

ALTERNATIVE, RENEWABLE AND NOVEL FEEDSTOCKS FOR PRODUCING CHEMICALS

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Alternative, Renewable and Novel Feedstocks for Producing Chemicals

Study Conducted By:

Chemical Industry Vision2020 Technology Partnership

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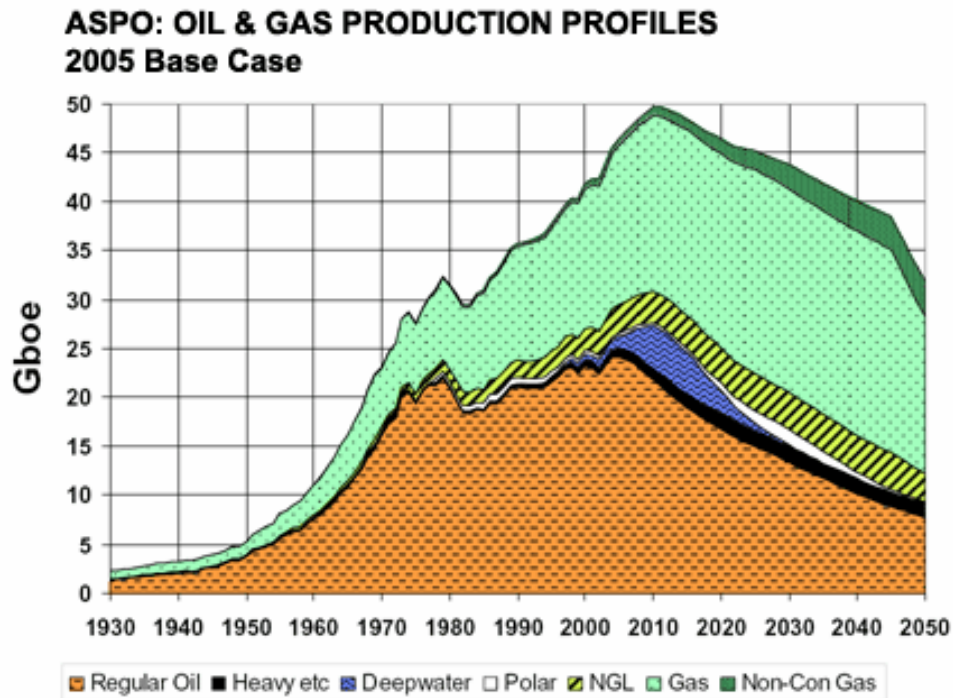


Chart from the Association for the Study of Peak Oil and Gas shows a compilation of worldwide oil and gas data based on information obtained by the independent national associations in Australia, Austria, Canada, China, Egypt, France, Germany, Ireland, Israel, Italy, Japan, Korea, Mexico, New Zealand, Norway, Portugal, Russia, South Africa, Spain, Sweden, Switzerland, United Kingdom and the United States. Many other organization and government agencies show similarly shaped profiles. (Gboe – giga barrels oil equivalent)

<https://aspo-ireland.org/Newsletter.htm>

Preface

Industrial chemistry has evolved from using natural plant oils, coal tars and wood tars to an industry that today generates in the United States alone over 160 million tons/yr of products from petroleum (~85%) and natural gas (~15%). The change in feedstock choice over the last century is the result of the components in petroleum and natural gas providing chemists with the lowest combined cost of raw materials and processing. Starting in 2000, the United States experienced a rapid increase in the price of petroleum and natural gas. Wellhead gas price went from an average of \$4.01/million Btu in 2000 to an average of \$7.62 in 2005, with short periods of over \$10/million Btu. Crude petroleum likewise rose rapidly from \$33/bbl in 2000 to \$56/bbl in 2005 and even higher in 2006. The rapid increases with significant fluctuations were the result of numerous production trends, booming Asian growth, short-term events (e.g., hurricanes), and the geopolitics of oil. These rate increases and fluctuations contribute to uncertainty in the near-term price of feedstocks and encumber U.S. chemicals producers as they compete in a global marketplace.

This recent price and supply volatility foretells a not-to-distant future when even more pronounced volatility will occur. It is well recognized that the natural gas and petroleum production will "peak," plateau and then decline. Although, when the "peak" will occur is speculative, its eventual arrival is not. Approaching the "peak" will be disruptive, add considerably to supply and price pressures and hasten the industry's move from petroleum and natural gas to less volatile "*alternative*" feedstocks such as coal or biomass. Alternative feedstocks will consume more energy and emit more CO₂ per unit of product produced. Biomass may be an exception to higher energy and CO₂ emissions depending on how the CO₂ is accounted for. Planning for and developing new technologies to ease the eventual transition to alternatives and manage CO₂ needs to be initiated by all industry stakeholders.

The *Chemical Industry Vision2020 Technology Partnership* (Vision2020), an industry-led organization several years ago recognized the need to examine alternative fuels and feedstocks. Vision2020, in partnership with DOE Industrial Technologies Program (ITP), directed a ChemicalsPlus project (completed in 2003, <http://www.chemicalvision2020.org/>) which examined alternative heat and power options for the industry. Vision2020 and ITP also directed a second project, *Alternative, Renewable and Novel Feedstocks*, to identify industrial options and to determine the work required to make alternative, renewable and novel feedstock options attractive to the U.S. chemicals industry. This report presents the *Alternative, Renewable and Novel Feedstocks* project findings which were based on a technology review and industry workshop.

The technology and know-how required to produce chemicals from alternative, renewable, and novel feedstocks is available and currently practiced at large scales in many parts of the world. These existing plants are the result of governments providing significant incentives for their construction and operation. Similar construction and operation of U.S. chemical manufacturing facilities using alternative, renewable and novel feedstock will occur only when the economics or government policies support the work. The economics of establishing such facilities can be made attractive by improving the technology. This report provides background information and suggests areas for technology improvement that will potentially enable wider use of alternative feedstocks for chemicals production.

Contents

Preface.....	g
Exhibits	i
Abbreviations, Chemicals & Terms.....	j
Executive Summary	I
1. Introduction.....	1
2. Current Status of Alternate Feedstocks Options and Related Processes	4
2.1 Coal	4
2.1.1 Coal Gasification.....	5
2.1.2 Coal Liquefaction	9
2.2 Biomass.....	10
2.2.1 Biomass Thermochemical Gasification.....	13
2.2.2 Biomass Fermentation.....	14
2.2.3 Pyrolysis	17
2.2.4 Biomass R&D Needs.....	18
2.4 Unconventional Natural Gas.....	20
2.5 Tar Sands/Heavy Oil.....	22
3. Research Needs and Recommendations	24
3.1 Relative Value of Alternative, Renewable and Novel Feedstocks	26
3.2 Ranking Alternative, Renewable and Novel Feedstock Opportunities for U.S. Chemicals Production	28
3.3 Gasification Issues for Alternative, Renewable and Novel Feedstocks	29
3.4 Syngas to End-Product Technical Issues	32
3.5 Feedstocks for Non-Gasification Routes to Chemical End Products	34
3.6 Workshop Summary of Research Needs and Recommendations.....	36
4. Conclusion	37
4.1 Existing Opportunities	37
4.2 Technology Needs to Improve Process Viability	39
4.3 Institutional Direction	40
Appendix 1: Vision2020 Task Force	42
Appendix 2: Alternate, Renewable, and Novel Feedstocks Workshop Attendees	43
Appendix 3: Large-Volume Chemicals Manufactured in the United States	44
Specialty Chemicals, Chemicals with Development Potential	45
Fuels, Hydrocarbons	45
References.....	47

Exhibits

Exhibit 1: Industrial Use of Energy	1
Exhibit 2: Coal Gasification Schematic.....	6
Exhibit 3: Coal Liquefaction Flow Diagram	10
Exhibit 4: Projected Level of Impact of Biomass R&D	11
Exhibit 5: Syngas Biomass Gasification Scheme	13
Exhibit 6: Top 12 Products from Sugar Fermentation.....	14
Exhibit 7: Flow Diagram for the Production of BioOil	17
Exhibit 8: UOP Methanol to Olefins Flow Diagram	21
Exhibit 9: Major Chemicals of Interest for Alternative, Renewable and Novel Feedstocks..	25
Exhibit 10: Relative Value of Alternative, Renewable and Novel Feedstocks	28
Exhibit 11: Ranking Probability of Feedstocks Chemical Route to Chemicals Production...	29
Exhibit 12: Major Concerns Identified for Viable Gasification Crosscutting All Feedstocks	31
Exhibit 13: Primary Concerns for Production of Products from Syngas.....	33
Exhibit 14: Major Hurdles to Implementing Production of Bio-chemicals.....	34
Exhibit 15: Carbon to Products Pathways	35
Exhibit 16: Major Chemicals of Interest for Alternative, Renewable and Novel Feedstocks	38
Exhibit 17: Implementation Potential for Feedstock Flexibility Program by Product	38
Exhibit 18: Implementation Potential for Feedstock Flexibility Program by Feedstock.....	39

Abbreviations, Chemicals & Terms

Acetone	dimethyl ketone or CH_3COCH_3
Acrylic acid....	$\text{CH}_2=\text{CHCOOH}$ or 2-propenoic acid is a chemical compound (formula $\text{C}_3\text{H}_4\text{O}_2$) is the simplest unsaturated carboxylic acid with both a double bond and a carboxyl group linked to its C_3
Bcfd.....	billion cubic feet per day
BDC	Bitumen derived crude
BTX.....	Benzene, toluene and xylenes
CBP.....	Consolidated bioprocessing approach
CPP.....	Catalytic process pyrolysis
CTL	Coal to liquid
DCC	Deep catalytic cracking
DME	dimethylether or CH_3OCH_3
DOE	U.S. Department of Energy
EERE	Energy Efficiency and Renewable Energy
FCC.....	Fluidic carbon cracking
FT.....	Fischer-Tropsch
Glycerol.....	also known as glycerin, glycerine, propane-1,2,3-triol, 1,2,3- propanetriol, and 1,2,3-trihydroxypropane
GTL	Gas to liquid
GW_t	Gigawatt thermal equivalent (10^9 watt thermal equivalent)
HGO.....	Heavy gas oil
IGCC.....	Integrated gasification combined cycle
ITM.....	Ion transport membrane
ITP	Industrial Technologies Program
Lactic acid	(2-hydroxypropanoic acid) or $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$
LNG.....	Liquefied natural gas
Methacrylic....	2-methyl-2-propenoic acid, is a low molecular weight carboxylic acid $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$
MEG.....	mono ethylene glycol or $\text{HOCH}_2\text{CH}_2\text{OH}$ or ethane-1,2-diol
MPG.....	mono propylene glycol or 1,2-propanediol
MTO.....	Methanol to olefin
MTG	Methanol to gasoline
MTP	Methanol to polymer, Methanol to propylene
MW_e	Megawatt electric equivalent (10^6 watt electric equivalent)
MW_t	Megawatt thermal equivalent (10^6 watt thermal equivalent)
PDH	Propane dehydrogenation
PLA	Polylactic acid
R-Cl.....	Chlorinated hydrocarbon
SAGC.....	Steam assisted gravity drainage
TCM	Trillion cubic meters (10^{12} cubic meter)
TPD.....	tons per day
Toluene	methyl benzene
WGS	Water gas shift
Xylenes	ortho (1,2-dimethylbenzene), meta (1,3-dimethylbenzene), and para (1,4-dimethylbenzene)

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Executive Summary

The U.S. chemicals industry operates in all 50 states, directly employs over 800,000 and generates more than \$400 billion in revenue. The nation depends on the industry to supply chemicals used in products for our homes, clothing, food, healthcare, potable water, transportation and many other items we take for granted. This vital industry relies on the carbon in natural gas and petroleum to provide the basic building blocks or feedstocks to produce over 160 million tons of materials required to manufacture the products we use everyday.

The natural gas and petroleum feedstocks used by the U.S. chemicals industry are equivalent to 3.4×10^{15} Btu/yr (3.4 quad/yr) of energy consumption, accounting for approximately half the chemical industry's energy use, 4% of the total U.S. energy consumption and 3% of the total U.S. natural gas consumption. The recent changes in availability and cost of these carbon sources have directly resulted in a decline in U.S. chemicals production, lower U.S. chemicals export (going from an 80-yr trade surplus peaking in 1995 at \$20 billion to a trade deficit beginning in 2002) and the loss of domestic chemicals manufacturing jobs. These declining trends from changes in energy availability and costs are cause for significant concern about the near- and long-term supply of carbon feedstocks and their economic impact on the domestic chemicals manufacturing industry. The chemicals industry is such a significant user of petroleum and natural gas that the use of alternate feedstocks must be implemented to meet national objectives of energy independence and to retain a domestic industry that is competitive on a global scale.

This report identifies feedstock options and the direction of work required to overcome the hurdles to make alternative, renewable and novel feedstocks attractive to the U.S. chemicals industry. These hurdles include technology, policy, and institutional constraints. The focus of this report is primarily research and development areas that will advance the technologies required to manufacture U.S. bulk chemicals from readily available domestic materials not derived from natural gas or petroleum. Significant policy and institutional solutions are equally important and are suggested although in brief. The successful pursuit of R&D will reduce U.S. dependence on foreign oil, lessen the demand for natural gas, lower the volatility of the carbon feedstock supply chain and increase the international competitiveness of the U.S. manufacturing industry.

The *Chemical IndustryVision2020 Technology Partnership* (Vision2020) formed a task force in early 2005 to evaluate alternative, renewable, and novel feedstocks for manufacturing chemicals, in recognition of the high risk to U.S. chemicals industry with continued dependence on petroleum and natural gas feedstocks. The alternative feedstock task force conducted a two-part effort:

1. Extensively reviewed literature to assess the current status of alternate feedstocks and the state of the art of the processes for conversion of these feedstocks to chemicals
2. Conducted a workshop subsequently for chemicals industry stakeholders to identify the most promising alternate renewable feedstocks and barriers that limit their usability in large-scale chemicals manufacturing

Alternate Feedstock Technology

Six alternative feedstock sources (coal, biomass, petroleum coke, tar sands and oil shale, organic municipal solid waste, and unconventional natural gas, including methane from “stranded” or “remote” sources, coal bed methane and gas hydrates) and five technologies (gasification, fermentation/extraction, pyrolysis, liquefaction, and coking) were reviewed for their potential application in production of chemicals. This study concluded that gasification of coal, petcoke, and biomass and fermentation/extraction of biomass have the highest probability of success, particularly for the near-term purposes; accordingly, efforts to identify R&D needs were focused on these areas. Chemical process chains were also reviewed to determine the application areas that will potentially yield maximum benefit from using these new technologies and feedstocks. All investigations focused on targeting manufacture of bulk organic chemicals, the path identified for the highest energy and economic impact potential.

a) Current Status of Alternate Feedstock Technologies

Gasification technologies utilizing coal are mature and widely used for power and liquid fuels. However, improvements in gasification and ancillary equipment are needed to make the process more economical at the scale of most chemical plants and to provide CO₂ management before wide-spread production of chemicals in the United States will occur. Small-scale 100 – 500 MW_{th} gasifiers will be required for standalone bulk chemical manufacturing (U.S. DOE, 2006). This scale is not economical for integrated gasification combined cycle (IGCC) power production or Fischer-Tropsch production of transportation fuels. IGCC provides significant improvements in energy efficiency and the ability to manage CO₂. Future power and/or fuel IGCC facilities that provide feedstock to chemical plants, in a relationship similar to the crude oil refining industry, are likely to evolve.

Gasification of biomass is less advanced and will require more R&D than coal and petcoke feedstocks. The type and size of gasification systems developed will have a major impact on the economics for application in chemicals industry. Chemical production requires medium- to high-Btu syngas; air-blown gasifiers developed for power and fuel applications will not be viable for chemical production because they produce low-Btu syngas (U.S. DOE, 2003).

“First generation” biomass fermentation processes are technically and commercially ready for small specialty chemicals using sugar-based feedstock and are emerging in the market place today. However, economical production of bulk chemicals will require “second generation” processes that use cellulose-based feedstock – a large step forward that requires significant R&D to address the technical hurdles to make the processes technically viable and economical. Co-production of bio-fuels and chemicals, such as in a biorefinery, will likely improve the economics for both processes.

b) R&D Needs

Technological advances are a major constraint to hasten the adoption and lessen the economic and environmental impact of transitioning from traditional chemical feedstocks to alternative, renewable and novel feedstocks. An initial set of R&D needs was developed from a preliminary literature review and from teleconferences with the industrial working group:

- R&D needs must be focused on production of bulk chemicals (i.e., those produced at levels > 1,000,000 tons/year) to create a significant impact on the domestic chemicals industry.
- Near-term opportunities should focus on alternative feedstock substitutions or augmentation to make current products with minimal changes in existing manufacturing facilities, i.e., for near-term impact, only those processes that are one or two unit operations different than the traditional chemical practices should be investigated and developed. On the other hand, long-term opportunities should involve manufacture of new products via new chemistries and new processing equipment.
- All technologies must offer the potential to advance the state of the art, be cost effective relative to current techniques using conventional feedstocks, and be applicable to the broad goals of industry and society toward reduced consumption of petroleum and natural gas, and environmental sustainability.

More specifically, technology improvements which will hasten the transition to alternative, renewable and novel feedstocks in the chemicals industry require focus on R&D in the following areas:

- Novel Carbon Conversion Technologies
 - Novel process developments (e.g., plasma gasification [U.S. Patent Application 20030024806] and rocket hydrogenation [U.S. Patent 4323538]) are examples of novel untested technologies that maybe advantageous for chemicals production, particularly since their scale may be more suitable than gasification
- Novel Separations
 - Novel separations technologies that are energy efficient, highly selective and economic for a) oxygen from air, b) separations of gasifier reaction products, c) separation of liquefaction reaction products, and d) CO₂ separation, capture and control
- Reactions Processes
 - New enzymes that can utilize low-cost “waste” and cellulose-based biomass in the production of chemicals
 - Scalable fermentation processes for biomass conversion to chemicals
 - Radically improved Fischer-Tropsch process for chemicals from coal to reduce waste generation and energy consumption
 - Direct liquefaction process for chemicals from alternative feedstocks
- Process Scale-Down
 - The economies-of-scale for gasification units and ancillary equipment are best fitted to the production of power and fuels. Even the largest world-class chemical plants use carbon feedstocks on a relatively small scale compared to a utility. Therefore, development of new gasification systems (design and materials) that are less sensitive to economies-of-scale is required.
- Materials of Construction
 - Gasifier unit internals require significant maintenance which is costly, both in terms of downtime and capital. New construction materials can assist with alleviating these costs.
- Process Control Technologies and Plant Design
 - Energy savings and emission control strategies

➤ CO₂ Technology

- Technologies and planning options for the control, capture, marketing or sequestration of CO₂ is essential for the success of non-biomass alternative feedstocks.

Specific applications which have the highest probability for near-term success and therefore, should be the focus of initial R&D programs include:

- (1) gasification of coal to olefins and aromatics, and
- (2) fermentation and/or extraction processes for conversion of lignin to aromatics.

Policy Requirements

Changing raw materials for chemicals manufacturing is a major business model shift, as risky as the move of the agriculture industry from a supplier food stocks to transportation fuels—a practice that has been federally subsidized for over two decades. Therefore, in addition to technology development, state and federal energy policies will be needed to assist with the risks associated with high capital investments for new feedstock facilities in an environment of fluctuating energy prices.

New federal policies will be required to ensure adequate and diverse energy supplies. They can contribute to hastening the adoption and lessening the economic and environmental impact of transitioning from traditional chemical feedstocks to alternative, renewable and novel feedstocks. Significant policy considerations include:

- **Alternative Carbon Subsidy** – The federal government has subsidized fuel ethanol production over the past 25 years. This subsidy (\$0.51/gallon) is equivalent to \$0.15 per pound of carbon. The chemicals industry carbon use is about one-tenth that of the transportation fuel industry. An equivalent subsidy would significantly lower the economic risks associated with development and construction of alternative feedstock manufacturing facilities.
- **Carbon Dioxide (CO₂) Emissions** – The federal and state governments need to establish a clear long-term CO₂ policy and/or trading programs in order to remove economic uncertainties associated with CO₂ emissions. This is particularly necessary in the case of non-biomass alternative feedstock which will likely result in substantial additional CO₂ emissions compared to traditional chemical feedstocks.
- **Loan Guarantees** – Federal loan guarantees for construction and performance of new chemical plants based on the use of alternative feedstocks would lower the risk of early adopters and hasten the feedstock transition.

Institutional Changes

Institutional changes, both in traditional chemicals industry partners and government funding emphasis, are essential to the future success of transitioning to alternative feedstocks. The chemicals industry is conservative and has long established ties with petroleum-based raw material suppliers. The use of alternative feedstocks will require the industry to develop an understanding and build new relationships with potential feedstock suppliers that have not been chemical industry stakeholders. In addition, there appears to be economically beneficial

scenarios where it will be advantageous for the chemicals producer to co-locate with an alternative fuel or power utility producer and/or near alternative feedstock source. In these instances, the chemical plant could co-produce chemicals and fuel/power and/or becomes dependent on the utility for the supply of its raw material. The chemicals industry must explore and begin to work with these new raw material suppliers and possibly new production partners.

The Path Forward

Several current DOE programs are addressing reductions in energy usage and replacement of fossil fuels for transportation and power, but there are presently no major efforts to replace use of petroleum and natural gas as raw materials for feedstocks in manufacturing of chemicals. The current federal R&D emphasis on transportation fuels and power generation and overlooks the large reduction potential (3.4 quad) in the use of imported petroleum and domestic natural gas by promoting alternative feedstocks in the manufacturing sector. Alternative feedstocks will provide a route to improving the nation's long-term manufacturing viability and international competitiveness.

Recognizing that the chemicals industry is the single largest non-utility user of natural gas and a significant user of petroleum second only to transportation, it is recommended that DOE lead an initiative to reduce petroleum and natural gas use as chemical feedstock. DOE Industrial Technologies Program (ITP) is well positioned within DOE to implement an R&D platform to address the issues specifically related to replacing petroleum-based feedstocks with coal or biomass feedstocks. DOE's Biomass program has published a study, *Top Value Chemicals from Biomass* (Werpy and Peterson, 2004), that has identified 12 chemicals producible from sugars that are of interest to biorefiners. None of the identified chemicals are in the top 100 bulk chemicals produced in the United States. Likewise, DOE's Fossil Energy program is focused on large-scale gasification and CO₂ sequestration to support conversion of natural gas power plants to coal-based power production. It does not address small/medium gasification systems required for chemical feedstock production. An industrial manufacturing focused program within ITP would interface and compliment, but not duplicate, ongoing efforts in EERE Biomass and Fossil Energy programs which focus on alternative transportation fuel production and power production, respectively.

The technology R&D work needs to begin now in order to lessen the energy and environmental impact of the eventual change over to alternative, renewable and novel feedstocks for the chemicals industry. Industry stakeholders will need to work closely for the transition within the United States to be successful.

1. Introduction

The U.S. chemicals industry consumed ~7.7 quads (1 quad = 10^{15} Btu)* of primary energy† in 2004 and accounts for approximately 6.4% of the total U.S. energy consumption. It is by far the largest industrial user of energy in the United States (Exhibit 1). Approximately 48% of this energy was attributable to the fuel consumed for heat and power production to operate equipment such as heaters, dryers, reactors, columns, pumps, and compressors. The remaining 52% (~4.0 quads) was used as feedstock or the basic building blocks required for producing the thousands of chemicals used in manufacturing of plastics, rubbers, fibers, soaps, paints, and fertilizers—products that we consume in our everyday activities. Petroleum contributes about 85% or 3.4 quads to this annual feedstock supply, while natural gas constitutes the remaining 15% or 0.6 quad. Several industrial and government programs are underway to reduce heat and power energy consumption, but no significant efforts are in place to address the enormous dependence on carbon-based feedstock by the chemicals industry.

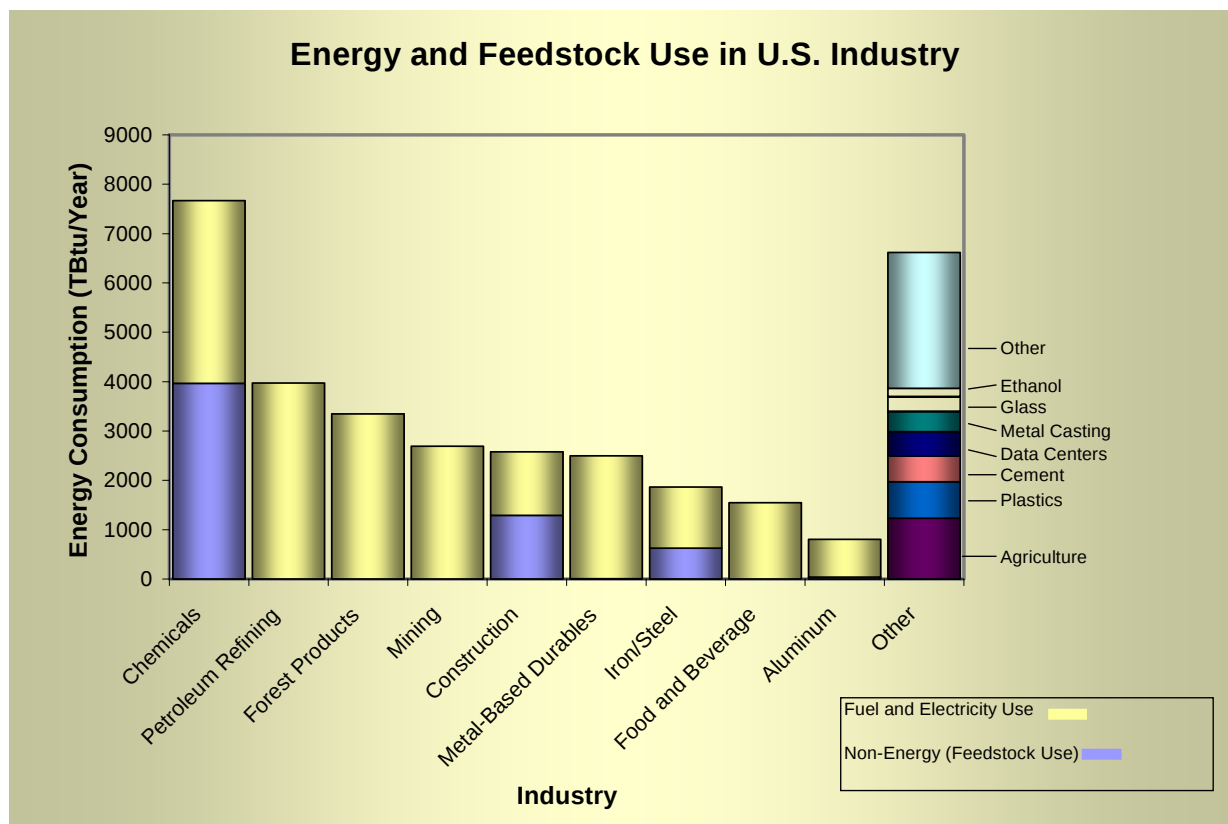


Exhibit 1: Industrial Use of Energy

(Source: DOE Annual Energy Outlook 2007 Supplemental Tables: Table 27)

The domestic supply of natural gas and petroleum feedstocks for chemicals manufacturing is constrained and their prices have risen dramatically over the past five years. Roughly 50% of the methanol, 45% of the ammonia, and 15% of the ethylene capacities in the United States were

* Annual Energy Outlook 2007 Supplemental Tables: Table 27

† Primary energy consumption is the amount of site consumption, plus losses that occur in the generation, transmission, and distribution of energy

shutdown primarily as a result of rising natural gas prices in 2004. The domestic demand for these products was met by importation and has resulted in a U.S. chemical industry trade deficit for the first time in the industry's history. This lost productivity is unlikely to return to the United States and the trend to transfer chemicals industry operations overseas will continue if the energy situation is not addressed. The impact of these trends spreads beyond the chemicals industry, negatively affecting the U.S. GDP, process equipment manufacturers, plant service providers and employment at chemical manufacturing plants. The chemicals industry stakeholders (i.e., corporations, federal and state governments, labor, NGOs, etc.) must address the growing environmental, supply, and price issues related to energy. Otherwise, the United States will increasingly depend on foreign natural gas and petroleum supplies to produce the chemicals the U.S. manufacturers and consumers need, leading to an increased vulnerability of the American economy to foreign instabilities.

The *Chemical Industry Vision2020 Technology Partnership* (Vision2020), an industry-led organization for accelerated innovation and technology development, recognizes the potential impact that our strong dependence on natural gas- and petroleum-based fuels and feedstocks could have on the industry and the nation. In 2001, Vision2020 formed a task force to identify the key barriers limiting more widespread use of biomass for heat and power production in the chemicals industry. The study, *Highlights of Biopower Technical Assessment: State of the Industry and Technology*, completed in 2003, (<http://www.chemicalvision2020.org/>) made the following key conclusions:

- Gasification is the least technically developed, but the most efficient bio-based heat and power generation process.
- Secondary waste treatment from a biorefinery heat and power plant could be 10% of the total capital equipment costs.
- Experience from near-term projects to produce power from woody-type biomass would be useful for designing biorefinery waste treatment facilities.

Vision2020 formed a new task force in early 2005 to evaluate alternative, renewable, and novel feedstocks for manufacturing chemicals, in recognition that feedstocks represent over half of the industry's energy use (see Appendix 1). The goal of the feedstock task force was to identify specific research requirements that could guide the allocation of R&D funding resources toward collaborative industry-academic-government programs geared to address technical challenges associated with implementing alternative feedstocks. The feedstock task force conducted the study in two parts:

1. Extensively reviewed literature to assess the current status of alternate feedstocks and the state of the art of the processes for conversion of these feedstocks to chemicals
2. Conducted a workshop subsequently for chemicals industry stakeholders to identify the most promising alternate renewable feedstocks and barriers that limit their usability in large-scale chemicals manufacturing

This report summarizes the results of the above efforts and consists of a technology review which assesses alternative, renewable and novel feedstocks options, current technology status and R&D activities (section 2), and the feedstock options and R&D needs identified as priorities as a result of the industry workshop (section 3). (See Appendix 2 for list of workshop attendees).

While this report presents a compilation of research needs and opportunities identified, the data-gathering activities were limited by time, scope, and degree of participation. As a result, the report may not fully capture all viewpoints. Although efforts were made to incorporate a broad range of views, some valid ideas may have been excluded based on judgments made in combining and prioritizing information to produce a final report.

2. Current Status of Alternate Feedstocks Options and Related Processes

Most of the currently available studies on alternative feedstocks focus on energy production, either for electricity, liquid fuels from syngas, or bio-based ethanol. A recent study by George Olah (2005) discusses the potential of methanol economy, i.e., methanol as a viable alternative to fossil fuel resources for energy and feedstock needs. The Vision2020 task force undertook an extensive literature review to study the state of the art of using alternative, renewable, and novel feedstocks for large-scale manufacturing of chemicals.

The goal of the literature review was to build a framework for guiding future research efforts toward enabling replacement of petroleum-based feedstocks with renewable feedstocks in a manner that would generate savings in supply and cost. The review aimed to determine the level to which alternate feedstocks process technologies have been developed and the extent of market penetration of these technologies.

The alternatives to conventional petroleum- and natural-gas-based feedstocks include coal, biomass, unconventional natural gas (such as methane from “stranded” or “remote” sources, coal bed methane and gas hydrates), and unconventional oil derived from oil shale and tar sands. Much of the findings presented below are sourced from reports prepared for the National Commission on Energy Policy in November 2004 (Mann 2004, Williams 2004a and 2004b, Hirsch et al. 2006, Ragauskas et al. 2006).

2.1 Coal

Substantial U.S. coal reserves make coal an attractive alternative to natural gas and petroleum. There have been several assessments of the use of coal for generation of syngas and fuel liquids through Fischer-Tropsch process. While several coal gasifiers are already running in the United States, new pilot gasification plants are being built for power production using clean coal technology. Other coal-based technologies, such as gas-to-liquid plants, are being pilot-tested around the world. Many of these initiatives are being undertaken outside of North America in areas where petroleum supply is limited and can take advantage of regional supplies of coal. For example, syngas to fuels is being done by Sasol in South Africa, and China has invested in coal liquefaction to fuels. Although these plants are focused on fuel manufacture, the lessons learned will be applicable to production of chemical building blocks.

Historically, research in coal gasification has focused on energy fuels, and more recently on power production, with less emphasis on commodity chemicals production. For example, DOE’s FutureGen project seeks to improve coal gasification for power production. The U.S. government provides far less funding for research on chemical production from coal.

The economics of coal-to-chemicals production varies around the world. Chemicals are presently produced from coal in regions with an abundance of low-cost coal, such as South Africa, Eastern Europe, and China. The following sections of this report summarize the global status of coal gasification and coal liquefaction technologies.

2.1.1 Coal Gasification

Coal provides the strongest long-term option for alternate feedstock in the United States because of its large domestic reserves. Coal gasification technology has been under development for decades, having been used in Germany in WWII (Becker, 1981) and in South Africa to produce liquid fuels in combination with Fischer-Tropsch processing. Small-scale gasification facilities are producing chemicals in the U.S., but replacement of commodity chemical production on the scale and breadth of current petrochemical plants will require additional development to reduce costs and technical uncertainties.

Worldwide Status

The status of coal gasification for applications including production of chemical feedstock is reflected in its already wide practice worldwide, with 117 plants (385 gasifiers)[‡] operating in 24 countries in 2004. The majority of existing gasification plant capacity utilizes coal (i.e., 49 percent of capacity provided by 22 plants). It is also projected that coal will be the feedstock of choice for most new capacity planned for installation between 2005 and 2010, with coal expected to feed 29 of the 38 new plants; 24 of these 29 new plants will be located in China. At existing plants, a slight majority (37 percent of capacity at 81 plants) generates feedstock for chemical production, closely followed by Fischer-Tropsch liquids production (i.e., 36 percent of capacity at 4 plants). Of the 38 new plants, 24 (63 percent of the total) will produce syngas for chemical feedstock. In terms of capacity, however, Fischer-Tropsch liquids will be the dominant gasification product at 43 percent, and chemicals will come in second at 34 percent (BCS, Inc., 2007).

Coal gasification is being used today for small-scale chemicals production in the United States and elsewhere. In the US and elsewhere coal gasification is mainly being used for electricity production, but chemicals are being produced in the US from gasifiers. In 2004, there were 366 gasifiers worldwide producing 42.7 GW_t/year of syngas, 27 GW_t/year of that from coal (Williams, 2004a & 2004b). Other estimates provide gasification production in GW_t equivalents as 24 GW_t/year chemicals, 23 GW_t/year electric, and 14 GW_t/year synfuels. The U.S. currently accounts for 15 percent of world gasification capacity. Seven of the U.S. plants currently operate on coal and/or petroleum coke, three of which produce syngas as feedstock for the production of chemicals or fertilizer. There are firm plans to build six new plants in the U.S. that will run on coal and/or petroleum coke by 2010, with possibility of coal-based IGCC[§] plants added to that mix (BCS, Inc., 2006).

Coal Gasification Process

The process starts with the production of syngas in a gasifier (coal + steam/O₂) to give hydrogen (H₂) and carbon monoxide (CO) – the primary syngas constituents. Further catalysis assists the reaction of CO to CO₂ in presence of water to produce H₂ (e.g., at Dakota Gasification Company). Subsequently, ammonia can be produced, or methanol, alcohols, and aldehydes by oxosynthesis. A Fischer-Tropsch process can be used to produce alkanes, which are building blocks for many large-volume chemicals.

[‡] This is the total number of plants with capacity exceeding 100 MW electric (MW_e) equivalent included in the world gasification survey as reported in USDOE (2002). These plants equaled a total capacity of over 25,000 MW_e, which equated with approximately 45,000 MW thermal (MW_{th}) capacity.

[§] Integrated coal gasification combined cycle (IGCC) systems are environmentally friendly alternative to coal-fired power plants that combine coal gasification unit with a gas-fired combined cycle power generation unit.

A generic oxygen-blown gasification system is illustrated in Exhibit 2 and comprises the following main steps:

- (i) Reaction with oxygen or steam at 70 atm
- (ii) Quenching with water to remove particles and cool syngas
- (iii) Water-gas shift reaction (WGS) to produce H_2 and CO_2
- (iv) Removing H_2S and CO_2 simultaneously, using physical solvents

Solvents are recovered by depressurization. H_2S is converted to sulfur in a two-step process by first heating in oxygen to produce SO_2 , which then reacts further with H_2S to produce sulfur and steam.

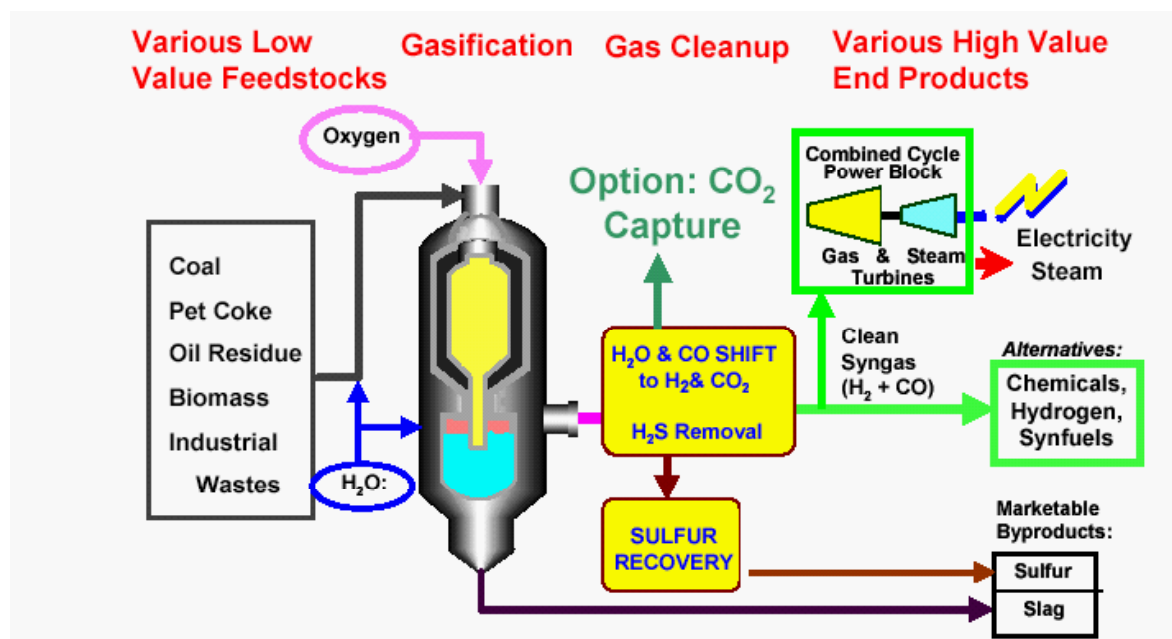


Exhibit 2: Coal Gasification Schematic
(Source: Williams, R.H. 2004b.)

State of the Art of Coal Gasification Technologies

Currently, three gasification technologies dominate the market (i.e., account for 94 percent of the 2004 total capacity) – Sasol Lurgi (41 percent), GE Energy (34 percent), and Shell (19 percent) technologies. This percentage distribution is expected to change by 2010, however, with Shell growing to produce 43 percent of syngas capacity, and Sasol Lurgi dropping to 27 percent. The GE Energy and Conoco-Phillips technologies are planned for use at six new plants each. Thus, Shell's oxygen-blown, high-temperature, slagging entrained-flow technology will dominate the near-term growth in gasification projects. (BCS Inc., 2007)

The U.S. gasification facilities are built based on the following home-grown technologies for chemicals production:

- **E-Gas Technology** – purchased by Conoco Phillips and operated under strategic alignment with Fluor
- **Shell** (http://www.gasification.org/Docs/2005_Papers/05CHHO.pdf)
- **GE Gasifier** (technology acquired from Chevron Texaco)

One successful example of this is Eastman Gasification Services located at Kingsport, TN. This facility produces all of the acetic anhydride and acetic acid needed for in-plant production. The facility has reported a reliability of 97.7% for the production of 80,000 gal/day of methanol (US DOE, 1997). Another facility, the Great Plains Synfuels plant in Beulah, ND, produces 7 million gallons per year of naphtha and 33 million pounds per year of phenol (<http://www.Dakotagas.com>). Recent developments include gasification facilities at petroleum refineries and chemical plants for ammonia production and industrial polygeneration (chemicals along with electricity) (Simbeck, 2001), based on the premise that syngas from residuals is less costly than reformation of methane on a lifecycle basis.

DOE is actively supporting the development of coal gasification for electricity production not only because of feedstock concerns, but also as a means to enable carbon capture. Coal integrated gasification combined cycle (IGCC), a promising clean coal technology with the potential for lower-cost carbon capture, was successfully demonstrated between 1984 and 1989 at Cool Water, California, in the United States. Since then, the following IGCC plants based on oxygen gasification of coal have been built (with subsidy support):

- 250 MWe Demkolec plant at Buggenum, The Netherlands (Shell gasifier and Siemens gas turbine) – Started up in January 1994; only 43% capacity factor at first because of integration between gas turbine and air separation unit (de Lange et al., 2001);
- 262 MWe Wabash project in Indiana (E-Gas gasifier, now ConocoPhillips and GE gas turbine) – Started up in October, 1995;
- 253 MWe Tampa Electric project in Florida (ChevronTexaco gasifier, now GE and GE gas turbine) – Started up in September 1996; and
- 310 MWe ELCOGAS project in Spain (Prenflo gasifier, now joint with Shell and Siemens gas turbine) – Started up in December 1997 (Coca et al., 1998).

Unfortunately, without the ongoing subsidy support and the relatively low cost of petroleum and natural gas until recently, these gasifiers proved to be unprofitable.

Most U.S. government-directed research effort has focused in the past on electricity generation and production of transportation fuels, rather than developing pathways for the production of commodity chemicals. (The gasification technology for power production is described at <http://www.fossil.energy.gov/programs/powersystems/gasification/> and <http://www.gasification.org/Presentations/2005.htm>).

Factors Limiting Widespread Commercialization

Although IGCC was successfully demonstrated for electricity production at Cool Water, gasification has not become an industry standard for coal conversion into power and chemicals. The primary reasons given are the low costs of petroleum and natural gas when the project was completed in the mid-1980s, reliability concerns, installation cost (new technologies must be cheaper than current methods to justify the capital investment), and cultural mismatch and institutional challenges (Williams, 2004a & 2004b). Benefits, such as low pollutant emission, reduced solid waste management, and oil supply/security issues are of public concern rather than private companies. Therefore, promotion by the public sector or federal government is critical for achieving widespread implementation of coal gasification. Since power producers are not comfortable with adopting new technology in the current economic climate, risk-sharing option will also add a boost.

Power regulators also complicate the commercialization of IGCC. IGCC facilities have higher capital costs, ~50% higher than a standard coal plant and ~100% higher than a natural gas plant. Historically, regulators have allowed power companies to easily pass on their fuel costs to electric customers but have been more restrictive in allowing capital costs to be passed on. This trend ignores the longer term benefits provided by IGCC (i.e., more efficient use of coal and the potential to capture CO₂).

There is an argument that generators of power through gasification are mainly focused on competition with traditional coal/steam electric supply, and may not be amenable to the diversion of syngas for chemical production. However, this suggestion has been refuted by chemical industry representatives, suggesting that symbiotic co-generation agreements can be fostered, with chemical manufacture occurring during off-peak hours of electricity production.

Another hurdle is the large quantities of CO₂ produced in gasification which poses the engineering challenge of carbon capture. Use of captured CO₂ in a chemical plant or for direct marketing is currently not economically feasible. However, captured CO₂ can be used for enhanced oil recovery as demonstrated in the joint effort of Dakota Gasification and EnCana, where CO₂ is piped across the Canadian border to enhance recovery from aging wells in Weyburn, SK (Williams, 2004a & 2004b).

The dramatic drop in the price of petroleum at the end of the 20th century has made gasification technology relatively uneconomical and less appealing in most instances. Although research in gasification dates back to the 1920s, there are minimal research funds *currently* directed by DOE Fossil Energy toward chemical feedstock production from coal. 1970s marked a fairly significant effort, however, it reached a low ebb before the 1990s start up of pilot- scale operations. One example of a pilot-scale development for production of chemicals was the co-production of dimethyl ether and electricity (International Dimethyl Ether Association). In addition, a pilot combined-cycle coal gasification project is currently being evaluated for Gilberton, PA (DOE/EIS, 2005). The primary focus of this facility is to gasify waste coal for electricity production and liquid fuel manufacture, the latter through Fischer-Tropsch processing of the syngas. The Gilberton plant is not designed for sequestration of CO₂, but this functionality could be added later.

Technical Uncertainties

Coal type (lignite, bituminous, or sub-bituminous) is expected to affect the efficiencies and economics of gasification. United States has the largest coal reserves in the world, estimated to be at 270 billion tons in recoverable reserves or a 250-year supply at the current rate of consumption, as per Energy Information Administration. However, approximately 40% of the U.S. coal is sub-bituminous coal from the Powder River Basin, and gasification efficiencies are lower and costs higher for sub-bituminous coal because of its high moisture and ash content. Since essentially any organic material can be gasified, existing gasifier designs can be adapted to use any type of coal as gasifier feed. Thus, coal characteristics do not pose insurmountable obstacles to its use for syngas production as a first step to chemicals or fuel production, but instead simply drive the economics of its use (BCS, Inc., 2007).

Minor impurities in coal that do not impact power generation, may affect chemical manufacture and byproduct formation. For instance, impurities such as alkalis may poison catalysts used in chemical production, but do not impact power production.

The development of a process control system that can handle changes in syngas end use in one plant, perhaps on an hourly, daily, monthly, or yearly basis is needed. These variations may include changes in feedstock composition or end product requirements.

Gas separation is another significant issue. Ion transport membranes (ITM) may be used for gas phase separations in place of the current cryogenic-based separations, not only for impurity removal but also for chemical synthesis.

The economics of Fischer-Tropsch will depend on the product desired and the hydrogen-carbon ratio from the syngas, which is not necessarily the same as for fuels production. For example, the use of H_2 in syngas to produce methanol shows heat losses in the production of H_2 in syngas of up to 20% of the total energy input to the system (Olah, 2005).

Environmental considerations will also affect the economics of gasification and liquefaction. For example, emissions of particulates, SO_x , NO_x , mercury and other heavy elements should be reduced with the use of advanced technologies, because gasification and liquefaction have the potential to remove sulfur and mercury more effectively than remediation of flue gas from power plants. Carbon capture as a byproduct may assist the economics of gasification for chemicals manufacture. For example, the proximity of the Dakota gasification plant to injection well sites allows sequestration of CO_2 , improving the economics of both the gasification plant and the gas field. CO_2 may also be used as a reagent to produce liquid fuels by reaction with H_2 to produce CH_4 .

Technologies for the co-firing of multiple feedstock inputs, such as a mixture of coal and biomass, could also enhance the gasification economics and need to be developed for process optimization.

2.1.2 Coal Liquefaction

Coal can also be liquefied directly to produce synthetic fuels and chemical feedstocks, as opposed to indirect coal liquefaction where coal is first gasified to produce syngas, which is then converted to a liquid through the Fischer-Tropsch process. Called the Bergius process, direct coal liquefaction is a decade older than the Fischer-Tropsch process and frequently termed “coal-to-liquid” or CTL. Liquefaction uses lignite distillation and hydrogenation where hydrogen is added to a coal-water slurry. The slurry increases the H/C ratio comparable to a crude oil ratio and removes impurities such as sulfur. Coal liquefaction provides better coal utilization (capturing 55% of the coal energy value compared to 45% for Fischer-Tropsch) but is technically more complex. A technology status review of coal liquefaction by the United Kingdom Department of Trade and Industry (1999) discusses the advantages and disadvantages of the technology and attributes the commercial viability of the process to its overall economics, especially in comparison with that of processing fossil fuels.

Coal liquefaction technology is of particular interest in areas of the world with large deposits of coal, like Japan, China, India, the Philippines and South Africa. A full-scale production facility is being built in China (at Shenhua in Inner Mongolia province) for direct liquefaction of coal to transportation fuels. The plant is scheduled to produce 20,000 bbl/day at the end of 2007 and 50,000 bbl/day when all reactors are in place.

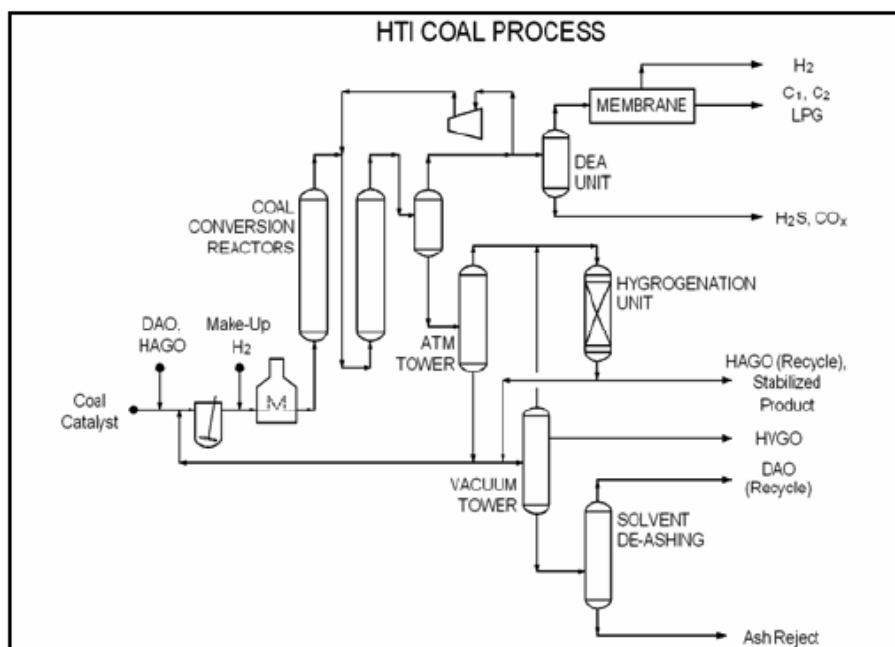


Exhibit 3: Coal Liquefaction Flow Diagram (Source: Shenhua Group Corporation)

2.2 Biomass

Biomass, referring to plant and plant-derived materials, can be used to manufacture chemicals through gasification, pyrolysis, and fermentation in dedicated plants or in biorefineries. In general, the fermentation of sugar from crops such as corn and sugarcane will provide oxygenated organics, but these are often small-volume niche chemicals with limited potential for large-scale manufacture. Co-production of byproducts formed in production of transportation fuels, such as biodiesel, may be used in bulk chemical manufacture, an example being glycerin. Efficient utilization of such intermediate reagents will require investment in the development of new synthesis pathways, or optimization of synthetic routes that are currently only being done in the laboratory. Currently, research is being conducted to explore bench-scale and pilot-scale processes of biomass gasification, fermentation of sugars, decomposition of cellulose, separation of lignin and other plant components, high-temperature pyrolysis, and biorefining of wood and waste materials. The primary issues limiting the replacement of petroleum with biomass feedstocks include impurities, feedstock composition variability, distributed supply, scalability and pathways for breakdown of cellulose. Studies on the use of biomass feedstocks in the production of commodity chemicals is primarily available from research conducted by Holtzaple and co-workers on biomaterials and Olah et al. on olefin synthesis.

Thousands of years of innovations in agriculture have concentrated on optimizing crops for food and fiber production, but not for energy production. The recent development of biomass-ethanol for fuel production needed government support to become viable. In general, the fermentation of sugar from crops such as corn and sugarcane will provide oxygenated organics, but these are often small-volume niche chemicals with limited potential for large-scale manufacture. Although some large-scale chemicals are produced as byproducts of fuel production, widespread use of biomass feedstocks for commodity chemical manufacture is not yet viable.

The escalating demand for energy worldwide and the accompanying increase in prices of crude oil and natural gas has deepened U.S. interest in the use of biomass to make biofuels such as ethanol and biodiesel. Biofuels provide energy security, support local agriculture, and reduce net emissions of CO₂ to the atmosphere. However, the use of biomass to make chemicals has received less public attention to date. For the most part, chemical manufacturers currently use sugar-based biomass to make high-priced specialty chemicals. Examples of chemicals being produced from biomass include organic acids, textile fibers, polymers, adhesives, lubricants and greases, and soy-based inks, amounting to a total of 12.7 billion pounds in 2004 (Biomass Technical Advisory Committee 2003). But even so, this represents only ~5% fraction of the potential > 200 billion-pound market.

The Biomass Technical Advisory Committee outlined the means to increase co-production of chemicals from biomass in *Roadmap for Biomass Technologies in the United States* (2003). The Roadmap highlighted research needs in three areas: biomass feedstock production, processing and conversion, and product use and distribution. The Committee assessed the extent of impact of R&D in the feedstock processing and conversion areas. The analysis suggests major benefits from research in bioconversion and biorefinery integration (Exhibit 4). The Biomass Technical Advisory Committee estimates an optimistic timeframe for deployment of biotechnologies, with large-scale technologies like 100 ton/day gasification and 200,000 lbs per day black liquor production from wood products likely to be implemented in the next 4-10 years.

Crosscutting Benefits of Processing and Conversion R&D			
Major R&D Needs	Biofuels Impact	Biopower Impact	Bioproducts Impact
Thermochemical Conversion:			
- Co-Firing	L	H	L
- Direct Combustion	L	H	L
- Gasification	L	H	L
- Anaerobic Fermentation	L	H	L
- Modular Systems	L	H	L
- Pyrolysis	L	H	M
Bioconversion:			
- Physical/Chemical Pretreatment	H	M	H
- Fractionation and Separation	H	M	H
- Residual Solids and Liquids	H	M	H
- Chemical/Enzymatic Conversion	H	M	H
- Catalytic and Chemical Conversion	H	M	H
- Inhibitory Substances	H	M	H
- Separation and Purification	H	M	H
- Biomass Fermentation and Hydrolysis	H	M	H
- Syngas Fermentation	H	M	H
Biorefinery Integration	H	H	H

H – High impact; M – Medium impact; L – Low impact

Exhibit 4: Projected Level of Impact of Biomass R&D
(Source: The Biomass Technical Advisory Committee, 2003)

Biorefinery is the concept equivalent to the prevalent ways of the petrochemical industry where chemicals, fuels, power and products are produced simultaneously at an integrated facility. The biorefinery process generally involves feeding biomaterials, along with waste oils and other carbon-based materials, into steam or catalyst crackers to make chemicals. Alternatively, these feedstocks may be hydroprocessed directly. Mills are used to process biomass (corn, pulp) to produce carbohydrates, oils, lignin, and fuel compounds. Once broken down, fermentation will produce alcohols from sugars and starch.

Biorefining feedstocks include crops, waste plant or animal material, and recycled fibers. Eventually, the conversion process will not only utilize the starch or sugar component of biomaterials, but also consume lignin, hemicellulose, and cellulose, in value-added processes beyond the current practice of burning these materials for fuel. Advances in biorefining have been recently presented by representatives from industry, academia, and government at a special biorefining session of the American Chemical Society Conference, August 28-Sept 1, 2005, in Washington, D.C. One example was the bioconversion of sugars to produce polyols (building block chemicals). For instance, International Polychemicals has joined with Global Biochemicals of China to construct a 10,000 tonne/yr glycol facility in China, with a 200,000 tonne/yr facility under development. Conversion of vegetable oils to lubricants, hydraulic fluids and monomers, is another example of biorefining.

Biorefining has been strongly embraced by Brazil, which has had a concerted effort over the last 30 years to home-grow its fuel for automobiles. Brazil produced over 3.7 billion gallons of ethanol from sugarcane in the 2003/2004 season.

Bioprocessing of corn to produce ethanol, as practiced in the United States, can be either done by wet milling or dry milling process. The dry process yields ethanol only, while wet-milling produces gluten feed, gluten meal, and corn oil, as well as ethanol. In spite of additional expenses incurred for separations equipment and operation, these byproducts can be sold to improve the economics of ethanol production. Wet mills are large, and generally require a coal-fired plant to operate, where as dry mills (~40 M gal) are smaller, and use natural gas. The byproduct of sugarcane processing is bagasse, which can be burned for fuel, providing sufficient energy to run the processing plant.

A review of the energy balance between inputs, farming costs, and energy output in the bioprocessing of starch and cellulose to produce ethanol revealed that starch-based ethanol was more energy efficient than gasoline, and in most cases ethanol showed a small net positive energy output (Hammerschlag, 2006). Ethanol production from cellulose and hemicellulose could be even more energy efficient than ethanol produced from starch, but there are large uncertainties in the calculation because the technology is much less developed.

Production of biodiesel (fatty acid methyl esters) from feed and biomass residues is of interest particularly in the developing world. Petrobras, Brazil's state-owned oil company, has developed processes for manufacturing diesel directly from castor beans, or from the esterification of castor bean oil. An alternative to fermentation, use of reactive distillation to produce esters of dibasic acids takes advantage of differences in volatility to give high purity products.

Biorefining becomes more cost effective when coupled with production of food, feed, power, and industrial and consumer products, and also has the advantage of reducing waste. One example of increased effectiveness is from a Danish plant, Grenaa, in which coal is burned for a straw pulping process, in tandem with ethanol production (Nikolaisen et al., 1998). For the best chance of success in the near term, however, biorefining must be operated on a small scale – in comparison with a petroleum refinery – relying as it does on a distributed supply of feedstock materials.

The production of biofuels will have a direct impact on the chemicals industry. For example, glycerine produced in Tavaux, France, as byproduct of biodiesel manufacture, will supplant propylene as a feedstock in the production of epichlorohydrin en route to epoxy resins. Other

chemical companies are taking advantage of similar opportunities (Chemical and Engineering News, 2006).

The current development of biorefinery technologies for producing commodity chemicals is explored below by investigating the three pathways for the extraction of chemicals from biomass: thermochemical gasification (or conversion), fermentation, and pyrolysis.

2.2.1 Biomass Thermochemical Gasification

Syngas for commodity chemical production can be derived from biomass. An example of the thermal gasification process for biomass is shown in Exhibit 5. Issues such as the production of clean syngas via biomass thermochemical processing are similar to the issues associated with coal gasification. Gasification of biomass can take place under slightly milder conditions than coal gasification (800 to 1,000°C at 20-30 bar instead of 1,400°C at 20 to 70 bar). Biomass (feedlot and chicken litter) can also be combined with a coal-syngas feedstock (Priyadarsan et al. 2004, 2005).

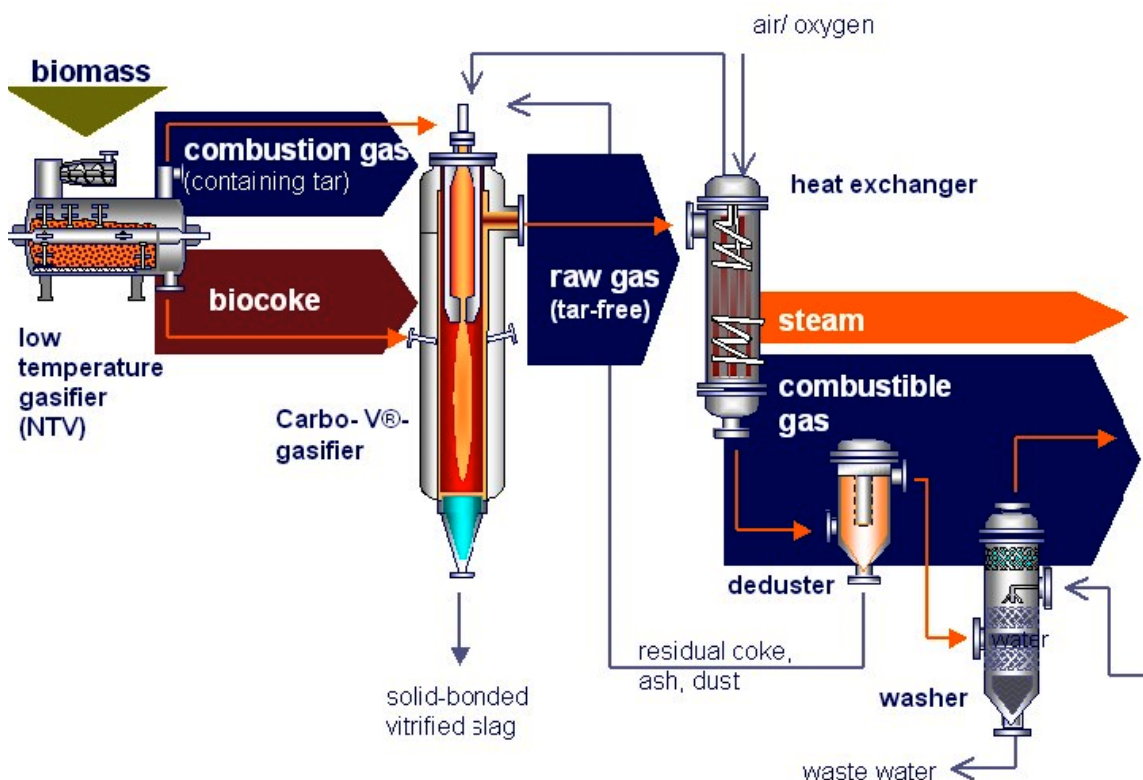


Exhibit 5: Syngas Biomass Gasification Scheme

Source: www.choren.de

Some pretreatment issues are unique to gasification of biomass. Biomass has a large water content that must be removed before gasification; the Choren process requires that starting material contain less than 35% water. Biomass components (alkali metals, halides, sulfur compounds, and tars) have a significant potential to poison downstream noble metal catalysts used in the production of syngas and chemicals (Raguaskas et al., 2006). Technologies have been developed to handle these impurities, but they add to the complexity and cost of the gasification process.

In addition, because production of biomass requires a large land base, feedstocks are spread wide, and manufacturing is distributed (e.g., forest pulp mills). Hence, innovative methods, such as feedstock densification or onsite drying prior to shipping, will assist with achieving economies of scale.

Many of the R&D areas identified by the Biomass Technical Advisory Committee (2003) in thermochemical processing are also relevant to the use of biofuels in electricity production. The Committee also noted that scalability from small scale to industrial scale is not well understood for thermochemical conversion and requires developments in analysis of costs, performance and emissions.

A pilot-scale project at the University of Utah-Institute for Combustion and Energy Studies is currently conducting gasification of black liquor, the lignin-based material produced during the pulping of paper. The project, funded by DOE, has two separate units, a pressurized fluidized bed steam reformer and an entrained flow gasifier (under construction for 2006 start up).

2.2.2 Biomass Fermentation

2.2.2.1 Sugar Fermentation

A second pathway of using biomass as feedstock for production of chemicals is through fermentation. A team of experts from the Pacific Northwest National Laboratory (PNNL), the National Renewable Energy Laboratory (NREL), and EERE short listed the top 12 target products from sugar fermentation using biomass for the most viable building blocks for manufacturing high-value products (Exhibit 6). The team screened 300 chemicals based on the following criteria: functional groups that give rise to building block chemicals, alignment with petrochemical pathways, availability of chemical data and market data, reliable property information, performance of production from sugar fermentation, and the industrial experience of authors.

Building Blocks
1,4 succinic, fumaric and malic acids
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

Exhibit 6: Top 12 Products from Sugar Fermentation

Source: Werpy and Peterson, 2004

The PNNL-NREL-EERE team identified the most promising building block chemicals from sugar fermentation by first grouping chemicals into direct replacements for petroleum-based

feedstock, novel building blocks, or intermediates. The chemicals were also classified from C1-C6 and evaluated for functional groups and reactivity. Since at the time of the study, biomass production was not cost competitive with other alternative technologies, commodity chemicals were excluded from the list and hence, methanol was not considered. While the production volumes of the identified diacids (2 carboxylic acid groups, e.g., succinic, fumaric and malic acids) and itaconic acid currently do not compare with the top-ranked commodity chemicals listed in Exhibit 9, these specialty chemicals have the potential for large-scale development, and so are of particular interest to the chemical manufacturing community. New chemical pathways may be engineered based on these bioproducts, leading to increased demand and larger-scale production.

However, many of the processes to produce chemicals from sugar fermentation are not commercially practiced, with the production of ethanol from fermentation being a notable exception (Hammerschlag, 2006). Formation of lactic acid from corn dextrose is a million kg/year industry in the U.S. (Ragauskas et al., 2006), but still small scale in comparison with the production rates of commodity chemicals listed in Exhibit 9.

Fermentation of sugars is often aerobic, using bacteria, yeast or fungi. Synthesis routes using the fermentation-based approach include the oxaloacetate bioconversion in Krebs's cycle to give aspartic acid (both fermentation and enzymatic conversion pathways are possible), aerobic fungal fermentation of sugar to produce itaconic acid, and enzymatic transformation of sugar to give glycerol (Biomass Technical Advisory Committee, 2003). Anaerobic processes can also be used, such as in the production of diacids and glutamic acid, and methane (section 2.4).

Chemical transformation of sugars can take place by oxidation (e.g., of starch), oxidative dehydration (of C6 sugars), hydrogenation (sometimes acid-catalyzed) of cellulose and sugars, acid amination, and esterification of oils. These products can be further converted to derivatives by chemical reactions like oxidation (which tends to be less important for biomass as these compounds are already oxidized), hydrogenation and dehydration, bond cleavage and direct polymerization. Biological reactions can also be used to produce derivatives, with the advantage that they are generally enzymatic and so very selective, and may go directly from sugar to the end product. However, conditions must be mild, which may be difficult to achieve after a harsh pretreatment.

2.2.2.2 Non-Sugar Fermentation

Annual crops such as corn that have a high sugar yield are typically difficult to grow and need fertilization, irrigation, herbicides and pesticides. In addition, these crops have been engineered for food production, rather than for efficiency of photosynthesis, or energy or chemicals production (Ragauskas et al., 2006). It has been suggested that it would be more economical to work with waste biomass, or cellulosic crops such as perennials that are easy to grow over much of the United States, because cellulose is the most abundant part of the plant (Mann, 2004). Use of cellulose from waste biomass would allow raw material to come from corn stalks (Thanakoses et al., 2003a), wood, bagasse from sugarcane (Thanakoses et al., 2003b), and even animal products (if proteins can be used). Additionally, fermentation of municipal waste, industrial waste and paper to produce carboxylic acids has been examined (Chan and Holtzapfel, 2003; Aiello-Mazaarri et al., 2005, 2006; and Domke et al., 2004).

Conversion of cellulose to fuel and hydrocarbons is a multistage process. The biomass must first be physically or chemically broken down to separate the cellulose from other components, such as lignin. Pretreatment issues dominate cellulose and lignin processing, and often involve acid- or base-catalyzed hydrolysis to facilitate enzymatic breakdown. The cost of pretreatment is high, but there is a potential for major technical improvement in the chemical or acid processing (Mann, 2004). However, pretreatment is an active area of research, an example being investigating improvement of lime pretreatment (Chang and Holtzapple, 2000; Chang et al., 2001a, 2001b).

The DOE-EERE's Biomass program is currently supporting R&D to improve the pretreatment of wood-based materials. This work, which could be applied to any of the biomass-based technologies, investigates improving the mechanical breakup of biomaterials into fine particles, which can then be fluidized and reacted. Many of these involve engineering challenges to study the best means to transport biomass particulates from separators to reactors, and the effect of moisture content and particle size on reaction kinetics. A different approach to pretreatment issues is to use genomics and plant science to develop biomass crops with enhanced decomposition rates, such as those with cell walls more easily digested by bacteria (Ragauskas et al., 2006). Delignification of corn stover is currently actively being investigated (Kim and Holtzapple, 2005, 2006a & 2006b).

Once isolated, the next step is the breakdown of cellulose to form sugars. The natural rotting process, facilitated by bacteria or fungi, is slow. Enzymatic hydrolysis will speed the process, but large facilities are required to sustain a reasonable throughput. The bacteria involved in the breakdown of cellulose consume a considerable amount of raw material, lessening the efficiency. Byproducts pose a problem when the processes of oxidation produce aldehydes and acids along with sugars. Once produced, these sugars can be fermented and processed by conventional means.

Hence, the key research needs for fermentation of biomass includes development in microbiology of bacteria that break down cellulose quickly. These bacteria, along with target crops, will be developed using genomics and DNA-modification technology. A goal could be to produce bacteria that increase the conversion rate of cellulose to sugar from the current 5% to 50%. Lowering the consumption of raw material by bacteria will also increase the efficiency. Other goals may be the investigation of different conversion pathways (such as developing a type of bacteria that uses parazoline) or a consolidated bioprocessing approach (CBP) that uses one bacterium to go straight from cellulose to ethanol (Lynd, 1996). Bacteria that consume sugars from hemicellulose – a raw component of biomass – are also desirable. The true step-change in economics is awaiting the successful development of enzymes that can utilize low-cost biomass, such as corn stover, rather than corn. If that route can be made competitive, experts say that the U.S. could quickly develop a significant agricultural-based petrochemical industry (Chemical Week, 2006)

Separations are important in handling of the varied and variable biofeedstocks: separation of cellulose from lignin and other plant materials, and separations of byproducts after fermentation is complete. A separation step in itself may allow production of a value added chemical, such as the production of xylitol from the pretreatment of cellulose.

The use of black liquor left over from wood pulping has been a subject of research for over two decades. Black liquor is lignin that has been separated from cellulose, mixed with water and the

chemicals used for the separation. Black liquor has been used as fuel, but there has been research into production of value-added chemicals. For instance, caustic-catalyzed treatment of lignin will allow it to depolymerize into phenolic compounds, which can be processed to form alkyl benzenes (Ragauskas et al., 2006). Another avenue of research has been to graft copolymers on the lignin. Depending on the monomer selected, a wide variety of materials may be created for different applications (Meister, 2002). An ongoing EERE-supported project is attempting to separate esterified wood-fiber-based polyesters using cyclone technology. These efforts though are still in R&D stage and not ready for commercialization.

2.2.3 Pyrolysis

A third means of extracting chemicals from biomass is through pyrolysis (Hallet et al., 2002). Biomass feedstocks can be wood wastes, bark, or other forest products, and pyrolysis products are oils, comprised of oxygenated organic compounds, and water. Pyrolysis is complex, incorporating both evaporation and combustion of a viscous and sticky fuel. The process involves the heating and vaporization of water, which takes a lot of energy, separation of more volatile components, microexplosions, and formation of a porous char or cenosphere from the heavy non-volatile components. Unlike direct combustion, pyrolysis occurs at high temperatures, $\sim 400^{\circ}\text{C}$ with ignition temperature of 730°C .

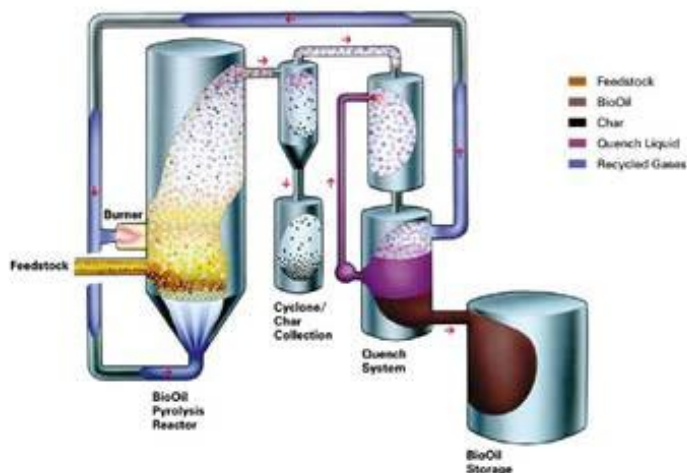


Exhibit 7: Flow Diagram for the Production of BioOil

DynaMotive Corporation
<http://www.dynamotive.com/>

A Canadian company, DynaMotive Corporation has established a plant that will manufacture 70 tons of bio-oil from 100 tons of wood per day, with 20 tons of char and 10 tons of associated gases (Exhibit 7). Half of the bio-oil will be used to generate electricity and the remaining shipped to the United States. The process involves heating the wood to $450\text{--}500^{\circ}\text{C}$ in a bubbling fluidized bed reactor in the absence of oxygen. The plant will eventually be used to convert other biofeedstocks, such as bagasse and sawdust.

High-temperature pyrolysis has been suggested as a more effective method of black liquor gasification than traditional lower temperature approaches because tarry residues are less of a problem. The tars, semi-volatiles and non-volatile char were identified from the heating of black liquor between 700 and $1,000^{\circ}\text{C}$ (Sricharoenchaikul et al., 2002). A suite of aromatic compounds were observed, from single benzene rings up to pyrene and fluoranthrene (4-ring

compounds). It is suggested that the products from the high-temperature pyrolysis are comparable to those created during the gasification of coal.

2.2.4 Biomass R&D Needs

Government-funded R&D has not focused on investigating production of commodity chemicals from biological sources, with the exception of glycerine. The research needs identified by literature survey for commodity chemical production from biomass feedstocks are provided below. These exclude R&D requirements in plant science, genomics and microbiology, that have been detailed elsewhere (Ragauskas et al., 2006).

Biofeedstocks come from a variety of sources and have a wide range of physical and chemical properties. The physical properties of the biofeedstock will affect pretreatment and processing conditions. Biomass fractionation, which will depend on the characteristics of the crop being processed as well as the processing method, and separation methods are primary areas of research interest. Although this is an active area of research, there are products, such as glycerine, where biodiesel-derived material is already supplanting that from natural sources. Biofeedstocks need improved thermal stability so that chemical and physical transformation occurs under controlled conditions. Pretreatment options for the breakdown of lignocellulosics to produce lignin and sugars are being investigated by programs funded by DOE.

The cleanliness of syngas in chemical manufacture will affect the performance of syngas catalysts. This will set the requirements for pretreatment of biomaterials for thermochemical gasification. For example, feedstock purity is critical in the commercial production of lactic acid and the production 1,3 propane diol (Ragauskas et al., 2006).

The infrastructure for separation of biomaterials (mechanical, chemical, air, and steam) must be engineered to handle a variety of materials in the input stream. Biological feedstocks will have variable compositions, impurity levels, and moisture content. EERE's biomass research on renewable feedstocks is investigating the effect of biomass moisture on size reduction in mechanical processing

(http://www.eere.energy.gov/state_energy_program/grants_by_state.cfm/state=TN#a200)

Fluidization of a variety of particle sizes is also being examined. Also, the feasibility of biological materials is being considered for their use as feedstocks in a conventional refinery or tandem process (involving mixed inputs or outputs).

Research into fermentation of sugars is needed in the following areas:

- pathway engineering to increase efficiency;
- reduction of cost by increasing the mass transfer of oxygen and nutrients to participating microorganisms;
- direct production of derivatives;
- improved biocatalysts to reduce acid byproducts and increase yields, resistance to inhibitors, and the ability to handle a variety of sugar types.

Solid catalysts are desired that function well under messy fermentation conditions, are resistant to impurities and more robust and longer lived. More selective catalysts are also needed. (Note

that the catalyst technology for the production of oxygenates, such as ethanol, is well established.)

New bacterial strains are needed for faster cellulose breakdown, to be more efficient, or to generate a different chemical pathway (e.g., direct conversion of cellulose to ethanol). Hydrolysis of the fiber, oil, starch and protein fractions of crops needs to be better understood. Research activities will develop a better understanding of cell biology, metabolic pathways and enzyme functioning. Nutrients must be cheap, like corn liquor, and not expensive, like biotin or yeast extract. The role of processes competing with fermentation, such as enzymatic oxidation, must also be understood.

Areas for research in the chemical processing of biological materials include:

- new catalysts that are longer lived, more robust, tolerant to inhibitory components, solid acidic substrates to replace liquid catalysts, and that allow heterogeneous catalysis
- milder oxidation, with less exotic oxidants and lower concentrations
- milder reduction, management of acid salts
- more selective hydrogenation, dehydration, reduction and oxidation processes, better yields
- improvements to the direct polymerization process, control of branching, rates, condensation of polymers
- better control of bond cleavage
- continuous rather than batch processing
- new pathways for alcohols to acids, aldehydes to acids, alcohols to aldehydes, acids to alcohols, dehydration to lactones and anhydrides

Downstream recovery costs need to be reduced by achieving a higher final titer, lower pH operation to remove need for neutralization, and optimized handling of wastes – primarily salts. Mixed sugar streams must be more effectively utilized, or separations of sugars must be improved. Separations and purification processes need to be developed and optimized. Unwanted acid coproducts must be reduced, and uses need to be found for residual solids.

Finally, the economics and feasibility of different methods for production of chemicals from biobased feedstocks should be compared (e.g., the manufacture of ethanol from the fermentation of sugar versus ethanol from the hydration of ethylene). One of the most important aspects is a reduction of cost to allow bio-based processes to be competitive with other technologies. Scale up of biologically based processes is difficult, particularly for enzymatic or bacterial conversions. Government protection of agriculture and its investment for energy security purposes complicates the issue of economic analysis. Hence, the commercial feasibility of a particular process will vary over time and geographic location (i.e., proximity to markets for products), as well as direct costs and sales of products (Gallagher et al., 2006).

2.4 Unconventional Natural Gas

Unconventional or stranded natural gas is being evaluated as an alternative to alleviate current shortages in natural gas supply. Stranded or unconventional natural gas is that which is not easily transported from source to end use by pipeline, or is uneconomical to transport as a gas.

Unconventional natural gas may come from a variety of sources: methane hydrates, stranded or geographically remote methane, such as that from sites in Alaska or the Rocky Mountains, coal bed methane, and methane from anaerobic fermentation such as occurs in landfills.

Supply of conventional natural gas in the United States is limited, although its known reserves are abundant. Worldwide there is a 70-year supply (180 Tcm) of gas, 7 Tcm of that in Central and South America, 7 Tcm in North America, 14 Tcm in Africa, 14 Tcm in Asia Pacific, 64 Tcm in Europe and Eurasia, and 73 Tcm in Middle East (Fleisch and Sills, 2005). However, not all these reserves are currently available, and recent increased demand for natural gas has caused prices to increase to the point where methanol and ammonia production are no longer economical in North America. A report from the National Academy of Sciences (Doyle et al., 2004) on hydrates predicts that there will be a shortfall in conventional and unconventional natural gas by 2020.

The chemicals industry uses 26% of the total natural gas consumed in the United States, 75% of which is used for heat and power. Separation processes are especially energy intensive, particularly for the refining, forest products, and chemicals industries. These three industries consume more natural gas for powering of separation processes than all of the other industries combined consume for both feedstock and power. If the chemical industry is faced with shortages in supply, the replacement of natural gas, or construction of small plants to take advantage of stranded methane may be a partial solution.

Until recently, natural gas has been relatively inexpensive, with the current world consumption reaching 260 bcfd; being easily available, technology for conventional use is well understood. Hydrogen production from natural gas uses 12 bcfd for ammonia production, 6 bcfd for refineries, and 3 bcfd in methanol production. The production of syncrude and methanol are particularly important to the chemicals industry.

Gas from unconventional sources must be controlled, concentrated, or converted to a liquid form or stabilized in some manner before being transported to the manufacturer, power plant, or end user. An alternative to transporting the gas is to develop modular plants that can be scaled down so that the stranded methane could be used in situ. These modular plants could be small scale with microturbines, fuel cells, or distributed systems that could be incorporated into farms, mills, or remote settings. The conversion of methane to a liquid product, such as methanol, will allow easier transportation of materials from remote sites.

Liquid products can be made from natural gas through a syngas process. Some synthesis routes, such as the production of diesel fuel, are well understood (Renesme et al., 1992). Gas to liquid refineries to give syncrude is predicted to operate at 0.7 bcfd in 2006, to be ramped up to 4 bcfd by 2012. Syncrude may then be converted to clean diesel, jet fuel, n-paraffins, lubricants, naphtha, olefins, etc. One example of gas to liquids is the Fischer-Tropsch production of liquid fuels such as done by Sasol, or methanol to gasoline (MTG) done by Mobil (<http://nzic.org.nz/ChemProcesses/energy/7D.pdf>).

Methanol is a primary natural gas product of the Lurgi process and is commercially produced in Trinidad (http://www.methanex.com/ourcompany/locations_trinidad.html). The 5,000 TPD Atlas plant is the biggest in the world and has been operated by Methanex and BP since June 2, 2004. The Atlas and Titan plants in Trinidad produce 8% of world's methanol at \$100/ton, at a rate cost competitive at \$20 bbl oil. Methanol can be used to produce a number of building block chemicals: acetic acid, dimethyl ether, gasoline (MTG), formaldehyde, olefins (MTO, MTP), ethane and propane.

The UOP/Norsk technology reacts CH_3OH at $425\text{-}500^\circ\text{C}$ in contact with a SAPO-34 catalyst (lattice with 3.8 Angstrom holes) at a 99.5% conversion rate. The exothermic reaction is carried out in a fluidized bed reactor, giving a 75-80% carbon yield in ethane and propane (byproducts are butanes, C_5^+ , $\text{C}_1\text{-C}_4$ paraffins, water, oxygenates, coke, H_2 , CO_x). A first plant is planned for Nigeria (Eurochem/Nigeria), for a gas to polymers process, yielding 7,500 TPD methanol via MTO (<http://www.uop.com>).

In the case of methanol to olefins (MTO), technologies are under development by UOP/Norsk Hydro and Exxon Mobil (Exhibit 8). The Lurgi methanol-to-propylene (MTP) process is ready for licensing and implementation (<http://www.lurgi.de/english/nbsp/>).

Rather than making methanol through an indirect route involving syngas, methanol can also be produced by direct oxidative conversion of methane over a catalyst. Since syngas production involves at least two process steps under very different conditions, a one-step route will represent savings in operating and capital costs. However, improvements in yield and catalyst performance are needed before this technology can be implemented commercially (Renesme et al., 1992).

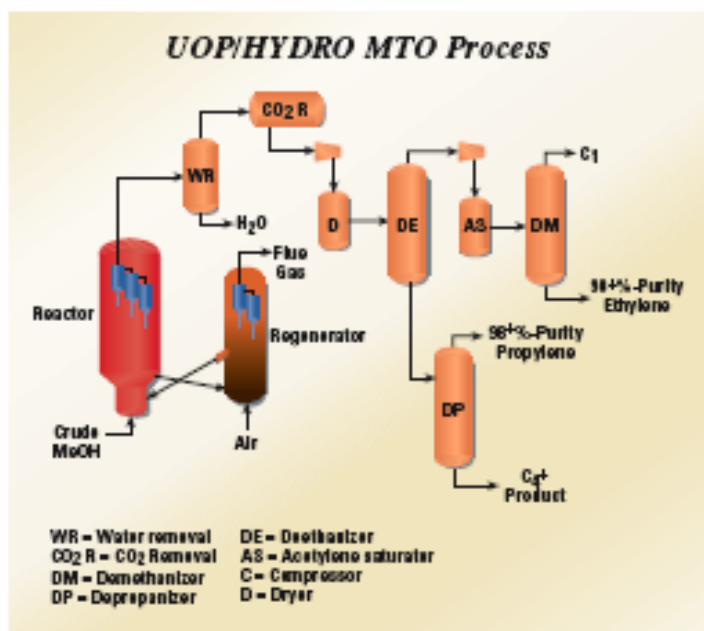


Exhibit 8: UOP Methanol to Olefins Flow Diagram

<http://www.uop.com/lightolefins/5033.html>

Methane from anaerobic fermentation can be generated from animal manure, biomass (e.g., methane from grain stillage, <http://www.lurgi.de/english/nbsp/>), waste water digestion gas, sewage treatment, as well as from landfills. The potential for anaerobic fermentation to be a source of useable methane rather than a source of pollution will require research into improvements in process control, operating efficiencies, and rate of digestion, targeting small-scale technologies that could use 10-300 Btu/cu. ft. of gas (Biomass Technical Advisory Committee, 2003).

2.5 Tar Sands/Heavy Oil

Unconventional sources of petroleum include the Canadian Athabasca tar sand, Venezuelan heavy oil, and oil shale in the Western U.S. Historically, the relatively high cost of extraction of these hydrocarbons has been a major detriment to the use of heavy oil. These feedstocks are now more competitive due to the high prices of conventional resources.

The extraction of bitumen-derived crude (BDC) follows several steps. The first step is the extraction of the heavy oil from the rock. Tar sands (7% bitumen by weight from the tar sands) and oil shale contain relatively low concentrations of hydrocarbons. Some loss (<10% of bitumen) occurs in the primary extraction process. Increased mechanical breakup or froth treatment can increase the yield. Current research is focused on making the extraction of unconventional crude more sustainable with less of an environmental impact, including better handling of mine tailings and the water entrained in the bitumen as it is extracted from the tar sands.

Placement of in situ cracking towers has been proposed for processing the bitumen. However, the physical and chemical properties of bitumen render it inherently unfriendly to standard refining methods, and the location of heavy oil and tar sands are far from the end users of hydrocarbon-based chemicals. So the next practical step for the bitumen is to lower the viscosity and density of the fluid so that it can be more easily transported to a refinery. The process will also permit removal of some impurities and entrained water.

Alternative in situ hydrocarbon production, as proposed for oil-shale deposits in the Western U.S., does not involve mining of the rock. Instead downhole combustion or gasification may be performed, which is predicted to give yields of up to 40-70%. Development activities for another in situ technology, steam assisted gravity drainage (SAGD), include design of reliable pumps and ways to recycle the water used in the steam process. One advantage of in situ production over traditional mining is that the product is ready for immediate refining.

Most of the BDC now goes to fuel production, i.e., 65% to sweet crude. However, many of the methods developed to extract hydrocarbons from the heavy gas oil (HGO) derived from bitumen are also appropriate to petrochemical manufacture. These include hydrocracking, fluidic carbon cracking (FCC), PetroFCC from UOP, deep catalytic cracking (DCC), and the catalytic pyrolysis process (CPP)^{**}. A key technical requirement for the use of heavy gas oil is development of new catalysts, such as that used for selective cycloparaffinic ring opening. These catalysts must be resistant to impurities such as sulfur and nitrogen-containing compounds, and coating with ultra-fine particles. Chemical processes that minimize the use of hydrogen are desirable, as this currently comes from natural gas.

^{**} Chinese RIPP, Stone & Webster

Technology development in the processing of tar sands and heavy oils has been primarily done without DOE financial assistance. Tar sands work has been spearheaded by Canadian agencies (Canadian Energy Research Institute, The Alberta Research Council, The National Centre for Upgrading Technology and Natural Resources Canada) and industries (Nova Chemicals Inc., Suncor Energy Inc., Shell Chemicals Canada, and Petro-Canada).

3. Research Needs and Recommendations

Over the last 70+ years, alternatives to conventional petroleum and natural gas feedstocks for the chemicals industry have been developed and demonstrated on large scale, but have limited implementation in the United States. The ChemicalsPlus team organized *Alternative, Renewable, and Novel Feedstocks Workshop* in Washington, DC on June 21, 2006 with the goal of reaching a consensus on the most likely feedstock options and to identify the research needed to overcome the barriers that have limited the use of these alternative, renewable, and novel feedstocks by the U.S. chemicals industry.

The workshop participants included representatives from ten major U.S. chemical manufacturers, one university, three national laboratories, and two Department of Energy programs (Appendix 1). The workshop began with a general discussion focused on answering two vital questions:

- Which alternative, renewable, and novel feedstocks can strengthen the U.S. chemicals industry in such a manner that production within the United States remains globally competitive?
- What alternative, renewable, and novel feedstocks are “good” for the industry and the citizenship?

Workshop participants agreed that the first priority in selecting potential feedstocks was to develop the ideal feedstock criteria. If the intention is to strengthen U.S. chemicals industry’s worldwide competitiveness and to help the industry recreate a net exporter position, then the focus rapidly narrows to those feedstocks suitable for the production of large-volume (>1,000,000 ton/yr) chemicals. These large-volume chemicals are the basic building blocks of the industry and are the beginning of the chemical chains (Appendix 3); they are the starting material for the thousands of domestic manufacturers that produce products from these chemicals. These large-volume chemicals would have the greatest impact on transforming the U.S. industry while providing the nation with the largest offset to imported petroleum and a large reduction in domestic natural gas consumption. Hence, the first criterion is that the feedstock must be available in quantities large enough to fill the supply needs of the industry as reliably as or more reliably than the currently employed feedstocks.

The chemicals that have large production volumes and are at or near the beginning of the chemical chains are shown in Exhibit 9. These chemicals represent over 50 million tons of carbon-based materials. The large-volume inorganic chemicals like ammonia, ammonia derivatives (i.e., ammonia nitrate, urea, etc.), sulfuric acid, oxygen, nitrogen and chlorine were not included in this analysis. Ammonia production is based on the production of hydrogen from a carbon source, frequently natural gas, and already has a well developed and practiced production route using alternative feedstock technology (i.e., coal). Sulfuric acid uses sulfur feedstock that is piling up at numerous refineries and the starting feedstocks for oxygen, nitrogen and chlorine (i.e., air and salt) are lower costs and ubiquitous.

Chemical	U.S. Production (x10 ⁶ tons) 2004	Alternative Chemical Route	End Use
Olefins: Ethylene (C ₂ H ₄) Propylene (C ₃ H ₆) 1,3-Butadiene (C ₄ H ₆)	28.3 16.9 2.4	Gasification of coal or biomass to methanol or ethanol to olefins	R-Cl, oxide, polymers
Aromatics: Benzene(C ₆ H ₆) Toluene Xylenes	7.5 4.1 4.0	Gasification to methanol (gas-to-liquids)	Polymers, cyclohexane
Oxygenated Hydrocarbons Acetone (CH ₃ COCH ₃) Formaldehyde (H ₂ CO)		Acetone – Gasification Formaldehyde - Gasification from methanol	Intermediate Olefin, wood products

- Toluene is methyl benzene
- Xylenes are: ortho (1,2-dimethylbenzene), meta (1,3-dimethylbenzene), and para (1,4-dimethylbenzene)

Exhibit 9: Major Chemicals of Interest for Alternative, Renewable and Novel Feedstocks

Additional criteria associated with alternative, renewable and novel feedstocks that would strengthen the industry and be "good" for the nation are:

- Collection, delivery and process technology are known and ready for commercialization;
- “One degree of separation” (i.e., one processing step more than traditional routes);
- Economically competitive in terms of:
 - providing stable low delivered cost feedstocks (i.e., decreases the volatility of the supply chain)
 - resulting products are competitive on price and performance (i.e., no trace elements in the feedstock impact product performance);
- Feedstocks are fungible;
- Sustainable – technically, economically and environmentally;
- Byproducts are valuable or their “last resort” value (boiler fuel) is acceptable;
- Similar or smaller waste footprint than current feedstocks;
- Similar or lower CO₂ emission than current feedstocks;
- “Green Premium” acceptance, perception and/or price;
- Has the ability to augment existing supplies (i.e., can be introduced slowly and used with existing equipment); and,
- Does not compete with or has no to very minor impact on feed/food supply and price.

3.1 Relative Value of Alternative, Renewable and Novel Feedstocks

The relative value of alternative, renewable and novel feedstocks is determined by a combination of feedstock accessibility, impact on CO₂ production, the readiness of the technology, and price premium from environmentally friendly production.

Economic access or availability of potential feedstocks is a paramount criterion. Alternative renewable and novel feedstocks must have the carbon concentration, location, transportation and storage properties that make them stable and low-cost feedstocks. Economic access or availability of potential feedstocks can be compared as follows:

- Coal currently matches these criteria the best. It has the best access, found in localized deposits large enough to supply a world-class chemical facility through the life of the plant (30+ years). Coal is easily transported and stored compared to other feedstocks and it contains very high quantities per mass of the desired component carbon. Importantly, coal has a long history of stable price and supply (very low price volatility).
- Biomass is more distributed and must be collected over a large area in order to supply a facility. It is not a concentrated source of carbon and when collected, can contain >50% moisture. The high moisture content will necessitate drying and will contribute to the overall waste footprint. Biomass supply can be seasonal and yields can vary. Transportation and storage can be problematic also.
- Oil shale and tar sands are similar to coal in that the deposits are large and localized. However, they require extensive processing to petroleum-like fluids in order to make them suitable for transportation and storage.
- Residuals oils and petcoke have medium level availability. They are localized, being generated at a refining/petrochemical complex. The localized quantity depends on refinery capacity, design and product slate. They can be shipped and stored without unusual problems.
- Organic waste such as corn stover or municipal solid waste (MSW) are distributed, pose economies of scale problems, may have health concerns, have diverse composition, and not concentrated in terms of carbon. They are the only material that can not be used for something more useful – as waste, they usually have a negative cost associated with them (i.e., a facility is paid to take it).
- Stranded gas, in terms of composition, is very desirable, however, its access is limited and is not transportable. Methane hydrates are a potential alternative source of carbon; however their carbon concentration is low, are difficult to access, and the costs of making chemical products are likely high.

CO₂ production is a major concern in utilizing alternative feedstocks. The production of chemicals from alternative feedstocks, with the possible exception of biomass, will result in increased energy consumption and increased CO₂ emissions. CO₂ policy in the United States and globally adds economic uncertainty to the planning of chemicals production from alternative, renewable and novel feedstocks. California's "Bill 35" and other states that may follow its example will significantly affect the planning and logistics for handling CO₂.

CO₂ emissions will increase as fossil-based feedstocks move from natural gas (stranded gas) to more carbon-rich petroleum, to petcoke and to coal feedstocks (i.e., moving from lower to higher carbon oxidation states, C⁻⁴ to C⁰) for the production of organic chemicals. Technologies are available to process CO₂ when generated at point sources. It is possible to capture, bury,

sequester or sell CO₂ (for enhanced oil recovery, dry ice, soda fizz, etc.). These options can add costs and in the case of selling, logistics will require the purchaser to be nearby. The CO₂ accounting for biomass is complex and no national or international standards have been established. Biomass use by itself is near zero in CO₂ emissions. However, depending on the specific crop or wood, its growth needs (fertilizer, pesticides, herbicides, etc.), tending, harvesting, storing, transportation, drying, etc., the CO₂ balance can shift to positive levels of emissions. On the other hand, biomass gasification with CO₂ capture could produce negative levels of emissions (or create carbon credits). CO₂ accounting for organic wastes is complex since it depends on the origin/composition of the waste.

Feedstock conversion technologies may be technologically ready, but not commercially competitive. The science and engineering of the technology may be demonstrated, but implementation will be delayed until the economics of the technology are viable. For these technologies significant R&D may be required to refine the science and “value engineer” the system so that it is commercially competitive.

The ability to rapidly commercialize alternative, renewable and novel feedstocks is highly desirable. The technologies required for commercialization include: the infrastructure for extracting/harvesting, transporting and storing feedstocks; the process equipment for converting feedstocks into intermediate chemicals; the ancillary process equipment (e.g., air separation unit (ASU), carbon capture and sequestering units, etc.); and the final conversion chemical process equipment.

The workshop attendees described the technology readiness of potential feedstocks for chemicals production as follows:

- Coal is a technically proven feedstock and in some site-specific cases commercially viable.
- Biomass is technically ready and commercially ready for small specialty chemicals (Note: Fuel ethanol is currently subsidized which contributes to its commercial viability to a certain degree).
- Tar sands are technically ready and commercially ready. Today tar sands are being converted to synthetic crude oil and shipped to refineries in Canada and the United States. Technology for converting tar sands into chemical products exists.
- Oil shale lags tar sands in terms of development (5 – 6 years further out).
- Residual oils, petcoke and stranded gas are technologically ready and in some site-specific cases, commercially viable.
- Organic waste is more logistically limited than technologically limited. Currently, it is used for power production.

A “green premium,” is a selling price that may be associated with products produced from more environmentally favorable feedstocks.

Exhibit 10 summarizes the relative value of the alternative, renewable, and novel feedstocks that meet the initial feedstock criteria as assessed by the workshop participants.

Resource	Access	Price Premium	CO ₂ Produced	Technology Readiness
Coal	High – localized and concentrated (lb C / lb), can ship and store easily	Low	More - produces more than oil but can be captured in process	Ready and Commercial
Biomass	Medium – less localized than coal, distributed, not uniform or concentrated	High	Neutral to Negative (if captured)	Ready for small chemicals (fuel ethanol is subsidized)
Oil Shale Tar Sands	High – can't ship without initial processing to petroleum	Mid to High	More – H ₂ deficient but can be captured in process	Oil Sands Ready in 5-6 yrs, longer for Shale Oils
Residual PetCoke	High to Medium – localized at refineries, can ship	Low	More – H ₂ deficient but can be captured in process	Ready and Commercial
Organic Wastes (MSW)	Low – distributed not concentrated, health concerns (?), only Resource not suitable for something more useful	High	Insignificant	Limited – requires more collection, community support, and political will than technology development
Stranded Gas	Low – not transportable, difficult to access	Low depends on source	Low – less than coal or oil	Ready

Exhibit 10: Relative Value of Alternative, Renewable and Novel Feedstocks

Future economic access or availability of the feedstocks in Exhibit 10 could change significantly. Coal accessibility will change dramatically as crude oil approaches its “peak” production and coal is more commonly used to produce fuels on a very large scale. This change however might benefit the production of chemicals. Fischer-Tropsch processing like crude oil refining produces carbon-based byproducts of low value. It is possible that these byproducts will be suitable as feedstock for chemical production. Likewise, as fuel ethanol/biodiesel/biorefineries develop into large-scale operations, the price and supply of biomass could become an issue.

3.2 Ranking Alternative, Renewable and Novel Feedstock Opportunities for U.S. Chemicals Production

The workshop participants matched feedstock characteristics with chemical products and ranked the practical chemical pathways for production of bulk chemical depending on their likelihood of being developed (Exhibit 11). This likelihood or probability ranking only considers the chemical pathway and assumes that competitive engineering/process economics are achievable. The most probable route for deriving olefins from alternative feedstocks will likely come from the coal gasification to methanol to olefin (MTO) pathway. There is also a high probability for producing ethylene from biomass by fermentation to ethanol and then dehydration. Biomass has a high potential for aromatic production if a chemical pathway could be developed using lignin as the feedstock. Oxygenated hydrocarbons (e.g., glycerin, alcohols, acids, PG, and phenolics) and halogenated hydrocarbons also have potential for production from biomass by processes other than gasification.

“One degree of separation” (i.e., one processing step more than traditional routes) is a desirable criterion. In general, the fewer unit operations away from traditional processing, the likelihood

that a viable chemical pathway could be commercialized will be greater. (Note: A good chemist, not necessarily an alchemist, can convert any carbon-based chemical to another chemical, given unlimited steps, equipment and finances.)

There is a medium probability that biomass gasification alone would be practical for the production of large-volume chemicals. The probability would increase if biomass could be co-fired with coal or the biomass was used to produce Fischer Tropsch fuels from which a byproduct stream is used for chemicals. Stranded gas has a low probability for the production of syngas alone since syngas transportation would be difficult. Stranded gas to syngas to chemicals is slightly more probable but the remoteness of the stranded gas may make it impractical. Residual and petcoke would be similar to coal. Tar sands and oil shale are low probability since these would need to be extracted and then transformed into a crude like product before being useful.

Probability Ranking	Coal	Biomass	Organic Wastes	Stranded Gas	Petcoke Residual	Tar Sands Oil Shale
Olefins: Ethylene Propylene Butadiene	High - with gasification	High - ethanol fermentation and dehydration to ethylene Medium - with gasification (not as attractive economically)	Medium - gasification	Low - not practical to pipe ethylene	High - with residual gasification No – with Petcoke	Low – since conversion to crude must occur first
Aromatics: BTX	High - with gasification	High - from lignin				N/R- Aromatics from shale (not gasification)
Oxygenated Hydrocarbons		N/R-PG, EG, alcohols, acids, phenol (not gasification)	N/R-PET and PC recovery and depolymerization			
Halogen Hydrocarbons		N/R-HCl + Biomass				
Paraffinic	N/R- Microbial production from coal					

- EG is ethylene glycol, ethane-1,2-diol, $\text{HOCH}_2\text{CH}_2\text{OH}$
- PG is propylene glycol, propane-1,2-diol, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$
- Phenol is carbolic acid, $\text{C}_6\text{H}_5\text{OH}$
- N/R, Probability not ranked

Exhibit 11: Ranking Probability of Feedstocks Chemical Route to Chemicals Production

3.3 Gasification Issues for Alternative, Renewable and Novel Feedstocks

The large economies of scale typically associated with the production of bulk chemicals and their immediate down-chain chemicals will tend to drive production processes of alternative, renewable and novel feedstocks toward gasification. Gasification is likely to have a smaller physical footprint than fermentation and requires less water handling and clean-up. Coal, residual oils and petcoke, all of which will require gasification, have high availability, low price and can

be gasified with readily available technologies to syngas and processed into products. These insights led the workshop participants to examine feedstock gasification issues.

The first issue was a recognition that even though gasification has been used and is used in a very limited fashion today for chemicals production (unique market situations), the gasification business is mainly coupled with electric power and Fischer-Tropsch fuels. The established gasification business base (utilities, fuel producers and their construction firms) do not wholly overlap with the traditional business partners/investor groups for the chemicals industry. In addition, alternative, renewable and novel feedstock providers are not the traditional supplies of raw materials to the U.S. chemicals industry. New non-traditional business relationship will need to be developed in order for the industry to transition to alternative, renewable and novel feedstocks. Building these relationships will require time and effort.

Gasifier units like most reactors have very large economies of scale. A modern gasification unit will process about 800 tons of coal per day. To ensure continuous supply (i.e., little downtime), multiple gasification units are installed. The magnitude of this scale and the benefit of multiple units may require the chemicals industry to transform into a combination of fuel/power/chemical supplier. It requires about four gasifiers to have an economical Fischer-Tropsch facility. This scale facility could provide fuel and a CO slipstream for chemicals. The scale in most planning scenarios is not economical for the complexity that IGCC would add but could be economical as a fuel/chemical plant. Future chemical plants may co-locate with the coal mine operations. This would provide feedstock on a “just-in-time” basis which may lower operational costs. Location does not impact the economies of scale. A mine site chemical plant might be of a scale that would produce not only the slate of products of the plant owner but may use the larger scale to produce methanol for shipment to other chemical industry operations. Future chemical plants may find it advantageous to co-locate with a power utility. This would provide economies of scale, however, storage and surge capacity would need to be integrated with peak power supply and the 24/7 steady state conditions required by chemicals production. Methanol production may be an important component of managing peak electric supply and steady state operation.

Gasification technology for fuel and power production is established. Adapting gasification technology into general use for the large-volume chemicals will require optimizing these systems around a different set of parameters than power or fuel production. Capital and operating costs per unit of syngas are major issues for the chemicals industry. The gasification unit and its ancillary equipment (air separation units or ASU), impurity removal, and downstream separation will likely add significant additional costs compared to traditional chemical feedstocks (Note: ASU and heat exchangers are both larger investments than the actual gasifier unit). These costs need to be engineered down to competitive levels. One attendee reported that capital cost allocations have 50-60% costs in gasifier and ancillaries and 20% in methanol to olefin operation.

Additionally, compared to power and fuels, chemicals production is likely to require much more sophisticated reaction, temperature and pressure controls and integration across multiple-unit downstream operations. The gasification unit operation will likely be much more sensitive to the following factors:

- Syngas composition. The gasification and shift reaction optimizations will be end-product specific; and

- Feedstock impurities. They may need removal or control in order to protect downstream catalyst.

Exhibit 12 lists the major issues associated with gasification identified at the workshop.

Issue Category	Issue	Resolution
Partnerships	Change from Traditional Partners	Need to work closely with utility/power industry, Fisher-Tropsch fuel producers and mining industry
Capital Costs	Nitrogen/Oxygen Separation – ASU scale typically requires cryogenic separations which are high capital, high energy consuming operations.	New separation technologies membranes vs. cryogenics
		Remove N ₂ from product stream to eliminate ASU
	Materials R&D needed	Refractory for lower construction and operating costs Corrosion resistance for lower construction and operating costs
Economies of Scale	Gasifier unit size (~ 800 tons/day) requires very large scale plants	Need to develop unit designs and materials of construction that are less cost sensitive to scale
Reliability	System reliability can not be fully addressed at Lab or Pilot scale	Demonstration Plant Loan guarantees
Composition	Shift Reaction Prediction and Control	Modeling for prediction and real-time modification Membranes/catalyst
	Impurities – can impact product and catalyst	Separation and control, up-stream and/or down-stream of the gasification unit
Process Control	Complex Modeling Integration (mass/energy)	Sensors, controls and software
CO ₂	Capture at pressure Must have strategy	Sequester, sale, other, ...
Water/Heat Management	High temperature typically required for slag control	Non-slagging, lower temperature (650°C) gasifier
	High Pressure, High Temperature (1,200°C) heat transfer equipment	New materials/designs
Mixed Feedstock Designs	Feedstock flexibility – gasifier designs are feed specific	New feed systems capable of coal/biomass/... and controls

Exhibit 12: Major Concerns Identified for Viable Gasification Crosscutting All Feedstocks

Biomass feedstocks present additional issues to the gasification platform. Raw biomass can contain >50% moisture and is biodegradable. Aging, damp biomass has perceptible odor and possibly health issues associated with its storage. Some moisture can be removed with field drying. However, frequently kiln or other energy-consuming drying methods have to be used to remove the moisture and make the biomass more suitable for transportation and storage.

Biomass gasification feedstock issues and possible solutions can be summarized as below:

Combination, Flexibility, Pretreatment	Liquefy, fluidize, homogenize
Heat Content / Surface Area.....	Pretreatment
Heterogeneous feeds	Composition Monitors
Storage.....	Liquefy, fluidize, homogenize
Locality.....	Modular gasifier moves to silos

3.4 Syngas to End-Product Technical Issues

Once carbon has been gasified, additional engineering and cost issues are encountered in converting the single carbon molecule (CO) in syngas to multi-carbon end products. These issues are end-product specific and many face the challenge of having the “one degree of separation” (i.e., one processing step more than traditional routes) that is desired to keep operating and capital costs low. Today, traditional ethylene and propylene production routes "surgically" produce products in specific ratios (i.e., feedstock and production equipment are tailored for specific end-product ratios). These processes use catalyst that are highly selective for ethylene and propylene and not higher olefins which require cracking and reprocessing. Syngas production of these olefins will likely go through the methanol route (MTO). This route will utilize different catalysts and have different driving equilibrium parameters which are not likely to result the same end-product ratios. These new routes will add unit operations and complexity to olefin production processes.

Ideally, a more direct and efficient process would be to build ethylene from ethanol rather than from methanol. However, there is no efficient route to produce ethanol from syngas (particularly syngas with high CO₂ concentrations). Similarly, the production of aromatics (BTX), oxygenated hydrocarbons, or any of the C₃ and C₄ backbones in one or two process steps (i.e., not going through the syngas/CO route) would be very desirable. This chemistry would require significant research on process reactor and development of catalyst (with desired selectivity and activity) .

Exhibit 13 highlights the primary issues that the attendees rapidly identified associated with the production of end products using gasification of alternative, renewable and novel feedstocks.

Issue Category	Issue	Resolution
General	As, H ₂ S, Hg, and other elements have undesired impact on product and catalyst	Trace component control, separation, and removal
Olefins: Ethylene Propylene Butadiene	Separation Costs	Olefins separated cryogenically are capital intensive. Need lower-cost more-efficient technologies to separate olefins
	Syngas to ethylene/ propylene	Tailored C2 : C3 ratios - high selectivity catalyst and controls to few C4 and greater (Don't want to spend energy to crack > C4s)
	MTP, MTO	Better catalyst and separation technologies
	Syngas direct to C4 backbones	Eliminate the syngas olefin step, don't go over C4 catalyst – selectivity and activity Better C4 to C5 separations
Aromatics: BTX	Benzene to Styrene	Direct and more selective production. Today the problems are the catalysts coke.
		Lacking fundamental process development
		Need MTO that coproduces aromatics
Oxygenated Hydrocarbons	Syngas to EG, syngas to acrylic acid, syngas to methacrylic acid, etc	Syngas direct to EG – new catalyst process development
		Methanol to EG improvement would be beneficial
		Better and more selective catalysts, stability to separate out the products
		New ways to make vinyl acetate - unique processing steps may enable these but have not to date.
	Syngas to ethanol (not good option)	Need to have CO ₂ down from 15% to 2%
		There is room clearly for improvement on the catalysts on the ethanol side
	DME	Processing/catalyst for not making CO ₂

- Acrylic acid $\text{CH}_2=\text{CHCOOH}$ or 2-propenoic acid is a chemical compound (formula $\text{C}_3\text{H}_4\text{O}_2$) is the simplest unsaturated carboxylic acid with both a double bond and a carboxyl group linked to its C_3
- Methacrylic acid, or 2-methyl-2-propenoic acid, is a low molecular weight carboxylic acid $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$
- DME – dimethylether CH_3OCH_3
- MEG – mono ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$ ethane-1,2-diol
- MPG – mono propylene glycol 1,2-propanediol
- Acetone CH_3COCH_3

Exhibit 13: Primary Concerns for Production of Products from Syngas

3.5 Feedstocks for Non-Gasification Routes to Chemical End Products

The global interest and the economies of scale that favor carbon gasification to CO for chemical end products may overshadow the potential to produce profitable chemical products by other means. Biomass fermentation is already recognized as a production route for ethanol, glycerol (which can be processed to propylene, glycol ethers, etc.), lactic acid (Cargill) and butanol (C₄H₁₀O). The challenges of commercializing chemicals production from biomass fermentation have been documented extensively by the DOE Office of Biomass Program. The workshop attendees rapidly listed out the major challenges to implementing biomass production of chemicals (Exhibit 14).

Issue Category	Issue	Resolution
General	Produces crude building blocks for high value materials	Complex downstream cleaning (separations) and processing
		Direct chemical reforming of Biomass
	Salts contained in biomass impact product quality and catalyst performance	Salt removal technologies (membranes, electrodialysis, ...)
Production Rate /Crop Intensity	Seasonal and dispersed	
Drying	Crop drying for transportation and storage	
Fermentation	Cost	
	Yield	
Separation	Product separation	
	Product drying	
Olefins	Biomass ethanol is a possible production route for olefins	Fuel ethanol will be a significant competitor
Aromatics - BTX	Lignin to aromatics not demonstrated	Demonstrations
Oxygenated Hydrocarbons	C ₃ oxygenates, glycerin, lactic acid and PLA, poly-glycol, phenyls	Ability to clean up glycerin and make high-valued materials from product
	Glycerol from biomass has a mix of bad actors for catalyst	Techniques to clean crude glycerin
Other	Direct biomass sugar/starch derivatives without fermentation	

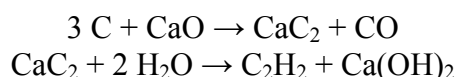
- Glycerol, also known as glycerin, glycerine, and as propane-1,2,3-triol, 1,2,3-propanetriol, and 1,2,3-trihydroxypropane
- Lactic acid (2-hydroxypropanoic acid) CH₃CH(OH)COOH

Exhibit 14: Major Hurdles to Implementing Production of Bio-chemicals

There may be other opportunities, for example in developing processes to take advantage of the inherently aromatic rich nature of tar sands to produce BTX and their derivatives or developing in situ pyrolysis to chemical end products. Other significant opportunities may lie along other production routes, for example:

- Parrafinics from microbial methane – Coal
- Aromatics from oil shale (which is more cyclic, less alkane than crude)
- Oxygenated hydrocarbons from depolymerization of polymers – Organic wastes
- Parrafinics from microbial methane – Stranded gas

It may be worthwhile to reinvestigate alternative feedstocks using acetylene chemistry (ethyne, $\text{HC}\equiv\text{CH}$). This historic chemical production route may again prove competitive at the economics and scale needed by today's chemicals industry. Acetylene is produced using coal and limestone.



Acetylene can be used as building block for numerous products. Catalytic addition of water to acetylene gives acetaldehyde from which acetic acid and other compounds can be made. Catalytic addition of acetic acid to acetylene gives vinyl acetate and addition of alcohols yields vinyl ethers. Addition of cyanide gives acrylonitrile. Also numerous other reaction products can be derived from acetylene building block chemistry.

Issue Category	Issue	Resolution
General	Need to understand Lifecycle Issues (e.g., CO_2) from a process and engineering perspective	Ring opening Catalyst
Tar Sands	Tar sands produce an aromatic rich stream	Ring opening Catalyst
In-situ Pyrolysis	Coal, tar sands and possibly shale can be pyrolyzed in-situ resulting in potential chemical feedstock production	Early stage R&D
Acetylene Chemistry	Re-examine acetylene chemistry	

Exhibit 15: Carbon to Products Pathways

3.6 Workshop Summary of Research Needs and Recommendations

The major technology improvements, identified during the workshop, which will hasten the transition to alternative, renewable and novel feedstocks in the chemicals industry should focus on advancing R&D in the following areas:

- Gasifiers
 - Economic scale down of gasifiers to the size needed for chemicals production
 - Economic and energy efficient air separations (N_2/O_2)
 - CO_2 handling equipment for separation, capture and control (including sequestration)
- Gasification system down stream of gasifier
 - Catalysts to achieve desired feedstock chemical composition
 - Separations to remove impurities for chemical plant feedstock
 - Replacement for energy-intensive cryogenic separations, i.e. nitrogen/oxygen and olefin separations
- Fermentation and extraction for biomass
 - Catalysis to utilize low-cost cellulose-based biomass
 - Salt removal separations processes

Specific applications which have the highest probability for near-term success and therefore, should be the initial focus of R&D programs, include:

- (1) gasification of coal to olefins and aromatics, and
- (2) fermentation and/or extraction processes for conversion of lignins to aromatics.

4. Conclusion

This report summarizes actions identified by the workshop as required to overcome hurdles to viably implementing alternative feedstocks in the U.S. chemicals industry. Six alternative fuel sources – coal, biomass, petroleum coke, tar sands and oil shale, organic municipal solid waste, and unconventional natural gas (including methane from “stranded” or “remote” sources, coal bed methane and gas hydrates) – and five utilization technologies (gasification, fermentation/extraction, pyrolysis, liquefaction, and coking) were reviewed for potential application to production of chemicals. Chemical process chains were also reviewed to determine the highest impact application areas for using these new technologies and feedstocks. Production of bulk organic chemicals was identified as the best target for focusing these efforts.

The following broad conclusions were drawn from the investigation:

- *Existing Opportunities* – There are known technologies and processing techniques that can utilize alternative feedstocks to manufacture the bulk chemicals that make up a major portion of the industry.
- *Technology Needs to Improve Process Viability* – New R&D is needed to improve the process economics and environmental impact of known alternative feedstock technologies and to develop novel feedstock technologies.
- *Institutional Direction* – The chemicals industry must examine its working relationship with alternative supplies both as a primary user and as a slipstream processor. The federal and state governments must address economic and environmental policies that impact the development of alternative feedstock.

4.1 Existing Opportunities

The literature review and workshop were focused on the identified alternative feedstocks and production of bulk organic chemicals. New opportunity resources were sought in terms of current practices, accessibility, process adaptability and the research and development needs to hasten their commercialization.

Natural gas and petroleum are not the only sources of feedstock available to the chemicals industry. However, they are currently the most economic and widely used feedstock sources. The Vision2020 feedstock task force identified coal, petroleum coke, heavy oil from tar sands or oil shale, renewable sources such as biomass and municipal solid waste (MSW) and unconventional reserves such as stranded natural gas as potential alternative feedstocks having economic and technical merit. These alternatives could provide the industry with significant opportunities to move away from natural gas and petroleum.

The *Alternative, Renewable, and Novel Feedstocks* workshop participants identified large-volume organic chemicals as providing the best opportunity to utilize alternative feedstocks as a means of reducing dependency on natural gas and petroleum. Organic chemicals are primarily derived from natural gas or petroleum feedstocks. Exhibit 16 lists commodity chemicals which could be produced using alternative feedstocks that are of interest to the chemicals industry.

These chemicals are generally those with U.S. volumes of production of at least 2 billion lbs/yr to over 50 billion lbs/yr. It should be noted that some low-volume specialty chemicals and those with future potential or an underdeveloped market have also been considered, especially in the case of bio-based feedstocks (www.acs.org, Chemical Manufacturers Association). Chemicals that are derived from inorganic sources, such as sulfuric acid or chlorine, were not included in this study.

Chemical	U.S. Production (x10 ⁶ tons) 2004	Alternative Chemical Route	End Use
Olefins: Ethylene (C ₂ H ₄) Propylene (C ₃ H ₆) Butadiene (C ₄ H ₆)	28.3 16.9 2.4	Gasification of coal or biomass to methanol or ethanol to olefins	R-Cl, oxide, polymers
Aromatics: Benzene(C ₆ H ₆) Toluene Xylenes	7.5 4.1 4.0	Gasification to methanol (gas-to-liquids) Extraction from lignins	Polymers, cyclohexane
Oxygenated Hydrocarbons Acetone (CH ₃ COCH ₃) Formaldehyde (H ₂ CO)		Acetone – Gasification Formaldehyde - Gasification from methanol	Intermediate Olefin, wood products

- Toluene is methyl benzene
- Xylenes are: ortho (1,2-dimethylbenzene), meta (1,3-dimethylbenzene), and para (1,4-dimethylbenzene)

Exhibit 16: Major Chemicals of Interest for Alternative, Renewable and Novel Feedstocks

Assessment of alternative fuels and utilization processes for replacing natural gas and petroleum as chemical industry feedstocks are summarized below (Exhibits 17 and 18).

Alternative Chemical Pathways	Alternative Fuel Sources		
	Coal	Biomass	Petcoke & Residual Gas
Olefins	Gasification - High	Gasification –Med Fermentation – High for ethanol dehydration	Gasification – High for Residual Gas
Aromatics	Gasification – High	Extraction - High from lignin	
Oxygenated Hydro-carbons		Fermentation - Med	
Halogen Hydro-carbons		Fermentation - Med	
Paraffinic	Fermentation - Med		

Exhibit 17: Implementation Potential for Feedstock Flexibility Program by Product (Areas in blue – Recommended for pursuing initially)

Alternative Fuel Sources	Alternative Fuel Industrial Utilization Pathways				
	Gasification	Fermentation	Pyrolysis	Liquefaction	Coking
Coal	High	Low	Low	Medium	Low
Biomass	Medium	High	Medium	Low	Low
Petroleum Coke	High	Low	Low	Medium	Low
Tar Sands & Oil Shale	Medium	Low	Low	Low	Low
Organic Waste (MSW)	Low	Low	Low	Low	Low
Stranded Gas	Low	Low	Low	Low	Low

Exhibit 18: Implementation Potential for Feedstock Flexibility Program by Feedstock
(Areas in blue – Recommended for pursuing initially)

It was concluded that gasification and fermentation/extraction of coal, petcoke, and biomass have the highest probability of success, particularly in the near term, and efforts to identify R&D needs were therefore focused on these areas.

4.2 Technology Needs to Improve Process Viability

Over the last 70 years, there has been much activity in the development of processes that utilize alternative feedstocks, but little progress in bringing the developed technologies into common use. The vast majority of these activities have been focused on coal conversion for power and/or Fischer-Tropsch fuel/chemicals production. Building and operation of alternative chemicals feedstock plants has only occurred where normal private investment markets do not function (such as when heavily subsidized in times of war, or in petroleum embargoed nations). The major impediment to the building and operation of alternative feedstock chemical plants rests on the economics and associated risks of the alternative processes.

Development of new technologies and processes focused on the production of major chemical products represents one of the most significant contributions to changing alternative feedstock economics so as to enable these feedstocks to be cost competitive with tradition chemicals production. R&D efforts are needed to make these alternative processes more efficient, environmentally benign, and less financially risky before becoming more common domestically.

Although using coal to make chemicals is not new, it is currently limited to a small number of production operations. Large-scale production and new constructions primarily occur in locations outside the U.S. where extremely cheap coal reserves, coal-based infrastructures and government financial support are available, such as in China or South Africa. Some technologies for chemicals production from coal are mature, such as coal gasification and are ready for implementation when economically feasible. Coal liquefaction is an older process than gasification and produces more products per pound of coal than Fischer-Tropsch synthesis.

However, liquefaction is significantly more complex and not proven on a large scale. Advances in gasification and liquefaction technology are needed to make these conversion processes more economically attractive and reliable.

International crude oil prices have made tar sands a practical feedstock for the large-scale production of synthetic crude oil. Synthetic crude production opens a new alternative feedstock source for chemicals production, using feedstocks that are significantly similar to feedstocks used in traditional chemicals manufacture. This may provide synthetic crude with a more attractive feedstock status than gasification and liquefaction. Technologies will need to be examined to exploit the byproducts of synthetic crude production. Oil shale technology and economy lags tar sands but large-scale production is not too far off.

Production of chemicals from biomass with the exception of transportation fuels, i.e., ethanol and biodiesel, is presently limited to relatively small-volume specialty chemicals using sugar- or starch-derived raw materials. Use of biomass for commodity chemical manufacture will require research and development in a variety of fields such as plant science, microbiology, genomics, catalysis, and chemical separations technologies. Large-scale chemicals production in the United States will require significantly new technological processes capable of utilizing low-cost biomass feedstocks (e.g., cellulose) on a large scale that do not compete with the corn and sugar used for fuels, livestock feed and human food. A true step-change in economics is awaiting the successful development of enzymes that can utilize low-cost biomass. If an enzymatic route can be made competitive, experts say that the United States could quickly develop a significant agricultural-based bulk chemicals industry (Chemical Week, 2006).

4.3 Institutional Direction

Development of alternative feedstocks is a critical change necessary to the domestic chemicals industry that will reduce U.S. dependence on foreign oil, reduce domestic natural gas consumption, and aid in sustaining the viability of U.S. manufacturing. Chemicals industry stakeholders (chemical companies, local state and federal governments, labor, shareholders, suppliers, environmental organizations, etc.) must examine the long-term dynamics and impacts of a changing industry. Private and/or public initiatives to replace oil and gas in manufacturing feedstocks will need to be recognized and implemented toward very significant technical, policy and economic issues. The industry and the federal government are the two largest stakeholders with the most influence. The industry must look beyond its normal business models to a future where carbon resources could be very constrained and business alignments with new suppliers and end users will be needed. The government must examine its role in promoting and maintaining this change.

The most economical investment in new gasification facilities will be in combining the needs of electricity/fuels production and chemicals manufacture. These initiatives will need investment in the development of methods of syngas storage and advanced control systems to switch from one activity to another.

Large integrated gasification combined cycle (IGCC) facilities utilizing alternative feedstocks are becoming more economically competitive for power and fuel production. IGCC competitiveness with conventional technologies depends on the current predicted prices of natural gas or petroleum and alternative feedstocks, current and predicted levels of subsidy and

the local costs of acquiring, and transporting and storing alternative fuels. The recent increase in the price of natural gas and petroleum makes IGCC alternative processes more economically attractive. However, conversion to use of alternative feedstocks requires a large investment of capital and is unlikely to occur when feedstock prices remain variable and unpredictable. Scale-up from successful pilot processes will benefit if feedstocks for the chemicals industry can be coupled with power production or other needs. This requires communication and planning across industrial and utility sectors of the economy, which currently do not collaborate closely.

Appendix 1: Vision2020 Task Force

John Carberry – Dupont
Terri Grocela-Rocha – General Electric
Mark Jones – Dow Chemical Company
Frank Lipiecki – Rohm & Haas Company
Joanna McFarlane – Oak Ridge National Laboratory (ORNL)
David Mobley – General Electric Company
Brendan Murray – Shell
Ravi Prasad – Praxair
Sharon Robinson – Oak Ridge National Laboratory (ORNL)
Jeff Siirola – Eastman Chemical Company
Cheryl Sabourin – General Electric Company
Clark Simmons – Innovene LLC
David Södeberg – BP
Tyler Thompson – Dow Chemical Company
Phillip Winkler – Air Products and Chemicals Inc.
Joe Zoeller – Eastman Chemical Company

Appendix 2: Alternate, Renewable, and Novel Feedstocks Workshop Attendees

Attendee	Company
Brendan Murray	Shell
Jeff Siirola	Eastman
John McDermott	GE Global Research
Joseph Zoeller	Eastman Chemical
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Carl Irwin	WVU
Don Anthony	CCR
Emory Ford	MTI
John C. Chen	AIChE (Lehigh U)
Daniel Cicero	NETL
Dickson Ozokwelu	U.S. DOE
Drew Ronneberg	U.S. DOE
Elliott Levine	U.S. DOE
Harold Sturm	SRNL
Ram Srivastava	SAIC/U.S. DOE
Sara Dillich	U.S. DOE
Sharon Robinson	ORNL
Karla Bell	BCS, Incorporated
Roy Tiley	BCS, Incorporated
William Choate	BCS, Incorporated

Appendix 3: Large-Volume Chemicals Manufactured in the United States

Chemical	Production** 10 ⁶ tons (US, 2004)	Alternative Feedstock or precursor	Industry/Product
Olefins: Ethylene Propylene Butadiene (1,3-)	28.29 16.89 2.42	Gasification of coal, biomass, DME* Methanol (MTO*, MTP*)	Gas to polymers
Ammonia	11.87	Gasification of coal, biomass Natural gas, Haber cycle	Fertilizer, reagent, explosives
Chlorinated organics: Ethylene dichloride Vinyl chloride Methyl chloride	13.35 8.00 0.62	Chlorination of olefins	Polyurethanes, solvents, pulp and paper solvents,
MTBE	6.39	CH ₃ OH+isobutylene	Fuel additive
Aromatics: Benzene Ethylbenzene Toluene P-xylene Cumene	8.73 6.37 4.13 4.58 4.10	Gasification of coal, biomass From methanol from GTL* Friedel-Crafts alkylation	Polymerization/surfactants
Methanol	3.24	Gasification of coal, biomass Fischer-Tropsch	Building block
Urea	6.34	Ammonia, CO ₂	Fertilizer, resins, adhesives
Styrene	6.03	ethylbenzene	Polystyrene
Terephthalic acid	2.20	p-xylene	Intermediate
Aldehydes: Formaldehyde	4.53	From methanol (natural gas)	Building block for olefins
Oxygenated organics: Ethylene oxide Propylene oxide	4.00 -	Gasification of coal, biomass, through ethylene oxide	Building block, reagent
Ethylene glycol Propylene glycol	3.18 -	Hydration of ethylene oxide	Polyester
Carboxylic acids: Acetic anhydride	0.89	Gasification of coal, biomass, Methanol from syngas	Adds C ₂ , reagents and intermediates
Phenol Bis phenol A	2.66 -	Cumene	Resins, paints, adhesives, coatings, solvents, polycarbonate
Acrylonitrile	1.73	NH ₃ + propylene/propane	Acrylic fibers
Esters: Vinyl acetate Methyl methacrylate	1.65 0.86	From ethylene	Intermediate Coatings, plastics
Acetone	-	Gasification of coal, biomass, BTEX	Intermediate
Cyclohexane	-	Hydrogenation of benzene	Intermediate
Caprolactam	-	Oxidation of cyclohexane	Nylon
Aniline	0.88	Nitro or chlorobenzene	Intermediate
Isopropyl alcohol Butanol	- 1.06	Gasification of coal, biomass, propylene	Intermediate

*Abbreviations given at beginning of document

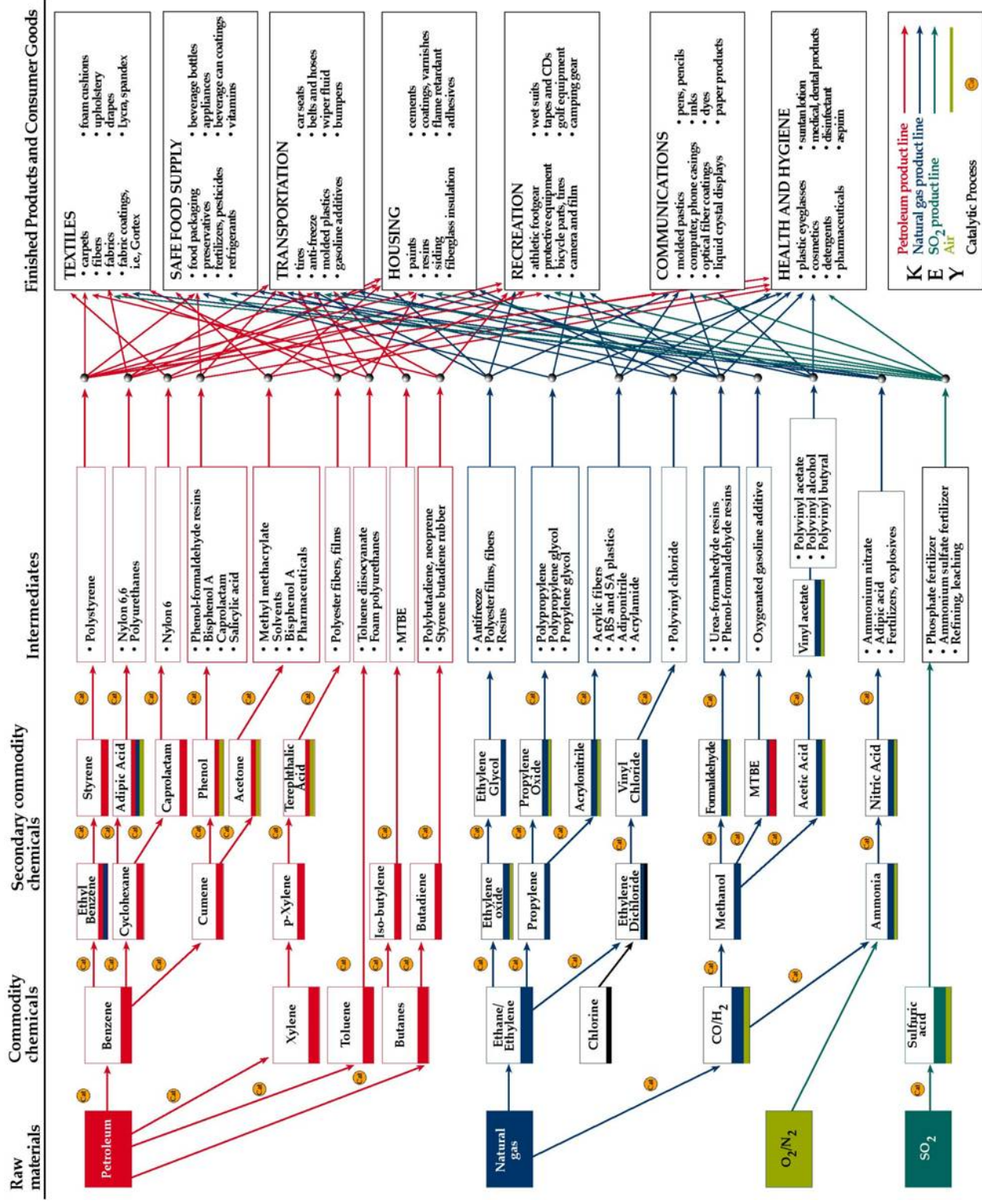
** *Guide to the Business of Chemistry 2005*, American Chemistry Council

Specialty Chemicals, Chemicals with Development Potential

Chemical	Alternative Feedstock or precursor	Industry/Product
Adipic acid	Alternative Feedstock	Intermediate
Ascorbic acid	Kreb's cycle	Building block
Diacids	fermentation	Replace petrochemical maleic acid, polymers
Aspartic acid	Amination of fumaric acid, or enzymatic conversion	Amino C4 acids, polymers
Itaconic acid	Fungal fermentation of sugar	Specialty monomer
FCDA 2,5 furan dicarboxylic acid	Oxidative dehydration of sugar	Polyethylene terphthalate
Glutaric acid	Oxidation of starch	Building block from carbohydrate
Levulinic acid	Dehydration of cellulotics, sugars	Building block from carbohydrate
HPA – hydroxy propionic acid	Fermentation	Acrylates, malonic acid, diol
Xylitol	Pretreatment of cellulose	Xylaric, arabonic acids, polymers
Sorbitol	Hydrogenation of glucose	Polymers, propylene glycol, lactic acid, polysaccharides
Hydroxy butyrolactone	Oxidation of starch	Furans, polymers

Fuels, Hydrocarbons

Chemical	Alternative Feedstock or precursor	Industry/Product
Paraffins: Ethane propane butanes	Gasification of coal, biomass Methanol dehydrogenation Fischer-Tropsch liquid	Fuel, building block
Ethanol	Fermentation of biomass Gasification of coal, biomass	Fuel
Biodiesel, Glycerol	Enzymatic transformation of biomass Transesterification of oils	Fuel, Building block Polyurethane, glycol, 1-propane diol, biodiesel
Dimethyl ether		Replacement for propane



An Example of a Flow-Chart for Products from Petroleum-based Feedstocks (Top Value Added Chemicals From Biomass Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas, Pacific Northwest National Laboratory and the National Renewable Energy Laboratory, August 2004)

References

Aiello-Mazzarri, C., Coward-Kelly, G., Agbogbo, F.K., Holtzapple, M.T. 2005. Conversion of municipal solid wastes into carboxylic acids by anaerobic countercurrent fermentation – Effect of using intermediate lime treatment, *Applied Biochemistry and Biotechnology* 127(2), 79-93.

Aiello-Mazzarri, C., Agbogbo, F.K., Holtzapple, M.T. 2006. Conversion of municipal solid wastes into carboxylic acids using a mixed culture of mesophilic microorganisms, *Biobioresource Technology* 97(1), 47-56.

Anderson, J. 2005. On-purpose propylene production. In *Technology and More*, October 2005. UOP LLC 4488/10/05, p.1. www.uop.com

BCS Inc., 2007, Coal as an Alternative Feedstock for Use in U.S. Manufacturing Industries, in progress

Becker, P., “The Role of Synthetic Fuel in World War II Germany,” *Air University Review*, July-August 1981, online at <http://www.airpower.maxwell.af.mil/airchronicles/aureview/1981/jul-aug/becker.htm>.)

Biomass Technical Advisory Committee. 2003. Vision for Bioenergy and Biobased Products in the United States.
http://www.bioproducts-bioenergy.gov/pdfs/BioVision_03_Web.pdf

Biomass Technical Advisory Committee. 2003.
Roadmap for Biomass Technologies in the United States
<http://www.bioproducts-bioenergy.gov/pdfs/FinalBiomassRoadmap.pdf>

Canadian Energy Research Institute. <http://www.ceri.ca/>

Chan, W.N., Holtzapple, M.T. 2003. Conversion of municipal solid wastes to carboxylic acids by thermophilic fermentation, *Applied Biochemistry and Biotechnology* 111(2), 93-112.

Chang, V.S., Holtzapple, M.T. 2000. Fundamental factors affecting biomass enzymatic reactivity, *Applied Biochemistry and Biotechnology* 84(6), 5-37.

Chang, V.S., Kaar, W.E., Burr, B., Holtzapple, M.T. 2001a. Simultaneous saccharification and fermentation of lime-treated biomass, *Biotechnology Letters* 23(16), 1327-1333.

Chang, V.S., Nagwani, M., Kim, C.H., Holtzapple, M.T. 2001b. Oxidative lime-pretreatment of high-lignin biomass – Poplar wood and newspaper, *Applied Biochemistry and Biotechnology* (94)1, 1-28.

Chemical Industry Vision2020 Technology Partnership. 2003 Highlights of Biopower Technical Assessment: State of the Industry and Technology. <http://www.chemicalvision2020.org/>

Chemical and Engineering News. 2006. Glycerin surplus. American Chemical Society, February 6, 2006, p. 7.

Chemical Manufacturers Association. 1998. U.S. Chemical Industry Statistical Handbook 1998. Arlington, VA.

Chemical Week, 2006. Alternative Feedstocks Warming Up to Coal, March 8, 2006.

Coca, M.T., Mendez-Vigo, I., Elias, F.A. 1998. Coal gasification. Conception, implementation and operation of the ELCOGAS IGCC power plant, ELCOGAS, Madrid, Spain, January 1998. http://www.worldenergy.org/wecgeis/publications/default/tech_papers/17th_congress/2_3_13.asp

Consortium for Premium Carbon Products from Coal (CPCPC) – Penn State, W. Virginia, NETL, <http://www.energy.psu.edu/cpcpc/overview.shtml>

de Lange, T.J., Beeldman, M., Kiel, J.H.A., den Uil, H., Veenkamp, J.N. 2001. Coproduction of fuels as an option for Demkolec? ECN Biomass, ECN-C—01-004, March 2001.

Deutsch, C.H. 2006. Dupont looking to displace fossil fuels as building blocks of chemicals, New York Times, February 28, 2006.

DOE/EIS. 2005. EIS 3057. Draft EIS for the Gilberton Coal-to-Clean Fuels and Power Project November 2005.

Domke, S.B., Aiello-Mazzarri, C., Holtzapple, M.T. 2004. Mixed acid fermentation of paper fines and industrial biosludge, Bioresource Technology 91(1), 41-51.

Doyle, E.H. (chair). 2004. Charting the future of methane hydrate research in the US. National Academy of Sciences, The National Academies Press, Washington, D.C., <http://www.nap.edu>

Energy Information Administration, February 2006, Annual Energy Outlook 2006

Fleisch, T.H. and Sills, R.A., BP, Innovation day Sept 7, 2005, Philadelphia

Foley, T., Anderson, J. 2005. Methanol to olefins (MTO). In Technology and More, October 2005. UOP LLC 4488/10/05, p.3. www.uop.com

Gallagher, P., Schamel, G., Shapouri, H., Brubaker, H. 2006. The international competitiveness of the US corn industry: A comparison with sugar-ethanol processing in Brazil, Agribusiness 22(1), 109-134.

Gregor, J., Anderson, J. 2005. Propane dehydrogenation (PDH). In Technology and More, October 2005. UOP LLC 4488/10/05, p.2. www.uop.com

Gregor, J., James, B. 2005. Olefin cracking. In Technology and More, October 2005. UOP LLC 4488/10/05, p.4. www.uop.com

Hallett, W.L.H., Clark, N.A., and M. White, Evaporation of Biomass Pyrolysis Oil Droplets – II, Combust. Inst. (Canadian Sect.) 2002 Spring Technical Meeting,

Hammerschlag, R. 2006. Ethanol's energy return on investment: A survey of the literature 1990-present, *Environ. Sci. Technol.* 40, 1744-1750.

Hirsch, R.L., Bezdek, R., and R. Wendling. 2006. Peak of World Oil Production and Its Mitigation, *AIChE Journal* 52(1), 2-8.

International Dimethyl-ether Association. 2002. <http://www.vs.ag/ida/ida brochure.pdf>

Kim, S., Holtzapple, M.T. 2005. Lime pretreatment and enzymatic hydrolysis of corn stover. *Bioresource Technology* 96(18), 1994-2006.

Kim, S., Holtzapple, M.T. 2006a. Effect of structural features on enzyme digestibility of corn stover. *Bioresource Technology* 97(4), 583-591.

Kim, S., Holtzapple, M.T. 2006b. Delignification kinetics of corn stover in lime pretreatment. *Bioresource Technology* 97(5), 778-785.

Kniel, L. and O. Winter. 1984. "Ethylene", in *Encyclopedia of Chemical Processing and Design*, Volume 20, McKetta, J.J. and W.A. Cunningham (Eds). Marcel Dekker, Inc., New York, 80-159.

Lynd, L.R. 1996. Overview and evaluation of fuel ethanol from cellulosic biomass: Technology, economics, the environment and policy, *Annual Review of Energy and the Environment* 21, 403-465.

Mann, R. Nov. 2004. National Commission on Energy Policy. Ethanol from Biomass

Meister, J.J. 2002. Modification of lignin. *J. Macromolecular Science – Polymer Reviews* C42(2), 235-289.

National Energy Technology Laboratory web site
<http://www.netl.doe.gov/coalpower/gasification/description/gasifiers.html>.

Nikolaisen, L. (Ed.), Nielsen, C., Larsen, M.G., Nielsen, V., Zielke, U., Kristensen, J.K., Christensen, B.H. 1998. Straw for energy production: Technology, environment, economy. Copenhagen Center for Biomass Technology/Danish Energy Agency.

Olah, G.A. 2005. Beyond oil and gas: The methanol economy. *Angew. Chem. Int. Ed.* 2636-2639.

Olah, G.A., Doggweiler, H., Feldberg, J.F., Frohlich, S., Gridinia, M.J., Karpeles, R., Keumi, T., Inaba, S-i., Ip, W.M., Lammertsma, K., Salem, G., Tabor, D.C. 1984. Onium ylide chemistry 1. Bifunctional acid-base-catalyzed conversion of heterosubstituted methanes into ethylene and derived hydrocarbons. The onium ylide mechanism of the $C_1 \rightarrow C_2$ conversion.

Priyadarsan, S., Annamalai, K., Sweeten, J.M., Muhktar, S., Holtzapple, M.T. 2004. Fixed bed gasification of feedlot manure and poultry litter biomass, *Transactions of the ASAE* 47(5), 1689-1696.

Priyadarsan, S., Annamalai, K., Sweeten, J.M., Holtzapple, M.T., Muhktar, S. 2005. Co-gasification of blended coal and feedlot and chicken litter biomass, *Proceedings of the Combustion Institute* 30, 2973-2980.

Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Caimey, J., Eckert, C.A., Frederick, W.J. Jr., Hallet, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., and T. Tschaplinski. 2006. The Path Forward for Biofuels and Biomaterials. *Science* 311, 484-489.

Renesme, G., Saintjust, J. and Y. Muller. 1992. Transportation fuels and chemicals directly from natural-gas – How expensive?, *Catalysis Today* 13(2-3), 371-380.

Shenhua Group Corporation,
<http://www.htigrp.com/data/upfiles/pdf/DCL%20Technology%2023Feb05.pdf>

Simbeck, D.R. 2001. CO₂ mitigation economics for existing coal fired power plants. *Pittsburg Coal Conference*, Dec. 4, Newcastle, New South Wales, Australia.

Söderberg, D.J. 2004. Vision 2020 Steering Team Priority Research Brainstorming Session, Dec. 1, 2004.

Sricharoenchaikul, V., Frederick, Jr., Wm.J., Agrawal, P. 2002. Black liquor gasification characteristics. 2. Measurement of condensable organic matter (tar) at rapid heating conditions, *Ind. Eng. Chem. Res.* 41, 5650-5658.

Spath, P. and D. Dayton, Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas. NREL Technical Report NREL/TP-510-34929. Dec 2003.

Thanakoses, P., Black, A.S., Holtzapple, M.T. 2003a. Fermentation of corn stover to carboxylic acids, *Biotechnology and Bioengineering* 83(2), 191-200.

Thanakoses, P., Mostafa, N.A.A., Holtzapple, M.T. 2003b. Conversion of sugarcane bagasse to carboxylic acids using a mixed culture of mesophilic microorganisms, *Applied Biochemistry and Biotechnology* 105, 523-546.

United Kingdom Department of Trade and Industry. 1999. *Technology Status Report, Coal Liquefaction*, TSR010, Oct. 1999.

United States Department of Energy. 2003. *Assessment of the Commercial Potential for Small Gasification Combined Cycle and Fuel Cell Systems: Phase II Final Draft Report*. HM Associates Inc, Princeton Energy Resources International, LLC and TFB Consulting.

United States Department of Energy. 2006. *Coal Gasification: an Alternative Carbon Source for U.S. Manufacturing*. Internal Report. BCS, Inc.

United States Department of Energy, Office of Energy Efficiency and Renewable Energy. 2005. 27th Symposium on Biotechnology for Fuels and Chemicals.

http://www.eere.energy.gov/biomass/biotech_symposium/

United States Department of Energy, Techline May 20 1997. Clean Coal Technology Project Produces First Methanol from Coal.

http://www.netl.doe.gov/publications/press/1997/tl_kngs.html

Werpy, T., Peterson, G., Eds. 2004. Top value added chemicals from biomass, Volume I: Results of screening for potential candidates from sugars and synthesis gases, Pacific Northwest National Laboratory, National Renewable Energy Laboratory, DOE Office of Biomass Program, Energy Efficiency Renewable Energy, August 2004.

Wham, R.M., Fisher, J.F., Forrester, R.C., III, Irvine, A.R., Salmon, R., Singh, S.P.N., and W.C. Ulrich. 1981. Liquefaction technology assessment. Phase 1: Indirect liquefaction of coal to methanol and gasoline using available technology, Oak Ridge National Laboratory ORNL-5664.

Wham, R.M. Stability of short-contact-time coal liquefaction products. Oak Ridge National Laboratory ORNL/TM-8651.

Williams, R.H. 2004a. Towards polygeneration of fluid fuels and electricity via gasification of coal and biomass, National Commission for Energy Policy. November, <http://www.energycommission.org/research/>

Williams, R.H. 2004b. IGCC Next Step on the Path to Gasification-Based Energy from Coal. National Commission for Energy Policy. November, <http://www.energycommission.org/research/>