of Roseau Public Works staff and Community Power Corporation of Littleton Colorado. AURI is leading the project and is coordinating all aspects of the project.

The technology being used for this project is a gasification unit that will produce 25kw of energy (Phase I – DOE Project) or 25 gallons of synthetic diesel (Phase II) per day. The technology was originally developed for military application to be used with garbage and other frontline waste products and is in testing stage at various military bases around the US. The unit is designed to utilize multiple biomass feedstocks.

The gasification power production process will be supplied by Community Power and is based on previous testing of ag biomass material conducted at our Waseca lab and assisted in identifying a densification system that allow the use of light fluffy ag materials which is densified prior to gasification. The project, which is located in Roseau, Minnesota, will be accomplished in two phases:

- Phase I – Install and demonstrate a small scale biomass to synthesized gas to run an engine to produce electricity for the Roseau school district (DOE Portion of the Project)
- Phase II – Install and demonstrate a biomass to synthetic diesel utilizing the Fischer–Tropsch process which is a catalyzed chemical reaction in which synthesis gas, a mixture of carbon monoxide and hydrogen, is converted into synthetic diesel.

The project was on track to accomplish the set goals of commissioning and feedstock testing by the end of June until a local electrician noticed a couple of electrical components did not have UL ratings. He contacted the state electrical inspector and the unit was locked out until the issue could be resolved.

It turns out that under Minnesota state law a demonstration unit does not need all components to be UL rated, but the state inspector requires to have the unit certified that the unit will not cause electrical harm to an operator or the grid.

The electrical engineer was contracted to conduct the certification and the electrical engineers final certification report was submitted to the state electrical inspector and approved in the middle of August. The vendor was not able to schedule engineers to return to the site until mid-September and are currently doing trouble shooting and test firing of the unit. Once the unit is test fired and dialed in on certain feedstocks the unit will be commissioned and the training of the operator, AURI staff and City of Roseau Staff will happen. We were able to secure funding to hire an operator for the unit for the next year. The sources of the funds are from AURI and the Northwest Minnesota Foundation. This individual will be hired by the City of Roseau under a contract with AURI.

Collaborative Financial Partners and Funding Request

Phase I (Biomass to Electricity and Heat)

AURI	
AURI Energy Initiative Funds	\$59,500
National Farmers Union	\$100,000
AURI	
Federal DOE Grant funds	\$200,000
MN Wheat Research and Promotion Council	\$15,000
MN Turf Seed Council	\$15,000
Northwest Minnesota Foundation	\$19,000
City of Roseau	\$300,000

Total Project Costs Phase I	\$708,500

Phase II (Biomass to Synthetic Diesel)

AURI	
Department of Commerce Grant (Committed)	\$150,000
MN Corn Growers (Committed)	\$150,000

Total Project cost Phase II	\$300,000