the Energy to Lead

TECHNICAL REPORT

Refinery Upgrading of Hydropyrolysis Oil from Biomass

Reporting Period:

Jan 1, 2013 through Aug 31, 2015

DOE Award Number:

U.S. DOE Award DE-EE-0005992

Prepared For:

U.S. Department of Energy

GTI Technical Contact:

Michael Roberts, Project Manager
Terry Marker, Principal Investigator
847-544-3491; terry.marker@gastechnology.org

Contributors:

GTI: Terry Marker; Michael Roberts, Martin Linck; Larry Felix; Pedro Ortiz-Toral; Jim Wangerow, Dan Swanson
CRI Catalyst: Celeste McLeod; Alan Del Paggio, Vikrant Urade Madhusudhan Rao, Laxmi Narasimhan
Johnson Timber: John Gephart
Cargill: Jack Starr; John Hahn, Daniel Stover
Valero: Martin Parrish, Carl Maxey
MTU: David Shonnard, Robert Handler, Jiquig Fan

Gas Technology Institute (GTI)
1700 South Mount Prospect Road
Des Plaines, Illinois 60018
www.gastechnology.org

Refinery Upgrading of Hydropyrolysis Oil from Biomass

Table of Contents

Table of Contents - Appendices

List of Figures

Table of Tables

Executive Summary

Cellulosic and woody biomass can be converted to bio-oils containing less than 10% oxygen by a hydropyrolysis process. Hydropyrolysis is the first step in Gas Technology Institute's (GTI) integrated Hydropyrolysis and Hydroconversion IH^2®. These intermediate bio-oils can then be converted to drop-in hydrocarbon fuels using existing refinery hydrotreating equipment to make hydrocarbon blending components, which are fully compatible with existing fuels. Alternatively, cellulosic or woody biomass can directly be converted into drop-in hydrocarbon fuels containing less than 0.4% oxygen using the IH^2 process located adjacent to a refinery or ethanol production facility. Many US oil refineries are actually located near biomass resources and are a logical location for a biomass to transportation fuel conversion process.

The goal of this project was to work directly with an oil refinery partner, to determine the most attractive route and location for conversion of biorenewables to drop in fuels in their refinery and ethanol production network. Valero Energy Company, through its subsidiaries, has 12 US oil refineries and 11 ethanol production facilities, making them an ideal partner for this analysis. Valero is also part of a 50-50 joint venture with Darling Ingredients called Diamond Green Diesel. Diamond Green Diesel's production capacity is approximately 11,000 barrels per day of renewable diesel. The plant is located adjacent to Valero's St Charles, Louisiana Refinery and converts recycled animal fats, used cooking oil, and waste corn oil into renewable diesel. This is the largest renewable diesel plant in the U.S. and has successfully operated for over 2 years

For this project, 25 liters of hydropyrolysis oil from wood and 25 liters of hydropyrolysis oils from corn stover were produced. The hydropyrolysis oil produced had 4-10% oxygen. Metallurgical testing of hydropyrolysis liquids was completed by Oak Ridge National Laboratories (Oak Ridge) and showed the hydropyrolysis oils had low acidity and caused almost no corrosion in comparison to pyrolysis oils, which had high acidity and caused significant levels of corrosion.

The hydropyrolysis oil was then upgraded at standard refinery diesel hydrotreating conditions to remove the oxygen and sulfur to then produce gasoline and diesel blending components. We have therefore shown hydropyrolysis oils could theoretically be upgraded in existing refinery hydro-processing units to produce valuable gasoline and diesel blend components. However, the diesel produced from standard hydrotreating has only a 27 cetane index which would limit its value.

Additionally, 25 liters of IH^2 oil were produced from wood and 25 liters of IH^2 oil were produced from corn stover. This IH^2 product is 100% gasoline plus diesel boiling range hydrocarbons and contains no detectable oxygen. The IH^2 diesel has a low cetane of 27, exactly like that produced from standard refinery hydrotreating, which limits the level that could be blended into a standard diesel fuel. However, the use of an integrated third stage to ensure the aromatic saturation of IH^2 diesel at 500psi, with an aromatic saturation catalyst, produced diesel with 43 cetane, which meets the US specifications. This additional integrated third stage is extremely desirable since it allows IH^2 to directly produce a fuel meeting the US gasoline and diesel specifications.

Valero performed a risk analysis. It is indicated in the near term, there is too much risk to introducing **any** oxygen containing feeds in their refinery equipment. To be profitable, refineries need to maintain a high operating factor and the Valero concern is on the metallurgy and other issues in existing equipment leading to excessive downtime for bio-oil co-processing equipment. For a first plant, they prefer to have drop in blending components such as those provided by IH^2 which requires no further upgrading. Likewise, a RIN (Renewable Identification Number) analysis by Life Cycle Associates confirms the biooil intermediates would not qualify for RINs by the EPA unless the rules in this area are changed. The barriers for co-processing biooil intermediates make this an unlikely route for rapid introduction of cellulosic biofuels in the US. Furthermore, most refineries do not have aromatics saturation units available and therefore would be unable to upgrade the diesel cetane to 43 as can easily be done in IH^2.

An engineering/capital cost study of hydropyrolysis versus IH^2 also shows the difference between IH^2 costs and hydropyrolysis costs is very small and does not justify the risk of petroleum refinery processing of an oxygen containing biooil intermediate. For this reason, processes such as IH^2 which produce high quality drop in fuels are much more likely for rapid commercial acceptance than processes which require upgrading of intermediates.

Two sites were studied for IH^2 or hydropyrolysis processes and both sites were adjacent to a Valero refinery. These sites were located in St Charles, Louisiana and Memphis, Tennessee. The sites process wood available from the surrounding countryside or shipped on the Mississippi River and utilize the refinery infrastructure and trained personnel. The wood could be sized and dried at remote locations and shipped to a refinery via barge, railroad, and truck or simply shipped as wet microchips. An analysis showed the Memphis site has lower cost wood feeds because much of the wood in the St. Charles area is going to pellet mills for ultimate shipment to Europe to burn for electrical generation. Another advantage of location of an IH^2 plant near a refinery, such as on a major river, is it allows the transportation and conversion of a variety of biomass feeds at a central location. This allows the initial plant to start with wood, but later process a variety of feedstocks such as corn stover, algae, or bagasse as these feeds became available at reasonable costs.

Cargill evaluated the price for corn stover moved to corn ethanol locations and found the price of corn stover is \$119.5/ton, which is \$47.5/ton more than that of wood. Most of the corn stover cost is in harvesting and nutrient replenishment. Corn stover also has a lower liquid yield than wood in hydropyrolysis (as has been reported for pyrolysis as well). This makes wood a more viable commercial feedstock than corn stover for conversion in the near term. Wood has a lower cost and has a higher liquid production per ton.

The Life Cycle Analysis (LCA) of IH^2 showed that for wood, the greenhouse gas reduction is 89% as long as the hydrogen is generated from the C1-C3 produced from the process. If natural gas derived methane is used for the hydrogen production, the greenhouse gas reduction decreases to 68%. Therefore, use of C1-C3 from the hydropyrolysis or from an IH^2 process is important in order to minimize the greenhouse gas production. The RIN analysis showed that IH^2 should qualify for RINs under several pathways.

The IH^2 process is utilizing US domestic renewable biomass resources to create transportation fuels, sufficient in quantity and quality to substantially reduce our reliance on foreign crude oil. Thus, the IH^2 technology offers a path to genuine energy independence for the US, along with the creation of a significant number of new US jobs to plant, grow, harvest, and process biomass crops into fungible fuels. Further development of this technology through demonstration scale and long term pilot scale testing is highly recommended.

Project Objectives

The IH^2 process (1)(2)(3)(4)(5)(6)(7) is a true game changing technology, by utilizing U.S. domestic renewable biomass resources to create transportation fuels, sufficient in quantity and quality to substantially reduce our reliance on foreign crude oil. The first goal of this project was to develop a cost effective route for converting biomass to transportation fuels by first converting biomass to hydropyrolysis oil and then upgrading the hydropyrolysis oil in a petroleum oil refinery using existing refinery equipment. This approach was compared to locating an IH^2 unit next to a refinery or corn ethanol plant and producing finished drop in blending components instead. A secondary goal was to produce a preliminary engineering design package for a commercial scale facility to be located adjacent to a Valero refinery. A third goal was to evaluate a case for locating a hydropyrolysis unit to convert corn stover to hydropyrolysis oil at one of Valero’s midwest corn ethanol plants and ship the hydropyrolysis oil to a nearby refinery for further upgrading.

For this project, GTI produced hydropyrolysis oil and IH^2 oil from wood and corn stover for testing, using an existing 50kg/day catalytic hydropyrolysis pilot unit. CRI Catalyst Company (CRI) then upgraded the hydropyrolysis oil and IH^2 oil in their existing hydrotreating test facilities at typical diesel hydro-processing test conditions. CRI also tested upgrading of the IH^2 diesel to improve its cetane using aromatic saturation at mild conditions.

A key step in the project was the risk analysis, completed by Valero, on upgrading hydropyrolysis oils in existing refinery equipment and whether a typical refiner is willing to accept this risk. Hydropyrolysis oil is an ideal intermediate feed for oil refineries since it has a low acid number and a low oxygen content compared to pyrolysis oil or partially upgraded pyrolysis oil.

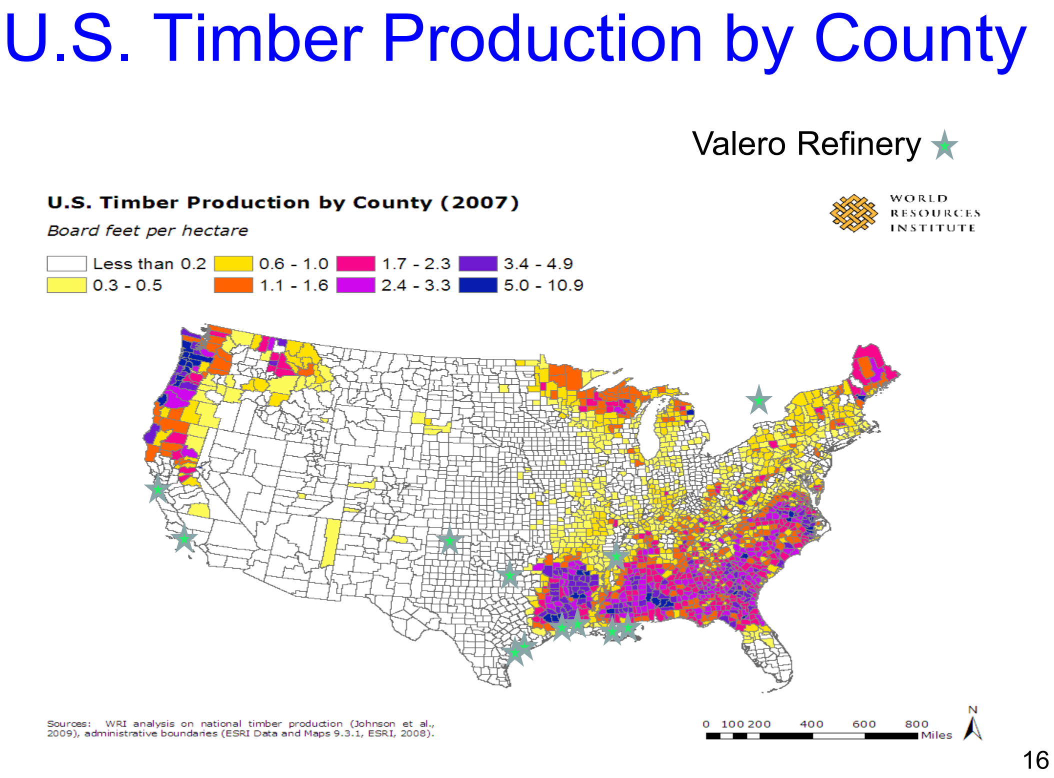
Another aspect of the study was to identify costs and logistics for moving feeds to a refinery and corn ethanol locations. Cargill, Inc. (Cargill) supplied information on the logistics and prices for moving corn stover to corn ethanol locations and Johnson Timber Cooperation (JT) supplied information on the logistics and prices for providing wood to a commercial hydropyrolysis or IH^2 units located adjacent to specific Valero refineries.

Another step of the project was to develop capital costs for an IH^2 or hydropyrolysis unit located adjacent to a refinery, which could use the refinery infrastructure such as the hydrogen plant and/or upgrading equipment in the case of hydropyrolysis alone. Utilization of refinery infrastructure significantly reduces capital costs, however, refinery upgrading of biofuels containing any oxygen was judged too risky for most refiners. An ideal case is to locate an IH^2 unit near a refinery and provide oxygen free gasoline and diesel blend stocks to a refinery for direct use.

Upgrading of both hydropyrolysis oil and IH^2 oil was done as part of the study in order to determine how upgrading is handled in a refinery. Also, it was to determine the capability of standard refinery upgrading technology to produce finished gasoline and diesel blending components from hydropyrolysis oil. It was determined the hydropyrolysis oil can be upgraded at standard diesel hydrotreating conditions, although the risk was judged too high for immediate use. However, location of an IH^2 unit right next door to a refinery can be an ideal approach especially in the many situations where biomass is located near to a refinery.

Background

Wood and corn stover are the 2 largest sources of currently available US biomass according to the Billion Ton Study(8). Many US refineries are located near biomass feedstocks as can be seen by comparing Figure 1(9) and 2(10) which show timber and corn stover production with Figure 3(11) showing oil refinery location. Oil refineries located near biomass feedstocks represent an ideal situation for biomass upgrading to transportation fuels. In this case, biomass transportation costs are minimized when they are transported to nearby refineries and the product oil is immediately blended into the transportation pool. Oil refineries are familiar with operating thermochemical conversion units, have skilled workers, and typically have enough capital to invest in new process units.


U.S. Timber Production by County

Valero Refinery ★

Sources: WRI analysis on national timber production (Johnson et al., 2009), administrative boundaries (ESRI Data and Maps 9.3.1, ESRI, 2008).

16

Figure 1 - US Timber Production

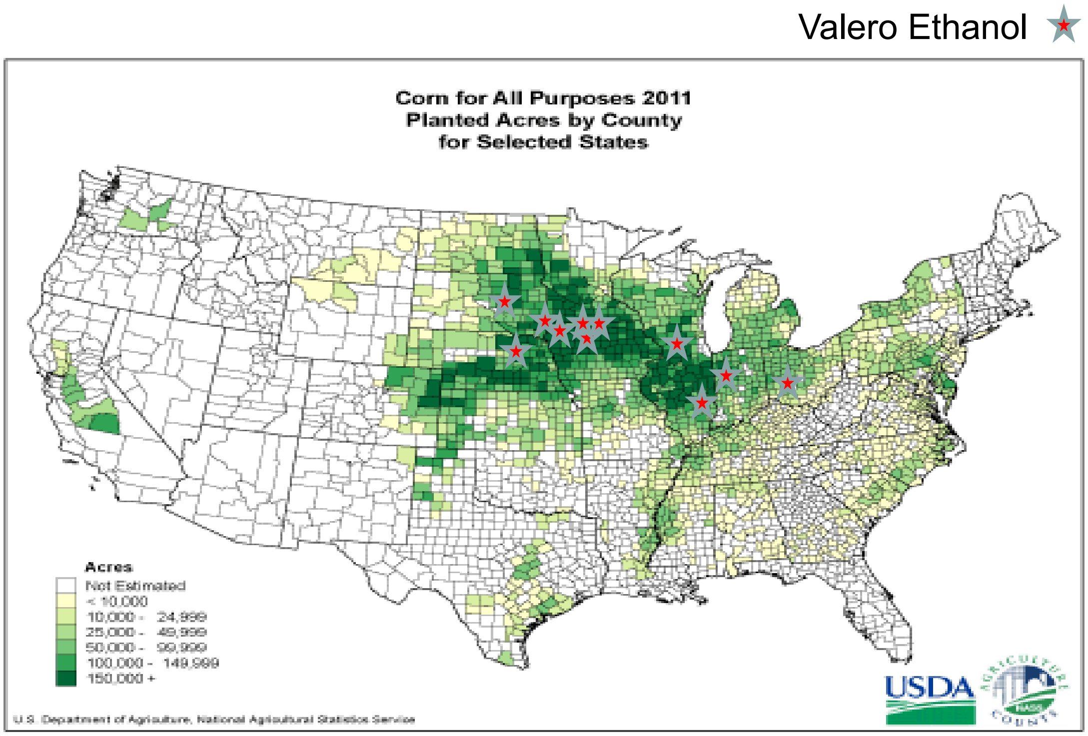


Figure 2 - US Corn Production

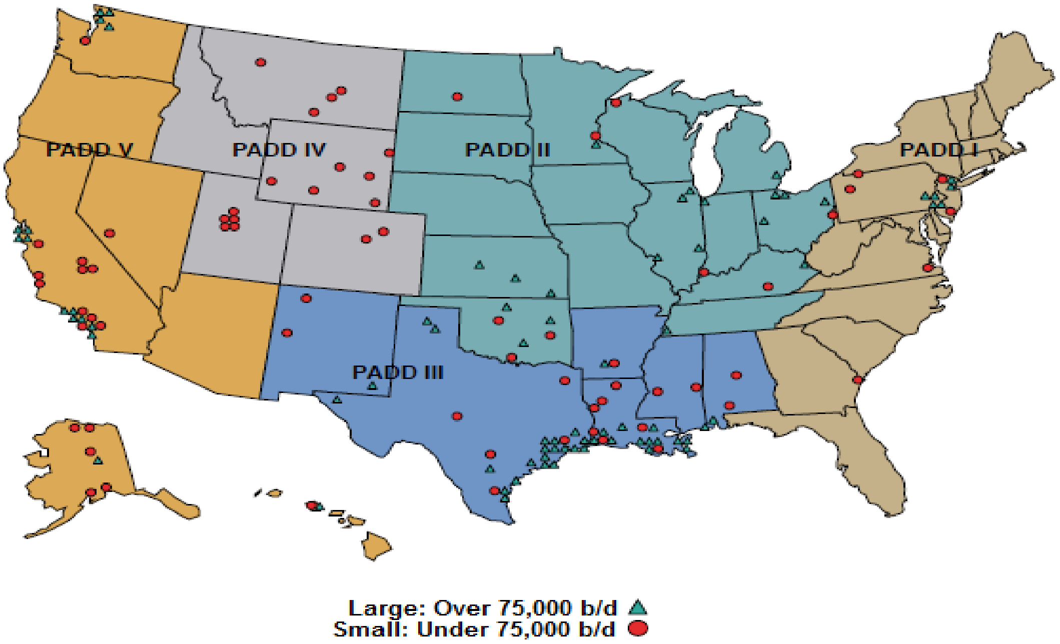
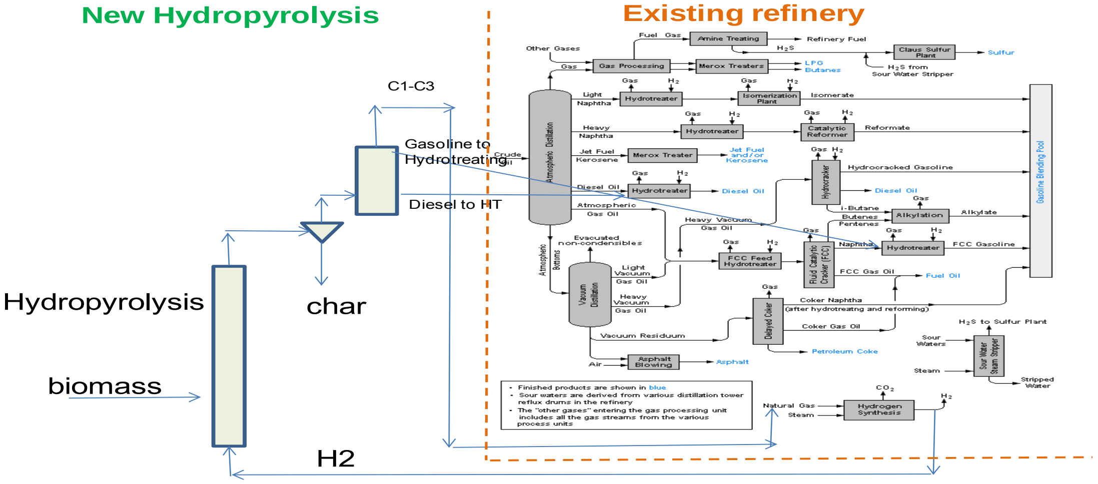


Figure 3 - US Oil Refinery Location

The advantages of locating biomass conversion process units adjacent to a refinery has been successfully demonstrated in Europe where many biodiesel units have been built right outside the refinery gate. The Diamond Green Diesel plant, located adjacent to Valero's St. Charles, Louisiana Refinery, converts recycled animal fats, used cooking oil, and waste corn oil into renewable diesel. This is the largest renewable diesel plant in the U.S. and has successfully operated for over 2 years. A hydropyrolysis unit located adjacent to an oil refinery, as pictured in Figure 4, has the advantages of integrating with the refinery hydrogen plant and utilities system so that the capital investment is minimized and the economics for investment are very favorable.

Adjacent Hydropyrolysis Integration With a Refinery



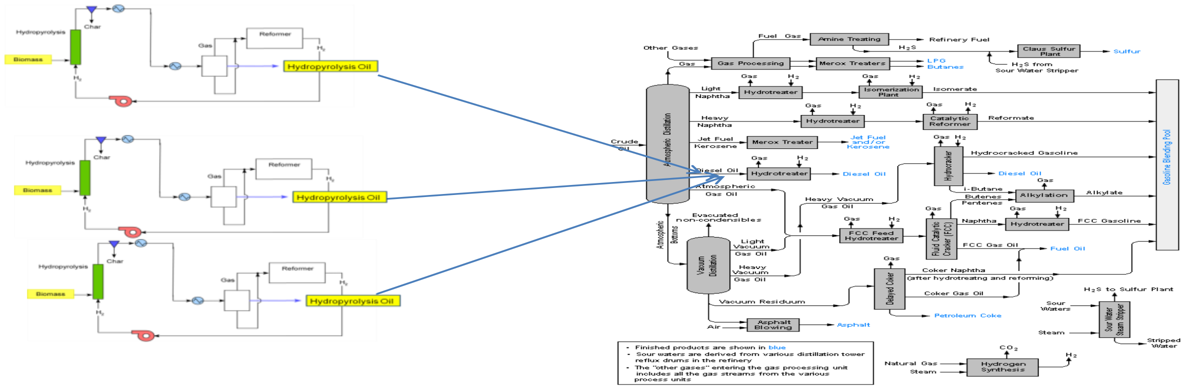
Best Integration system depends on Oil Refinery specifics-Hydropyrolysis products have low TAN's and can be blended into Refinery streams – Capital cost could be <$50MM for 2000 t/d of biomass feed

Figure 4 - Hydropyrolysis Adjacent to a Refinery

Valero owns 11 ethanol facilities which convert corn to ethanol. The hydropyrolysis unit converting corn stover to hydropyrolysis oil could be located adjacent to Valero's existing ethanol production facilities using locally produced corn stover as shown in Figure 5.

Distributed Hydropyrolysis Sites Feeding an Existing Refinery

Multiple Remote Standalone Hydropyrolysis Sites **Existing Refinery**



Hydropyrolysis products sent for further upgrading in existing refinery hydrotreaters

Figure 5 - Distributed Hydropyrolysis with Biooil Products Sent to a Refinery

Technical Background

GTI has completed more than 4000 hours of IH^2 experiments using a continuous 50 kg/day IH^2 pilot plant. The weight percent liquid yields from these tests are shown in Figure 6. These tests show very consistent liquid yields for wood, as long as the wood has not been severely dried. If wood is severely dried, some of the hydrocarbon liquids are lost in the drying step and the liquid yields are reduced.

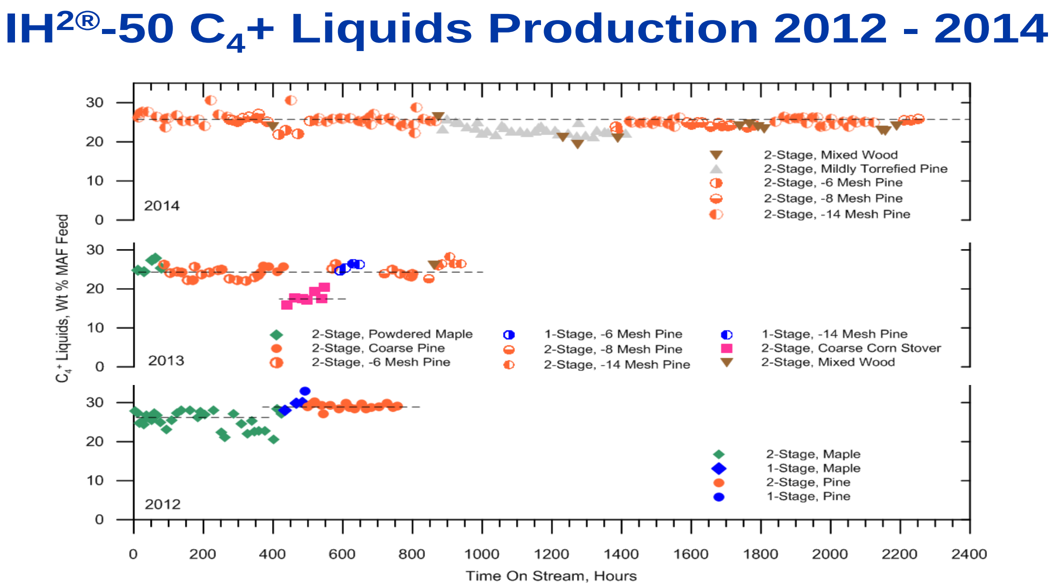


Figure 6 - C4+ Liquids Production from IH^2 50kg/d Pilot Plant

GTI has also completed more than 50 semi-batch proof of principle tests on IH^2 with a variety of feedstocks including wood, corn stover, and algae. Comparisons of the yield from various feeds are shown in Table 1.

Table 1- IH^2 Yields and Liquid Product Properties from Feedstocks in the Semi Batch IH2 pilot plant

	Wood	Lemna	Algae	Bagasse	Macroalgae (seaweed)	Corn Stover
Typical C4+ Liquid yield (MAF)	26-28	30	46	30	35	21
C4+gallon/ton (MAF)	86-92	100	157	100	119	67
% Oxygen	BDL	BDL	BDL	BDL	BDL	BDL
TAN	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Note : BDL= below detectable limit

In catalytic hydropyrolysis, biomass is converted in a fluidized bed of catalyst under hydrogen pressure of 20 to 35 bar and temperatures of 350-460°C. Catalytic hydropyrolysis removes oxygen as water and CO_X, while minimizing the undesirable acid catalyzed polymerization, aromatization and coking reactions which is typical in standard fast pyrolysis. Furthermore, catalytic hydropyrolysis with an active catalyst is an exothermic process since oxygen is removed and hydrogen is added to the hydrocarbon structure. With catalytic hydropyrolysis, biomass can be directly converted to a hydrocarbon product which can be moved to a refinery for polishing or further polished on the spot in an integrated hydrotreating reactor to stabilize and upgrade the product.

In IH^2, the extra hydroconversion reactor is added to process the vapor phase to produce a completely deoxygenated drop-in fuel. A unique and distinctive feature of the GTI hydropyrolysis or IH^2 process is that all of the process hydrogen required for carrying out hydropyrolysis is produced within the process by reforming light gases (C_1-C_3 hydrocarbons and CO). An initial economic analysis shows that both hydropyrolysis and the IH^2 process reduces the costs of converting biomass to drop in fuels biomass compared to pyrolysis plus upgrading or catalytic pyrolysis plus upgrading.

It should be noted that the alkali metal attack and catalyst regeneration problems which can cause issues in catalytic pyrolysis applications, which is run at low pressure with a ZSM-5 catalyst, without hydrogen, have not been found with IH^2. IH^2 does not regenerate its catalyst, and runs under medium pressure hydrogen, with a different type of catalyst. This comparison of the two technologies is shown in Table 2. They are fundamentally different processes, just like Fluid Catalytic Cracking is fundamentally different than hydrotreating. IH^2 also has much higher yields than catalytic pyrolysis.

Table 2 - Comparison of IH^2 versus Typical Catalytic Pyrolysis

	IH^2	**Catalytic Pyrolysis**
Hydrogen	Yes	No
Regeneration	No	Yes
Liquid Yield Gallon/ton MAF from Wood	86	40
Temperatures,C	350-460	500-600
Pressure, barg	20-35	1.5-2

A key question studied here is the advantage of performing hydropyrolysis alone and doing upgrading at a petroleum refinery to use the existing petroleum refinery upgrading equipment versus the use of an integrated IH^2 system next to a refinery to produce finished hydrocarbons for blending and minimize refinery risk. A simplified process flow diagram of the hydropyrolysis system is shown in Figure 7.

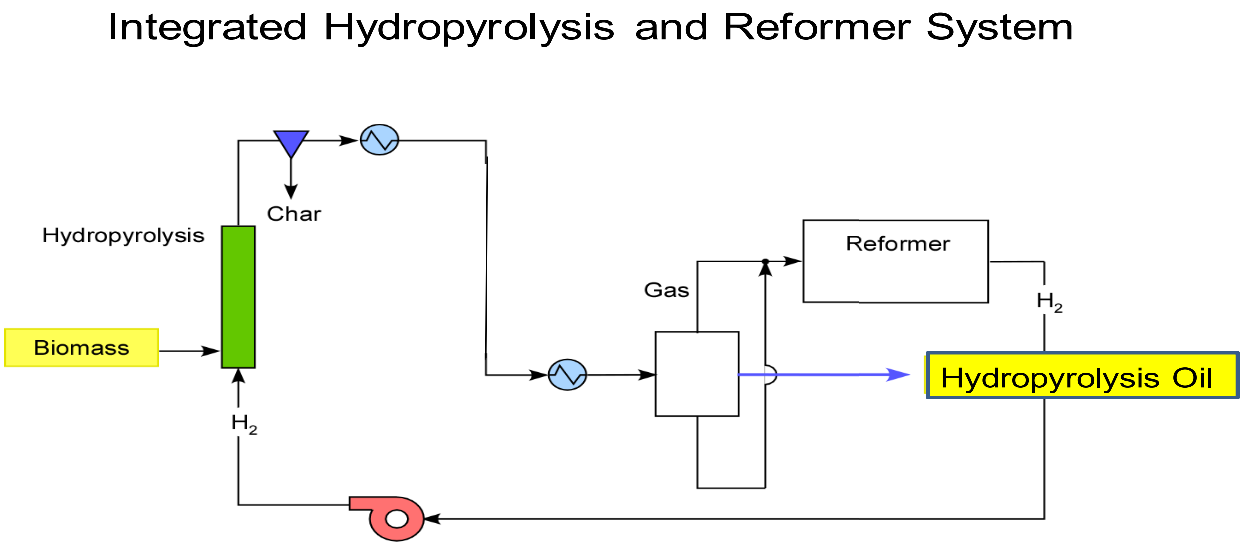


Figure 7 - Simplified Process Flow Diagram of Integrated Hydropyrolysis and Reforming

A simplified process flow diagram of the IH^2 process is shown in Figure 8.

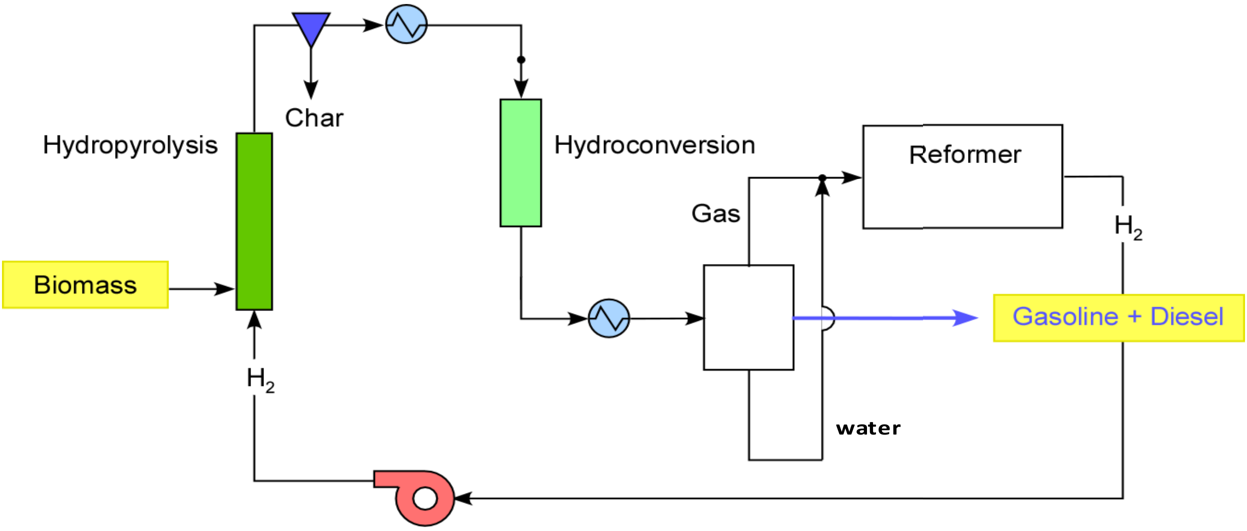


Figure 8 - Simplified Process Flow Diagram of IH^2 Process

Feedstock Analysis

The two biomass feeds used for this study were wood and corn stover, which are the two feeds currently most readily available in the US. The feedstock analysis is shown in Table 3.

Table 3 - Feedstock Analyses

	Wood pine 1	**Wood pine 2**	**Corn stover**
Feed wt % Carbon (dry basis)	51.62	51.34	42.81
Feed wt % Hydrogen (dry basis)	6.23	6.09	5.08
Feed wt % Oxygen (dry basis)	41.62	42.23	38.44
Feed wt % Nitrogen (dry basis)	0.18	0.08	0.93
Feed wt % Sulphur (dry basis)	0.01	0.01	0.09
Feed wt % Ash (dry basis)	0.35	0.30	12.65
Feed wt % Moisture	8.93	7.36	6.87
Feed H/C	1.45	1.42	1.42
Heating value Btu/lb dry basis calc. from Dulong Btu/lb=145.44*C+620.28*H+40.5*S-77.54*O	8145	7970	7090
Chloride, ppm			1420

The corn stover particles were smaller than 0.5mm. Larger sized wood feeds were used for these pilot plants by modifying the plant to run larger size wood particles than had been used in previous work. The feedstock particle size distribution is shown in Figure 9.

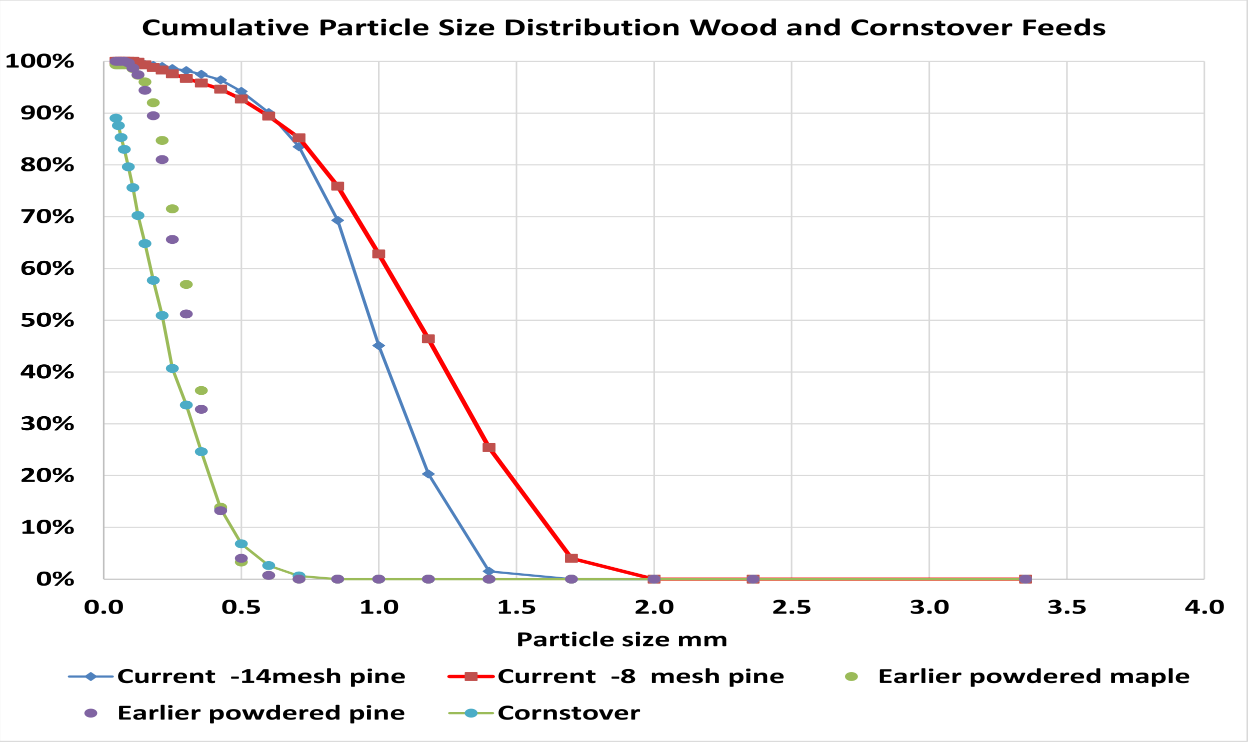


Figure 9 - Feedstock Particle Size Distribution

Previous studies had used wood feeds less than 0.5mm with an average size of 0.25mm. For the work reported here, the wood feed was primarily between 0.5mm and 2mm with an average size of 0.9-1.3mm. The larger wood particle tests were run to show the liquid yields and product quality remain the same for larger size feed particles, within the range tested.

Pilot Plant Tests to Make Hydropyrolysis and IH^2 Oil

The IH^2 50kg/hr continuous pilot plant was used to make the feeds for upgrading. A schematic drawing of the pilot plant is shown in Figure 10. A picture of the IH^2 Continuous pilot plant is shown in Figure 11.

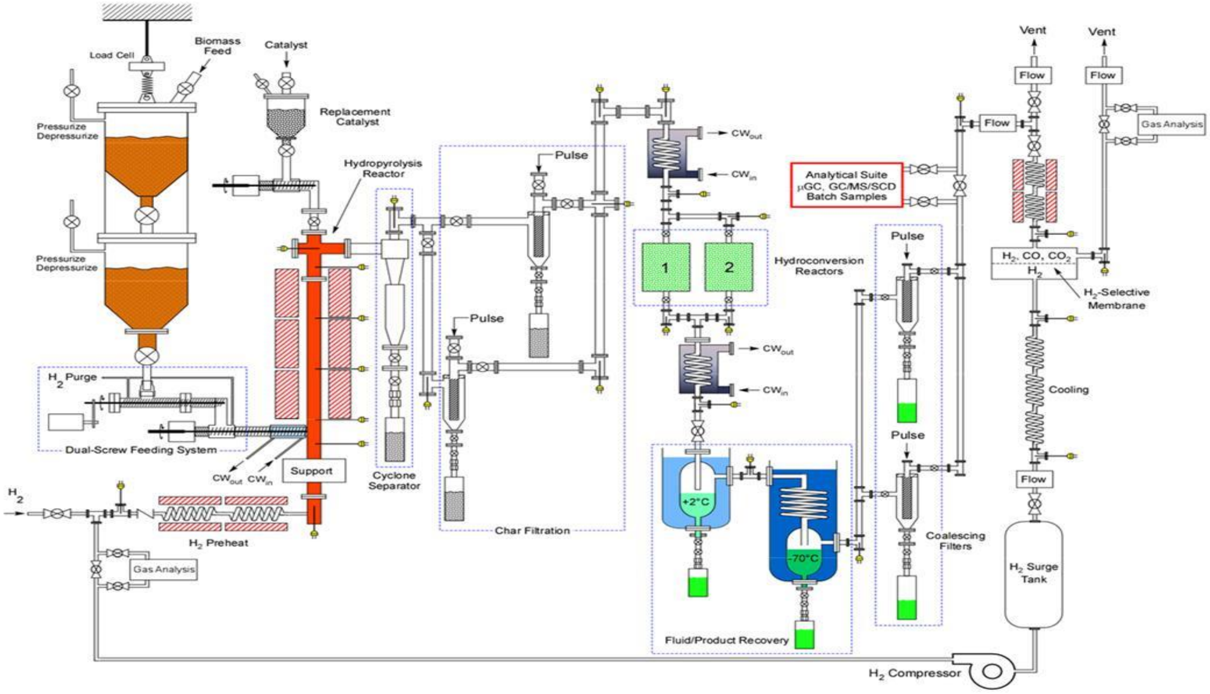


Figure 10 - Schematic Drawing of the IH^2 Continuous Pilot Plant

Figure 11 - Picture of the IH^2 Continuous Pilot Plant

To make the hydropyrolysis liquid in this pilot plant, the IH^2 second stage is by-passed and the plant is run the same in all other respects. The hydrocarbon product from the first stage hydropyrolysis still separates away from the water when only one stage is used but the separation is less clean, as expected, with product containing some oxygen. The product is also much darker than the light yellow liquid produced from IH^2 produced when essentially all of the oxygen has been removed from the products.

The IH^2 liquid yields produced from the larger wood particles were approximately the same as those produced from smaller wood particles as shown in Table 4.

Table 4 - Effect of Wood Particle Size of Liquid yields for IH2

Average Wood Size, mm	Average Wt% Liquid Yield
0.2	26
0.9	26.2
1.2	25.8

The main difference between the large size and small size particle yields is in the CO_2 production and the char production. The larger the size of the feed, the more char and less CO_2 which is produced. The CO_2 production and char yield is also affected by the residence time of the char in the char separation system. The longer the residence time in the char separation system, the larger the amount of CO_2 is evolved by the system and the smaller the yield of char.

Corn stover liquid yields were lower than wood yields, as shown in Figure 5. This same yield loss has been reported for standard pyrolysis of wood versus corn stover. The optimal temperature required for corn stover was also hotter than for wood feeds and the char yield was higher for corn stover than wood.

Table 5 - Optimal IH^2® Yields from Corn stover

	Analysis
Wt% C4+Liquids produced (MAF)	21
Wt% C1-C3 gas produced (MAF)	11
Wt% Char yield produced (MAF)	23
Wt % $CO+CO_2$ produced (MAF)	12
Wt % Water produced (MAF)	38
Wt% Total produced (MAF)	105
Wt% Hydrogen added (MAF)	5

The hydropyrolysis and IH^2 product for upgrading were produced and sent to CRI Catalyst for distillation and upgrading. Altogether more than 100 liters of product was sent to CRI Catalyst for distillation and upgrading.

The average product properties for the samples prepared are shown in Table 6.

Table 6 - Average Product Properties of Hydrocarbon Liquids from Hydropyrolysis and IH^2 Pilot Plant

	Hydropyrolysis Product from Wood	IH^2 of Wood	Hydropyrolysis of Corn stover	IH^2 of Corn stover
Wt % Carbon	84.71	88.62	80.39	86.10
Wt % Hydrogen	10.25	11.69	10.00	12.48
Wt % Nitrogen	<0.1	<0.1	1.19	0.24
Wt % Sulphur	<0.1	<0.1	0.14	<0.1
Wt % Oxygen	4.96	<0.4	8.29	1.18
Density g/ml	0.850	0.789	0.874	0.792
TAN	4.4	<0.05	9.95	0.05
% Gasoline	59	76	59	70
% Diesel	41	24	41	30
Liters prepared	25+	25+	25+	25+

There was some variation in analysis of first stage liquids between GTI, Oak Ridge National Laboratory, and CRI, probably due to stratification of sample. The corn stover first stage and second stage product were less upgraded at the same conditions as wood, which means that larger catalyst loadings and a lower

WHSV (weight hourly space velocity) would be needed for commercial designs for corn stover feeds compared to wood feeds to achieve complete deoxygenation.

Table 7 shows a comparison of the water produced using hydropyrolysis and IH^{2} using wood and corn stover feeds.

Table 7 - Analysis of Water Produced from Wood and Corn stover through Hydropyrolysis and IH^{2}

	Hydropyrolysis Wood	**IH^{2} Wood**	**Hydropyrolysis Corn stover**	**IH^{2} Corn stover**
% C	1.91	<0.5	6.35	0.88
Ammonia ppm	500	812	4,950	10,600
pH	5	8	6.5	10
Color	Slightly brown	Clear	Brown	Yellow

Water produced from IH^{2} has significantly lower levels of carbon than the water produced from hydropyrolysis. This is consistent with literature data, which consistently shows that a high level of deoxygenation must be achieved to produce a clean water fraction with low levels of carbon. The water produced from IH^{2} is also more basic and contains more ammonia than water produced from hydropyrolysis alone. The low % C in water from IH^{2} reduces water cleanup costs and carbon losses compared to hydropyrolysis or other conversion processes which only partially upgrade the hydrocarbons.

Char Analysis from IH^{2} – Larger size wood feeds used in 2013-2014

In 2013 and 2014, the IH^{2} pilot unit was shifted to running larger size feeds, which naturally produced larger sized char. The size analysis is shown in Figure 12. As before, the char is significantly smaller than the feed. In the commercial unit, the catalyst, char and feed will be even larger than this. For the commercial unit we have begun testing 2mm microchipped feeds, which can be prepared directly from wood.

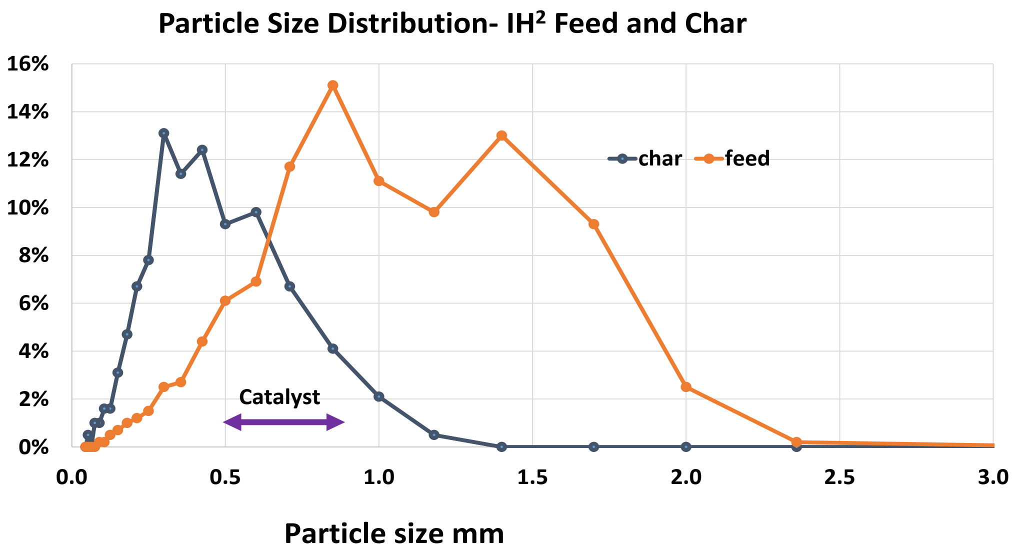


Figure 12 - Feed vs Char Particle Size Distribution in IH^{2}- 50kg/d Pilot Plant

In Table 8 some typical data for larger size char from IH^{2} of wood is shown.

Table 8 - IH^2 Typical Char Analysis from Large Sized Wood Feeds

	Sample 1	Sample 2
% Carbon (mf)	77.60	77.25
% Hydrogen (mf)	4.46	4.35
% Nitrogen (mf)	0.22	0.21
% Sulfur (mf)	0.24	0.16
% Oxygen (mf)	13.24	15.01
% Ash (mf)	4.25	3.02
% Moisture	0.73	0.97
% Volatiles	Nm	Nm
Gross Calculated Heating Value Btu/lb (from Dulong)	13,034	12,776

The char from hydropyrolysis or IH^2 retains most of the biomass potassium, sodium, and phosphorous. Metals analysis of char and feed is shown in Table 9. In IH^2 this char is removed from the reactor and burned separately so the metals in the char do not get deposited on the catalyst. By contrast, processes which require catalyst regeneration, such as catalytic pyrolysis, will deposit most of these metals on the catalyst. Metals analysis of char and feed is shown in Table 9.

Table 9 - Typical Metals Analysis in Char and Feed

	Feed 1	**Char 1**	**Char 2**
Potassium, wt%	0.03	0.29	0.31
Sodium, wt%	0.01	0.03	0.05
Phosphorous, wt%	<0.01	0.03	0.06

Corrosion Testing of Hydropyrolysis Oil

Corrosion tests of hydropyrolysis oils were completed at Oak Ridge National Laboratory(ORNL) and compared to those of typical pyrolysis liquids. These results are shown in Tables 10, 11, 12, and 13. As expected, exposure of metals to hydropyrolysis liquids resulted in much lower corrosion rates than exposure of metals to pyrolysis oils.

Table 10 - Corrosion Rates of Metals Exposed to Hydropyrolysis Oil from Wood

Exposure time (hr)	Carbon steel		2¼ Cr-1 Mo steel		409 stainless steel		304L stainless steel		316L stainless steel	
	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C GTI sample C (wood)										
250 hr	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1000 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Samples immersed in 50°C GTI sample C (wood)										
250 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1000 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table 11 - Corrosion Rates of Metals Exposed to Pyrolysis Liquids from Wood

Exposure time (hr)	Carbon steel		2¼Cr-1Mo steel		409 stainless steel		304L stainless steel		316L stainless steel	
	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C GTI sample C (wood)										
250 hr	1.35	1.41	2.07	1.95	0.12	0.12	<0.01	<0.01	<0.01	<0.01
500 hr	0.90	1.04	1.61	1.46	0.06	0.08	<0.01	<0.01	<0.01	<0.01
1000 hr	0.69	0.99	1.46	1.41	0.03	0.04	<0.01	<0.01	<0.01	<0.01
Samples immersed in 50°C GTI sample C (wood)										
250 hr	5.05	5.21	4.08	4.25	0.89	1.79	<0.01	<0.01	<0.01	<0.01
500 hr	2.96	2.90	2.45	2.61	0.44	0.90	<0.01	<0.01	<0.01	<0.01
1000 hr	1.66	1.62	1.59	1.77	0.23	0.45	<0.01	<0.01	<0.01	<0.01

Table 12 - Corrosion Rates of Metals Exposed to Hydropyrolysis Liquids from Corn stover

Exposure time (hr)	Carbon steel		2¼Cr-1Mo steel		409 stainless steel		304L stainless steel		316L stainless steel	
	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C GTI sample B (corn stover)										
250 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1000 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Samples immersed in 50°C GTI sample B (corn stover)										
250 hr	0.09	0.08	0.07	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	0.06	0.06	0.04	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1000 hr	0.04	0.07	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table 13 - Corrosion Rates of Metals Exposed to Pyrolysis Oil from Corn stover

Exposure time (hr)	Carbon steel		2¼Cr-1Mo steel		409 stainless steel		304L stainless steel		316L stainless steel	
	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C GTI sample B (corn stover)										
250 hr	0.75	1.52	1.27	1.86	0.29	.26	<0.01	<0.01	<0.01	<0.01
500 hr	1.25	1.25	1.48	1.71	0.20	.20	<0.01	<0.01	<0.01	<0.01
1000 hr	1.01	1.31	1.48	1.67	0.16	.15	<0.01	<0.01	<0.01	<0.01
Samples immersed in 50°C GTI sample B (corn stover)										
250 hr	4.86	4.88	5.84	5.91	3.85	3.52	<0.01	<0.01	<0.01	<0.01
500 hr	3.41	3.31	4.97	5.20	3.0	1.76	<0.01	<0.01	<0.01	<0.01
1000 hr	2.14	2.07	3.69	3.83	1.52	0.88	<0.01	<0.01	<0.01	<0.01

Additional corrosion tests were done by placing pieces of tubing with various metallurgy into the pilot plant and exposing them to 700 hours of pilot plant testing. The tubing was obtained from Oak Ridge National Laboratory and was examined by scanning electron microscope and light microscopes by Oak Ridge National Laboratory after the 700 hours of testing was complete. Alloys of 304L, 316L, 317L, 310, 800H and 825H were tested. The tubing was placed at the outlet of the hydropyrolysis reactor (exposed to char) and also between the filter and second reactor (not exposed to char). Oak Ridge National Laboratory reported little corrosive attack on any of the pieces of tubing. More details and pictures are shown in Appendix A.

Detailed Analysis of Hydropyrolysis Oil

Analysis of the hydropyrolysis oil liquid for acid content is shown in Table 14. Hydropyrolysis oil has much lower levels of acids and TAN than does pyrolysis oil. The most important difference between the ORNL modified TAN and standard TAN is that ORNL uses an aqueous extraction; the water matrix efficiently extracts lower molecular weight carboxylic acids while maintaining a solvent environment ideal for utilization and accurate functioning of a glass pH electrode.

Table 14 - Analysis of Pyrolysis Liquids versus Hydropyrolysis Liquids (ORNL)

	Pyrolysis oil from Wood	**Pyrolysis Oil from Corn stover**	**Hydropyrolysis Oil from Wood**	**Hydropyrolysis Oil from Corn stover**
ppm formic acid	4855	2317	297	0
ppm acetic acid	30819	13871	309	0
ORNL modified TAN	119	93	14	16
Standard TAN			4.4	15

Detailed analysis of the wood hydropyrolysis oil is shown in Table 15.

Table 15 - Analysis of Compounds in Hydropyrolysis Oil from Wood from CRI

Compound type	**Wt %**
C5-C11 Monocyclics (saturates and olefins)	9
Linear paraffins	5
C17-C18 Olefin isomers	1
Groups of saturated fused ring systems	11
Monoaromatics	19
Indanes/Indenes	8
Phenols	9
2 ring aromatics (naphthalenes)	9
Naphthalenes with additional saturated ring	6
3 ring aromatics	6
3 ring aromatics with additional saturated ring	2
Unknowns	16

A gas chromatograph/mass spectrometer (GC/MS) analysis of hydropyrolysis oil of wood and corn stover from Oak Ridge National Laboratory is shown in Figure 13.

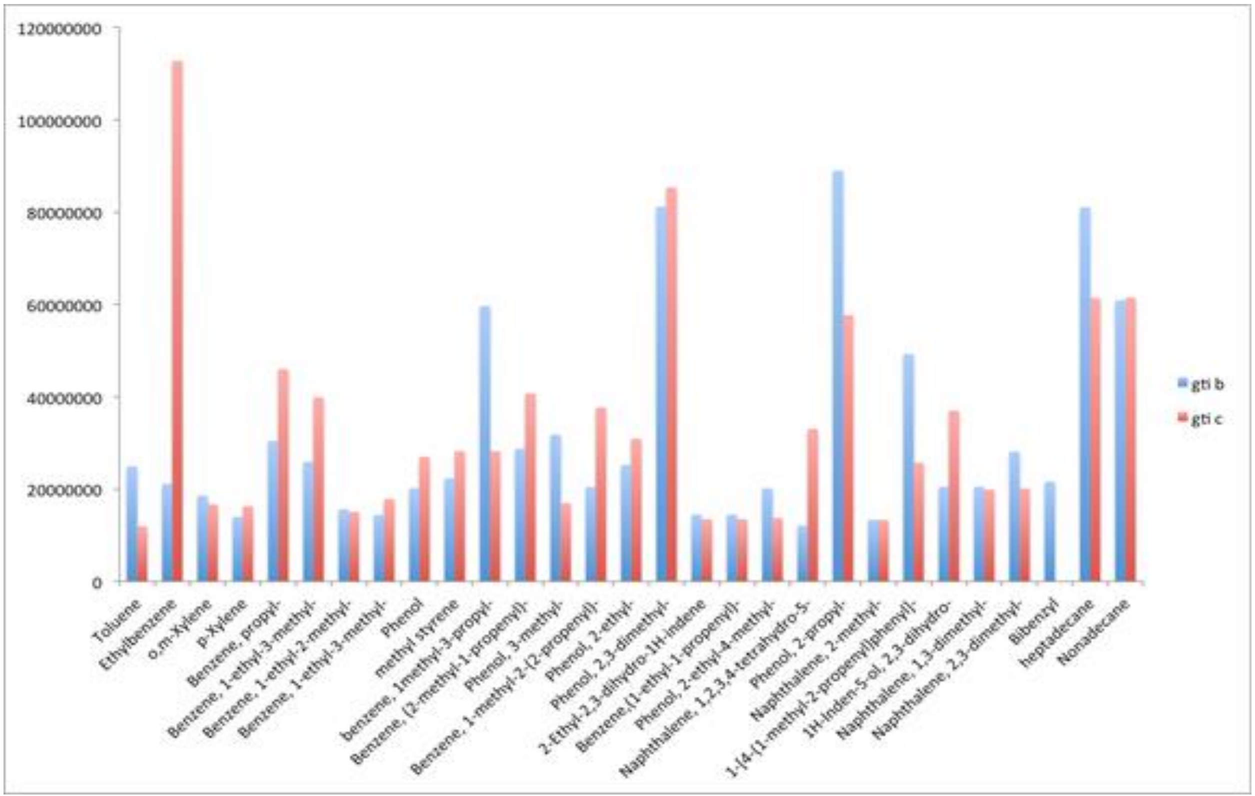


Figure 13 - Area Comparison of the Volatile Organic Species Identified from the Thermo GC/MS

Note: Where GTI B in blue is hydropyrolysis oil from corn stover and GTI C in red is hydropyrolysis oil from wood.

Oak Ridge National Laboratory also identified a number of other oxygenated compounds in the hydropyrolysis oil from wood and corn stover however, there is no quantitation of the compounds. This information is included in Appendix B.

A GC x GC analysis of the hydropyrolysis oil from wood from CRI is shown in Figure 14. This shows the primary compounds present at higher boiling point are aromatics and the primary oxygen component identified was phenol.

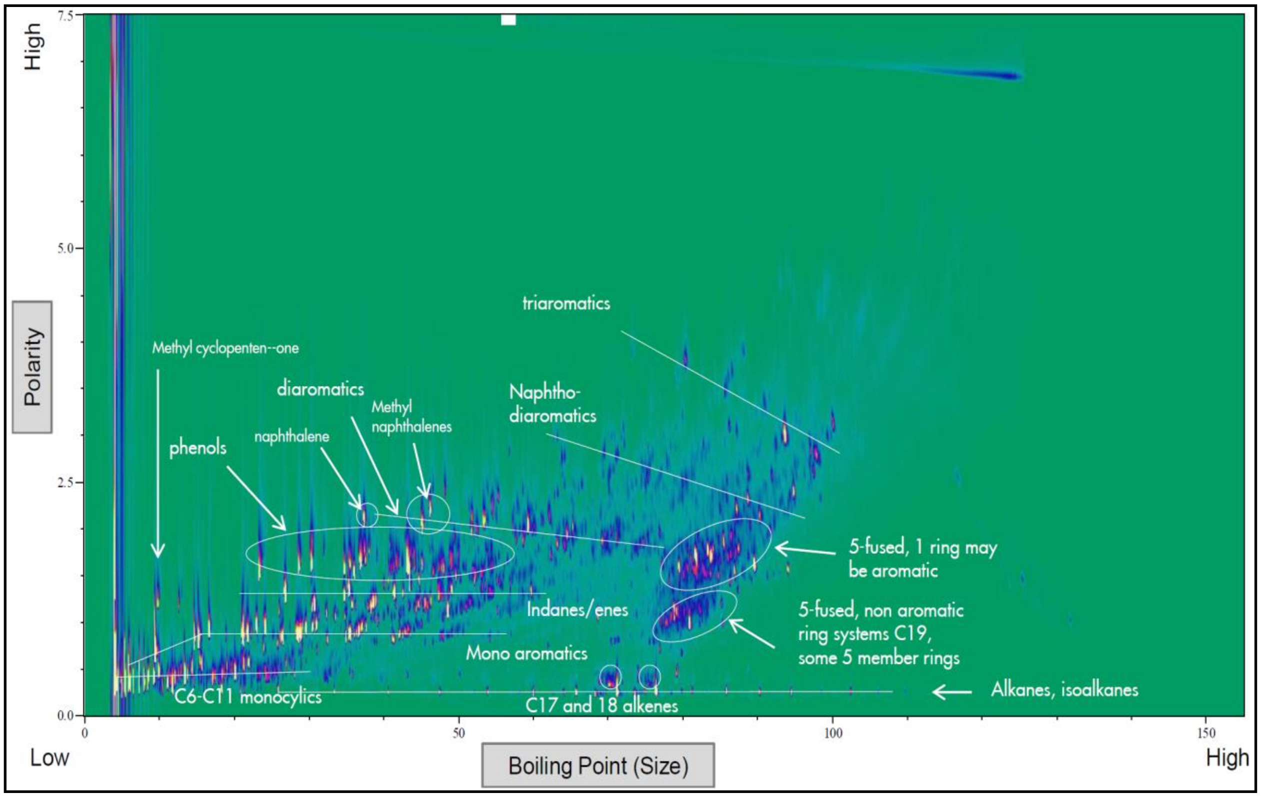


Figure 14 - GCxGC of First Stage hydropyrolysis Liquid from Wood

Hydropyrolysis Oil Upgrading

CRI Catalyst did studies of hydropyrolysis oil hydrotreating at pressure of 500psi and typical diesel hydrotreating upgrading conditions using a typical diesel hydrotreating catalyst. This work went well and resulted in product similar to that produced through IH^2. CRI tested quite a number of catalysts as shown in Figures 15, 16, and 17 and each achieved complete deoxygenation at mild conditions.

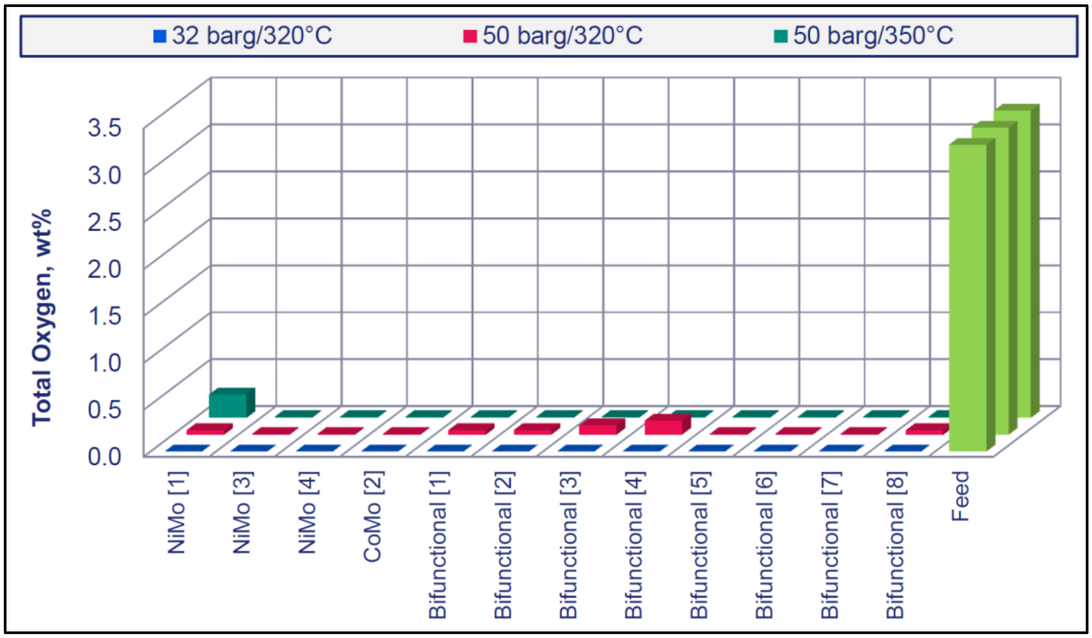


Figure 15 - Oxygen Content of Hydro-treated Hydropyrolysis Oil Using Various Catalyst

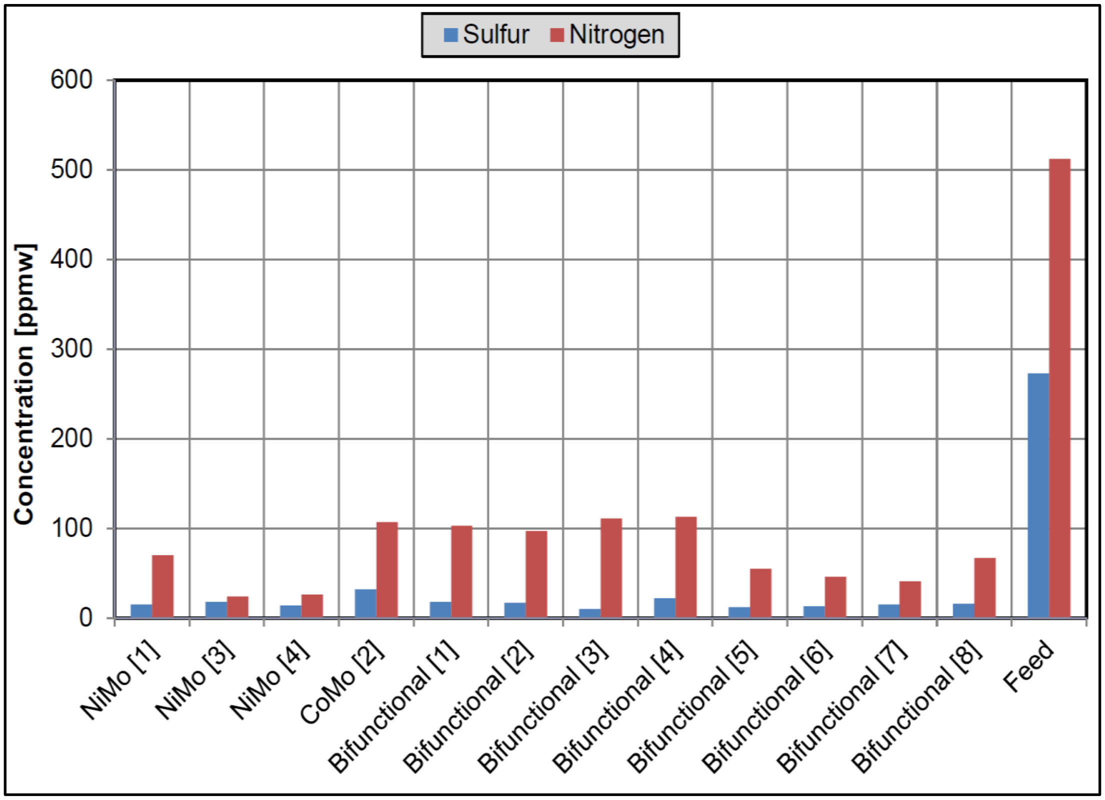


Figure 16 - Sulfur and Nitrogen Content of Upgraded Hydropyrolysis Oil Using Various Catalysts

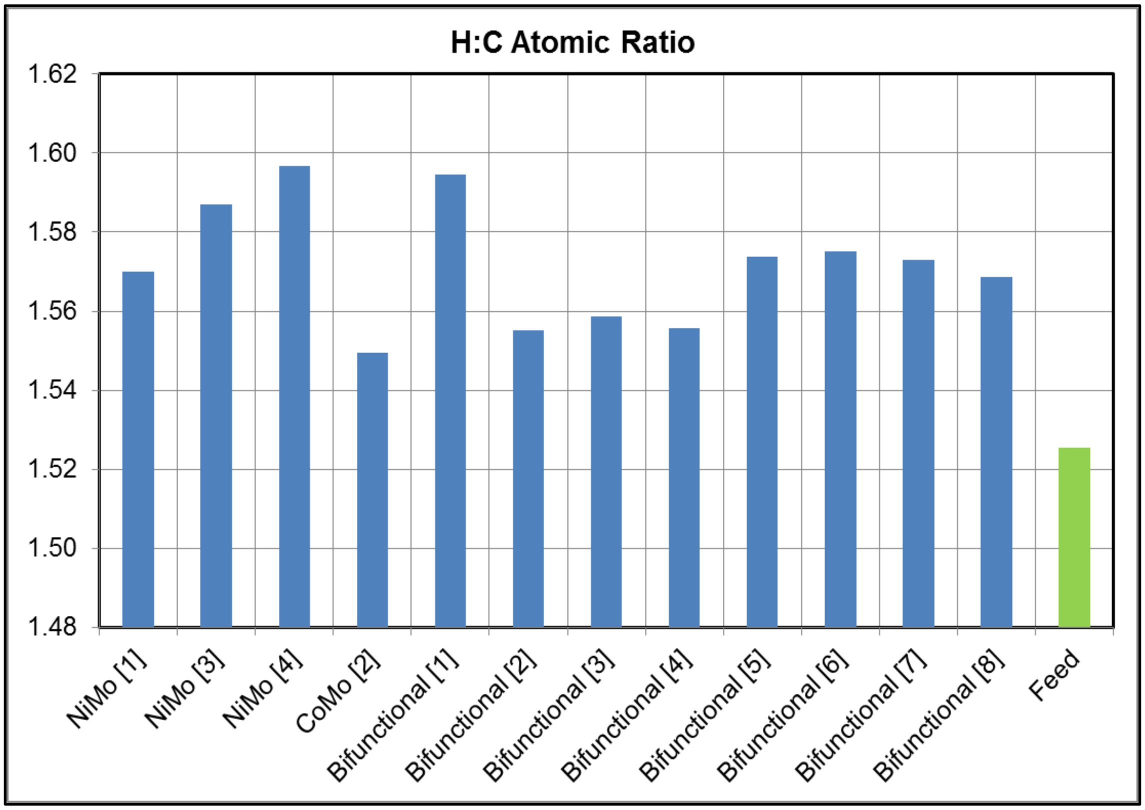
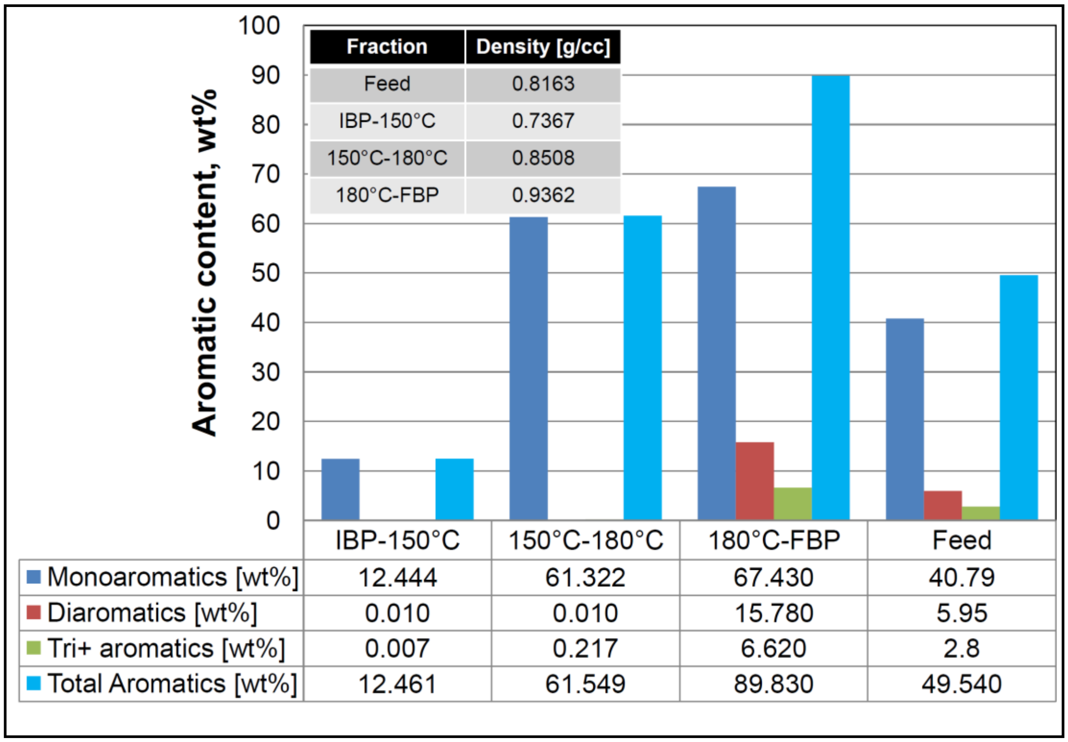


Figure 17- H/C Ratio of Hydro-treated Hydropyrolysis Oil from Various Hydrotreating Catalyst Systems

More details on hydropyrolysis oil upgrading can be found in Appendix C.

IH^2 Oil Upgrading to improve Diesel Cetane

The IH$^{2®}$ process makes high quality gasoline product that can be used as a premium RBOB in the US, and a high quality diesel blendstock. The oxygen content of the hydrocarbon products is well below 0.1 wt%. However, the diesel produced in a 2-stage IH$^{2®}$ process has one disadvantage; the cetane index was only 27. The high aromatic content of the fuel hindered the auto-ignition of the diesel fuel, and cetane number in an engine test could not be measured. The US diesel specification is 40 and the diesel produced from the 2nd stage of the IH$^{2®}$ process requires improvement on the cetane number front.



Fraction	Density [g/cc]
Feed	0.8163
IBP-150°C	0.7367
150°C-180°C	0.8508
180°C-FBP	0.9362

	IBP-150°C	150°C-180°C	180°C-FBP	Feed
🟦 Monoaromatics [wt%]	12.444	61.322	67.430	40.79
🟥 Diaromatics [wt%]	0.010	0.010	15.780	5.95
🟩 Tri+ aromatics [wt%]	0.007	0.217	6.620	2.8
🟦 Total Aromatics [wt%]	12.461	61.549	89.830	49.540

Figure 18 - Aromatic contents of various IH^2 product fractions.

The aromatic distribution of the liquid product is shown in Figure 18. In the gasoline range, only monoaromatics are seen, while in the diesel range, a significant amount of di and tri+ aromatics are also present. CRI developed an integrated third stage for upgrading IH$^{2®}$ diesel to meet US cetane specifications through aromatic saturation. They evaluated a number of aromatic saturation catalysts to convert aromatics into naphthenes and thereby improve the diesel cetane. They found reduced nickel aromatic saturation catalysts were especially effective for this application since they were effective at pressures as low as 367 psig and temperatures as low as 200°C. Figure 19 shows a comparison of the aromatic content of diesel fuel produced using various aromatic saturation catalysts tested to provide cetane improvement for the IH$^{2®}$ diesel. Upon further optimization of operating conditions, upgraded diesel products with less than 5 wt% total aromatics were produced (Appendix C).

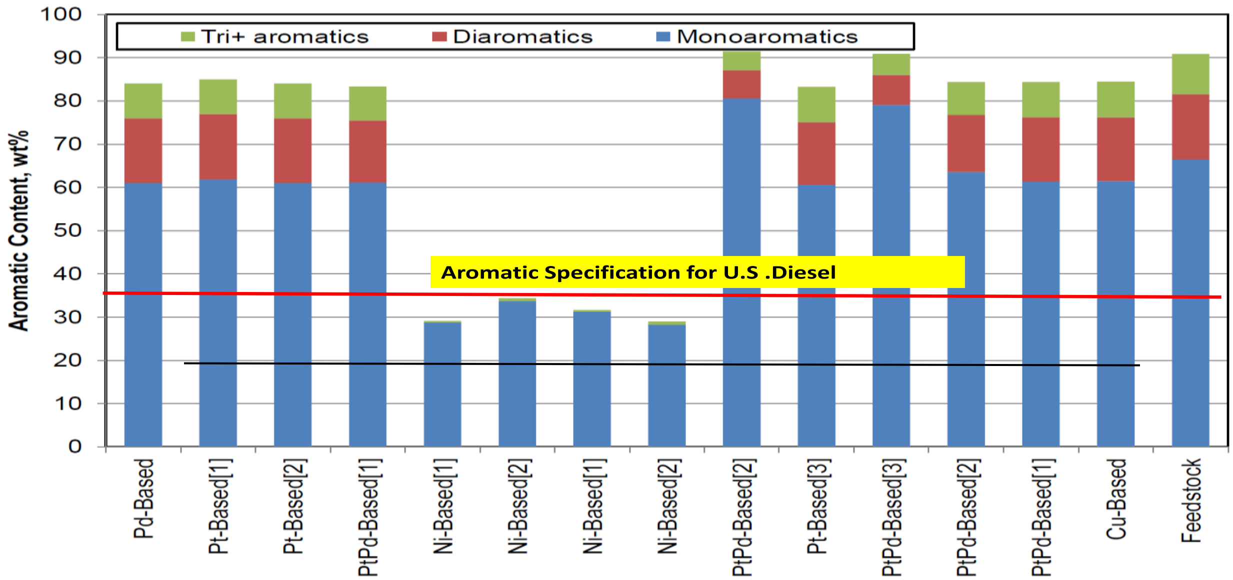


Figure 19 - Comparison of Diesel Product after Third Stage Aromatic Saturation Using Various Aromatic Saturation Catalysts

Once these screening tests were completed, a large batch of upgraded high cetane diesel was prepared using a nickel based aromatic saturation catalyst. This catalyst was also simultaneously used to eliminate the benzene from an IH^2 gasoline benzene cut to ensure IH^2 gasoline will meet the benzene specification for gasoline. The detailed properties of the third stage upgraded diesel product is shown in Table 16.

Table 16 - Fuel Properties of 3rd Stage IH2 Diesel Compared to ASTM D975 Specifications

Property	Specification	Analysis Method	IH^2 Third Stage Diesel
Cetane Number, min	40	ASTM D976	43.7
Sulfur, ppmw, max	15	ASTM D5453	6
Viscosity at 40°C, cSt, max	4.1	ASTM D445	4.1
T90, °C, max	338	ASTM D86	341.9[2]
Flash Point, °C, min	52	ASTM D93	Meets specification
Carbon Residue 10%, wt%, max	0.35	ASTM D524	0.15
Water and Sediment, vol%, max	0.05	ASTM D2709	NA[1]
Ash, wt%, max	0.01	ASTM D482	<0.001
Lubricity, Diameter at 60°C, micron, max	520	ASTM D6079	400[3]
Copper Corrosion, 3 hr at 50°C, max	No. 3	ASTM D130	1A

1. The sample quantity available was inadequate to complete this test. However, diesel fraction distilled to meet EU specifications, which has a lower initial boiling point, had a flash point of 58°C. Hence, the US-cut diesel with a higher IBP is expected to meet the flash point specification.
2. This parameter can be easily met by modifying the boiling range of the diesel feed to third reactor train.
3. Low-sulfur diesel fuels generally do not meet lubricity specifications without any lubricity improvers. This is true for IH^2 third stage diesel also. Lubricity specification can be met by adding lubricity improvers.

More details on IH^2 oil product quality upgrading are in Appendix C.

Valero Refinery Risk Analysis of the Upgrading of Hydropyrolysis and IH^2 Liquid in a Refinery

Preface:

The decision to put a new stream into a refinery is always highly scrutinized. Engineering data for a new feed stream is usually limited in both quantity and detail. Refiners have developed correlations for erosion, corrosion, fouling, etc. based on bulk properties of the hydrocarbons (i.e., sulfur, TAN, etc.). These correlations have been derived from years of inspection and process data from various grades of crude/hydrocarbon streams. A stream with properties that fall outside of the historic dataset are reviewed carefully and monitored frequently until a suitable history for such a stream is developed. Refining personnel are understandably cautious with putting operation of a 200,000 bpd refinery at risk to make a small margin on a few thousand bpd of a new stream. Reliability is a major key to the safety and profitability of a plant. Refiners will naturally err on the side of being cautious.

Regarding pyrolysis streams with high oxygen content:

To maximize output the first units should be dedicated hydro-processing units. In our experience, there are significant engineering risks associated with high oxygen content bio-feedstocks in hydro-processing units. Even a design based on the best pilot/demo data available has a high potential for engineering design challenges with a potential to create lost opportunity(ies) for a refinery. A pilot plant or demonstration plant will not cover the full range of commercial operation. The actual commercial feed properties will likely vary more than the range tested during pilot/demonstration testing. The higher the level of oxygen or other contaminants in the stream, the greater the potential for engineering challenges. Unsaturated pyrolysis derived streams are expected to have higher polymerization/fouling tendencies than saturated bio-based feeds. In addition to oxygen, bio-derived feedstocks are expected to contain higher levels of chlorides, silicon, metals, ash, etc.

- Chlorides, oxygen and water w/olefins - Polymerization/fouling, even at trace levels
- Chlorides – Corrosion at dew point
- Other contaminants – Poisons and catalyst life impact. This can be piloted and projected pretty well if the contaminant levels are known.

The actual quantity of these contaminants will vary based on biomass collection method and the mineral content of the soil the biomass was grown on.

Commercial validation of the full range of oxygen, chlorides, or other metals with the potential to impact catalyst life is a key step in the process of qualifying a bio-derived feedstock as suitable feedstock for a refinery unit. With the various elements that are commercially unknown, we conclude there are too many engineering risks to put a high oxygen pyrolysis stream into a refining unit. Commercial validation in a dedicated unit is necessary to make the correct metallurgy, polymerization, exchanger fouling, and catalyst life design-decisions for co-processing in a refinery unit.

Even with commercial experience (i.e., having generated dataset and quantified calculated erosion, corrosion, fouling, etc. rates for a range of feedstocks in dedicated unit), we expect there would be a fair amount of capital required to run a significant quantity of a high oxygen content feed in a unit originally designed for crude kerosene/diesel. The issues are but not limited to:

- Water - Significantly more water generated than the refining hydrotreating unit design. Potential separator and water draw line hydraulics issue.
- Heat recovery/heater impacts - Heat recovery is typically limited to an approach to the water dew point. Either significant changes in metallurgy or changes to the heat recovery required.
- Saturation - Different reaction/different exotherm. Reactor bed count, height, and hydrogen quench capacity may limit how much high oxygen feedstock a unit can process.

- Hydrogen circulation - Coking in reactors is highly dependent on reactor outlet hydrogen partial pressure. With higher hydrogen consumption, higher circulation may be required to maintain run length.

Regarding the IH2 streams with significantly lower oxygen content:

With the lower oxygen content, the risks are lower. The metallurgy concerns are diminished compared to the high oxygen content pyrolysis derived streams. Industry data does not include sufficient experience for what happens in between high oxygen content and very low oxygen content.

- We feel certain the 5-10% oxygen presents serious engineering challenges and risks.
- Trace or "non-detect" oxygen levels are a much more manageable issue (i.e., can monitor with high frequency inspection, corrosion coupons, etc. and determine impact).
- Maintaining the oxygen content at very low levels as pyrolysis plant feeds change is key.

As mentioned above, bio-derived feedstocks are expected to contain higher levels of chlorides, silicon, metals, ash, etc. The actual quantity of these contaminants will vary based on biomass collection method and the mineralogy of the soil the biomass was grown on. Commercially validation of the full range of oxygen, chlorides, silicon, or other metals with the potential to impact catalyst life is a key step in the process of qualifying a bio-derived feedstock as suitable feedstock for a refinery unit.

Our view is that the first unit for IH^2 upgrading should also be a dedicated unit. We would want to see it commercially demonstrated for full IH^2 catalyst cycle before introducing the IH^2 stream in a refinery unit. We recommend proving upgrade of neat IH^2 liquid and upgrade of IH^2 w/Light Cycle Oil (LCO) /Diesel mix to de-risk fouling/polymerization potential**.** We conclude that it is possible that a commercial trial in a dedicated unit will prove lower oxygen content IH^2 pyrolysis derived oils suitable for co-processing in a conventional refinery hydrotreater. We expect some capital investment in the hydrotreater and possibly pretreatment of the bio-oil to reduce contaminants would be required.

Regarding the IH^2 treated streams - without integrated third stage:

The IH^2 treated streams are acceptable for blending into finished products, however, the value will be relatively low given the blending limitations outlined below.

Gasoline range cut:

The octane and RVP (Reid Vapor Pressure) are within the expected ranges for gasoline. Its value calculation is based on the blend value of this stream relative to gasoline based on a market call for butane (basis for $/RVP bbl) and market call for premium gasoline relative to regular gasoline (basis for $/octane bbl).

The property of greatest concern is the aromatics content. Gasoline aromatics specifications will likely limit the volume of IH^2 gasoline that can be blended with conventional hydrocarbon gasoline. Each refinery has different gasoline grades/specifications and refinery configuration. The amount of a high aromatics stream that can be blended will be very different at each refinery. Known issues are:

- Defining location for the gasoline from the first plant. It will become more challenging to blend the high aromatics gasoline from subsequent plants.
- Aromatics saturation is one way to further upgrade this stream. Saturation is costly (requires hydrogen) and lowers the octane.
- The BTX portion of the aromatics can be extracted. The BTX components are typically very high value. The raffinate octane will be fairly low (lower value), but easy to blend into gasoline.
- BTX recovery is capital intensive. It is beneficial to run the gasoline through a gas chromatograph and characterize the aromatics. The stream may be better suited for sale as feedstock to a BTX recovery plant.

Kerosene range cut:

- The neat kerosene cut will not make jet or kerosene specifications. The aromatics level is too high.
- Some refineries operate against cetane constraints due to their refinery configuration and the crudes/feedstocks they process. Such a plant could not blend any 24 cetane kerosene/diesel.
- Other refineries have some room in their kerosene/diesel pools on cetane. Even a refinery with some room on cetane will be quite limited on how much 24 cetane kerosene/diesel they can blend. Blending may be workable for the first plant. Blending will be more difficult for subsequent plants. Eventually, aromatics saturation will be required.

Diesel range cut:

- Same concerns as the jet fuel cut.
- Aromatics are very high and cetane is very low.
- A large volume of diesel would be required to blend off the low cetane diesel.
- Some refineries are already at cetane limits and could not blend any.

Note the GTI document(1) (Dec 2012) valued the distillate cut at LCO market value (similar aromatics and cetane). LCO is typically processed through a medium pressure hydrotreater to saturate the aromatics which results in a volume gain. The value of LCO as a direct blending component would be much lower than the LCO market value (i.e., priced at feedstock to saturation units).

The good news is that if the IH^2 treated kerosene/diesel streams are commercially proven (first in dedicated units) to be suitable for co-processing in a refinery unit, then finding a use for the high aromatics oil seems reasonable (pending capital investment requirement for co-processing low oxygen content feeds).

General comments regarding hydrocarbon TAN

The analysis in Table 6 for IH2 product shows TAN <0.1. For comparison, West Texas Intermediate crude oil (WTI) has a whole crude TAN of 0.1. WTI acid is a non-issue. Whole crude TAN of 0.4-0.5 requires significant design changes. The refining industry has general engineering practices covering design and metallurgy selection for high acid crude.

- Reduce velocity or adjust metallurgy: 5% and 9% chromium are no better than carbon steel against acid, need nickel or more expensive alloys. High acid, high sulphur is fairly straightforward. **But high acid and low sulphur can be more complex.** Acid corrosion is generally viewed as an erosion/corrosion mechanism. Erosion of sulfide (passivation layer) and subsequent corrosion by acid attack on bare metal.
- Most of the acid is in the heavy end of crudes: However, corrosion rates in the kerosene/distillate sections can be as bad as or worse than for heavy oil sections.
- Counterintuitive: Sulphur in kerosene/light diesel is an order of magnitude lower than it is in the heavy oil. As such, re-passivation is much slower. While acid in kerosene is lower than in the heavy end of the crude, there is more bare metal to attack due to the slower re-passivation. **Without commercial experience with high acid, in combination with low sulphur, there is a level of uncertainty, (co-processing with high sulphur feeds may be required).** The concern would be consistency of the oxygen content, knowing this is a nil sulphur stream.
- Based on this risk analysis, it would appear that an IH^2 unit including the integrated third stage to improve cetane to above 40 would be best from a refiners' point of view to substantially reduce risk and produce drop-in fuel components meeting the required specifications.

Wood Feedstock Logistics

A report was completed by Johnson Timber on the logistics and price of supplying wood to the Valero St. Charles Refinery, and the Valero Memphis Refinery. The Valero Memphis Refinery was chosen as the best Valero refinery location for a hydropyrolysis or an IH^2 plant based on wood feedstock costs and supplies. The wood prices on the gulf coast have increased due to European pellet demands and the Valero St. Charles Refinery is located further from wood supplies. Figure 20 shows the acres of wood near the Memphis site versus distance.

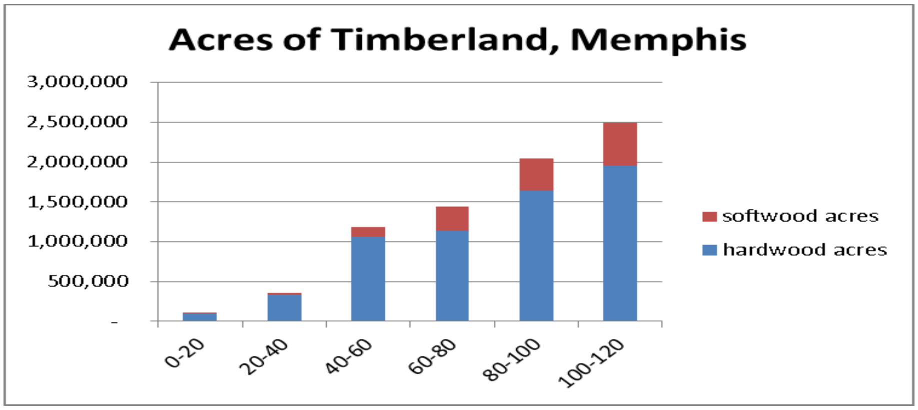


Figure 20 – Acres of Timberland vs Distance (in miles) from Memphis Valero Refinery site

Table 17 shows the average haul distance of the wood to the Memphis refinery and the average cost of the wood. As the size of the plant increases, the haul distance increases and therefore the wood cost increases.

Table 17 - Average Haul Distance in Miles from the Point of Origin (Forest or Mill) and Delivered Cost for Wood at Memphis Location for each IH^2 Plant Size

	250 ton/day Plant	500 ton/day Plant	1000 ton/day Plant
Average Distance in Miles	70	73	82
Delivered Wood Cost $/bone dry ton	69	72	76

Feedstock preparation, especially size reduction and drying, adds additional costs to the wood. There is variation in the cost of this step depending on the type of size reduction and drier system used. Table 18 shows a comparison of standard DOE estimated wood preparation costs with those estimated based on Johnson Timber experience if hammermill size reduction is included. The variation is understandable considering the wide variety of feedstock preparation options and this represents an important area for future optimization.

Table 18 - Wood Feed Cost Comparison - 500t/d Plant - Delivered to Memphis assuming Hammermilled Feed Preparation Required

	DOE standard (1)	Johnson Timber est.
Delivered Feed price, $/ton	72	72
$/ton Preparation	29	34
$/ton after Feed Preparation	101	106

1 Source: Jacobson, J.J.; Cafferty, K.; Roni, M.S.; Lamers, P.; Kenney, K. *Biomass Feedstock and Conversion Supply System Design and Analysis.* INL/EXT-14-32377. Idaho Falls, ID: Idaho National Laboratory, 2014.

Feed preparation costs can be considerably reduced if feed preparation is done using in field micro-chippers, followed by microchip drying at the IH^2 site to utilize low grade IH^2 energy. Under these conditions, feed preparation cost could be potentially reduced to $10/ton. GTI and KBR are currently studying the best optimization for this step. Initial microchipping tests results show that reasonably small sizes suitable for IH^2 use can be obtained by direct microchipping.

Another scenario considered is offsite collection and feed preparation. A suitable site was found in Yellow Creek Mississippi, which is 120 miles from Memphis. Offsite feed preparation would enable the refinery location to concentrate on the upgrading step and reduce the biomass conversion footprint, but because of the additional transportation distance this would add an additional $10/ton in cost unless a closer, suitable offsite site can be found.

Many refineries in the US are located near wood which is a readily available commoditized feed. These refineries represent ideal locations for hydropyrolysis or IH^2 plants because they have the workforce, are typically located near transportation by water, or rail and have the infrastructure all in place. In addition to the Valero Memphis Refinery and the Valero St. Charles Refineries, there are other US refineries (non-Valero) located in Wisconsin, Washington state, Virginia, Georgia, Mississippi, Alabama, West Virginia, and Arkansas that are ideally suited to have an IH^2 or hydropyrolysis unit located right outside the refinery gates. Economics based on green field sites for biomass conversion are unnecessarily expensive compared to these refinery sites.

More details related to the wood logistics are located in Appendix D.

Corn Stover Feedstock Logistics

Cargill completed a study of moving corn stover to Valero's corn ethanol plants and also investigated the possibility of moving corn stover to refinery locations. To complete the study Cargill developed a model of the costs of providing corn stover to a Valero ethanol plant and Valero refinery locations. Key assumptions used in the model are shown in Table 19.

Table 19 - Key Assumptions in Corn Stover Price Estimate

Harvesting Costs	
Corn mass per bushel	47 lb/BU db
Stover mass ratio to grain	1.0
Moisture content of harvested Stover	15%
Farmer payment	$14.5/MT db
Farmer participation rate	30%
Chopping/windrowing cost	$4.8/MT db
Baling cost	$21.7/MT db
Stover collection efficiency	30%
Stacking cost	$10.4/MT db
LOCAL STORAGE	
Transport cost to local storage	$9.3/MT db
Storage cost	$4.0/MT db
Losses during storage	4.8%
Fraction of total nearby corn stover available to Valero	8.6%
TRANSPORTATION	
Cargo weight per load	11.3 MT db
Transportation cost up to 25 miles	$2.03 /mi
Transportation cost 25-100 miles	$2.03/mi
Transportation cost greater than 100 miles	$2.0 /mi
Unloading cost	$2.04/MT db
NUTRIENT REPLACEMENT COST	$30.3/MT db
ADMINISTRATIVE COST FOR CORN STOVER SUPPLIER	$6.4/MT db
PARTICLE SIZE GRINDING AND HAMMERMILL	$7.9/MT db

It was more cost effective to provide corn stover to existing Valero ethanol plants than Valero refinery locations since the ethanol plants are located closer to the corn stover production. The draw radius for various plant sizes and several locations is shown in Table 20.

Table 20 - Average Draw Radius in Miles for Corn Stover to Typical Ethanol Plants and the Memphis Refinery Location for Different IH^2 Plant Sizes

City, State Location	250 ton/day Plant	500 ton/day Plant	1000 ton/day Plant
Welcome, MN Ethanol Plant	25.9	32.7	47.1
Albion NE, Ethanol Plant	31.8	33.6	53.0
Memphis, TN Refinery	76.7	94.8	132.2

The Valero Memphis Refinery location had a lower cost for corn stover than most other Valero refinery locations and is included for comparison. The corn stover costs for several locations at different draw radii are shown in Table 21. As the amount of feed increases the price for the feed increases, as was also the case for wood, because the distance for transportation increases.

Table 21 - Average Delivered Corn Stover Cost $/ton at Typical Ethanol Plants and Memphis Refinery Location for each IH^2 Plant Size

City. State, Location	250 ton/day Plant	500 ton/day Plant	1000 ton/day Plant
Welcome, MN Ethanol Plant	99.3	101.6	104.5
Albion, NE Ethanol Plant	100.2	102.5	105.1
Memphis, TN Refinery	109.9	114.0	119.5

The breakdown of contributing factors for corn stover feed cost at 500t/d size is shown in Figure 21.

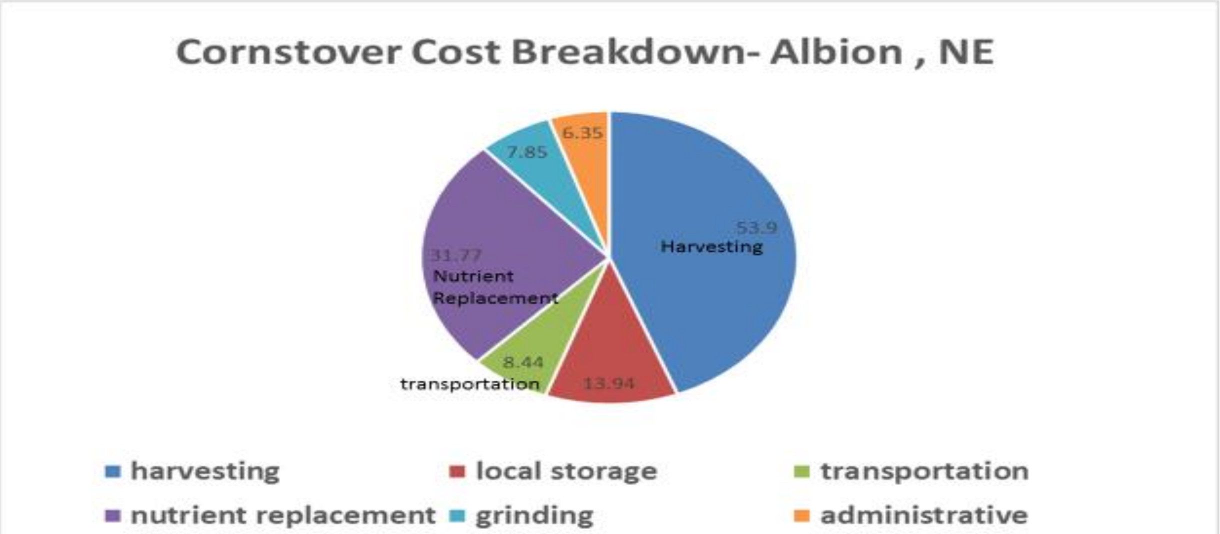


Figure 21- Corn Stover Cost Breakdown – Albion, NE Location

The cost of corn stover harvesting and nutrient replacement had the biggest impact on the price of the corn stover feedstock.

The corn stover feed was a more costly feed than wood in this project. Since corn stover also has lower yields for hydropyrolysis or IH^2 than wood, as shown in Table 22, wood will be a more likely first feedstock for early US adapters than corn stover.

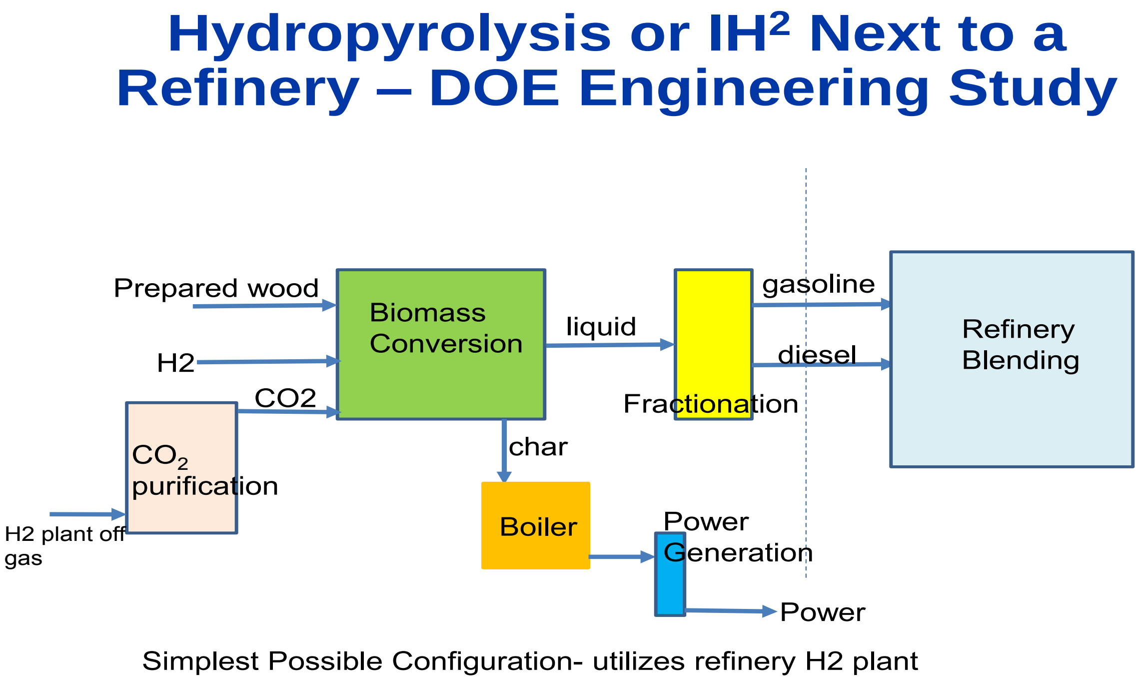
Table 22 - Yield Comparison Wood and Corn Stover

	Wt % C4 Liquid Yield	Gallon per Ton
Wood	26-30	86-92
Corn Stover	21	67

More Information on the Cargill Study is in Appendix E.

Engineering Study for a IH^2 or Hydropyrolysis unit Adjacent to a refinery

Since KBR has been doing the engineering studies for commercial IH^2 facilities, they were utilized for the current DOE analysis. For Case 1 the hydrogen production was assumed to be coming from an adjacent refinery hydrogen plant. Therefore, the hydrogen was made from natural gas and the light gas byproduct was burned as fuel to make electricity along with the char.



Hydropyrolysis or IH^2 Next to a Refinery – DOE Engineering Study

Simplest Possible Configuration- utilizes refinery H2 plant

Figure 22 - Case 1 Engineering Study Configuration

There was very little savings in capital or utilities ($3.4MM) by eliminating the second stage and making a hydropyrolysis product which required further refinery upgrading as compared to making a finished IH^2 product. The cost of the integrated hydrotreating reactor is small compared to the rest of the plant. Integrated systems, such as IH^2, have a natural cost advantage compared to separate systems requiring intermediate storage, and separate pumps and compressors, such as pyrolysis plus upgrading.

Table 23 - Capital Cost in Millions – Case 1-IH^2 adjacent to a Refinery

	500 t/d	1000 t/d
Biomass Conversion	18.7	28.4
Hydrotreating Section	2.5	3.8
Hydrocarbon Separation	10.8	16.3
Hydrogen Auxiliaries	3.0	4.5
Amine Regenerator	6.0	9.1
Char Boiler	18.5	28.0
Power Generation	11.1	16.8
Cooling Tower System	3.6	5.4

Total Capital	74.1	112.3
Catalyst	2.0	4.0
Infrastructure	11.2	17.0
Field Cost Total Direct	87.3	133.2
Total Indirects	43.7	64.6
Total Project	131.0	197.9

Table 24 shows the utilities produced from IH^2 in the case where the wood is pre-prepared and the hydrogen is available from the refinery.

Table 24 - Case 1- IH^2 Utilities

	500t/d	1000t/d
MW Power produced	12	24

In Case 2, shown in Figure 23, it is assumed the IH^2 is located next to the refinery, has its own hydrogen plant, and has an integrated third stage upgrading system for the drop in gasoline and diesel development. The fuels meeting the US specifications can be produced for direct blending. This case adds capital cost, yet allows the C1-C3 from the process to be used to make the hydrogen required in the process. In many cases, hydrogen plant providers (such as Air Products) will build the plant and sell the hydrogen to a customer in order to minimize or even eliminate hydrogen plant costs.

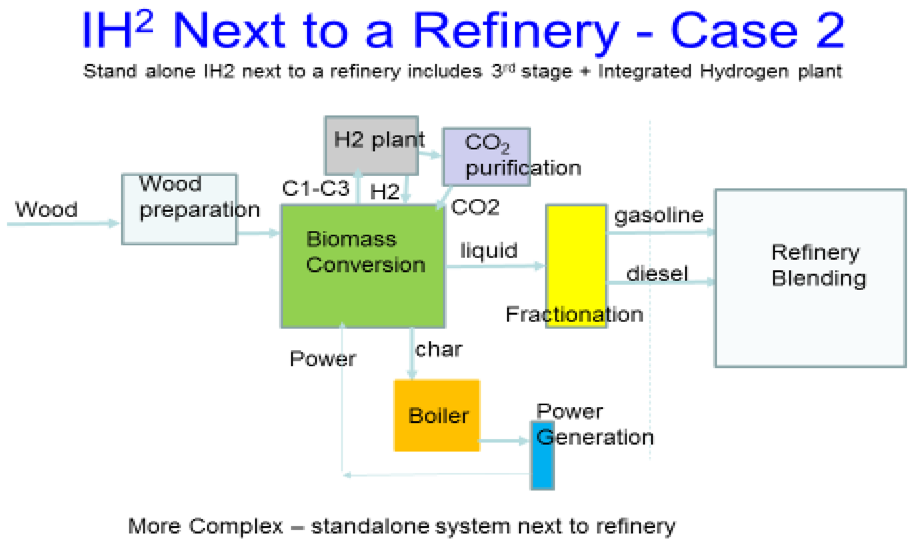


Figure 23 - Stand Alone IH^2 Next to a Refinery

Table 25 shows the additional capital costs for Case 2 over Case 1.

Table 25 - Case 2 - 500t/d-Capital Cost in $Millions - KBR

	500 t/d
Case 1 cost	131
Additional third stage costs	10
Additional hydrogen plant costs	38
Total Case 2 cost	179

For larger plants IH^2 capital scales up using a 0.6 factor. Utilities scale up linearly. In Case 2 utilities are required, since the C1-C3 from IH^2 are used to produce the hydrogen and are not burned to generate power. Case 2 utilities are shown in Table 26.

Table 26 - Case 2 - IH^2 Utilities Required

	500 t/d
Electricity, MW	2.0
Raw Makeup Water, l/s	17.9
Wastewater out, l/s	7.1
Nitrogen, kg/hr	<2.5

More details on the IH^2 engineering design are shown in Appendix F.

LCA Analysis

Michigan Technological University (MTU) completed the LCA analysis. The 2 cases were compared: 1) where an IH^2 process is next to a refinery (case 1 Figure 16) and uses refinery hydrogen generated from natural gas and 2) where an IH^2 process is next to a refinery or ethanol plant yet generates its own hydrogen from the C1-C3 produced in the process (Case 2 Figure 17). These are the same cases studied by KBR.

The inventory inputs for the LCA for forest residues harvest and collection are shown in Table 27.

Table 27 - Inventory inputs of forest residues harvest and collection

in gallons unless stated otherwise		**250 tons/day (bone dry)**	**500 tons/day (bone dry)**	**1000 tons/day (bone dry)**
Raw material processing in woods	Diesel	396	706	1,281
	Lubricating oil	5	10	21
	Hydraulic fluid	5	11	22
	Grease	14	29	58
	Gasoline	14	29	60
Trucking from woods to facility	Diesel	290	608	1,372
	Lubricating oil	1	2	4
	Grease		1	1
Yard equipment	Diesel	50	100	200
	Lubricating oil	4	8	16
	Hydraulic fluid	4	8	16
	Grease	11	21	43
Feedstock processing and drying	Energy in kWh (size reduction)	7,460	14,920	29,840
	Energy in kWh (drying) *	6,378	12,757	25,513

The inventory inputs for the LCA for corn stover is shown in Table 28.

Table 28 - Inventory Inputs of Corn Stover as Transported

Materials		
Diesel, low-sulfur (corn stover collection)	10.9	lb
Diesel, low-sulfur (corn stover loading)	0.238	lb
Fertilizer (K_2O)	31.5	lb
Fertilizer (P_2O_5)	5.2	lb
Ammonium nitrate, as 100% $(NH_4)(NO_3)$ (NPK 35-0-0)	17*0.2	lb
Ammonia, as 100% NH_3 (NPK 82-0-0)	17*0.3	lb
Di ammonium phosphate, as 100% $(NH_3)_2HPO_4$ (NPK 22-57-0)	17*0.1	lb
Urea, as 100% $CO(NH_2)_2$ (NPK 46.6-0-0)	17*0.4	lb
HDPE(high density polyethylene) pipes E	0.74	lb
Processes		
CO_2 emissions from diesel/gasoline combustion	10.9+0.238	lb
CO_2 emissions from urea application (Nitrogen in urea)	17*0.4	lb
N_2O emission at corn stover storage	1	ton
Transport, truck 10-20t, EURO1, 100%LF	95*1.609	tkm
Transport, truck 10-20t, EURO1, 100%LF, empty return	95*1.609	tkm

Greenhouse gas emissions of the two feedstocks, forest residues and corn stover, are illustrated in Figure 24. Corn stover bears more environmental burden, due to the synthetic fertilizer needed to replace the nutrients on corn fields, and it also requires a longer transport distance to the IH^2 facility.

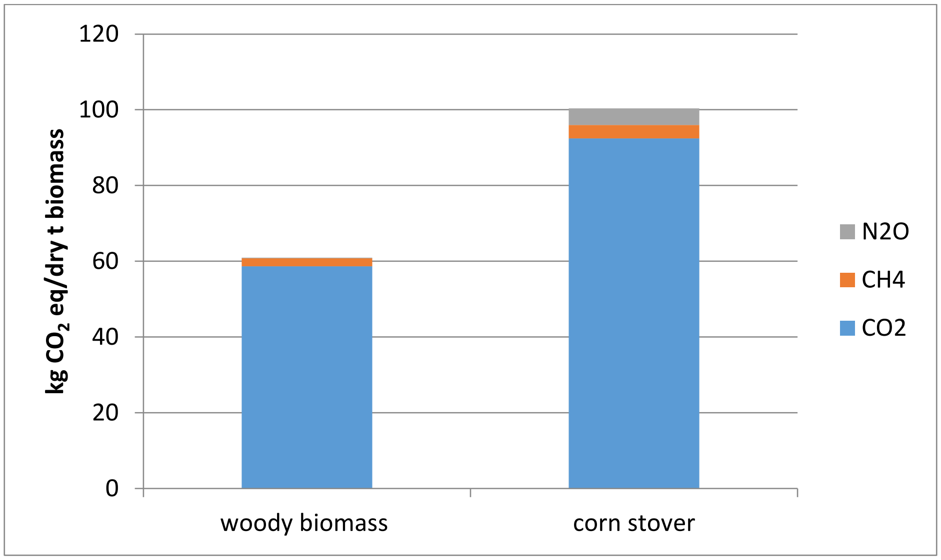


Figure 24 - GHG Emissions of Forest Residues and Cornstover

Greenhouse gas emission results of IH^2 renewable fuel blend from forest residues and corn stover are tabulated in Table 29, and are compared to petroleum diesel and gasoline. Net CO_2 emissions of renewable fuel blend at the combustion stage are considered carbon neutral because CO_2 is sequestered by photosynthesis during the growth of biomass.

*Table 29 - **Life cycle GHG emissions of IH^2 Renewable fuel blend***

g CO_2 eq/MJ	Woody biomass case 1	Woody biomass case 2	Woody biomass case 3	Corn stover case 1	Corn stover case 2	Petroleum Diesel	Petroleum gasoline
Feedstock	3.75	3.75	3.90	5.45	5.67	6.29	6.94
Feedstock transport	1.60	1.60	1.66	6.59	2.38	1.25	1.36
Fuel production	22.52	17.63	3.47	16.71	-0.26	9.05	9.27
hydrogen	61.42	51.00	0.00	69.87	0.00		
other inputs[1]	0.37	0.33	3.80	0.45	0.18		
credit from electricity	-38.96	-33.39	0.00	-53.18	0.00		
Credit from ammonia	-0.31	-0.31	-0.32	-0.43	-0.44		
Waste treatment	0.07	0.06	0.06	0.13	0.13		
Fuel transport	0.85	0.85	0.85	0.85	0.85	0.85	1.03
Use						72.7	72.6
Total	28.78	23.89	9.95	29.74	8.77	90	91.3
GHG reduction[2]	68%	73%	89%	67%	90%		

1: other inputs include electricity, water, inerting gas, etc
2: GHG reductions are compared to petroleum gasoline

For wood and corn stover feeds the greenhouse gas reduction is larger when the hydrogen is derived from IH^2 produced gas rather than natural gas. More details of the LCA analysis is in Appendix G.

Renewable Fuel Credits from IH^2

To improve IH^2 economics in the United States, it is important for the IH^2 gasoline and diesel to qualify for a renewable fuel credit which are typically valued from $.50/gal to $1.0/gal.

A **Renewable Identification Number** (or **RIN**) is a serial number assigned to a batch of biofuel for the purpose of tracking its production, use, and trading as required by the US Environmental Protection Agency's Renewable Fuel Standard (RFS) implemented according to the Energy Policy Act of 2005. The RIN system allows the EPA to monitor compliance with the RFS, a federal program that requires transportation fuels sold in the US to contain minimum volumes of renewable fuels. In order to get the RIN credit a biofuel must first be certified by the EPA.

Life Cycle Associates completed a study of the IH^2 process to determine if the IH^2 process would likely qualify as a renewable fuel under the RFS standards. This study is available in its entirety in Appendix F. The current standard requires a renewable fuel have greater than a 60% greenhouse gas reduction, so IH^2 fuel from waste wood and corn stover would meet that requirement for all scenerios studied. The IH^2 would likely qualify under pathways M or L. Pathway M is specific to catalytic pyrolysis yet IH^2 could be seen by the EPA as an improved type of catalytic pyrolysis and so it is likely to qualify there. Pathway L is only for making bio-jet fuel, biodiesel and bio-fuel oil so is more limited. The standard also requires no electricity be used in biofuel production. IH^2 is using electricity in most embodiments but this requirement could be met by burning a small amount of biomass feed to make the electricity required or by requesting a waiver from the EPA in this area.

In the current ruling slash, pre-commercial thinnings and residues including treetops, branches, and bark qualify as acceptable wood feeds to qualify for renewable fuel credits. So a specific study for the site chosen would be needed to determine the amount of these woody materials available in that specific area.

Life Cycle Associates also reports that the EPA currently does not grant RINs to an intermediate that requires further upgrading in a refinery. One can always petition the EPA for a special allowance of biofuel intermediate production followed by refinery upgrading to qualify under the RFS, however it would be a more problematic path than production of drop-in fuels like those produced through IH^2. The EPA has historically not allowed RINS for vegetable oil refinery co-processing. This is seen as a negative precedence for the case of intermediate upgrading in a refinery.

The fuel producer ultimately will have to register IH^2 fuels to qualify for RIN credits. Based on this analysis, the path for this would seem to be relatively straightforward for IH^2 technology with no significant barriers.

More details on IH^2 RFS credits are in Appendix H.

Future Work

A key step forward for the IH^2 process is the construction of a larger demonstration scale plant to reduce the risk associated with scale up of IH^2 technology to commercial size and thereby increase the ease of raising funds for a commercial IH^2 investment. Studies which provide data to model the hydrodynamics, heat transfer, and kinetics in the hydropyrolysis reactor are also recommended. More long term testing to look at first stage catalyst activity versus time and catalyst make up rate are also recommended.

Conclusions

Gas Technology Institute has developed a new breakthrough catalytic technology, IH^2, that thermochemically converts biomass directly into drop in gasoline and diesel. Testing shows hydropyrolysis oil, which is the oil from the first stage of IH^2, can be co-processed in standard refinery equipment, at standard refinery hydrotreating conditions, to remove the oxygen and acidity and produce drop in diesel or gasoline blending components. Therefore, refiners could theoretically complete this upgrading step themselves.

However, after a risk analysis, Valero concluded it is unlikely that a refiner would be able to take the risk of upgrading bio-oils in their refinery since refineries require high throughput and high operating factors to make money. Problems caused by processing small amounts of bio-oils in their refinery could lead to costly refinery downtime. Valero also concluded in the near term, refiners would much prefer to utilize processes such as IH^2 located near a refinery which directly produced drop in quality gasoline, diesel, and jet fuel.

Life Cycle Associates reports that an IH^2 unit located next to a refinery is also more consistent with the current RIN regulations as well, which only provide credits for finished biofuels.

The KBR engineering study showed that for the IH^2 process, the costs of adding the additional second stage reactor were minimal and most likely offset by the costs of condensing intermediate products and the more expensive water cleanup needed when only one stage is used. Therefore, the driving force for partial upgrading of bio-oils is offset by the negatives of refinery upgrading risks and intermediate handling and water cleanup. The best option for refiners is to use drop in product produced when IH^2 has the additional diesel upgrading step so that 43 cetane diesel is directly available for blending.

GTI believes that locating an IH^2 process next to a refinery, near wood, is an extremely cost effective method of effectively deploying the IH^2 process in the US. The capital costs are then reduced and the infrastructure is already in place. Building an IH^2 process near a refinery also makes it flexible to process a variety of biomass feeds such as algae or corn stover that could become available in the future.

GTI believes that the IH^2 technology, when fully commercialized, will be a game-changing technology, by reducing US dependence on foreign crude, reducing greenhouse gas emissions, creating US jobs and producing high quality and low-priced transportation fuels from US grown biomass resources. Based on this study, GTI believes that commercial deployment of IH^2 near refineries would be a logical and cost effective commercialization strategy.

References

1. Marker, T., Felix, L., Linck, M., Roberts, M., ”Integrated Hydropyrolysis and Hydroconversion(IH2) for the Direct Production of Gasoline and Diesel Fuels or Blending Components from Biomass, Part 1: Proof of Principle Testing”, Environmental Progress and Sustainable Energy, Vol 31, No. 2, p.191-199, July 2012.
2. Marker, T., Felix, L., Linck, M., Roberts, M. Ortiz-Toral, P., Wangerow, J., “Integrated Hydropyrolysis and Hydroconversion (IH2) for the direct production of gasoline and diesel fuels or blending components from biomass, Part 2: Continuous Testing”, Environmental Progress and Sustainable Energy, Vol 33, No. 3, p 762–768, October 2014.
3. Marker, T., et. al., “Biomass to Gasoline and Diesel Using Integrated Hydropyrolysis and Hydroconversion”, DOE final report U.S. DOE Award DE-EE-0002873, Dec 28, 2012
4. Marker, T., et al. “Long Term Processing using Integrated Hydropyrolysis and Hydroconversion(IH2) for the Production of Gasoline and Diesel from Biomass”, DOE Final Report , DOE Award DE-EE-0004390. March31, 2013.
5. Marker. T., et al. US 8,841,495 "Bubbling bed catalytic hydropyrolysis utilizing large catalyst particles and small biomass particles featuring an anti-slugging reactor”, Sept 23, 2014
6. Felix, L. et al. US 8,816,144 “Direct production of fractionated and upgraded hydrocarbon fuels from biomass”,, Aug 26, 2014
7. Marker, T., US 8,492,600 “Hydropyrolysis of Biomass for Producing High Quality Liquid Fuels”, July 23, 2013
8. Oak Ridge National Laboratory, “US. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry,” A Study Sponsored by the US. Department of Energy, Energy Efficiency and Renewable Energy, Office of the Biomass Program, DE-AC05-00OR22725, August, 2011 (http://www1.eere.energy.gov/biomass/pdfs/billion_ton_update.pdf)
9. US Timber production by County , World Resources Institute
10. USDA National Agricultural Statistic Map of corn planted http://www.nass.usda.gov/Charts_and_Maps/Crops_County/cr-pl.asp
11. NPRA refinery Statistics, http://old.npra.org/ourIndustry/refineryFacts/?fa=refineryStatistics

Appendix A - Oak Ridge Metallurgy Report

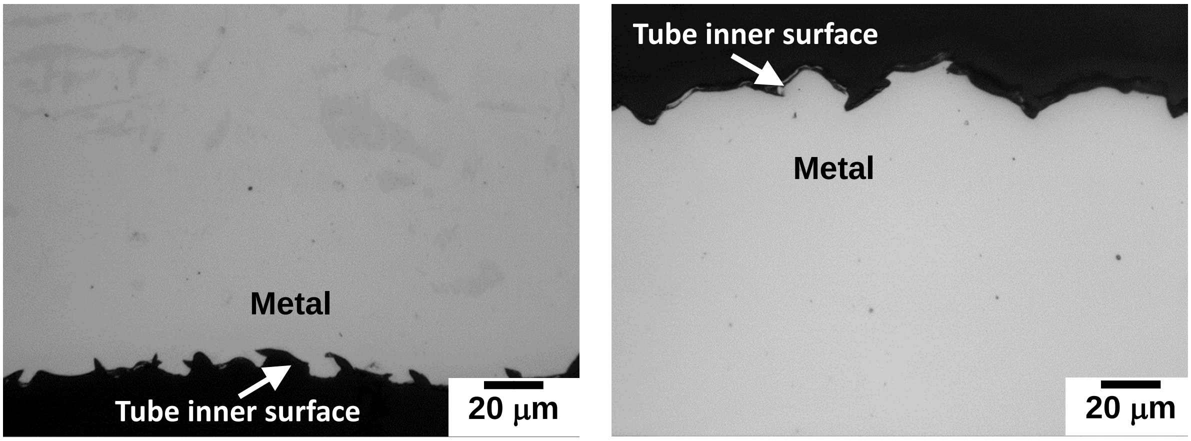
Two sets of nominal ¾" outer diameter (OD) tube samples of 6 alloys (Table 1) were exposed to high temperature gas from the GTI biomass liquefaction system for ~ 700 hours (h). Set #1 was exposed to the outlet from vessel R112, and this stream contained solids. Set #2 was located between vessels R126 and R131, and this stream did not contain solids. Exposed tube samples were sectioned and mounted to determine the extent of reaction with the high temperature gas stream that flowed through the tubes. Non-aqueous polishing fluids were used since some potential reaction products (e.g. chlorides) could be water soluble. The polished cross-sections were analyzed by light microscopy and by scanning electron microscopy (SEM) with energy dispersive x-ray analysis for elemental makeup.

Table 1- Nominal base compositions (weight percent) of the alloys tested (listed in approximate order of least to most expensive, cost driven primarily by Ni and Mo content).

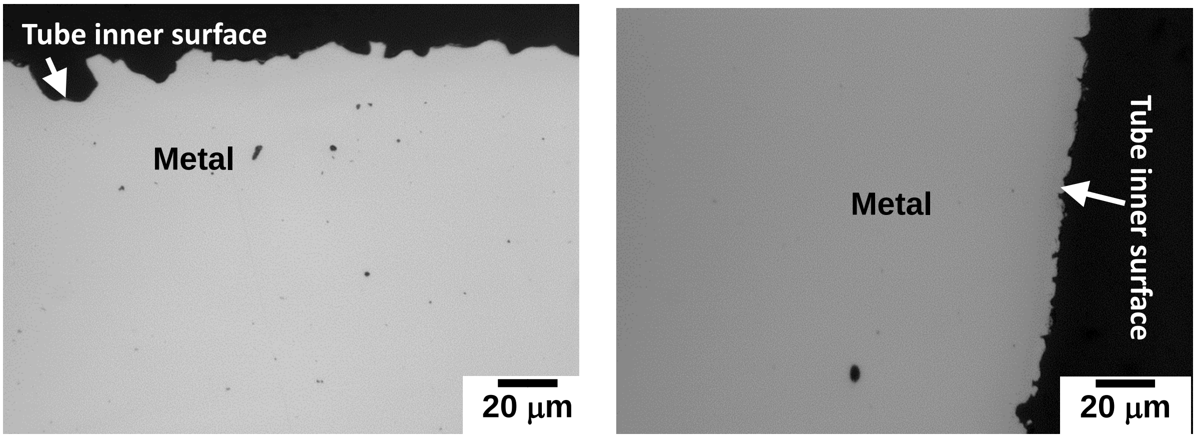
Alloy	Fe	Ni	Cr	Mo	Mn	Si	C	other
304L	balance	8-12	18-20		2 max	0.75 max	0.03 max	0.1N max
316L	balance	10-14	16-18	2-3	2 max	0.75 max	0.03 max	0.1N max
317L	balance	11-15	18-20	3-4	2 max	0.75 max	0.03 max	0.1N max
310	balance	19-22	24-26		2 max	1.5 max	0.25 max	-
800H	balance	30-35	19-23		1.5 max	1 max	0.1 max	Al, Ti 0.15-0.6
825	min 22	balance	19.5-23.5	2.5-3.5	1 max	0.5 max	0.05 max	1.5-3Cu, 0.6-1.2 Ti

Figure 1 shows light microscopy cross-sections of the as-received tubes prior to exposure. The inner surfaces of the tubes were found to be quite rough and irregular, with sharp inward penetrating features and occasional minor localized surface cracking. Figure 2 shows cross-section SEM images of the 6 test alloys after 700 h exposure at the outlet from vessel R112 (set #1, stream contained solids). The rough, irregular features observed in as-received (no exposure) tubing was again evident in the 700 h set #1 cross-sections. Minor local scaling generally less than 5 µm in thickness was observed for all alloys, indicating little corrosive attack. Qualitatively, slightly thicker scales were observed for 316L and 825; however, the extent of attack was minor and these differences in apparent scale thickness may simply be an artifact of the location sectioned and local scale and deposit adherence. Similar cross-sections and only minor extent of corrosion were observed for set #2 after 700 h of exposure at the location between vessels R126 and R131 (stream contained no solids) (Figure 3).

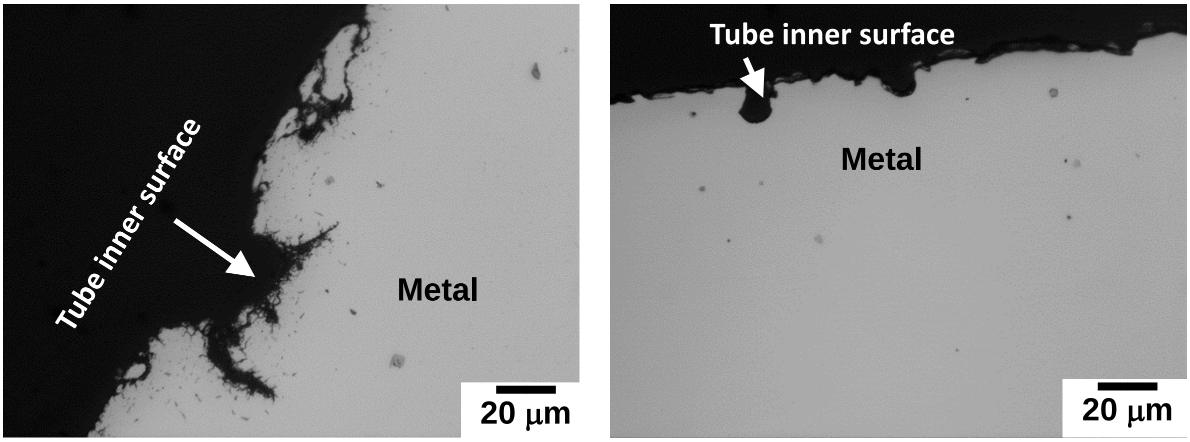
Energy dispersive x-ray analysis (EDS) was performed for all alloy sections and for both sets #1 and #2. The outer diameter (OD) surfaces showed primarily oxide products (C was also detected, but likely resulted primarily from beam overlap with the polymer mount used for sample preparation). Trace amounts of Ca, K, Cl were also occasionally registered. In contrast, the scale regions observed for the inner diameter (ID) surfaces of tubes also nearly always contained large EDS peaks consistent with Mo or S, which were associated with Cr and Fe (shown for set #2 304L and set #1 316L and 825 in Figure 4). Peak overlap in EDS spectra between Mo and S complicate a definitive identification of Mo vs S (wavelength dispersive analysis in electron probe microanalysis is typically used to distinguish between them); however, a large Mo/S peak was observed for 304L (Fig 4a), which does not contain Mo as an intentional alloy addition (Table 1), strongly suggesting that the inner scale regions contain significant quantities of S. The scales also contained minor amounts of O (and C), but the scales were sufficiently thin and subject to beam overlap with surrounding mount, possible deposit, and metal regions that it was not possible to determine if the scales were likely sulfides, or mixtures of oxides and sulfides. As the extent of scaling was relatively minor, it is not yet clear if this possible local sulfidation is an issue for long-term durability under the conditions examined. Additional and longer term exposures are needed to more definitively address the potential significance of this sulfidation attack.


a) 304L Inner Surface

b) 316L Inner Surface

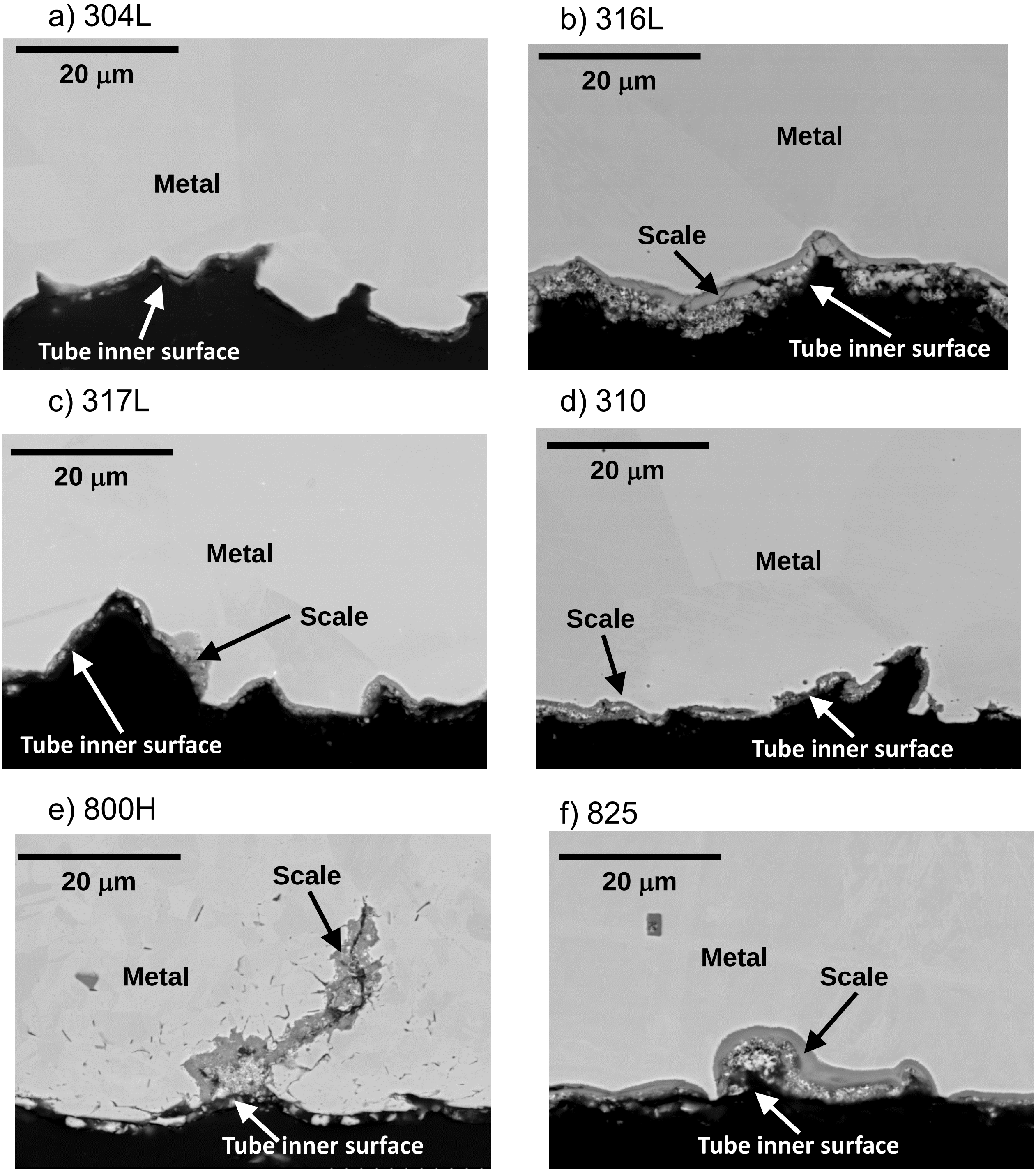

c) 317L Inner Surface

d) 310 Inner Surface


e) 800H Inner Surface

f) 825 Inner Surface

Figure 1- Light microscopy cross-section images of as-received (not exposed) alloy tubes showing rough, irregular inner diameter surface features.



a) 304L

b) 316L

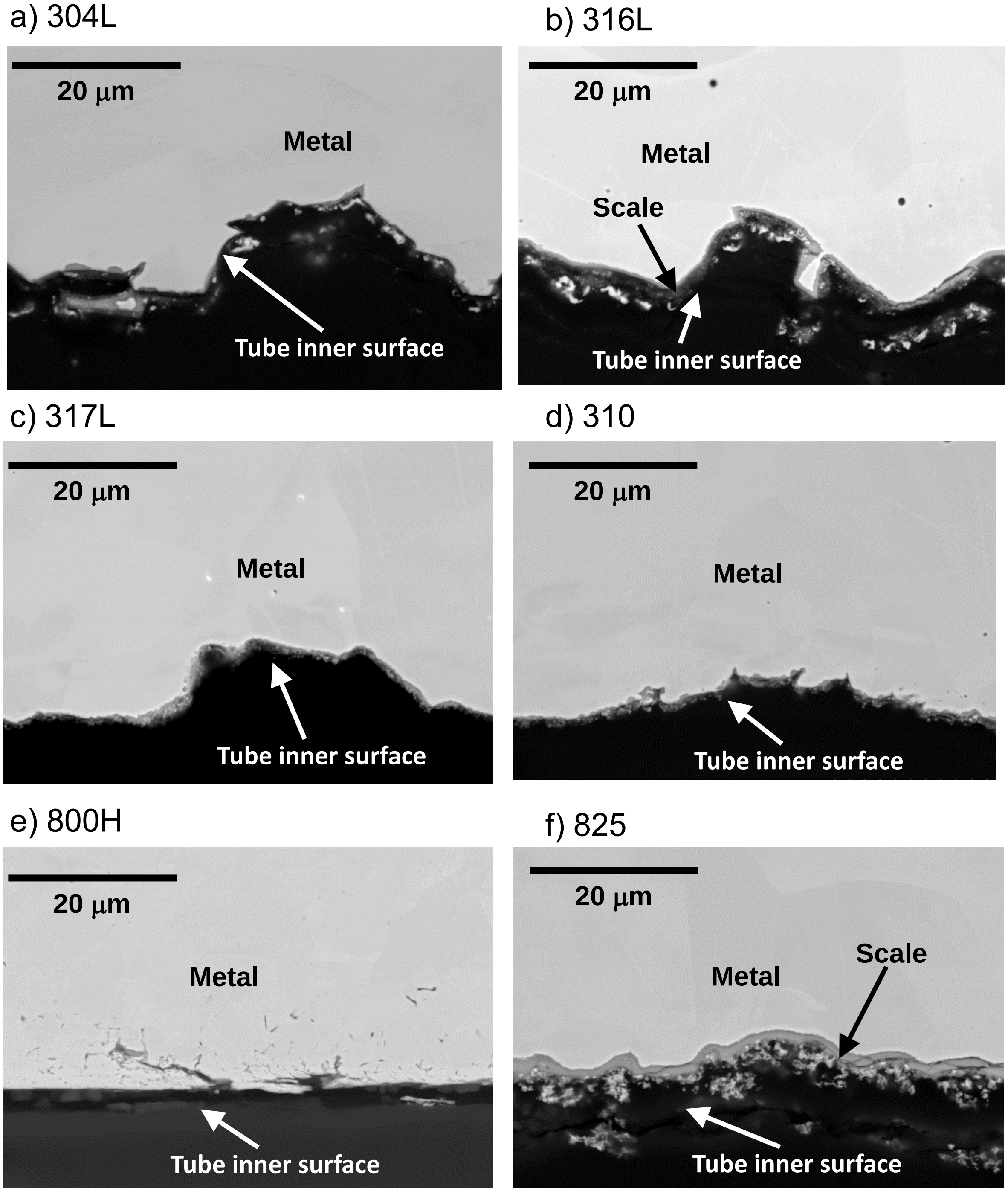
c) 317L

d) 310

e) 800H

f) 825

Figure 2- Scanning electron microscopy (SEM) backscattered electron images of alloy tube samples after 700 h exposure to high-temperature gas from the GTI biomass liquefaction system at the outlet from vessel R112 (stream contained solids). Only minor oxide scaling (< 5 μm) of the initially rough tube inner surfaces was evident, with no major differences in the extent of corrosion among the alloys exposed.



a) 304L

b) 316L

c) 317L

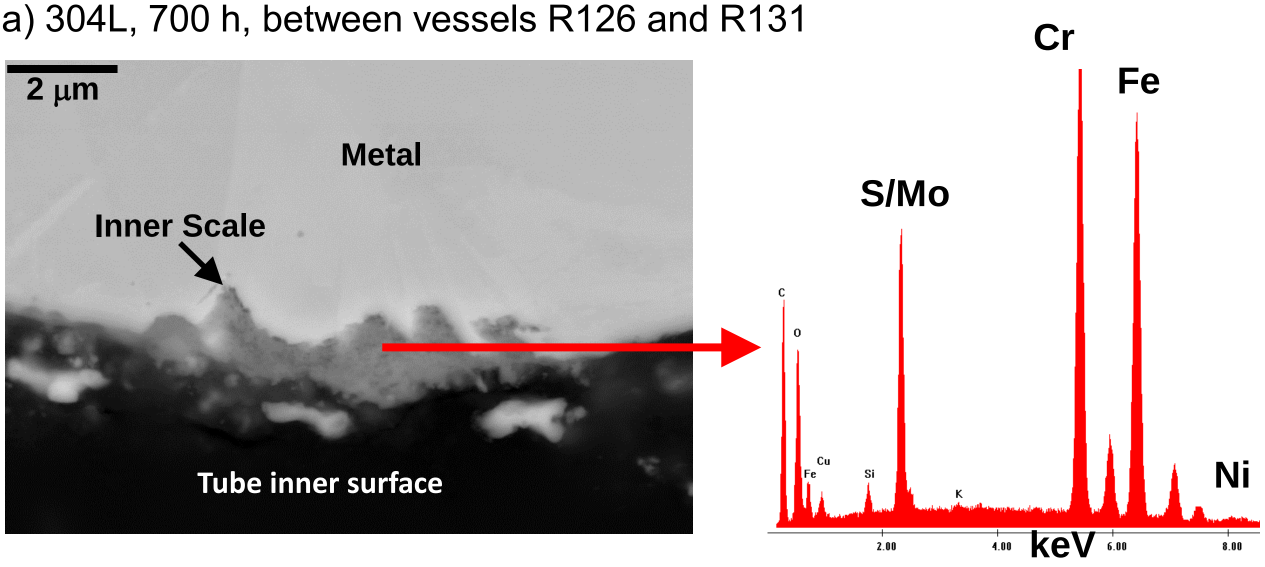
d) 310

e) 800H

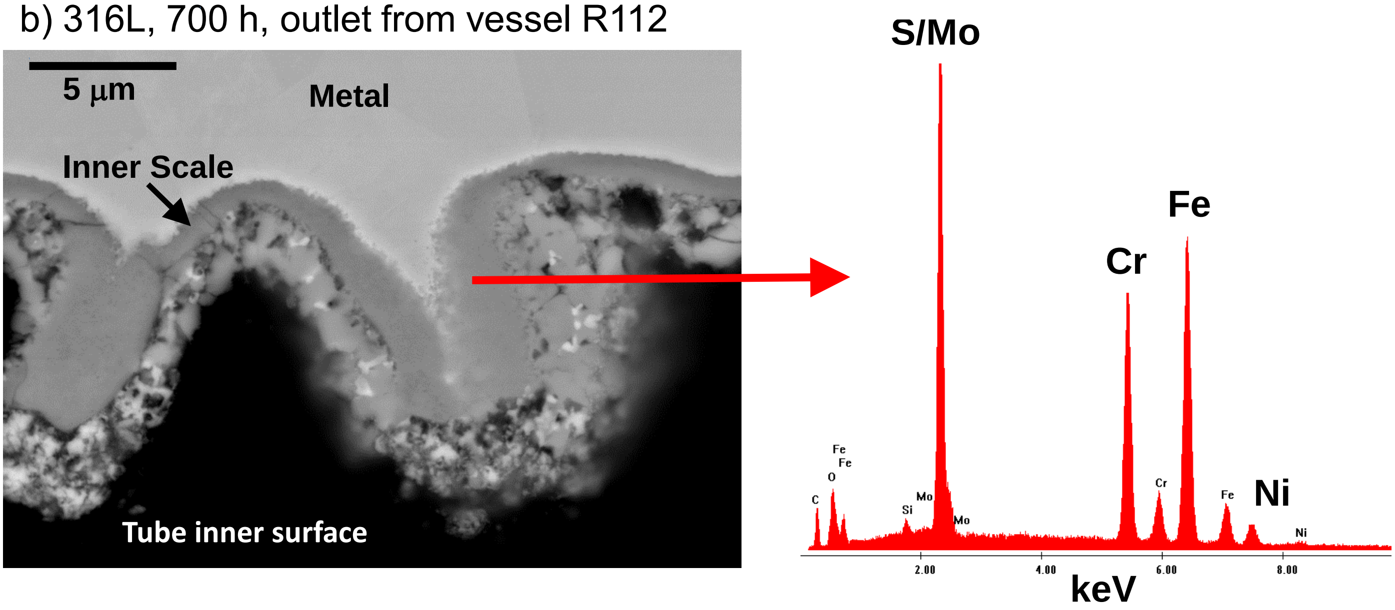
f) 825

Figure 3- Scanning electron microscopy (SEM) backscattered electron images of alloy tube samples after 700 h exposure to high-temperature gas from the GTI biomass liquefaction system between vessels R126 and R131 (stream contained no solids). Only minor oxide scaling (< 5 μm) of the initially rough tube inner surfaces was evident, with no major differences in the extent of corrosion among the alloys exposed.

a) 304L, 700 h, between vessels R126 and R131



b) 316L, 700 h, outlet from vessel R112



c) 825, 700 h, outlet from vessel R112

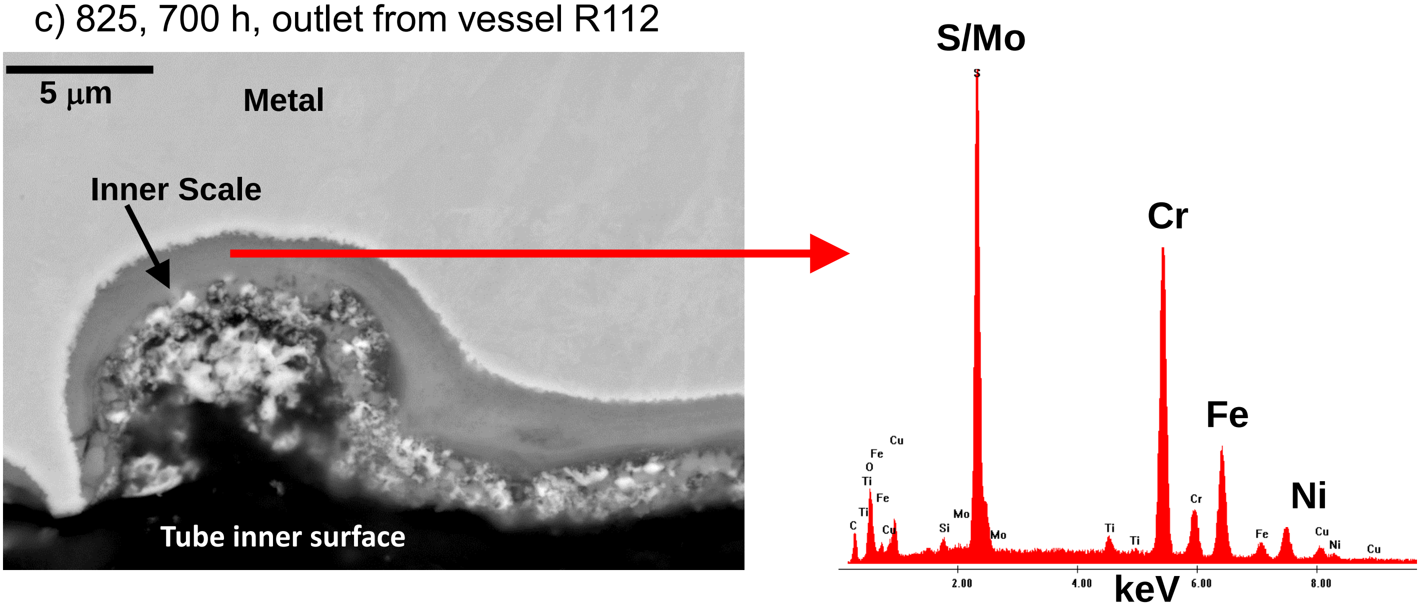


Figure 4- Representative SEM energy dispersive x-ray analysis (EDS) suggested the inner scale regions were locally rich in S: observed for all alloys examined (S and Mo peaks overlap in EDS)

Appendix B - Oakridge Analysis of First Stage Liquids

The organic analysis of GTI samples B (Hydropyrolysis oil from cornstover) and C (hydropyrolysis oil from wood)

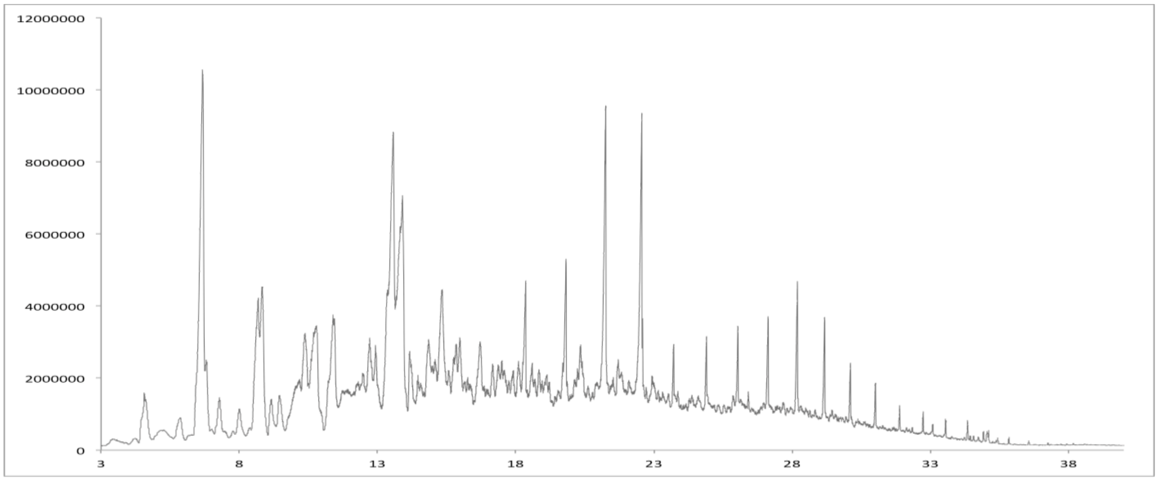
The bio-oil samples (liquids) were divided into two subsamples. One subsample was analyzed by thermo/pyrolysis gas chromatography/mass spectrometry (thermo gc/ms). The other subsample was analyzed by capillary electrophoresis/ electrospray/ mass spectrometry (ce/ms).

The experimental setup for the thermo gc/ms used a 10mg sample that was weighed into a thermo-sample vessel. The thermo program started at an initial temperature of 40C then ramped to 350C at 100C/min, with a final holding time of 5 min. The desorbed compounds were cyro-focused onto a 5 % phenyl/95% methyl coated gas chromatograph column. The gas chromatograph temperature program set an initial temperature of 40C, and ramped 5C/min to 320C with a holding time of 5min. The mass spectrometer was scanned from 40 to 500 daltons per 0.5 sec.

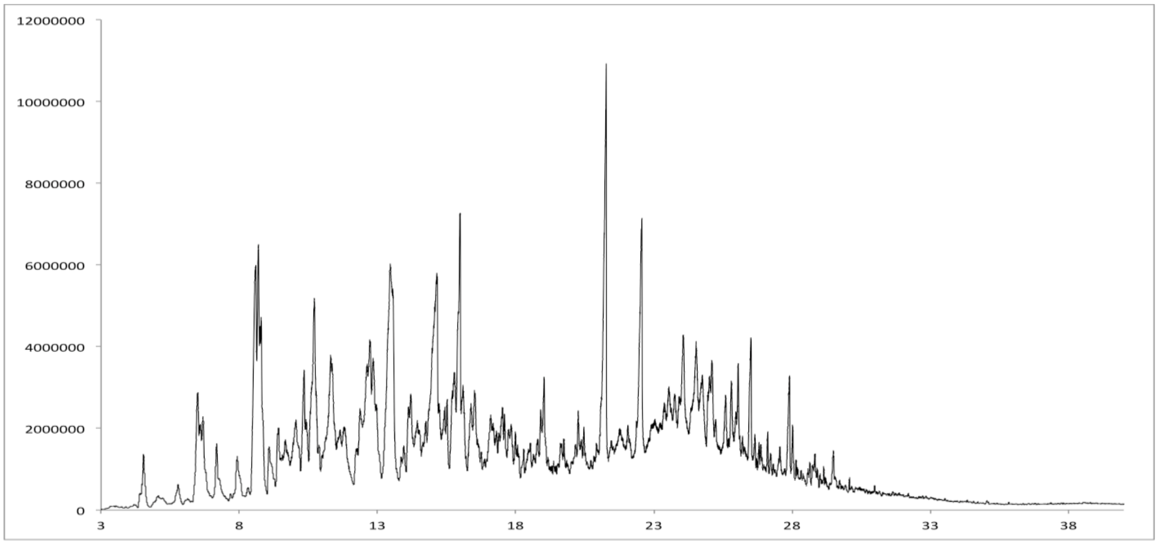
The sample preparation for the ce/ms used a100ul sample diluted 3:1 in a solution of 50:50, water:methanol with 100ul diethylamine . The diluted sample was sonicated for 10min. The ce column was 70cm long with an 100 um ID. The column was treated with a dynamic coating. The sample injection was 50bar for 10secs. The column-applied voltage was -30kv. The electrospray was operated in negative mode at 3.5KV. A makeup solution of 50:50, methanol:water with 10% NH_4OH was used. The makeup solution ensures proper electrospray ionization/osmotic flow is maintained and prevents stoppage of osmotic flow in the column. The mass spectrometer was scanned from 50 to 1000 daltons at a scan rate of 0.5 sec and operated in negative ms and ms/ms modes.

The following chromatographs were obtained from the thermo gc/ms analysis. The left scale is total ion counts and the bottom is time.

GTI B

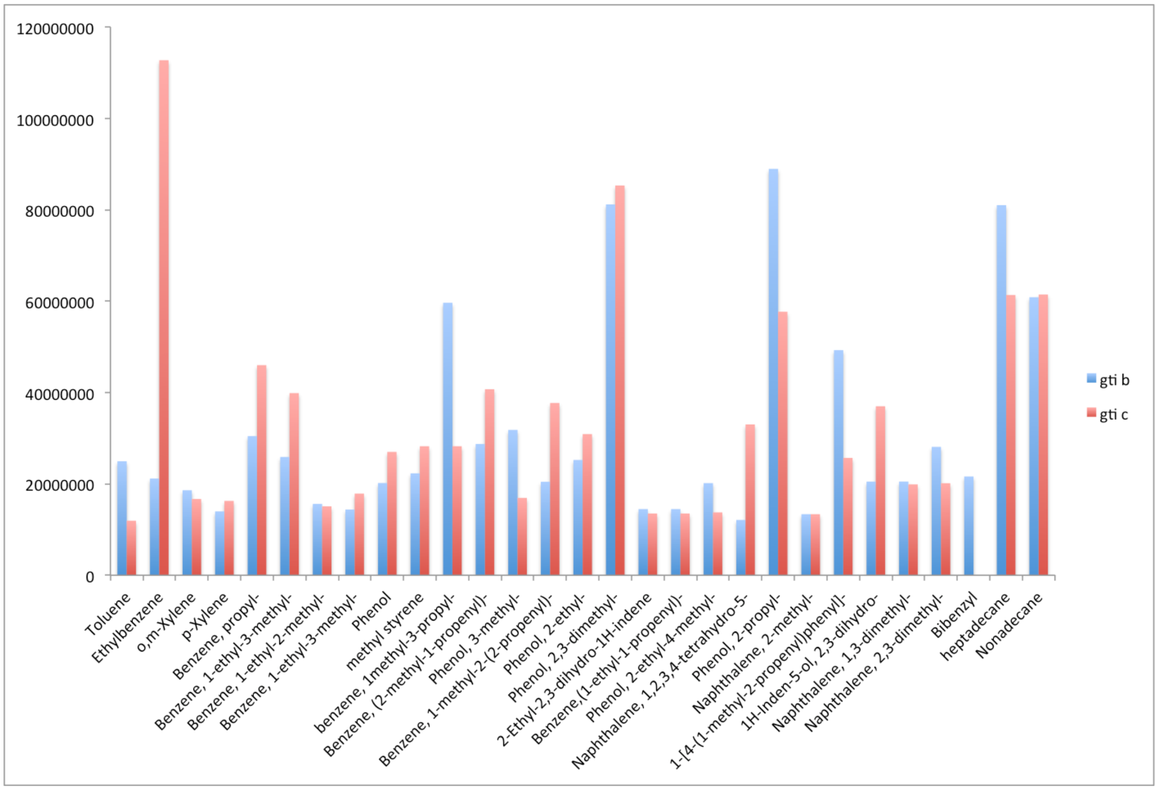


GTI C



Generally, the data from the gc/ms analysis shows the GTI B sample contains more alkanes than GTI C. Both samples have a large number of mono aromatic and phenolic compounds. Chart 1 is a comparison of area counts for the volatile organic species identified from the thermo GC/MS analysis. Quantitative values could not be calculated.

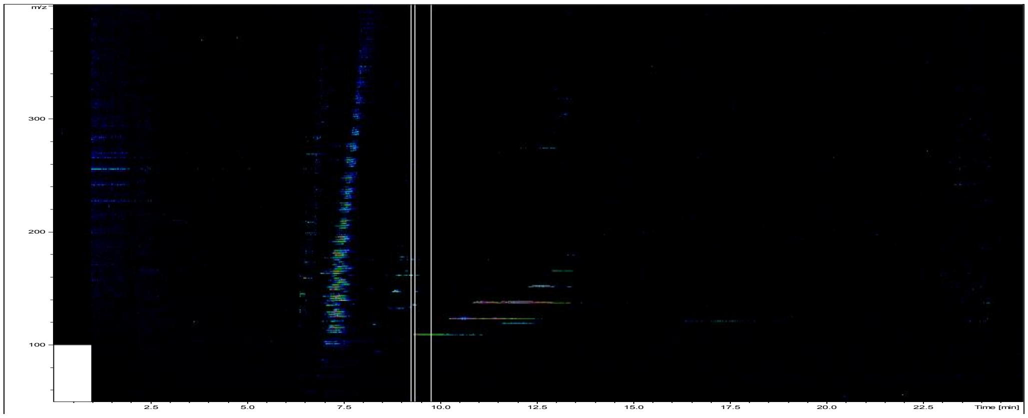
Chart 1



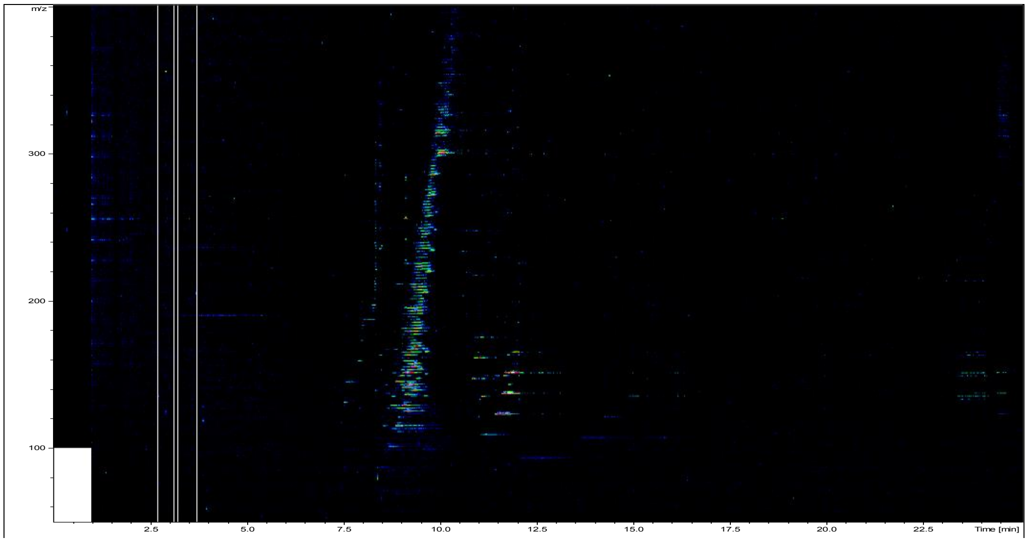
CE/MS Results:

The following electrophographs were obtained from the ce/ms analysis. The left scale is the mass range. The bottom scale is time. The color scale is blue to red with red being the highest intensity.

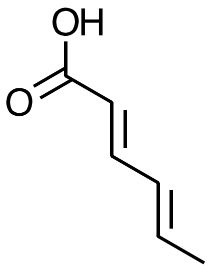
GTI B



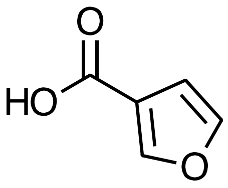
GTI C

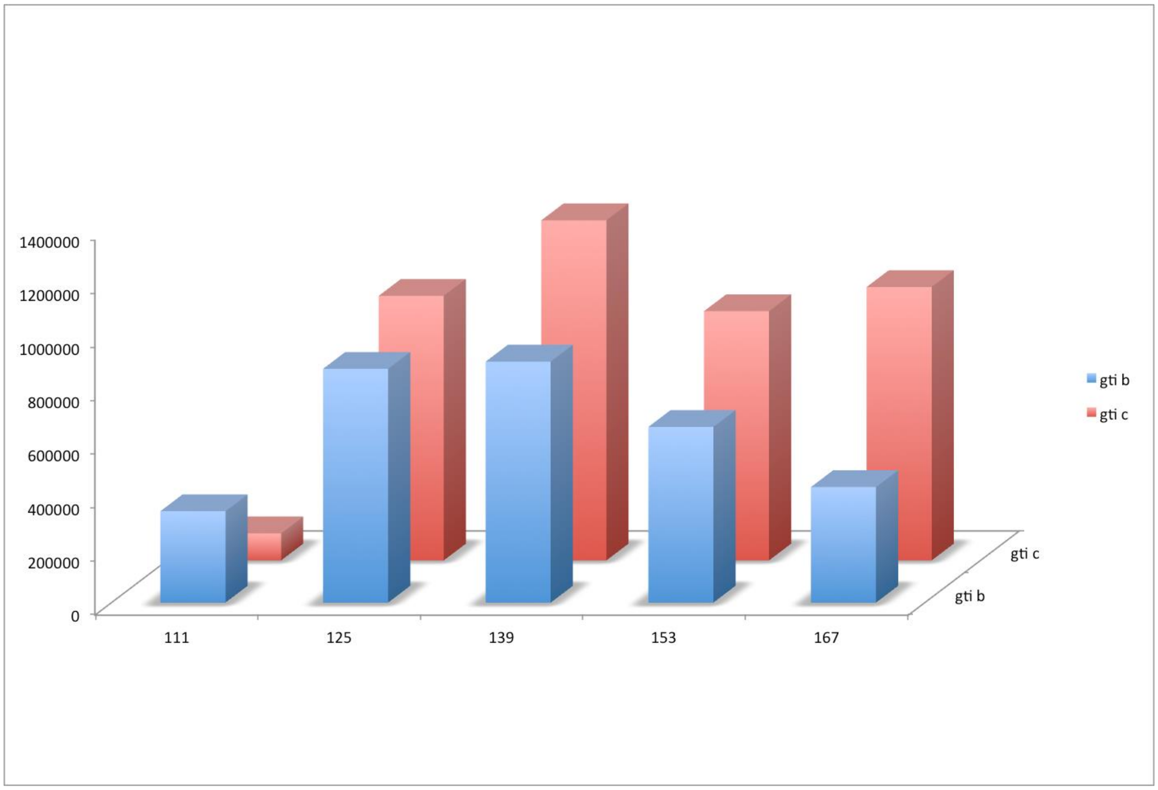


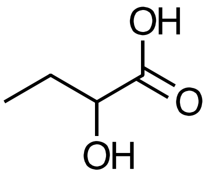
Generally, the data from the ce/ms analysis show the GTI C sample contains more organic anions than GTI B. Both samples have a large number of homologs of organic anions with molecular weight range of 100 to greater than 400 amu. The charts below are comparisons of area counts for different methylene(-CH2-) homologs series. The structure at the top of each chart is the estimated root structure. Quantitative values could not be calculated.

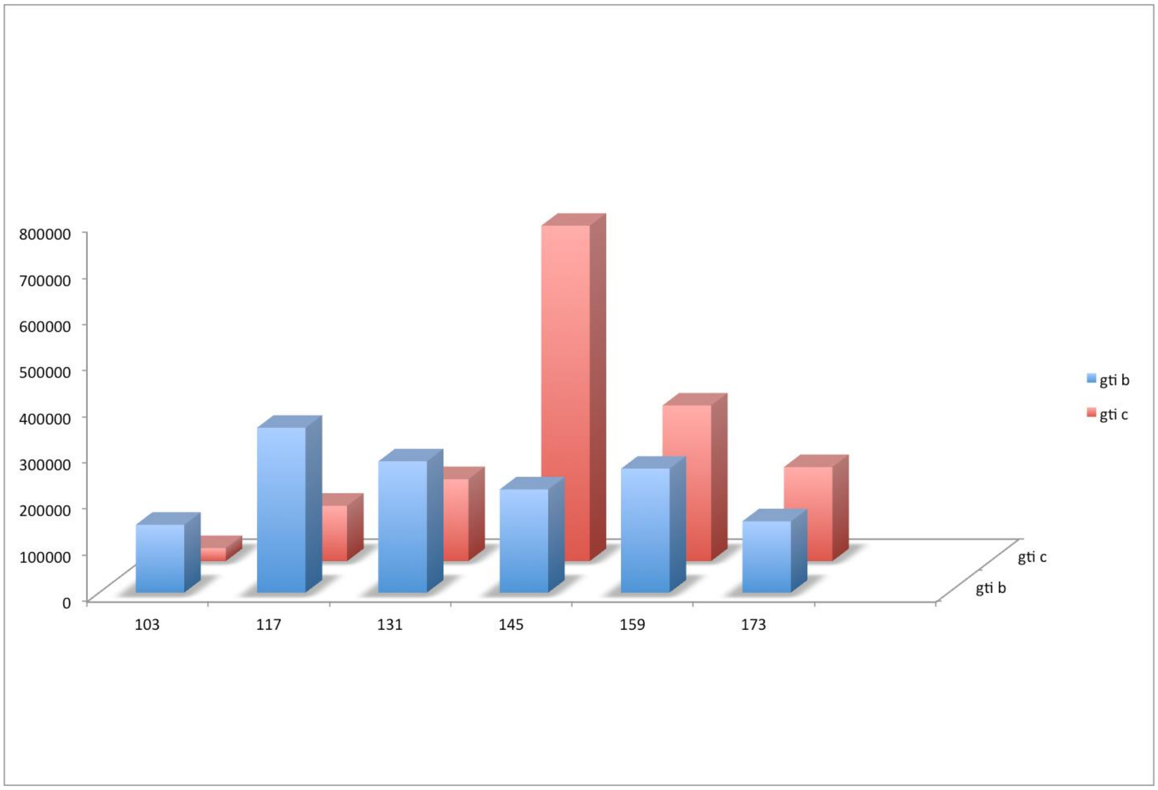

OH
O

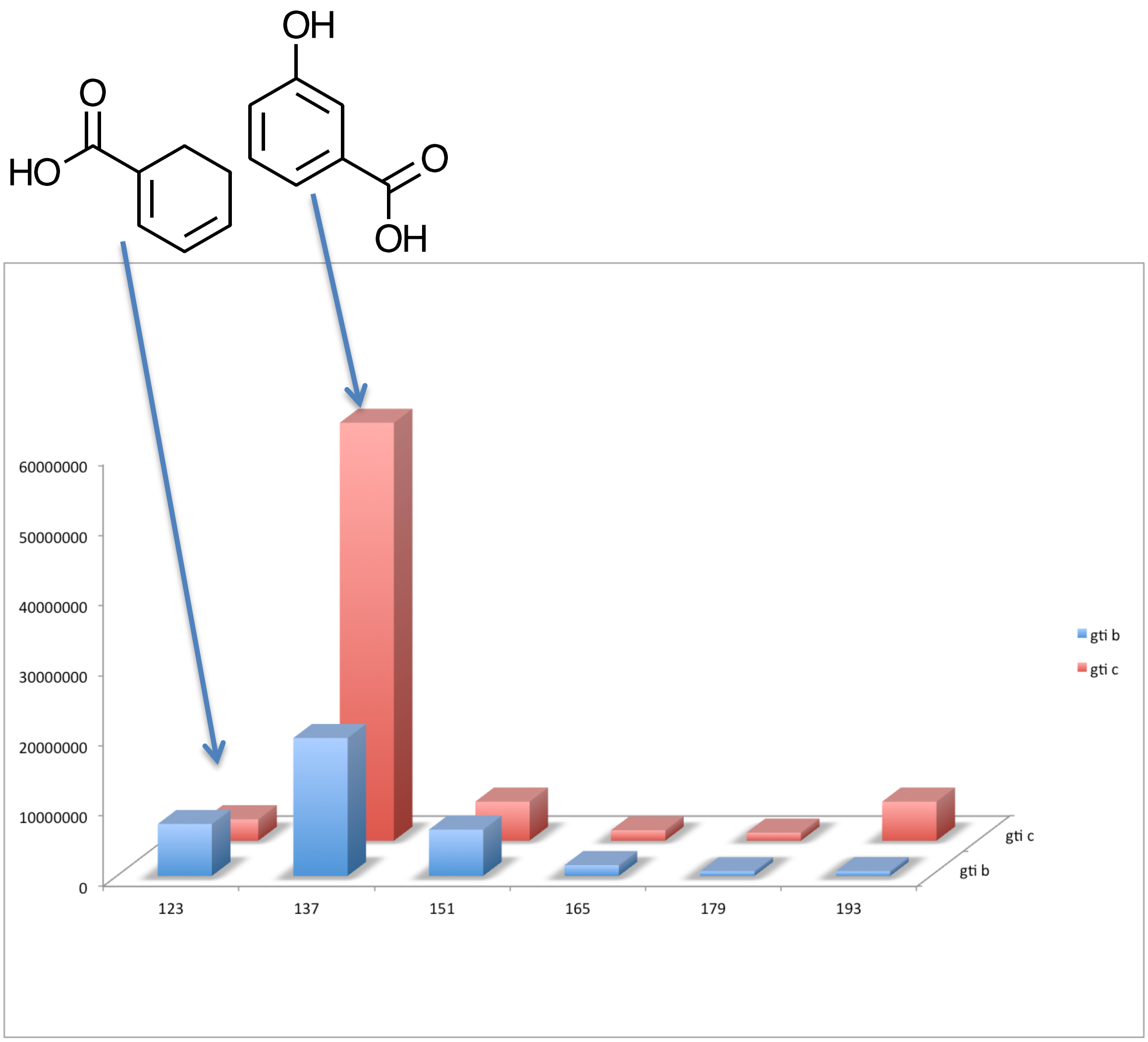
or

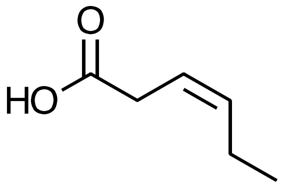

O
HO
O

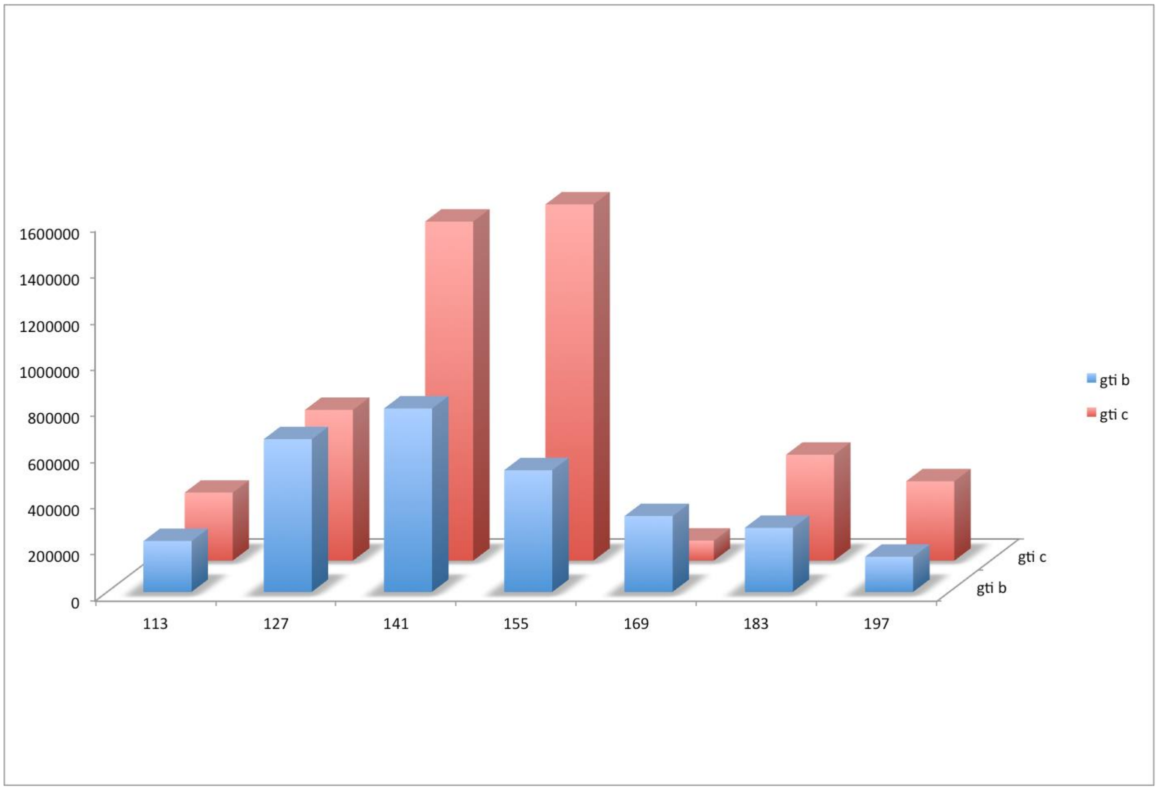

1400000
1200000
1000000
800000
600000
400000
200000
0
111
125
139
153
167
gti b
gti c
gti b
gti c

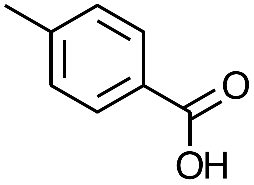

OH
O
OH

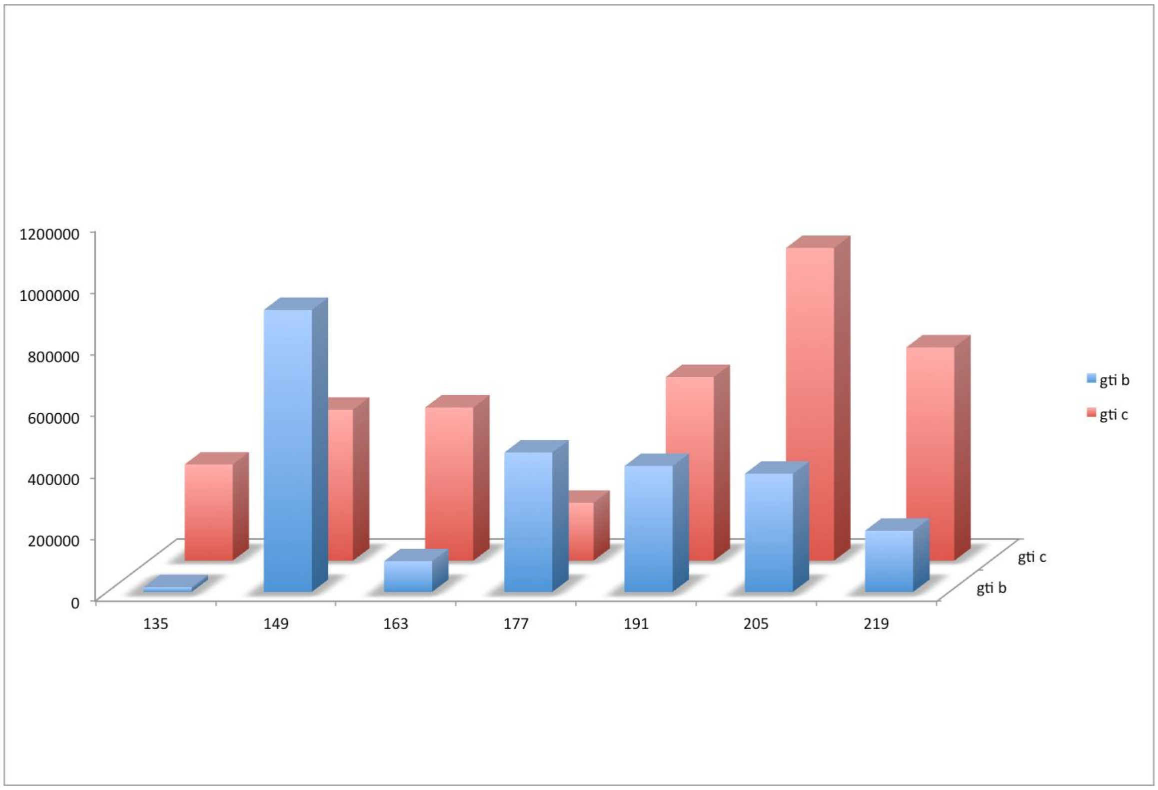

800000
700000
600000
500000
400000
300000
200000
100000
0
103
117
131
145
159
173
gti c
gti b
gti b
gti c

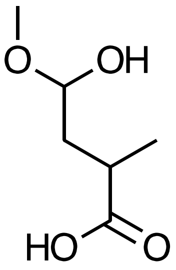

O
HO
OH
O
OH
60000000
50000000
40000000
30000000
20000000
10000000
0
123
137
151
165
179
193
gti c
gti b
🟦 gti b
🟥 gti c


O
HO

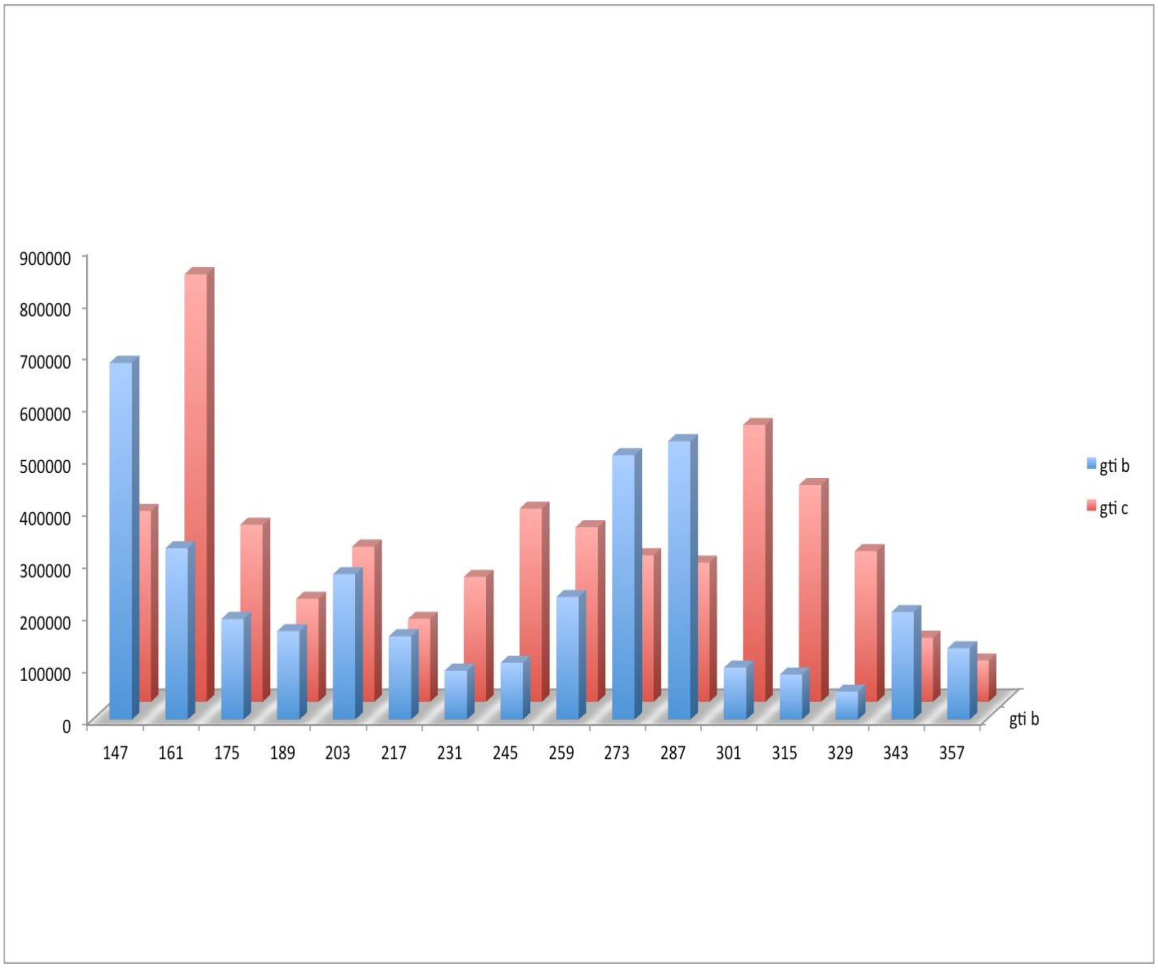

1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
113
127
141
155
169
183
197
gti c
gti b
gti b
gti c


O
OH


1200000
1000000
800000
600000
400000
200000
0
135
149
163
177
191
205
219
gti c
gti b
🟦 gti b
🟥 gti c

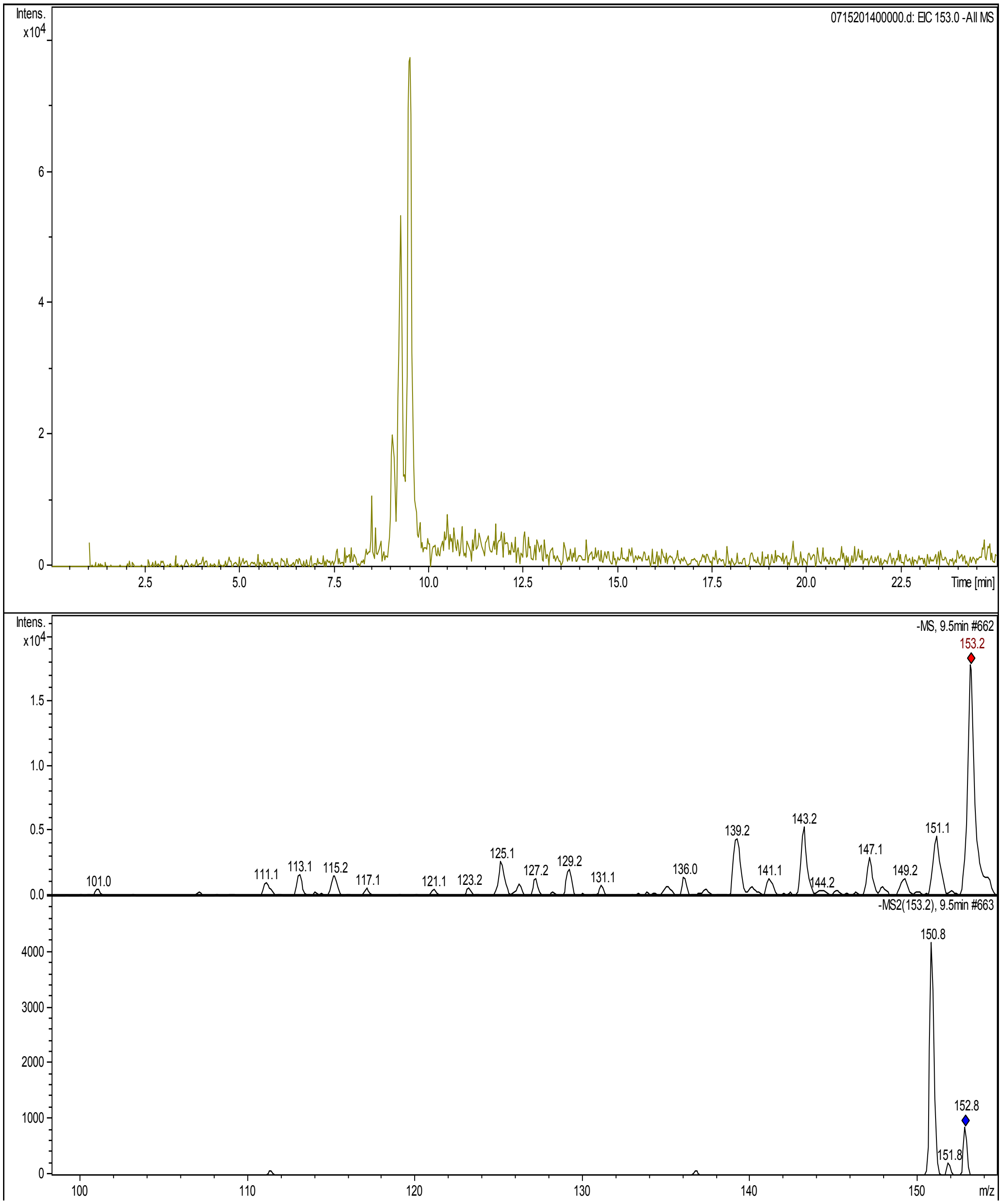


OH
O
HO
O



900000
800000
700000
600000
500000
400000
300000
200000
100000
0
147
161
175
189
203
217
231
245
259
273
287
301
315
329
343
357
gti b
gti b
gti c

The top panel of the figure below is a trace of mass 153 with the left scale being intensity and the bottom trace is time. The bottom panel is mass spectrum at 9.5min and the ms/ms spectrum of 153 ion. The three peaks of the 153 trace indicates there are probably 3 isomers. The mass/mass spectrum of the 153 is representative of the majority of the mass/mass of the bio oil products with neutral losses of 2, 16 and 42.



Appendix C

Upgrading of First Stage and Second Stage Liquids Produced in the IH$^{2®}$ Process

A Report on Upgrading Work on Wood Based and Cornstover
Based Hydrocarbons Carried out at Shell Technology Center on
Liquids Received from Gas Technology Institute

Acknowledgements

The authors wish to acknowledge the contribution from the broader team at Shell Technology Center to the product quality upgrading effort. Specifically, Anuj Chaudhary and Vedant Pande are acknowledged for their contributions towards high throughput catalyst and process parameter screening program, and Harish Balam and Baiju Methale Vilayil are acknowledged for their work on the microflow unit operation. Acknowledgements are also due to the Analytical team for their contributions towards developing deeper understanding of product quality through various stages of upgrading.

Contents

Table of Figures

Executive Summary

The IH$^{2®}$ process is a versatile and feedstock agnostic process to convert woody biomass, agricultural residues and sorted municipal solid waste into hydrocarbon liquid fuels boiling in the gasoline, kerosene and diesel range. The process, in its most widely known configuration, uses a series of two reactors to convert the solid biomass or sorted MSW feedstocks to hydrocarbon fuels. The first reactor is a bubbling fluidized bed reactor containing a proprietary catalyst fluidized in a stream of hydrogen. The solid feedstock is converted to hydrocarbons by devolatilization followed by in-situ hydrodeoxygenation. The products of the first reactor are sent to the second reactor, which is a fixed bed vapor phase hydrotreater. The hydrocarbon product of the second stage reactor is oxygen-free, zero TAN liquid boiling in the gasoline, kerosene and diesel range. The second-stage gasoline and diesel products produced from wood are high quality blendstocks for both US and EU gasoline specifications.

It is desirable to have near R100 quality gasoline and diesel (meeting existing specifications without blending with any petroleum-derived fractions) produced within the IH$^{2®}$ process itself. Near R100 product quality will help improve the economics of the process further, and allow for the bypassing of the existing refining and distribution infrastructure to send the fuels from the IH$^{2®}$ process plant directly to a retail outlet. With this objective, an upgrading program was undertaken to improve the quality of the second-stage gasoline and diesel fuels produced from woody biomass and cornstover. It was demonstrated that the quality of the diesel product could be updated to R100 quality for the US market, i.e. the diesel produced in the IH$^{2®}$ process met all the specifications of ASTM D975 diesel. The upgraded gasoline product met all US gasoline specifications, and constitutes a premium renewable RBOB. It is expected that a blend of upgraded gasoline from the IH$^{2®}$ process with 10% ethanol will meet the anti-knock index requirements in the US. For the EU market, the upgraded gasoline and diesel products were found to be high quality blendstocks, with an estimated blend level of at least 70% (R70 quality). Further development activities are underway to improve the quality of gasoline and diesel for the EU market to near R100 quality.

1. Understanding Liquid Quality

To drive the devolatilization of biomass, the IH$^{2®}$ process employs temperatures of 400-450°C and pressures of 22-35 barg in the first stage. The temperatures employed are 100-130°C higher than those in the hydroprocessing (hydrotreatment) of conventional fossil fuels, while the pressures are comparable to the lowest pressures at which conventional hydrotreatment is carried out. The operating conditions as listed above promote devolatilization of biomass, and help in boosting liquid yields. They are also effective in carrying out complete hydrodeoxygenation of the products of biomass devolatilization, allowing for production of oxygen-free, zero TAN (total acid number) hydrocarbons.

To understand the upgrading challenge, it is necessary to understand the quality of oxygen-free hydrocarbons produced in the 2nd stage. It is also necessary to understand the quality of the first stage intermediate product to evaluate the feasibility of co-processing it in a refinery. An extensive characterization of the first and second stage liquids was therefore carried out which is presented in this section of the report.

1.1. Bulk Property Analyses of First Stage Liquids

The first stage liquids produced from wood and cornstover in the IH$^{2®}$-50 pilot plant at GTI's Des Plaines facilities was analyzed for bulk properties, and a detailed fingerprinting analysis using two-dimensional gas chromatography was also carried out.

Table 1-1 Bulk Property Analysis of First Stage Cornstover and Wood Derived Liquid

Property	Method	Cornstover (1st Stage)	Wood (1st Stage)
Sulfur, ppmw	ASTM D 2622	1491	273
Nitrogen, ppmw	ASTM D 4629	7898	512
Density [15°C] g/cc	ASTM 4052	*	0.8643
Carbon, wt%	ASTM D5291	82.29	85.69
Hydrogen, wt%	ASTM D5291	10.7	10.97
Oxygen, wt%		6.072	3.272
TAN, mg KOH/g	D664	17.4	2.3

*Stable density could not be measured by densitometer due to emulsion-like nature of the sample.

Table 1-1 summarizes the bulk property analyses carried out on first stage cornstover and wood derived liquids. The visual appearance of both cornstover and wood derived first stage liquids was dark (photographs can be seen in the next section) and opaque.

Wood-derived first stage liquid had a high content of heteroatoms (oxygen, sulfur and nitrogen), with oxygen content of approximately 3.3 wt%. Its acid number was 2.3 mg KOH/g. The sulfur content was also quite high at 272 ppmw. For comparison, a fully deoxygenated 2nd stage wood-derived liquid has oxygen below detectable limit (<0.05%) and an essentially zero acid number (<0.01). The sulfur content of 2nd stage wood based liquid is typically 10-30 ppmw. The heteroatom content of wood based 1st stage total liquid product (TLP), while high, is manageable for processing in a typical refinery metallurgy designed for a TAN of around 2. The liquid was also stable and no precipitation of solids was seen during storage. (Precipitation of solid residues upon storage due to condensation reactions of reactive oxygenated and unsaturated molecules is a major problem with incompletely deoxygenated biomass-derived liquids produced by thermal conversion processes).

The picture of cornstover derived first stage liquid, however, was not as encouraging. The liquid was quite unstable during storage and continuous precipitation of solids was observed during storage. To make it easy to handle and analyze the liquid, it was subjected to filtration to remove the solid precipitates. However, the filtered liquid continued to precipitate solids over time. The liquid also had an emulsion-like appearance, and it appeared to contain water droplets in a continuous oil phase.

The heteroatom content was much higher in cornstover derived 1st stage product liquid than in the corresponding wood analogue – oxygen content was about 6 wt%, sulfur content was about 1491 ppmw and nitrogen content was extremely high at about 7898 ppmw. The acid number of cornstover derived liquid was very high at about 17.4 mg KOH/g. The liquid produced from cornstover is thus unstable and corrosive, and the feasibility of processing such a liquid in a typical refinery unit will be a challenged proposition.

1.2. 2-Dimensional GC Analyses of First Stage Liquids

Two-dimensional (2-D) gas chromatography analyses were carried on first stage liquids to understand the nature of chemical species present in the liquid. This information will help in understanding of reaction mechanisms and thus help in proposing strategies for improving product quality and yield structures.

Two-dimensional gas chromatogram separates molecules based on both the vapor pressure/boiling point of the molecule, and on polarity of the molecule. The separation along the horizontal axis in all 2-D chromatograms shown in this section is based on vapor pressure or boiling point of the molecule, whereas the separation along the vertical axis is based on the polarity of the molecule being analyzed. Saturates (alkanes) tend to be appear at the bottom (low retention time on the polar column), and alkenes slightly more towards the top in relation to the alkanes. Linear alkanes are seen as periodic dots at the bottom. Cyclic molecules that are more polar than alkanes and alkenes appear at a higher retention time on the polar axis, and aromatics, which are more polar than cyclics appear further up. The higher the number of fused rings, the more polar the aromatic and it appears further towards the top. Oxygenates have some polarity, eluting away from the bottom, how much depends on the exact nature of oxygenated group. Two-dimensional GC resolves the molecules or groups of molecules in the sample into clusters or bands containing similar types of molecules grouped together, helping in their identification.

Prior to analyses, the samples were phase-separated to obtain a polar extract and a non-polar extract. The phase separation was carried out by dissolving the sample in dichloromethane as a solvent followed by addition of hexane or methanol to separate polar and non-polar phased. The wood sample was also analyzed as-is i.e., without any phase separation. Most of the material in polar and non-polar extracts, even with cornstover derived first stage liquid, was easily within the GC range (well below carbon number of 30).

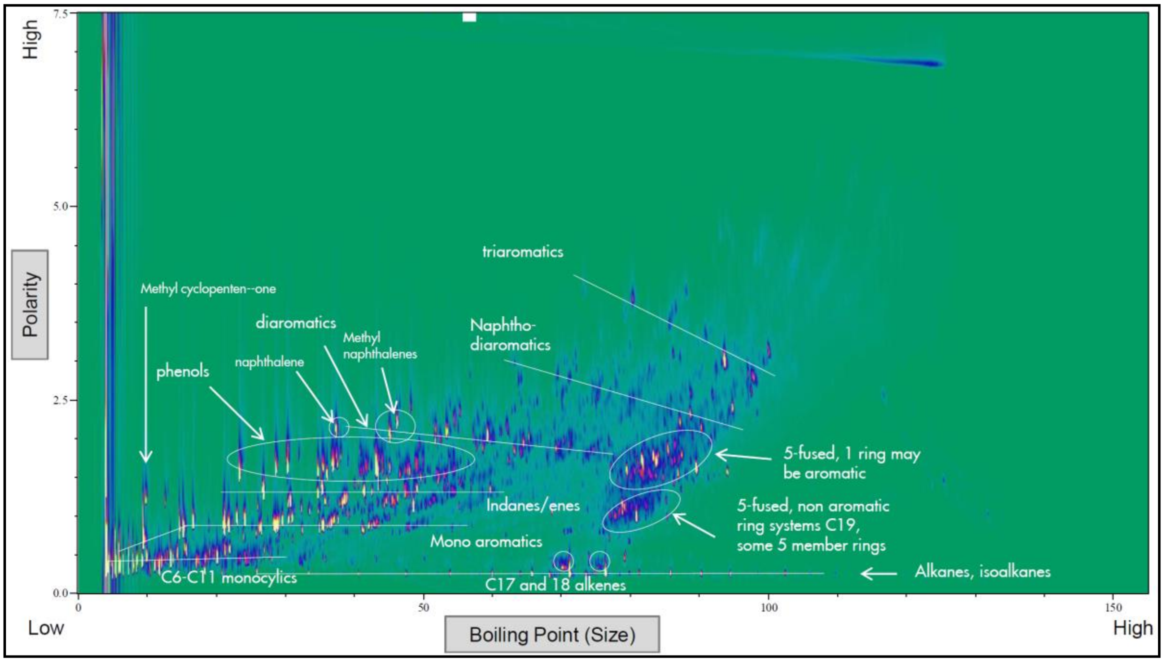


Figure 1 GC×GC with FID (Flame Ionization Detector) chromatogram for first stage wood total liquid product

Figure 1 shows two-dimensional gas chromatogram collected on an instrument with an FID detector for hydrocarbon detection and quantification (GC×GC-FID). Such a detector has a nearly linear response to hydrocarbons, making it possible to identify and quantify the molecular species in the liquid.

As seen in Figure 1, the 1st stage wood derived liquid has a very low content of linear alkanes and branched alkanes (band indicated at the bottom of Figure 1). The most dominant class of molecules in the gasoline range (having 10 or less carbon atoms) is naphthenes (indicated as ‘C6-C11 monocyclics’ in Figure 1), while in the kero/diesel range (C11+ hydrocarbons), aromatics dominate.

The first stage wood derived liquid had about 3.3 wt% residual oxygen. Interestingly, nearly all of this oxygen appears to be present in phenolic compounds, which are derived from the lignin present in the biomass. Oxygenated molecules derived from cellulose and hemicellulose present in the biomass (e.g. levoglucosan, cellobiosan, furan and furan derivatives etc) were not detected at all in the GC×GC analysis, indicating complete deoxygenation of those molecules to corresponding hydrocarbons. It is known from literature that the initial devolatilization temperature (IDT) of lignin is much lower than that of cellulose or hemicellulose. Yet, oxygenates produced from lignin appear to be more refractory in nature (resistant to oxygen removal) than those produced from cellulose and hemicellulose.

An effort was made to quantify the molecules present in wood 1st stage total liquid product. The results of the quantification are presented in Table 1-2.

Table 1-2 Quantification of molecules detected by GC×GC-FID

Compound Group	**Wt%**
C5-C11 Monocyclics (Cycloalkanes and Cycloalkenes)	9%
Linear Alkanes	5%
C17 and C18 Alkene Isomers	1%
Groups of Mostly Saturated Fused Ring Systems	11%
Monoaromatics (1 Ring)	19%
Indanes/Indenes	8%
Phenols	9%
2 Ring Aromatics (Naphthalenes)	9%
Naphthalenes with Additional Saturated Ring	6%
3 Ring Aromatics (Anthracenes/Phenanthrenes)	6%
3 Ring Aromatics with Additional Saturated Ring	2%
Unknowns	15%

As seen from Table 1-2, aromatics are the most predominant species in the liquid followed by naphthenes. Various classes of aromatics noticed in the liquid are monoaromatics (benzene and its derivatives), naphthenic monoaromatics (indanes/indenes), diaromatics (naphthalene and its derivatives), naphthenic diaromatics (naphthalenes with an additional saturated ring), triaromatics (anthracene, phenanthrene and their derivatives), and naphthenic triaromatics (triaromatics with an additional fused saturated ring). Amongst naphthenes, C5-C11 cyclic molecules and poly-fused ring compounds (having 5 fused rings) were seen as predominant species in gasoline and diesel range, respectively. Oxygenated molecules noticed were all phenol and phenol derivatives, accounting for about 9% of the total liquid by mass. Identified alkanes and alkenes accounted for only about 6% of the total liquid.

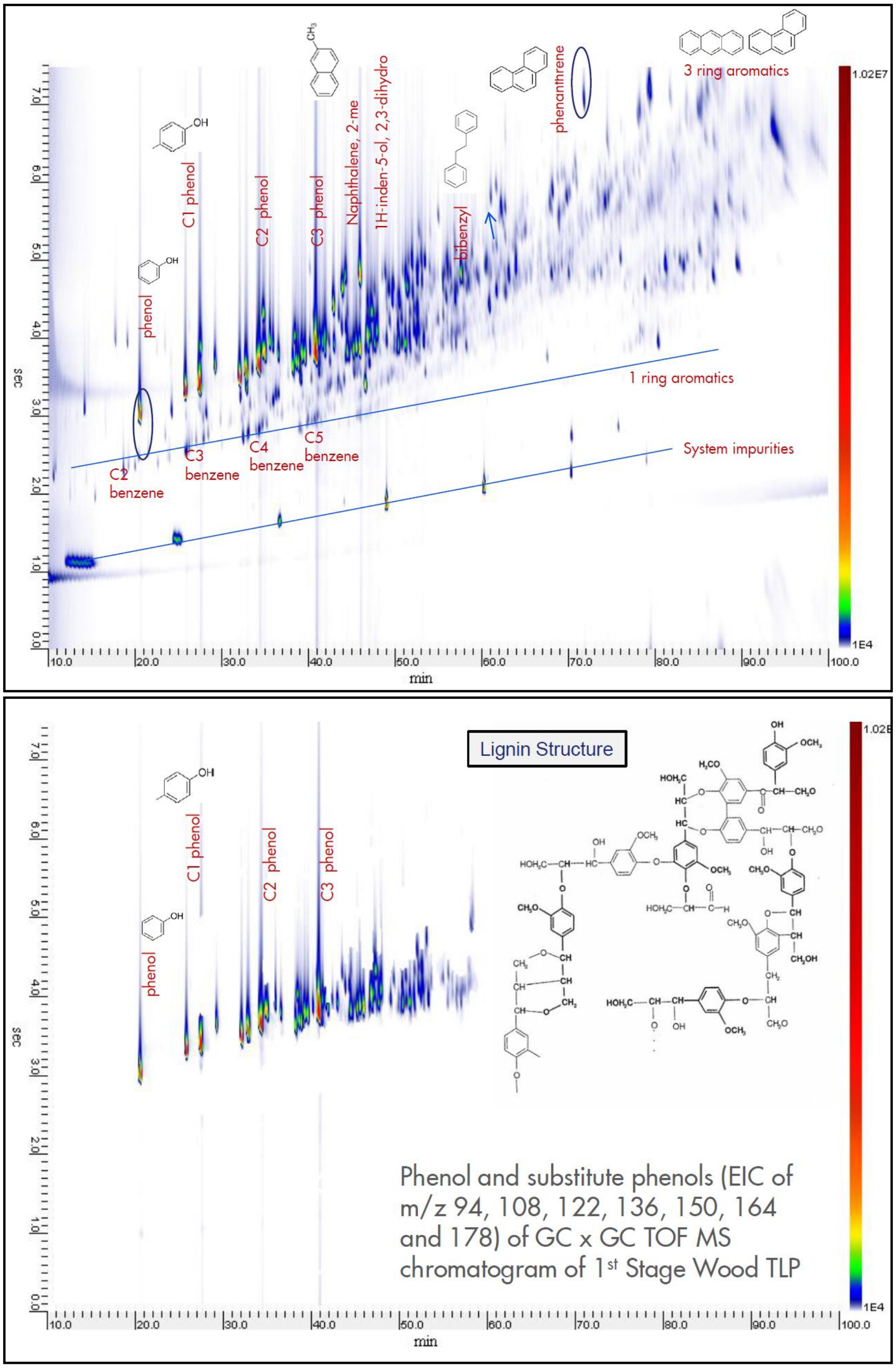


Figure 2 GC×GC TOF-MS chromatogram of polar extract of 1st stage wood TLP (Top), the same chromatogram filter by the charge to mass ratio of ions to reveal phenolics

The 1st stage wood product sample was extracted into a polar phase and an apolar phase by first dissolving it in dichloromethane and then adding a mixture of hexane and methanol to cause phase separation. The polar and apolar phases were then injected into a GC×GC instrument equipped with a time-of-flight mass spectrometer (TOF-MS) for detection. This method of detection allows for detection of a number of hydrocarbons and oxygenated molecules but is less accurate quantitatively. A combination of TOF-MS detector for identification and FID for quantification was employed for identifying and quantifying the species and generated the data reported in Table 1-2. The 2D-chromatogram collected by the GC×GC TOF-MS is shown in the top of Figure 2. Any residual oxygenated hydrocarbons in 1st stage liquid are expected to appear in the polar extract. The analysis of the chromatogram shows phenol and upto C3 phenol derivatives as the only oxygenates in the liquid. Phenolics seen in the product of pyrolysis or hydropyrolysis are produced almost exclusively from lignin in the biomass. This observation indicates that other types of oxygenates produced from cellulose and hemicellulose constituents of biomass are completely converted under the operating conditions of the 1st stage reactor when the biomass feedstock was processed. In hydrodeoxygenation of biomass derived oxygenates, phenolics are thus the equivalents of refractory sulfur compounds (benzothiophenes and dibenzothiophenes) in hydrodesulfurization of conventional fossil-fuel derived feedstocks.

First (1st) stage cornstover product, on the other hand, was difficult to analyze by GC×GC due to unstable nature of the sample. Ignoring the semi-solid precipitates found in this liquid, attempts were made to analyze the rest of the sample. The sample was analyzed by 1D GC-MS after extraction into CH_2Cl_2. Figure 3 shows the 1D-GC chromatogram of the polar extract of the sample.

There were nearly no pure hydrocarbons identified in this sample. All identified molecules had either an oxygen atom or a nitrogen atom in the structure. This observation is consistent with the high oxygen content (about 6 wt%) and high nitrogen content (about 0.8 wt%) in 1st stage cornstover liquid. Even though GC-MS is not fully quantitative technique for analysis, it can be seen from Figure 3 that the most intense peaks can be attributed to phenol and phenol derivatives (methylphenol, ethylphenol, hydroquinone and methyl hydroquinone).5-member cyclic ketones were also seen (cyclopentanone, Corylon).

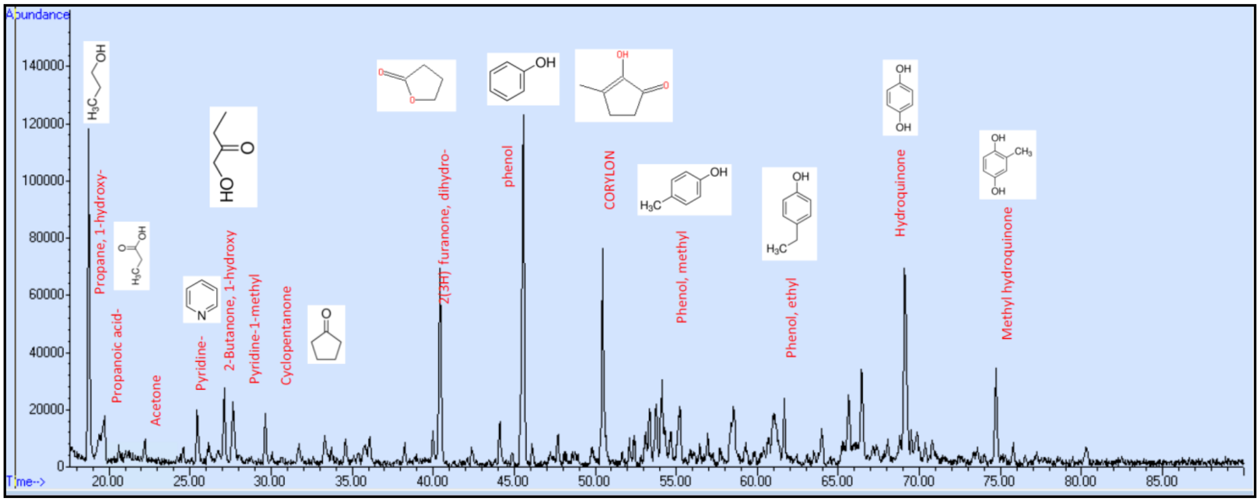


Figure 3 1-D GC-MS chromatogram of polar extract of cornstover liquid showing major components

In conclusion, both first stage total liquid products (wood based and cornstover based) showed a residual oxygen content and residual TAN. However, the wood based product was completely amenable to further processing considering its stability, relatively low TAN of 2.3 and fairly low oxygen content of 3.3 wt%. Both the hydrocarbons and oxygenates in wood based TLP are stable, non-reactive molecules (aromatics, saturated ring compounds and phenolics). Cornstover based TLP, on the other hand, displayed a tendency to precipitate with time which can be attributed to its high oxygen content of about 6 wt% which is present in the form of reactive oxygenated molecules (alcohols, acids, ketones). Its acid number is also quite high at 17.4. Hence cornstover based liquid could not be upgraded further as part of this work.

1.3. Quality of Second Stage Liquid from Wood

The second stage in the IH$^{2®}$ process is a fixed bed vapor-phase hydrotreater. The objective of this reactor is complete removal of all heteroatoms (sulfur, nitrogen, oxygen) to produce pure hydrocarbons. The IH$^{2®}$-50 pilot plant at Gas Technology Institute's Des Plaines campus has produced oxygen-free, zero TAN hydrocarbons from wood. Various batches of wood-derived total liquid product have been prepared and shipped to Shell's R&D facilities overseas for further upgrading to meet US and EU fuel specifications. Before describing the upgrading strategy and results of the upgrading program, the properties of the 2nd stage liquids are described in some detail in this section to elucidate the objectives and challenges in upgrading 2nd stage liquid to US and EU fuel quality specifications.

Distillation of 2nd stage total liquid product

For understanding the properties of various boiling fractions of the 2nd stage total liquid product, it was subjected to fractional distillation following the ASTM D2892 method (batch distillation in a distillation set-up having 15 theoretical stages). Three different fractions were recovered: a gasoline-range fraction (boiling below 150°C), an intermediate fraction (150°C to 180°C) and a diesel-range fraction (boiling above 180°C). Depending on which fuel specifications are targeted, the cut points between gasoline and diesel can be adjusted. The intermediate fraction can either become part of the gasoline pool or the diesel pool based on fuel specifications. Currently, jet fuel is not a prime focus product for the IH$^{2®}$ process. Given very large volumes and long timeframes needed to register jet fuel, the focus for commercialization is on gasoline and diesel.

ASTM D2887 Simulated Distillation

ASTM D2887 boiling curves for the total liquid product, as well as the three fractions as described above, are presented in Figure 4. The TLP had >97 wt% recovery at or below a boiling point of 370°C, indicating essentially no hydrocarbons boiling in the vacuum gasoil range. (ASTM D2887 provides true component boiling points based on a calibration curve. A >97 wt% recovery at or below 370°C on ASTM D2887 scale translates into a >>97 wt% recovery on the ASTM D86 scale.) Another prominent feature noticed was presence of distinct steps in the boiling curve in the gasoline fraction. Such steps are an indication of a discrete number of molecules in the liquid. The steps correlate well with boiling points of pentane (36.1°C), cyclopentane (49°C), hexane (68°C) and cyclohexane (80.7°C). Presence of these C5 and C6 molecules was also confirmed by the DHA PIONA discussed next. The abundance of C5 and C6 molecules in the gasoline range can be explained by the presence of C5 sugars in hemicellulose component of wood, and presence of C6 sugars in the cellulose component.

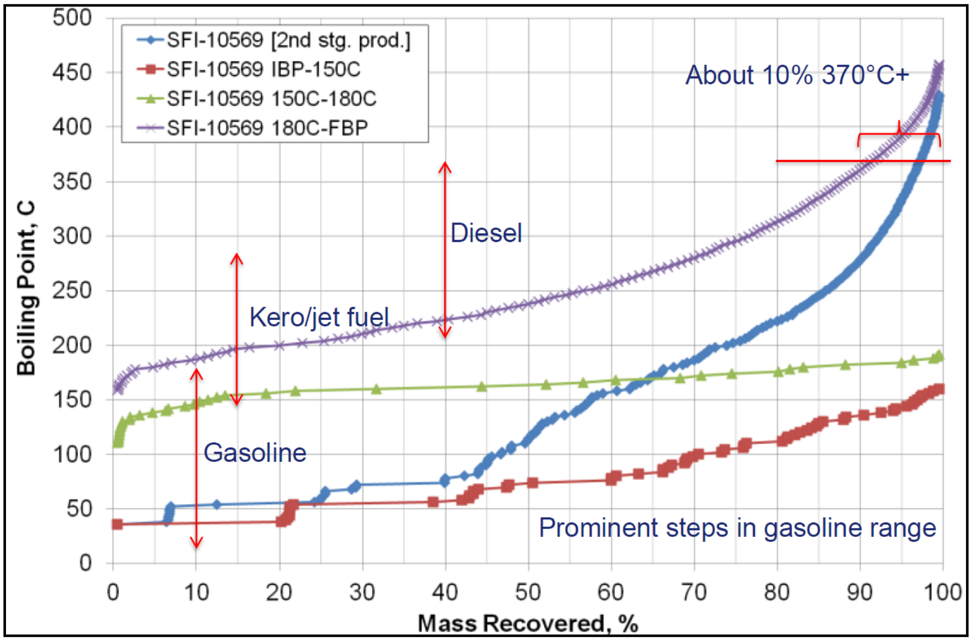


Figure 4 ASTM D2887 Boiling Curves of the TLP and various fractions distilled from the TLP

For the intermediate fraction and the diesel fraction, the boiling curve was smooth, without any steps. More than 90% of the total mass of the diesel fraction, as measured using ASTM D2887, boiled at or below 370°C. Thus, even in the diesel fraction, the concentration of vacuum gasoil range materials was quite low. Any residual 370°C+ hydrocarbons had no impact on the fuel properties as will be described in the next sections.

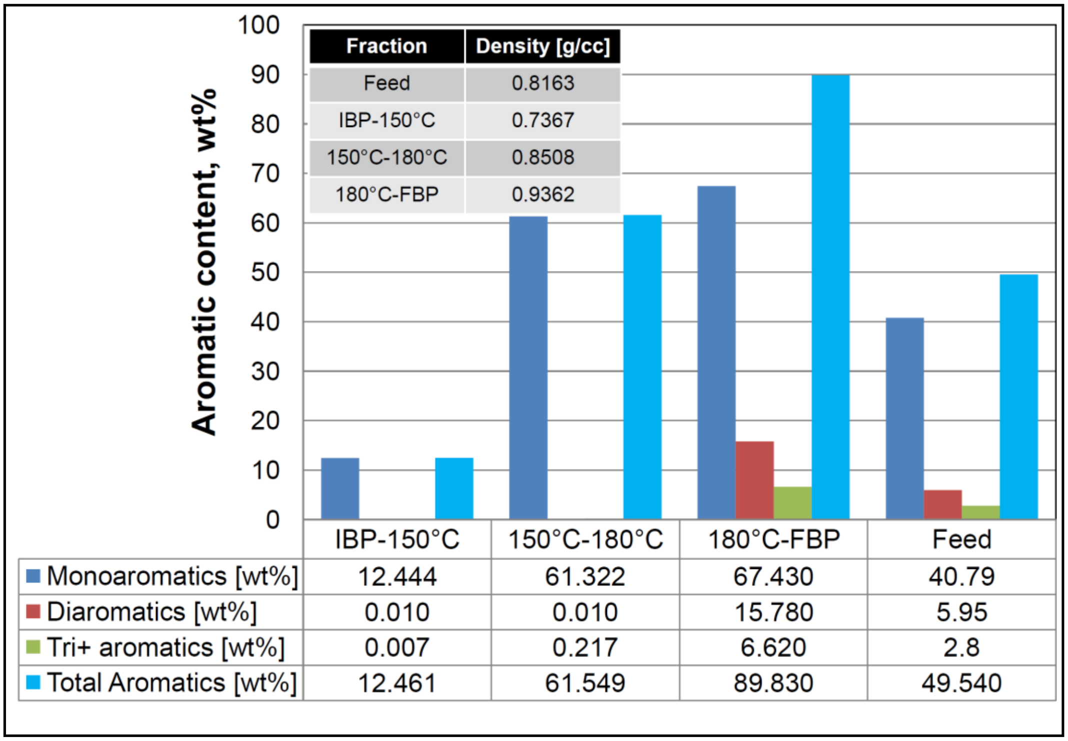
Aromatic Content and Density

The aromatic content of the total liquid product and individual fractions was analyzed using the IP-391 method. It was found that the aromatics were concentrated in the diesel range (Figure 5). While the gasoline fraction (boiling below 150°C) had only about 12.5 wt% total aromatic content, the intermediate cut (150°C-180°C) had about 61.6 wt% aromatics and the diesel fraction (boiling above 180°C) had nearly 90 wt% total aromatics. The amount of polyaromatics in the diesel fraction was also quite high at 22.4 wt%, while gasoline and intermediate fractions had very low polyaromatic content.

While the gasoline fraction had a low aromatic content, its benzene content was about 2 wt%, which is above the summer or winter gasoline specifications for the US and EU regions.

The high aromatic content of the diesel fraction resulted in a high density as well. While the gasoline fraction had a density of 0.734 g/cc, the diesel fraction had a density as high as 0.936

g/cc. Overall aromatic content of the total liquid product was about 49.5 wt% and its density was 0.816 g/cc.



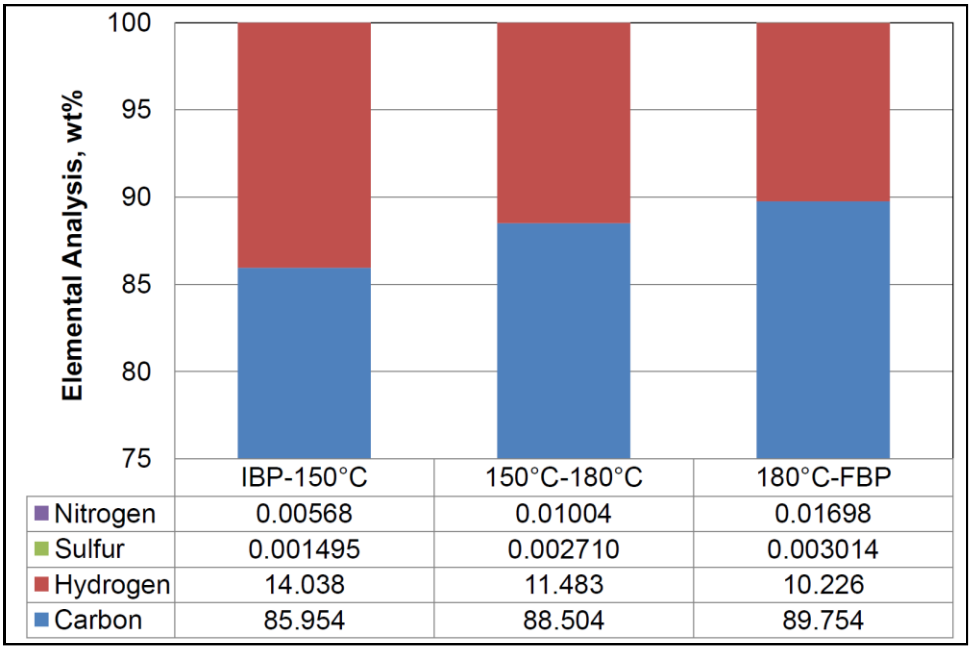
Fraction	Density [g/cc]
Feed	0.8163
IBP-150°C	0.7367
150°C-180°C	0.8508
180°C-FBP	0.9362

	IBP-150°C	150°C-180°C	180°C-FBP	Feed
🟦 Monoaromatics [wt%]	12.444	61.322	67.430	40.79
🟥 Diaromatics [wt%]	0.010	0.010	15.780	5.95
🟩 Tri+ aromatics [wt%]	0.007	0.217	6.620	2.8
🟦 Total Aromatics [wt%]	12.461	61.549	89.830	49.540

Figure 5 IP-391 Aromatics data and density data from TLP and individual fractions

Elemental Analysis

The elemental analysis of the total liquid product and individual fraction is shown in Figure 6. The oxygen content of the liquid was below detection limit in all cases, and the content of other heteroatoms was also low – total sulfur in gasoline fraction was about 15 ppmw and that in the diesel fraction was about 30 ppmw. The atomic ratio of hydrogen-to-carbon for the gasoline fraction was 1.946, which is comparable to a gasoline product meeting ASTM and EU specifications. The diesel product, on the other hand, had a low hydrogen-to-carbon ratio of only 1.358, which is significantly below the ratio of ~1.80 in diesel product meeting ASTM or EU specification.



	IBP-150°C	150°C-180°C	180°C-FBP
🟪 Nitrogen	0.00568	0.01004	0.01698
🟩 Sulfur	0.001495	0.002710	0.003014
🟥 Hydrogen	14.038	11.483	10.226
🟦 Carbon	85.954	88.504	89.754

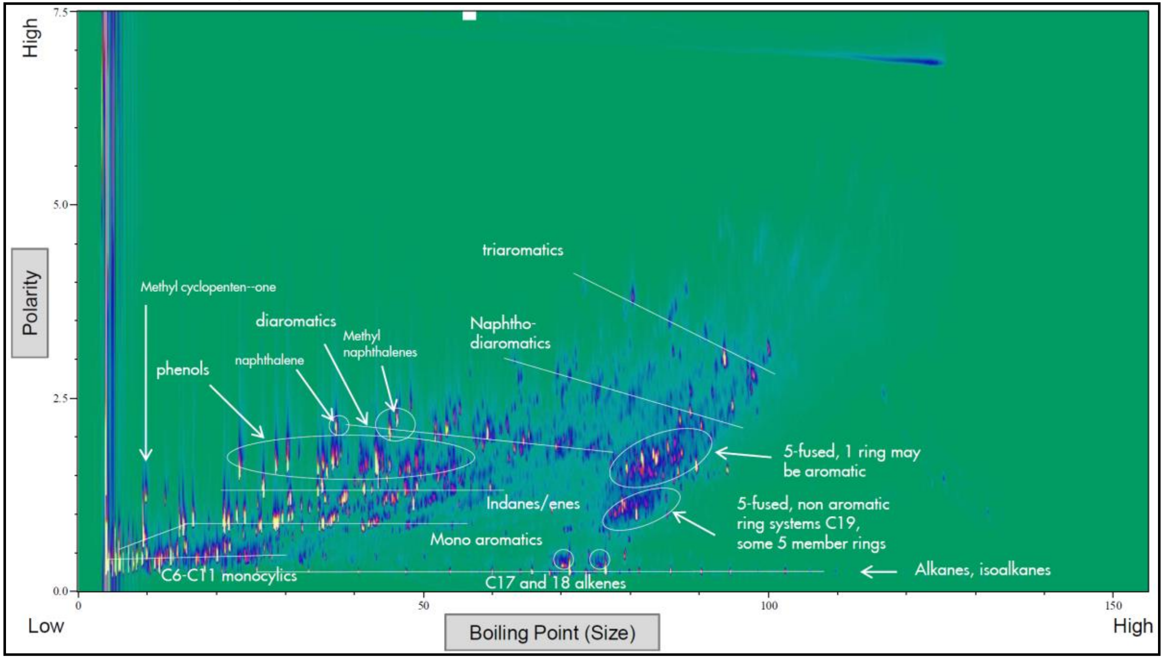
Figure 6 Elemental analysis of various fractions distilled from the total liquid product

The diesel product from the 2nd stage of the IH2® process is, thus, quite hydrogen-deficient.

Detailed Hydrocarbon Analysis (DHA) of TLP

The total liquid produced from wood was subjected to a detailed hydrocarbon analysis (DHA) following ASTM D6730 method. The DHA data was converted to a PIONA graph as shown in Figure 7. The DHA technique used for this analysis analyzes only the front end of the liquid - any hydrocarbons heavier than C14 are not analyzed by the DHA and do not show up on the graph.

There are 3 peaks centered at carbon numbers of 6, 9 and 12 in the graph, with the peak at carbon number 6 having a prominent shoulder at carbon number 5. The peaks can be broadly attributed to hydrocarbons produced from 6-carbon sugars present in cellulose, 5-carbons sugars present in hemicellulose, repeating structures in the phenolics found in lignin containing 9 carbons atoms and dimeric hydrocarbons produced from 6-carbon sugar. As seen in Figure 7, the overall trends seen in the analysis of various fractions described above were confirmed in the DHA graph. For example, the DHA shows aromatics as the most dominant class of molecules for carbon numbers of 8 and above. This observation matches well with the high aromatic content of the intermediate cut (boiling between 150°C-180°C) and the diesel cut (boiling at 180°C and above).



In the gasoline range, naphthenes were noticed as the predominant products, followed by linear alkanes. The high naphthene content is consistent with the observations shown in Figure 1 of a high content of C5-C10 cyclics in the gasoline carbon number range of the first stage liquid from wood.

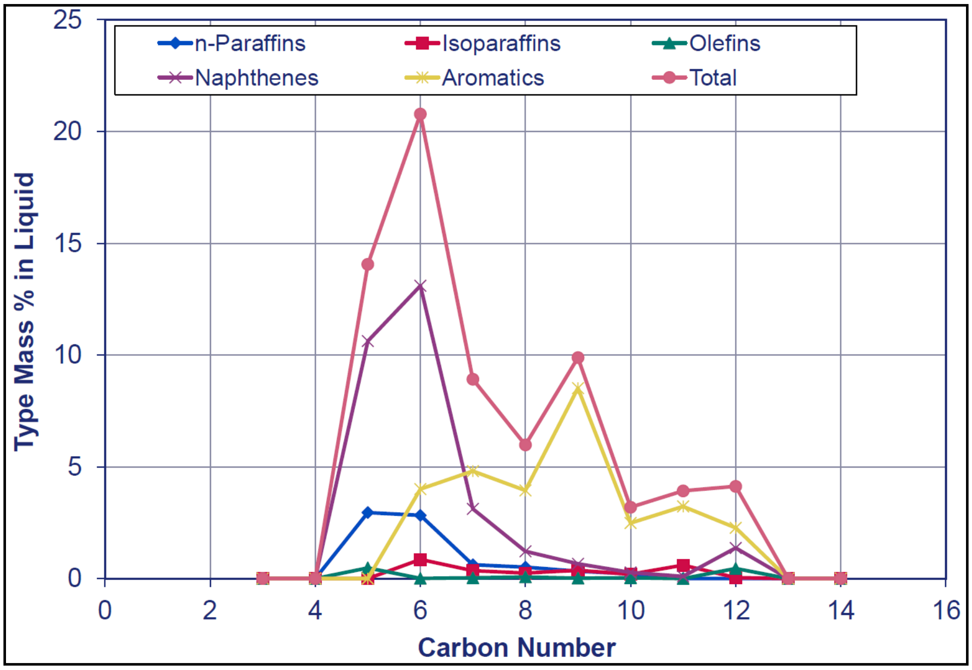


Figure 7 Detailed Hydrocarbon Analysis (DHA) PIONA of total liquid product

2. The Upgrading Challenge

Having established a detailed analysis of both 1st and 2nd stage total liquid product, and various fractions obtained from it, it is now possible to compare the limiting, or challenged, properties against both US and EU specifications. The main parameters on which the 2nd stage diesel product from the IH$^{2®}$ process falls short with respect to US and EU specifications are the aromatic content, the density and the ignition quality (cetane number). These gaps are summarized in Table 2-1.

The US specifications for No. 2-D diesel require a cetane number of 40, while the EU specifications (EN 590 diesel) require a minimum cetane number of 51. 2nd stage diesel product from the IH$^{2®}$ process (defined here as boiling above 150°C, with intermediate cut described above being blended to the diesel fraction), when subjected to a cetane number measurement in a diesel engine, would not combust due to very high autoignition temperature of the aromatic species in the diesel. In addition to the cetane number, US specifications also require compliance with one of the two requirements: either the cetane index must be 40 or above, or the total aromatic content must be below 35 vol%. EU specifications do not impost any limit on the total aromatic content. However, they do require a cetane index of 46 and above. 2nd stage diesel product from the IH$^{2®}$ process had a total aromatic content of 83 wt%, and had a cetane index of 27. It should be noted here that the cetane index does not correlate well with cetane number for the highly aromatic diesel product from the IH$^{2®}$ process, and for the 2nd stage product, cetane index over-estimates cetane number.

Table 2-1 Limiting (difficult-to-meet) US and EU diesel specifications for wood-based IH$^{2®}$ diesel product

	No. 2-D Diesel (North America)	**EN 590 Diesel (Europe)**	**2nd Stage Wood-Based Product, 150°C+ Cut**
Cetane Number, min	40	51	Not measurable[1]
Aromatics, max	35 vol% or[2]	No specification	83 wt%
Cetane Index, min	40	46	27[3]
Polyaromatics, max	No specification	11 wt%	17 wt%
Density@15°C	No specification	0.820-0.845	0.907
Hydrogen content	No specification	No specification	10.5 wt%

1. The fuel does not combust in a diesel (compression ignition) engine.
2. US specifications require compliance with either the maximum aromatic specification or the cetane index specification, but not both.
3. Cetane index overestimated the cetane number of the 2nd stage diesel product of IH$^{2®}$ process, considering lack of combustion in internal combustion engine. Cetane index-cetane number correlation is quite poor for diesel products from the IH$^{2®}$ process.

EU diesel also has a maximum specification of 11 wt% on polyaromatics. The 2nd stage diesel product, with 17 wt% polyaromatics, does not meet this specification. EU diesel has a density specification of 0.820-0.845 g/cc. The 2nd stage diesel product of the IH$^{2®}$ process, with a density of 0.907 g/cc, does not meet this specification either. US diesel does not have any specification for polyaromatics or for density, and it is adequate to simply meet the total aromatic specification and cetane number specification for US diesel. While neither US nor EU diesel have any specification on the hydrogen content, as shown in Table 2-1, the total hydrogen content of 2nd stage diesel is only 10.5 wt%, much lower than the typical hydrogen content of ~13% found in US and EU diesel.

All of the product quality deficiencies in the 2nd stage diesel with respect to US and EU specifications boil down to high aromatic nature of the diesel. Aromatics in the diesel contribute to the high autoignition temperature and consequent lack of combustion in a diesel engine, and also contribute to the high density of the product. Thus, the challenge of upgrading the quality of the diesel product from the IH$^{2®}$ process boils down to the challenge of destroying aromatics in this diesel, while retaining the overall economic attractiveness of the process. This means conducting aromatics conversion under conditions of pressure comparable to those in the 1st and 2nd stages of the IH$^{2®}$ process (20-35 barg). Compared to typical pressures used for aromatic saturation in refinery operations, these are moderate pressures.

Coupled with the problem of high aromatic content of the 2nd stage diesel, the issue of excessive benzene concentration in the gasoline fraction also needs to be addressed. However this reaction is an aromatic saturation reaction similar to reactions to which aromatics in the diesel range can be subjected, and hence the upgrading challenge for gasoline and diesel collectively can be considered as an aromatic saturation challenge.

In addition to saturating the aromatics to corresponding naphthenes, other strategies of minimizing aromatics can also be looked into. These include selective ring opening and mild hydrocracking. In selective ring opening (Figure 8, bottom), one or more of the rings in the ring structure of an aromatic is opened to produce a minimally branched monoaromatic molecule or a minimally branched alkane molecule. Ideally, selectivity towards mono-branched monoaromatics or mono-branched naphthene is desirable as these molecules tend to have high cetane numbers. However, doing ring opening selectively remains a challenge, and an elusive goal even after significant amount of R&D effort being put into it, for example, to upgrade light cycle oil produced in a cat cracker unit in a refinery. Often, multiply branched alkanes, poly-branched monoaromatics or naphthenes are produced, which have a lower cetane number than the starting aromatic molecule. While aromatic saturation can be done with both sulfided metal systems (similar to sulfided NiMo/alumina catalysts used for hydrotreating) and reduced base or noble metal systems, ring opening requires a combination of acid sites (in the form of a zeolite or amorphous silica-alumina) and metal sites.

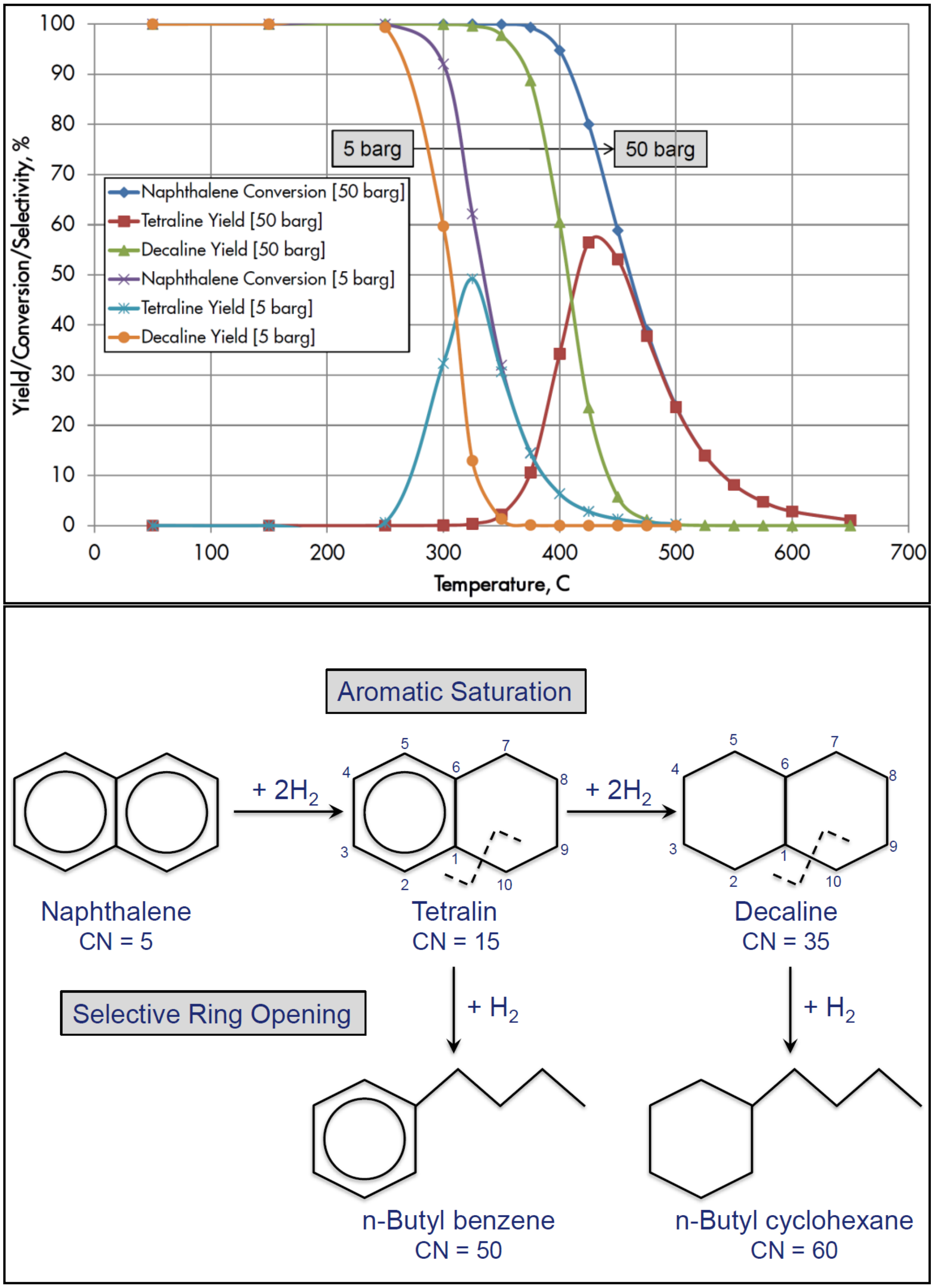


Figure 8 (Top) Illustrative diaromatics saturation equilibrium at 5 barg and 50 barg and (bottom) illustrative gains to be had in cetane number for aromatic saturation and for selective ring opening

In mild hydrocracking pathway, the aromatics in the diesel range are subjected to hydrocracking on a zeolite or amorphous silica-alumina based catalyst also containing metal sites. The hydrocracking pushes some of the aromatics from the diesel range to the gasoline range (hence benefitting the octane number of the gasoline), while some are saturated and ring opened but remain in the diesel range. Mild hydrocracking results in some loss of diesel product and some loss of overall liquid product as well. While we have investigated all three strategies for liquid quality improvement, greatest success has been obtained with aromatic saturation, and hence this report focuses on description of catalyst systems used and results obtained with aromatic saturation as strategy for upgrading.

Aromatic saturation is an equilibrium-limited reaction, and it is promoted by high pressure or low temperatures. Illustrative diaromatic saturation equilibrium is shown in Figure 8, top. The Figure at the top shows the results of Gibbs free-energy based equilibrium calculations for the aromatic saturation scheme shown in the bottom (Naphthalene → Tetralin → Decaline) conducted using SimSci Pro/II® process simulation software. As seen from this Figure, an increase in pressure from 5 barg to 50 barg broadens the window of temperature over which complete diaromatic saturation is expected by about 100°C, from 250°C and lower temperatures at 5 barg to ~350°C and lower temperatures at 50 barg. Likewise, lower temperatures promote aromatic saturation. For example, at 250°C, both 5 barg and 50 barg conditions lead to nearly complete naphthalene conversion, while at ~350°C, only the higher pressure condition leads to nearly complete naphthalene conversion. One of the attractive features of the IH$^{2®}$ process is its ability to produce pure hydrocarbons from biomass or residual feedstocks under moderate conditions of pressure. It is desirable, therefore, that any upgrading of the 2nd stage liquid products be done successfully at pressures that are comparable to that used in the 1st or 2nd stage of the process, namely, between 20 and 35 barg. Because of equilibrium limitations, this means the catalyst selected must be active at temperatures of 300°C or lower. A preferred operating condition (based on thermodynamic considerations alone) is 25 barg and 200-250°C.

Two types of catalysts systems were investigated for aromatic saturation. The first type of catalysts include sulfided catalysts, most commonly sulfided NiMo or CoMo on an alumina support, similar to the catalysts used in conventional hydrotreating of fossil-fuel derived feedstocks in petroleum refining. These catalysts are active at temperatures above 300°C, and consequently require pressures of 50 barg or above to produce adequate hydrogenation activity. The other catalyst system includes non-sulfided i.e. reduced metal systems, comprising of base metals (e.g. nickel) or noble metals (e.g. Pt or Pd) supported on an oxidic support. The later type of catalysts are quite active at temperatures below 300°C and pressure of 20-35 barg, provided the feed being hydrogenated does not contain any appreciable amounts of sulfur. Often, with reduced metal system, a hydrodesulfurization step using sulfided CoMo or sulfided NiMo catalysts must be carried out to reduce the sulfur content and gain optimal activity out of a reduced metal catalyst system used in a subsequent, downstream reactor. If the feedstock being hydrogenated has low sulfur levels, it is advantageous to use reduced metal systems and gain the benefits of mild operating conditions. If the feedstock has high sulfur content, it is necessary to desulfurize the feed first and then use reduced metal systems for aromatic saturation. Alternatively, sulfided catalyst systems may be used to do both desulfurization and aromatic saturation in one reactor; albeit at the expense of having to operate the single reactor under more severe operating conditions than needed for reduced metal systems.

The sulfur content of the 2nd stage product is already quite low (15 ppmw for the gasoline fraction and about 30 ppmw for the diesel fraction), and the use of reduced metal systems become feasible. Some of the reduced metal systems we investigated required a hydrodesulfurization step to be carried out before aromatic saturation, while some systems had a high sulfur tolerance and could carry out aromatic saturation without any prior hydrodesulfurization. However, since both US and EU specifications for ultra-low sulfur diesel require a sulfur content of less than 10 ppmw, it is anyway necessary to carry out hydrodesulfurization to manage the product sulfur content (even though the reduced metal catalyst can tolerate the higher sulfur content).

3. Results of Upgrading of 1st Stage Product

The integration of hydropyrolysis and *in-situ* catalytic conversion of the products of hydropyrolysis in the 1st stage (bubbling fluidized bed) of the IH2® process, offers the possibility of producing a substantially fully deoxygenated liquid in the first stage itself. This possibility has indeed been demonstrated in the IH2®-50 pilot plant and IH2®-Miniature Benchscale Unit (MBU) at Gas Technology Institute in a test with woody biomass as the feedstock - the oxygen content of the liquid hydrocarbon product was lowered from about 10.4 wt% (corresponding to an extent of deoxygenation of 76%) to about 0.5 wt% (corresponding to an extent of deoxygenation of 99%) when the residence time of vapors in the first stage was increased from 1.6 sec to 2.6 sec. The 1st-stage-only IH2® process can potentially be deployed in a distributed manner to convert the solid feedstock into a densified, nearly oxygen-free hydrocarbon liquid, and the liquid thus produced can be transported to and upgraded in a centralized processing facility to produce on-spec gasoline and diesel. The upgrading can be done neat (i.e. without mixing the liquid product of the IH2® process with any fossil-derived feedstocks), or in a co-processing mode. In this work, efforts were focused on doing neat processing, as the learnings of neat processing can readily be extended to co-processing.

As described in §1.1. Bulk Property Analyses of First Stage Liquids, the oxygen in wood-based 1st stage liquid is contained predominantly in the phenolic compounds. No other oxygenated molecules were found to be present in this liquid to any significant extent. This liquid is therefore quite stable during handling and storage. While its total acid number (TAN) of 2.3 mg KOH/g is slightly higher than the typical TAN of about two that the refinery infrastructure is designed for, handling of this liquid with existing refinery infrastructure is possible. Cornstover-based 1st stage liquid, on the other hand, has a very high TAN of 17.4. It also has a high oxygen content of 6.1 wt% and a high nitrogen content of 0.8 wt%. It is quite unstable and shows a tendency to precipitate solids upon storage. We made attempts to dilute this liquid with fossil-derived gasoil feedstocks (i.e. do co-processing instead of neat processing, given its high TAN). While the liquid did appear to be miscible with gasoil, there was precipitation of solids even after blending it with gasoil. At the typical upgrading temperatures of 300°C-400°C, the polymerization reactions that form the precipitates in the cornstover based 1st-stage liquid are expected to worsen and result in clogging of the reactor system or process tubing. Therefore, it was decided not to upgrade the cornstover based 1st stage liquid and focus our attention on wood-based 1st stage liquid instead.

The upgrading of wood-based 1st stage liquid was carried out in a high-throughput fixed-bed catalyst testing unit having 16 parallel reactors manufactured by *hte*® GmbH. The catalysts were chosen to address 2 different objectives at the same time.

1. Remove the residual oxygen, sulfur and nitrogen to produce a true hydrocarbon liquid from the feedstock.
2. Explore changing the gasoline to diesel ratio in the product either in favor of more gasoline or more diesel (in addition to, of course, removing the residual heteroatoms and producing a true hydrocarbon liquid).

To address the first objective, several sulfided NiMo or CoMo catalysts were used in the test and a range of different operating conditions were investigated. The liquid hourly space velocity was kept nearly constant at ~0.7 mL feed/(mL catalyst.hr). The gas-to-oil ratio was kept fixed at 750 Nl H_2/kg feed. At each operating condition, the product was analyzed for residual oxygen and other elements (sulfur, nitrogen, carbon and hydrogen). Given aromatics are the most dominant molecules in the 2nd stage product of a two-stage $IH^{2®}$ process, the upgraded product from the one-stage $IH^{2®}$ process was analyzed for its aromatic content as well. To measure the gasoline to diesel ratio in the upgraded 1st-stage product, the product was subjected to a simulated distillation following the ASTM D2887 method.

The elemental composition of the product of various catalyst systems, under different operating conditions studied, is shown graphically in Figure 9. As seen in this Figure, at a temperature of 320°C and a pressure of 32 barg, all the catalyst systems achieved complete deoxygenation of the feed, and had produced essentially oxygen-free hydrocarbon product. It should be noted that this temperature is about 80-100°C lower than the typical temperatures employed in the 1st stage of the $IH^{2®}$ process. The sulfur content of the product was also lowered from 273 ppmw to 10-30 ppmw under these relatively mild operating conditions. The nitrogen content was lowered from 512 ppmw in the feed to 20-110 ppmw in the product. All of the catalyst systems thus achieved a significant heteroatom removal under all conditions studied.

As seen in Figure 9, the hydrogen to carbon atomic ratio showed a marginal increase from about 1.53 to about 1.60 after the upgrading. The hydrogen to carbon ratio in typical diesel product meeting all US or EU specification is typically about 1.80. The modest boost achieved in the hydrogen to carbon ratio indicates that the product of the processing of the 1st stage liquid requires further upgrading to improve its quality against US or EU specifications. A stronger hydrogenation function is required to improve the quality further, and such a stronger hydrogenation function can be provided by a reduced metal catalyst system (As discussed in §2, the Upgrading Challenge). Since the first stage product has a high sulfur content of 273 ppmw, reduced metal systems can’t be used with this feed. The central upgrading facility for first stage hydrocarbon liquid, therefore, will require multiple reactors to do heteroatom removal, interstage H_2S removal and finally either aromatic saturation or a combination of aromatic saturation and ring opening.

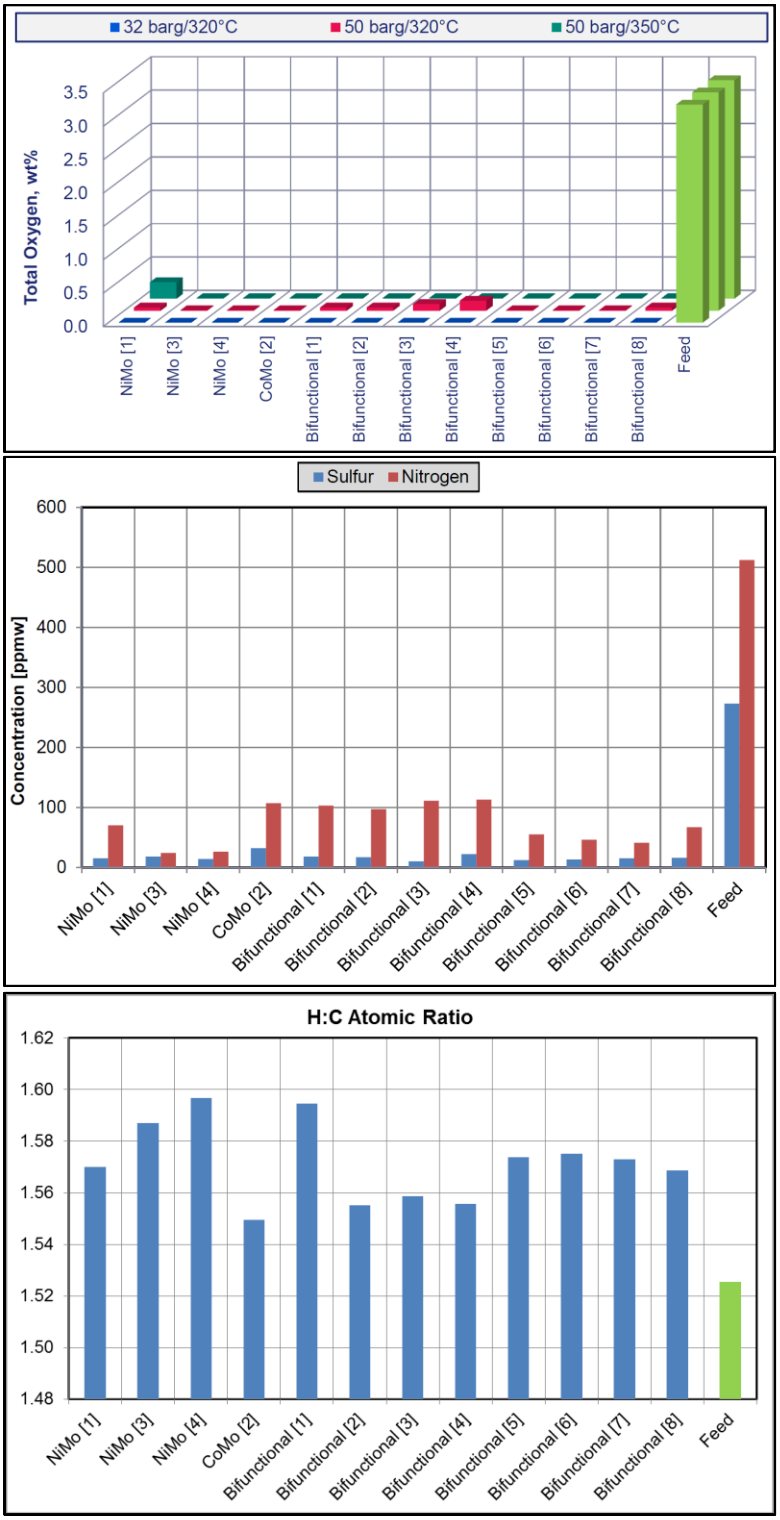


Figure 9. Elemental Composition of the Product for Various Catalyst Systems Studied. Oxygen content of the product at various operating conditions (top), sulfur and nitrogen content (middle) and the hydrogen to carbon atomic ratio (bottom)

To understand the quality of the hydrocarbon liquid produced further, the liquid product of all reactor systems was subjected to ASTM D2887 SIMDIS analysis and IP-391 aromatics analyses. These analyses are shown in Figure 10.

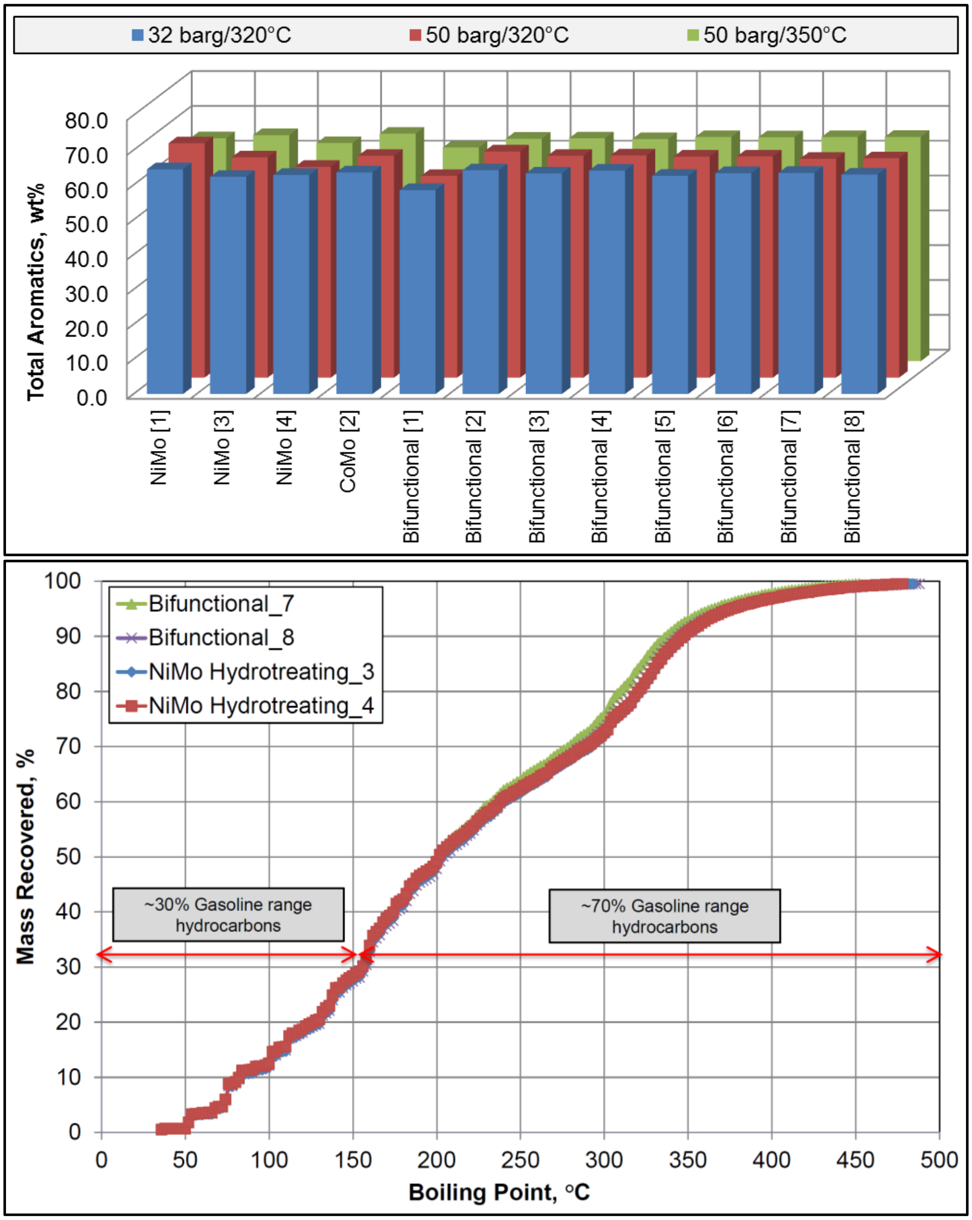


Figure 10. Total aromatic content of the products of various reactors (Top); ASTM D2887 SIMDIS analyses of the hydrocarbon TLP of different reactor systems (bottom)

In spite of the different types of catalyst systems used for the upgrading of the first stage wood-based liquid, the quality of the product produced was remarkably similar across the different catalyst systems, within the window of different operating conditions investigated. The total aromatic content of the product (Figure 10, top) varied from about 58 wt% to 67 wt% for all the catalyst systems studied at a temperature range of 320°C-350°C, and pressures of 32 barg and 50 barg. The distribution of the aromatics across mono-, di- and tri+ aromatics was also very similar for the various catalyst systems. The SIMDIS D2887 boiling profiles for four of the systems studied are shown in Figure 10, bottom. The curves show a nearly complete overlap with each other. These two observations support the conclusion that the predominant chemistry happening on the catalyst surface under the operating conditions investigated is heteroatom removal, without a major shift in the boiling range of the hydrocarbon liquid product produced.

It should be pointed out here that the typical gasoline to diesel ratio in the hydrocarbon total liquid product (TLP) from wood in a two-stage IH$^{2®}$ process varies from 70 : 30 to 65 : 35. Here gasoline is defined as hydrocarbon liquid boiling at or below an atmospheric equivalent boiling point of 150°C, and diesel is defined as hydrocarbon liquid boiling above an atmospheric equivalent boiling point of 150°C, recovered by a D2892 distillation. The ratio of SIMDIS D2887 yields of gasoline and diesel is comparable to this range. As seen in Figure 4, the gasoline to diesel ratio as measured from D2887 data for 2nd stage wood-based TLP is 60 : 40. The ratio of gasoline to diesel in the products of hydrodeoxygenation of wood-based first stage TLP, on the other hand, is found to be quite different at 30 : 70. The unexpectedly different ratio of gasoline to diesel in the product of upgrading of the first stage wood-based liquid can be explained in two different ways (or by a combination of both).

1. The first stage hydrocarbon liquid from wood has about 3.3 wt% oxygen. The first-stage aqueous product from wood has about 1.91 wt% carbon. The pH of the aqueous product from the first stage is 5, while the aqueous product from a typical two-stage IH$^{2®}$ process has a pH of 8-9.5. The presence of carbon in water and oxygen in hydrocarbon product suggests the potential for partitioning of some of the lighter, naphtha-range oxygenated hydrocarbon molecules into the aqueous phase. Such a portioning of lighter oxygenates molecules into water would also lower the pH of the water produced, which is indeed experimentally observed. It is thus plausible that the some of the light naphtha range oxygenated molecules have been lost to the aqueous phase and have simply not been recovered into the hydrocarbon phase, making the hydrocarbon phase appear richer in diesel. This would be an artefact and not a true representation of the yield profile from wood at the end of the first stage. The aqueous phase was however not preserved for detailed analysis, and hence it is not possible at this stage to verify this hypothesis.

2. Given the oxygen content of 3.3 wt%, and the presence of phenolics in the liquid, it is also plausible that there are slow polymerization reactions going on within the first stage liquid during storage. A period of several months had passed between the collection of these liquids at

GTI's facilities in Des Plaines, and there upgrading at the Shell Technology Center. These polymerization reactions will also lower the gasoline to diesel ratio in the final product.

In conclusion, it is possible to upgrade the first stage liquid from wood in a centralized facility by hydrodeoxygenation and produce oxygen-free hydrocarbons. The product of hydrodeoxygenation of the first stage liquid is rich in aromatics and will require further upgrading to meet fuel property specifications (similar to those applied for the second stage liquid, described in §4 below). The centralized upgrading facility is thus likely to have a hydrotreating unit and an aromatic saturation or ring opening/mild hydrocracking unit, followed by a product work-up section. The facility would need to be supplied with hydrogen (or would need to have its own hydrogen manufacturing unit). Given the most capex-intensive equipments in a two-stage IH$^{2®}$ process are the hydrogen manufacturing unit, the solid handling system and the first stage reactor, all of which will also be required for a one-step IH$^{2®}$ process, the choice between doing a central upgrading of first stage liquid or doing distributed upgrading at the two-stage IH$^{2®}$ plant site, is a decision that will have to be driven by economics.

4. Results of Upgrading of 2^{nd} Stage Products by Aromatic Saturation

In this section, we present results on upgrading of diesel and gasoline fractions of the 2^{nd} stage TLP from the $IH^{2®}$ process by aromatic saturation to address the fuel quality deficiencies identified above. We begin by describing the results achieved with sulfided catalyst systems, and then move on to results obtained with reduced metal systems. Initially, the results obtained using a high-throughput screening tool 'hte$^{®}$ unit' (containing 16 parallel reactors of 0.5 cc catalyst volume each) are described. The most optimal systems were then studied on a larger 'microflow' scale (reactors with catalyst volume of about 30 cc), and these are then described.

4.1. Screening of Sulfided Catalyst Systems using the hte$^{®}$ Tool

Initially, the focus of the program was on the use of sulfided catalyst systems (sulfided NiMo and CoMo supported on alumina) to conduct the aromatic saturation. Several NiMo and CoMo catalyst systems were selected for testing. Eleven of these catalysts were loaded (with some in duplicates) on a ~0.5 cc scale each in hte$^{®}$ reactors. The catalysts used in hte$^{®}$ unit are prepared by crushing commercial sized extrudates and sieving to obtain 40-80 mesh fraction. The diesel-range fraction of the 2^{nd} stage product (boiling above 150°C based on ASTM D2892 distillation) was used as the feed for the reaction. Given the low sulfur content of the 2^{nd} stage diesel product (~30 ppmw), the feed was doped with DMDS (dimethyl disulfide, CH_3-S-S-CH_3) to keep the catalysts fully sulfided. The amount of DMDS added was such that the H_2S concentration in the gas phase, assuming complete conversion all sulfur in the doped feed to H_2S, would be about 1500 ppmv. The liquid hourly space velocity (LHSV) for all reactors was kept constant at approximately 1 mL feed/(mL catalyst.hr). The ratio of hydrogen to the feedstock at reactor inlet was either 1200 Nl H_2/kg feed, or 2000 Nl H_2/kg feed. The ratio was selected to have 3-5 times the stoichiometric excess of hydrogen for complete conversion of the aromatics in the feed to corresponding naphthenes. Prior to introduction of the feed, the catalysts were converted to their sulfide form by a liquid-phase sulfidation procedure. The procedure uses a temperature program applied under hydrogen and sulfiding feed flow. Straight-run gasoil spiked with DMDS was used as the sulfiding feed.

The sulfided catalysts typically are most active above 300°C, therefore, temperatures of 330°C, 360°C and 390°C were investigated. These relatively high temperatures necessitate the use of high pressure to make the aromatic saturation reaction thermodynamically favorable, and pressures were varied between 50 barg and 100 barg for various temperatures. Each operating condition (combination of temperature and pressure) was operated for a minimum of 3 days, and the samples collected on the 3^{rd} day were subjected to a full suite of analyses. The analyses done on the samples include measurement of aromatics by IP-391 method, density measurement, SIMDIS D2887, elemental analysis and estimation of cetane index using the four-point method (ASTM D4737).

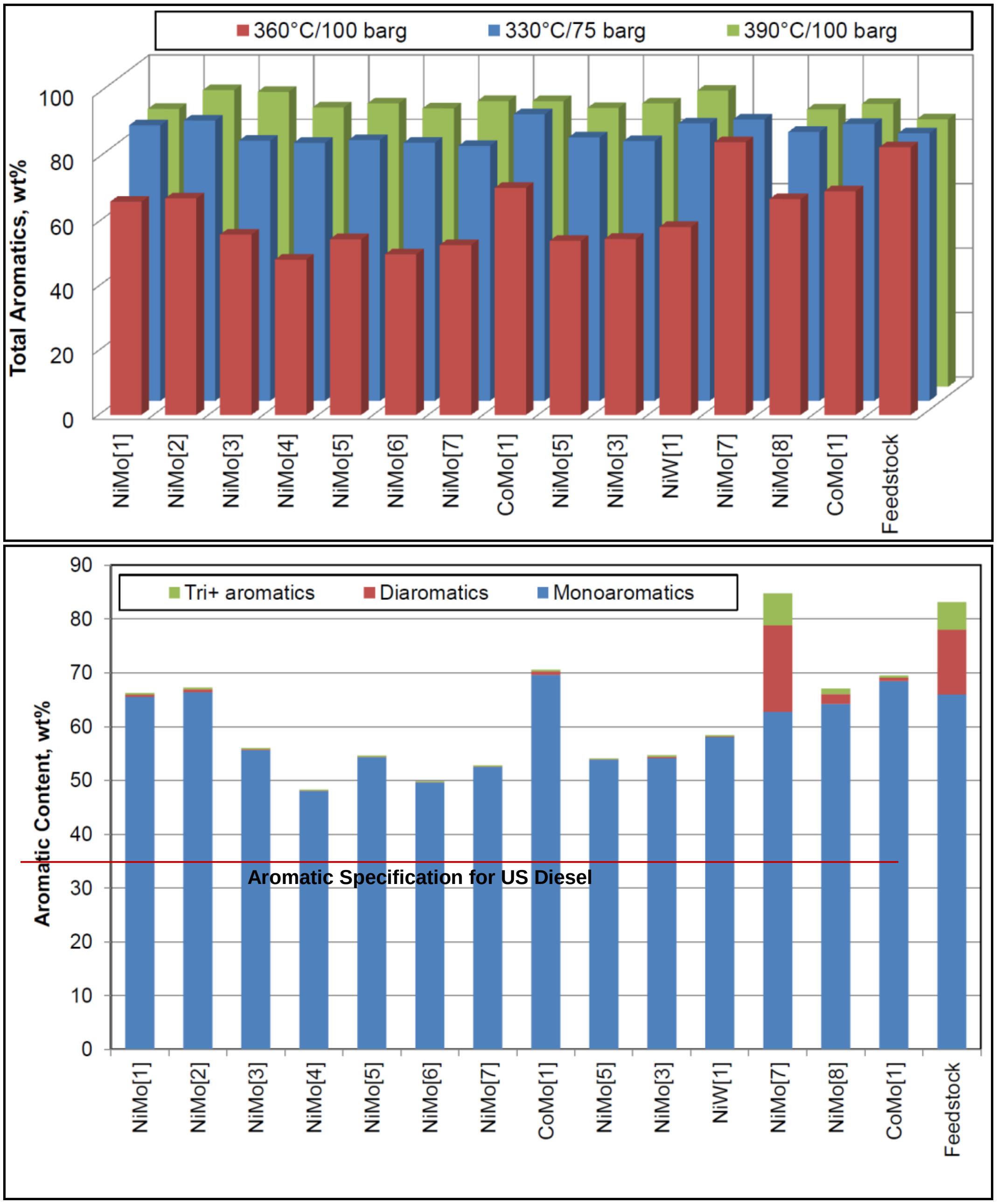


Figure 11 Summary of aromatic saturation results with sulfided catalysts systems (Top); Aromatics distribution under most optimal condition studied (bottom)

A summary of much of the dataset generated in this experiment is shown in Figure 11. At 330°C and 75 barg, none of the catalysts showed any appreciable activity towards aromatic saturation, and the total aromatic content was comparable or only marginally lower than that in the feed. To promote higher aromatic saturation, pressure was increased to 100 barg and temperature was increased to 360°C to get higher catalyst activity. At this condition, the most active catalyst (NiMo[4]) achieved 42% reduction in total aromatic content, and more than 99% reduction in polyaromatics. While the aromatic content in the product was lowered to 48 wt% with the most optimal combination of catalysts and operating conditions, it was still substantially higher than the US diesel specification of 35 vol%. At temperatures higher than 360°C at 100 barg pressure, thermodynamics is no longer favorable to the aromatic saturation reaction. Pressures above 100 barg were not investigated, as such high pressures deviate from the philosophy of keeping the IH$^{2®}$ process a moderate pressure process and would impact the economics of the process negatively.

Even under the most optimal condition, product density was reduced only to 0.8693 g/cc, about 0.025 units higher than the maximum density specification for EU diesel. Cetane index for the feed was 27.25, and for the product under the most optimal conditions, the cetane index increased to 30.01. Since cetane index is not a reliable measure of cetane number, a derived cetane number (DCN) measurement was done. DCN involves an engine test with a small compression ignition engine and is an approved ASTM method (ASTM D7170). Since the product generated from any one hte$^{®}$ reactor at any one operating condition wasn't adequate for a DCN test, a representative sample was prepared by mixing the products with lowest aromatic content from multiple reactors to have a sample containing about 60 wt% total aromatics, mainly monoaromatics. Even with a sample with this relatively high aromatic content, the sample did ignite in a cetane engine and gave a derived cetane number of 25 (an effective cetane increase of 25 units). It was decided to target deeper aromatic saturation based on this result. Since sulfided catalysts are typically not used for deep aromatic saturation, non-sulfided, base and noble metal based reduced metal catalysts were chosen as focus for subsequent investigation in hte$^{®}$ unit.

4.2. Screening of Reduced Metal Catalyst Systems using the hte$^{®}$ Tool

Several base-metal (nickel) based and noble metal (Pt, Pd and bimetallic systems) based hydrogenation catalysts supported on silica, alumina or titania were selected as candidates for screening using the hte$^{®}$ tool. Eleven different catalyst systems were studied, some in duplicates to ensure reactor to reactor repeatability. The 150°C+ fraction of the 2nd stage total liquid product was used as the feed for the test. The feed had about 30 ppmw sulfur. The feed used was not subjected to any desulfurization treatment prior to testing it for aromatic saturation with reduced metal systems, given the relatively short duration of the high-throughput screening test (2-3 weeks) and the purpose of such a test (identifying most optimal system for further testing). As described later, when the most promising system was tested on a larger scale, the feed used was subjected to hydrodesulfurization followed by aromatic saturation. Similar to the test with sulfided catalyst, the liquid hourly space velocity (LHSV) was kept fixed at approximately 1 mL feed/(mL catalyst.hr). The hydrogen to diesel feed ratio was kept fixed at 1200 Nl H_2/kg feed, which is about 3 times the stoichiometric amount of hydrogen needed for complete conversion of aromatics in the feed to corresponding naphthenes. Prior to the introduction of the feed into the reactors, the active metals on the catalyst were reduced to zero oxidation state in a flow of hydrogen with an appropriate temperature program applied. The reduced metal catalysts are active at temperature range of 170°C to 300°C. Three temperatures of 200°C, 240°C and 300°C were investigated. The low temperature activity of these catalysts facilitates aromatic saturation even at lower pressures, and hence most of the testing was done at a pressure of 25 barg. The 300°C condition was also evaluated at a pressure of 50 barg. Similar to the test with sulfided systems, each operating condition (combination of temperature and pressure) was run for a minimum of 3 days, and the samples collected on the 3rd day were subjected to full analyses. The analyses done on the samples include measurement of aromatics by IP-391 method, density measurement, SIMDIS D2887, elemental analysis and estimation of cetane index using the four-point method (ASTM D4737). Both feed and product samples were also analyzed using a 2-dimensional GC equipped with a flame ionization detector for detailed speciation. Finally, pooled sample from the best performing catalysts was subjected to a derived cetane number (DCN) test.

Figure 12 summarizes the results obtained with the reduced metal catalysts under various operating conditions at a glance. As seen in this Figure, the reduced metal system display a high aromatic saturation activity even under very mild operating conditions of 200°C-240°C/25 barg. Nickel-based reduced metal catalysts were found to be more active than noble metal based catalysts under the conditions studied with this feed. They achieved the same aromatic reduction (40%-45%) at 25 barg and 200°C as achieved by NiMo sulfided systems at 100 barg and 360°C. When temperature was increased from 200°C to 240°C at the same pressure of 25 barg, the extent of aromatic saturation increased from 40% to 68%, and all of the nickel-based catalyst systems produced product that meets the maximum specification of 35% for US diesel. When temperature was increased further from 240°C to 300°C at the same pressure of 25 barg, thermodynamic limitation on aromatic saturation became apparent, and the extent of aromatic saturation reduced from 68% to only 23%. The negative effect of higher temperature on aromatic saturation equilibrium could be easily countered by increasing the pressure - when pressure was increased from 25 barg to 50 barg at 300°C, the most active nickel based catalyst achieved greater than 72% aromatic reduction.

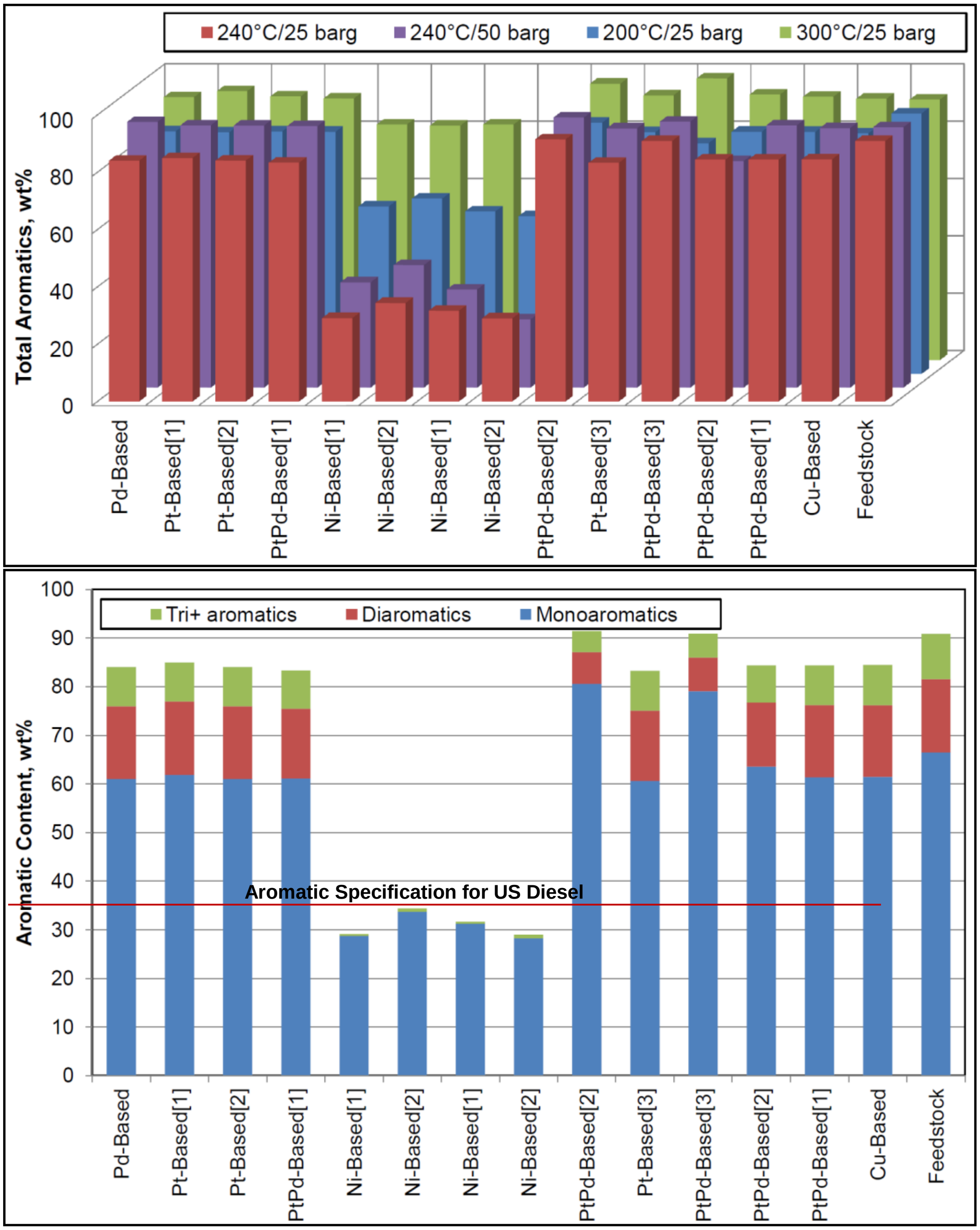


Figure 12 Summary of aromatic saturation results with reduced metal systems (Top); Aromatics distribution under most optimal condition studied with various reduced metal systems (bottom)

Given the goal of maintaining the operation of the entire IH$^{2®}$ process, including the fixed-bed 2nd stage liquid product upgrading section, the operating condition of 240°C/25 barg with nickel based systems appeared promising for further scale-up. The detailed analysis of the product upgraded on nickel based catalysts at this condition showed a density of 0.8708 g/cc. While this density is higher than the maximum density specification of 0.845 g/cc for EU diesel, greater than 0.05 units of density reduction was achieved with aromatic saturation alone. The cetane index estimated using the 4-point method was 34.50, showing a >7 units increase in the cetane index over the feed. The hydrogen to carbon atomic ratio also showed a significant increase from 1.37 for the feed to 1.69 for the product, although it fell short of the stated target of 1.80. The sulfur content of the product was also extremely low (<2 ppmw), as the nickel based catalyst also picks up the sulfur from the feed. The best products from nickel-based catalysts were all pooled together to generate adequate sample for a derived cetane number test. The resulting sample had about 40% aromatics. This sample did ignite in a compression ignition engine and had a derived cetane number of 36. Thus, a 36 unit cetane improvement was seen with the pooled product. GC×GC-FID analyses of feed and product showed aromatic saturation to be the mechanism of aromatic removal, and production of naphthenes from the aromatics in the feed without any further conversion of the naphthenes produced. There was no increase in the linear or branched alkane content of the product in relation to the feed.

Overall, the strategy of using reduced metal based catalyst systems for aromatic reduction appeared quite promising. It was decided to investigate this strategy further on a somewhat larger ‘microflow’ scale, and the results of microflow tests are described in the next section.

5. Microflow Unit (MFU) Scale Upgrading of 2nd Stage Diesel and Gasoline

Detailed analysis of the 2nd stage gasoline and diesel fractions was presented in §1.3. Quality of Second Stage Liquid from Wood. As a summary, the main upgrading objectives for gasoline and diesel are restated below.

1. Increase the cetane number of the 2nd stage diesel for both the US and EU. For US, attempt to meet the specification of a cetane number of 40 without adding any blendstock or cetane improvers. For EU, improve the value of the diesel as a blendstock for producing final diesel product with a cetane number of 51.

2. Reduce the density of the 2nd stage diesel to improve its value as a blendstock for EU diesel.

3. Reduce the aromatic content of 2nd stage diesel to meet US and EU aromatics specifications.

4. Reduce the sulfur content of 2nd stage diesel to meet ultra-low sulfur diesel specifications in the US and EU.

5. Reduce gasoline benzene content from 2 wt% to 0.6 vol% (summer gasoline) or 1.3 vol% (winter gasoline).

Given the superior performance of nickel-based reduced metal catalyst for aromatic saturation, this catalyst was selected for aromatic saturation. Nickel-containing catalysts are tolerant to a few ppm levels of sulfur in the feed, but are deactivated irreversibly when exposed to feeds containing sulfur. The rate of deactivation depends on the sulfur content of the feed. With feed containing 2 ppmw of sulfur, the catalyst is expected to have a useful life of about 1.5 years. Since the diesel fraction contains about 30 ppmw sulfur after the 2nd stage, it is necessary to remove this sulfur from the feed before subjecting it to aromatic saturation using the nickel based catalysts. Further, while benzene in gasoline can be removed using the same aromatic saturation strategy, it is undesirable to subject the entire 2nd stage TLP to aromatic saturation. Doing so will severely degrade the octane number of gasoline as non-benzene aromatics in gasoline will also be saturated by the catalyst to corresponding naphthenes. Replacement of high-octane aromatics with very low-octane naphthenes in gasoline, at a penalty of added hydrogen consumption, is an undesirable consequence of subjecting full-range gasoline to hydrodesulfurization and aromatic saturation. Hence, it was proposed to distil the gasoline fraction and recover only benzene-rich stream of this fraction, and subject it to aromatic saturation along with the entire diesel fraction of 2nd stage TLP. Most of the benzene in gasoline (>80%) was presented in the fraction boiling between 60°C and 80°C when distillation was carried out according to the ASTM D2892 method. Such an upgrading scheme addressing gasoline benzene content and diesel cetane number challenges together is presented in Figure 13.

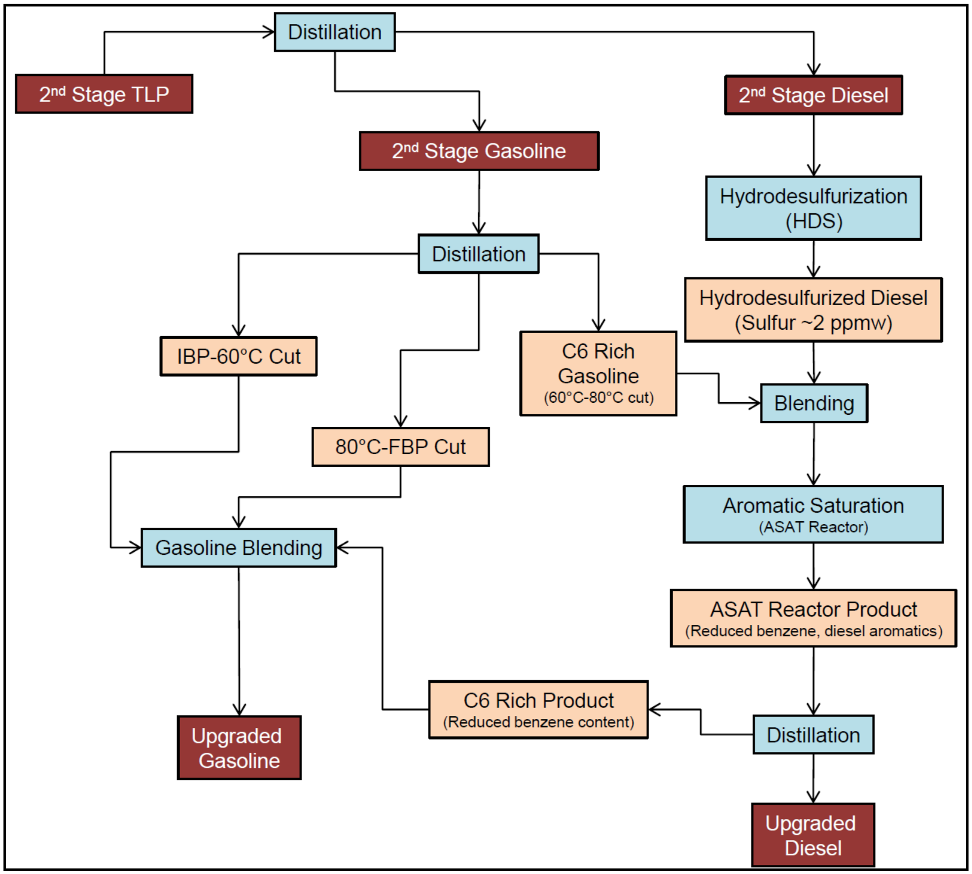


Figure 13 2nd stage gasoline and diesel upgrading simulation carried out on microflow units

After aromatic saturation, the product is distilled again to separate the upgraded diesel fraction from the upgraded gasoline-boiling fraction. The gasoline boiling fraction is blended back into the rest of the gasoline pool (gasoline fractions boiling below 60°C and above 80°C). The cut-point between gasoline and diesel was dependent on which specifications were being targeted. For US specifications, 200°C was chosen as the cut-point between gasoline and diesel (for the first distillation of 2nd stage TLP), while for EU specifications, a cut-point of 150°C was chosen.

5.1. Results of Microflow-Scale Upgrading Simulation of 3rd Reactor Train with 2nd Stage Wood Based Product as the Feed

As described above, microflow units (MFUs) have a catalyst volume of about 30 cc and use commercial-sized catalysts in extrudate form (typically trilobes of 1.3 mm nominal diameter, and 3-5 mm in length). First the diesel feed was hydrodesulfurized to reduce its sulfur content to ~1 ppmw, and the product of hydrodesulfurization was collected. The hydrodesulfurization catalyst used was a sulfided CoMo catalyst supported on alumina commercially available from CRI/Criterion. Prior to the introduction of the feed the hydrodesulfurization catalyst was subjected to a liquid-phase sulfidation treatment. To ensure no sulfur contamination between sulfidation feed and actual test feed (the 2nd stage diesel product of the $IH^{2®}$ process), the unit was thoroughly flushed with a light solvent (typically heptane) before introducing the test feed. The hydrodesulfurization step was carried out at a pressure of 32 barg, and the temperature applied was between 330°C and 333°C. The hydrogen gas to liquid feed ratio was kept at 250 Nl H_2 per liter of liquid feed. The liquid hourly space velocity was maintained at 1 lit feed/(lit catalyst.hr).

Figure 14 shows an evolution of the sulfur content of the HDS reactor product as a function of catalyst age. As seen in this Figure, it was possible to maintain extremely low product sulfur content of 1 ppmw consistently over several hundred hours of catalyst age with the catalyst system and operating conditions chosen. With 1 ppmw sulfur in the product of HDS reactor (which is feed to the aromatic saturation reactor), catalyst life of 2-3 years can be expected for the nickel based reduced metal catalyst, which makes the upgrading process commercially feasible.

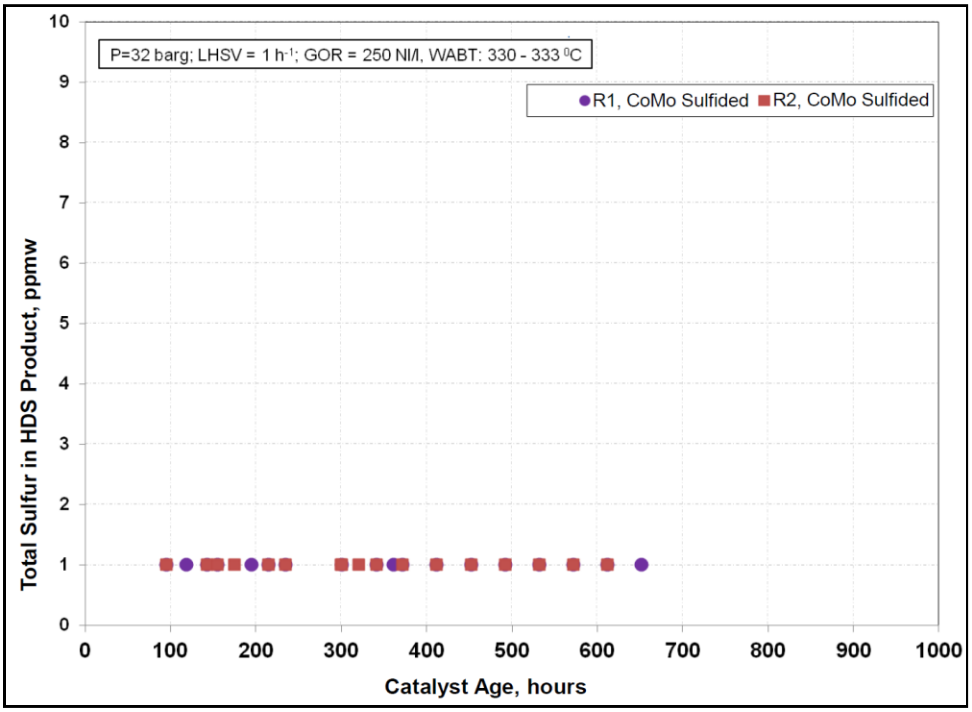


Figure 14 Total sulfur content of the total liquid product of hydrodesulfurization reactor as a function of catalyst age

Complete analyses of the feed and product to the HDS reactor are shown in Table 5-1. The feed to the HDS reactor had 32 ppmw sulfur, while the product had only 1 ppmw sulfur. There was a minor decrease in the density after upgrading of 0.009 units. While the total aromatics content remained unchanged after the HDS step, there was an increase in monoaromatics and a decrease in di- and tri+ aromatics, indicating saturation of polyaromatics even with the CoMo based catalyst under these conditions. There was a minor shift in boiling point towards the gasoline range as indicated by a reduction of ~20°C in the initial boiling point, although the 5 wt% recovery point shifted down by only 2°C.

Table 5-1 Properties of the feed to the HDS reactor and the diesel fraction of the product

Parameter	**Method Used**	**HDS Feed (150°C+)**	**HDS Product (150°C+)**
Total Sulfur, ppmw	MultiTek	32	1
Total Nitrogen, ppmw	MultiTek	99	5
Carbon, wt%	ASTM D5291	88.92	89.09
Hydrogen, wt%	ASTM D5291	10.64	10.96
Density [g/mL, 15°C]		0.9149	0.9060
Monoaromatics, wt%	IP-391	57.2	66.9
Diaromatics, wt%	IP-391	12.7	6.8

Tri+ Aromatics, wt%	IP-391	7.2	4.4
Total Aromatics, wt%	IP-391	77.1	78.1
SIMDIS	ASTM D2887		
IBP		136	117
5%		158	156
10%		162	161
20%		182	180
30%		200	198
40%		214	212
50%		232	232
60%		258	256
70%		292	290
80%		318	318
90%		356	354
95%		388	384
98%		422	418
FBP		460	456

In summary, the sulfided CoMo catalyst removed sulfur from the 2nd stage diesel to produce a product with 1 ppmw sulfur, while saturating about 43% of the polyaromatics in the feed to monoaromatics. This product was collected for use as feed to the aromatic saturation reactor.

Separately, gasoline fraction was distilled to recover the benzene-rich fraction (60°C-80°C cut). The benzene-rich gasoline fraction was then blended with hydrodesulfurized diesel, and resulting blend had about 1 ppmw sulfur. The blend was then subjected to an aromatic saturation step over the nickel based reduced metal catalyst. About 35 cc of aromatic saturation catalyst was loaded in a microflow reactor, and the nickel was reduced to its metallic state in a flow of hot hydrogen prior to introduction of the feed. The aromatic saturation reactor was operated at a pressure of 32 barg and a liquid-hourly space velocity of 1 lit feed/(lit catalyst.hr). The hydrogen to liquid feed ratio was maintained at 1000 Nl H_2/lit feed. The reaction was carried out at a temperature of 200-205°C. Aromatic saturation is a highly exothermic reaction, and in commercial operation, either a liquid quench (by diluting the feed with inert/saturated product) or a gas quench (by injecting hydrogen interstage) is practiced. However, on MFU reactor scale, such quenching is not necessary, as the heat of exotherm can easily be dissipated to the reactor wall and to the furnace surrounding the reactor and a runaway is avoided.

Table 5-2 Properties of the blended feed product (distilled diesel cut) of aromatic saturation

Parameter	Method Used	HDS Diesel (150°C+)/ Naphtha 60°C-80°C Cut	ASAT Diesel Cut (150°C+)	Gasoline (After blending)
Sulfur, ppmw	MultiTek	1	1	18
Nitrogen, ppmw	MultiTek	6	<1	12
Carbon, wt%	ASTM D5291	88.4	86.32	85.95
Hydrogen, wt%	ASTM D5291	11.6	13.97	14.30
Density, g/mL at 15°C	ASTM D4052	0.8686	0.8600	0.7385
Benzene, wt%	DHA	1.158	NA	0.204
Monoaromatics, wt%	IP-391	54.7	6.9	8.8
Diaromatics, wt%	IP-391	5.1	0	0
Tri+ aromatics, wt%	IP-391	3.8	0	0
Total Aromatics, wt%	IP-391	63.5	6.9	8.8
Cu Strip Corrosion		NA	1A (Pass)	<1A (Pass)

The upgraded product was distilled to separate diesel, which was subjected to a detailed analysis. Adequate upgraded product was generated to do both typical laboratory analyses (elemental analysis, SIMDIS, density, GC×GC, PIONA etc) and fuel property testing at a 3rd-party laboratory. About 2 lit each of gasoline and diesel products were produced for both US and EU fuel testing at 3rd-party laboratory, which included an engine test as well.

Table 5-2 shows the analyses of the blended feed to the aromatic saturation reactor, and those of distilled products (diesel recovered from the distillation of the aromatic saturation product, and gasoline prepared by blending the C6-rich gasoline fraction distilled after aromatic saturation and the unprocessed 2nd stage gasoline cuts). As seen from this Table, the total aromatics in the diesel are reduced by more than 90% from 77.1 wt% in the diesel feed to the HDS reactor to only 6.9 wt% in the product. The diesel product produced is an extremely low sulfur diesel - it has only 1 ppmw sulfur. The density of the diesel is reduced from 0.9149 g/cc to 0.8600 g/cc after the aromatic saturation step. The hydrogen to carbon atomic ratio also improved substantially from 1.43 for the 2nd stage diesel to 1.93 for the 3rd stage diesel, which is comparable to the retail diesel sold in the US and EU. These results largely parallel those achieved in the smaller hte® unit.

Finally, the upgraded fuels were subjected to fuel quality testing in a 3rd-party laboratory. The diesel product was compared to US diesel specifications ASTM D975 and gasoline was compared against ASTM D4814-10b. The upgraded diesel was found to have a cetane number of

43.7, which exceeds the cetane number requirement of 40 under ASTM D975. The upgraded diesel met every specification it was tested for, except the T90 specification and lubricity specification. It is relatively straightforward to meet these specifications by minor tweaking of the boiling range of the product, and by addition of lubricity improvers (nearly all ultra-low sulfur diesel fuels require lubricity improvers). Thus, the upgrading strategy produced a fully renewable diesel fuel from solid biomass that can meet all specifications for US diesel and can be sold at retail outlets without having to use any blendstocks of petroleum origin. The fuel properties which were tested against ASTM D975 specification are summarized in Table 7-1 in the Appendix.

Upgraded gasoline also met the two quality gaps identified in the 2nd stage product - the benzene content was lowered from 2 wt% to 0.2 vol%, which is well within the specifications for winter (1.3 vol%) and summer (0.62 vol%). The copper strip corrosion rating also improved from Class 2 before upgrading to Class 1A after upgrading. It was noticed, however, that the anti-knock index (AKI) for upgraded product was only about 79. This reduction in octane number resulted from two factors: (1) When diesel was saturated, the reduction in initial boiling point of diesel resulted in the production of a gasoline-range hydrocarbon stream as a byproduct after distillation. This stream contains naphthenic gasoline range molecules. Naphthenes have a poor octane value, and when this stream was blended back into the gasoline pool, the AKI of gasoline was lowered as a result. (2) Benzene, a high octane molecule in gasoline, was over-saturated. The product had a benzene content of only 0.2 vol%. The specification allows upto 1 vol% benzene. Benzene is a high octane component and it should be saturated only to the extent needed to meet the specifications. The main challenge with gasoline is, therefore, to increase the octane number for which several upgrading strategies are being pursued.

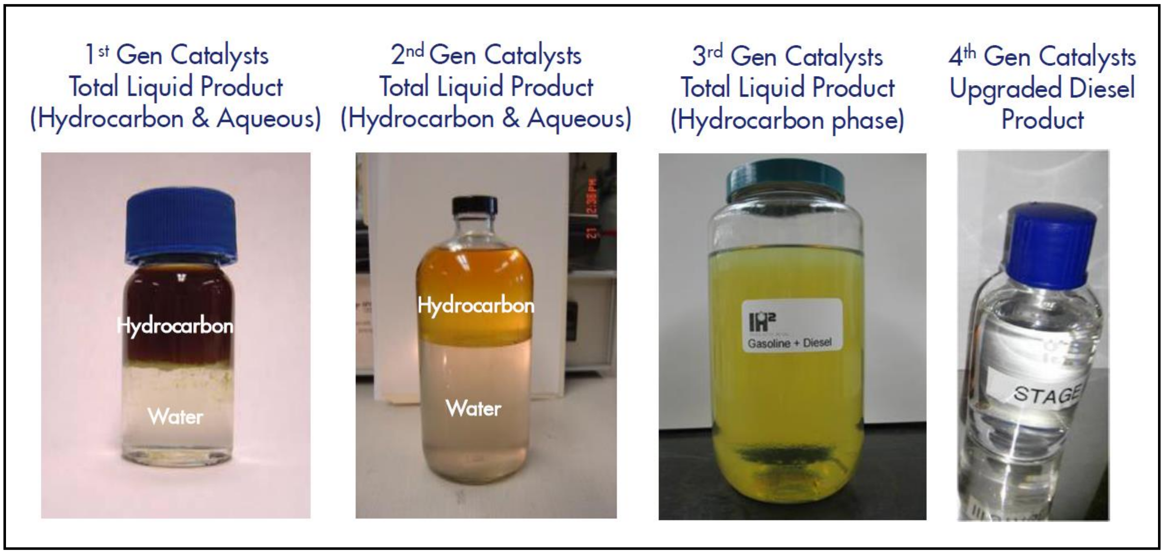


Figure 15 Visual improvement of the hydrocarbon products of the IH$^{2®}$ process. From the 1st generation product produced in 2009 (left) to the upgraded diesel product meeting all US specifications in 2014 (right)

Finally, there was a significant improvement in the visual quality of the products produced. Both gasoline and diesel products after upgrading were water-white in color, due to their extremely low sulfur, nitrogen and polyaromatic content. Superior visual appearance is a desirable characteristic for acceptance of these products in the market place. Figure 15 shows the evolution of the visual appearance of the hydrocarbon products from the IH$^{2®}$ process using the 1st generation catalysts (produced in 2009 on GTI's Miniature Benchscale Unit) to the 4th generation catalysts, upgraded through the third reactor train on microflow units at Shell Technology Center Bengaluru.

5.2. Upgrading of Cornstover-Derived Diesel in the 3rd Reactor Train

The strategy of using hydrotreating followed by aromatic saturation to upgrade the 2nd stage diesel and gasoline product derived from wood can also be applied to 2nd stage product from cornstover. Since the difference between fuel specifications and actual quality parameters is greater for 2nd stage diesel product than it is for gasoline, attention was focused on upgrading cornstover derived 2nd stage diesel only.

With this objective, the 2nd stage, cornstover-based, total hydrocarbon liquid product was distilled into gasoline and diesel fractions. For consistency, the boiling range chosen for the gasoline fraction was IBP to 150°C, and that for the diesel fraction was 150°C-FBP, the same as those for wood-derived gasoline and diesel. Using ASTM D2892 fractional distillation method, the yield of the gasoline fraction was 52.8 wt% of the TLP, while the diesel yield was 47.2 wt%.

The upgraded diesel product from cornstover was subjected hydrodesulfurization using the same sulfided CoMo catalyst supported on alumina as that used for hydrotreating of wood-based 2nd stage diesel product. The hydrotreating was at two different pressures (32 barg, the same pressure as that for wood, and 60 barg) and at about 10°C higher temperature than that used for wood based diesel product upgrading. The analysis of the feed and the product after hydrotreating and after aromatic saturation is presented in Table 6.

As seen from Table 6, the cornstover based diesel product has a significantly higher content of nitrogen than wood based diesel product, at 4550 ppmw. The total aromatic content of cornstover based diesel product is somewhat lower than that of wood based diesel, at about 60.6 wt%. After hydrotreatment at 32 barg pressure, the sulfur content was reduced from 52 ppmw to about 9 ppmw, however the nitrogen content could only be reduced to 2900 ppmw. Since refractory nitrogen compounds can be removed by promoting hydrogenation followed by heteroatom removal at higher pressures, enhanced hydrodenitrogenation was attempted at a higher pressure of 60 barg with the same catalyst system. The increase in pressure did lead to further reduction in the nitrogen content of the product to 1968 ppmw, and sulfur was reduced to 8 ppmw. However, the sulfur and nitrogen content in the product of hydrotreatment of cornstover based 2nd stage diesel remain substantially higher than those in the wood case. As seen from Table 5-2, the hydrotreatment of wood based 2nd stage diesel led to a product that had less than 10 ppmw sulfur and less than 10 ppmw nitrogen.

The increased nitrogen content of the product of hydrotreatment reactor appeared to hinder the aromatic saturation reactions on both noble metal and nickel based catalysts systems. As seen in Table 6, the total aromatic content could only be reduced to about 42.1 wt% at a pressure of 32 barg with the noble metal based system. With nickel based catalysts, the total aromatic content could be reduced to about 35.9 wt%. The aromatic content of upgrade cornstover based diesel product, therefore, remains much higher than that of wood-based diesel product (*cf*. Table 5-2).

The aromatic saturation catalysts require a feedstock that has <10 ppmw, preferably <5 ppmw of sulfur and nitrogen, to display the desired activity for aromatic saturation. The hydrotreatment of cornstover based gasoline and diesel product, therefore, requires further work to select an optimal combination of catalyst and operating conditions to produce a hydrotreated product having sufficiently low sulfur and nitrogen to upgrade successfully through the 3rd reactor train.

Table 6. Summary of upgrading results for cornstover based 2nd stage diesel

	Method Used	**150°C+ fraction from Cornstover (SFI-10611)**	**32 bar HDS TLP (SFI-10649)**	**60 bar HDS TLP (SFI-10652)**	**ASAT Product of Noble Metal Catalyst** (32 bar HDS product as feed)	**ASAT Product of Nickel Based Catalyst** (60 bar HDS product as feed)
Sulfur [ppmw]	MULTITEK	52	9	8	9	4
Nitrogen [ppmw]	MULTITEK	4550	2900	1968	2848	1770
Carbon [wt%]	ASTM D5291	89.02	88.55	88.50	86.95	86.79
Hydrogen [wt%]		10.98	11.16	11.30	12.76	13.03
Density at 15°C [g/mL]	ASTM D4052	0.9133	0.9004	0.8950	0.8694	0.8632
∆Density over 2nd stage diesel [g/mL]			0.0129	0.0183	0.0439	0.0501
Aromatics [wt%]	IP-391					
Monoaromatics		40.7	49.27	51.87	40.7	34.9
Diaromatics		11.2	11.25	10.09	0.0	0.0
Tri+ aromatics		8.7	7.25	6.21	1.4	1.0
Total Aromatics		60.6	67.76	68.16	42.1	35.9
SIMDIS - Mass Recovered [wt%]	D-7169					
0.5		136	100	100	100	100
1.0		143	111	110		
2.0		153	136	131		
5.0		160	152	146	131	131
10.0		167	162	161	157	156
20.0		184	179	177	173	172
30.0		202	196	194	189	187

40.0	217	212	211	206	204
50.0	235	233	231	227	225
60.0	257	257	256	253	256
70.0	286	287	286	281	284
80.0	317	317	317	311	312
90.0	363	364	362	350	349
95.0	398	399	397	385	382
98.0	435	437	433	422	418
99.5	479	486	478	469	463

6. Conclusion and Directions for Future Research Efforts

In conclusion, the nature of the liquid product produced in the IH$^{2®}$ process from wood post the 1st stage, 2nd stage and now the 3rd stage was understood in detail by a combination of several analytical techniques. The first stage product from wood had low oxygen content (below 5 wt%) and it was a stable product that can be fractionated. The oxygen in the product was contained almost exclusively in the phenol and phenol derivatives class of molecules. The phenol and phenol derivatives originate predominantly from the lignin fraction of the biomass, and the products of devolatilization of cellulose and hemicellulose appeared to have been fully deoxygenated to corresponding hydrocarbons. Under the process conditions investigated, the 1st stage liquid product produced from cornstover had a high oxygen content of 6.1 wt% and a high total acid number (TAN) of 17.4. It showed a tendency to continuously precipitate solids upon storage. However, the experience of processing wood through the 1st stage suggests possibilities of improving the quality of cornstover based 1st stage liquid product substantially by increasing the severity of 1st stage operation (e.g. by operating the 1st stage at a lower weight-hourly space velocity and a higher temperature than what was done as part of this work).

Wood based 2nd stage product was investigated in detail for its quality, and also its fuel properties. The deficiencies in quality of wood based 2nd stage diesel were attributed to its high aromatic content. It was demonstrated through a campaign of high-throughput catalyst testing that the aromatics in the diesel can be successfully eliminated under moderate conditions of temperature and pressure using CRI's high activity aromatic saturation catalysts. The resulting upgraded diesel product meets all specifications of US No. 2 diesel (ASTM D975) without the need to add any other blendstock. It is therefore possible to go from the biomass directly to the pump by converting wood using the IH$^{2®}$ process and upgrading the resultant diesel by the process scheme proposed here. The gaps in gasoline quality were mainly in its benzene content and its copper strip corrosion rating. Both the quality deficiencies were successfully addressed by the upgrading strategy used. The upgraded gasoline was found to be a premium renewable RBOB that is expected to meet existing US gasoline specifications after blending with 10% ethanol (R90/E10 blend). Research activities are currently underway to improve the anti-knock index of gasoline further to meet existing US specifications without having to blend ethanol in.

Cornstover based 2nd stage product was found to contain a high amount of nitrogen. It required more severe operating conditions for upgrading that those used for wood-based 2nd stage product, and yet the nitrogen content of upgraded product was found to remain high. It was possible to achieve a reduction in density of cornstover based 2nd stage diesel that was comparable to that obtained with 2nd stage wood-based diesel, however the aromatic content of cornstover diesel remained high after upgrading. Additional focused efforts are required to investigate both hydrotreatment step and aromatic saturation step with cornstover based gasoline and diesel to improve the product quality.

7. Appendix

Tabular summary of all properties of the upgraded fuels which were tested against respective diesel specifications (ASTM D975) and gasoline specifications (ASTM D4814-10b) is included in the Appendix.

Properties of upgraded diesel

Table 7-1 Fuel properties of upgraded US diesel against ASTM D975 specifications

Property	**Specification**	**Analysis Method**	**3rd Stage Diesel from IH2® Process**
Cetane Number, min	40	ASTM D976	43.7
Sulfur, ppmw, max	15	ASTM D5453	6
Viscosity at 40°C, cSt, max	4.1	ASTM D445	4.1
Distillation			
T90, °C, max	338	ASTM D86	341.9[2]
Flash Point, °C, min	52	ASTM D93	NA[1]
Carbon residue 10%, wt%, max	0.35	ASTM D524	0.15
Water and sediment, vol%, max	0.05	ASTM D2709	NA[1]
Ash, wt%, max	0.01	ASTM D482	<0.001
Lubricity, diam at 60°C, micron, max	520	ASTM D6079	400[3]
Copper corrosion, 3 hr at 50°C, max	No. 3	ASTM D130	1A

1. The sample quantity available was inadequate to do this test.
2. This parameter can be easily met by tweaking the boiling range of the diesel feed to 3rd reactor train.
3. Low-sulfur diesel fuels generally don't meet lubricity specifications without any lubricity improvers. This is true for the 3rd stage diesel also. Lubricity specification can be met by adding lubricity improvers.

Properties of upgraded gasoline

Table 7-2 Fuel properties of upgraded US gasoline against ASTM D4814-10b specifications

Property	**Specification**	**Analysis Method**	**3rd Stage Gasoline from IH2® Process**
Antiknock Index (MON+RON)/2, calculated, min			78.8[1]
Sulfur, ppmw, max	40	ASTM D 5453	18[2]
RVP at 37.8°C (100°F), kPa, max	103	ASTM D 5191	47.3
Distillation Specifications		ASTM D 86	
IBP, °C, max	Report		38.7
T10, °C, max	70		57.0
T50, °C, max	121		98.3
T90, °C, max	190		173.6
FBP, °C, max	225		190.0
Residue, vol%, max	2		Meets
Oxidation stability (Induction period), minutes, min	240	ASTM D 525	>360
Copper corrosion, 3hr at 50°C, merit (Class)	1	ASTM D 130	1A[3]

1. The anti-knock index is lowered due to two reasons: a. Boiling point shift of diesel during aromatic saturation step creates a small amount of naphthene-rich gasoline-range byproduct. This blendstock has poor octane value, and when blended with rest of the gasoline, lowers gasoline octane. b. Benzene was oversaturated - the product had a benzene content of only 0.2 vol%. The specification allows upto 1 vol% benzene. Benzene is a high octane component and it should not be oversaturated.
2. Gasoline sulfur content of 18 ppmw has been reduced in subsequent batches of 2nd stage TLP produced at GTI's IH2®-50 pilot plant.
3. Copper strip corrosion test was met after upgrading, even though only the 60°C-80°C fraction was upgraded.

Appendix D – Wood procurement for IH2 Refinery Project Report

Wood procurement for IH2 Refinery Project Report
October 8, 2014

The purpose of this report is to present the findings for a feedstock supply study undertaken for the purpose of an IH2 processing facility next to an existing refiner. Two sites were chosen from a list that was provided by GTI. These were Valero refineries located in St. Charles, Louisiana and Memphis, Tennessee Three plants sizes were plant sizes of 250, 500, and 1,000 bone dry tons per day were evaluated (based on a 2,000 pound ton).

The St. Charles site is located only a few miles north of New Orleans and is extremely limited on resource availability. Resource supply to the site is strongly influenced by the Gulf of Mexico, the Mississippi River delta, and a combination of urban, agricultural, and industrial development. Sources of wood feedstock generally lie beyond a 75-100 miles distance to the north east and north west. However, recent development of the European wood pellet export industry has significantly reduced any excess resource supplies that may have existed. The area around the St. Charles site itself has been highly developed and appeared to have limited space for an expansion that would accommodate the handling and storage of feedstock.

The Memphis site is limited on resource availability to the west by the Mississippi River delta and to the east by extensive urban development and agricultural. The site appeared to have room in an adjacent industrial park to accommodate the handling and storage of feedstock. Sources of feedstock were located beyond a 50 mile zone to the east of Memphis.

After site visits and a review of the resources it was determined that efforts would be focused on the Valero Memphis Tennessee location. In addition to the three plant sizes three scenarios for the Memphis site were evaluated.

The first scenario assumed that all feedstock would be delivered to Memphis at which point it would be processed and dried. In the second scenario an offsite location for receipt of feedstock and for processing was evaluated. This site was located approximately 120 miles (east) of Memphis. Prepared feedstock would then be transferred to the Memphis site. The third scenario was added during the final review of the report. It is similar to the first scenario in which the feedstock is direct shipped to Memphis; however, in this scenario the feedstock is limited to in woods produced microchips approximately less than 6mm in length.

To allow for a comparison of transfer methods off-site locations were chosen for evaluation that included rail, barging, and trucking. To refine the analysis only one of the offsite locations was selected for detailed analysis. Briefly rail was eliminated due to the relatively short distance and the need to utilize multiple rail line companies. Barging at first appeared to have merit however after analysis the site locations were significantly closer by truck than by barge (120-150 miles by truck compared to 300-400 miles by barge). In addition the carrying capacity of barges (80,000 -100,000 cubic feet) and the low bulk density of wood feedstock (10-25 pounds per cubic foot) resulted in significantly higher per ton transfer rates than traditional barge cargos (for example grain products typically have bulk densities of 55 pounds per cubic foot.) In the final analysis only transfer trucking was considered.

IH2 Feedstock Requirements and Types

The final desired feedstock characteristic for the IH2 process is a thin rectangular particle (microchip). The current feedstock specifications are shown are:

- 100% less than 4.76mm
- 5% max above 4mm
- 7% less than 0.3mm
- Arithmetic mean diameter = 2mm+/- .38mm

There are challenges to achieve this feedstock geometry. Recent developments in the area of micro-chipping have shown promise. The use of equipment such as grinders or hammermills that result in the crushing of wood fibers need to be avoided.

The process can use feedstock with high moisture content. However, to reduce the amount of water produced in the process moisture content of 10% is desired. Feedstock's high in ash (such as bark) are acceptable. While the chemical composition of different tree species (softwoods and hardwoods) and tree components (bole, bark, tops) differ the process is not limited to any one species or species group. For the purposes of this analysis feedstock information is presented as either softwood or hardwood. Feedstock sources have been grouped by mill residues, forest residues, and commercial forest feedstock from growing stock volume. Commercial sources have also been divided into sub groups of merchantable and under-utilized.

Site Locations

St. Charles, Louisiana

The St. Charles, Louisiana location appeared to not to have suitable undeveloped land adjacent to the facility (Figures 1 and 2).The site was served by secondary road system with difficult travel from the interstate system. It is along the river and had barge and rail service. The site was not in close proximity to the feedstock supply.

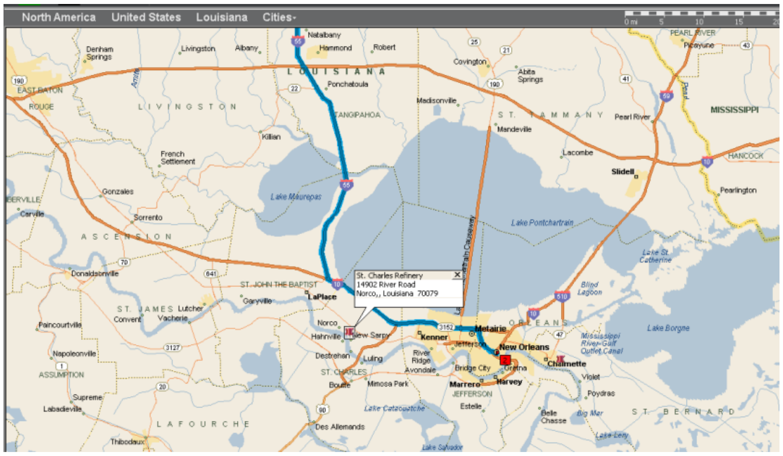


Figure 1: Location of St. Charles Refinery in Louisiana

Figure 2: Satellite Image of St. Charles Refinery Site location in Louisiana

Memphis, Tennessee

The Memphis site appears to have undeveloped property adjacent to the facility available for development; it is directly accessible from the interstate system; and has rail and barge services available (see figures 3 and 4). However the Memphis site is limited on resource availability within the first 50 miles, the area deemed critical for reliable low cost feedstock. Figure 5 illustrates the accumulative acres of commercial forest land by distance from Memphis. These limitations are due to a number of factors. To the west of Memphis is the Mississippi River, an area that has been heavily transformed into agricultural and extends nearly 100 miles. To the east the first 50 miles is a combination of urban development and agriculture.

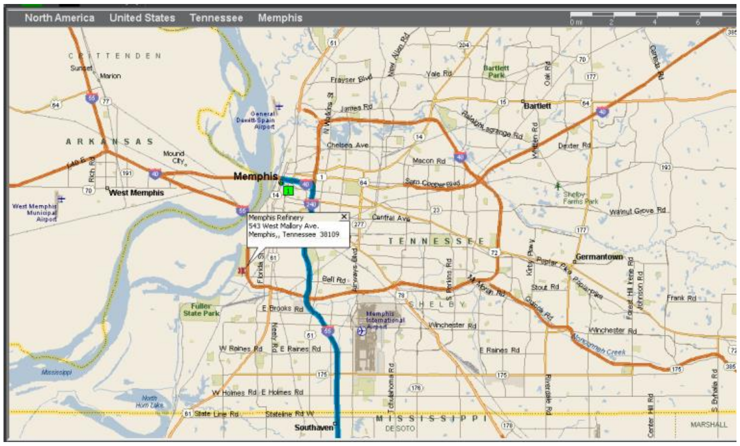


Figure 3: Map showing the Valero Refinery Location in Memphis, Tennessee

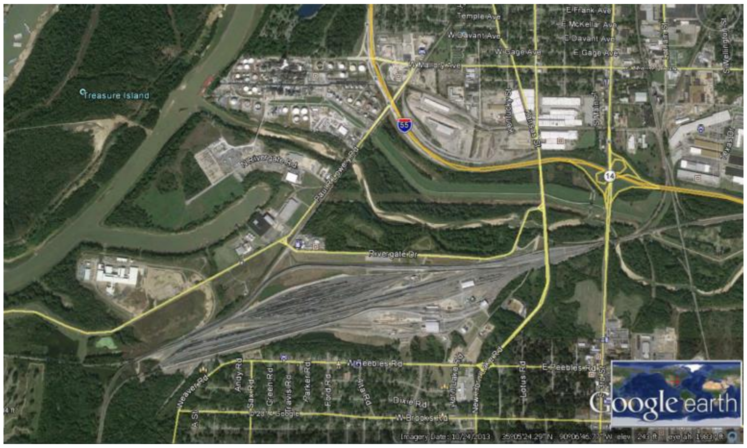


Figure 4: Satelite Image of the Valero Refinery, Memphis Tennessee.

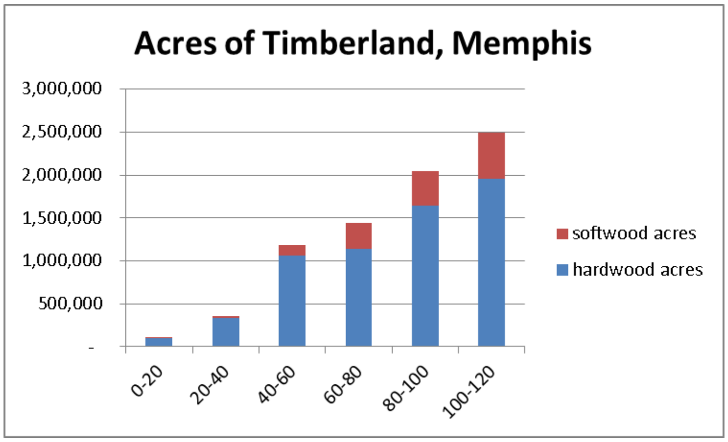


Figure 5: Accumulative Acres of Softwood and Hardwood Timberland by Trucking Distance from the Valero Refinery site in Memphis

.

Offsite Locations

Four off site locations were initially selected for analysis (Figure 6). These sites included New Johnsonville, Tennessee; Clarksville, Tennessee: Florence Alabama: and the Port of Yellow Creek, Mississippi. These are examples of potential sites. Considerable work will be needed to confirm if they would be suitable for actual development. Table 1 lists these locations and the transfer distances by barge, rail, and truck. In all cases truck transfer has the shortest distance, followed by rail, and the barge.

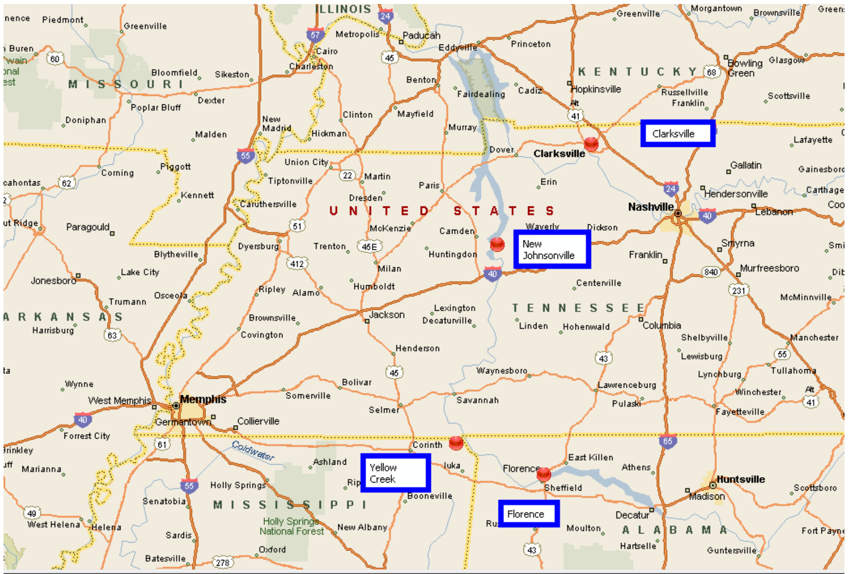


Figure 6: Offsite Receiving and Processing Locations

Table 1: Transfer Distance by Transfer Method from Possible Offsite Receiving and Processing Facilities

Transfer Method	**Florence, Al**	**New Johnsonville, TN**	**Clarksville, TN**	**Yellow Creek, MS**
Barge	515	360	370	475
Rail	160	175	290	130
Truck	150	155	210	120

In consultation with Tennessee Department of Natural Resources an offsite processing facility was identified at the Yellow Creek Port located in Mississippi near the juncture of the Tennessee and Alabama borders. Figure 7 shows the routes taken from the Port of Yellow Creek, Mississippi to Memphis. As can be seen the most direct route is by truck or rail.

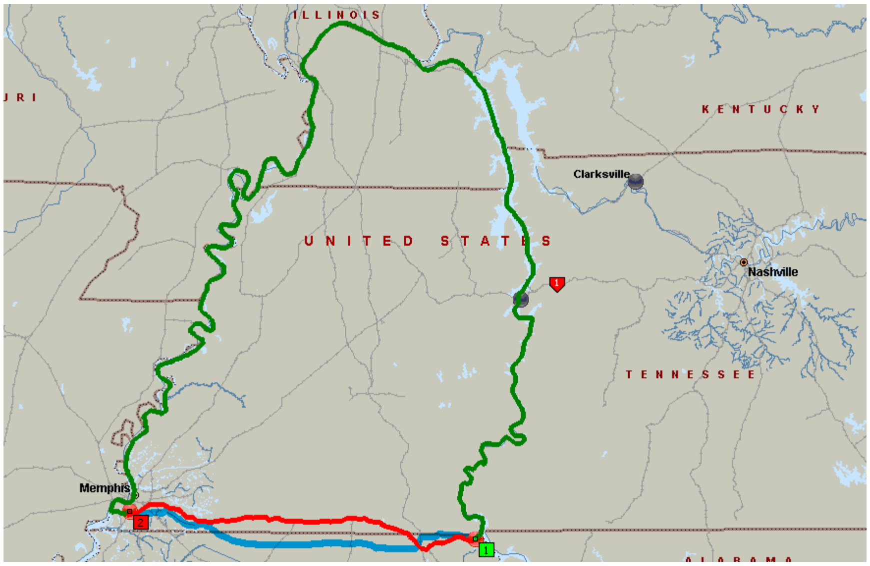


Figure 7: Map for Offsite Facility Showing Transfer Routes for Barge (green), Rail (red), and by Trucks (blue)

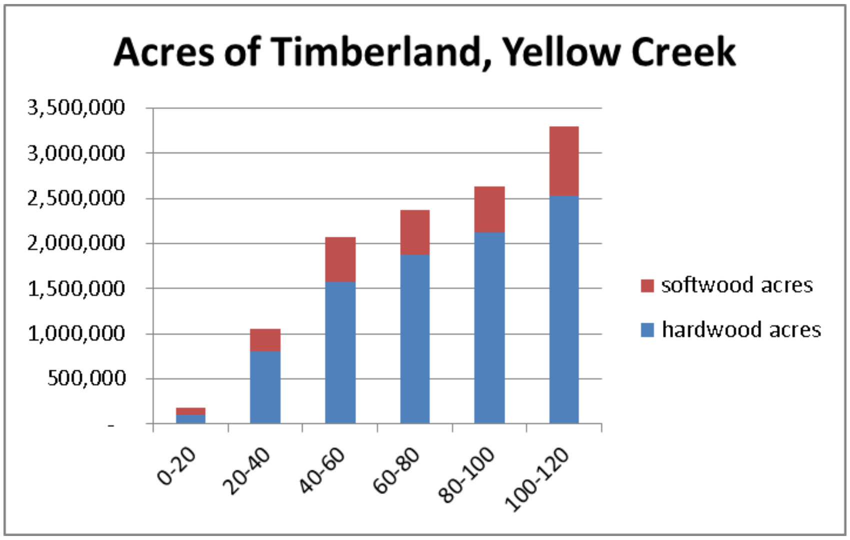


Figure 8: Accumulative Acres of Softwood and Hardwood Timberland by Trucking Distance to the Offsite Facility

Estimating Feedstock Supply

To estimate feedstock supply sources of information were gathered and combined. The first consisted of data derived from the USFS Forest Inventory Data Online (FIDO) website that was aggregated at the county level. In addition to the USFS data unpublished mill residue was utilized for estimating unused feedstock. The second set of data consisted of highway transportation distances from the center of each county to the both the Memphis site and to the offsite processing facility. Combining this data provides a basic distance and feedstock cost supply curve for the resource to the refinery.

Produce standard FIA reports on your own selection of states, counties, and survey year(s) ... You can also select from a wide range of custom filters.

Customize a retrieval for your own specific needs or build new, user-defined report templates.

Forest Inventory Data Online (FIDO)

Welcome to FIDO!

FIDO gives you access to the National FIA (Forest Inventory and Analysis) databases. You now have the ability to generate tables and maps of forest statistics through a web browser without having to understand the underlying data structures.

With FIDO, you will be able to run any of the standard reports for a specific area of interest and survey year or, if you are an advanced user, create completely customized reports based on whatever criteria you choose. As an advanced user, you can also save your work to your hard drive to load/rerun your custom FIDO retrievals at a later time.

User Alert -- April 11, 2014

FIA, in conjunction with the Forest Service Chief Information Office, will be implementing changes to the FIADB structure and data the third and fourth weeks of April. During that time, FIADB and the online tools will remain available; however, the data will consist of a mix of version 5.1 and 6.0 data. The most visible change is in the interpretation of the definition of reserved status. All annual data have been reanalyzed in accordance with this interpretation and some previously published values have been changed. Change estimates have been recomputed to account for any modifications. For more details please consult the FIADB User's Guide (http://www.fia.fs.fed.us/library/database-documentation/).

Figure 9: Forest Service FIDO Online Data Service

Data Analysis

Data analysis was accomplished using a modified program developed for GTI in an earlier project. This analysis combined wood feedstock availability estimates by type (mill residues, forest residues, merchantable and un merchantable); quantity (green tons), properties (chemical composition, ash content, moisture content); costs for collection, processing , and transfer; costs for final processing including sizing and drying.

Data Output for Direct Haul to Memphis and to an Offsite Facility

Appendix A consists of 21 data tables detailing information on types of feedstock, chemical composition, costs, and information for use in an LCA study. Table’s 1 through 7 present the model output for Scenario 1 in which the feedstock will be shipped, as is, from its point of origin directly to the Memphis site. Tables 8 through 14 present data for Scenario 2 in which all of the feedstock was delivered as is to an offsite location for processing and drying. The feedstock in Scenario 2 would be transferred by truck as needed to Memphis. Tables 15 through 21 present the model output for Scenario 3. Scenario 3 is similar to 1 but all feedstock is delivered in the form of microchips.

Summary Discussion and Recommendations

Table 2 shows a cost comparison for the three scenarios of direct receiving of feedstock in Memphis, for an offsite facility, and for direct haul of microchips to Memphis. In all cases costs increase with plant size, direct haul to Memphis is approximately $10.00 per bone dry ton less than an offsite facility. The costs for micro-chips to Memphis increase more dramatically with plant size than in the other scenarios. This increase is due to the need to reach out further for feedstock. There are number of important issues to take into account some of which are:

Figures 10, 11 and 12 show the procurement profiles for a 500 ton per day facility for the three scenarios. As discussed earlier the lack of adequate forest resources near Memphis result in a procurement profile (Figure 10) shifted to the right with a feedstock makeup based primarily on unmarketable roundwood and biomass. In comparison the procurement profile for the offsite facility has a more desirable left hand profile (Figure 11) and has a makeup with more biomass and mill residues. The procurement profile for the third scenario (Figure 12) has profile that is shifted further to the right than in Figure 10. Having profiles similar Figure 11 to 12 increases the percentage of feedstock that would like qualify for RIN credits. However a supply profile similar to Figure 11 is more desirable in that it has less supply uncertainties associated with more distant feedstock sources.

Direct hauling from the forest to Memphis in Scenarios 1 and 3 will occur primarily during the day time hours when traffic is at its greatest. Transfer trucks in Scenario 2 will have greater latitude for scheduling for arrival during low traffic periods.

Truck turnaround time from the forest to the receiving location is extremely important, especially for low cost feedstock. Table 3 shows a comparison of the average hauling distance from the point of origin for the feedstock to the receiving facility. An offsite facility has significantly shorter hauls than direct hauling into Memphis.

Weather is a significant factor in the delivery of feedstock from the forest to a receiving location. To address this receiving facilities require large raw material inventories. An offsite receiving and processing location would be better suited for maintaining large inventories than a location near downtown Memphis.

While there are greater costs to having an offsite facility there is significantly lower risk and uncertainty for the feedstock supply.

The costs and feedstock haul distances in Scenario 3 can be decreased over time through the development of a supply chain infrastructure.

Table 2: Per Bone Dry Ton Costs Comparisons for Three Scenarios

		Plant Size in Bone Dry Tons per Day		
		250	**500**	**1000**
Scenario 1	**Direct Haul to Memphis**	$102.38	$105.47	$110.29
Scenario 2	**Delivered to Offsite Facility**	$112.56	$116.45	$120.71
Scenario 3	**Direct Haul of Microchips to Memphis**	$105.44	$110.00	$118.18

Table 3: Average Haul Distance from the Point of Origin (forest or mill) for each Scenario and Plant Size

		Plant Size in Bone Dry Tons per Day		
		250	**500**	**1000**
Scenario 1	**Direct Haul to Memphis**	70	73	82
Scenario 2	**Delivered to Offsite Facility**	50	56	57
Scenario 3	**Direct Haul of Microchips to Memphis**	70	87	117

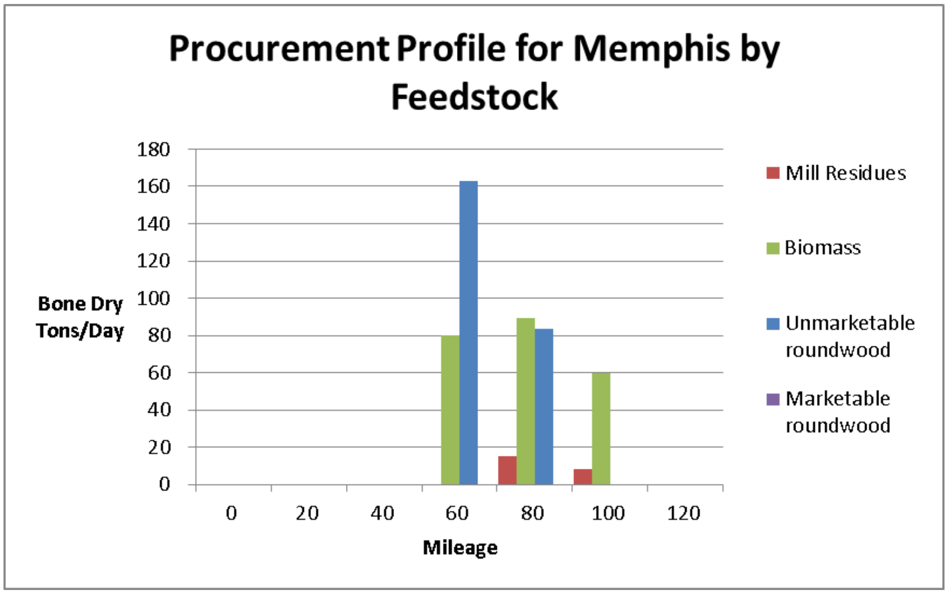


Figure 10: Procurement Profile for a 500 Bone dry ton/day facility in Memphis by Feedstock (Scenario 1)

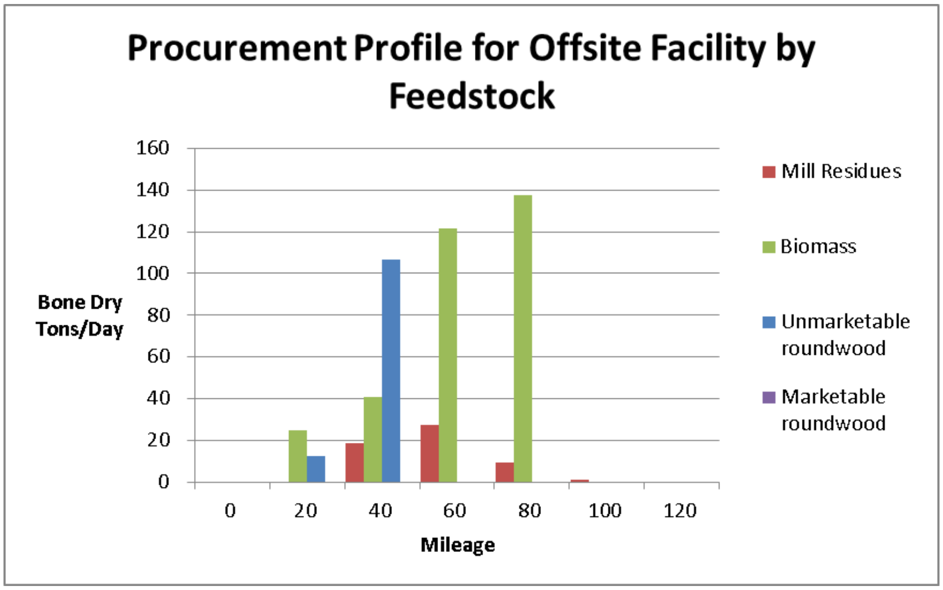


Figure 11: Procurement Profile for a 500 Bone dry ton/day Offsite Facility by Feedstock (Scenario 2)

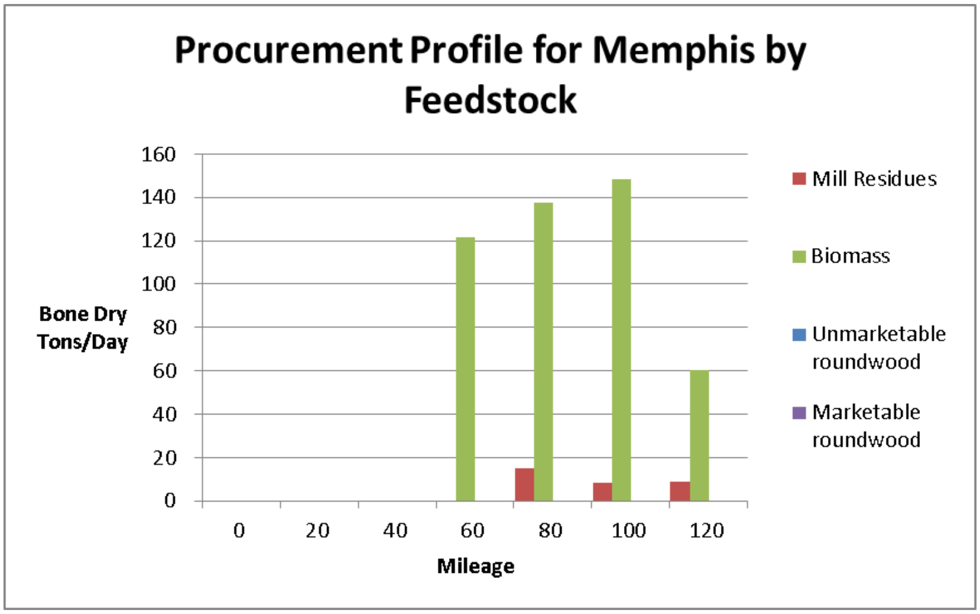


Figure 12: Procurement Profile for a 500 Bone dry ton/day in Memphis limited to Biomass Feedstock (Scenario 3)

Appendix A

Scenario 1: Summary Bone Dry Ton by Plant Size

Scenario 1: Memphis		**250 bone dry tons per day**	**500 bone dry ton per day**	**1000 bone dry ton per day**
Table 1: Types and Sources of Feedstock		**Plant Size in Bone Dry Tons per Day**		
Origin	**Description**	**250**	**500**	**1000**
Mill Residues	mill residues	23	23	32
	sub total	**23**	**23**	**32**
Forest Sources	biomass	170	230	313
	underutilized roundwood	57	247	562
	merchantable roundwood	0	0	92
	sub total	**227**	**477**	**968**
	total	**250**	**500**	**1,000**

Table 2: Major Species Groups		**Plant Size in Bone Dry Tons per Day**		
	Description	**250**	**500**	**1000**
	hardwoods	242	489	944
	softwoods	8	11	56
	total	**250**	**500**	**1,000**

Table 3: Moisture Content, HHV , and Composition		**Plant Size in Bone Dry Tons per Day**		
		250	**500**	**1000**
Average Green Moisture Content		45%	45%	45%
HHV of feedstock	**BTU's**	**8,503**	**8,453**	**8,437**
Chemical Composition				
	Ash Content	1.7%	1.5%	1.3%
	Carbon	46.9%	46.8%	46.8%
	Hydrogen	6.2%	6.2%	6.2%
	Oxygen	44.8%	45.1%	45.3%
	Nitrogen	0.4%	0.3%	0.3%
	Sulfur	0.04%	0.04%	0.03%
	total	**100.0%**	**100.0%**	**100.0%**

Table 4: Total Costs		**Plant Size in Bone Dry Tons per Day**		
Processing step		**250**	**500**	**1000**
Raw Materials	base costs (stumpage)	$2,793.71	$5,933.62	$14,010.53
	collection	$6,719.30	$13,959.98	$28,134.37
	delivery	$7,748.34	$15,870.21	$33,865.83
Delivered costs	**sub total**	**$17,261.35**	**$35,763.81**	**$76,010.73**
Manufacturing	yarding/procurement	$750.00	$1,500.00	$3,000.00
	holding	$617.89	$1,299.70	$2,638.82
	processing	$3,414.40	$7,071.32	$14,434.77
	drying	$3,551.14	$7,102.27	$14,204.55
Total Manufacturing	**sub total**	**$8,333.42**	**$16,973.29**	**$34,278.14**
total	**total without transfer**	$25,594.77	$52,737.10	$110,288.86
Transfer Cost	**from offsite processing facility to refinery**	**$0.00**	**$0.00**	**$0.00**
Total Delivered Cost		**$25,594.77**	**$52,737.10**	**$110,288.86**

Table 5: Costs per Bone Dry Ton		**Plant Size in Bone Dry Tons per Day**		
Processing step		**250**	**500**	**1000**
Raw Materials	base costs (stumpage)	$11.17	$11.87	$14.01
	collection	$26.88	$27.92	$28.13
	delivery	$30.99	$31.74	$33.87
Delivered Costs	**sub total**	**$69.05**	**$71.53**	**$76.01**
Manufacturing	yarding/procurement	$3.00	$3.00	$3.00
	holding	$2.47	$2.60	$2.64
	processing	$13.66	$14.14	$14.43
	drying	$14.20	$14.20	$14.20
Total Manufacturing	**sub total**	**$33.33**	**$33.95**	**$34.28**
Total	**total without transfer**	**$102.38**	**$105.47**	**$110.29**
Transfer Cost	**from offsite processing facility to refinery**	**$0.00**	**$0.00**	**$0.00**
Total Delivered Cost		**$102.38**	**$105.47**	**$110.29**

Table 6: Total Fuel and Lubricants		**Plant Size in Bone Dry Tons per Day**		
		250	**500**	**1000**
Raw material processing in woods	**Lubricants/Fuel**			
	diesel gallons	396	706	1,281
	lubricating oil gallons	3	3	3
	hydraulic fluid gallons	5	11	22
	tubes of grease	14	29	58
	gasoline gallons	14	29	60
Trucking from point of origin in woods to processing facility	**Lubricants/fuel**			
	diesel gallons	290	608	1,372
	lubricating oil gallons	1	2	4
	hydraulic fluid gallons	0	0	0
	tubes of grease	0	1	1
Yard Equipment	**Lubricants/fuel**			
	diesel gallons	50	100	200
	lubricating oil gallons	4	8	16
	hydraulic fluid gallons	4	8	16
	tubes of grease	11	21	43
Transfer Trucking	**Lubricants/fuel**			
	diesel gallons	0	0	0
	lubricating oil gallons	0	0	0
	hydraulic fluid gallons			
	tubes of grease	0	0	1
Feedstock Processing and Drying	**electrical power to process feedstock KwHr**	7,460	14,920	29,840
	electrical power for drying feedstock KwHr	6,378	12,757	25,513
	Total	**13,838**	**27,677**	**55,353**
Feedstock Drying	based on excess heat from IH2			

Table 7: Summary of Fuel and Lubricants by Plant size

		Plant Size in Bone Dry Tons per Day		
Summary		**250**	**500**	**1000**
Lubricants/fuel	diesel (gallons)	737	1,414	2,853
	lubricating oil (gallons)	8	12	23
	hydraulic fluid (gallons)	9	19	38
	tubes of grease (14 oz)	25	51	103
	gasoline (gallons)	14	29	60
	electrical power (KwHr)	13,838	27,677	55,353

Scenario 2: Summary Bone Dry Ton by Plant Size

Scenario 2: Offsite		250 bone dry tons per day	500 bone dry ton per day	1000 bone dry ton per day

Table 8: Types and Sources of Feedstock		Plant Size in Bone Dry Tons per Day		
Origin	**Description**	**250**	**500**	**1000**
Mill Residues	mill residues	51	56	65
	sub total	**51**	**56**	**65**
Forest Sources	biomass	187	324	415
	underutilized roundwood	12	119	349
	merchantable roundwood	0	0	170
	sub total	**199**	**444**	**935**
	total	**250**	**500**	**1,000**

Table 9: Major Species Groups		Plant Size in Bone Dry Tons per Day		
	Description	**250**	**500**	**1000**
	hardwoods	242	479	939
	softwoods	8	21	61
	total	**250**	**500**	**1,000**

Table 10: Moisture Content, HHV , and Composition		Plant Size in Bone Dry Tons per Day		
		250	**500**	**1000**
Average Green Moisture Content		45%	45%	45%
HHV of feedstock	**BTU's**	**8,533**	**8,504**	**8,468**
Chemical Composition				
	Ash Content	2.0%	1.8%	1.4%
	Carbon	47.1%	46.9%	46.9%
	Hydrogen	6.2%	6.2%	6.2%
	Oxygen	44.3%	44.7%	45.1%
	Nitrogen	0.4%	0.4%	0.3%
	Sulfur	0.04%	0.04%	0.03%
	total	**100.0%**	**100.0%**	**100.0%**

Table 11: Total Costs		**Plant Size in Bone Dry Tons per Day**		
Processing step		**250**	**500**	**1000**
Raw Materials	base costs (stumpage)	$2,991.09	$5,652.38	$13,815.96
	collection	$5,962.91	$13,149.04	$27,327.88
	delivery	$5,664.52	$12,084.01	$24,253.75
Delivered costs	**sub total**	**$14,618.52**	**$30,885.43**	**$65,397.59**
Manufacturing	yarding/procurement	$750.00	$1,500.00	$3,000.00
	holding	$543.62	$1,210.16	$2,548.71
	processing	$3,333.74	$6,839.27	$14,188.45
	drying	$3,551.14	$7,102.27	$14,204.55
Total Manufacturing	**sub total**	**$8,178.50**	**$16,651.71**	**$33,941.71**
total	**total without transfer**	$22,797.02	$47,537.13	$99,339.30
Transfer Cost	**from offsite processing facility to refinery**	**$5,343.75**	**$10,687.50**	**$21,375.00**
Total Delivered Cost		**$28,140.77**	**$58,224.63**	**$120,714.30**

Table 12: Costs per Bone Dry Ton		**Plant Size in Bone Dry Tons per Day**		
Processing step		250	500	1000
Raw Materials	base costs (stumpage)	$11.96	$11.30	$13.82
	collection	$23.85	$26.30	$27.33
	delivery	$22.66	$24.17	$24.25
Delivered Costs	**sub total**	**$58.47**	**$61.77**	**$65.40**
Manufacturing	yarding/procurement	$3.00	$3.00	$3.00
	holding	$2.17	$2.42	$2.55
	processing	$13.33	$13.68	$14.19
	drying	$14.20	$14.20	$14.20
Total Manufacturing	**sub total**	**$32.71**	**$33.30**	**$33.94**
Total	**total without transfer**	**$91.19**	**$95.07**	**$99.34**
Transfer Cost	**from offsite processing facility to refinery**	**$21.38**	**$21.38**	**$21.38**
Total Delivered Cost		**$112.56**	**$116.45**	**$120.71**

Table 13: Total Fuel and Lubricants		**Plant Size in Bone Dry Tons per Day**		
		250	**500**	**1000**
Raw material processing in woods	**Lubricants/Fuel**			
	diesel gallons	386	768	1,350
	lubricating oil gallons	3	3	2
	hydraulic fluid gallons	5	10	21
	tubes of grease	12	27	56
	gasoline gallons	12	27	58
Trucking from point of origin in woods to processing facility	**Lubricants/fuel**			
	diesel gallons	207	469	945
	lubricating oil gallons	1	1	3
	hydraulic fluid gallons	0	0	0
	tubes of grease	0	0	1
Yard Equipment	**Lubricants/fuel**			
	diesel gallons	50	100	200
	lubricating oil gallons	4	8	16
	hydraulic fluid gallons	4	8	16
	tubes of grease	11	21	43
Transfer Trucking	**Lubricants/fuel**			
	diesel gallons	533	1,067	2,133
	lubricating oil gallons	1	2	4
	hydraulic fluid gallons			
	tubes of grease	0	1	1
Feedstock Processing and Drying	**electrical power to process feedstock KwHr**	7,460	14,920	29,840
	electrical power for drying feedstock KwHr	6,378	12,757	25,513
	Total	**13,838**	**27,677**	**55,353**
Feedstock Drying	based on excess heat from IH2			

Table 14: Summary of Fuel and Lubricants by Plant size		**Plant Size in Bone Dry Tons per Day**		
Summary		**250**	**500**	**1000**
Lubricants/fuel	diesel (gallons)	1,177	2,404	4,629
	lubricating oil (gallons)	8	14	25
	hydraulic fluid (gallons)	9	18	38
	tubes of grease (14 oz)	23	49	101
	gasoline (gallons)	12	27	58
	electrical power (KwHr)	13,838	27,677	55,353

Scenario 3: Summary Bone Dry Ton by Plant Size

Scenario 3: Biomass only to Memphis		250 bone dry tons per day	500 bone dry ton per day	1000 bone dry ton per day

Table 15: Types and Sources of Feedstock		**Plant Size in Bone Dry Tons per Day**		
Origin	**Description**	**250**	**500**	**1000**
Mill Residues	mill residues	15	32	51
	sub total	**15**	**32**	**51**
Forest Sources	biomass	235	468	949
	underutilized roundwood	0	0	0
	merchantable roundwood	0	0	0
	sub total	**235**	**468**	**949**
	total	**250**	**500**	**1,000**

Table 16: Major Species Groups		**Plant Size in Bone Dry Tons per Day**		
	Description	**250**	**500**	**1000**
	hardwoods	246	478	934
	softwoods	4	22	66
	total	**250**	**500**	**1,000**

Table 17: Moisture Content, HHV , and Composition		**Plant Size in Bone Dry Tons per Day**		
		250	**500**	**1000**
Average Green Moisture Content		45%	45%	45%
HHV of feedstock	**BTU's**	**8,537**	**8,547**	**8,554**
Chemical Composition				
	Ash Content	1.9%	1.9%	1.8%
	Carbon	46.6%	46.7%	46.8%
	Hydrogen	6.2%	6.2%	6.2%
	Oxygen	44.9%	44.7%	44.7%
	Nitrogen	0.4%	0.4%	0.4%
	Sulfur	0.04%	0.04%	0.04%
	total	**100.0%**	**100.0%**	**100.0%**

Table 18: Total Costs		**Plant Size in Bone Dry Tons per Day**		
Processing step		**250**	**500**	**1000**
Raw Materials	base costs (stumpage)	$2,141.06	$4,745.40	$10,483.08
	collection	$7,047.55	$14,027.01	$28,466.88
	delivery	$7,781.48	$17,457.50	$41,649.73
Delivered costs	**sub total**	**$16,970.09**	**$36,229.91**	**$80,599.69**
Manufacturing	Yarding	$1,886.36	$3,772.73	$7,545.45
	Holding	$640.69	$1,275.18	$2,587.90
	processing	$3,311.15	$6,622.29	$13,244.58
	Drying	$3,551.14	$7,102.27	$14,204.55
Total Manufacturing	**sub total**	**$9,389.33**	**$18,772.47**	**$37,582.48**
total	**total without transfer**	$26,359.42	$55,002.38	$118,182.17
Transfer Cost	**from offsite processing facility to refinery**	**$0.00**	**$0.00**	**$0.00**
Total Delivered Cost		**$26,359.42**	**$55,002.38**	**$118,182.17**

Table 19: Costs per Bone Dry Ton		**Plant Size in Bone Dry Tons per Day**		
Processing step		**250**	**500**	**1000**
Raw Materials	base costs (stumpage)	$8.56	$9.49	$10.48
	Collection	$28.19	$28.05	$28.47
	Delivery	$31.13	$34.91	$41.65
Delivered Costs	**sub total**	**$67.88**	**$72.46**	**$80.60**
Manufacturing	yarding/procurement	$7.55	$7.55	$7.55
	Holding	$2.56	$2.55	$2.59
	processing	$13.24	$13.24	$13.24
	Drying	$14.20	$14.20	$14.20
Total Manufacturing	**sub total**	**$37.56**	**$37.54**	**$37.58**
Total	**total without transfer**	**$105.44**	**$110.00**	**$118.18**
Transfer Cost	**from offsite processing facility to refinery**	**$0.00**	**$0.00**	**$0.00**
Total Delivered Cost		**$105.44**	**$110.00**	**$118.18**

Table 20: Total Fuel and Lubricants		**Plant Size in Bone Dry Tons per Day**		
		250	**500**	**1000**
Raw material processing in woods	**Lubricants/Fuel**			
	diesel gallons	470	935	1,898
	lubricating oil gallons	3	4	4
	hydraulic fluid gallons	5	11	22
	tubes of grease	14	28	57
	gasoline gallons	15	29	59
Trucking from point of origin in woods to processing facility	**Lubricants/fuel**			
	diesel gallons	293	725	1,943
	lubricating oil gallons	1	2	6
	hydraulic fluid gallons	0	0	0
	tubes of grease	0	1	2
Yard Equipment	**Lubricants/fuel**			
	diesel gallons	50	100	200
	lubricating oil gallons	4	8	16
	hydraulic fluid gallons	4	8	16
	tubes of grease	11	21	43
Transfer Trucking	**Lubricants/fuel**			
	diesel gallons	0	0	0
	lubricating oil gallons	0	0	0
	hydraulic fluid gallons			
	tubes of grease	0	0	0
Feedstock Processing and Drying	**electrical power to process feedstock KwHr**	7,460	14,920	29,840
	electrical power for drying feedstock KwHr	6,378	12,757	25,513
	Total	**13,838**	**27,677**	**55,353**
Feedstock Drying	based on excess heat from IH2			

Table 21: Summary of Fuel and Lubricants by Plant size		**Plant Size in Bone Dry Tons per Day**		
Summary		**250**	**500**	**1000**
Lubricants/fuel	diesel (gallons)	813	1,760	4,041
	lubricating oil (gallons)	8	14	26
	hydraulic fluid (gallons)	9	19	38
	tubes of grease (14 oz)	25	50	102
	gasoline (gallons)	15	29	59
	electrical power (KwHr)	13,838	27,677	55,353

Engineering R&D

APPENDIX E

Refinery Upgrading of Hydropyrolysis Oil from Biomass

Corn Stover Supply Chain Economics

Daniel Stover
December 31, 2014

Keywords: Corn stover, biomass, hydropyrolysis, supply chain cost analysis, Monte Carlo simulation, sensitivity analysis

SUMMARY

Gas Technology Institute (GTI) is leading a project, "Refinery Upgrading of Hydropyrolysis Oil from Biomass," funded by the US Department of Energy, to explore production of transportation fuels from biomass using its Integrated Hydropyrolysis and Hydroconversion Process (IH2). As part of this project, Cargill has been asked to provide a supply chain cost analysis for corn stover as a biomass feedstock for the IH2 process. The analysis considered fuel production at each of Valero's 23 US facilities, 12 refineries and 11 ethanol plants.

We surveyed several published models of similar scope and compiled cost information related to the corn stover supply chain components of harvesting, local storage, transportation, nutrient replacement, grinding, and administration. For many of these model inputs, the cited references had differing values, so to account for these differences of opinion, we employed Monte Carlo simulation to understand the effect of uncertainty in the model inputs on the predicted stover supply costs.

Supply of stover to Valero's ethanol plants, which are located in corn producing regions, is predicted to have a cost advantage over supply to the refinery locations. The lowest cost site per our model is the ethanol plant in Welcome, MN, with a single-point (all inputs at median value) estimate of $102.77/MT and an expected value via Monte Carlo simulation of $107.80/MT (range $99.85 to $116.53/MT). At the other end of the spectrum, the highest cost site per our model is the refinery in Wilmington, CA, with cost of delivered corn stover more than triple that for any of the ethanol plants.

The cost differences among Valero locations are due to differences in transportation cost depending on distance from corn producing areas. For the low cost site, the predicted draw radius is only 33 miles, while for the high cost site, it is 1145 miles. The predicted draw radius is impacted significantly by anticipated low farmer participation and low stover collection efficiency. Farmer participation may be impaired by market uncertainty and environmental concerns.

The largest non-transportation contributors to stover feedstock cost are harvesting cost and nutrient replacement costs. For the low cost site, the model variables contributing the greatest uncertainty to overall stover cost per the Monte Carlo simulation are windrowing cost, transportation to local storage, and baling cost, with more than 60% of cost variance explained by those three inputs.

An alternative supply chain analysis conducted by Johnson Timbers for wood as a biomass feedstock to IH2 predicted a lower cost for wood than for corn stover, and feedback from the project team has indicated that wood may perform better than stover in the hydropyrolysis process. Therefore, wood looks to be the preferred raw material for the IH2 process.

TABLE OF CONTENTS

1 Introduction

A description of the overall project is provided in the project proposal for the US Department of Energy:

> *"The overall goal of this project is to develop a cost effective route for biomass to transportation fuels by first converting biomass to hydropyrolysis oil and then upgrading the hydropyrolysis oil in a petroleum oil refinery using existing refinery equipment. This will be accomplished by working closely with Valero Energy Corporation (Valero), one of the largest US. oil refiners with over 12 domestic refineries and a combined production capacity of more than 2.9 million barrels of oil per day. A secondary goal is to produce a preliminary engineering design package for a pilot-scale hydropyrolysis facility and commercial scale facility to be located adjacent to a Valero refinery, which would represent sufficient economic advantage to justify rapid commercial deployment. A third goal will be to develop an engineering design package for locating a hydropyrolysis unit converting cornstover to hydropyrolysis oil at one of Valero's 10 Midwest corn ethanol plants and shipping the hydropyrolysis oil to a nearby refinery for further upgrading.*
>
> *Hydropyrolysis oil can be an excellent feed for oil refineries since it has a low acid number and a typical oxygen content below the detection limit (BDL) of standard direct oxygen analyzers (< 1% oxygen). However, no studies have been completed concerning the upgrading of hydropyrolysis oils produced from rapid catalytic hydropyrolysis since this is a newly developed novel process. The diesel cut of hydropyrolysis oil should be easily upgraded in either a standard diesel hydrotreater or a hydrocracker to increase its cetane number and remove any remaining oxygen. Also, the gasoline cut should also be easily upgraded in a gasoline hydrotreater to remove oxygen.*
>
> *In this project, Gas Technology Institute (GTI) will produce hydropyrolysis oil from wood and corn stover for testing, using an existing 50kg/day catalytic hydropyrolysis pilot unit that employs GTI's Integrated Hydropyrolysis and Hydroconversion Process (IH2). CRI Catalyst Company (CRI) will then carry out upgrading studies of the hydropyrolysis oil in their existing hydrotreating test facilities while working closely with Valero to select an appropriate processing regimen.*
> *Valero will study the insertion of hydropyrolysis oil at several of their specific refineries for various refinery processing units and assess the required feed properties for proper insertion. Valero will compare the economics and risks for the refinery upgrading of IH2 oils along with petroleum oils versus the blending of finished IH2 oils into the product pool. Valero is participating in the project with a goal to potentially build a hydropyrolysis or IH2 unit directly outside one of their refineries to be fed with locally grown biomass feedstocks or potentially build a hydropyrolysis or IH2 process unit at one of their 10 Midwest ethanol production facilities. The study will detail and assess the best approach, based on risk and economic attractiveness.*
>
> *One of the goals of the study will be to identify an optimal design for a hydropyrolysis process unit, adjacent to a refinery which is integrated into the refinery and supplied with wood and cornstover feeds. Cargill, Inc. (Cargill) and Johnson Timber Cooperation (JT) will supply information on the logistics and prices for providing corn stover and wood to a commercial and demonstration scale hydropyrolysis unit located adjacent to specific Valero refineries and compare these costs to the supplying feedstocks to remote hydropyrolysis units which would provide hydropyrolysis oils to a Valero refinery. The study will also produce a preliminary engineering design package of a hydropyrolysis pilot scale facility to be located adjacent to a Valero refinery and for a hydropyrolysis unit located at one of Valero's corn ethanol locations."*

This report summarizes the corn stover supply chain analysis in support of the overall effort to optimize process economics for GTI's hydropyrolysis to be performed at one of Valero's ethanol plants or refinery facilities.

2 Methods and Materials

2.1 Modeling Approach

2.1.1 Corn Stover Availability

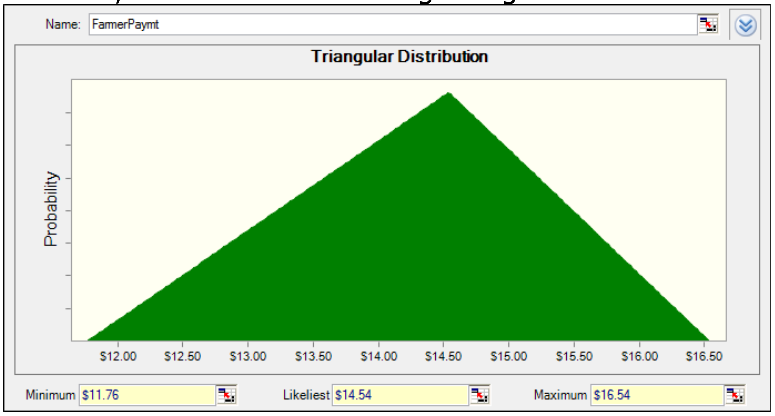
In order to estimate the stover supply availability to each of Valero's refinery and ethanol production locations, we compiled corn production data for each county in the United States. This data was downloaded from USDA's National Agricultural Statistics Service website[10] and compiled by Cargill's Trading Analytics group.

Using the latitude and longitude coordinates of Valero's locations and of the county centers, we could then compute the distances of each county's corn supply from each Valero location and sort from nearest to farthest, giving corn supply and, by extension, stover supply as a function of distance from the refinery location. Other factors detailed below, including farmer participation rate and stover collection efficiency, are also considered to determine stover availability.

2.1.2 Monte Carlo Simulation

To account for differing estimates for model inputs among the resources cited and to understand the sensitivities of stover supply chain costs to uncertainty in the model inputs, we performed Monte Carlo simulation using Crystal Ball software (from Oracle, version 11.1.1.3). This numerical technique allows us to specify statistical distributions for model inputs rather than using a single value. The distributions are defined by low, most likely, and high values obtained from the references. For example, for farmer payment upon harvesting, we have estimates ranging from a low of \$11.76 to a high of \$16.54 per dry basis MT, with a most likely (median) value of \$14.54/dry MT.

From these parameters, we derive the following triangular distribution:



Name: FarmerPaymt

Minimum \$11.76

Likeliest \$14.54

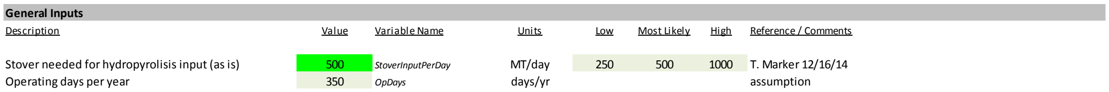
Maximum \$16.54

Triangular distributions were chosen (as opposed to normal or other types), because (1) they have finite bounds, thus mitigating risk of instability in calculations due to divideby-zero errors or nonsensical results, and (2) they allow us to define skewed distributions when an input's upside and downside are not the same.

With distributions defined for our model inputs, the Monte Carlo simulation performs a series of trials (we used 1000 here), in which random values are taken from each input distribution, and the spreadsheet is recalculated. This then gives us a distribution of outputs (corn stover cost for each Valero location), from which we see the range of outcomes and sensitivity information we seek.

2.2 *Model Inputs*

2.2.1 General



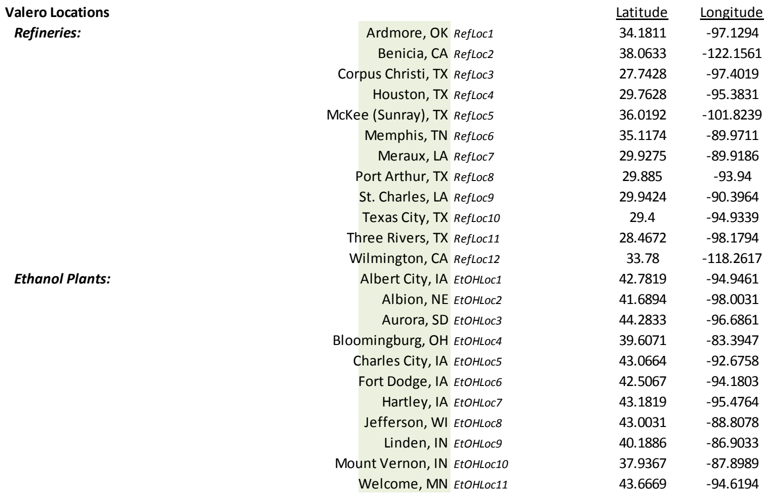
General Inputs

Description	Value	Variable Name	Units	Low	Most Likely	High	Reference / Comments
Stover needed for hydropyrolisis input (as is)	500	*StoverInputPerDay*	MT/day	250	500	1000	T. Marker 12/16/14
Operating days per year	350	*OpDays*	days/yr				assumption

The project team indicated that the target production basis is 500 MT/day incoming corn stover. It was requested, however, that we look at a range of production scales, so the model included a range from 250 – 1000 MT/day incoming stover.

It was assumed that the hydropyrolysis and refining processes would operate 350 days per year.

Following is the list of Valero US locations modeled, which came from Valero's website: http://www.valero.com/OurBusiness/OurLocations/Pages/Home.aspx.



Valero Locations

			Latitude	Longitude
Refineries:	Ardmore, OK	*RefLoc1*	34.1811	-97.1294
	Benicia, CA	*RefLoc2*	38.0633	-122.1561
	Corpus Christi, TX	*RefLoc3*	27.7428	-97.4019
	Houston, TX	*RefLoc4*	29.7628	-95.3831
	McKee (Sunray), TX	*RefLoc5*	36.0192	-101.8239
	Memphis, TN	*RefLoc6*	35.1174	-89.9711
	Meraux, LA	*RefLoc7*	29.9275	-89.9186
	Port Arthur, TX	*RefLoc8*	29.885	-93.94
	St. Charles, LA	*RefLoc9*	29.9424	-90.3964
	Texas City, TX	*RefLoc10*	29.4	-94.9339
	Three Rivers, TX	*RefLoc11*	28.4672	-98.1794
	Wilmington, CA	*RefLoc12*	33.78	-118.2617
Ethanol Plants:	Albert City, IA	*EtOHLoc1*	42.7819	-94.9461
	Albion, NE	*EtOHLoc2*	41.6894	-98.0031
	Aurora, SD	*EtOHLoc3*	44.2833	-96.6861
	Bloomingburg, OH	*EtOHLoc4*	39.6071	-83.3947
	Charles City, IA	*EtOHLoc5*	43.0664	-92.6758
	Fort Dodge, IA	*EtOHLoc6*	42.5067	-94.1803
	Hartley, IA	*EtOHLoc7*	43.1819	-95.4764
	Jefferson, WI	*EtOHLoc8*	43.0031	-88.8078
	Linden, IN	*EtOHLoc9*	40.1886	-86.9033
	Mount Vernon, IN	*EtOHLoc10*	37.9367	-87.8989
	Welcome, MN	*EtOHLoc11*	43.6669	-94.6194

2.2.2 Harvesting Costs

Harvesting Costs

Description	Value	Variable Name	Units	Low	Most Likely	High	Reference / Comments
Corn mass per bushel, dry basis	47	*CornLbsPerBu*	lb/Bu db				Reference iii
Stover mass ratio to grain, dry basis	1.0	*StoverMassRatio*	lb/lb db				Reference iii
Moisture content of harvested stover	15%	*StoverMst*	%	15%	15%	16%	Low: Ref i; Likely: Ref iv; High: Ref iii
Farmer payment	$14.54	*FarmerPaymt*	$/MT db	$11.76	$14.54	$16.54	Low: Ref v; Likely: Ref ii & iv avg; High: Ref i
Farmer participation rate	30%	*FarmerParticipation*	%	20%	30%	50%	Low: Ref iv; Likely: Ref vii; High: Ref iii
Chopping / windrowing cost	$4.84	*WindrowCost*	$/MT db	$2.74	$4.84	$15.53	Low: Ref i; Likely: Ref v; High: Ref vii
Baling cost	$21.66	*BalingCost*	$/MT db	$14.54	$21.66	$26.35	Low: Ref v; Likely: Ref i & ii avg; High: Ref vii
Stover collection efficiency	30%	*CollectionEff*	%	27%	30%	40%	Low: Ref ii; Likely: Ref i; High: Ref iii
Stacking cost	$10.35	*StackingCost*	$/MT db				Reference vii

Since we know corn production by county in bushels, we can determine the associated mass of corn stover using the mass of corn per bushel, 47 dry basis lbs per bushel, and the ratio of stover mass to corn mass, 1.0 lb/lb dry basis, both as cited by Petolia[3].

To convert as-is stover mass to dry basis stover mass, we need the moisture content of the stover. Both Carlson School of Management[1] and Laboreiro et al[4] cite this value as 15%, and Petrolia[3] reports 16%.

There is compensation to farmers for their time and effort to harvest stover. The farmer payment used in the model ranges from a low of $10.00/MT ($11.76/MT dry basis) per Sokhansanj et al[5] to a high of $15.00/MT ($16.54/MT dry basis) per Carlson School of Management[1], with most likely taken as the average of $11.97/MT ($14.08/MT dry basis) and $15.00/dry MT cited by Laboreiro et al[4] and Cook[2], respectively.

Even with compensation, not all farmers can be expected to be willing to participate in harvesting their stover. Laboreiro et al[4] estimates 20% farmer participation, while Shah[7] and Petrolia[3] assume a farmer participation rate of 30%.

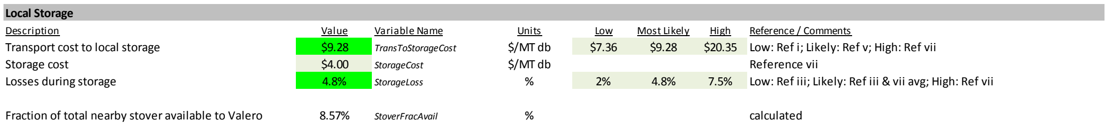
In addition to farmer payments, there are variable costs associated with equipment and fuel usage for the stover collection steps. Windrowing, the process of chopping to separate corn stalks from roots and soil, is estimated to cost $10.35/acre ($2.74/dry MT, low) per Carlson School of Management[1], $4.11/MT ($4.84/dry MT, most likely) per Sokhansanj et al[5], and $13.20/MT ($15.53/dry MT, high) per Shah[7].

The cost of baling used in the model ranges from a low of $12.36/MT ($14.54/dry MT) per Sokhansanj et al[5] to a high of $22.40/MT ($26.35/dry MT) per Shah[7], with most likely taken as the average of $9.60 per bale ($19.05/dry MT) and $11.70 per bale ($24.27/dry MT) as reported by Cook[2] and Carlson School of Management[1], respectively.

Stover collection efficiency is the fraction of stover biomass that is successfully captured into a bale. For round bales, this fraction is estimated to be 27% by Cook[2], 30% by Petrolia[3], and 37% by Laboreiro et al[4]. For square bales, collection efficiency is assumed to be 30% by Carlson School of Management[1] and 40% by Petrolia[3]. For the model, we assumed the range defined by the low (27%), median (30%), and high (40%) of these assorted values.

Finally, stacking bales of corn stover ahead of transporting to local storage is estimated to cost $8.80/MT ($10.35/dry MT) by Shah[7].

2.2.3 Local Storage



Local Storage

Description	Value	Variable Name	Units	Low	Most Likely	High	Reference / Comments
Transport cost to local storage	$9.28	*TransToStorageCost*	$/MT db	$7.36	$9.28	$20.35	Low: Ref i; Likely: Ref v; High: Ref vii
Storage cost	$4.00	*StorageCost*	$/MT db				Reference vii
Losses during storage	4.8%	*StorageLoss*	%	2%	4.8%	7.5%	Low: Ref iii; Likely: Ref iii & vii avg; High: Ref vii
Fraction of total nearby stover available to Valero	8.57%	*StoverFracAvail*	%				calculated

The estimated cost to transport harvested stover to local storage ranges from $3.55 per bale ($7.36/dry MT) per Carlson School of Management[1] to $17.30/MT ($20.25/dry MT) per Shah[7], with a median value of $4.64 per bale ($9.28/ dry MT) cited by Sokhansanj et al[5].

The cost of local storage is reported by Shah[7] to be $3.40 per MT as-is ($4.00/dry MT). Note that this cost of local storage is less than the cost of transportation to local storage.

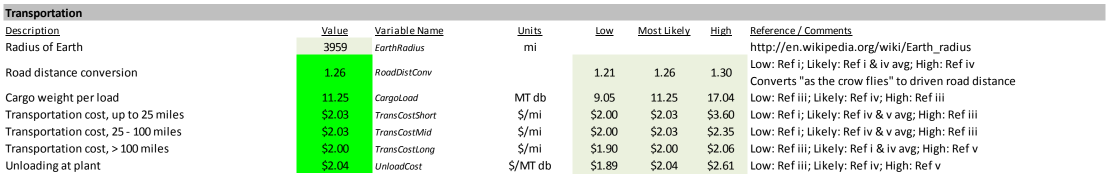
A fraction of harvested stover is lost somewhere between harvesting and final delivery. This loss rate is estimated to range from 2% per Petrolia[3] to 7.5% per Shah[7].

The effect of low farmer participation, low stover collection efficiency, and losses during storage and/or transportation is that only a small fraction of stover theoretically available is truly available for processing to biofuels. For example, with model inputs at the median (most likely) values, the estimated fraction of local stover available to Valero would be:

30% farmer participation x 30% collection efficiency x (100% - 4.8% losses) = 8.57% stover availability

Because of this low rate of stover availability, the necessary draw radius expands significantly, increasing transportation costs.

2.2.4 Transportation



Transportation

Description	Value	Variable Name	Units	Low	Most Likely	High	Reference / Comments
Radius of Earth	3959	*EarthRadius*	mi				http://en.wikipedia.org/wiki/Earth_radius
Road distance conversion	1.26	*RoadDistConv*		1.21	1.26	1.30	Low: Ref i; Likely: Ref i & iv avg; High: Ref iv Converts "as the crow flies" to driven road distance
Cargo weight per load	11.25	*CargoLoad*	MT db	9.05	11.25	17.04	Low: Ref iii; Likely: Ref iv; High: Ref iii
Transportation cost, up to 25 miles	$2.03	*TransCostShort*	$/mi	$2.00	$2.03	$3.60	Low: Ref i; Likely: Ref iv & v avg; High: Ref iii
Transportation cost, 25 - 100 miles	$2.03	*TransCostMid*	$/mi	$2.00	$2.03	$2.35	Low: Ref i; Likely: Ref iv & v avg; High: Ref iii
Transportation cost, > 100 miles	$2.00	*TransCostLong*	$/mi	$1.90	$2.00	$2.06	Low: Ref iii; Likely: Ref i & iv avg; High: Ref v
Unloading at plant	$2.04	*UnloadCost*	$/MT db	$1.89	$2.04	$2.61	Low: Ref iii; Likely: Ref iv; High: Ref v

The latitude and longitude data were used to compute distance from each Valero location to each corn producing county in its vicinity. The distance calculation is as follows (with latitudes & longitudes converted to radians):

$$Distance = acos(sin(Lat_1)*sin(Lat_2)+cos(Lat_1)*cos(Lat_2)*cos(Long_2-Long_1))*R,$$
$$\text{where } R \text{ is the radius of the Earth, 3959 miles.}$$

This formula gives the distance between any two points “as the crow flies.” What impacts transportation cost, however, is the road distance between those two points, so a road distance conversion factor is also applied. This multiplier is estimated by Carlson School of Management[1] to be 1.21 and by Laboreiro et al[4] to be 1.30.

An important factor to transportation cost per MT is the quantity of stover that will fit in a truckload. Petrolia[3] reports 23,760 lbs/load (low, 9.05 dry MT/load) for round bales and 44,736 lbs/load (high, 17.04 dry MT/load) for square bales, and Laboreiro et al[4] assumes 29,197 lbs/load (median, 11.25 dry MT/load) for round bales.

Transportation cost per mile is cited by both Carlson School of Management[1] and Laboreiro et al[4] at $2.00. Sokhansanj et al[5] indicates $9.98 per bale, or $2.06 per mile (for 18 bales per load, distance of 140 miles round trip). Petrolia[3] breaks it down in more detail, listing $3.60/mile for distances 25 miles or less, $2.35/mile between 26 and 100 miles, and $1.90/mile for distances greater than 100 miles. For the model, we also utilize these distance categories with corresponding low, median, and high values defining the range. The per mile costs are applied to round trip distances between corn producers and Valero sites (“as the crow flies” distance x road conversion factor x 2).

The final transportation cost component is unloading at the biorefinery. Petrolia[3] cites this cost as $1.15 per bale (low, $1.89.dry MT), Laboreiro et al[4] lists $1.00 per bale (median, $2.04/dry MT – *note: different bale weights for these sources*), and Sokhansanj et al[5] reports $2.22 per MT (high, $2.61/dry MT).

2.2.5 Nutrient Replacement

Nutrient Replacement							
Description	Value	Variable Name	Units	Low	Most Likely	High	Reference / Comments
Nitrogen							
Cost of Nitrogen per lb.	$0.517	*NitrogenCost*	$/lb N	$0.463	$0.517	$0.571	Low: Ref i; Likely: Ref i & ii avg; High: Ref ii
Nitrogen lost per MT stover	17.0	*NitrogenLoss*	lb N/MT db	14.0	17.0	20.0	Low: Ref i; Likely: Ref i & vii avg; High: Ref vii
Phosphorous							
Cost of Phosphorous per lb.	$0.776	*PhosphorusCost*	$/lb P	$0.663	$0.776	$0.889	Low: Ref i; Likely: Ref i & ii avg; High: Ref ii
Phosphorus lost per MT stover	5.2	*PhosphorusLoss*	lb P/MT db	5.2	5.2	6.5	Low: Ref ii; Likely: Ref i; High: Ref vii
Potassium							
Cost of Potassium per lb.	$0.526	*PotassiumCost*	$/lb K	$0.525	$0.526	$0.526	Low: Ref i; Likely: Ref i & ii avg; High: Ref ii
Potassium lost per MT stover	31.5	*PotassiumLoss*	lb K/MT db	30.9	31.5	32.4	Low: Ref ii; Likely: Ref i; High: Ref vii
Soil							
Cost of Soil per lb.	$0.003	*SoilCost*	$/lb soil				Reference ii
Soil lost per MT stover	286.7	*SoilLoss*	lb soil/MT db				Reference ii
Cost of nutrient replacement (fertilizer value, total)	$30.26	*NutrientReplCost*	$/MT db				Calculated

As corn stover is removed from the cornfield, essential nutrients are removed with it, and the farmer must eventually increase fertilizer usage to replace these nutrients. The farmer must be compensated for this added cost.

The estimated amount of nitrogen lost ranges from 10.8 lb/ton (14.0 lb/dry MT, Carlson School of Management[1]) to 15.4 lb/ton (20.0 lb/dry MT, Shah[7]). The estimated value of this nitrogen ranges from $0.463/lb (Carlson School of Management[1]) to $1.26/kg ($0.571/lb, Cook[2]).

The estimated amount of phosphorus lost is reported to be 2.35 kg/MT (low, 5.2 lb/dry MT, Cook[2]), 4 lb/ton (median, 5.2 lbs/dry MT, Carlson School of Management[1]), and 5 lb/ton (high, 6.5 lb/dry MT, Shah[7]). The estimated value of this phosphorus ranges from $0.663/lb (Carlson School of Management[1]) to $1.96/kg ($0.889/lb, Cook[2]).

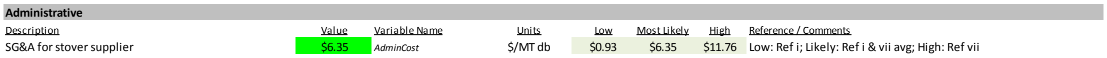
The estimated amount of potassium lost is reported to be 14 kg/MT (low, 30.9 lb/dry MT, Cook[2]), 24.25 lb/ton (median, 31.5 lb/dry MT, Carlson School of Management[1]), and 25 lb/ton (high, 32.4 lb/dry MT, Shah[7]). The estimated value of this potassium ranges from $0.525/lb (Carlson School of Management[1]) to $1.16/kg ($0.526/lb, Cook[2]).

Cook[2] also accounts for loss of soil during stover collection, citing 130 kg per MT stover (287 lb/dry MT) and a replacement value of $0.007/kg ($0.003/lb).

For the median values above, this give a breakdown of nutrient loss values as follows:

Component	Loss value ($/dry MT)
Nitrogen	$8.79
Phosphorus	$4.03
Potassium	$16.53
Soil	$0.91
Total nutrient replacement value	$30.26

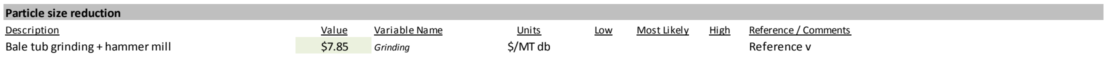
2.2.6 Administrative



Administrative							
Description	Value	Variable Name	Units	Low	Most Likely	High	Reference / Comments
SG&A for stover supplier	$6.35	*AdminCost*	$/MT db	$0.93	$6.35	$11.76	Low: Ref i; Likely: Ref i & vii avg; High: Ref vii

The models from Carlson School of Management[1] and Shah[7] account for overhead costs to the stover supplier, citing $350,000 per year ($0.93/dry MT) and $10 per MT ($11.76/dry MT), respectively.

2.2.7 Particle Size Reduction



Particle size reduction							
Description	Value	Variable Name	Units	Low	Most Likely	High	Reference / Comments
Bale tub grinding + hammer mill	$7.85	*Grinding*	$/MT db				Reference v

The project team has indicated that for efficient hydropyrolysis, the corn stover needs to be ground to a 3 mm particle size. The Sokhansanj et al[5] model considers similar grinding (before feeding to a biomass boiler) and cites a cost of $5.72/MT for bale tub grinding and $0.95/MT for hammer mill usage ($7.85/dry MT total).

3 Results and Discussion

3.1 Corn Stover Cost Summary

The table below summarizes the model results. Values are cost of delivered corn stover in $/MT as-is. The base case estimate is the single-point result obtained with all model inputs at their most likely value. The Monte Carlo results indicated are the average output of the 1000 trials along with the range defined by 5th and 95th percentiles (i. e., the 90% confidence interval).

Refineries ($/MT as-is)				
Location	Base case estimate	Monte Carlo results		
		average	90% confidence interval	
Ardmore, OK	$161.29	$161.51	$142.23	$181.95
Benicia, CA	$334.81	$307.68	$207.89	$396.51
Corpus Christi, TX	$168.46	$170.29	$142.74	$207.20
Houston, TX	$148.26	$151.05	$132.15	$173.13
McKee (Sunray), TX	$115.05	$119.67	$108.36	$132.47
Memphis, TN	$118.44	$123.13	$113.26	$133.80
Meraux, LA	$166.76	$167.52	$150.43	$186.00
Port Arthur, TX	$164.65	$165.34	$148.14	$183.78
St. Charles, LA	$162.34	$163.41	$146.80	$181.09
Texas City, TX	$156.75	$158.39	$139.08	$179.90
Three Rivers, TX	$158.41	$162.62	$136.85	$199.23
Wilmington, CA	$369.75	$345.18	$280.78	$411.91
Ethanol Plants ($/MT as-is)				
Location	Base case estimate	Monte Carlo results		
		average	90% confidence interval	
Albert City, IA	$103.69	$108.93	$101.06	$117.58
Albion, NE	$103.96	$108.97	$100.93	$117.66
Aurora, SD	$104.79	$110.18	$102.17	$119.07
Bloomingburg, OH	$105.08	$110.57	$102.52	$119.66
Charles City, IA	$104.17	$109.40	$101.54	$118.08
Fort Dodge, IA	$104.26	$109.32	$101.36	$117.99
Hartley, IA	$103.58	$108.81	$101.00	$117.53
Jefferson, WI	$107.18	$112.61	$104.59	$121.80
Linden, IN	$103.78	$108.99	$101.11	$117.64
Mount Vernon, IN	$104.47	$109.85	$101.41	$118.74
Welcome, MN	$102.77	$107.80	$99.85	$116.53

We see that the location with lowest delivered cost stover cost is the ethanol plant in Welcome, MN, and the location with highest delivered cost is the refinery in Wilmington, CA. The reason for the cost differences is the difference in transportation cost determined by proximity to corn supply.

To illustrate, the table below breaks down the supply chain costs for these two locations.

Costs ($/dry MT)	Welcome, MN	Wilmington, CA
Harvesting	$53.96	$53.96
Local storage	$13.94	$13.94
Transportation	**$7.05**	**$321.13**
Nutrient replacement	$31.77	$31.77
Grinding	$7.85	$7.85
Administrative	$6.35	$6.35
Total cost per dry MT stover	$120.91	$435.00
Total cost per as-is MT stover	$102.77	$369.75

For Welcome, MN, the required draw radius for corn stover supply is 33 miles, and for Wilmington, CA, the required draw radius is 1,145 miles. Note that this analysis assumes truck transportation for all cases (as did all the published models from which data were pulled). For extremely large distances, transportation by rail may reduce the expense somewhat, but that will not change the conclusion that locations requiring large draw radii will be at a significant raw material cost disadvantage.

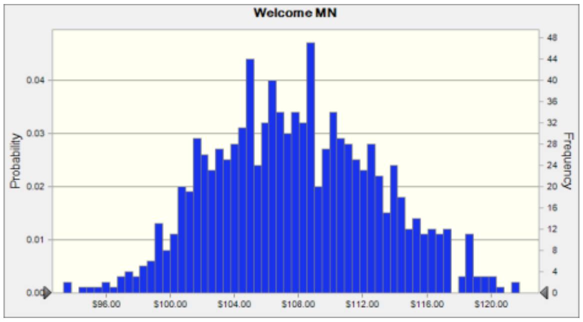
We also see from this that the top three non-transportation contributors to stover cost are harvesting, nutrient replacement, and local storage.

In the Appendix to this report are full model results for each location, including the detailed single-point corn stover costs, results and summary statistics from the Monte Carlo simulation, and sensitivity charts showing contribution to variance for each model input (discussed in next section).

3.2 Sensitivity Analysis

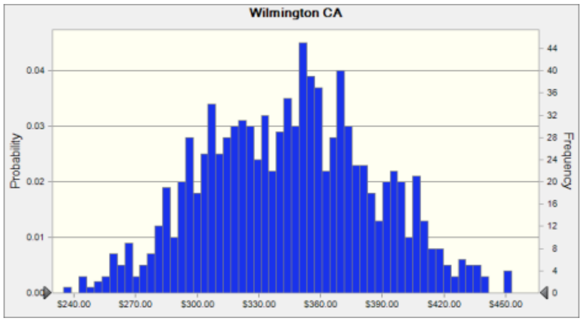
An important result of the Monte Carlo simulation is the sensitivities of each location's stover cost to the uncertainties of the model inputs. The sensitivity charts in the Appendix show model variables' contribution to variance, i. e., the fraction of the uncertainty of the forecast (stover cost) explained by the uncertainty of the model input. In each chart, model inputs are sorted from most important to least important to variance. The colored bars indicate the percent contribution to variance, and the direction indicates whether the variable is positively or negatively correlated to stover cost.

If we look at the low cost location (Welcome, MN), the Monte Carlo simulation predicts an expected delivered corn stover price (average of 1000 trials) of $107.80, with 90% of the trials falling between $99.85 and $116.53. The full histogram of results looks like:



The top five variables explaining the variance in predicted corn stover cost for Welcome, MN are: windrowing cost (27.7%), transportation to local storage (20.7%), baling cost (16.9%), administrative cost (11.0%), and production capacity (4.6%).

For the high cost location (Wilmington, CA), the Monte Carlo simulation predicts an expected delivered corn stover price of $345.18, with 90% of the trials falling between $280.78 and $411.91.



The top five variables explaining the variance in predicted corn stover cost for Wilmington, CA are: truckload capacity (65.2%), production capacity (19.5%), farmer participation (10.0%), collection efficiency (1.5%), and road distance multiplier (0.7%). Not surprisingly, each of these variables are related to transportation cost – figuring into draw radius, quantity of stover required, and number of truckloads required.

3.3 Other Considerations

In the model, we assume a farmer participation rate of 20 – 30%. To understand why this may be so low, Klingenfeld[8] lists some important barriers to farmers' wanting to harvest corn stover for biofuels, paraphrased below:

- Soil health: There is concern about the sustainability of harvesting stover due to soil erosion and maintaining organic carbon levels.
- Harvest technology: Without clear market demand, the rate of deployment of specialized harvesting equipment may be hindered.
- Storage: A distributed storage system requires coordination between many parties, and financing may be a concern with more complex supply chains.

- Transportation: Fear of risk due to uncertain economics of biomass transport may limit available capacity.
- Willingness to supply: Market uncertainty and environmental concerns may limit farmers' willingness to supply stover and to invest in technology.

To mitigate these concerns, Klingenfeld suggests education and outreach, formation of farmer co-operatives for knowledge sharing, government subsidies, public-private partnership for demonstration projects, and land management plans to address environmental concerns.

Moreover, Tyndall et al[9] suggest a substantial learning curve for farmers regarding corn stover. Among the concerns are that harvesting stover will require large capital investment, management systems, and a well-developed support infrastructure. They also point to environmental concerns as a significant barrier for farmers.

4 Conclusions and Recommendations

It is not a surprise that corn stover supply costs are lower for a facility that is near the corn producers. What may be a surprise is the magnitude of the cost difference as a function of distance. For the Valero ethanol facilities, all located near corn producing areas, we see draw radii ranging from 33 to 54 miles and resulting corn stover supply costs (single point results) ranging from \$102.77 to \$107.43 per MT as-is.

For the Valero refineries, though, the draw radii for corn stover range from 109 miles to 1145 miles, and resulting supply costs range from \$115.05 to \$369.75 per MT as-is. For the two west coast refinery locations in particular, cost of delivered corn stover more than triples because of the long haul distances.

The effect of transportation costs is exacerbated by anticipated low farmer participation rates and low collection efficiency, each of which reduces the available stover supply from a given corn production area and, therefore, expands the draw radius required to get the amount of stover needed.

An alternative supply chain analysis was conducted by Johnson Timbers for wood as a biomass feedstock to hydropyrolysis. This analysis predicted delivered feedstock cost ranging from \$102.38 to \$120.71 per dry MT of wood, depending on production capacity and whether supply is by direct haul or via and offsite facility. By comparison, the lowest cost corn stover supply predicted from this analysis is to Valero's Welcome, MN ethanol plant: a range of \$117.47 and \$137.10 per dry MT of corn stover (from the Monte Carlo simulation). Feedback from the project team has indicated that wood may perform better than stover in the hydropyrolysis process.

Given the performance difference and the lower cost for delivered wood, it seems that wood would be the preferred raw material for the IH2 process over corn stover. However, there may be other economic drivers in the overall analysis (e. g., subsidies, incentives) that could make corn stover more attractive.

5 References

1. Carlson School of Management, University of Minnesota, Corn stover supply chain economic analysis (report and model), Cargill contracted, Cargill proprietary, 2013
2. Cook, "Economics of Alternative Corn Stover Logistics Systems," University of Wisconsin, 2011
3. Petrolia, "The Economics of Harvesting and Transporting Corn Stover for Conversion to Fuel Ethanol: A Case Study for Minnesota," University of Minnesota, 2006
4. Leboreiro et al, "Analysis of Supply Chain, Scale Factor, and Optimum Plant Capacity for the Production of Ethanol from Corn Stover," Archer Daniels Midland, 2013
5. Sokhansanj et al, "Techno-economic Analysis of Using Corn Stover to Supply Heat and Power to a Corn Ethanol Plant – Part 1: Cost of Feedstock Supply Logistics," Oak Ridge National Laboratory, 2009
6. Webster, "Single-pass Corn Stover Harvest System Productivity and Cost Analysis," Iowa State University (MS thesis), 2011
7. Shah, "Techno-economic Analysis and Life Cycle Assessment of the Corn Stover Biomass Feedstock Supply Chain System for a Midwest-based First-generation Cellulosic Biorefinery," Iowa State University (PhD thesis), 2013
8. Klingenfeld, "Corn Stover as a Bioenergy Feedstock: Identifying and Overcoming Barriers for Corn Stover Harvest, Storage, and Transport," Harvard Kennedy School, 2008
9. Tyndall et al, "Corn Stover as a Biofuel Feedstock in Iowa's Bio-economy: an Iowa Farmer Survey," Iowa State University, 2011
10. USDA, National Agricultural Statistics Service website: http://nass.usda.gov/index.asp

6 Appendix

The following pages show detailed single-point and Monte Carlo results of delivered corn stover cost for each Valero location modeled.

Ardmore, OK

Draw radius **304.2 miles**

Stover cost summary (single point)

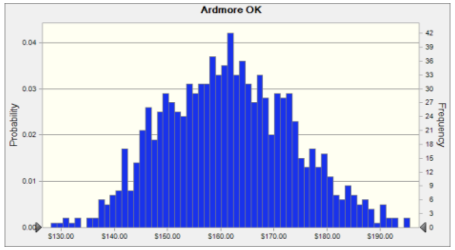
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$75.89***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$189.76***
Total cost per as-is MT stover	***$161.29***

Monte Carlo results

Forecast: Ardmore OK **Cell: U14**

Summary:

Entire range is from $128.18 to $200.42
Base case is $161.29
After 1,000 trials, the std. error of the mean is $0.38

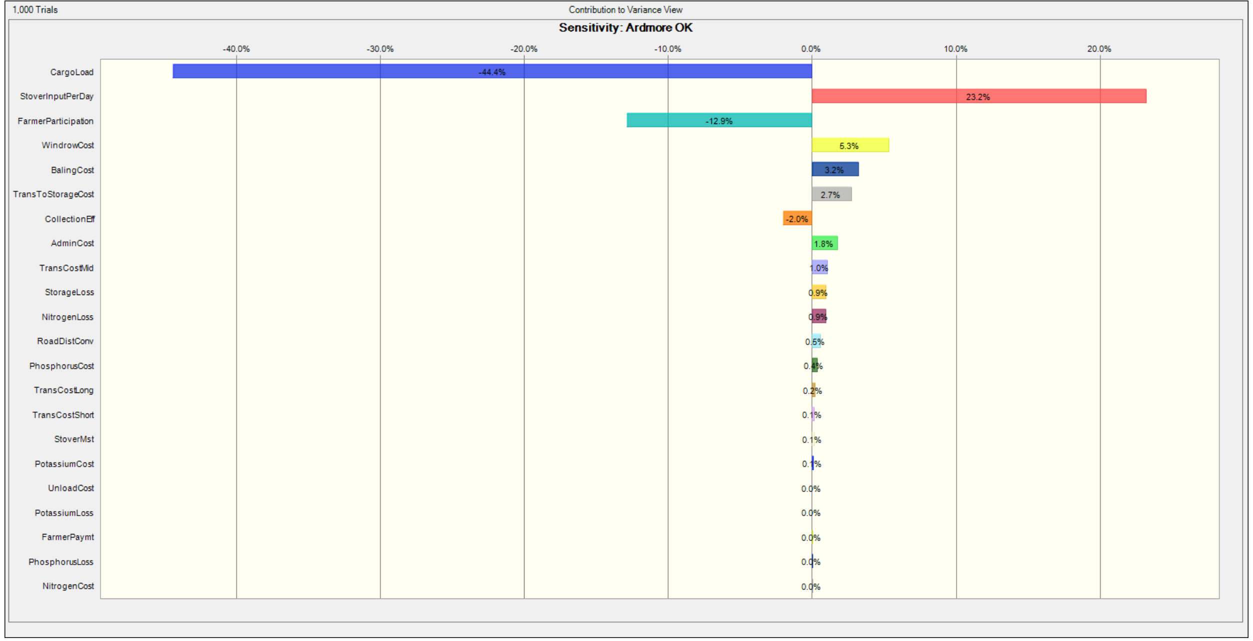


Statistics:	Forecast values
Trials	1,000
Mean	$161.51
Median	$161.33
Mode	---
Standard Deviation	$12.13
Variance	$147.15
Skewness	0.1549
Kurtosis	2.69
Coeff. of Variability	0.0751
Minimum	$128.18
Maximum	$200.42
Range Width	$72.24
Mean Std. Error	$0.38

Forecast: Ardmore OK (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$128.18
10%	$145.96
20%	$150.30
30%	$154.50
40%	$158.22
50%	$161.31
60%	$164.23
70%	$167.83
80%	$172.03
90%	$177.68
100%	$200.42

Sensitivity Chart (contribution to variance)



Benicia, CA

Draw radius **1278.4 miles**

Stover cost summary (single point)

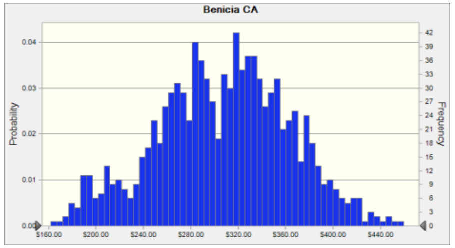
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$280.03***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$393.90***
Total cost per as-is MT stover	***$334.81***

Monte Carlo results

Forecast: Benicia CA **Cell: U14**

Summary:

Entire range is from $162.10 to $488.88
Base case is $334.81
After 1,000 trials, the std. error of the mean is $1.77

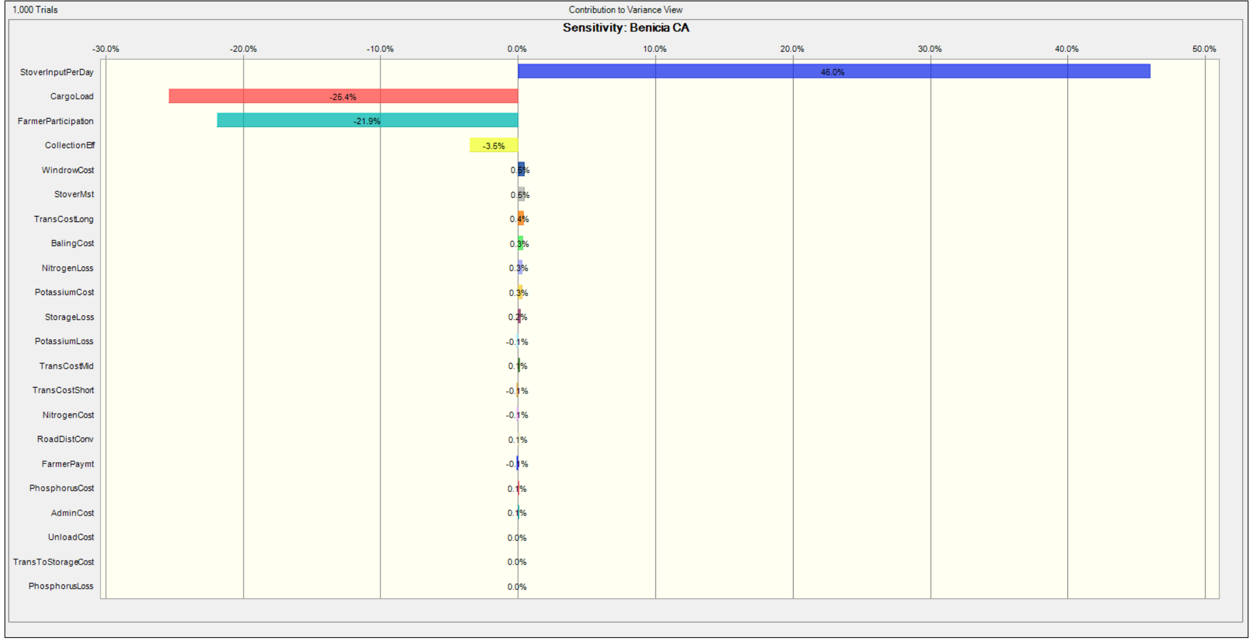


Statistics:	Forecast values
Trials	1,000
Mean	$307.68
Median	$310.60
Mode	---
Standard Deviation	$55.96
Variance	$3,131.58
Skewness	-0.0879
Kurtosis	2.70
Coeff. of Variability	0.1819
Minimum	$162.10
Maximum	$488.88
Range Width	$326.78
Mean Std. Error	$1.77

Forecast: Benicia CA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$162.10
10%	$234.48
20%	$260.81
30%	$277.99
40%	$292.20
50%	$310.52
60%	$324.22
70%	$338.42
80%	$355.07
90%	$378.50
100%	$488.88

Sensitivity Chart (contribution to variance)



Corpus Christi, TX

Draw radius **474.7 miles**

Stover cost summary (single point)

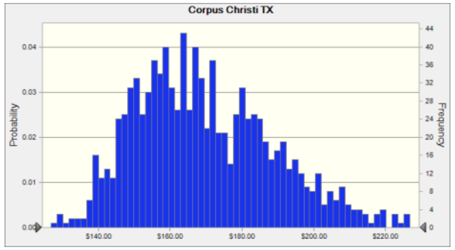
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$84.32***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$198.18***
Total cost per as-is MT stover	***$168.46***

Monte Carlo results

Forecast: Corpus Christi TX **Cell: U14**

Summary:

Entire range is from $126.87 to $248.30
Base case is $168.46
After 1,000 trials, the std. error of the mean is $0.64

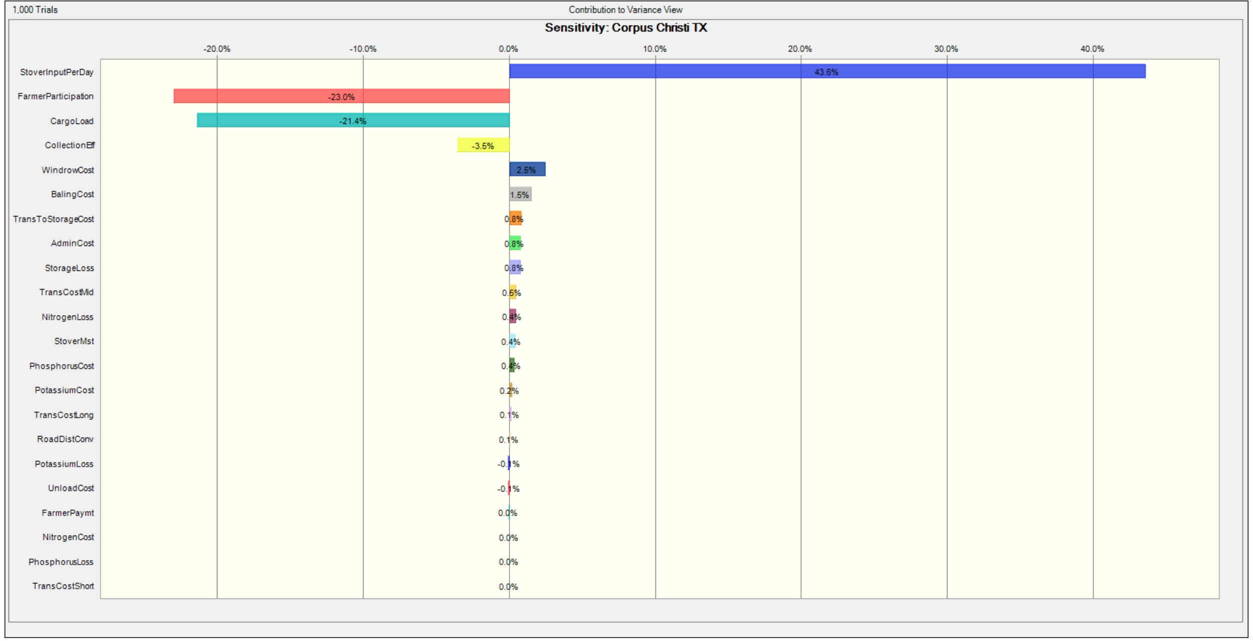


Statistics:	Forecast values
Trials	1,000
Mean	$170.29
Median	$167.44
Mode	---
Standard Deviation	$20.15
Variance	$405.89
Skewness	0.6872
Kurtosis	3.33
Coeff. of Variability	0.1183
Minimum	$126.87
Maximum	$248.30
Range Width	$121.43
Mean Std. Error	$0.64

Forecast: Corpus Christi TX (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$126.87
10%	$147.21
20%	$152.54
30%	$157.67
40%	$162.56
50%	$167.39
60%	$172.54
70%	$179.88
80%	$186.84
90%	$197.10
100%	$248.30

Sensitivity Chart (contribution to variance)



Houston, TX

Draw radius **283.4 miles**

Stover cost summary (single point)

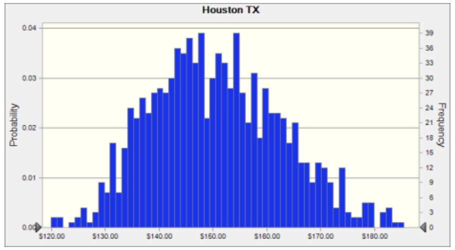
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$60.56***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$174.42***
Total cost per as-is MT stover	***$148.26***

Monte Carlo results

Forecast: Houston TX **Cell: U14**

Summary:

Entire range is from $120.00 to $196.50
Base case is $148.26
After 1,000 trials, the std. error of the mean is $0.40

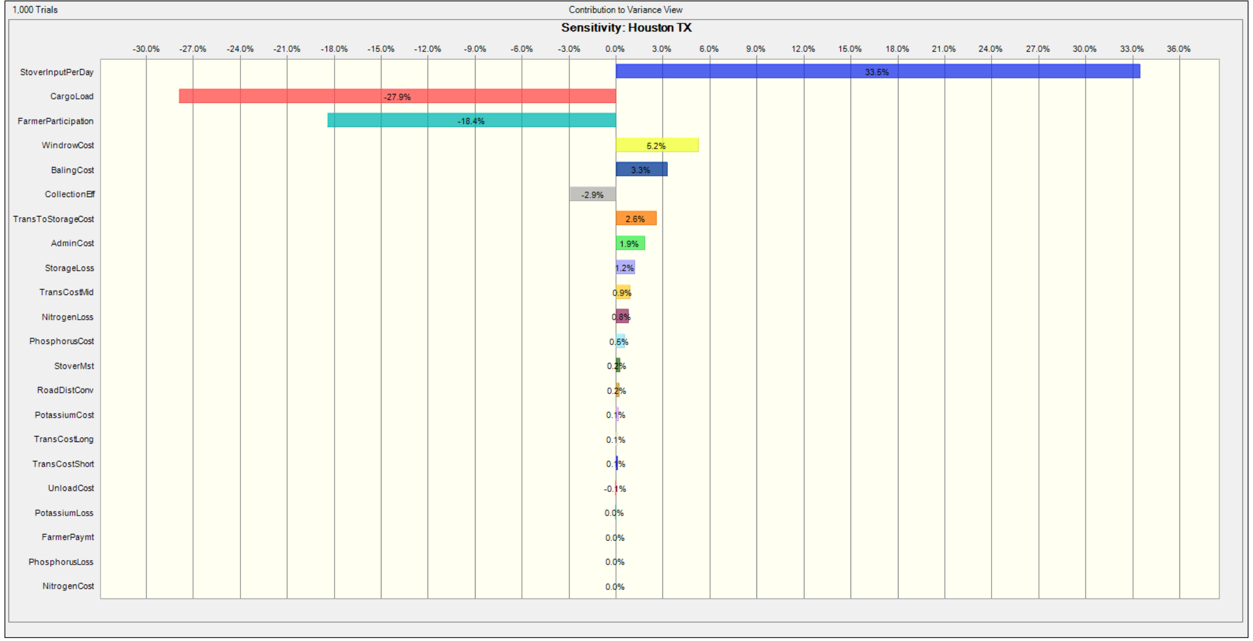


Statistics:	Forecast values
Trials	1,000
Mean	$151.05
Median	$149.83
Mode	---
Standard Deviation	$12.66
Variance	$160.22
Skewness	0.4597
Kurtosis	3.09
Coeff. of Variability	0.0838
Minimum	$120.00
Maximum	$196.50
Range Width	$76.50
Mean Std. Error	$0.40

Forecast: Houston TX (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$120.00
10%	$135.41
20%	$139.88
30%	$143.41
40%	$146.49
50%	$149.83
60%	$153.50
70%	$157.21
80%	$161.71
90%	$167.77
100%	$196.50

Sensitivity Chart (contribution to variance)



McKee (Sunray), TX

Draw radius **108.5 miles**

Stover cost summary (single point)

Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$21.49***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$135.35***
Total cost per as-is MT stover	***$115.05***

Monte Carlo results

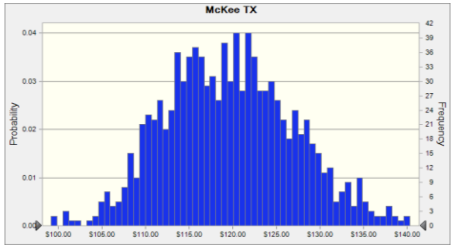
Forecast: McKee TX **Cell: U14**

Summary:

Entire range is from $99.20 to $141.89

Base case is $115.05

After 1,000 trials, the std. error of the mean is $0.23

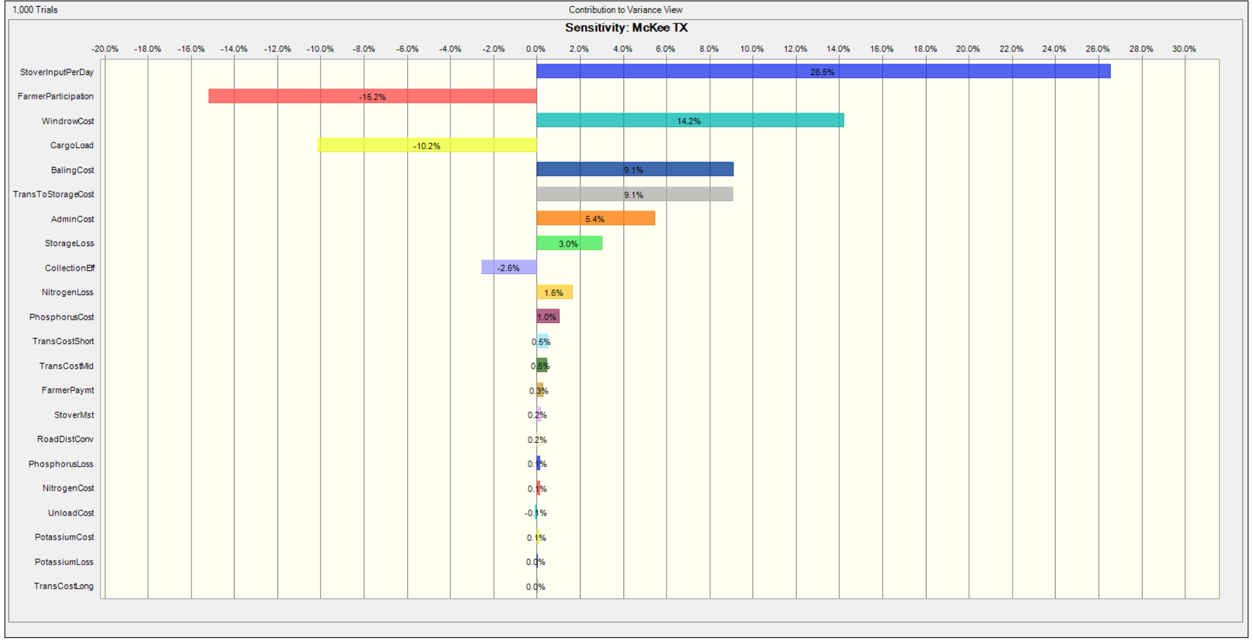


Statistics:	Forecast values
Trials	1,000
Mean	$119.67
Median	$119.46
Mode	---
Standard Deviation	$7.34
Variance	$53.89
Skewness	0.1901
Kurtosis	2.75
Coeff. of Variability	0.0613
Minimum	$99.20
Maximum	$141.89
Range Width	$42.69
Mean Std. Error	$0.23

Forecast: McKee TX (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$99.20
10%	$110.49
20%	$113.22
30%	$115.31
40%	$117.30
50%	$119.46
60%	$121.48
70%	$123.42
80%	$126.01
90%	$129.27
100%	$141.89

Sensitivity Chart (contribution to variance)



Memphis, TN

Draw radius	94.8 miles

Stover cost summary (single point)

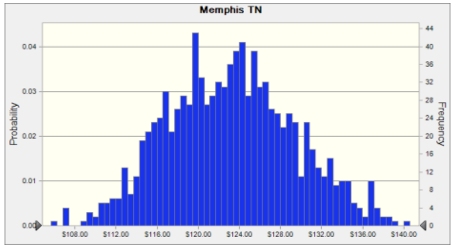
Harvesting	*$53.96*
Local storage	*$13.94*
Transportation	*$25.47*
Nutrient replacement	*$31.77*
Grinding	*$7.85*
Administrative	*$6.35*
Total cost per dry MT stover	*$139.34*
Total cost per as-is MT stover	*$118.44*

Monte Carlo results

Forecast: Memphis TN **Cell: U14**

Summary:

Entire range is from $105.13 to $140.90
Base case is $118.44
After 1,000 trials, the std. error of the mean is $0.20

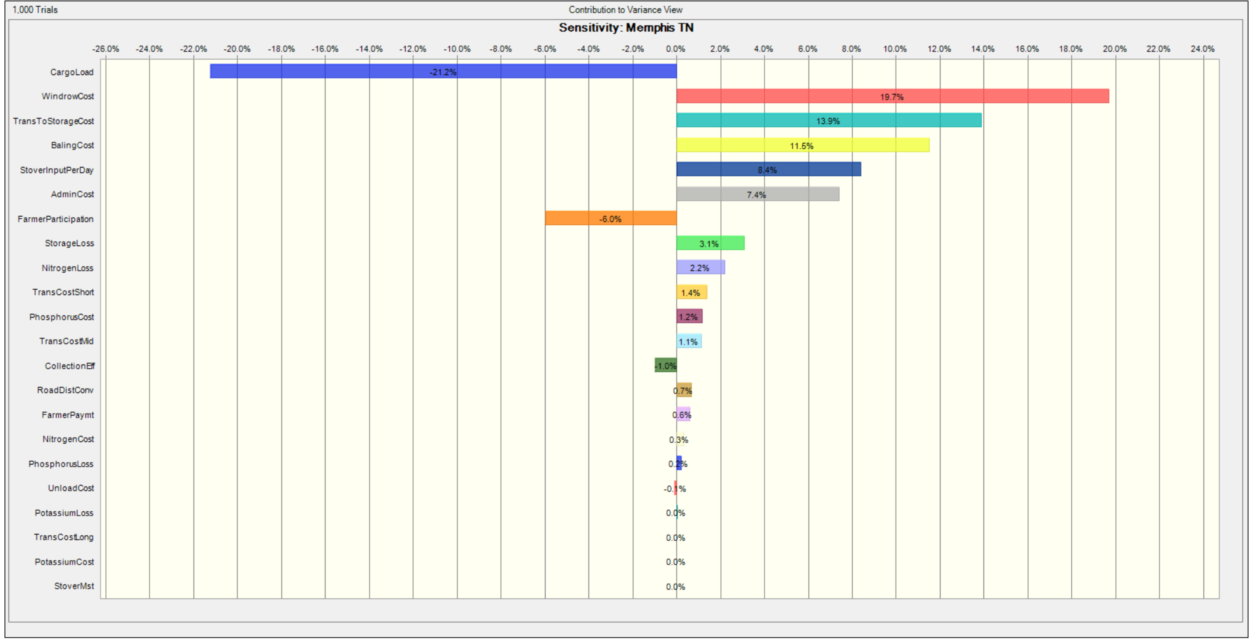


Statistics:	Forecast values
Trials	1,000
Mean	$123.13
Median	$123.18
Mode	---
Standard Deviation	$6.22
Variance	$38.71
Skewness	0.0871
Kurtosis	2.71
Coeff. of Variability	0.0505
Minimum	$105.13
Maximum	$140.90
Range Width	$35.77
Mean Std. Error	$0.20

Forecast: Memphis TN (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$105.13
10%	$115.26
20%	$117.58
30%	$119.56
40%	$121.32
50%	$123.17
60%	$124.61
70%	$126.33
80%	$128.52
90%	$131.41
100%	$140.90

Sensitivity Chart (contribution to variance)



Meraux, LA

Draw radius **265.4 miles**

Stover cost summary (single point)

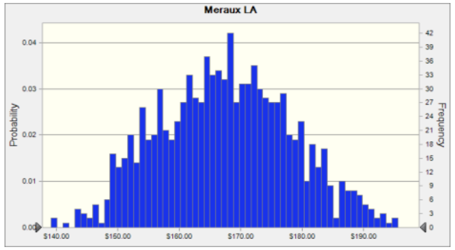
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$82.32***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$196.19***
Total cost per as-is MT stover	***$166.76***

Monte Carlo results

Forecast: Meraux LA **Cell: U14**

Summary:

Entire range is from $139.19 to $198.30
Base case is $166.76
After 1,000 trials, the std. error of the mean is $0.34

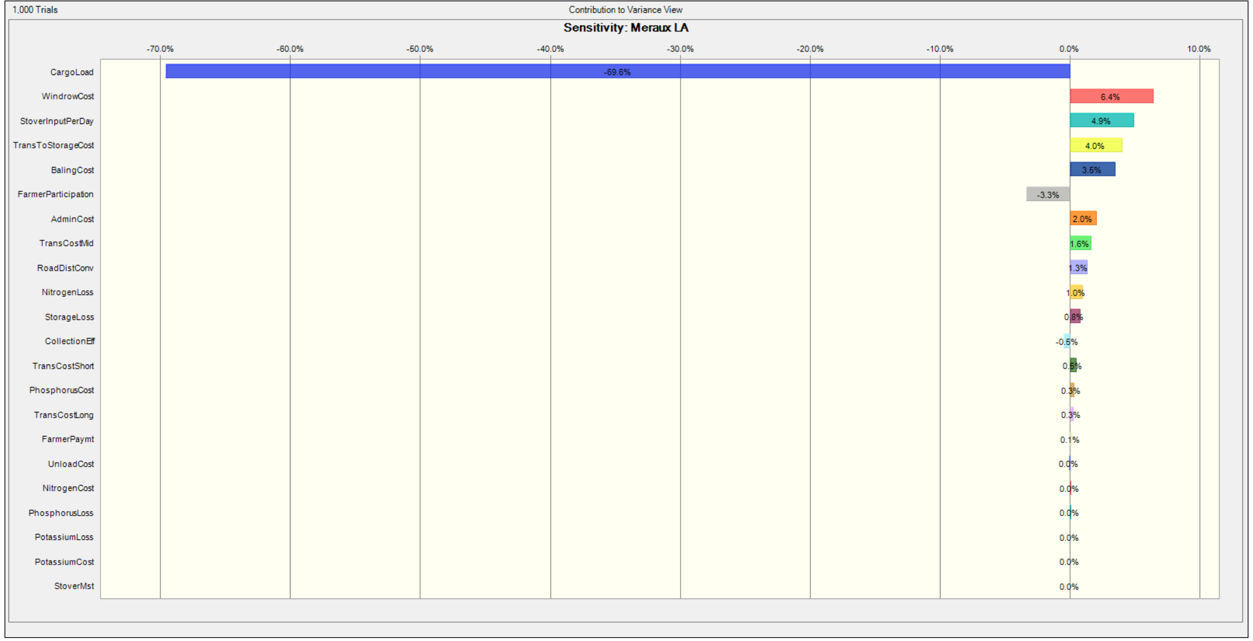


Statistics:	Forecast values
Trials	1,000
Mean	$167.52
Median	$167.40
Mode	---
Standard Deviation	$10.69
Variance	$114.21
Skewness	0.0899
Kurtosis	2.53
Coeff. of Variability	0.0638
Minimum	$139.19
Maximum	$198.30
Range Width	$59.11
Mean Std. Error	$0.34

Forecast: Meraux LA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$139.19
10%	$153.49
20%	$157.45
30%	$161.54
40%	$164.50
50%	$167.39
60%	$170.28
70%	$173.37
80%	$176.80
90%	$181.96
100%	$198.30

Sensitivity Chart (contribution to variance)



Port Arthur, TX

Draw radius	**267.4 miles**

Stover cost summary (single point)

Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$79.84***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$193.71***
Total cost per as-is MT stover	***$164.65***

Monte Carlo results

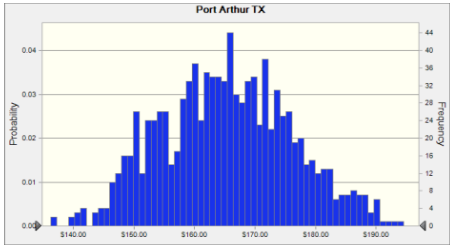
Forecast: Port Arthur TX **Cell: U14**

Summary:

Entire range is from $136.32 to $197.23

Base case is $164.65

After 1,000 trials, the std. error of the mean is $0.34

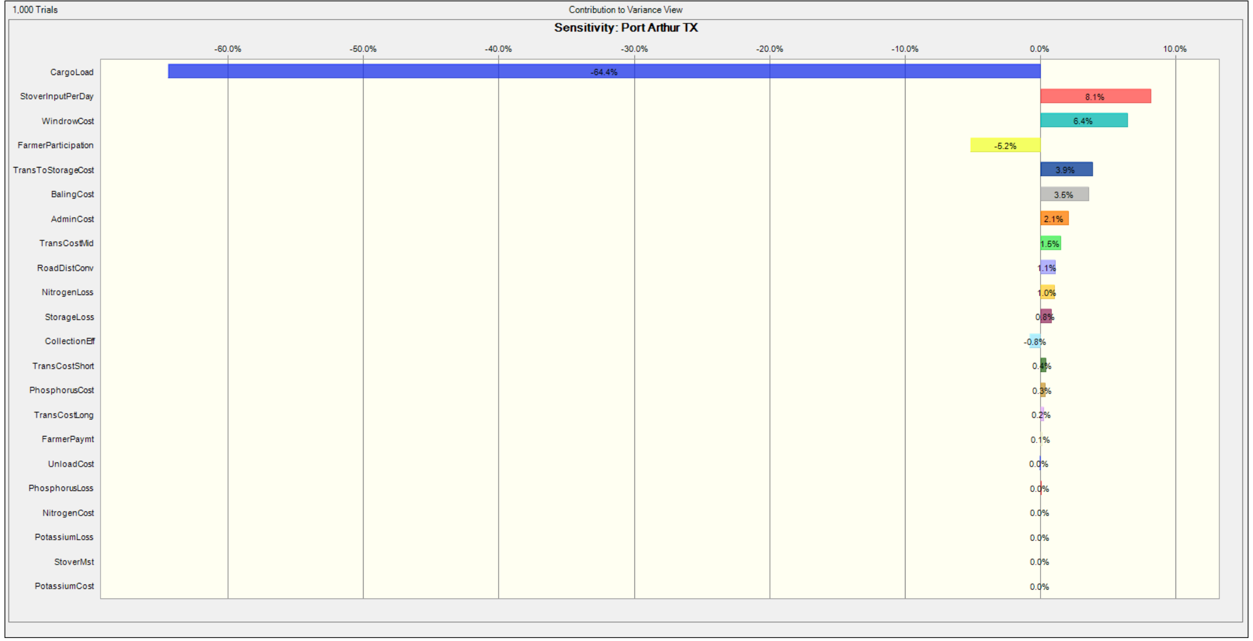


Statistics:	Forecast values
Trials	1,000
Mean	$165.34
Median	$165.29
Mode	---
Standard Deviation	$10.77
Variance	$115.94
Skewness	0.0995
Kurtosis	2.57
Coeff. of Variability	0.0651
Minimum	$136.32
Maximum	$197.23
Range Width	$60.91
Mean Std. Error	$0.34

Forecast: Port Arthur TX (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$136.32
10%	$150.80
20%	$155.18
30%	$159.46
40%	$162.41
50%	$165.25
60%	$167.99
70%	$171.31
80%	$174.71
90%	$179.73
100%	$197.23

Sensitivity Chart (contribution to variance)



St. Charles, LA

Draw radius **257.5 miles**

Stover cost summary (single point)

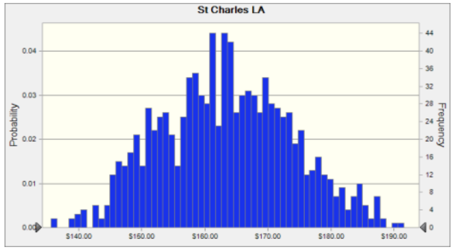
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$77.12***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$190.98***
Total cost per as-is MT stover	***$162.34***

Monte Carlo results

Forecast: St Charles LA **Cell: U14**

Summary:

Entire range is from $135.64 to $193.91
Base case is $162.34
After 1,000 trials, the std. error of the mean is $0.33

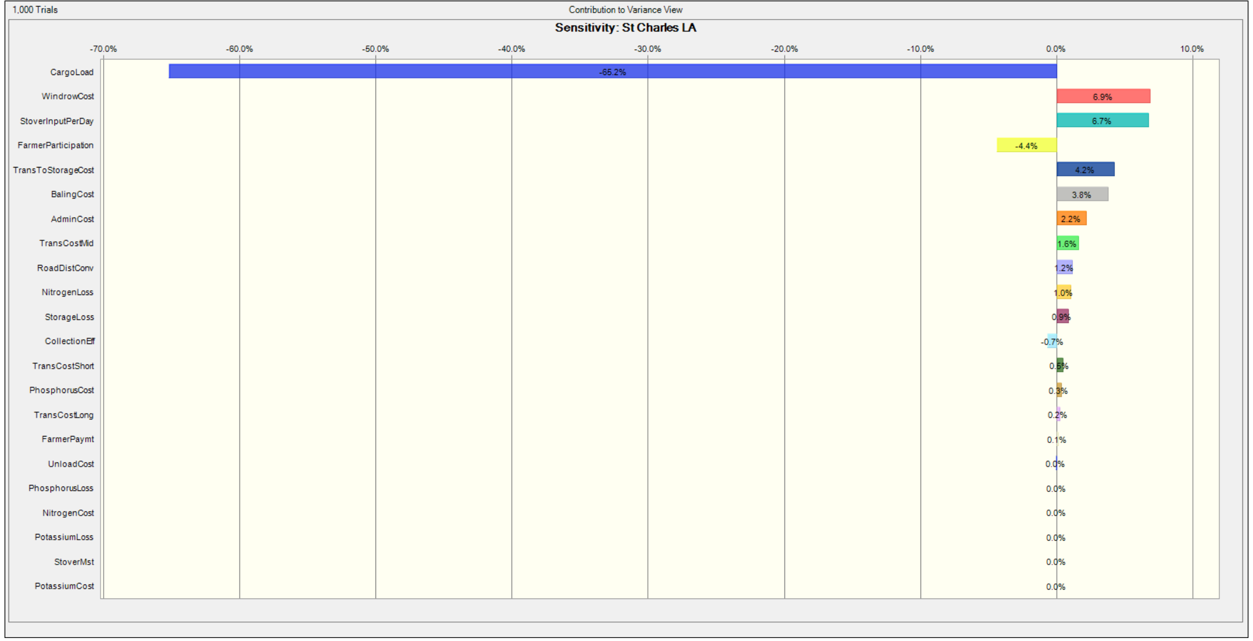


Statistics:	Forecast values
Trials	1,000
Mean	$163.41
Median	$163.32
Mode	---
Standard Deviation	$10.38
Variance	$107.67
Skewness	0.0998
Kurtosis	2.57
Coeff. of Variability	0.0635
Minimum	$135.64
Maximum	$193.91
Range Width	$58.26
Mean Std. Error	$0.33

Forecast: St Charles LA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$135.64
10%	$149.36
20%	$153.60
30%	$157.73
40%	$160.70
50%	$163.32
60%	$166.04
70%	$169.24
80%	$172.28
90%	$177.30
100%	$193.91

Sensitivity Chart (contribution to variance)



Texas City, TX

Draw radius	**303.0 miles**

Stover cost summary (single point)

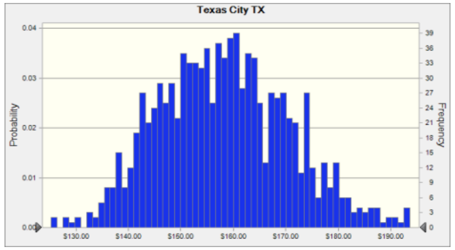
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$70.55***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$184.42***
Total cost per as-is MT stover	***$156.75***

Monte Carlo results

Forecast: Texas City TX **Cell: U14**

Summary:

Entire range is from $125.33 to $202.45
Base case is $156.75
After 1,000 trials, the std. error of the mean is $0.40

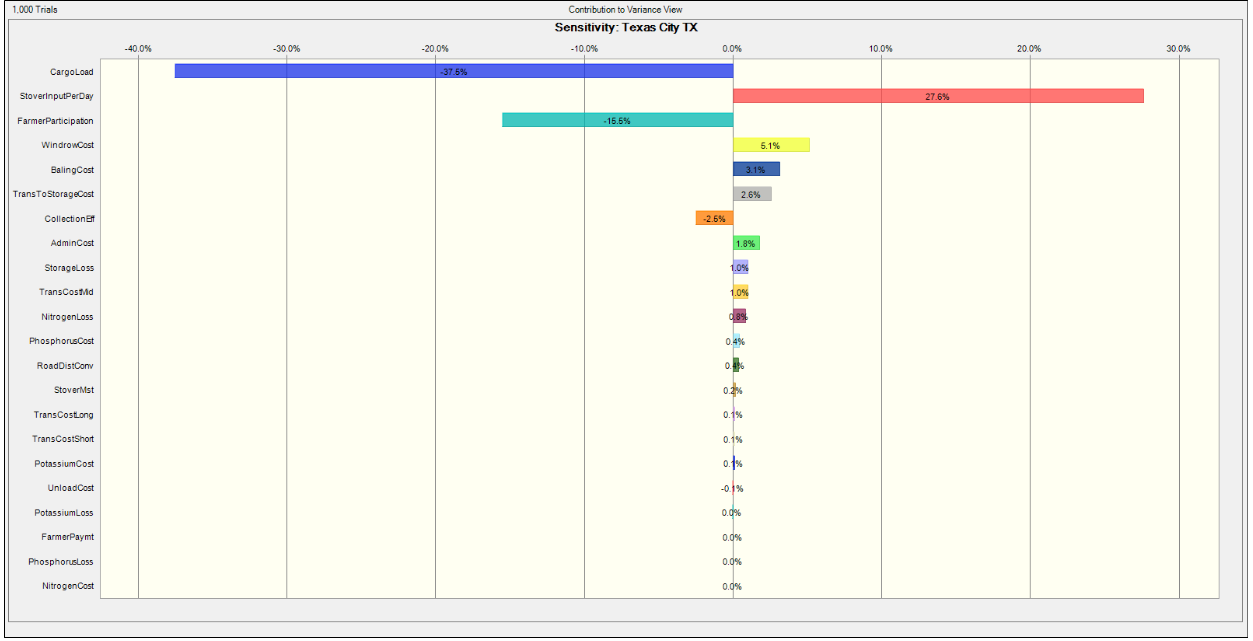


Statistics:	Forecast values
Trials	1,000
Mean	$158.39
Median	$157.89
Mode	---
Standard Deviation	$12.56
Variance	$157.81
Skewness	0.3143
Kurtosis	2.93
Coeff. of Variability	0.0793
Minimum	$125.33
Maximum	$202.45
Range Width	$77.13
Mean Std. Error	$0.40

Forecast: Texas City TX (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$125.33
10%	$142.65
20%	$147.09
30%	$151.08
40%	$154.50
50%	$157.89
60%	$160.81
70%	$164.30
80%	$169.17
90%	$174.42
100%	$202.45

Sensitivity Chart (contribution to variance)



Three Rivers, TX

Draw radius **460.7 miles**

Stover cost summary (single point)

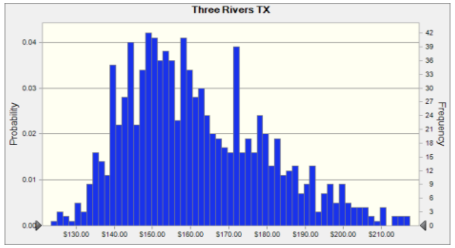
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$72.51***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$186.37***
Total cost per as-is MT stover	***$158.41***

Monte Carlo results

Forecast: Three Rivers TX **Cell: U14**

Summary:

Entire range is from $123.56 to $239.10
Base case is $158.41
After 1,000 trials, the std. error of the mean is $0.62

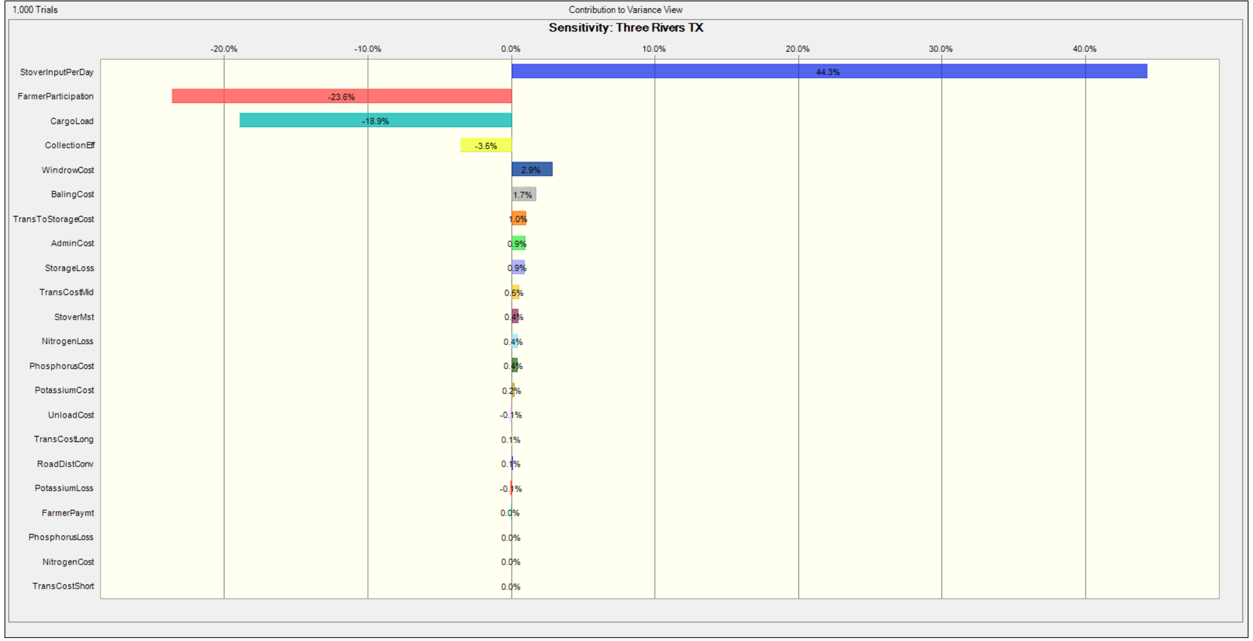


Statistics:	Forecast values
Trials	1,000
Mean	$162.62
Median	$158.79
Mode	---
Standard Deviation	$19.53
Variance	$381.31
Skewness	0.8303
Kurtosis	3.53
Coeff. of Variability	0.1201
Minimum	$123.56
Maximum	$239.10
Range Width	$115.54
Mean Std. Error	$0.62

Forecast: Three Rivers TX (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$123.56
10%	$140.46
20%	$145.81
30%	$149.97
40%	$154.15
50%	$158.77
60%	$163.84
70%	$171.63
80%	$178.44
90%	$189.43
100%	$239.10

Sensitivity Chart (contribution to variance)



Wilmington, CA

Draw radius	**1144.8 miles**

Stover cost summary (single point)

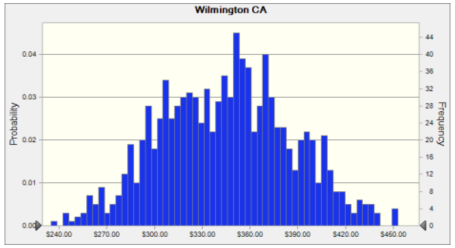
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$321.13***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$435.00***
Total cost per as-is MT stover	***$369.75***

Monte Carlo results

Forecast: Wilmington CA **Cell: U14**

Summary:

Entire range is from $235.13 to $482.74
Base case is $369.75
After 1,000 trials, the std. error of the mean is $1.30

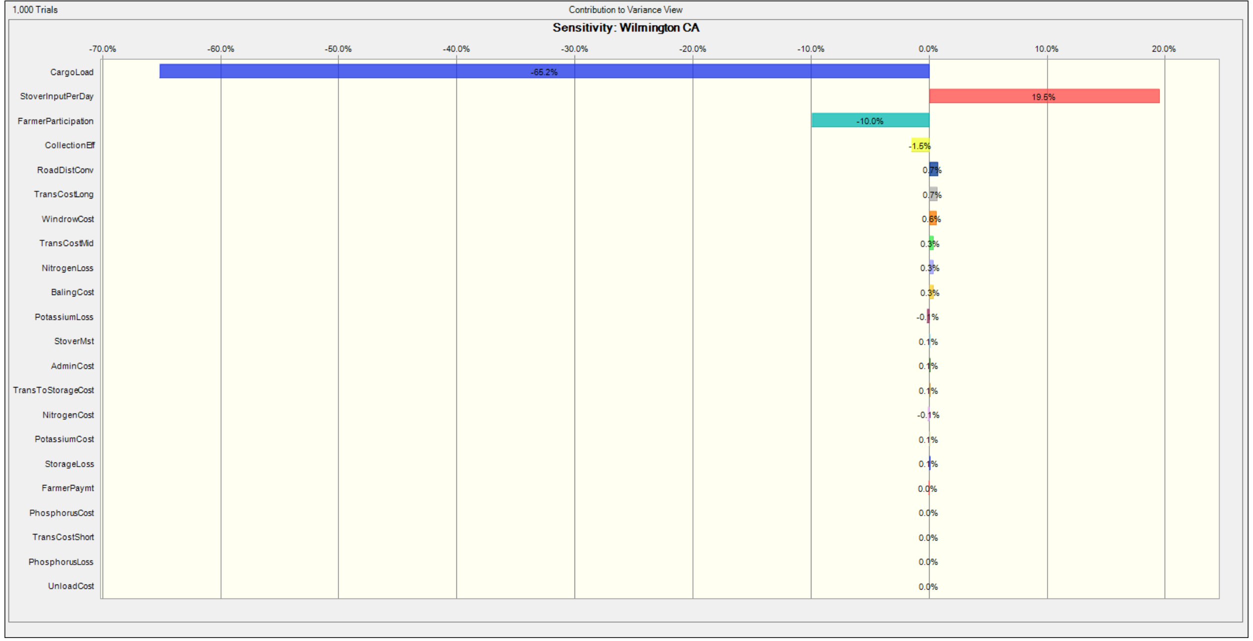


Statistics:	Forecast values
Trials	1,000
Mean	$345.18
Median	$346.21
Mode	---
Standard Deviation	$41.11
Variance	$1,689.83
Skewness	0.0694
Kurtosis	2.60
Coeff. of Variability	0.1191
Minimum	$235.13
Maximum	$482.74
Range Width	$247.60
Mean Std. Error	$1.30

Forecast: Wilmington CA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$235.13
10%	$292.82
20%	$307.64
30%	$320.78
40%	$333.26
50%	$346.07
60%	$355.48
70%	$368.04
80%	$380.30
90%	$400.22
100%	$482.74

Sensitivity Chart (contribution to variance)



Albert City, IA

Draw radius **36.2 miles**

Stover cost summary (single point)

Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$8.12***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$121.99***
Total cost per as-is MT stover	***$103.69***

Monte Carlo results

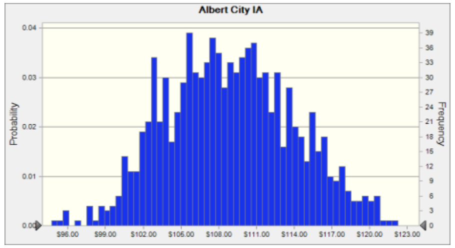
Forecast: Albert City IA **Cell: U14**

Summary:

Entire range is from $94.13 to $123.86

Base case is $103.69

After 1,000 trials, the std. error of the mean is $0.16

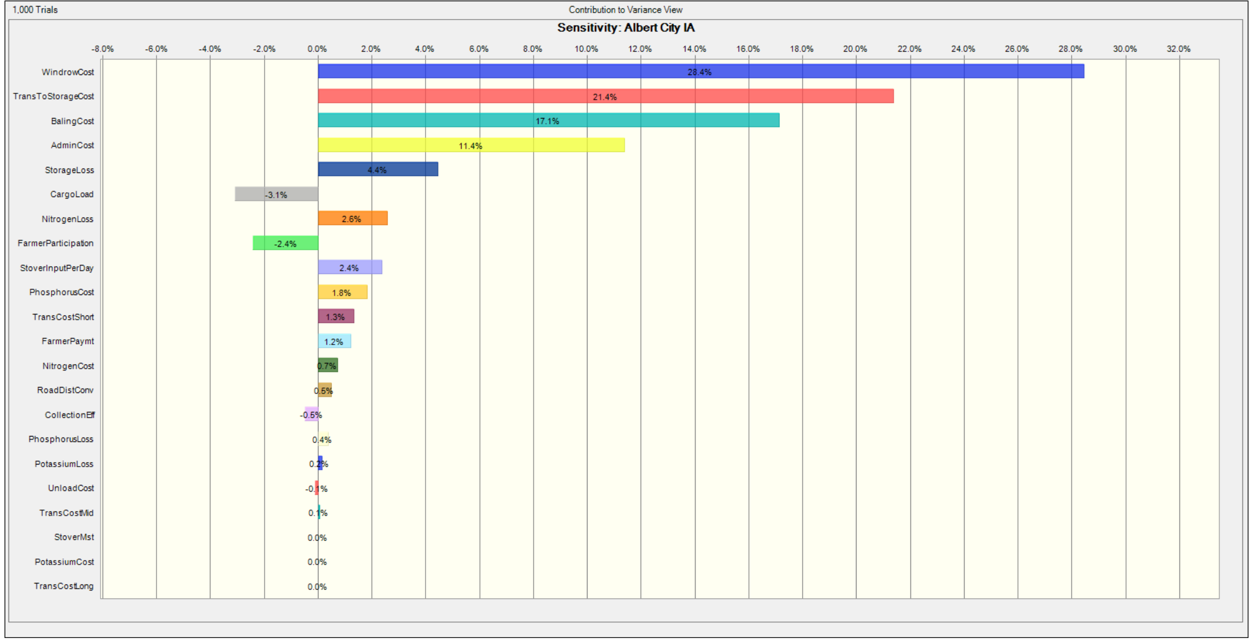


Statistics:	Forecast values
Trials	1,000
Mean	$108.93
Median	$108.82
Mode	---
Standard Deviation	$5.08
Variance	$25.84
Skewness	0.1118
Kurtosis	2.63
Coeff. of Variability	0.0467
Minimum	$94.13
Maximum	$123.86
Range Width	$29.73
Mean Std. Error	$0.16

Forecast: Albert City IA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$94.13
10%	$102.58
20%	$104.28
30%	$105.92
40%	$107.37
50%	$108.82
60%	$110.27
70%	$111.59
80%	$113.52
90%	$115.77
100%	$123.86

Sensitivity Chart (contribution to variance)



Albion, NE

Draw radius	**33.6 miles**

Stover cost summary (single point)

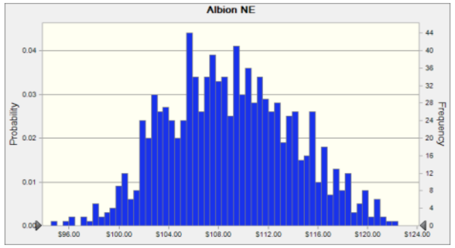
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$8.44***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$122.30***
Total cost per as-is MT stover	***$103.96***

Monte Carlo results

Forecast: Albion NE **Cell: U14**

Summary:

Entire range is from $93.83 to $123.72
Base case is $103.96
After 1,000 trials, the std. error of the mean is $0.16

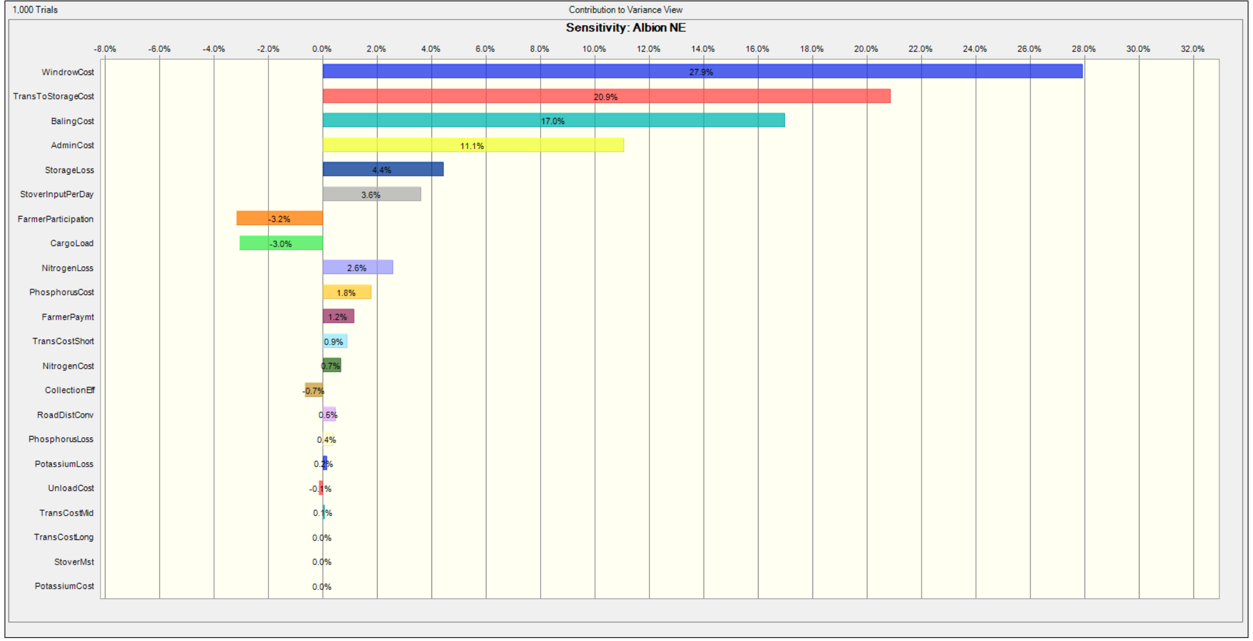


Statistics:	Forecast values
Trials	1,000
Mean	$108.97
Median	$108.83
Mode	---
Standard Deviation	$5.14
Variance	$26.44
Skewness	0.0959
Kurtosis	2.66
Coeff. of Variability	0.0472
Minimum	$93.83
Maximum	$123.72
Range Width	$29.90
Mean Std. Error	$0.16

Forecast: Albion NE (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$93.83
10%	$102.53
20%	$104.25
30%	$105.93
40%	$107.37
50%	$108.82
60%	$110.21
70%	$111.69
80%	$113.53
90%	$115.70
100%	$123.72

Sensitivity Chart (contribution to variance)



Aurora, SD

Draw radius	**45.6 miles**

Stover cost summary (single point)

Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$9.42***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$123.28***
Total cost per as-is MT stover	***$104.79***

Monte Carlo results

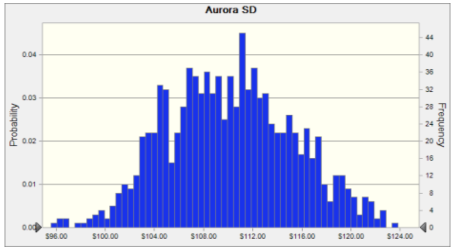
Forecast: Aurora SD **Cell: U14**

Summary:

Entire range is from $95.08 to $125.40

Base case is $104.79

After 1,000 trials, the std. error of the mean is $0.16

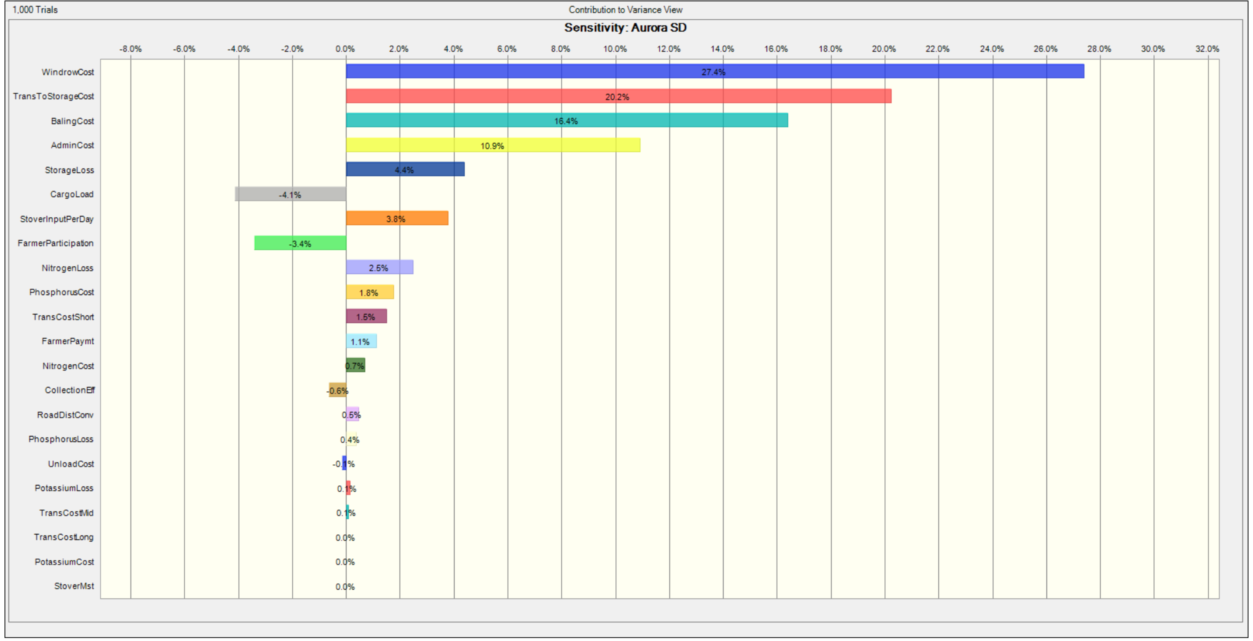


Statistics:	Forecast values
Trials	1,000
Mean	$110.18
Median	$110.12
Mode	---
Standard Deviation	$5.20
Variance	$27.08
Skewness	0.1074
Kurtosis	2.64
Coeff. of Variability	0.0472
Minimum	$95.08
Maximum	$125.40
Range Width	$30.33
Mean Std. Error	$0.16

Forecast: Aurora SD (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$95.08
10%	$103.63
20%	$105.37
30%	$107.14
40%	$108.53
50%	$110.12
60%	$111.42
70%	$112.90
80%	$114.92
90%	$117.15
100%	$125.40

Sensitivity Chart (contribution to variance)



Bloomingburg, OH

Draw radius **40.4 miles**

Stover cost summary (single point)

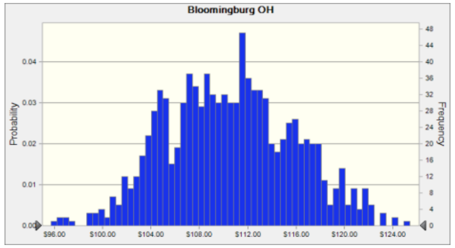
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$9.76***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$123.62***
Total cost per as-is MT stover	***$105.08***

Monte Carlo results

Forecast: Bloomingburg OH **Cell: U14**

Summary:

Entire range is from $95.47 to $125.91
Base case is $105.08
After 1,000 trials, the std. error of the mean is $0.17

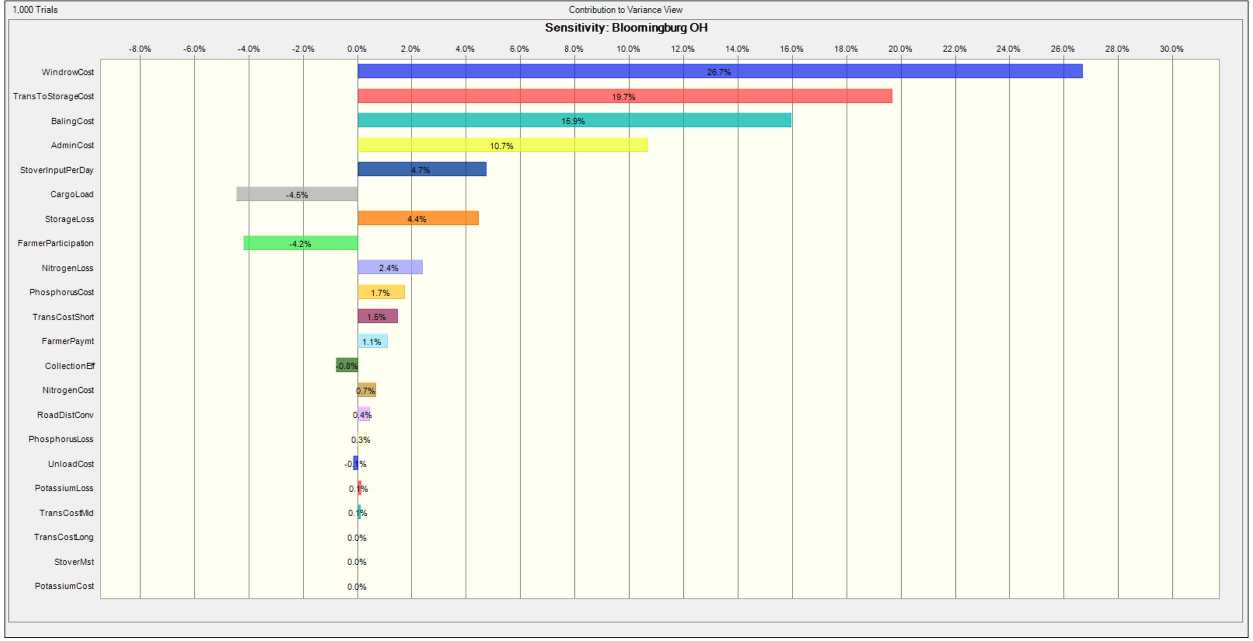


Statistics:	Forecast values
Trials	1,000
Mean	$110.57
Median	$110.46
Mode	---
Standard Deviation	$5.28
Variance	$27.92
Skewness	0.1143
Kurtosis	2.65
Coeff. of Variability	0.0478
Minimum	$95.47
Maximum	$125.91
Range Width	$30.44
Mean Std. Error	$0.17

Forecast: Bloomingburg OH (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$95.47
10%	$103.94
20%	$105.67
30%	$107.46
40%	$108.92
50%	$110.46
60%	$111.80
70%	$113.24
80%	$115.37
90%	$117.60
100%	$125.91

Sensitivity Chart (contribution to variance)



Charles City, IA

Draw radius	**33.6 miles**

Stover cost summary (single point)

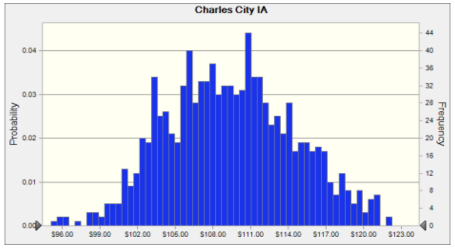
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$8.68***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$122.55***
Total cost per as-is MT stover	***$104.17***

Monte Carlo results

Forecast: Charles City IA **Cell: U14**

Summary:

Entire range is from $94.72 to $124.60
Base case is $104.17
After 1,000 trials, the std. error of the mean is $0.16

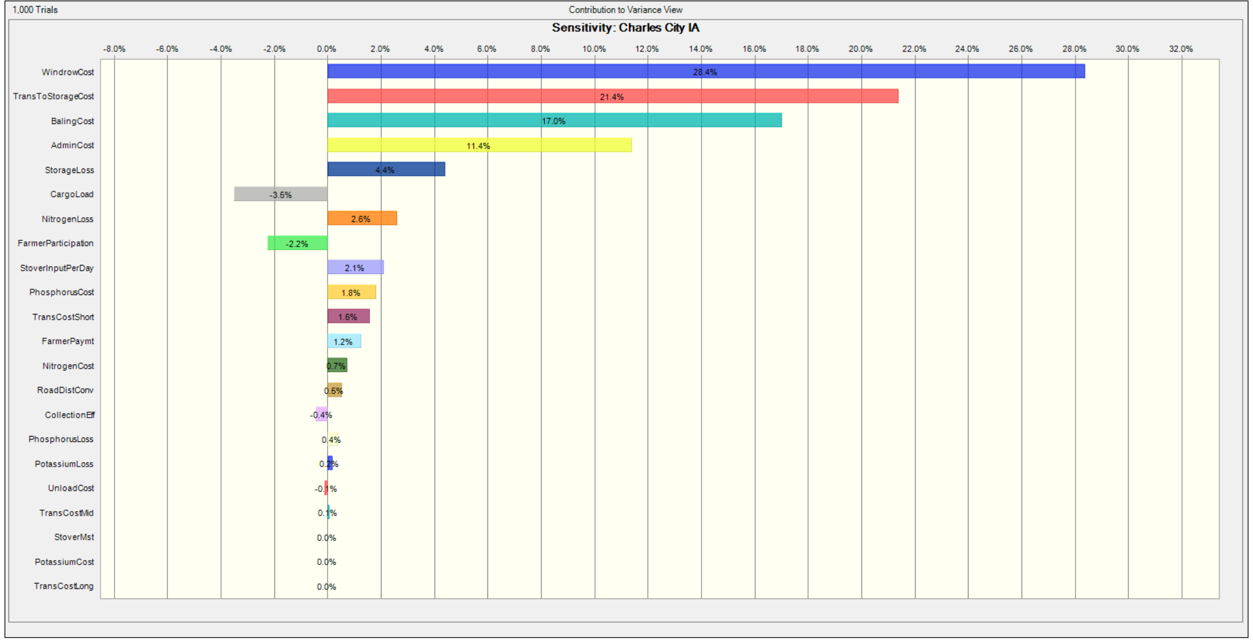


Statistics:	Forecast values
Trials	1,000
Mean	$109.40
Median	$109.25
Mode	---
Standard Deviation	$5.09
Variance	$25.91
Skewness	0.1144
Kurtosis	2.63
Coeff. of Variability	0.0465
Minimum	$94.72
Maximum	$124.60
Range Width	$29.87
Mean Std. Error	$0.16

Forecast: Charles City IA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$94.72
10%	$103.01
20%	$104.73
30%	$106.36
40%	$107.87
50%	$109.25
60%	$110.76
70%	$111.99
80%	$113.92
90%	$116.32
100%	$124.60

Sensitivity Chart (contribution to variance)



Fort Dodge, IA

Draw radius **34.7 miles**

Stover cost summary (single point)

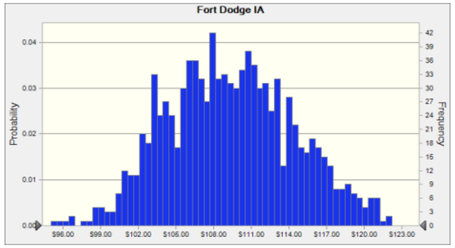
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$8.80***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$122.66***
Total cost per as-is MT stover	***$104.26***

Monte Carlo results

Forecast: Fort Dodge IA **Cell: U14**

Summary:

Entire range is from $94.52 to $124.42
Base case is $104.26
After 1,000 trials, the std. error of the mean is $0.16

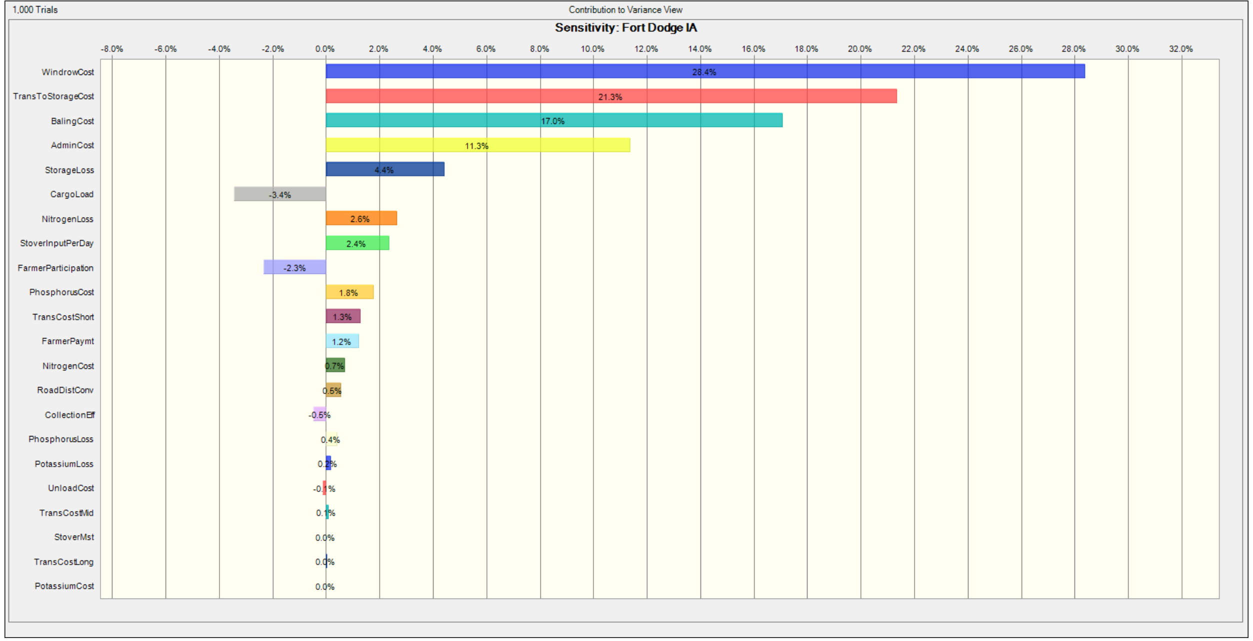


Statistics:	Forecast values
Trials	1,000
Mean	$109.32
Median	$109.19
Mode	---
Standard Deviation	$5.10
Variance	$25.96
Skewness	0.1063
Kurtosis	2.65
Coeff. of Variability	0.0466
Minimum	$94.52
Maximum	$124.42
Range Width	$29.90
Mean Std. Error	$0.16

Forecast: Fort Dodge IA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$94.52
10%	$102.93
20%	$104.64
30%	$106.34
40%	$107.79
50%	$109.18
60%	$110.67
70%	$111.99
80%	$113.88
90%	$116.17
100%	$124.42

Sensitivity Chart (contribution to variance)



Hartley, IA

Draw radius **39.5 miles**

Stover cost summary (single point)

Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$7.99***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$121.86***
Total cost per as-is MT stover	***$103.58***

Monte Carlo results

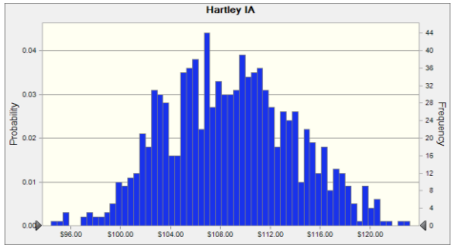
Forecast: Hartley IA **Cell: U14**

Summary:

Entire range is from $93.81 to $123.83

Base case is $103.58

After 1,000 trials, the std. error of the mean is $0.16

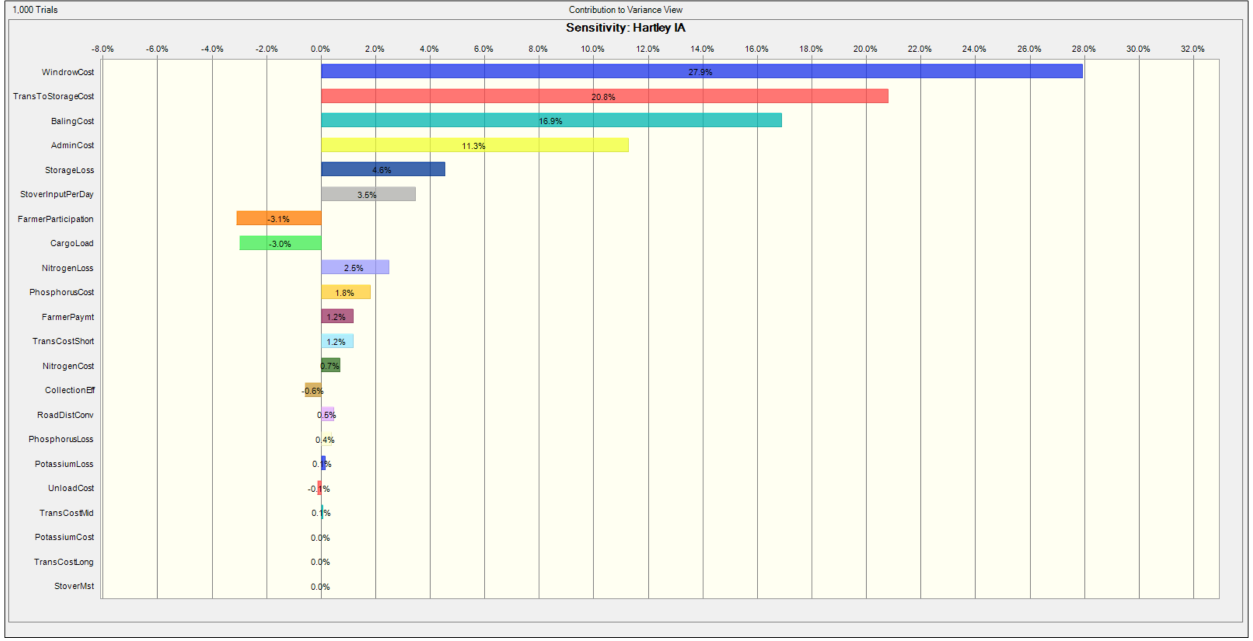


Statistics:	Forecast values
Trials	1,000
Mean	$108.81
Median	$108.71
Mode	---
Standard Deviation	$5.13
Variance	$26.30
Skewness	0.1094
Kurtosis	2.63
Coeff. of Variability	0.0471
Minimum	$93.81
Maximum	$123.83
Range Width	$30.02
Mean Std. Error	$0.16

Forecast: Hartley IA (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$93.81
10%	$102.34
20%	$104.17
30%	$105.79
40%	$107.14
50%	$108.70
60%	$110.05
70%	$111.46
80%	$113.35
90%	$115.65
100%	$123.83

Sensitivity Chart (contribution to variance)



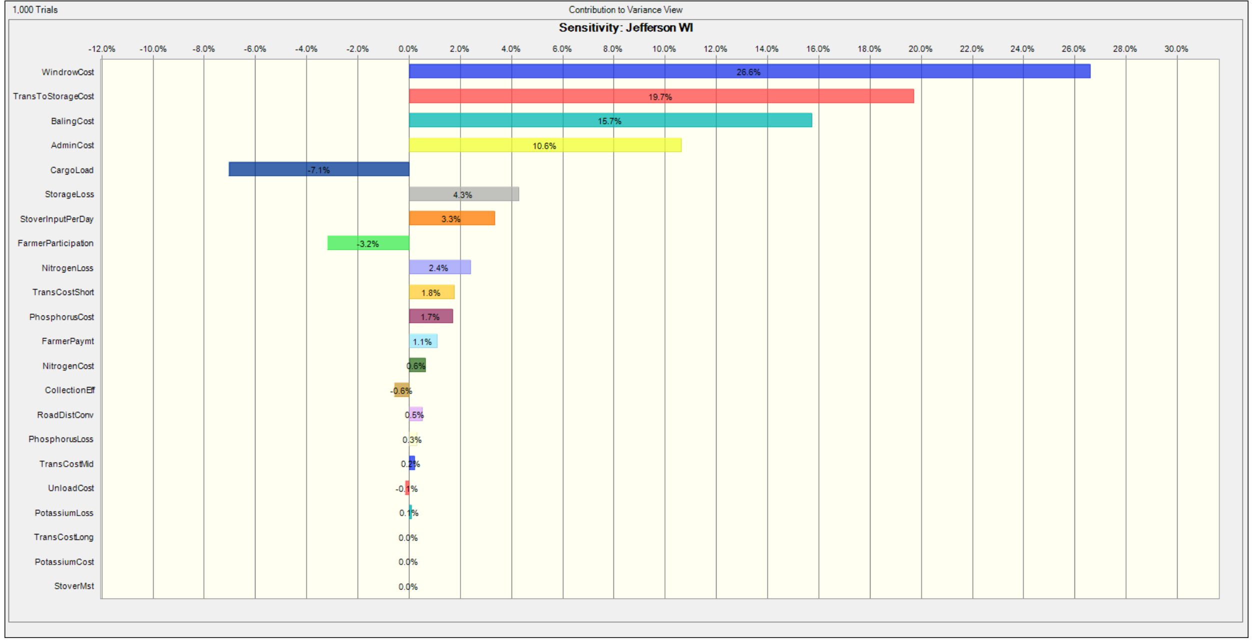
Jefferson, WI

Draw radius **52.2 miles**

Stover cost summary (single point)

Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$12.23***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$126.10***
Total cost per as-is MT stover	***$107.18***

Sensitivity Chart (contribution to variance)



Monte Carlo results

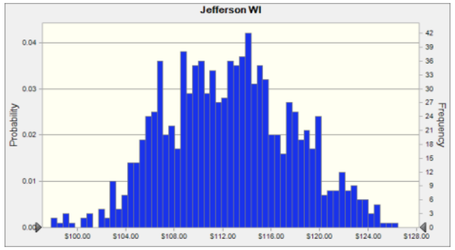
Forecast: Jefferson WI **Cell: U14**

Summary:

Entire range is from $97.87 to $128.37

Base case is $107.18

After 1,000 trials, the std. error of the mean is $0.17



Statistics:	Forecast values
Trials	1,000
Mean	$112.61
Median	$112.58
Mode	---
Standard Deviation	$5.29
Variance	$27.96
Skewness	0.1145
Kurtosis	2.63
Coeff. of Variability	0.0470
Minimum	$97.87
Maximum	$128.37
Range Width	$30.50
Mean Std. Error	$0.17

Forecast: Jefferson WI (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$97.87
10%	$105.84
20%	$107.71
30%	$109.52
40%	$111.00
50%	$112.55
60%	$113.92
70%	$115.29
80%	$117.37
90%	$119.70
100%	$128.37

Linden, IN

Draw radius **33.9 miles**

Stover cost summary (single point)

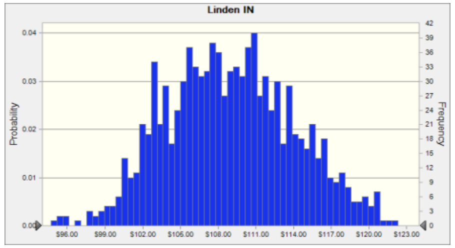
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$8.23***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$122.10***
Total cost per as-is MT stover	***$103.78***

Monte Carlo results

Forecast: Linden IN **Cell: U14**

Summary:

Entire range is from $94.11 to $123.92
Base case is $103.78
After 1,000 trials, the std. error of the mean is $0.16

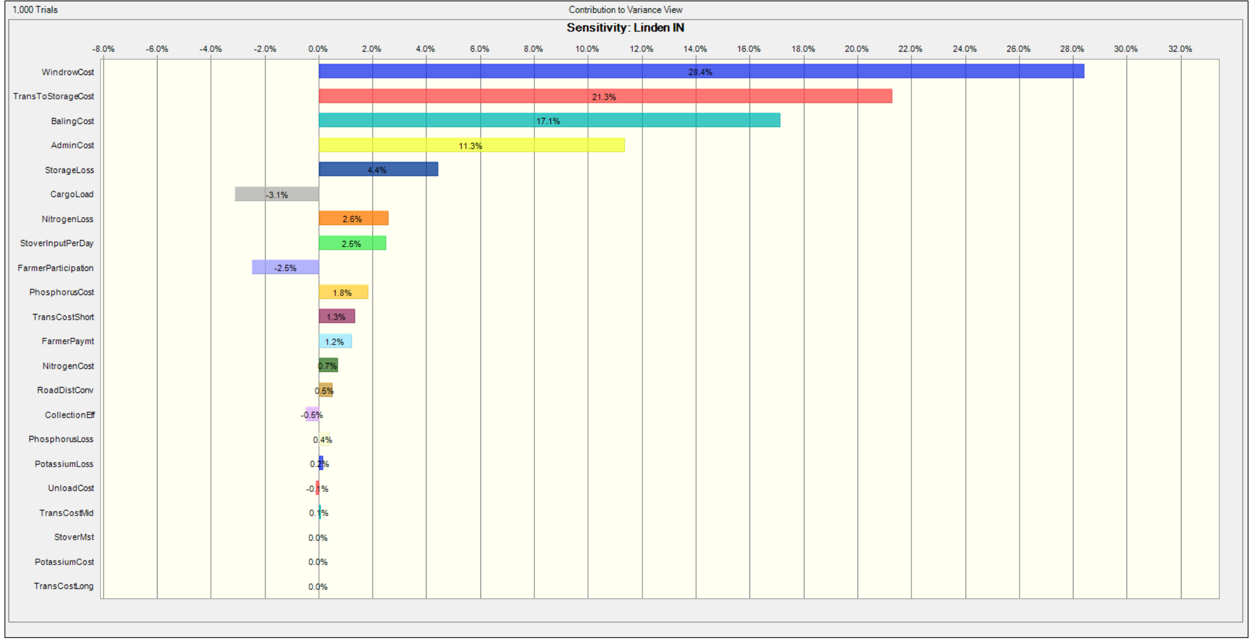


Statistics:	Forecast values
Trials	1,000
Mean	$108.99
Median	$108.90
Mode	---
Standard Deviation	$5.09
Variance	$25.88
Skewness	0.1117
Kurtosis	2.63
Coeff. of Variability	0.0467
Minimum	$94.11
Maximum	$123.92
Range Width	$29.81
Mean Std. Error	$0.16

Forecast: Linden IN (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$94.11
10%	$102.62
20%	$104.29
30%	$105.96
40%	$107.43
50%	$108.90
60%	$110.33
70%	$111.65
80%	$113.56
90%	$115.83
100%	$123.92

Sensitivity Chart (contribution to variance)



Mount Vernon, IN

Draw radius	**39.1 miles**

Stover cost summary (single point)

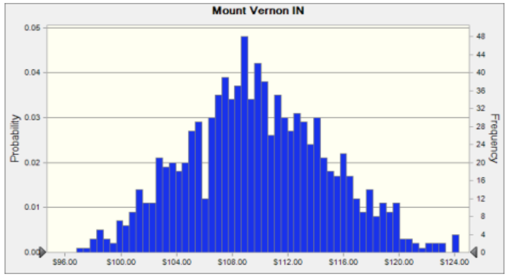
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$9.04***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$122.91***
Total cost per as-is MT stover	***$104.47***

Monte Carlo results

Forecast: Mount Vernon IN **Cell: U14**

Summary:

Entire range is from $95.28 to $128.96
Base case is $104.47
After 1,000 trials, the std. error of the mean is $0.16

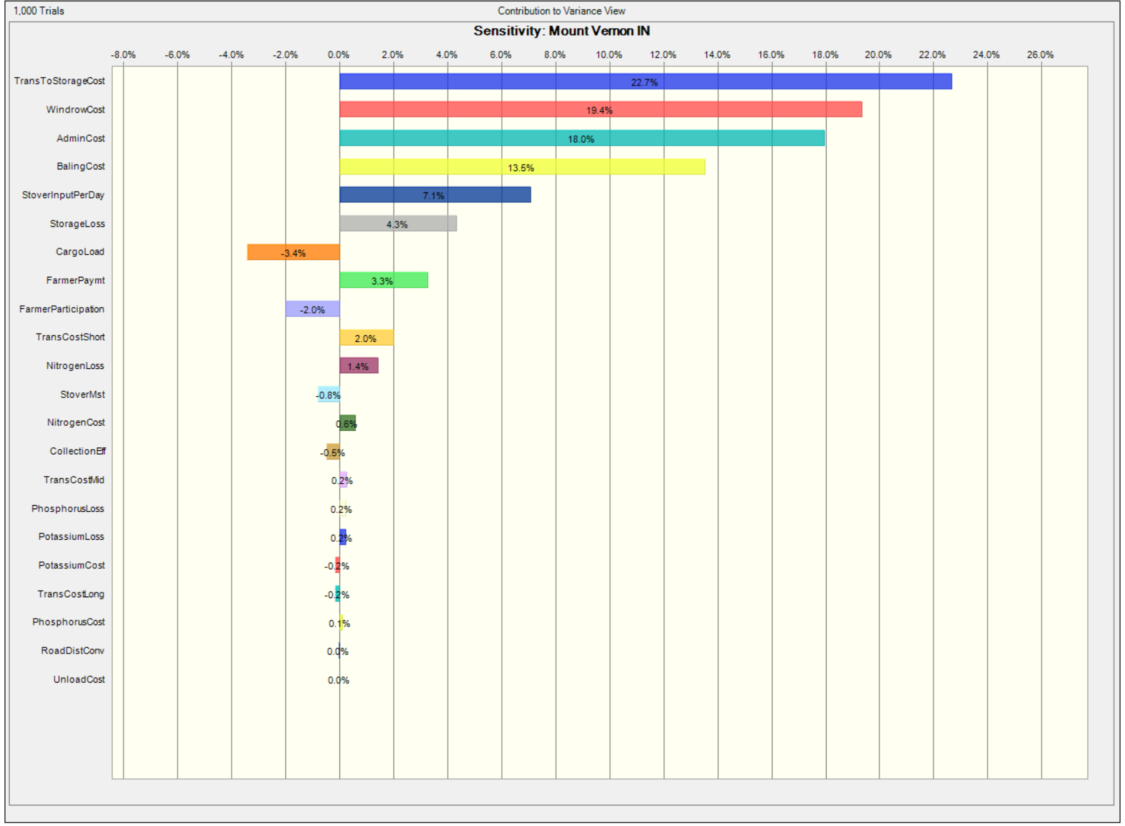


Statistics:	Forecast values
Trials	1,000
Mean	$109.85
Median	$109.64
Mode	---
Standard Deviation	$5.15
Variance	$26.54
Skewness	0.1755
Kurtosis	2.90
Coeff. of Variability	0.0469
Minimum	$95.28
Maximum	$128.96
Range Width	$33.68
Mean Std. Error	$0.16

Forecast: Mount Vernon IN (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$95.28
10%	$103.06
20%	$105.37
30%	$107.16
40%	$108.46
50%	$109.63
60%	$110.97
70%	$112.48
80%	$114.20
90%	$116.56
100%	$128.96

Sensitivity Chart (contribution to variance)



Welcome, MN

Draw radius **32.7 miles**

Stover cost summary (single point)

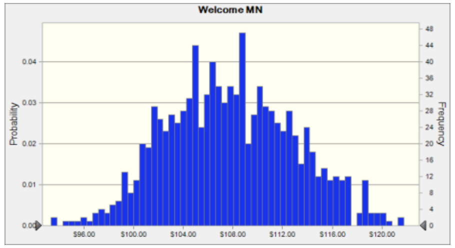
Harvesting	***$53.96***
Local storage	***$13.94***
Transportation	***$7.05***
Nutrient replacement	***$31.77***
Grinding	***$7.85***
Administrative	***$6.35***
Total cost per dry MT stover	***$120.91***
Total cost per as-is MT stover	***$102.77***

Monte Carlo results

Forecast: Welcome MN **Cell: U14**

Summary:

Entire range is from $92.46 to $122.75
Base case is $102.77
After 1,000 trials, the std. error of the mean is $0.16

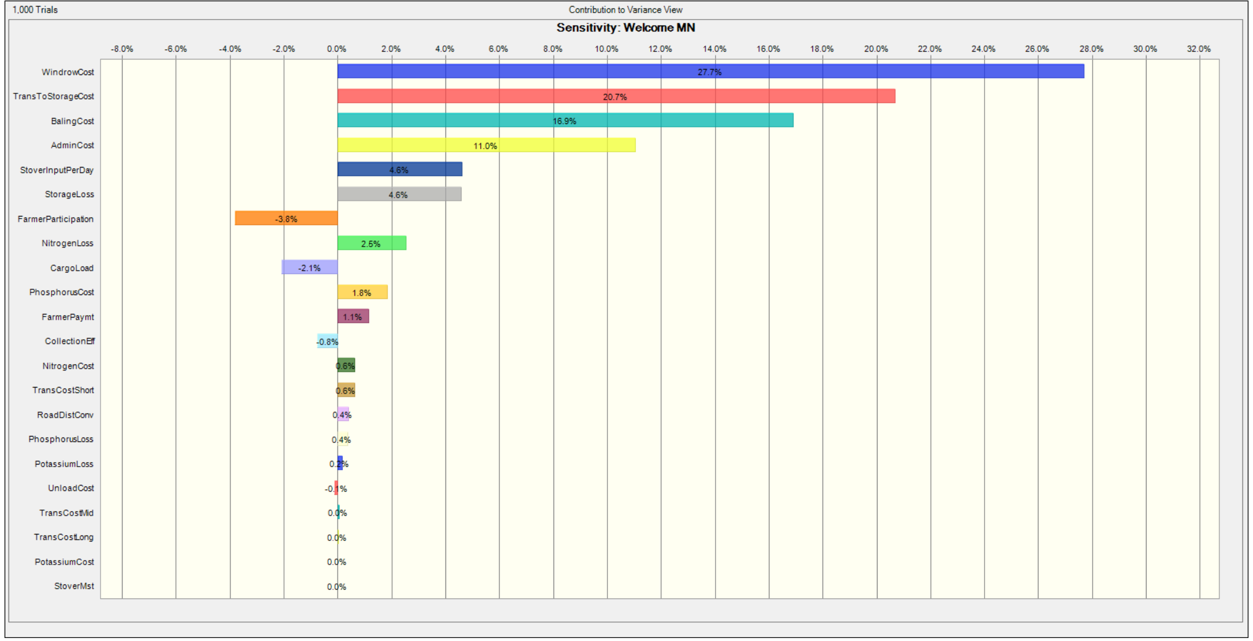


Statistics:	Forecast values
Trials	1,000
Mean	$107.80
Median	$107.60
Mode	---
Standard Deviation	$5.15
Variance	$26.52
Skewness	0.0952
Kurtosis	2.66
Coeff. of Variability	0.0478
Minimum	$92.46
Maximum	$122.75
Range Width	$30.29
Mean Std. Error	$0.16

Forecast: Welcome MN (cont'd) **Cell: U14**

Percentiles:	Forecast values
0%	$92.46
10%	$101.31
20%	$103.06
30%	$104.80
40%	$106.26
50%	$107.60
60%	$108.94
70%	$110.53
80%	$112.36
90%	$114.60
100%	$122.75

Sensitivity Chart (contribution to variance)



IH^{2}® Biomass-to-Fuels
GTI – DOE STUDY
DEPARTMENT OF ENERGY REFINERY INTEGRATED DESIGN

UNIT PROCESS DESCRIPTIONS

THIS DOCUMENT WAS PRODUCED BY KELLOGG BROWN & ROOT LLC USING INFORMATION FROM GAS TECHNOLOGY INSTITUTE (GTI).

Job No.: F-954

Document No.: F954-KBR-00-PR-GR10-0001

Rev.	Date	Issued for	Prepared	Reviewed	Approved	Approved
0	20-NOV-2014	ICR – ISSUED FOR CLIENT REVIEW	LAT	MHC	EJ	

Table of Contents

BIOMASS CONVERSION PROCESS

Biomass is trucked into the facility and is expected be ground and dried to the right specifications for processing (<3.3mm wood chips and 10% moisture). The trucks are off-loaded into solids storage tanks that feed into a lock hopper system. The lock hopper system is pressurizes with hydrogen to get the feed into the process.

The conversion process combines the biomass with catalyst and additional hydrogen in the 1st stage reactor to convert it into Fuel Gas, Naphtha, Diesel, BioChar, and Sour Water which are separated further downstream in the process.

The BioChar is removed from the 1st stage reactor effluent and then depressured, purged, and sent to the solids boiler.

After the BioChar is removed, the reactor effluent goes to the 2nd stage reactor for final hydrocarbon stabilization and then is cooled through a series of exchangers that make steam which is used in the process. The reactor effluent then goes to the Hydrocarbon Separation area.

Low Pressure and High Pressure Carbon Dioxide are used for purging and pressurizing of some of the solids systems in this area.

HYDROCARBON SEPARATION/TANKAGE

The cooled reactor effluent material goes to a three phase separator drum.

The gas from the three phase separator drum goes to a PSA (or membrane) where hydrogen is recovered and sent to the Hydrogen Auxiliaries and the residual gas goes to an Absorber Tower system to remove the butane and heavier components. The butane and heavier components go to the Primary Fractionator to be combined with the other Gasoline material from the reactors. The remaining light end hydrocarbons (Fuel Gas) are sent to a gas boiler.

The light liquid material (Gasoline & Diesel) from the three phase separator drum, along with the butane and heavier components from the gas stream, goes to the Primary Fractionator where Gasoline and light ends are separated from Diesel. The Gasoline is sent to a Splitter Tower that will remove any light ends that would cause the Gasoline RVP to be out of specification. The light ends from the Splitter Tower are combined with the light ends material from the Primary Fractionator and are sent to the Absorber Tower to combine with the gas phase light ends. Gasoline from the Splitter Tower goes to a product day tank where it can be tested before being blended into finished Gasoline. Diesel from the Primary Fractionator is dried and then sent to a product day tank where it can be tested before being blended into finished Diesel fuel. A recycle stream of Diesel is used as a sponge oil that runs between the Primary Fractionator and the Absorber Tower on the gas stream.

The heavy liquid material from the three phase separator drum is sour water. It is collected into a header along with water drains from the Primary Fractionator and the Splitter Tower. The header goes to a Degassing Drum and then the water is sent to a Sour Water Stripper in the co-located refinery.

HYDROGEN AUXILIARIES

The hydrogen auxiliaries' area combines the recovered Hydrogen from the gas section of Hydrocarbon Separation area with pure make-up hydrogen from the co-located refinery. This combined hydrogen is then cooled and/or heated as needed to be used in the Biomass Conversion Process.

AMINE REGENERATION UNIT (ARU)

An inert gas system is required for the purging and pressuring of the feed and Char handling systems. To facilitate this, an amine system is used to capture CO_2 from the co-located Hydrogen Plant syn gas. The syn gas from the hydrogen plant will go to an Amine Contact Tower where lean amine (activated MDEA) will absorb the required amount of CO_2. The rich amine from the bottom of this contactor goes to an Amine Regenerator Tower where the CO_2 is stripped out of the amine. The CO_2 is then dried and compressed to make a high and low pressure inert gas used in the Biomass Conversion Process.

BOILERS

There are two boilers in the system used to generate high pressure superheated steam. This steam is then sent to the Power Generation area. The solids boiler burns the BioChar and creates an ash product. The gas boiler burns all light ends (fuel gas) from the Absorber Tower.

POWER GENERATION

The high pressure superheated steam from the boilers is fed to a turbo-generator where power is made and fed back to the process as needed with the rest going to the power grid. The turbine is a condensing type with a surface condenser where the condensate is recycled back to the refinery.

COOLING TOWER

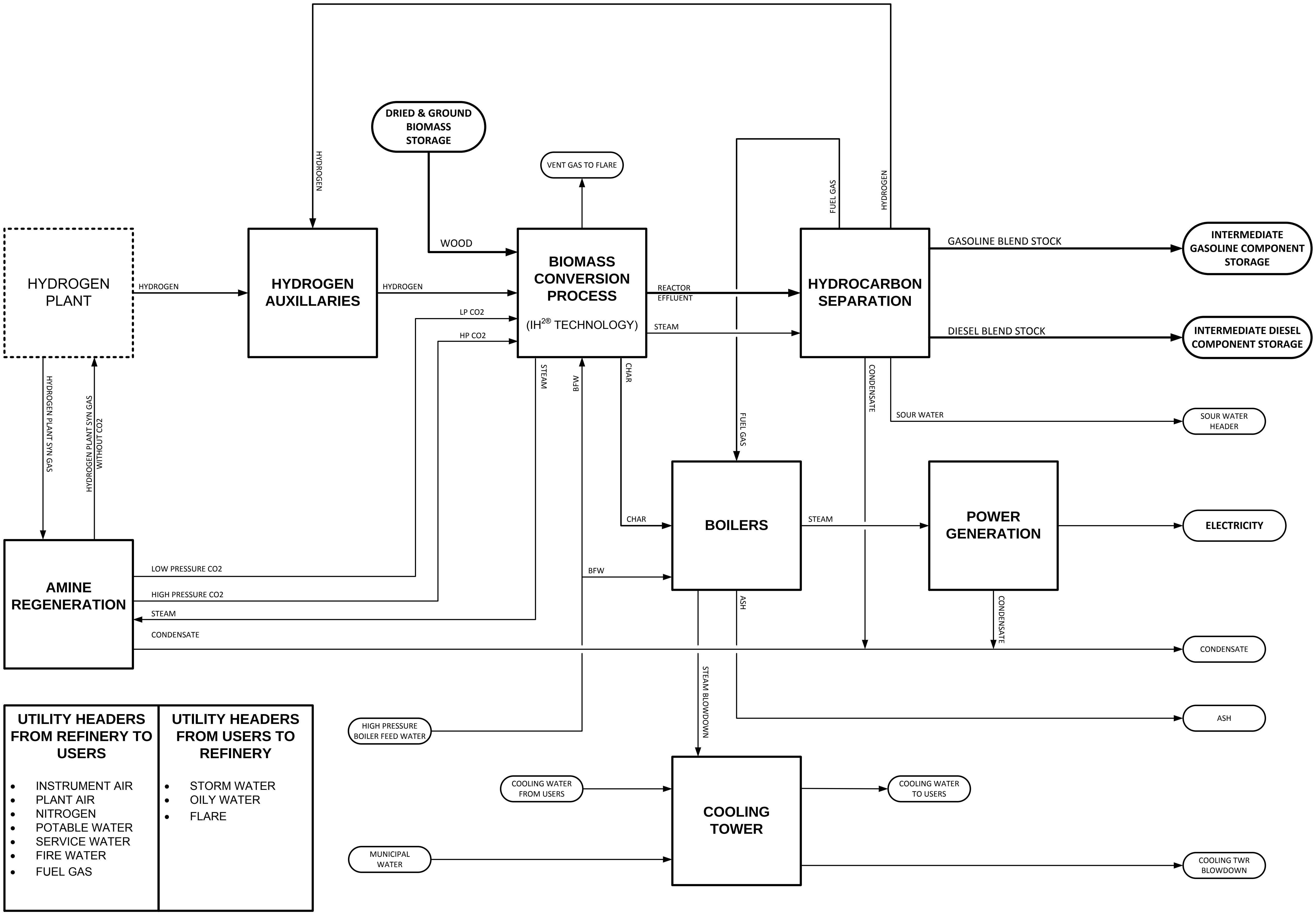
Due to the large amount of cooling required for the turbo-generator’s surface condenser, a separate cooling tower is added to provide cooling water to the entire facility.

IH$^{2®}$ UTILITY HEADERS

The following utilities cross the battery limits:

- Instrument Air
- Plant Air
- Nitrogen
- Potable Water
- Service Water
- Fire Water
- High Pressure Boiler Feed Water
- Condensate
- Fuel Gas
- Flare
- Oily Water Sewer
- Storm Water

Appendix F



<u>ASSUMPTIONS:</u>

1. WOOD ARRIVES AT FACILITY AT PROPER SIZED & MOISTURE CONTENT.
2. DESIGN INCLUDES 2 DAYS OF WOOD STORAGE (SILOS).
3. H2 PLANT ASSUMED TO HAVE SUFFICIENT EXCESS CAPACITY
4. HYDROGEN PLANT PURITY ASSUMED TO BE 99.9+ mole%
5. LOCKHOPPER PRESSURIZATION USES HYDROGEN
6. HYDROGEN PLANT FLOW TO AMINE CONTACTOR WILL BE CONTROLLED TO RECOVER ONLY THE AMOUNT OF CO2 REQUIRED BY THE PROCESS.
7. DESIGN INCLUDES AN AMINE CONTACTOR LOCATED IN THE HYDROGEN PLANT (OSBL) AND AN AMINE REGENERATOR LOCATED ISBL.
8. NO ENVIRONMENTAL LIMIT ON BURNING CHAR OR FUEL.
9. NO CHAR COOLING OR PASSIVATION SYSTEM INCLUDED.
10. FEEDS TO THE ABSORBER TOWER WILL BE CHILLED USING AN ABSORPTION CHILLER.
11. US GULF COAST (CONDITIONS & COST).
12. NAPHTHA TO GO TO 2 DAY TANKS.
13. DIESEL TO GO TO 2 DAY TANKS.
14. ONE SLOP/OFFSPEC TANK REQUIRED.
15. SITE WILL ALREADY BE CLEARED, ALLOWANCE WILL BE MADE FOR ALL OTHER SITE PREP.

<u>UTILITY/OSBL:</u>

1. SCOPE INCLUDES TWO HIGH PRESSURE SUPERHEATED STEAM BOILERS (CHAR & FUEL GAS)
2. SCOPE INCLUDES COOLING TOWER, PUMPS, & CW HEADERS
3. UTILITY HEADERS FOR ISBL ONLY (POTABLE WATER, BOILER FEED WATER, CONDENSATE, FIRE WATER, INSTRUMENT AIR, PLANT AIR etc.)
4. EXISTING REFINERY UTILITY SYSTEMS ASSUMED SUFFICIENT BOTH IN SIZE & QUANITY
5. SEWER SYSTEMS FOR ISBL ONLY (OILY WATER & STORM WATER)
6. REFINERY WASTE WATER TREATMENT SYSTEM ASSUMED SUFFICIENT
7. FLARE HEADER FOR ISBL ONLY – CURRENT FLARE ASSUMED SUFFICIENT

<u>LEGEND:</u>

———— IN SCOPE

- - - - - - NOT IN SCOPE

ICR	0	10OCT14	ISSUED FOR CLIENT REVIEW	LAT	AA	MHC	
ISSUE	REV	DATE	REVISION DESCRIPTION	BY	CHK	APP	CLIENT

THIS DOCUMENT WAS PRODUCED BY KELLOGG BROWN & ROOT LLC USING INFORMATION FROM GAS TECHNOLOGY INSTITUTE (GTI).

gti®

KBR
Engineering Services by KBR Technical Services, Inc.

BLOCK FLOW DIAGRAM
REFINERY INTEGTATED IH$^{2®}$ PROCESS
US GULF COAST

	CLIENT GTI	CLIENT		
	KBR F-954	KBR F954-KBR-00-PR-DBFD-0001	1 OF 1	0
CLASS	JOB NO.	DOCUMENT NO.	SHEET	REV

Appendix F

IH$^{2®}$ Biomass-to-Fuels

GTI - DOE STUDY

DEPARTMENT OF ENERGY REFINERY INTEGRATED DESIGN

BATTERY LIMIT SUMMARY

THIS DOCUMENT WAS PRODUCED BY KELLOGG BROWN & ROOT LLC USING INFORMATION FROM TO GAS TECHNOLOGY INSTITUTE (GTI).

Job No.: F-954

Document No.: F954-KBR-00-PR-SY30-0001

Rev.	Date	Issued for	Prepared	Reviewed	Approved	Approved
1	20-Nov-2014	RCR - REVISED FOR CLIENT REVIEW	MHC	LAT	MHC	
0	10-Oct-2014	ICR - ISSUED FOR CLIENT REVIEW	MHC	LAT	MHC	

Project:	F-954	Page:	1 of 1
Location:	US Gulf Coast	Date:	20-Nov-2014
Doc. #:	F954-KBR-00-PR-SY30-0001	Revision:	1

BATTERY LIMIT SUMMARY

Case 1: Hydrogen Recovery for recirculation via PSA

Case 2: Hydrogen Recovery for recirculation via Membrane

Inputs

Stream Description	Quality of Stream	Flow Rate Case 1	Flow Rate Case 2	Density	Pressure	Temperature
		kg/hr	kg/hr	kg/m^3	Bar(g)	°C
Wood (Note 1)	Less than 3.3mm in all dimensions 10 wt.% Moisture	46,296	46,296	160	atmospheric	ambient
Hydrogen	99.9% Purity Hydrogen from a PSA	2,617	2,173	0.085	37.5	38
Municipal Water	For Cooling Tower Makeup	290,000	256,800	1000	atmospheric	ambient
Boiler Feed Water	For Production of 41.5 Bar(g) Superheated Steam	258,000	234,500	1000	43.0	108
Instrument Air	Typical Refinery Quality	2,000	2,000	1.2	5.0	ambient
Nitrogen	Typical Refinery Quality	<300	<300	1.2	5.0	ambient
Fire Water	Typical Refinery Quality	Emergency use only. Design assumes that tying into the existing refinery header is adequate.				
Potable Water	Typical Refinery Quality	Intermittent use only. Design assumes that tying into the existing refinery header is adequate.				
Service Water	Typical Refinery Quality	Intermittent use only. Design assumes that tying into the existing refinery header is adequate.				
Plant Air	Typical Refinery Quality	Intermittent use only. Design assumes that tying into the existing refinery header is adequate.				
Fuel Gas	Typical Refinery Quality	Required only during Start-Up. Design assumes that tying into the existing refinery header is adequate.				

Note 1: Facility designed to process 1,000 metric tons per day on a moisture and ash free basis. Flow rate for wood above is based on 10 wt.% moisture.

Outputs

Stream Description	Destination	Flow Rate Case 1	Flow Rate Case 2	Density	Pressure	Temperature
		kg/hr	kg/hr	kg/m^3	Bar(g)	°C
Gasoline (blend stock)	Blended into Finished Gasoline	7325 (1575 BPD)	7325 (1575 BPD)	702	3.5	38
Diesel (blend stock)	Blended into Finished Diesel	3485 (675 BPD)	3485 (675 BPD)	779	3.5	38
Condensate	Refinery Deaerator	232,300	209,400	1000	3.5	100
Sour Water (Note 2)	Refinery Sour Water Stripper	20,550	22,425	998	3.5	38
Cooling Tower Blowdown	Refinery Waste Water Treatment Plant	62,400	55,370	1000	atmospheric	32
Ash	Trucks (transported OSBL for disposal)	160	160	n/a	atmospheric	ambient
Storm/Oily Water	Refinery Waste Water Treatment Plant	Intermittent use only. Design assumes that tying into the existing refinery header is adequate.				
Relief & Purge Gases	Refinery Flare Stack	Intermittent use only. Design assumes that tying into the existing refinery header is adequate.				
Electricity (Note 3) (Based on 18wt% Char yield)	For Sale or use in co-located Refinery	28 MW	24 MW			

Note 2: Sour Water composition by weight is 99.62% water, 0.26% ammonia, 0.12% carbon dioxide, and 25 ppm H_2S.

Note 3: One (1) wt% Reduction in Char yield will reduce electricity amount by 0.65 MW if everything else remains the same.

Appendix F

IH^{2}® Biomass-to-Fuels

GTI - DOE STUDY

DEPARTMENT OF ENERGY REFINERY INTEGRATED DESIGN

FEL-1 LEVEL COST ESTIMATE

THIS DOCUMENT WAS PRODUCED BY KELLOGG BROWN & ROOT LLC USING INFORMATION FROM GAS TECHNOLOGY INSTITUTE (GTI).

Job No.: F-954

Document No.: F954-KBR-00-PR-GG30-0001

Rev.	Date	Issued for	Prepared	Reviewed	Approved	Approved
0	10-Oct-2014	ICR - ISSUED FOR CLIENT REVIEW	LAT	MHC	EJ	

Project:	F-954	KBR	Page:	1 of 1
Location:	US Gulf Coast		Date:	10-Oct-2014
Doc. #:	F954-KBR-00-PR-GG30-0001		Revision:	0

FEL-1 LEVEL COST ESTIMATE

Process Equipment		
Biomass Conversion Process	*32.2*	
Hydrocarbon Separation	*16.3*	
Hydrogen Auxiliaries	*4.5*	
Amine Regeneration	*9.1*	
Boilers	*28.0*	
Power Generation	*16.8*	
Cooling Tower System	*5.4*	
TOTAL		**112.3 MM$**

Turnkey Items		
Catalyst	*4.0*	
TOTAL		**4.0 MM$**

Infrastructure	**17.0 MM$**

Total Direct Field Costs (w/o Turnkey)	**129.3 MM$**
Total Direct Field Costs (w/ Turnkey)	**133.2 MM$**

Total Indirect Costs	**64.6 MM$**

Total Project Costs	**197.9 MM$**

Michigan Technological University
1400 Townsend Drive
Houghton, MI 49931-1295

Sustainable Futures Institute
Office: 840 Dow Env. Sci. & Engr. Bldg.
Phone: 906-487-3612
Facsimile: 906-487-2943
email: sfi@mtu.edu
website: www.sfi.mtu.edu

APPENDIX G

Life Cycle Carbon Footprint of IH2® process from woody biomass and corn stover

June 2015

Jiqing Fan, Ph.D
Post-doc researcher

Dr. David Shonnard, Ph.D.
Professor and Robbins Chair in Sustainable Use of Materials
Department of Chemical Engineering

Sustainable Futures Institute
Michigan Technological University
Houghton, MI 49931 USA

Submitted to Terry Marker, GTI

Michigan Technological University
1400 Townsend Drive
Houghton, MI 49931-1295

Sustainable Futures Institute
Office: 840 Dow Env. Sci. & Engr. Bldg.
Phone: 906-487-3612
Facsimile: 906-487-2943
email: sfi@mtu.edu
website: www.sfi.mtu.edu

Table of Contents

List of Tables

List of Figures

Executive Summary

With an increasing focus on renewable fuels, it is vital to understand the environmental impacts from the various alternative transportation fuel products and processes under development. Current legislation aimed at sustainability regulates biofuels, adding greenhouse gas (GHG) emission reduction requirements for advanced biofuels, such as renewable gasoline and diesel from the IH2 process. Life cycle assessment (LCA) is the mandated methodology to evaluate and compare environmental impacts of alternative transportation fuels.

The goal of this LCA study is to quantify the life cycle carbon footprint of the renewable fuel blend (gasoline and diesel) produced from the IH2® process (GTI), and compare them to conventional petroleum gasoline and diesel. Two feedstocks were considered in this study: woody biomass (forest residues, unmarketable roundwood, and mill residues) and corn stover. The inputs for production of woody biomass were obtained from a supply chain study performed by Mr. John Gephart (North Shore Forest Products, Duluth, MN) and Johnson Timber Company (JTC, Park Falls, WI). Corn stover production data was obtained from personal communication with Daniel Stover of Cargill, and The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model by the Argonne National Laboratory. Inputs for the IH2 process were prepared by proprietary data from Gas Technology Institute (GTI) and engineering design data from KBR LLC. The scope of this study encompasses the entire life cycle of IH2 renewable fuel blend, including feedstock collection, transport and processing (size reduction and drying), renewable fuel blend production and final use in vehicles. The functional unit for this LCA is the quantity of renewable biofuel blend equal to one megajoule (MJ) of energy content. This is a suitable functional unit because transportation vehicle performance is largely based on the on energy content of fuel. Inventory data for all of the inputs to the life cycle reside in databases within the software used for this LCA, SimaPro 8.0. For this LCA, co-products such as electricity and ammonia were dealt with using system expansion (displacement) method, the recommended method by EPA. For GHG emissions, the results are given in grams of CO_2 equivalence emitted per MJ of fuel used by using global warming potentials for all greenhouse gases.

For woody biomass, cases 1 and 2 represent IH2 facility with H_2 from a steam methane reforming (SMR) facility, in which methane is an imported fossil resource. Case 2 includes updated (reduced) H_2 usage inputs obtained from GTI, which eliminates excess H_2 use in the reactor based on an updated engineering design from KBR. Case 3 assumes a stand-alone integrated IH2 facility, where H_2 is produced internally using C1-C3 co-products made in the process. In cases 1 and 2 for woody biomass, char produced in the IH2 process is combusted for internal consumption of heat and power, and where excess power is exported to the Tennessee grid. In case 1 of corn stover, feedstock is transported to the Memphis refinery where it is used to produce IH2 fuel blend with excess electricity exported to the Tennessee grid, and the same amount of H_2 as woody biomass case 2 is required for IH2 process (estimation), which is assumed to be produced from a SMR facility using imported fossil methane. In case 2, corn stover is processed at Welcome MN, where it has the lowest corn ethanol production cost. The IH2 facility is integrated with a third reactor unit where renewable diesel product is further hydrotreated to increase cetane number from 25 to 43, and H_2 is produced internally using the C1-C3 co-products. GHG savings of IH2 fuel blend are compared to the petroleum fuel counterparts (gasoline and diesel), which were obtained from a National Energy Technology Laboratory (NETL) report[1].

GHG emissions of IH2 fuel blend are summarized in Table ES.1. IH2 fuel from woody biomass show 68%, 73% and 89% of GHG reduction compared to fossil gasoline, depending on the H2 sources and requirements. Case 1 shows the least favorable results because of its largest H2 requirement, which is produced from fossil methane. Case 3 yields the lowest GHG emissions because H2 is produced internally from the C1-C3 co-products. But case 3 requires grid electricity, which results in higher emissions in the “other inputs” category. IH2 fuel blend from corn stover show 67% and 90% GHG reduction compared to fossil gasoline. With lower liquid yield, it requires more biomass and utilities to produce the same amount of fuel product. However, the process also produces more co-product char when corn stover is used as feedstock, which can be burned to generate electricity, which results in more GHG credits.

Table ES.1: Life cycle GHG emissions of IH2 renewable fuel blend

g CO_2 eq/MJ	Woody biomass case 1	Woody biomass case 2	Woody biomass case 3	Corn stover case 1	Corn stover case 2	Petroleum Diesel	Petroleum gasoline
Feedstock	3.75	3.75	3.90	5.45	5.67	6.29	6.94
Feedstock Transport	1.60	1.60	1.66	6.59	2.38	1.25	1.36
Fuel Production	22.52	17.63	3.47	16.71	-0.26	9.05	9.27
H_2	61.42	51.00	0.00	69.87	0.00		
other inputs[1]	0.37	0.33	3.80	0.45	0.18		
credit from electricity	-38.96	-33.39	0.00	-53.18	0.00		
credit from ammonia	-0.31	-0.31	-0.32	-0.43	-0.44		
Waste treatment	0.07	0.06	0.06	0.13	0.13		
Fuel Transport	0.85	0.85	0.85	0.85	0.85	0.85	1.03
Use						72.7	72.6
Total	28.78	23.89	9.95	29.74	8.77	90	91.3
GHG reduction[2]	68%	73%	89%	67%	90%		

1: other inputs include electricity, water, inerting gas, etc
2: GHG reductions are compared to petroleum gasoline

1. Introduction

Alternative transportation fuels, such as ethanol produced from corn and biodiesel from soybean, rapeseed, or other plant oils, are experiencing increased domestic and international market demand. This increased demand for biofuels is a response to concerns of reliance on imported petroleum, increasing fuel costs, domestic job creation, and a strong interest in reducing the impacts of human-caused global climate change. This trend in increased biofuels production is being supported at the highest levels of national governments, particularly in the most developed nations. For example, the energy independence and security act (EISA) of 2007[2] mandates renewable fuel production targets through the year 2022, at which time 36 billion gallons should be produced annually. This quantity would represent about 25% of current annual gasoline consumption in the US[2]. A report by the US Department of Energy [3] estimated that over 1 billion dry metric tons of biomass is available for collection per year in the US within sustainability constraints and for a price less than $60/dry ton (2011 basis). The majority of this biomass "billion ton vision" is woody (lignocellulosic) as opposed to the current biomass feedstocks for biofuels, corn starch, and plant oils. Anticipated conversion technologies for lignocellulosic biomass are either biochemical, including hydrolysis for production of sugars and fermentation production of biofuels, or thermochemical, which includes gasification, pyrolysis, or hydropyrolysis, plus a catalytic upgrading step to convert intermediate synthesis gas or pyrolysis oil to hydrocarbon "drop-in" biofuels [4].

The IH2 process developed by Gas Technology Institute (GTI) [5] is a thermochemical process for the conversion of a broad range of biomass types into liquid hydrocarbon biofuels spanning the range of gasoline and diesel. The process is carried out in two sequential yet integrated stages at moderate pressure (250–500 psi) and temperature ranging between 350 and 450°C. The first step involves exothermic catalytic fast hydropyrolysis and hydrodeoxygenation reactions carried out in a fluidized bed reactor at moderate hydrogen pressure. The product vapors from the first step are carried to the second conversion step, an exothermic polishing hydrodeoxygenation and hydroconversion fixed-bed reactor operating at essentially the same pressure as the first reactor. The hydrogen required for the IH2 process can be either imported from an external source such as steam methane reformer, or can be produced in a reformer using C1-C3 co-products. Other co-products are solid char, high pressure steam, and ammonia/ammonium sulfate. Solid char is combusted internally to provide heat for feedstock drying and process start-up, and generate electricity to export to electricity grid. Ammonia and hydrogen sulfide in the process condensate from the separator are stripped and oxidized to make an aqueous ammonia/ammonium sulfate product, which can be used as a fertilizer.

The purpose of our LCA study is to evaluate the life cycle GHG emissions of renewable fuel blend (gasoline and diesel) produced by the IH2 processes utilizing woody biomass (forest residues, unmarketable roundwood, and mill residues)and corn stover as feedstock. In this LCA study, the system boundaries include feedstock collection and transportation, feedstock processing (size reduction and drying), fuel production, waste treatment, transportation and use of final fuel product. The functional unit of the study is 1MJ of final fuel used, and all the inventory data were calculated based on this functional unit. The inputs of woody biomass were obtained from a supply chain analysis by Mr. John Gephart (North shore Forest Products, Duluth, MN) and Johnson Timber Company (JTC, Park Falls, WI). Corn stover inputs were obtained from personal communication with Daniel Stover of Cargill, and The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model by the Argonne National Laboratory. Inputs of the IH2 process were prepared by proprietary data from Gas Technology Institute (GTI) and engineering design data from KBR LLC.

2. Methods

2.1 Feedstock

2.1.1. Woody biomass

A forest feedstock supply study was undertaken by John Gephart to understand the economic feasibility of supplying woody biomass to an IH2 processing facility next to an existing refiner. Two Valero refineries were evaluated and located in St. Charles, Louisiana and Memphis, Tennessee. The St. Charles site was ruled out because of limited local feedstock supply and lack of space for an expansion that would accommodate the handling and storage of feedstock. It was determined that efforts would be focused on the Valero Memphis Tennessee location. Three plant sizes of 250, 500, and 1,000 bone dry tons per day were evaluated for the Memphis Tennessee location. The feedstock includes forest residues, unmarketable roundwood, and mill residues. Forest residues are collected using conventional logging equipment, converted roadside into chips, and hauled to the receiving location. Roundwood is processed into 8' and tree length logs using conventional logging equipment, transported to the receiving facility, and then converted into chips. Mill residues are collected in a sawmill facility, which include bark from round logs and pulpwood, sawdust and sawmill chips, and slabs. All feedstock is delivered to Memphis where they are processed and dried. The hauling distances vary from 70 to 82 miles depending on the plant capacity. The inputs of woody biomass feedstock supply are tabulated in Table 1.

Table 1: Inputs of woody biomass collection, transport and processing

in gallons unless stated otherwise		250 tons/day (bone dry)	500 tons/day (bone dry)	1000 tons/day (bone dry)
Raw material processing in woods	Diesel	396	706	1281
	Lubricating oil	5	10	21
	Hydraulic fluid	5	11	22
	Grease	14	29	58
	Gasoline	14	29	60
Trucking from woods to facility	Diesel	290	608	1372
	Lubricating oil	1	2	4
	Grease		1	1
Yard equipment	Diesel	50	100	200
	Lubricating oil	4	8	16
	Hydraulic fluid	4	8	16
	Grease	11	21	43
Feedstock processing and drying	Energy in kWh (size reduction)	7460	14920	29840
	Energy in kWh (drying) *	6378	12757	25513

*feedstock drying uses excess heat from the IH2 process, so these values do not represent actual inputs

2.1.2. Corn stover

Lignocellulosic biomass such as corn stover is a potential feedstock to produce biofuel and bioproducts[6]. With an estimated annual yield of 196 million tonne, corn stover can be collected at relatively low cost for biofuel production[7], while providing other benefits such as reducing nitrogen emissions[8].

Corn stover as a biomass feedstock for the IH2 process was studied by Cargill, Inc. The supply chain includes collection of stover in the field, local storage, transportation, nutrient replacement, and grinding. It was assumed that the IH2 refinery operate 350 days per year and the target production basis is 500 t per day. A range of production scales from 250 to 1000 t/day was analyzed in their study.

The inputs of corn stover are tabulated in Table 2. The main inputs are diesel for stover collection and loading, and synthetic fertilizers used to displace the nutrients in the corn stover which are removed from the corn field. The estimated amount of replacement N, P and K fertilizers were provided by Cargill. N fertilizer is assumed to be a combination of ammonium nitrate, ammonia, Di ammonium phosphate, and urea. Fossil C in urea ($CO(NH_2)_2$) is assumed to be released into atmosphere as CO_2. N_2O emission due to fertilizer application is not included, because the stover will produce the same amount of N_2O emission if they are left on the corn field. N_2O emission at storage is calculated as 0.048*0.0077*0.01*1000000*44/28/(1-0.048)/(1-0.02), where dry matter loss at storage is 4.8%, nitrogen accounts for 0.77% of biomass dry matter, 1% of nitrogen is assumed to be converted to N_2O, another 2% of dry matter loss at transport. The GREET model assumes no CH_4 emission at biomass storage. The transported distance of corn stover is predicted by Cargill as 95 miles for Memphis. A range of distances is assumed by Cargill in their supply chain study. The shortest draw radius for corn stover supply is 33 miles for Welcome, MN, and longest draw radius is 1,145 miles for Wilmington, CA, but the Wilmington case was not included in this study because it is not environmentally and economically feasible to haul feedstock for such a long distance.

Table 2: Inputs of corn stover as transported (basis 1 metric ton)

Materials		
Diesel, low-sulfur (corn stover collection)	10.9	lb
Diesel, low-sulfur (corn stover loading)	0.238	lb
Fertilizer (K_2O)	31.5	lb
Fertilizer (P_2O_5)	5.2	lb
Ammonium nitrate, as 100% $(NH_4)(NO_3)$ (NPK 35-0-0)	17*0.2	lb
Ammonia, as 100% NH3 (NPK 82-0-0)	17*0.3	lb
Di ammonium phosphate, as 100% $(NH_4)_2HPO_4$ (NPK 22-57-0)	17*0.1	lb
Urea, as 100% $CO(NH_2)_2$ (NPK 46.6-0-0)	17*0.4	lb
HDPE pipes E	0.74	lb
Processes		
CO_2 emissions from diesel/gasoline combustion	(10.9+0.238)*3.172	lb
CO_2 emissions from urea application (N in urea)	(17*0.4)*0.733	lb
N_2O emission at corn stover storage	6.63	g
Transport, truck 10-20t, EURO1, 100%LF	95*1.609	tkm
Transport, truck 10-20t, EURO1, 100%LF, empty return	95*1.609	tkm

2.2 IH2 processing

The IH2 processing data was provided by the proprietary data from GTI and engineering design data from Kellogg Brown & Root (KBR) LLC. Three cases were analyzed for the IH2 process from woody biomass: in the first two cases, H_2 required in the IH2 process is imported from a steam methane reforming (SMR) facility. Case 2 is updated from case 1 with more accurate H_2 use. The third case assumes a stand-alone integrated IH2 facility, where H_2 is produced internally using C1-C3 co-products made in the process. The IH2 process also includes a third stage where IH2 renewable fuel (diesel cut only) is further hydrotreated to increase cetane number from 25 to 43. Excess electricity is produced as a co-product and exported to the grid in the first two cases, while the third case requires electricity from the grid because the C1-C3 co-products are used to produce H_2 instead of electricity in this case. The system flow diagrams of IH2 process from woody biomass are illustrated in Figure 1 and 2.

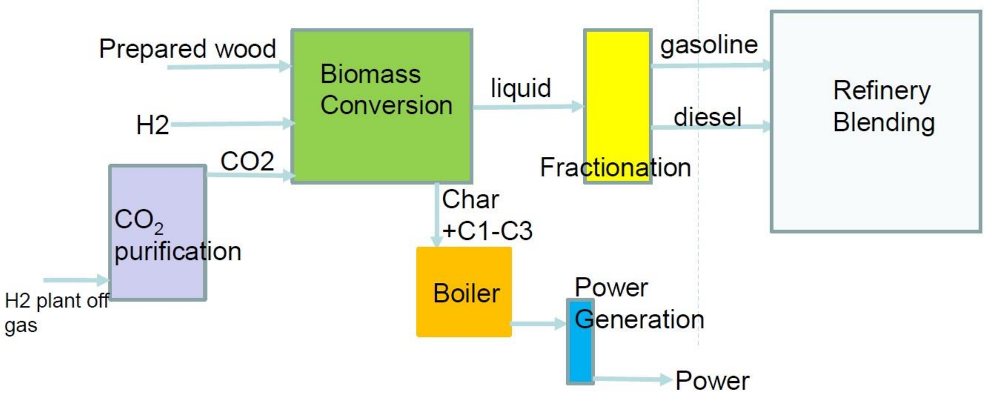


Figure 1: Engineering design of IH2 process, woody biomass case 1 and 2

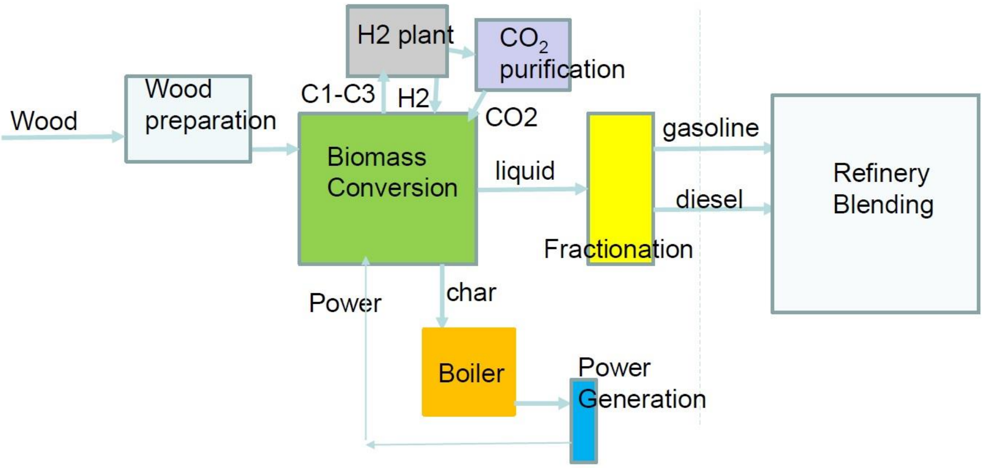


Figure 2: Engineering design of IH2 process, woody biomass case 3

Two cases of IH2 process from corn stover were analyzed. In case 1, corn stover is transported to the Memphis refinery where the feedstock is used to produce IH2 fuel blend with excess electricity exported to the grid. In case 2, corn stover is processed at Welcome MN, where it has the lowest corn ethanol production cost. The IH2 facility is integrated with a third stage unit where renewable diesel is further hydrotreated, and H_2 is produced internally using the C1-C3 co-products. The utilities use for corn stover processing is expected about the same as the woody biomass processing, and the amount of final fuel product would be approximately73% of the fuels produced in the case of the woody biomass. The difference in liquid yield is going to char, so the char yield increase is assumed to be the same as decrease in liquid fuel yield. Char is burned to generate electricity, with the same efficiency assumed in woody biomass case 1 and 2. The Tennessee (TN) and Minnesota (MN) electricity mix profile was created in SimaPro using literature data. The inventory inputs are tabulated in Table 3.

Table 3: Inventory inputs of TN and MN electricity generation mix

Electricity mix	TN	MN	
Electricity, electricity production, hard coal	0.527	0.572	kWh
Electricity, electricity production, nuclear	0.341	0.235	kWh
Electricity, electricity production, hydro	0.12	0.013	kWh
Electricity, biomass, at power plant	0.11	0.015	kWh
Electricity, electricity production, natural gas,	0.005	0.048	kWh
Electricity, electricity production, wind, >3MW turbine	0.001	0.094	kWh
Transmission network, electricity, high voltage	3.24E-08	3.24E-08	km
Sulfur hexafluoride, liquid	7.48E-08	7.48E-08	kg
Emissions to air			
Heat, waste	0.0192	0.0192	MJ
Sulfur hexafluoride	7.48E-08	7.48E-08	kg

The final fuel products (renewable diesel and gasoline blend) are assumed to be distributed to the adjacent Valero fuel terminal at Memphis, which are to be blended with fossil gasoline and diesel. Therefore, we assume the fuel transport the same as their fossil counterparts.

The IH2 process also produces a water-ammonia stream, which is sold as N fertilizer. Energy and GHG credits were assigned to this water-ammonia stream based on the environmental burden of synthetic N fertilizer. Ash is trucked and disposed of. Ash content in corn stover is approximately 10%, as compared to 0.5% in woody biomass. Thus more ash needs to be disposed of by landfill when the feedstock is corn stover. Cooling tower blowdown and storm/oily water are treated at the refinery waste water treatment plant. GHG emissions of waste treatment are estimated in Simapro as well.

3. Results and Discussion

GHG emissions of the two feedstocks, woody biomass and corn stover, are illustrated in Figure 3. Corn stover bears more environmental burden, due to the synthetic fertilizer needed to replace the nutrients on corn fields, and it also requires a longer transport distance to the IH2 facility for the Memphis location.

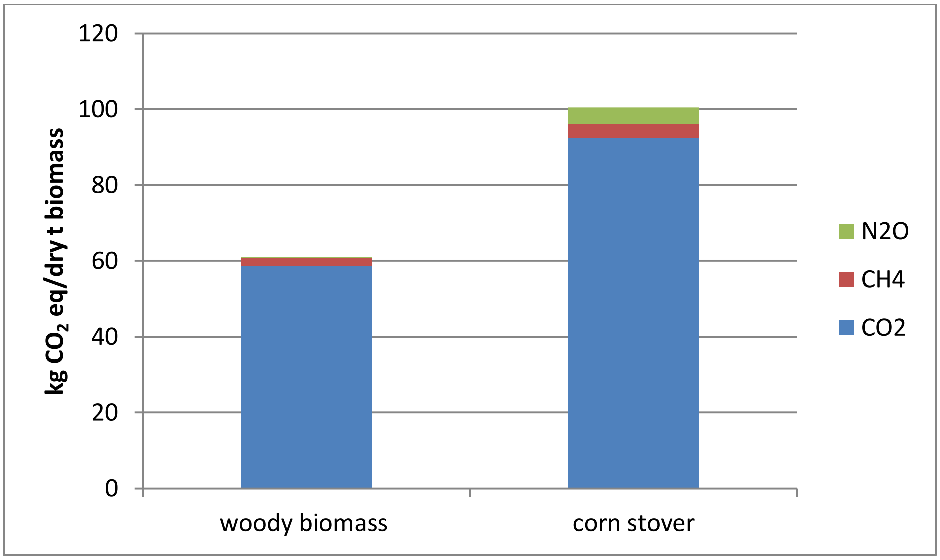


Figure 3: GHG emissions of woody biomass and corn stover

GHG emission results of IH2 renewable fuel blend from woody biomass and corn stover are tabulated in Table 4 and Figure 4, and are compared to petroleum diesel and gasoline. Net CO_2 emissions of renewable fuel blend at the combustion stage are considered carbon neutral because CO_2 is sequestered by photosynthesis during the growth of biomass.

Table 4: Life cycle GHG emissions of IH2 renewable fuel blend

g CO_2 eq/MJ	Woody biomass case 1	Woody biomass case 2	Woody biomass case 3	Corn stover case 1	Corn stover case 2	Petroleum Diesel	Petroleum gasoline
Feedstock	3.75	3.75	3.90	5.45	5.67	6.29	6.94
Feedstock Transport	1.60	1.60	1.66	6.59	2.38	1.25	1.36
Fuel Production	22.52	17.63	3.47	16.71	-0.26	9.05	9.27
H_2	61.42	51.00	0.00	69.87	0.00		
other inputs	0.37	0.33	3.80	0.45	0.18		
credit from electricity	-38.96	-33.39	0.00	-53.18	0.00		
credit from ammonia	-0.31	-0.31	-0.32	-0.43	-0.44		
Waste treatment	0.07	0.06	0.06	0.13	0.13		
Fuel Transport	0.85	0.85	0.85	0.85	0.85	0.85	1.03
Use						72.7	72.6
Total	28.78	23.89	9.95	29.74	8.77	90	91.3
GHG reduction*	68%	73%	89%	67%	90%		

* GHG reductions are compared to petroleum gasoline

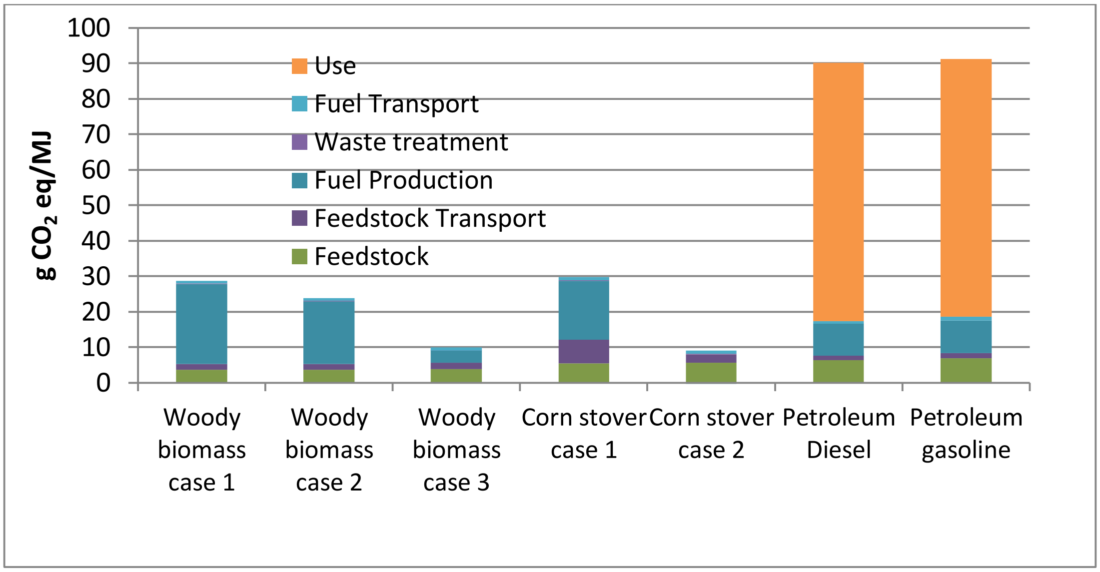


Figure 4: Life cycle GHG emissions of IH2 renewable fuel blend

GHG emissions of IH2 fuel blend from woody biomass are 28.78, 23.89, and 9.95 g CO_2 eq/MJ, for case 1, 2 and 3 respectively. Case 1 has the highest GHG emission because of its largest H_2 requirement, while case 3 shows the most favorable GHG results, because H_2 in case 3 is produced using C1-C3 co-products from the IH2 process. However, case 1 and 2 have GHG credits from exported electricity, while electricity is consumed in case 3. IH2 fuel blends from corn stover case 1 have higher GHG emissions than those produced from woody biomass. With lower liquid yield, more feedstock and utilities are used to produce the same amount of fuel products, corn stover cases benefit from electricity credits from burning co-product char. Corn stover case 2 shows the lowest GHG emission result because H_2 is provided from C1-C3 co-products, and electricity is provided by burning the char. Environmental burdens from waste treatment are higher for corn stover because of larger amount of ash produced. Woody biomass is transported 70-82 mi depending on the plant size. Diesel use for feedstock transport was provided by John. Emissions from diesel production and combustion were used to estimate the feedstock transport impact. Stover draw radius is 95 and 33mi for case 1 and 2, truck transportation ecoprofiles (w/ empty return) were used to estimate the feedstock transport impact. Transport emissions of woody biomass are significantly lower than corn stover, possibly because the diesel use of empty return is not included.

This final section of Results and Discussion deals with the issue of sustainable practices for biomass feedstock procurement of woody biomass and corn stover. This discussion will focus on issues that may affect the carbon footprint analysis in these forest and agricultural landscapes. One of the first concepts to acknowledge is that biomass carbon in and on soils is connected to atmospheric carbon (CO_2) through rapid cycles of photosynthesis and mineralization. Therefore, if C in biomass increases on the landscape and in soils then this increase corresponds to a proportional decrease of C (CO_2) in the atmosphere. Likewise, if landscape biomass C decreases, possibly due to unsustainable biomass collection practices, then C in the atmosphere will increase in a proportional manner. This could lead to an increase in greenhouse gas emissions from biofuels production systems. For example, if all corn stover is collected from the land surface after corn grain harvest, then over a long period of time, on the order of decades, the likely effects will be a decrease in soil C, increase in CO_2 in the atmosphere, increase in soil erosion, and loss of water from soils due to excessive runoff which the stover may have previously minimized. In the most recent national update on sustainable biomass supply[3], considering soil type, climate, tillage practice, and other crop management factors, stover retention coefficients were estimated for each crop management zone in the U.S. Although there are large regional differences, on a national basis stover retention coefficients for no-till corn are predicted to range between 55-50% from the present to 2030, while for reduced tillage the range will be from 82-74%. Corn farming using conventional (full) tillage must retain all stover to maintain soil quality. In forest landscapes a similar effect may be felt if excessive logging residue collection takes place. In forest landscapes where logging residues are collected, the depletion of C from the landscape may cause a delay of several decades for the benefits of biofuels displacing fossil fuels to be felt[9]. It is feasible to estimate these landscape effects through the use of appropriate carbon budget models in agricultural settings using the DAYCENT or iEPIC models and in forest landscapes using a model such as the Carbon Budget Model of the Canadian Forest System (CBM-CFS). In this LCA report, we have assumed that biomass collection for IH2 biofuel production using corn stover and forest residue collection would remain within sustainability constraints.

4. Conclusion

IH2 renewable fuels produced from woody biomass and corn stover show considerable GHG savings compared to their fossil fuel counterparts. Depending on the H_2 sources, IH2 fuel blend from woody biomass have 68-89% of savings and IH2 fuels from corn stover show 67-90% GHG reduction. Even with lower liquid fuel yield, corn stover is still a viable feedstock to produce renewable fuels from an environmental perspective, mainly because it produces more char as a co-product, which can be burned to generate electricity, thus providing a GHG credit.

Appendix

Table A.1: Inventory inputs of IH2 process (1000 metric ton dry biomass per day)

	Case 1	Case 2	Case 3	Comment
Inputs				
Tap water, at user	290000*24	256800*24	128520*24	municipal water for cooling tower makeup
Water, completely softened, from decarbonised water	258000*24	234500*24	0	boiler feed water for steam production
Nitrogen, via cryogenic air separation, production mix	300*24	300*24	5*24[a]	
H_2 from SMR	2617*24	2173*24	0[b]	
Outputs				
Gasoline	7325*24	7325*24	7325*24*0.96	
Diesel	3485*24	3485*24	3485*24*0.96	
Ammonia, as 100% NH3 (NPK 82-0-0)	10000*0.2	-10000*0.2	-10000*0.2	water-ammonia stream as fertilizer, 1% of total feed, 20% ammonia
Electricity	28*1000*24	-24*1000*24	3900*24[c]	elec output for sale or use in refinery

a: CO_2 recovered from the H_2 plant as inerting gas, instead of N_2, thus less N_2 required

b: H_2 is produced from C1-C3 made in the process

c: electricity is used internally for H_2 production and biomass feed processing

References

[1] Skone TJ, Gerdes K. Development of Baseline Data and Analysis of Life Cycle Greenhouse Gas Emissions of Petroleum-Based Fuels. National Energy Technology Laboratory (NETL) 2008, p. 310.

[2] EPA. Renewable fuel standard program (RFS2) regulatory impact analysis. Ann Arbor, MI: Assessment and Standards Division, Office of Transportation and Air Quality, U.S. Environmental Protection Agency; 2010.

[3] U.S. Department of Energy. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. In: Perlack RD, Stokes BJ, editors. Oak Ridge, TN.: Oak Ridge National Laboratory; 2011, p. 227.

[4] Brodeur-Campbell M, Martin-Garcia AR, Kalnes TN. Chapter 8. Chemical Engineering for Bioenergy Plants: Concepts and Strategies. In: Shonnard DR, editor. Handbook of Bioenergy Crop Plants: CRC Press; 2012, p. 133.

[5] Marker TL, Felix LG, Linck MB, Roberts MJ. Integrated Hydropyrolysis and Hydroconversion (IH2) for the Direct Production of Gasoline and Diesel Fuels or Blending Components from Biomass, Part 1: Proof of Principle Testing. Environ Prog Sustain 2012;31:191.

[6] Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol. In: Schoen P, Lukas J, Olthof B, Worley M, Sexton D, Dudgeon D, editors. Golden, Colorado: National Renewable Energy Laboratory; 2011, p. 147.

[7] Graham RL, Nelson R, Sheehan J, Perlack RD, Wright LL. Current and potential US corn stover supplies. Agron J 2007;99:1.

[8] Kim S, Dale BE. Life cycle assessment of various cropping systems utilized for producing biofuels: Bioethanol and biodiesel. Biomass Bioenerg 2005;29:426.

[9] Mckechnie J, Colombo S, Chen JX, Mabee W, Maclean HL. Forest Bioenergy or Forest Carbon? Assessing Trade-Offs in Greenhouse Gas Mitigation with Wood-Based Fuels. Environ Sci Technol 2011;45:789.

Appendix H

Life Cycle Associates

An Analysis of Renewable Fuel Credits Generated by the Production of Renewable Biofuels using the IH^2® Technology

LCA.8050.93.2014
January 2014

Prepared by:
Stefan Unnasch
Ashley Henderson

DISCLAIMER

This report was prepared by Life Cycle Associates, LLC for the Gas Technology Institute (GTI). Life Cycle Associates is not liable to any third parties who might make use of this work. No warranty or representation, express or implied, is made with respect to the accuracy, completeness, and/or usefulness of information contained in this report. Finally, no liability is assumed with respect to the use of, or for damages resulting from the use of, any information, method or process disclosed in this report. In accepting this report, the reader agrees to these terms.

ACKNOWLEDGEMENT

Life Cycle Associates, LLC performed this study under contract to GTI. Terry Marker of Gas Technology Institute was the project manager.

Contact Information:

Stefan Unnasch
Life Cycle Associates, LLC
1.650.461.9048
unnasch@LifeCycleAssociates.com
www.LifeCycleAssociates.com

Contents

Tables

Figures

Terms and Abbreviations

ARB	California Air Resources Board
Btu	British thermal unit
CA	California
CI	Carbon Intensity
EPA	Environmental Protection Agency
GHG	Greenhouse gas
GREET	Greenhouse gas, Regulated Emissions and Energy Use in Transportation (Argonne National Laboratory's well-to-wheels model)
LCA	Life cycle assessment
LCFS	Low Carbon Fuel Standard
LCI	Life cycle inventory
LHV	Lower heating value
MJ	Mega joule
ml	Milliliters
mmBtu	Million Btu
NG	Natural gas
NREL	National Renewable Energy Laboratory
RFS	Renewable Fuel Standard (U.S.)
TTW	Tank-to-wheels
U.S.	United States

Summary

The U.S. Renewable Fuel Standard 2 (RFS2) requires the addition of 36 billion gallons of renewable transportation fuels to the U.S. transportation fuel pool by 2022. The RFS2 established mandatory carbon intensity (CI) emission thresholds for renewable fuel categories based on% reductions from an established 2005 petroleum baseline. Within the total volume requirement, RFS2 established separate annual volume standards for cellulosic biofuels, biomass-based diesel, advanced biofuels, and renewable fuels. Figure 1 illustrates the RFS2 volume requirements per fuel category.

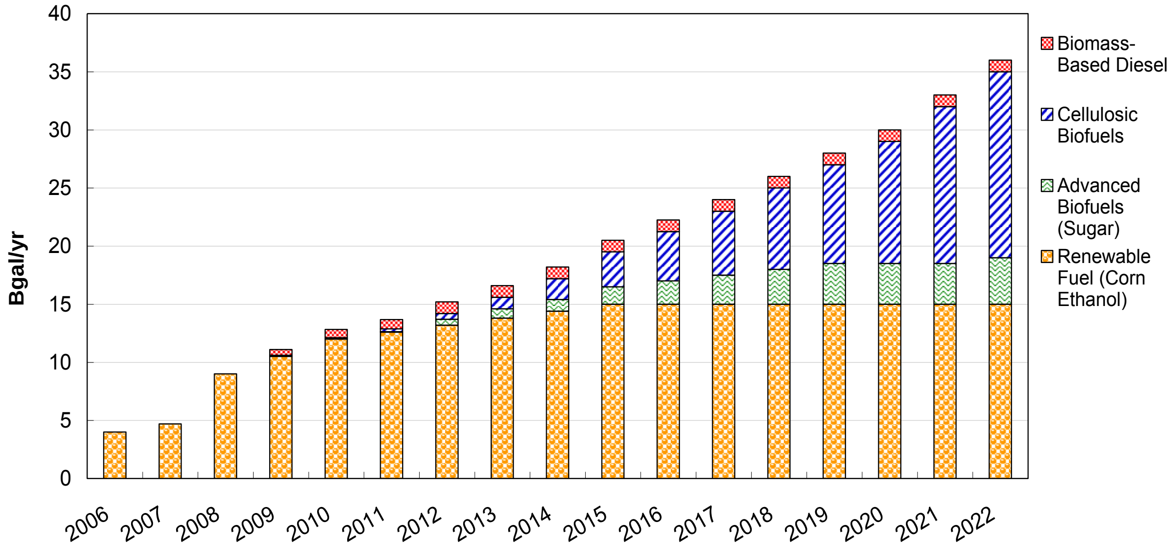


Figure 1. RFS2 renewable fuel volume requirements for the United States

Under the RFS2, gasoline and diesel fuel refiners and importers are required to purchase a certain amount of renewable fuels annually. This is called their Renewable Volume Obligation. In order to verify that their obligations have been met, refiners must submit renewable fuel credits to the EPA. The credits are quantified based on the volume of Renewable Identification Numbers (RINs) purchased or generated. RINs are generated only when renewable fuels can be shown to achieve a reduction in life cycle greenhouse gas emissions as compared to petroleum. The required reduction percentage varies by biofuel. Currently, this percentage is 20% for conventional renewable fuels, 50% for advanced biofuels, and 60% for cellulosic biofuels.

Only certain pathways qualify for RINs under RFS2. All of the pathways that are eligible for generating RINs are outlined in the RFS2 regulation. Pathways are defined by their renewable biomass feedstock input, the technology used for processing, and the fuel products made. Each pathway is assigned a D-code which groups all of the fuels associated with that pathway together. Table 1, below, provides the RFS2 definitions of the five different biofuel categories and their RIN D Codes. EPA makes D-code determinations by feedstock since the feedstock is typically the dominant driver in the GHG emissions. To receive a D3 or D7 RIN code, fuel must be derived from cellulosic feedstocks and achieve a 60% GHG reduction on a lifecycle basis relative to gasoline or diesel.

Table 1. Summary of RFS2 Fuel Requirements

Renewable Fuel Category	Definition	RIN D Code
Cellulosic Ethanol/Gasoline	Derived from cellulose with a 60% GHG reduction relative to petroleum fuels displaced.	3
Biomass Based Diesel	Biodiesel or renewable diesel with a 50% GHG reduction relative to petroleum fuels displaced.	4
Advanced Biofuel	Any renewable fuel other than corn ethanol with 50% GHG reduction relative to petroleum fuels displaced.	5
Conventional Renewable Fuel	Biomass based fuel with 20% GHG reduction relative to petroleum fuels displaced.	6
Cellulosic Diesel/Jet	Cellulosic diesel, jet fuel, or heating oil with 60% reduction relative to petroleum fuels displaced.	7

Source: 40 CFR 80.1426

The Gas Technology Institute (GTI), with initial funding from the Department of Energy (DOE), has developed a unique technology for directly converting cellulosic and woody biomass into hydrocarbon gasoline and diesel blending components. This economical new technology is referred to as integrated hydro-pyrolysis plus hydro-conversion, or IH²® for short, since it combines these two steps. While many different cellulosic feedstocks could be used in the IH²® technology, GTI has so far considered the following: forest resources, bagasse, corn stover, and microalgae. When these feedstocks are processed using the IH²® technology, they produce a high-quality gasoline, which is very close to a drop in fuel, and diesel blending components. Both products are fully compatible with petroleum-based gasoline and diesel.

A GHG-LCA analysis was performed on the IH²® production process by researchers at Michigan Technological University (MTU). They assessed the life cycle greenhouse gas (GHG) impacts of production with four different feedstock inputs: microalgae, bagasse, corn stover, and forest resources. They found that all IH²® biofuels except for microalgae reduced GHG emissions compared to petroleum by over 90%, meaning they exceed the 60% cellulosic biofuel threshold. They suggest also that microalgae IH²® biofuels could achieve qualifying GHG reductions if electricity input were to come from renewable sources.

Life Cycle Associates estimated the life cycle GHG emissions of the IH^2 technology using the EPA's methods, based on facility input and output life cycle inventory data from the MTU report and various progress reports to the Department of Energy, and up and downstream inventory data from GREET version 1.8. The carbon accounting approach taken here is more similar to the EPA method of quantifying carbon than that used by MTU, but results confirm the finding that IH²® products will generate GHG reduction levels that make them eligible for RINs. Figure 4 shows the comparison of emissions from production using different feedstocks to the baseline emissions from petroleum based gasoline. Forest residue feedstock without char electricity production shows an 87% reduction in CI, forest resources feedstock with char being burned for electricity production 93%, and corn stover feedstock 89%.

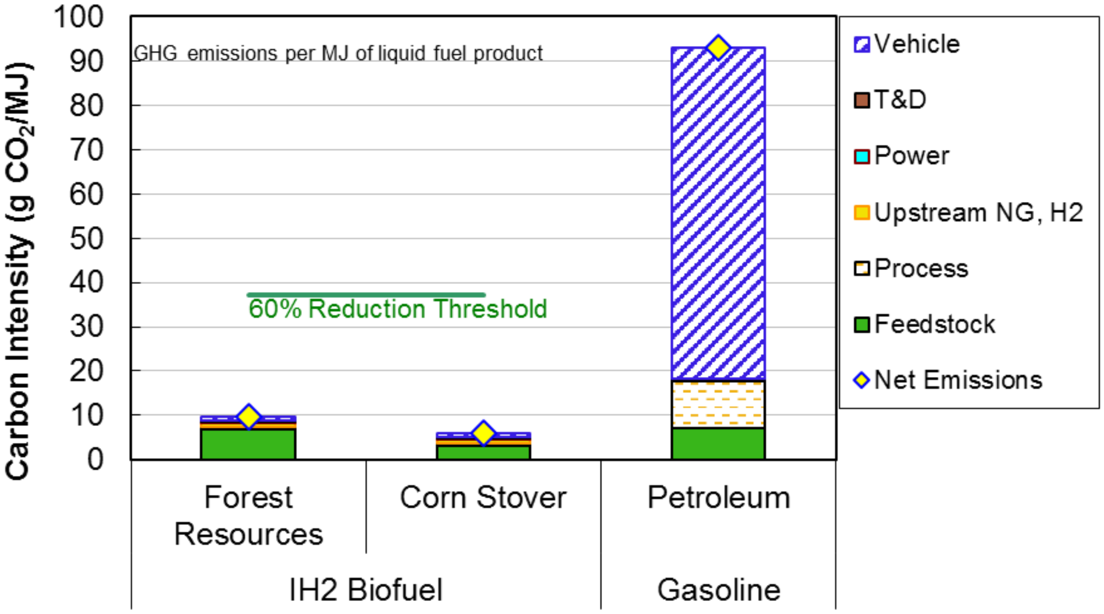


Figure 2. Life Cycle Associates GHG-LCA Analysis

Life Cycle Associates believes that the renewable gasoline and diesel fuels being produced by the IH²® technology developed by GTI will be able to generate RINS under RFS2. We find that, based on the carbon intensity findings of the GHG-LCA, IH²® fuels are likely to qualify for RINs under at least two pathways, pathways L and M, and will produce RINs with D-codes 7 and 3, corresponding to cellulosic biomass-based diesel and cellulosic biofuel.

Pathway L applies to the production of cellulosic diesel, jet fuel, or heating oil using cellulosic biomass feedstocks. Under pathway L, no specific requirements are listed regarding the technology process itself, only the types of feedstock and fuel products allowed. Any technology can be used here, thus catalytic pyrolysis is included.

Pathway M is specifically for renewable gasoline and renewable gasoline blendstocks produced with catalytic pyrolysis technology. Many different cellulosic feedstocks are accepted under pathways L and M, including cellulosic biomass from crop residue, tree slash, cover crops, yard waste, and municipal solid waste. Acceptable cellulosic biomass feedstocks are similar but not identical for the two pathways; pathway L includes the additional feedstocks of switchgrass, miscanthus, and energy cane.

This document describes some of the Federal and California mandates that are relevant to the production and use of renewable fuels. The GTI IH²® technology is described, and the applicable RIN pathways, pathways L and M, are discussed in detail. The volume of RINs that can be expected from production of biofuels using IH²® technology is calculated, and shown to be between 100 and 200 million gallons annuals, dependent on feedstock and based on a 2,000 moisture and ash free metric ton/day feedstock input.

1. Introduction

Transportation accounts for one half of the oil consumed in the world and one fourth of all greenhouse gases emitted. In the United States, these statistics are more like two thirds of oil consumed and one third of greenhouse gases emitted (Sperling & Yeh, 2009). For the most part, transportation fuels are petroleum-based. In order to reduce our global carbon emissions, we will need to reduce the GHG emissions from transportation sources. A significant step towards this goal will be to transition to transportation fuels that result in fewer harmful emissions for a given amount of energy.

Biofuels are transportation fuels that are made from biomass feedstocks, and they are an important source of low greenhouse gas emitting transportation fuel. This includes biofuels like ethanol, biodiesel, or renewable gasoline made from such feedstocks as corn, sugar cane, or woody biomass. Biofuels are usually blended with petroleum-based gasoline and diesel fuel, but they can also be used on their own (EIA.gov). In 2012, biofuels accounted for roughly 7.1 percent of total transport fuel consumption, or 13.8 billion gallons. 94% of biofuels produced in 2012 were corn ethanol (www.ers.usda.gov). The remaining 6% was made up of a variety of different diesel and gasoline like fuels. Almost all gasoline in the United States is already blended with 10 percent ethanol (E10) (EIA, 2012).

2. U.S. Regulation of Biofuels

Use of biofuels is on the rise in the United States. An important driver of the increased use of biofuels in the United States is the federal and state level regulations and tax incentives that have been passed over the past decades. Some of the relevant legislation will be discussed in this section, including the federal Renewable Fuel Standard and the Low Carbon Fuel Standard of California State.

2.1 Renewable Fuel Standard (Federal)

The Renewable Fuel Standard (RFS) was signed into law under the energy policy act of 2005, and was expanded through the Energy Independence and Security Act of 2007 (EISA). The RFS program sets requirements for the amount of renewable fuel that must be blended into on and off-road petroleum fuels, with the dual goals of increasing energy independence and reducing climate change impacts. The RFS legislation falls under the Clean Air Act (CAA) and the Environmental Protection Agency (EPA) has the responsibility of setting annual renewable standard amounts. The RFS2, the current set of regulations enacted in 2007, requires the use of 36 billion gallons of renewable fuel annually by 2022 in the United States, 21 billion of which must be non-cornstarch ethanol biofuels such as cellulosic biofuel or biomass-based diesel. It required the use of 16.55 billion gallons of renewable fuel in 2013, 1.28 billion gallons of which had to be biomass-based diesel substitutes. However production of cellulosic biofuels has so far been well below required levels (EIA, 2012).

Under the RFS2, gasoline and diesel fuel refiners and importers are required to purchase a certain amount of renewable fuels annually. This is called their Renewable Volume Obligation. In order to verify that their obligations have been met, refiners must submit renewable fuel credits to the EPA. These tradable credits are called Renewable Identification Numbers (RINs), which are generated through the production of biofuels. One RIN corresponds to 1 gallon of ethanol equivalent. RINs are generated when renewable fuels can be shown to achieve a certain percentage reduction in life cycle greenhouse gas emissions as compared to a petroleum fuel baseline. The emissions are measured in terms of kilogram of emissions per MJ of fuel, commonly known as a fuel's carbon intensity (CI). The required reduction percentage varies by biofuel. Currently, this percentage is 20% for corn ethanol, 50% for advanced biofuels, and 60% for cellulosic biofuels.

The EPA is proposing to set the 2014 cellulosic biofuel volume minimum at 17 million gallons, and the percentage standard, which corresponds to the ratio of renewable fuel volume to nonrenewable gasoline and diesel fuel volume, at 0.010%. However, the proposed standards are currently under review, and these numbers could change (EPA, 2013).

Each batch of renewable fuel is assigned a unique identifier that applies to a given calendar year and producer, and this is its renewable identification number (RIN). A batch can be any volume less than 1 million gallon-RINs. A RIN is assigned to a batch of fuel at the time when its ownership is being transferred (EPA, 2012).

2.2 Low Carbon Fuel Standard (California)

California's low carbon fuel standard (LCFS) is designed to reduce the greenhouse gas emissions from transportation fuels inside California. An executive order was passed in 2007 that called for a reduction in the carbon intensity of California's transportation fuels by 2020 by at least 10%. Carbon intensity is measured in grams of carbon dioxide equivalents (gCO2e) per unit energy (MJ) of fuel and is quantified on a lifecycle basis. The California air resources board (CARB) became responsible for implementing this standard in 2009, and the law went into effect in 2011.

The LCFS utilizes a market-based solution to the need to reduce carbon emissions. Regulated parties include all producers of transportation fuel sold in the state. Petroleum refiners who produce gasoline and diesel transportation uses are typically regulated entities. Renewable fuel producers of low carbon intensity products can opt into the system in order to be able to sell carbon credits. Each fuel provider is required to ensure that the carbon intensity of the suite of fuels they produce meets the carbon intensity target for that year. Yearly CI targets are reduced each year until 2020, at which point they should have achieved a 10% reduction.

Refiners have three options for complying with the CA LCFS. First, they can blend low carbon intensity fuels into petroleum-based gasoline and diesel to lower the aggregate CI of the fuels they produce. Second, they can buy or produce low CI fuels to lower the average carbon intensity of their suite of fuel products. Or, third, they can buy carbon credits from producers of low CI fuels in the carbon credit market (ARB, 2009).

3. Integrated Hydropyrolysis plus Hydroconversion (IH²®) Technology

3.1 IH²® Technology Description

The Gas Technology Institute (GTI), with initial funding from the Department of Energy (DOE), has developed a unique technology for directly converting cellulosic and woody biomass into hydrocarbon gasoline and diesel blending components. This economical new technology is referred to as integrated hydro-pyrolysis plus hydro-conversion, or IH²® for short, since it combines these two steps. While many different cellulosic feedstocks could be used in the IH²® technology, GTI has so far considered the following: forest resources, bagasse, corn stover, and microalgae. When these feedstocks are processed using the IH²® technology, they produce a high-quality gasoline, which is very close to a drop in fuel, and diesel blending components. Both products are fully compatible with petroleum-based gasoline and diesel.

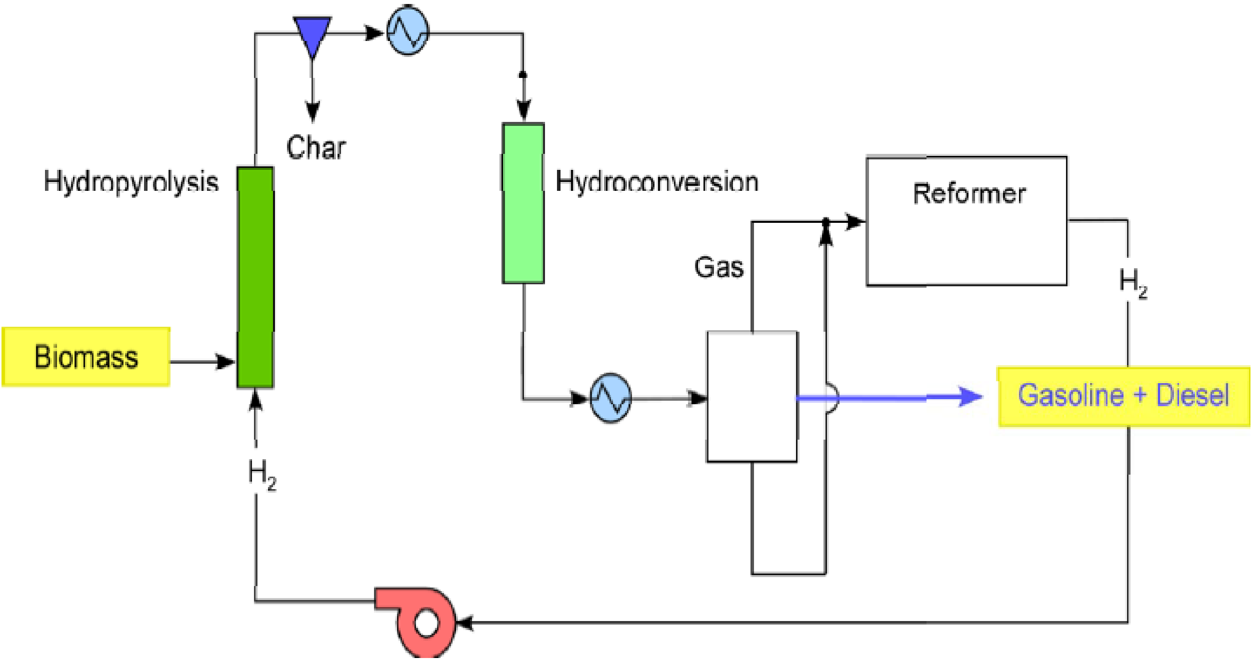


Figure 3. Process Flow Diagram of IH²® Process

Source: Shonnard, Maleche, & Glaser, 2011.

The biomass feedstock passes through a pressurized fluid bed in the presence of hydrogen, producing a gas and a liquid. The gas then undergoes a hydroconversion step, which removes oxygen and produces deoxygenated gasoline and diesel products. The liquid is condensed, and the vapors are sent to a steam reforming unit, where they are converted to the hydrogen that is used in the IH²® process. When the process is performed correctly, the hydrodeoxygenation and decarboxylation reactions are balanced so the full amount of hydrogen required for hydropyrolysis and hydroconversion is produced in the steam reformer. The hydropyrolysis reactor continuously separates char from the catalyst so that the majority of the active hydropyrolysis catalyst remains in the catalyst bed, continuing the reactions, and the char is separated, allowing for it to potentially be used as fuel. Figure 3 shows a process flow diagram that corresponds to the different steps that occur throughout the IH²® process.

Extensive assessment of this technology has already been performed. Initial lab tests and estimates were supported by testing of the process in a continuous 50 kg per day pilot facility. The plant was operated continuously for 750 hours and showed good operability, producing yields of 26% to 28% by weight high-quality gasoline and diesel fuels. The proprietary IH²® catalyst also showed good stability, and continuous testing of the char and catalyst separation by the hydropyrolysis reactor found it to be effective.

3.2 IH²® Life cycle GHG Emissions

A lifecycle assessment (LCA) of the greenhouse gas (GHG) emissions resulting from the IH²® process was performed by the Michigan Technological University (MTU). The results indicate that the IH²® process is a good candidate for generation of RINs due to the fact that it results in significantly lower GHGs than traditional petroleum fuels. The results of this analysis, and the GHG-LCA performed by Life Cycle Associates, are discussed further in Section 4.2.

4. Renewable Identification Numbers (RIN) Pathways

As mentioned above, only certain pathways qualify for renewable identification numbers (RINs). All of the pathways that are eligible for generating RINs are outlined in the RFS regulation (40 CFR part 80). Pathways are defined by their renewable biomass feedstock input, the technology used for processing, and the fuel products made. Each pathway is assigned a D-code which groups all of the fuels associated with that pathway.

Table 1, below, provides the RFS2 definitions of the five different biofuel categories and their RIN D Codes. Cellulosic Biofuel, with a RIN D code of 3 or 7, is the most desirable classification given its large reduction in GHG's relative to petroleum. To receive a D3 or D7, fuel must be derived from cellulosic feedstocks and achieve a 60% GHG reduction on a lifecycle basis relative to gasoline or diesel. EPA makes D-code determinations by feedstock since the feedstock is typically the dominant driver in the GHG emissions.

Table 2. Summary of RFS2 Fuel Requirements

Renewable Fuel Category	Definition	RIN D Code
Cellulosic Ethanol/Gasoline	Derived from cellulose with a 60% GHG reduction relative to petroleum fuels displaced.	3
Biomass Based Diesel	Biodiesel or renewable diesel with a 50% GHG reduction relative to petroleum fuels displaced.	4
Advanced Biofuel	Any renewable fuel other than corn ethanol with 50% GHG reduction relative to petroleum fuels displaced.	5
Renewable Fuel	Biomass based fuel with 20% GHG reduction relative to petroleum fuels displaced.	6
Cellulosic Diesel/Jet	Cellulosic diesel, jet fuel, or heating oil with 60% reduction relative to petroleum fuels displaced.	7

Source: 40 CFR 80.1426

In the RFS2 rulemaking, EPA provides a list of feedstocks and fuels in Table 1 of 40CFR§80.1426 that have already had RIN D codes assigned. Eligible feedstocks for renewable gasoline and diesel production include switch grass, crop residue, cover crops, and tree thinnings, among others. Renewable gasoline produced from these feedstocks qualifies as a cellulosic biofuel and will receive a RIN D code of 3. Renewable diesel produced from these feedstocks also qualifies as a cellulosic biofuel and will receive a RIN D code of 7. While these inputs affect GHG emissions, EPA has developed broad categories for feedstocks that they believe easily achieve the thresholds.

Many other potential feedstocks are not included in EPA list's (see Table 1 of 40CFR§80.1426). However, they consider new feedstock sources on a regular basis and update the regulation accordingly. On January 5, 2012, EPA issued a direct final rule expanding the list of cellulosic ethanol (RIN D Code 3) feedstocks to include energy cane (Federal Register, 2012).

> *EPA has evaluated these feedstocks and is now including the cellulose, hemicelluloses and lignin portions of renewable biomass from energy cane, giant reed, and napiergrass in Table 1 to § 80.1426 as approved feedstocks for cellulosic biofuel pathways.*

The rule was issued without a prior proposed rule because EPA considered the action noncontroversial. However, adverse comment was received, so EPA was obligated to withdraw and reconsider the rule. The main concerns of the adverse comments were the need for a more detailed analysis of indirect land use change and the potential for introduction of invasive species. EPA is revising the rule to reflect these comments and will reissue it as a final rule without a comment period in the next several months.

EPA also recently added forest based materials as eligible feedstocks. Materials such as lumber mill residue, pre-commercial tree thinnings, and slash are now eligible sources of cellulosic biomass. Feedstock from federal forestland is excluded in the RFS2 legislation, however.

EPA also continues to consider new technologies for biofuel production. In March of 2013, the EPA issued a final rule, to take effect in May 2013, amending the pathways and technologies that meet the requirements for renewable fuels under the RFS2. One of the changes included in this revision was the approval of a new category of fuel production technology. Renewable gasoline and renewable gasoline blendstocks made from cellulosic biomass using thermochemical pyrolysis technology now qualify as a source of RINs.

In making the ruling, the EPA considered the GHG emissions from a model of catalytic pyrolysis that combined an NREL study with a study by AspenPlus, as well as some literature sources. The catalytic pyrolysis and upgrading process described in the update to RFS2 involves rapid heating of biomass to 500degC (=932degF). The resulting liquid bio-oil can then be upgraded using conventional hydroprocessing technology and further separated into renewable gasoline, renewable gasoline blendstock and renewable diesel streams (cellulosic diesel from catalytic pyrolysis is already included as an acceptable pathway in the RFS program) (§ 80.1401). They grant a co-product credit since excess electricity is generated from the use of co-product coke/char and product gases. This is in addition to the electricity used to run the plant.

While the technology studied by the EPA is not identical to that used by GTI, the processes are very similar in that they both use catalytic hydropyrolysis, although at different temperatures and for different periods of time. It is expected that the IH²® technology will either be considered functionally identical or that a petition will be granted to include the IH²® technology under the RFS2. There are also some pathways for which any technology can be used.

As previously mentioned, there are three different components to a pathway: feedstock, production technology, and fuel type. The IH²® technology can accept a range of different cellulosic feedstocks and produces a fuel that is very similar to gasoline and another that is similar to diesel. The following sections consider the feedstock, fuels, and technology of the IH²® process in order to determine which pathways it may be eligible for.

4.1 What RFS2 qualifying feedstocks does IH²® use?

The definitions of these different feedstocks, fuels, and technologies are quite specific, and are important to consider when applying for RINs. The feedstocks so far considered by GTI include algae, bagasse, corn stover, and wood-based biomass.

The IH²® process has so far been designed to process the whole algae plant. While no pathways currently include algae as a feedstock, there are several pathways that include the processing of algal oil, the oil extracted from the fat content of the algae plant. Algal oil has been approved for certain biodiesel pathways, but it has not been approved for any pathways utilizing catalytic pyrolysis as the production process. The duckweed plant, which is most likely harvested as a waste product from wastewater treatment, is materially similar to algae. It is likely that the EPA would approve a petition for catalytic hydropyrolysis of the whole algae plant, provided that the greenhouse gas emissions savings relative to petroleum-based fuels meet the GHG reduction criteria under RFS2.

Bagasse, corn stover, and woody biomass, however, have the potential to qualify for RINs using the IH²® technology under the current regulations. Bagasse refers to the fibrous part of the stalk that remains after processing of sugar and energy cane to produce ethanol. Cellulosic biomass from crop residue is defined in Table 3, and included in pathways L and M, as shown in Table 8. Bagasse has the potential to meet this definition provided it is harvested from agricultural lands already in use. Corn stover, the stalks and leaves that remain after the processing of corn ethanol, has the potential to also qualify as cellulosic biomass from crop residue.

Slash and pre-commercial thinnings/tree residue are allowable feedstocks under RFS2 for pathways L and M. RFS2 requires that slash and pre-commercial thinnings be harvested from non-federal forestland that is not ecologically sensitive. Forestland is defined in 40 CFR 80.1401 as generally undeveloped land covering a minimum area of 1 acre upon which the primary vegetative species are trees, including land that formerly had such tree cover and that will be regenerated, and tree plantations.

Slash is defined as the residue, including treetops, branches and bark, left on the ground after logging or a natural disturbance such as a storm or a fire. The definition of slash excludes pulpwood from the actual sawforest resources trees, and only includes pulpwood from sawforest resources tree residues (treetops, branches and bark).

Pre-commercial thinnings is defined as trees removed to reduce stocking and concentrate growth on more desirable, healthy trees, or other vegetative material that is removed to promote tree growth. Trees that have been clear cut would not qualify, since thinning requires that a significant portion of the trees remain standing.

Tree residue is slash and any woody residue generated during the processing of planted trees from tree plantations for use in lumber, paper, furniture or other applications, provided that such woody residue is not mixed with similar residue from trees that do not originate in tree plantations.

GTI has also considered the use of lemna duckweed as a feedstock. This is technically feasible, but lemna does not currently fall under any of the RFS2 approved feedstock categories.

Table 3. Feedstock definitions under RFS2

Potential Feedstocks for IH²®	**Definition**
Cellulosic biomass from crop residue	Crop residue is the biomass left over from the harvesting or processing of planted crops from existing agricultural land and any biomass removed from existing agricultural land that facilitates crop management (including biomass removed from such lands in relation to invasive species control or fire management), whether or not the biomass includes any portion of a crop or crop plant.
Pre-commercial thinnings and tree residue	The term pre-commercial thinnings is defined in 40 CFR 80.1401 as trees, including unhealthy or diseased trees, removed to reduce stocking to concentrate growth of more desirable, healthy trees, or other vegetative materials that is removed to promote tree growth…. Thus, unmerchantable trees removed during a clear-cut would not be considered pre-commercial thinnings because the term thinning requires that substantial stock remains in the stand.
Slash	Slash is defined in 40 CFR 80.1401 as the residue, including treetops, branches and bark, left on the ground after logging or accumulating as a result of a storm, fire, delimbing or other similar disturbance.

4.2 What fuels can IH²® qualify for under RFS2?

Fuel products have specific criteria under RFS2 regarding the characteristics of the fuel, the feedstock used to produce it, and the amount of greenhouse gas reduction achieved in comparison to fuels.

In order to determine which fuel definitions the IH²® products meet, life cycle greenhouse gas emissions were taken from the MTU life cycle analysis and compared to the petroleum fuel greenhouse gas baseline used by the EPA. As can be seen in Table 4, all the feedstocks except for algae achieve over 90% reductions in greenhouse gas emissions compared to fossil fuels.

Table 4. Comparison of Life Cycle GHG Emissions from IH²® fuels vs. Petroleum Fuels

Fuel Produced	Life Cycle GHGs (gCO2e/MJ)	% Reduction from fossil gasoline	% Reduction from fossil diesel
2005 Gasoline Baseline	93.1	N/A	N/A
2005 Diesel Baseline	88.0	N/A	N/A
Algae (US Average Grid)	61.9	33%	30%
Bagasse (Char product)	2.1	98%	98%
Bagasse (Char burned)	2.6	97%	97%
Corn Stover (20% moisture)	6.6	93%	93%
Wood (30% moisture)	3.3	96%	96%
Wood (50% moisture)	3.6	96%	96%

Life Cycle Associates performed its own GHG-LCA for the forest resources and corn stover feedstocks, using facility input and output life cycle inventory data from the MTU report and various progress reports to the Department of Energy, and up and downstream inventory data from GREET version 1.8. Corn stover yield volumes were updated based on more current data provided by GTI staff, but other yield values were taken from the data reported by MTU in their life cycle assessment report. The carbon accounting approach taken here is more similar to the EPA method of quantifying carbon than that used by MTU, but results confirm the finding that IH²® products will generate GHG reduction levels that make them eligible for RINs.

Table 5 shows the numbers that were used to calculate the reduction in carbon intensity relative to petroleum, broken down by life stage to correspond with EPA methodology. It is assumed here that all char is being combusted for power generation onsite, which accounts for both the low electricity consumption levels and the lack of a co-product credit from char. 60% reduction refers to the threshold for net emissions required to achieve a 60% reduction from petroleum based gasoline.

Table 5. Total Greenhouse Gas Emissions Relative to Petroleum Baseline

	IH2 Biofuel		Gasoline
g CO2e/MJ	Forest Resources	Corn Stover	Petroleum
Feedstock	6.91	3.22	7.00
Upstream NG, H2	1.11	1.10	
Process	0.35	0.35	10.80
Power	0.27	0.15	
T&D	0.31	0.31	0.40
Vehicle	0.80	0.80	74.88
Net Emissions	9.74	5.93	93.08
-60% Threshold	37.23	37.23	
% Reduc. from Baseline	89.5%	93.6%	

Figure 4 graphs the comparison of emissions from production of renewable fuels from different cellulosic feedstocks to the baseline emissions from petroleum-based gasoline. Forest resources feedstock shows an 89.5% reduction in CI, and corn stover feedstock shows a reduction of 93.6%. These reductions are comparable to the numbers obtained by MTU, and confirm the finding that these two pathways qualify for cellulosic biofuel status, i.e. fall below the 60% reduction from petroleum baseline threshold.

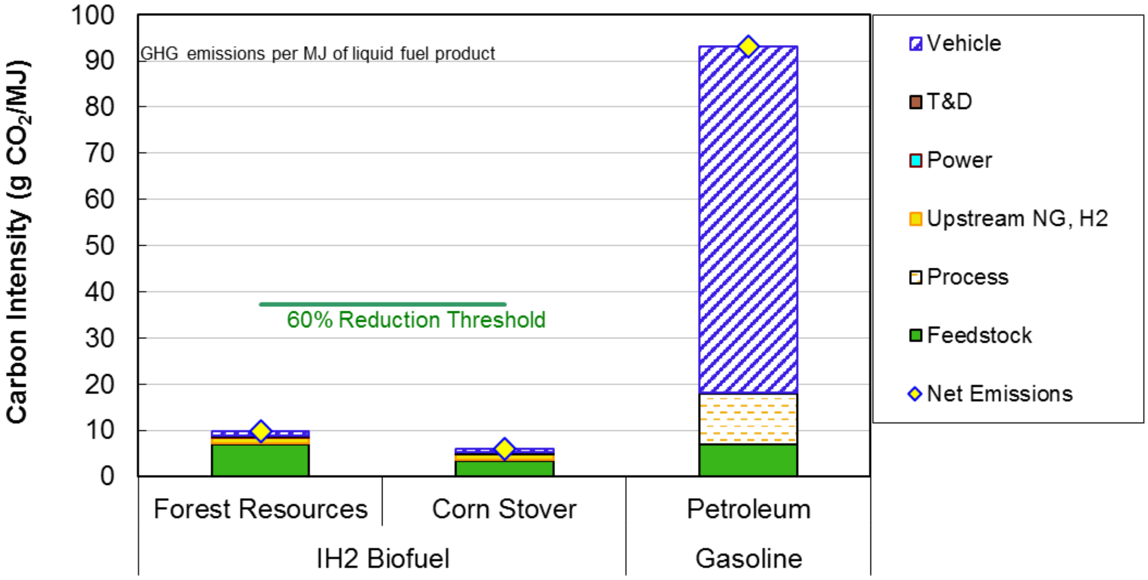


Figure 4. Life Cycle Associates GHG-LCA Analysis

Table 6 displays the official RFS definitions for all of the fuels relevant to assessment of the IH²® process. All of the fuel products except for those produced from algae qualify as cellulosic biofuels because they demonstrate GHG emission reductions of over 60%. The diesel fuel produced from non-algae feedstocks qualifies as both biomass-based diesel and cellulosic biodiesel, which means that it qualifies as cellulosic diesel as well. Because the renewable gasoline blendstock definition does not specify a greenhouse gas emission reduction percentage, all of the feedstocks can be used to produce gasoline that qualifies as renewable gasoline blendstock under RFS2.

Table 7 summarizes the fuel types for which the IH²® products qualify. “Rest” refers to forest resources, corn stover, and bagasse.

Table 6. Product definitions under RFS2

Products	**RFS2 Definition**
Advanced biofuel	means renewable fuel, other than ethanol derived from cornstarch, that has lifecycle greenhouse gas emissions that are at least 50 percent less than baseline lifecycle greenhouse gas emissions.
Biomass-based diesel	means a renewable fuel that has lifecycle greenhouse gas emissions that are at least 50 percent less than baseline lifecycle greenhouse gas emissions and meets all of the requirements of paragraph (1) of this definition: (1)(i) Is a transportation fuel, transportation fuel additive, heating oil, or jet fuel. (ii) Meets the definition of either biodiesel or non-ester renewable diesel. (iii) Is registered as a motor vehicle fuel or fuel additive under 40 CFR part 79, if the fuel or fuel additive is intended for use in a motor vehicle. (2) Renewable fuel that is co-processed with petroleum is not biomass-based diesel.
Biodiesel	means a mono-alkyl ester that meets ASTM D 6751 (incorporated by reference, *see* §80.1468).
Cellulosic biofuel	means renewable fuel derived from any cellulose, hemi-cellulose, or lignin that has lifecycle greenhouse gas emissions that are at least 60 percent less than the baseline lifecycle greenhouse gas emissions.
Cellulosic diesel	is any renewable fuel which meets both the definitions of cellulosic biofuel and biomass-based diesel, as defined in this section 80.1401. Cellulosic diesel includes heating oil and jet fuel made from cellulosic feedstocks.
Renewable gasoline blendstock	means a blendstock made from renewable biomass that is composed of only hydrocarbons and which meets the definition of gasoline blendstock in §80.2(s).
Non-ester renewable diesel (NERD)	means renewable fuel which is all of the following: (1) A fuel which can be used in an engine designed to operate on conventional diesel fuel, or be heating oil or jet fuel. (2) Not a mono-alkyl ester.

Table 7. IH²® Fuels under RFS2 Definitions

Meets Fuel Definition	**Advanced biofuel**	**Biomass-based diesel**	**Cellulosic biofuel**	**Cellulosic diesel**	**Renewable gasoline blendstock**	**NERD**	**Biodiesel**
Algae (US Average Grid)	No	No	No	No	Yes	No	No
Rest	Yes	Yes	Yes	Yes	Yes	Yes	No

4.3 What pathways can IH²® qualify for under RFS2?

Having established the feedstocks, fuels, and technology definitions IH²® products qualify for, we can now consider the RFS2 pathways for which they may be eligible. Table 8 shows the two pathways for which users of the IH²® technology are most likely to qualify, pathways L and M, producing cellulosic biofuel (table excerpted from 40 CFR 80.146).

Table 8. RIN pathways for Cellulosic Feedstocks

Path	Fuel Type	Feedstock	Production Process Requirements	D-Code
L	Cellulosic diesel, jet fuel and heating oil.	Cellulosic biomass from crop residue, slash, pre-commercial thinnings and tree residue, annual covercrops, switchgrass, miscanthus , energy cane Arundo donax and Pennisetum purpureum; cellulosic components of separated yard waste; cellulosic components of separated food waste; and cellulosic components of separated MSW	Any	7 (cellulosic biofuel or biomass-based diesel)
M	Renewable gasoline and renewable gasoline blendstock.	Cellulosic biomass from crop residue, slash, pre-commercial thinnings, tree residue, annual cover crops; cellulosic components of separated yard waste; cellulosic components of separated food waste; and cellulosic components of separated MSW.	Must utilize natural gas, biogas, and/or biomass as the only process energy sources	3 (cellulosic biofuel)

Pathway L describes the production of cellulosic diesel, jet fuel, or heating oil using cellulosic biomass feedstocks. Under pathway L, no specific requirements are listed regarding the technology process itself, only the types of feedstock and fuel products allowed. Any technology can be used here. This is not the case with pathway M, which is specific to catalytic pyrolysis, along with other processes specified in the legislation, used to produce renewable gasoline and renewable gasoline blendstocks. The regulations also specify that the technology must utilize natural gas, biogas, or biomass as the only process energy sources. Acceptable cellulosic biomass feedstocks are similar but not identical for the two pathways; pathway L includes the additional feedstocks of switchgrass, miscanthus, and energy cane.

Each pathway is assigned a D-code which groups all of the fuels associated with that pathway. Table 9 below provides the RFS2 definitions of the five different biofuel categories and their RIN D Codes. Cellulosic Biofuel, with a RIN D code of 3 or 7, is the most desirable classification given its large reduction in GHG's relative to petroleum. To receive a D3 or D7, fuel must be derived from cellulosic feedstocks and achieve a 60% GHG reduction on a lifecycle basis relative to gasoline or diesel. EPA makes D-code determinations grouped by feedstock since the feedstock is typically the dominant driver in the GHG emissions.

Table 9. Summary of RFS2 Fuel Requirements

Renewable Fuel Category	Definition	RIN D Code
Cellulosic Ethanol/Gasoline	Derived from cellulose with a 60% GHG reduction relative to petroleum fuels displaced.	3
Biomass Based Diesel	Biodiesel or renewable diesel with a 50% GHG reduction relative to petroleum fuels displaced.	4
Advanced Biofuel	Any renewable fuel other than corn ethanol with 50% GHG reduction relative to petroleum fuels displaced.	5
Renewable Fuel	Biomass based fuel with 20% GHG reduction relative to petroleum fuels displaced.	6
Cellulosic Diesel/Jet	Cellulosic diesel, jet fuel, or heating oil with 60% reduction relative to petroleum fuels displaced.	7

Source: 40 CFR 80.1426

In the RFS2 rulemaking, EPA provides a list of feedstocks and fuels in Table 1 of 40CFR§80.1426 that have already had RIN D codes assigned. Eligible feedstocks for renewable gasoline and diesel production include switch grass, crop residue, cover crops, and tree thinnings, among others. Renewable gasoline produced from these feedstocks qualifies as a cellulosic biofuel and will receive a RIN D code of 3. Renewable diesel produced from these feedstocks also qualifies as a cellulosic biofuel and will receive a RIN D code of 7. A biorefinery's choice of process heat and power does not affect the designation according to Vince Camobreco of EPA.

Table 10 and Table 11 show the possibility of generating RINs from IH²® under the two pathways given each of the possible feedstocks. Bagasse, corn stover, and woody biomass all currently qualify for pathway L using IH²® technology. The algae feedstock product does not currently meet the GHG emission reduction requirements necessary to be considered cellulosic biofuel and is therefore not eligible for pathway L. Under pathway M, all four feedstock possibilities result in eligible fuel products. Algal feedstock is not considered eligible but could potentially be approved under a petition.

Some questions remain regarding the eligibility of the technology. For one thing, the GTI process is slightly different from one described in the EPA ruling. For another, pathway M specifies that all process energy be produced from renewable sources or natural gas. The IH²® process currently involves the consumption of conventionally produced electricity, although only a very small amount, the difference of which is made up for by the combustion of biochar onsite. The use of electricity may be approved by the EPA, or it may be needed to petition the EPA for an exemption from this requirement for the small amount of electricity IH²® uses.

Table 10. IH²® Feedstocks under Pathway L

Meets Requirements for Pathway L	Fuel Produced	Feedstock	Process
Algae	No	No	Yes
Bagasse	Yes	Yes	Yes
Corn Stover	Yes	Yes	Yes
Woody Biomass	Yes	Yes	Yes

Table 11. IH²® Feedstocks under Pathway M

Meets Requirements for Pathway M	Fuel Produced	Feedstock	Process
Algae	Yes	Petition	Yes
Bagasse	Yes	Yes	Yes
Corn Stover	Yes	Yes	Yes
Woody Biomass	Yes	Yes	Yes

5. RINs Generated by IH²®

The following section makes the assumption that it will be possible to generate RINs using the IH²® technology, and calculates possible RIN volumes based on this assumption. Inventory data from the life cycle assessment (LCA) performed by the University of Michigan along with data from reports submitted to the Department of Energy (DOE) by GTI regarding the IH²® process were used to calculate the volume of RINs (vRIN) that are likely to be generated using different feedstocks. The formulas and calculations performed to determine vRIN are described in this section.

RIN volumes are based on the unit corn ethanol gallon equivalents. Therefore, in order to calculate the RIN volume of fuels other than corn ethanol, it is necessary to calculate their ethanol gallon equivalence value. The formula for calculating these numbers is taken from the RFS2 standard, section 80.1415, and is shown below. A lower heating value of 44 MJ/kg, for both gasoline and diesel products, is taken from the GTI progress report to DOE. The two fuels have different energy content values, however, because of their differences in density. The energy contents in Table 12 are expressed in BTU per gallon. Given that a typical gallon of gasoline contains 115,000 Btus and a gallon of pure benzene contains 127,000 Btus, an energy content of 122,425 for gasoline appears to be within the reasonable range of a highly aromatic fuel.

$$EV = (R/0.972) * (EC/77{,}000)$$

Where:
EV = Equivalence Value for the renewable fuel, rounded to the nearest tenth.
R = Renewable content of the renewable fuel. This is a measure of the portion of a renewable fuel that came from renewable biomass, expressed as a fraction, on an energy basis.
EC = Energy content of the renewable fuel, in Btu per gallon (lower heating value).

Table 12. Equivalence values for IH^2® fuel products

Equivalence Values	**Gasoline**	**Diesel**
R	1	1
EC (Btu/gal)	122,425.52	144,132.17
EV	**1.6**	**1.9**

In order to calculate the RIN volume, it is also necessary to know the energy content of the feedstocks. The equation for calculating the feedstock energy content is shown below. The majority of information about the feedstocks is taken from life cycle inventory data used in the life cycle assessment done by Michigan Technological University. Energy contents of the feedstocks are taken from the GTI progress report to DOE or from default values listed in the RFS2.

$$FE = M * (1 - m) * CF * E$$

Where:
FE = Feedstock energy, in Btu.
M = Mass of feedstock, in pounds, measured on a daily or per-batch basis.
m = Average moisture content of the feedstock, in mass percent.
CF = Converted Fraction in annual average mass percent, representing that portion of the feedstock that is converted into renewable fuel by the producer.
E = Energy content of the components of the feedstock that are converted to renewable fuel, in annual average Btu/lb, determined according to paragraph (f)(7) of this section.

Table 13. Feedstock Energy Content

FE = M * (1–m) * CF * E					
Feedstock Energy (FE)	**Algae**	**Bagasse**	**Corn Stover**	**Maple**	**Pine**
M(lb)	4409240	4409240	4409240	4409240	4409240
m (%)	0	0	0	0	0
CF	1	1	1	1	1
E (Btu/lb)	7940	7,300	7090	8490	8690
FE (mmBtu)	**35,009.37**	**32,187.45**	**31,261.51**	**37,434.45**	**38,316.30**

With the equivalence value goals produced in the energy contents feedstocks used as inputs, we can now calculate the volume of RIN gallons generated. The volume of gasoline and diesel fuel produced from each different feedstock is taken from the life cycle assessment done by Michigan Technological University. Table 14 displays the resulting volume of RINs generated on a daily and an annual (assuming 350 days of operation) basis.

$$V_{RIN} = EV * V_s * FE_R/(FE_R + FE_{NR})$$

Where:
V_{RIN} = RIN volume, in gallons, for use in determining the number of gallon-RINs that shall be generated for the batch.
EV = Equivalence value for the batch of renewable fuel per §80.1415.

V_S = Standardized volume of the batch of renewable fuel at 60 °F, in gallons, calculated in accordance with paragraph (f)(8) of this section.
FE_R = Feedstock energy from renewable biomass used to make the transportation fuel, heating oil, or jet fuel, in Btu.
FE_{NR} = Feedstock energy from non-renewable feedstocks used to make the transportation fuel, heating oil, or jet fuel, in Btu.

Table 14 shows the input values used to calculate the total RINs generated for each feedstock on a daily and annual basis, and the resulting volumes. These numbers are based on a 2,000 moisture and ash free (MAF) metric ton/day feedstock input. As can be seen below, the largest number of RINs is generated by algae feedstock, followed by bagasse, then corn stover and forest resources. These differences are primarily driven by the yield of product to feedstock. The yield of diesel product from algae is over three times greater than that of bagasse, which in turn has a significantly greater gasoline product yield than corn stover and forest resources.

Table 14. Volume of RINs Generated by IH^2® with 2000 MAF tonne/day Feedstock Input

$V_{RIN} = EV * Vs * FE_R/(FE_R + FE_{NR})$				
RINs Generated	**Algae**	**Bagasse**	**Corn Stover**	**Forest Res.**
Evgas	1.6	1.6	1.6	1.6
Evdies	1.9	1.9	1.9	1.9
Vs_{gas} (gal)	158,922	153,246	117,772	113,585.37
Vs_{dies} (gal)	141,458.79	44,205.87	40,416.80	53,032.69
FER (mmBtu)	35,009	32,187	31,262	37,875.37
FENR (mmBtu)	0	0	0	0
$VRIN_{gas}$ (gal)	259,954.84	250,670.73	192,645.10	185,796.43
$VRIN_{dies}$ (gal)	272,416.80	85,130.25	77,833.37	102,128.65
$VRIN_{tot}$ (gal)	**532,371.64**	**335,800.98**	**270,478.47**	**287,925.08**
Annual (million gal)	**186.3**	**117.5**	**94.7**	**100.8**

Because the IH^2® process is still undergoing improvements and experimentation, the volume of RINs generated may change slightly over time. Therefore, a sensitivity analysis was performed to demonstrate the impact on total RINs volumes if gasoline and diesel volumes change within a reasonable range. Table 15 shows the results of the sensitivity analysis. With a 10% increase in total fuel yield, the corresponding RINs range from 104 million gallons (corn stover) to 205 million gallons (microalgae). A 10% decrease in total fuel yield results in a range of 85 million gallons (corn stover) to 168 million gallons of RINs (microalgae). A 5% increase in gasoline yield, which implies a 5% decrease in diesel fuel yield, results in a small decrease in total RINs generation from algae, and a small increase in total RINs from bagasse, corn stover, and forest resources. A 5% decrease in gasoline yield, which implies a 5% increase in diesel fuel yield, results in slight decreases in total RINs generation across the board.

Table 15. RINs Volume Sensitivity Analysis

Annual RINs (mil gal)	Algae	Bagasse	Corn Stover	Forest Res.
Baseline Yields	*186.3*	*117.5*	*94.7*	*100.8*
+10% Total Yield	205.0	129.3	104.1	110.9
-10% Total Yield	167.7	105.8	85.2	90.7
+5% Gasoline	186.1	120.4	96.7	102.2
-5% Gasoline	185.9	117.2	94.4	100.5

6. Conclusion

The current analysis indicates that the IH²® technology should qualify for both pathway L and pathway M, and that the diesel and gasoline fuels it produces will be considered cellulosic biofuels under the RFS2 based on the information cited. Under the assumption that it does qualify, the process will result in anywhere from 94 to 186 million gallons of RINs annually at the plant capacity levels assumed with current the GTI model.

Life Cycle Associates also has several recommendations for areas of future research. As pointed out in the MTU report, microalgae has significantly higher moisture levels than the other feedstocks considered (80% compared to 20% for corn stover and bagasse, and 30-50% for woody biomass.) Drying the algae is quite energy intensive, causing the overall GHG balance of the algal feedstock scenario to have the lowest net benefits relative to petroleum fuels and to fail to qualify as an advanced or cellulosic biofuel. GTI should investigate possible alternative drying methods or fuel sources to improve the GHG profile of the algae feedstock pathway. Additionally, it will be important to verify with EPA that algal biofuels qualify using any process and from any state of algae processing.

It would be useful to recalculate GHG impacts and RINs generation once updated data are available, incorporating any changes to the IH²® process since the publishing of the MTU life cycle assessment. Data should be rechecked for both accuracy and consistency. Areas of particular concern include diesel fuel inputs, since some feedstock data reports the diesel fuel used in yard equipment while others report no yard equipment usage at all, and electricity usage, since char power production was not reported and electricity usage appears low.

The IH²® technology allows for the processing of biomass feedstock to a finished hydrocarbon product, that when distilled would either meet ASTM transportation fuel specifications, or be a high quality blend stock. However, an alternative option would be for the intermediate product, resulting from the processing solely through the1st stage hydropyrolysis reactor and still containing oxygen to be sold to a petroleum refinery. This intermediate could then potentially be co-processed and distilled into a finished product, potentially resulting in a less capital intensive pathway. However, even if this option proves technologically feasible, there is a possibility that the generation of RINs will be affected by the co-processing of renewable and non-renewable fuels. If one wants to investigate this option, it will be necessary to coordinate with the EPA, and a pathway petition may be needed

7. References

ARB (2009) California Low Carbon Fuel Standard Documents, Models and Methods/Instruction. http://www.arb.ca.gov/regact/2009/lcfs09/lcfs09.htm.

EIA. Biofuels: ethanol and biodiesel explained. Accessed 12/20/2013. http://www.eia.gov/energyexplained/index.cfm?page=biofuel_home

EPA (2012) Renewable Fuel Standard 2(RFS2), U.S. Environmental Protection Agency. http://www.epa.gov/otaq/fuels/renewablefuels/index.htm.

EPA (2013) EPA Proposes 2014 Renewable Fuel Standards, 2015 Biomass-Based Diesel Volume. http://www.epa.gov/otaq/fuels/renewablefuels/regulations.htm.

Federal Code of Regulations (2012) Volume 77 Number 3.

Federal Code of Regulations (2013) Title 40 Part 80 Subpart M.

GTI (2012a) Technical Report to DOE: Biomass to Gasoline and Diesel Using Integrated Hydropyrolysis and Hydroconversion.

GTI (2012b) Technical Report to DOE: Long Term Processing using Integrated Hydropyrolysis plus Hydroconversion (IH²®) for the Production of Gasoline and Diesel from Biomass.

Shonnard, D., E. Maleche, & R. Glaser (2011) GHG-LCA Analysis of IH²® Biofuels.

USDA. U.S. Bioenergy Statistics. Accessed 12/0/13. http://www.ers.usda.gov/data-products/us-bioenergy-statistics.aspx#.UrOJwvRDta8