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## TECHNICAL REPORT

# Long Term Processing using Integrated Hydropyrolysis plus Hydroconversion (IH<sup>2</sup>) for the Production of Gasoline and Diesel from Biomass

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## Executive Summary

Cellulosic and woody biomass can be directly converted to hydrocarbon gasoline and diesel blending components through the use of a new, economical, technology named integrated hydroprocessing plus hydroconversion (IH<sup>2</sup>). The IH<sup>2</sup> gasoline and diesel blending components are fully compatible with petroleum based gasoline and diesel, contain less than 1% oxygen and have less than 1 total acid number (TAN). The IH<sup>2</sup> gasoline is high quality and very close to a drop in fuel. The life cycle analysis (LCA) shows that the use of the IH<sup>2</sup> process to convert wood to gasoline and diesel results in a greater than 90% reduction in greenhouse gas emission compared to that found with fossil derived fuels. The technoeconomic analysis showed the conversion of wood using the IH<sup>2</sup> process can produce gasoline and diesel at less than \$2.00/gallon.

In this project, the previously reported semi-continuous small scale IH<sup>2</sup> test results were confirmed in a continuous 50 kg/day pilot plant. The continuous IH<sup>2</sup> pilot plant used in this project was operated round the clock for over 750 hours and showed good pilot plant operability while consistently producing 26-28 wt % yields of high quality gasoline and diesel product. The IH<sup>2</sup> catalyst showed good stability, although more work on catalyst stability is recommended.

Additional work is needed to commercialize the IH<sup>2</sup> technology including running large particle size biomass, modeling the hydroprocessing step, studying the effects of process variables and building and operating a 1-50 ton/day demonstration scale plant.

The IH<sup>2</sup> 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. Thus, the IH<sup>2</sup> technology offers a path to genuine energy independence for the U. S., along with the creation of a significant number of new U.S. jobs to plant, grow, harvest, and process biomass crops into fungible fuels.

## Project Objectives

Gas Technology Institute's (GTI) project goal was to demonstrate the long term processing and catalyst stability of a new, economical technology that integrates hydroprocessing (pyrolysis carried out in a pressurized hydrogen atmosphere) and hydroconversion(IH<sup>2</sup>), for the direct conversion of biomass into gasoline and diesel fuel. This technology utilizes our 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<sup>2</sup> technology offers a path to genuine energy independence for the U. S., along with the creation of a significant number of new U.S. jobs to plant, grow, harvest, and process biomass crops into fungible fuels. Commercialization of this technology will also reduce U.S. greenhouse gas emissions from transportation fuels made through this process, by 90%, compared to present levels.

The specific objective of this project is to show the long term operability, catalyst stability and high quality product made from IH<sup>2</sup> in a long term test using a continuous automated pilot plant which will convert biomass directly into high quality gasoline and diesel products. The IH<sup>2</sup> process consists of a pressurized fluidized-bed first stage reactor for hydroprocessing, followed by an integrated hydroconversion step, which together remove oxygen from the biomass and convert the biomass to gasoline and diesel products containing less than 1% oxygen. Commercially, light gas from the hydroconversion step is separated and sent to a steam reformer which produces the hydrogen used in the process. With this integration, and using the proper processing conditions, the process is self sufficient as it requires no external source of methane or hydrogen.

The specific objectives of this project were to demonstrate the following:

1. Long term operability of the IH<sup>2</sup> process

2. Catalyst stability for the catalyst used in IH<sup>2</sup> and detailed catalyst analysis
3. The production of gasoline and diesel fuels containing less than 1% oxygen which can be blended into ASTM petroleum fuels or further upgraded in existing petroleum refineries
4. Detailed characterization of the gasoline and diesel fuel produced from the process
5. Yields and material balances for the IH<sup>2</sup> products

## Process Overview

A simplified process flow diagram of the IH<sup>2</sup> process is shown in Figure 1.

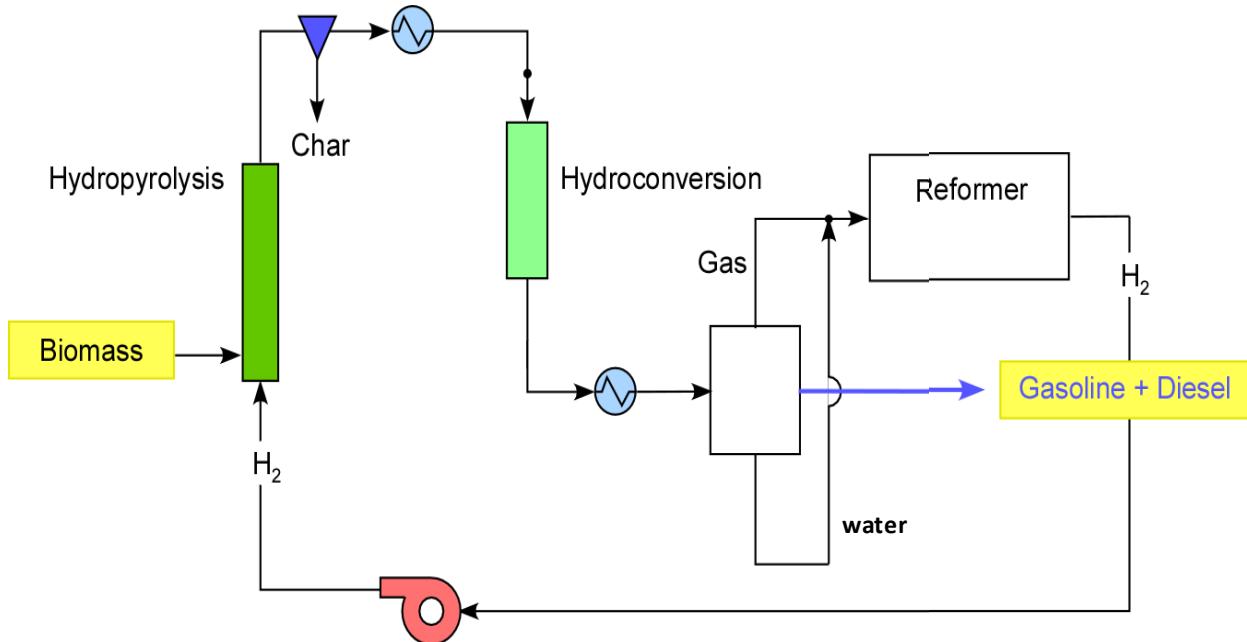


Figure 1-The IH<sup>2</sup> system, showing overall process flow.

Biomass is converted to gas, liquid and char in the presence of hydrogen in a pressurized fluid-bed hydropyrolysis stage, the char is removed, and the vapor from this stage is directed to a second stage hydroconversion unit which further removes oxygen and produces deoxygenated gasoline and diesel products. The liquid is condensed and the C<sub>3</sub>- gas from the process is sent to an integrated steam reformer. By running at the proper conditions with the proper catalyst, the hydrodeoxygenation and decarboxylation reactions are balanced so the hydrogen required for hydropyrolysis and hydroconversion is produced in the steam reformer. The hydropyrolysis and hydroconversion processes are exothermic and produce high levels of steam. The process steps are carried out at almost the same pressure except for pressure drops through the vessels, so the energy required to compress hydrogen and recirculate it back to the first stage is available from steam produced in the process.

The chemistry of the hydropyrolysis step is depicted in Figure 2. The hydropyrolysis step is the heart of the IH<sup>2</sup> process and the part which separates it from competing technologies. In the hydropyrolysis step, the biomass devolatilizes and then the volatile fragments are immediately hydrotreated to remove oxygen and add hydrogen to the structure. Polymerization also occurs since IH<sup>2</sup> products show a wide range of boiling points and chain length. 200-500 psi of hydrogen partial pressure is required for good yields and high oxygen removal. Since excess hydrogen is always present in IH<sup>2</sup>, the rate of hydrodeoxygenation is a function of hydrogen partial pressure. Residence time is also important since the biomass must have

sufficient time to devolatilize. Biomass will devolatilize more slowly at high pressures and moderate temperature than would occur in standard pyrolysis conditions.

## Chemistry Considerations in IH<sup>2</sup>

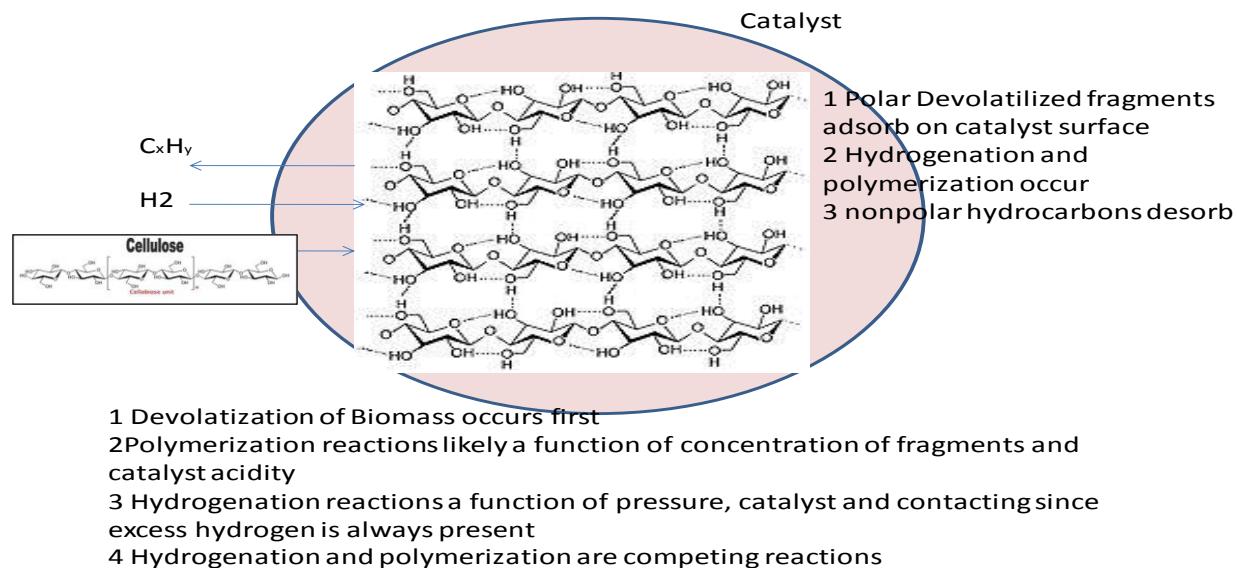


Figure 2-Chemistry of Hydropyrolysis

Hydropyrolysis as practiced in IH<sup>2</sup> occurs at the intersection of pyrolysis and hydrotreating as shown in Figure 3.

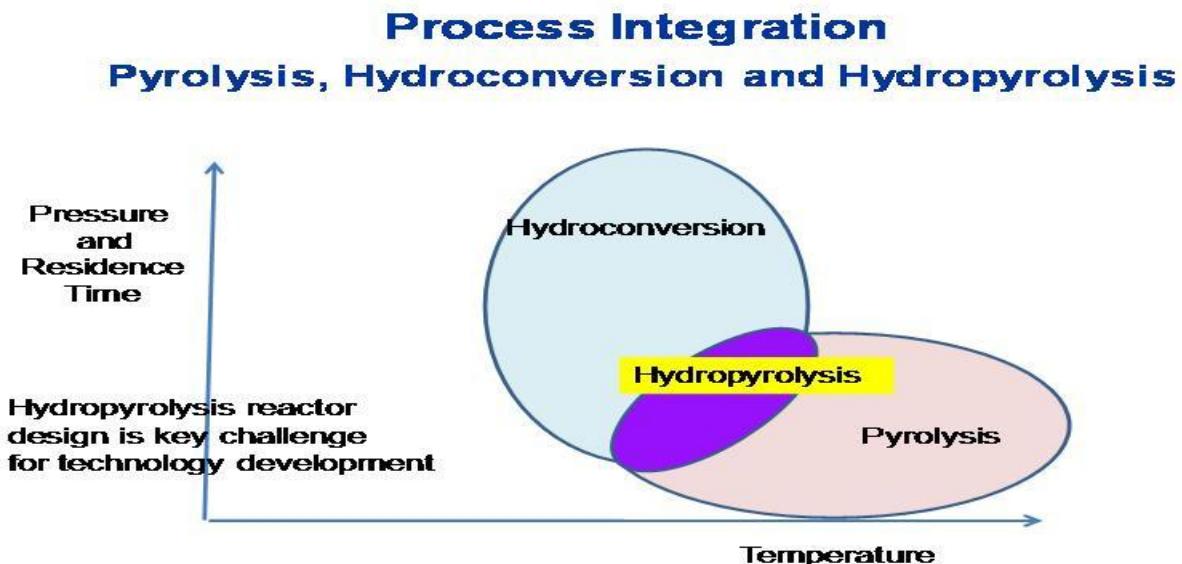


Figure 3-Hydropyrolysis Process Conditions

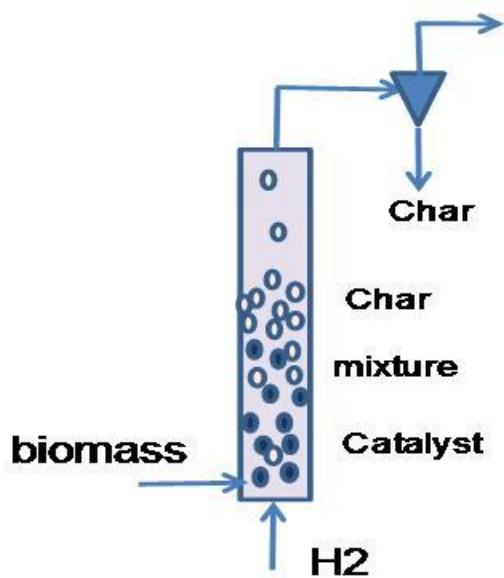
A comparison of standard pyrolysis conditions with those used in the hydropyrolysis step in IH<sup>2</sup> is shown in Table 1.

**Table 1- Comparison of Pyrolysis and IH<sup>2</sup> Hydropyrolysis conditions**

	Pyrolysis	Hydropyrolysis in IH <sup>2</sup>
Biomass/char Residence time	1-2 sec	minutes
Temperature , F	950-1000	775-850
Hydrogen partial pressure,psi	<1	200-500
Catalyst	no	Yes, with hydrogenation activity

Riser reactors would be a poor choice for hydropyrolysis since they don't have the residence time required for devolatilization at moderate temperatures. Running hydropyrolysis experiments at low hydrogen partial pressures (<100psi) will not be successful either since hydrogenation reactions require a high hydrogen partial pressure (200-500psi).

In addition to achieving the desired reactions, the hydropyrolysis reactor should continuously separate the char and catalyst, retaining the catalyst in the bed while allowing the char to pass through the bed and be removed continuously from the system. Proper design of the hydropyrolysis step therefore includes proper control and understanding of the reactor hydrodynamics and char-catalyst separation as shown in Figure 4.



**Figure 4- Hydropyrolysis Reactor- showing char catalyst separation**

## IH<sup>2</sup> Project Team

Our project team, shown in Figure 5, was well suited to successfully complete the project tasks and ultimately commercialize the IH<sup>2</sup> technology. The team included experts from the agricultural industry (Cargill), forest industry (Johnson Timber), and lemma microcrop industry (Parabel) who all have a stake in commercializing new technology for converting their feedstocks into fungible fuels.

## IH<sup>2</sup> Long Term Processing Team

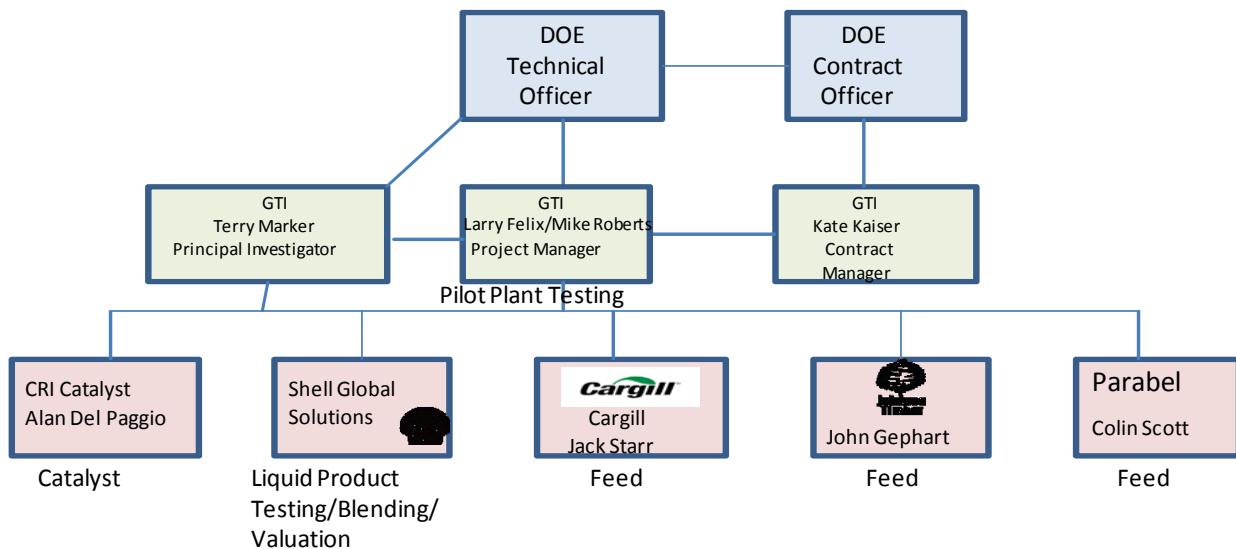


Figure 5-Project Team

A key team member is CRI Catalyst Company (CRI) who has developed and provided the catalysts used in the IH<sup>2</sup> development. CRI signed joint development and licensing agreements with GTI to commercially offer the IH<sup>2</sup> technology. The Shell Global Solutions laboratory at the Shell Westhollow facility in Houston, Texas completed the detailed IH<sup>2</sup> product analysis working with CRI.

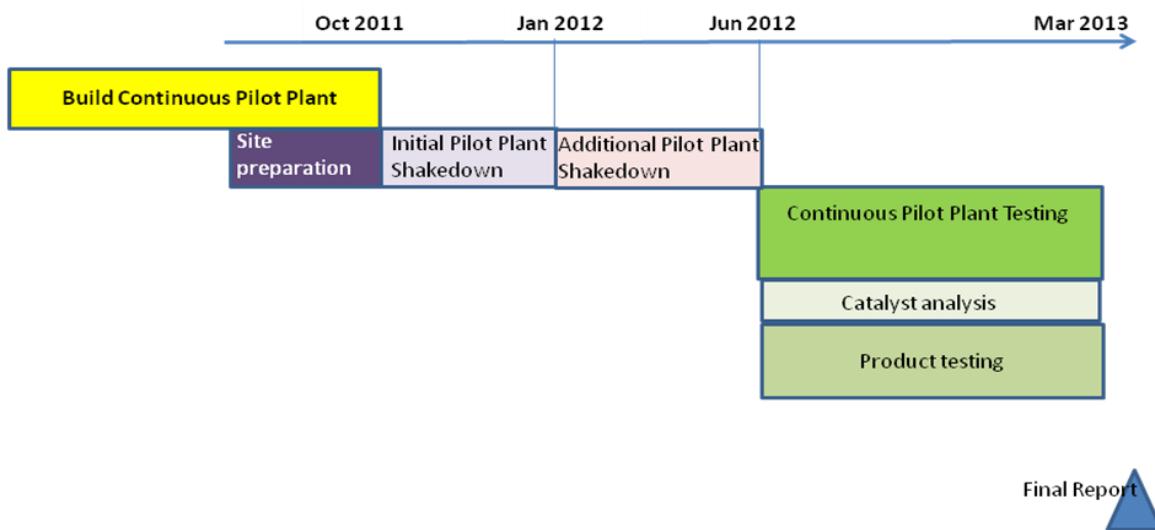
The Project Tasks and Timeline are shown in Figure 6. The construction of the 50 kg/day IH<sup>2</sup> pilot plant was outside the scope of the project and was funded by CRI and built by Zeton. The pilot plant was delivered on Sept 20, 2011 as expected. However this DOE project included the site preparation and pilot plant shakedown. The pilot plant shakedown task proved much more involved than originally anticipated and the timeline for that task had to be extended by 6-8 months which reduced the operational funds and time available for IH<sup>2</sup> testing.

# IH<sup>2</sup> Project Tasks and Timeline



U.S. DOE Award DE-EE-0004390

## Long Term Processing Using IH<sup>2</sup>



Project Partners are GTI, CRI Catalyst, Shell Global Solutions, Cargill, Johnson Timber, Parabel

Figure 6-IH<sup>2</sup> Project Timeline

Table 2-Project Task List

1	Pilot Plant Shakedown and Site Preparation
2	Feedstock Preparation
3	Long term IH <sup>2</sup> Catalyst Testing
4	Catalyst Analysis and Deactivation Rates
5	Liquid Product Distillation, Blending and Valuation
6	Corrosion Testing
7	Final Report

## Feedstock Analysis

The project plan was to run the IH<sup>2</sup> 50 kg/day pilot plant with a hardwood (maple) feed, a softwood (pine) feed, cornstover and lemma in separate campaigns. The maple feedstock was run as part of DOE DE-EE0002873 *Biomass to Gasoline and Diesel using Integrated Hydrolysis plus Hydroconversion process*. Table 3 shows analyses for the feeds to be used in the IH<sup>2</sup> 50kg/day pilot plant.

**Table 3- Feedstock Analyses**

	Wood maple	Wood pine	Corn-stover	Lemna derived
Feed wt % C (dry basis)	50.84	51.28	42.81	46.26
Feed wt % H (dry basis)	6.01	5.97	5.08	5.52
Feed wt % O (dry basis)	42.67	42.33	38.44	38.00
Feed wt % N (dry basis)	0.08	0.13	0.93	3.17
Feed wt % S (dry basis)	0.02	0.01	0.09	0.25
Feed wt % Ash (dry basis)	0.38	0.28	12.65	6.80
Feed wt % moisture	6.35	5.64	6.87	12.30
Feed H/C	1.42	1.40	1.42	1.43
Heating value Btu/lb dry basis	8490	8690	7090	7940
Chloride, ppm	182	110	1420	1220

For initial tests, the pilot plant was designed to run with feedstocks less than 500 micron in size to enable good char catalyst separation and minimize the required gas flow rates. In future tests, biomass particle size will be increased stepwise to reach 3.3 mm which is typical pyrolysis biomass feed size. Based on small scale semi-continuous pilot plant work, biomass particle size should not significantly affect yields as long as biomass is less than 3.3 mm. This is consistent with the particle size effects seen in pyrolysis.<sup>(1)</sup>

Lemna was obtained from Parabel (formerly Petroalgae) and was a lemna which had been extracted to remove much of the protein from the structure. The extracted lemna protein is sold as animal feed, while the remaining solid lemna (called lemna derived) was used as feed for the IH<sup>2</sup> process. The wood was obtained and prepared by Johnson Timber and the cornstover was obtained and prepared by Cargill. Preparation consisted of sizing and drying.

## Pilot Plant Site Preparation and Shakedown

Extensive site preparation was required to prepare the GTI space to house the IH<sup>2</sup> pilot plant. The site had important advantages such as a nearby hydrogen generator, high pressure hydrogen compressor and storage tanks, and good ventilation. But the site still required significant preparation to be suitable for the continuous IH<sup>2</sup> pilot plant. Key site preparation tasks included:

- Replacement of the standard overhead door with an enlarged automatic roll-up-door for process skid installation and safety which is shown in Figure 7.



Figure 7-IH<sup>2</sup> Automated roll-up-door to IH<sup>2</sup> Pilot Plant area

- b) Installation of improved process gas exhaust system.
- c) Relief vent purchase and installation.
- d) Maintenance of the existing GTI Proton Hogen hydrogen generation system (an electrolytic hydrogen generation system) shown in Figure 8.



Figure 8-IH<sup>2</sup> Hydrogen generation unit

- e) Water supply to deliver 15 lph Type II+ water quality for condenser system
- f) Added H<sub>2</sub> and CO gas sensors, flow sensors and fire detection.
- g) Added room alarm and safety interlock system
- h) Removed existing equipment and conduit from room A-101 near feeding cyclone of IH<sup>2</sup> skid.
- i) Added Chillers to provide cooling fluids to IH<sup>2</sup> Heat Exchangers
- j) Added nitrogen, hydrogen, vacuum and air delivery systems
- k) Added feed and sample preparation storage shed including electrical tie ins.
- l) Installed safety logic system and wiring.
- m) Prepared the adjoining room to be a control room for the IH<sup>2</sup> pilot plant
- n) Completed HAZOP review of IH<sup>2</sup> pilot plant process with IH<sup>2</sup> skid fabricator. .
- o) Completed hookup of electrical power to IH<sup>2</sup> skid, chiller units and biomass storage shed.
- p) Completed hookup and calibration of online GC

The IH<sup>2</sup> 50kg/day pilot plant was built by Zeton using private funding. It arrived on Sept 20<sup>th</sup>, 2011. This is the first continuous IH<sup>2</sup> pilot plant ever built so its engineering and design required real innovation. Pictures showing the pilot plant are shown in Figures 9, 10,11 and 12.



**Figure 9-IH<sup>2</sup> 50kg/day Continuous Pilot plant being Unloaded from Truck at GTI**



**Figure 10-New IH<sup>2</sup> Continuous Pilot Plant being Positioned in GTI building**

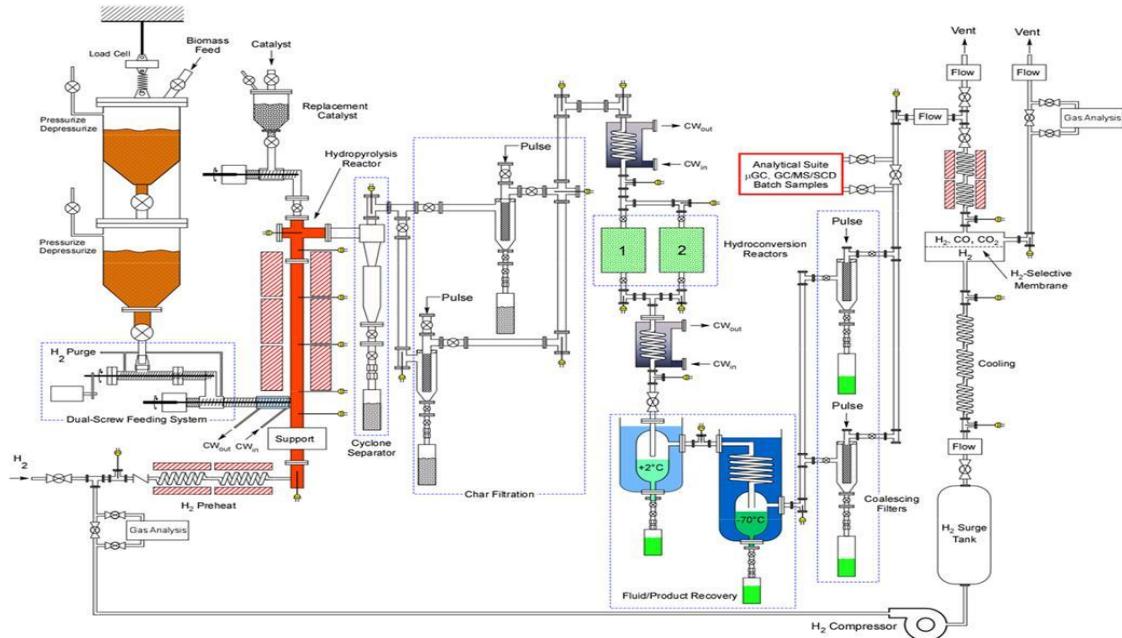


**Figure 11-Setup of Control Room for Continuous IH<sup>2</sup> Pilot Plant**



**Figure 12- IH<sup>2</sup> Pilot Plant**

A schematic diagram of the pilot plant is shown in Figure 13.



**Figure 13- Schematic Drawing of IH<sup>2</sup> 50kg/day pilot plant**

Initial phases of pilot plant shakedown included:

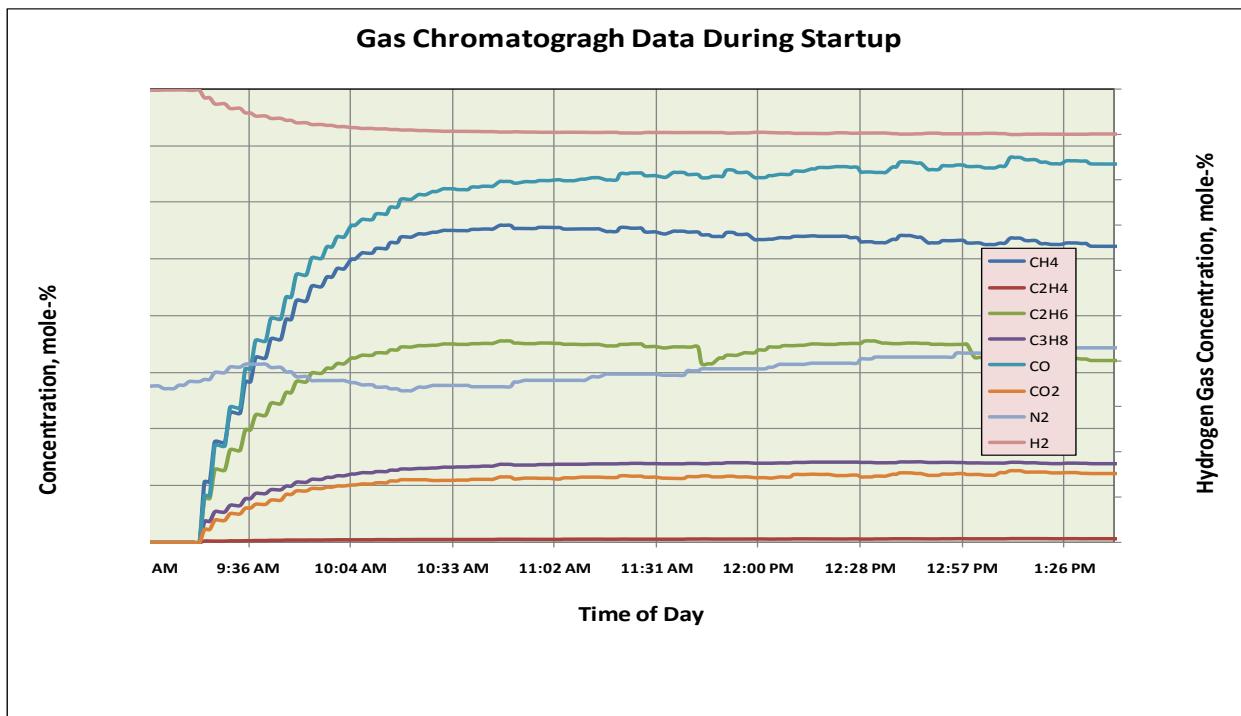
- a) Testing the lock-hopper system and feed handling system
- b) Testing the catalyst addition system
- c) Testing the char removal system
- d) Leak testing the system
- e) Insulating the system
- f) Testing the compressor and gas circulation system
- g) Testing the heaters
- h) Testing the liquid product collection system
- i) Testing the safety/alarm system
- j) Testing the online GC system
- k) Testing the data retrieval and daily spreadsheet update system

These tests revealed that certain parts of the pilot plant needed significant improvement before operation could begin. The safety displays required redesign so that alarms would be more obvious. The critical plant alarms are shown in Figure 14.

AREA SIS ALARMS				PROCESS ALARMS for ESD						DATE: 1/24/2013 TIME: 9:46:53 AM	
Description	High Alarm Status	High Alarm Status	High Alarm Status	Sensor	Description	High Alarm Status	High Alarm Status	High Alarm Status	Low Alarm Status	Low Alarm Status	Low Alarm Status
High H2 Level Rm A-101				PWR_IN	Control Output Power Status						
High CO Level Rm A-101				PI_1022	H2 Press at Bio-Mass Grav Feeder						
High H2S Level Rm A-101				PI_1108	H2 Static Press at R-111						
High HC's Level Rm A-101				PI_1328	Static Press at R-131						
High NH3 Level Rm A-101				PI_1329	Static Press at R-132						
Fire Alarm Rm A-101				PI_1507	Recyc Gas Compr Disch Press						
High HC'Level V-163 Enclosure				PDI_1207	H2 to Char Cyclone						
Vacuum C-101 High Alarm				PDI_1217	H2 Diff Press across Char Filters						
				PDI_1328	Diff Press across R-131						
				PDI_1329	Diff Press across R-132						
				PDI_1408	Diff Press across Cold Condensers						
				PDI_1507	Diff Press across HE-164/ C-151						
				PI_1502	Non-Cond Prdt Gas Press at Compr Cooler						
				LIT_1402A	Coalescer Top Level						
				LIT_1409	Cold Separator Level						

Figure 14- IH<sup>2</sup> Pilot Plant Alarm System Screen

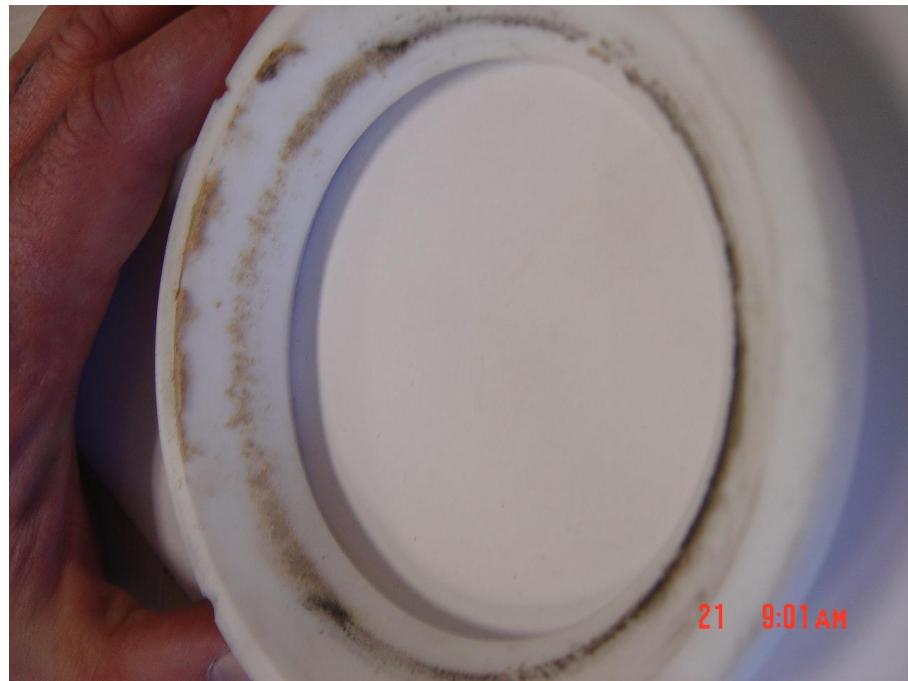
Auditory alarms were added to highlight emergency shutdowns. The pilot plant data system export system had to be improved so that key data could be exported each day and placed in a running spreadsheet to monitor pilot plant day to day yields and quality. .



*Figure 15- Start-up GC gas analysis plot*

The continuous GC results of the gas stream had to be displayed in the control room so operators could monitor the steadiness of operation. A typical start up GC display is shown in Figure 15. A molecular sieve drier had to be added to remove trace water and prevent the heat exchangers from freezing up. The catalyst screw feeder had to be replaced with a new one to prevent excessive breakage when the catalyst was fed to the unit.

The valves on the feed system and char removal system all leaked at high rates. It was found that tiny particles of wood or char would score the Teflon valve seats over time. These valves had to be replaced with more rugged metal seated valves in order to reduce leak rates.



*Figure 16- Leaking Teflon Valve Seat*

The char did not flow through valves as intended and tended to pack and plug. A stirrer or agitator had to be designed, fabricated and then added to the system to move the particles and help them drop down from vessel to vessel in the char removal system.

Automated sequencing of valves to add the feedstock and remove the char were developed. This is shown in Figures 17 and 18.

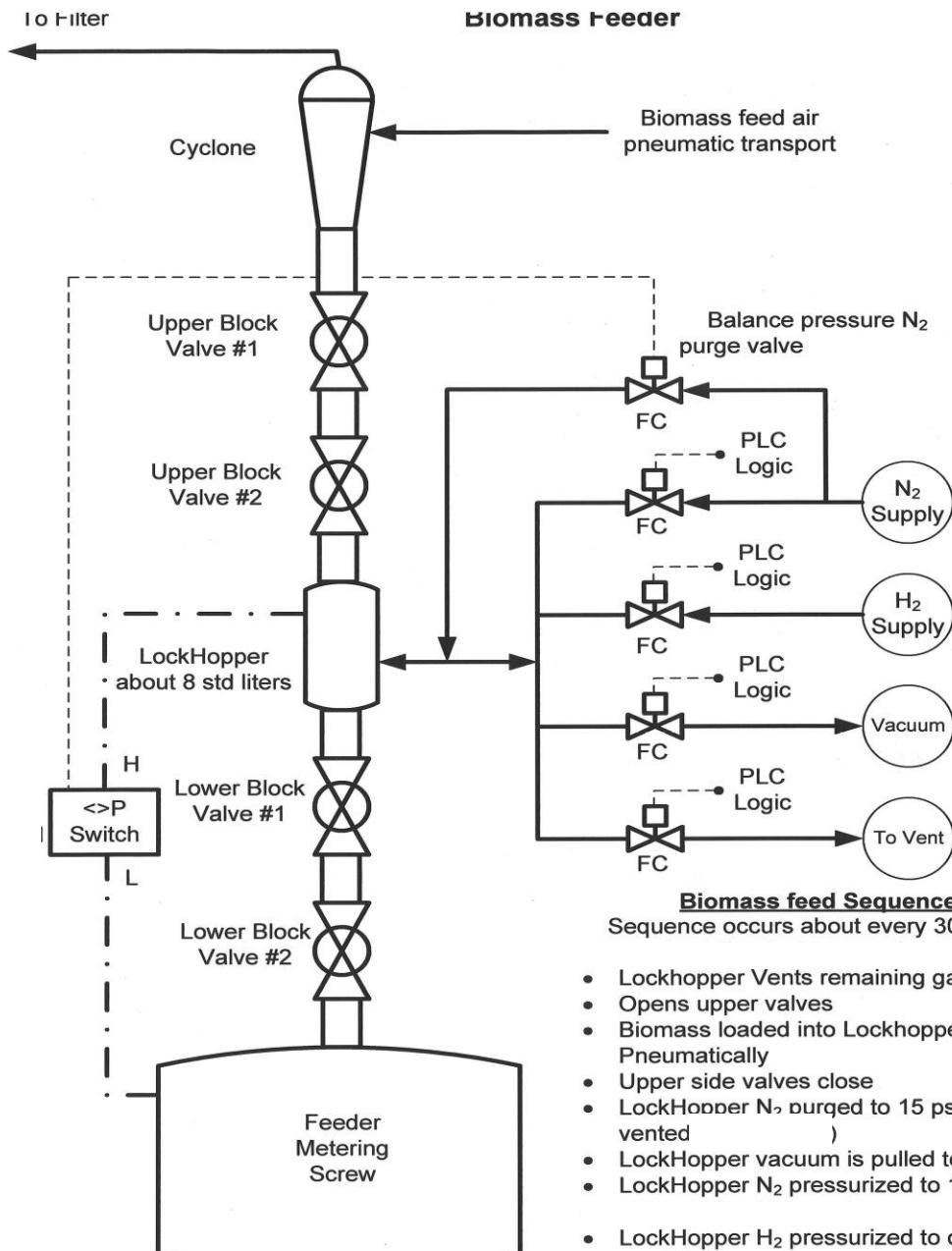
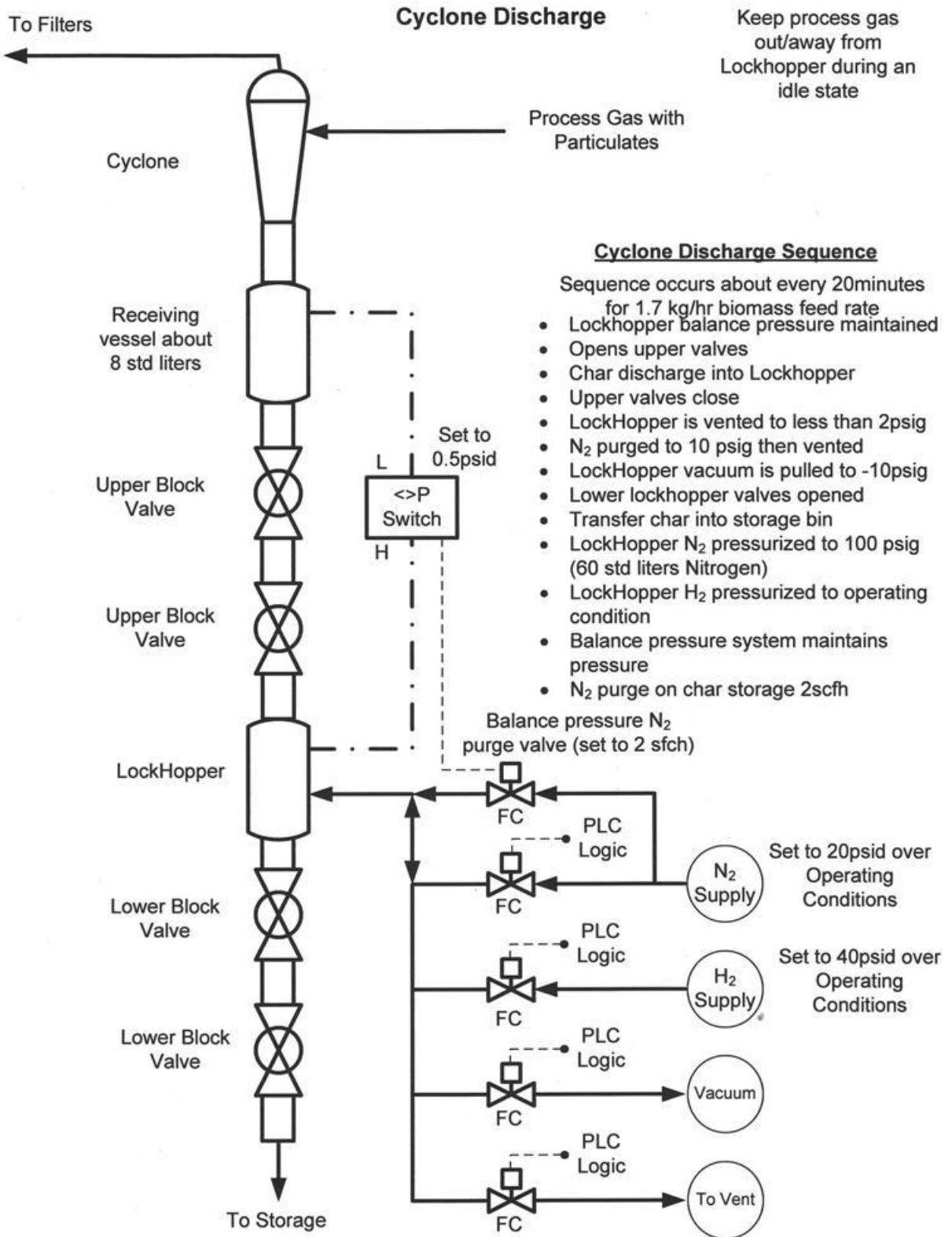


Figure 17- Biomass Feeder Operation



**Figure 18- Char Removal System**

Using these automated valves and procedures solid biomass was continuously added to the pilot plant and char was continuously removed. Liquid was continuously collected in the product receiver and removed once a day for analysis.

It was expected that debugging of the pilot plant would last 3-4 months but instead pilot plant debugging took 8 months to complete and cost more than expected. This reduced the amount of pilot plant run time possible with the funds available. As a result of the extended pilot plant shakedown, the experiments with cornstover and lemma were not completed and the project concentrated on testing with pine.

Once major issues were corrected, preliminary testing of the 50 kg/day IH<sup>2</sup> pilot plant began. Initial testing was done in 8 hours ( day shift only) with the unit put in hot idle overnight and restarted the next morning. Hot idle is a standby condition for the pilot plant, in which we keep the reactor temperature and pressure at standard test conditions, keep hydrogen in the pilot plant system, but do not add any new biomass feed , recirculate gas or add any makeup hydrogen. Hot idle conditions just maintain temperatures and pressures so restart is quicker. The goal of the initial 8 hour tests was to establish operating procedures and aid in pilot plant debugging.

The pilot plant then progressed to 24 hour a day operation with periodic shutdowns for maintenance. 24 hour operation for the IH<sup>2</sup> continuous pilot plant is much more efficient because it eliminates the need for startups, shutdowns and line out periods.

## Pilot Plant Testing Results

The first goal in testing was to achieve the same yields in continuous testing as were obtained in small scale batch testing reported in the final report for DOE DE-EE0002873 “Biomass to Gasoline and Diesel using Integrated Hydropyrolysis plus Hydroconversion process”<sup>(2)</sup> and the article *Integrated Hydropyrolysis and Hydroconversion (IH<sup>2</sup>) for the Direct Production of Gasoline and Diesel Fuels or Blending Components from Biomass*<sup>(3)</sup> published in Environmental Progress and Sustainable Energy.

Initial yields from the bench scale testing and continuous testing were quite close as shown in Table 4.

**Table 4-IH<sup>2</sup> Yield Comparison, Maple feed, MAF**

	<b>Bench scale test</b>	<b>50 kg/day continuous</b>
% C4+ Liquid hydrocarbon	26	26
% water	36	36
% char	13	14
% C1-C3	13	15
% CO+CO <sub>2</sub>	17	14
Total	105	105

A second goal was to produce high quality liquid hydrocarbon products as we had produced in the small scale batch testing.<sup>(2)(3)</sup> Liquid product quality was quite good as shown in Table 5 and Figures 19 and 20.

*Table 5- IH<sup>2</sup> Continuous Pilot Plant Liquid Analysis, Maple Feed*

	%
%C	<b>88.20</b>
%H	<b>11.60</b>
%S	<b>.02</b>
%N	<b>&lt;.1</b>
%O	<b>&lt;.1 (BDL)</b>
TAN	<b>&lt;1</b>
% Gasoline	<b>63</b>
% Diesel	<b>37</b>



*Figure 19 - IH<sup>2</sup> Total Hydrocarbon Product from 50kg/day Pilot Plant*

## Liquid Products Collected from Recent Continuous IH<sup>2</sup>-50 Testing with Wood

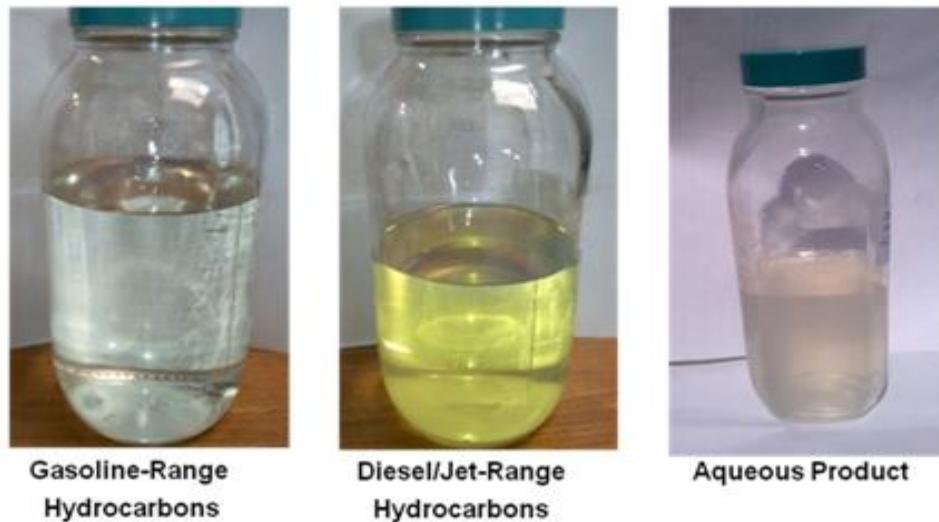


Figure 20- IH<sup>2</sup> Hydrocarbon Product cuts and water from 50kg/day Pilot Plant

The third goal was to show steady continuous operation over an extended period of time. The pilot plant was operated to get daily yields, material balances, and product analysis so that product quality and yields could be monitored versus time. The pilot plant was successfully operated for over 750 hours on stream for this test program. Data from the pilot plant versus hours on stream is shown in Figures 21-28. The maple feed was run under project DOE DE-EE0002873 and the pine feed was run under this project. All yields are reported on a moisture ash free (MAF) basis.

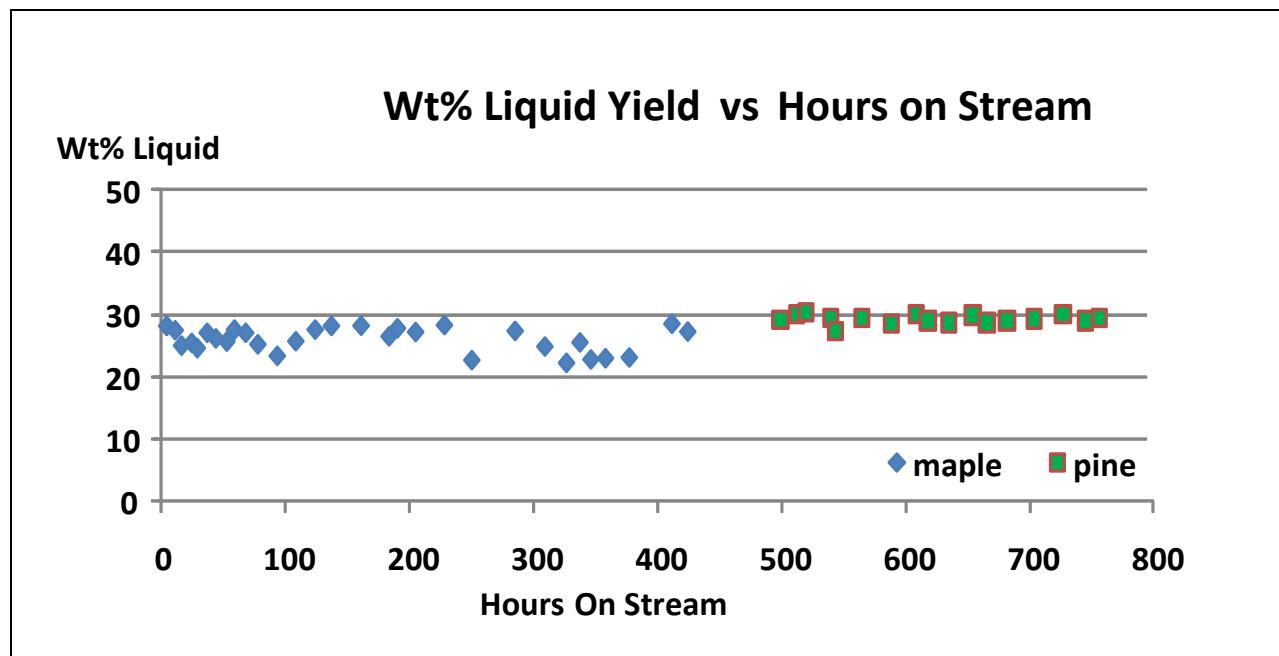


Figure 21-Wt% Hydrocarbon Liquid Yield versus Hours on Stream

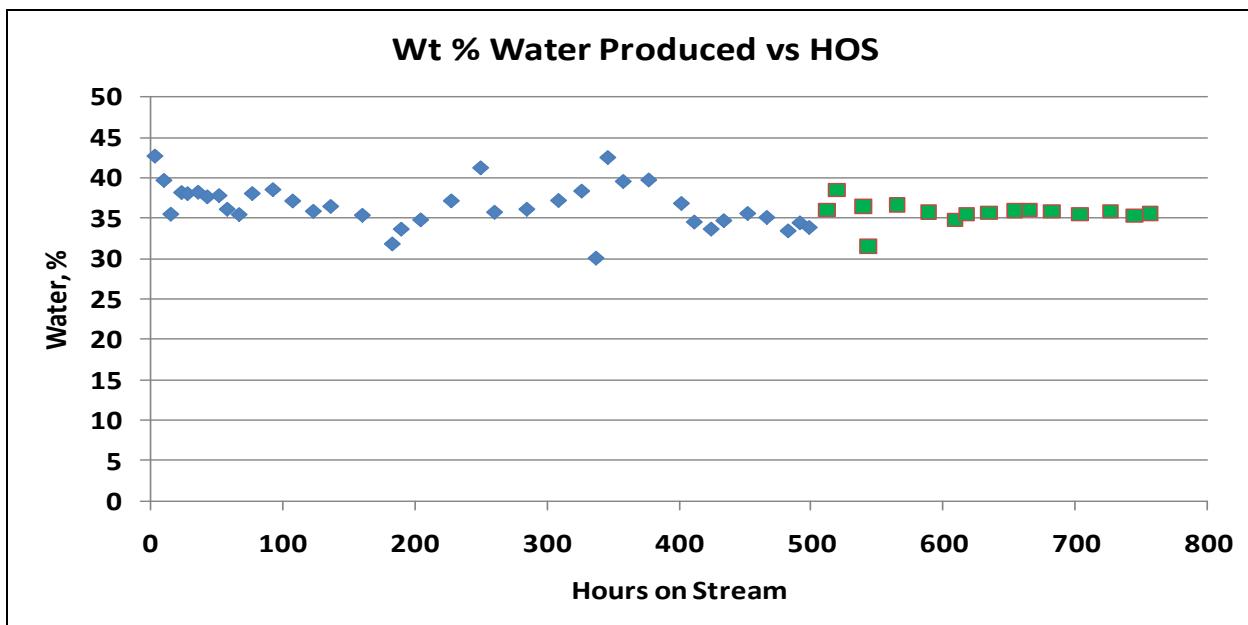


Figure 22-Wt% Water versus Hours on Stream

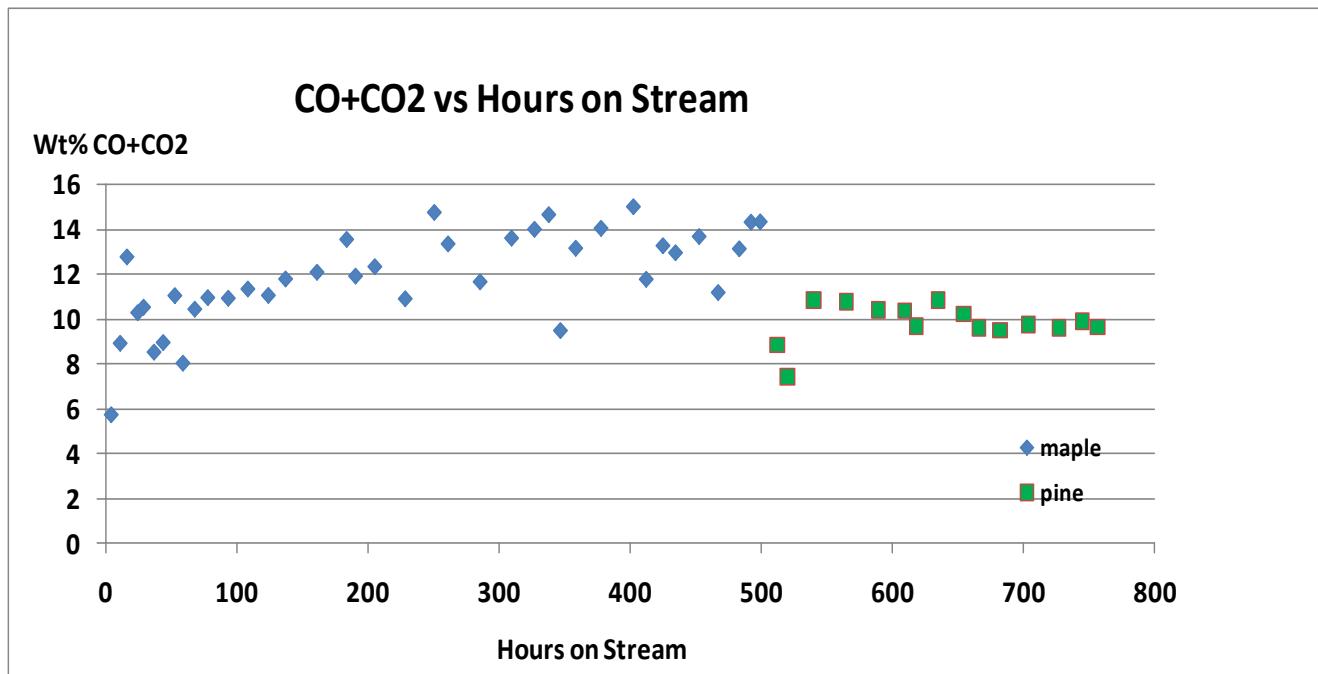


Figure 23-Wt% CO+CO<sub>2</sub> versus Hours on Stream

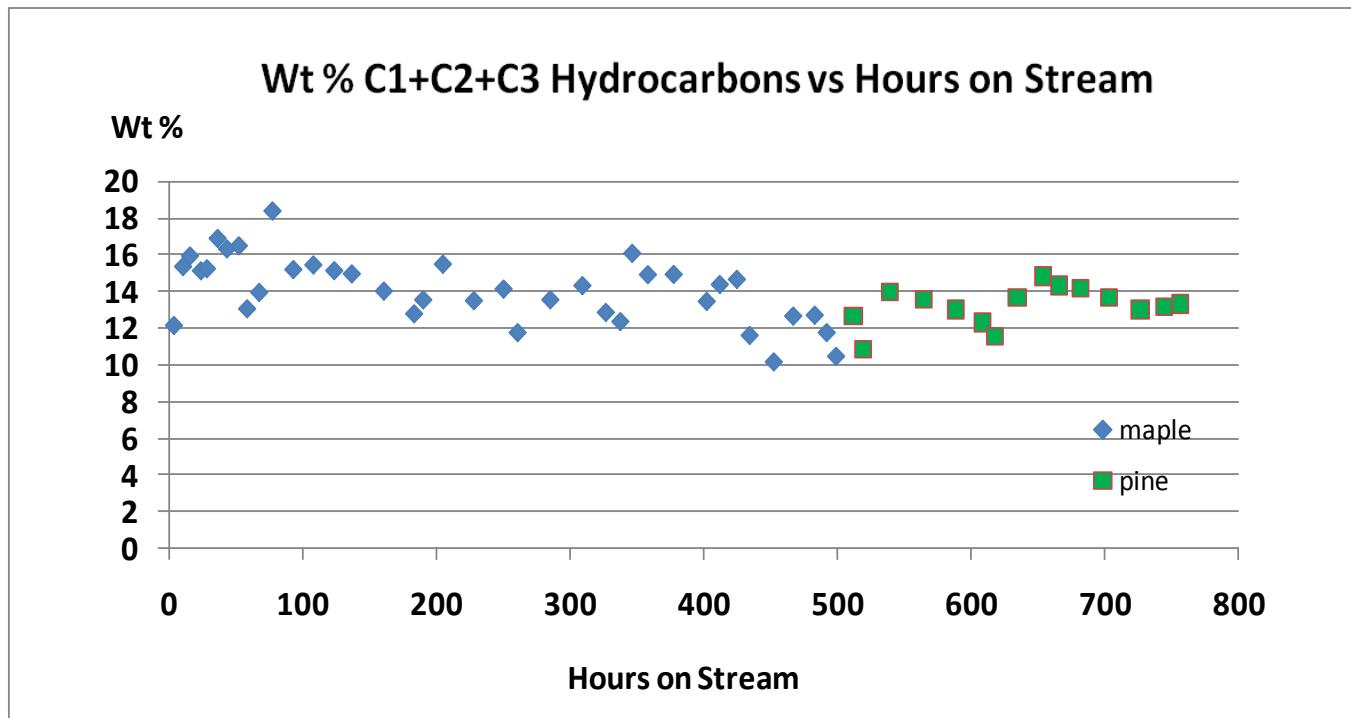


Figure 24-Wt% Methane +Ethane +Propane versus Hour on Stream

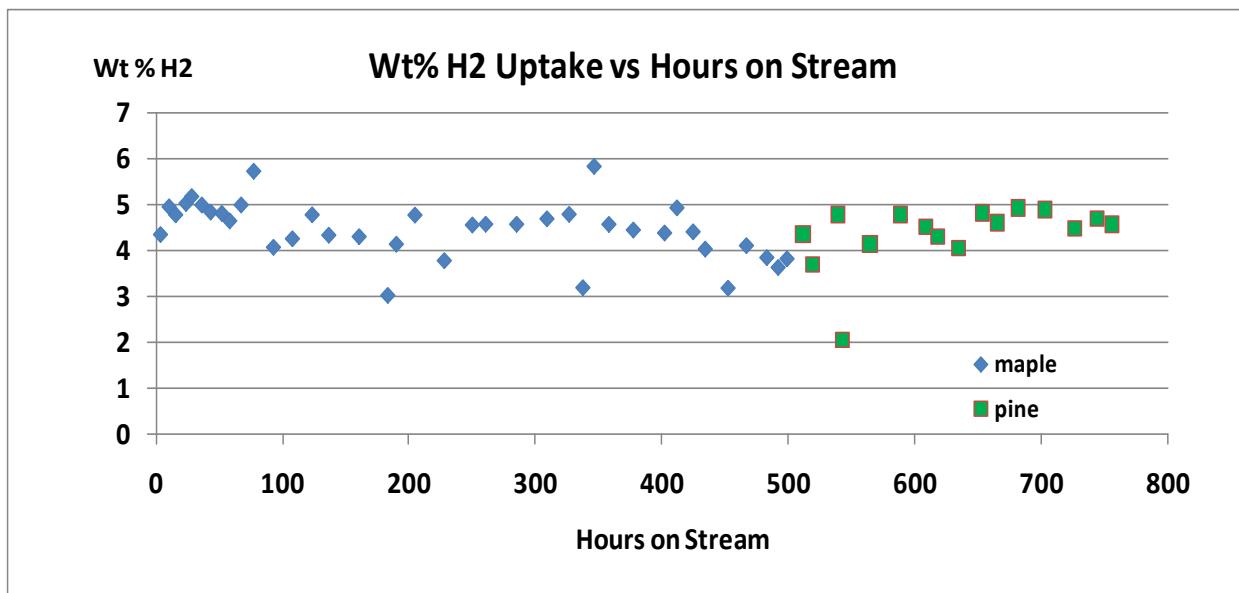


Figure 25-Wt% H<sub>2</sub> versus Hours on Stream

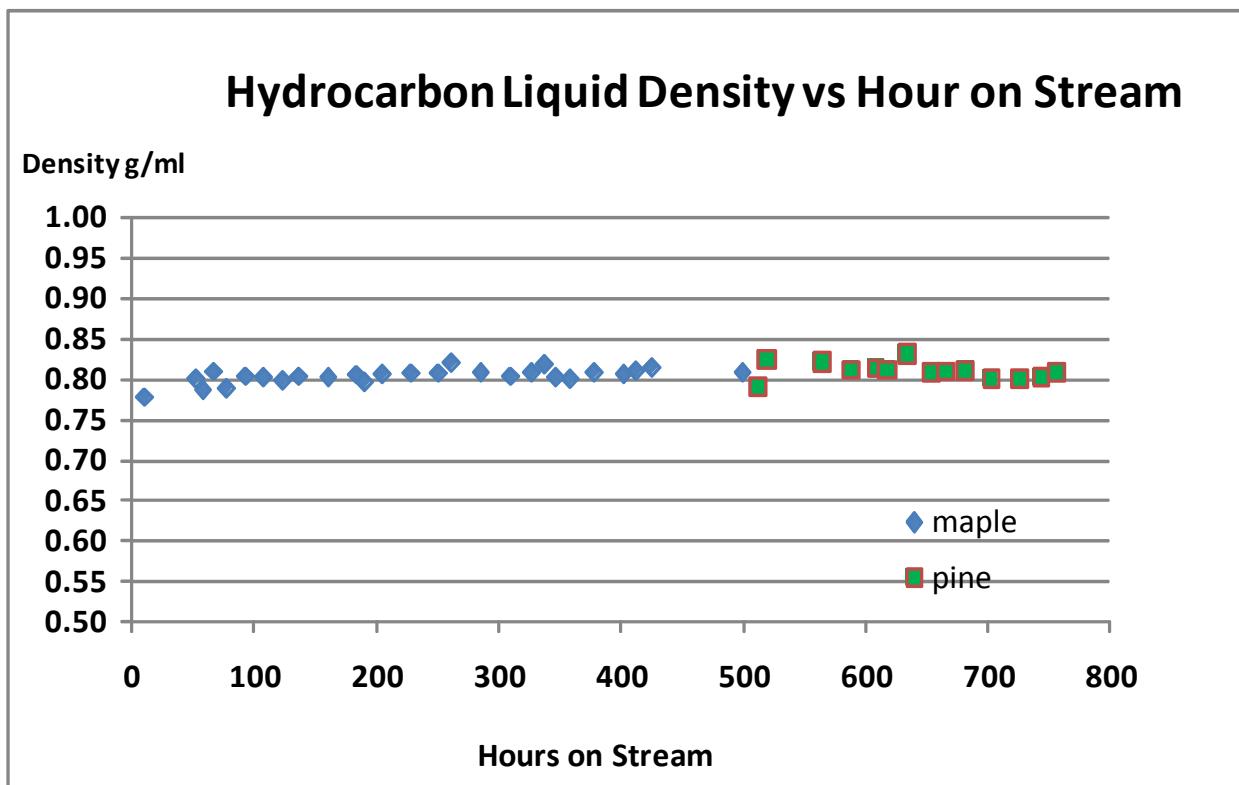


Figure 26-Hydrocarbon Product Density versus Hours on Stream

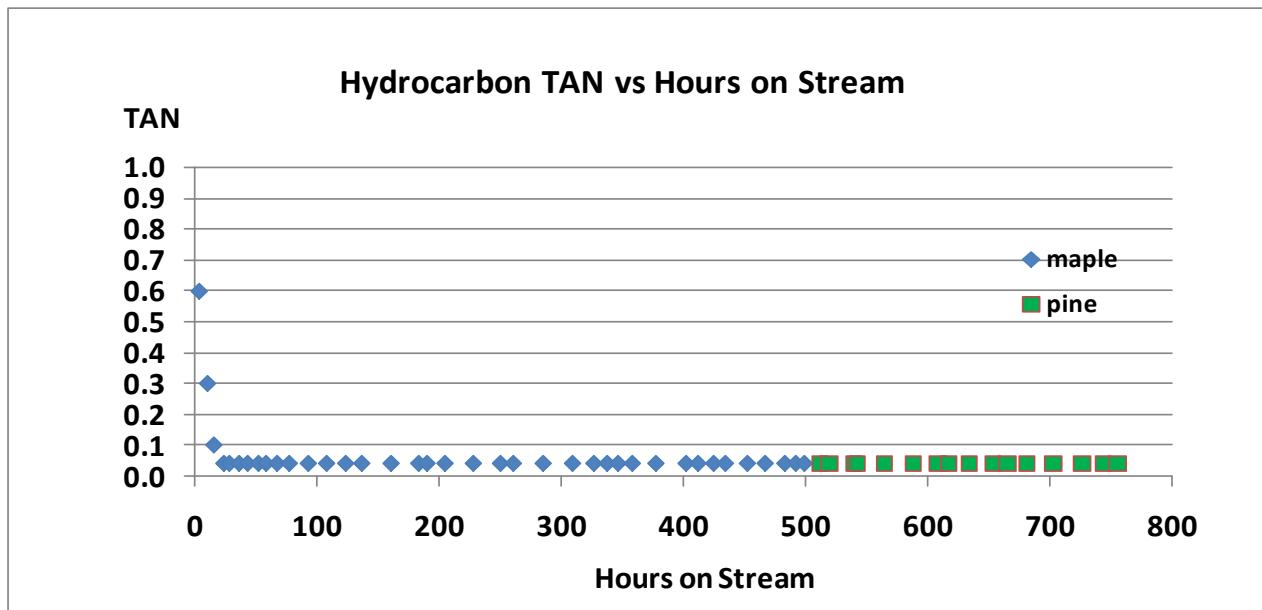


Figure 27-TAN versus Hours on Stream

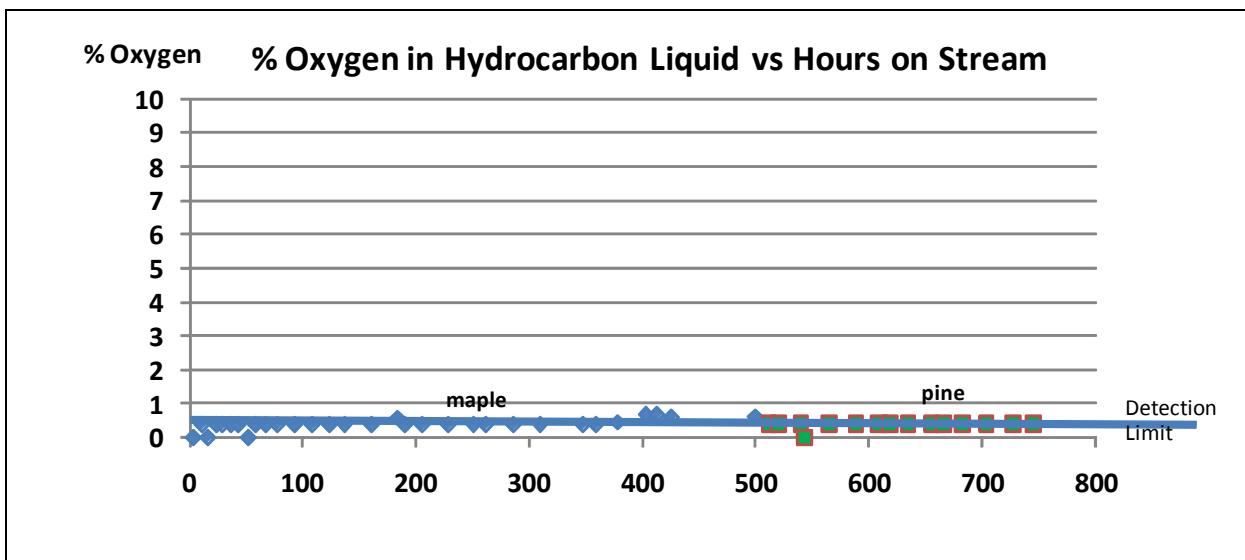


Figure 28-% Oxygen in Hydrocarbon Liquids vs. Hours on Stream

The yields of hydrocarbon liquids of 25-28% were very steady over the test period and the product quality was also quite good with less than 1wt% oxygen in the hydrocarbon liquid products..

## Char Analysis

The char from IH<sup>2</sup> continuous testing was analyzed as shown in Table 6. The IH<sup>2</sup> char could be used as a renewable fuel sent to a boiler and burned to make steam or electricity.

**Table 6- IH<sup>2</sup> Typical Char Analysis from Wood Feeds**

	Sample 1	Sample 2
% Carbon(mf)	77.95	79.74
% Hydrogen(mf)	2.57	3.79
% Nitrogen(mf)	.24	.22
% Sulfur(mf)	.03	.05
%Oxygen(mf)	15.45	13.37
%ash(mf)	2.57	2.83
Cl ppm	71	160
K, %	.40	nm
%Metal 1	<.05	.03
% Metal 2	.05	.06
% moisture	3.64	3.48
% Volatiles	31.37	29.07
Gross Calculated Heating Value btu/lb (from Dulong)	11734	12914
Calculated char yield from ash content*	12.8	11.7
Calculated % catalyst in char from metal 2	.43	.51
Calculated catalyst lost % of bed/day	2.4	2.9

- Assumes average feed ash of .33

As expected, the calculated char yield based on the ash balance is in rough agreement with the measured char yields. Gross Heating values were calculated based on the Dulong formula of:

Heating value btu/lb = $145.44*C+620.28*H=40.5*S-77.54*O$ . These calculated numbers compare well to a measurement made of char obtained from earlier experiments in our small batch pilot plant which showed a measured char heating value of 12,710 btu/lb . Coal typically has 12,000-13,000 btu/lb so heating value of the char and coal on BTU/lb basis is similar. One difference between char and coal is that char has a low bulk density of .35-.45 g/cm<sup>3</sup> whereas coal has a bulk density of .98g/cm<sup>3</sup>. The low bulk density of char suggests burning on site or that briquetting would be best for transportation. Literature data has shown that pyrolysis char can be briquetted<sup>(4)</sup>. Char from the small batch unit had a surface area of 16.7m<sup>2</sup>/g.

The char is much weaker in strength than the catalyst. Relative strength of char was measured in a modified Hargrove grindability index test is shown in Table 7.

**Table 7-Relative Strength via Modified Hardgrove Grindability Test**

	Catalyst	Char	Coal typical
Modified Hardgrove Grindability Index	70	146	100

The particle size of the char is smaller than the initial particle size of the wood feedstock which is probably the result primarily of attrition which occurs as it goes through the bed. This change in particle size is shown in Figure 29 and 30. It was also noticed that as the char is handled it continues to attrite and gets smaller and smaller.

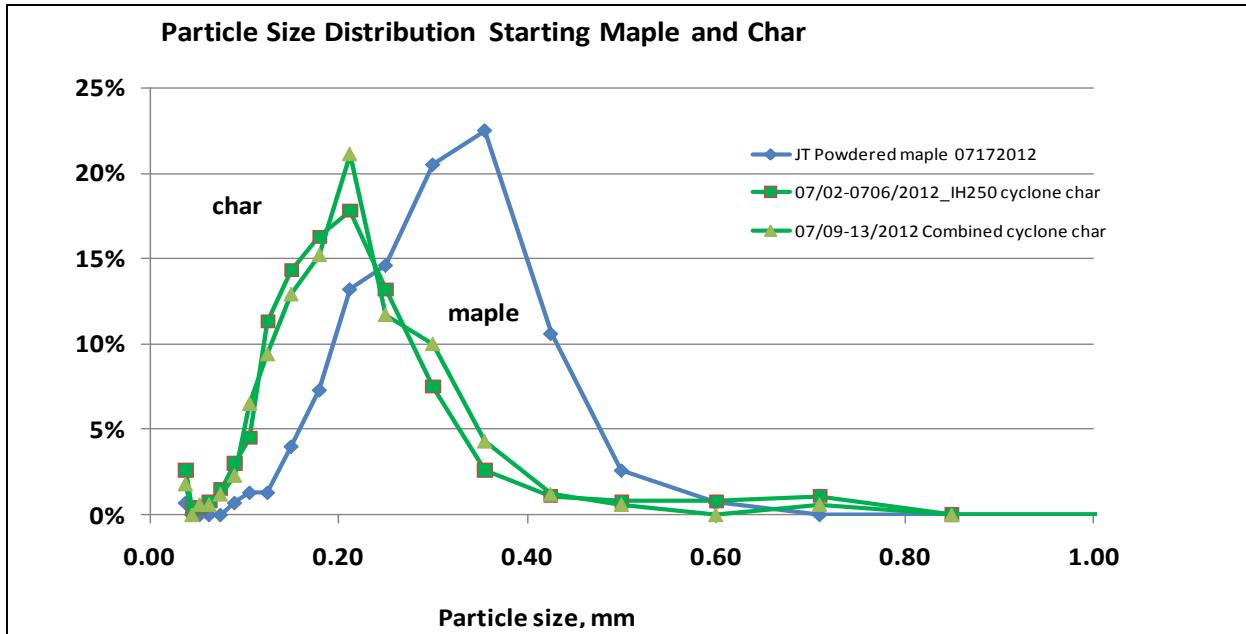


Figure 29- Particle Size Distribution of Maple and Char

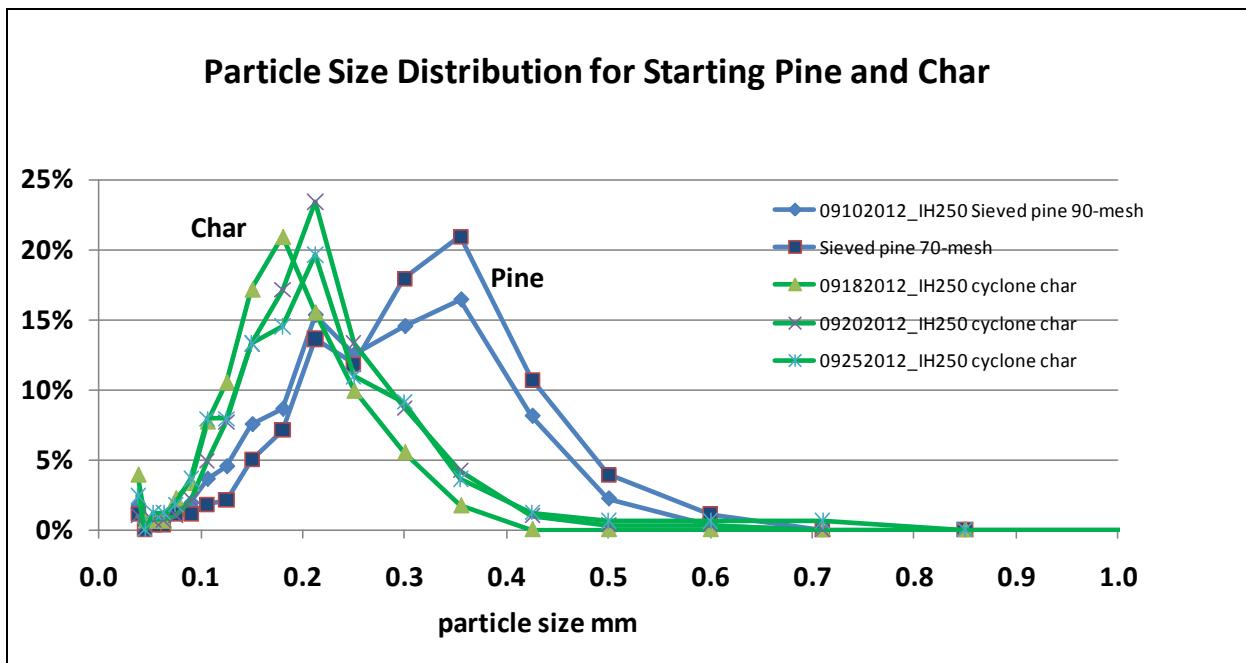


Figure 30- Particle Size Distribution for Starting Pine and Char

A key area for future study is to determine the residence time of the char in the bed. Fine char will pass through the fluidized bed more rapidly than coarse char.

Because of the presence of small amounts of catalyst metals in IH<sup>2</sup> char, the IH<sup>2</sup> char is valued based on its heating value rather than its use as a soil amendment. Our engineering design partner, has had discussions about the use of the IH<sup>2</sup> char in coal fired boilers, or in existing hog boilers and determined that it should work well in those applications.

## Water Analysis

The water was analyzed periodically to determine the level of hydrocarbon contamination. The water always had less than 1% carbon as shown in Figure 31. This was expected since it has been shown in the literature <sup>(5)</sup> that when high level of oxygen removal is achieved in the hydrocarbon phase, low levels of hydrocarbon contamination are present in the water phase. This trend is shown in Figure 32.

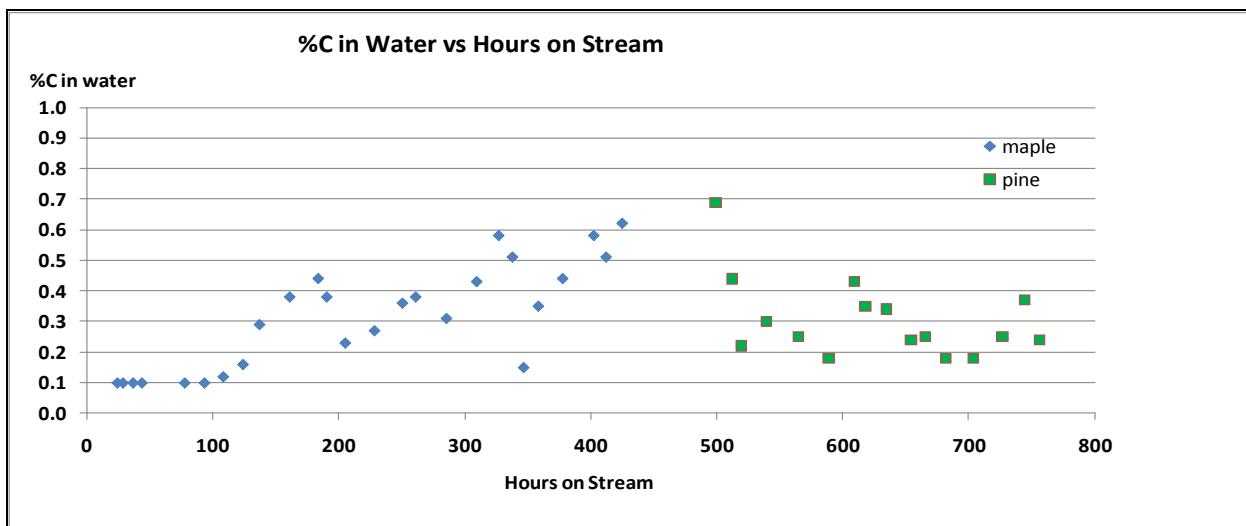


Figure 31-%C in Water from IH<sup>2</sup> vs. Hours on Stream

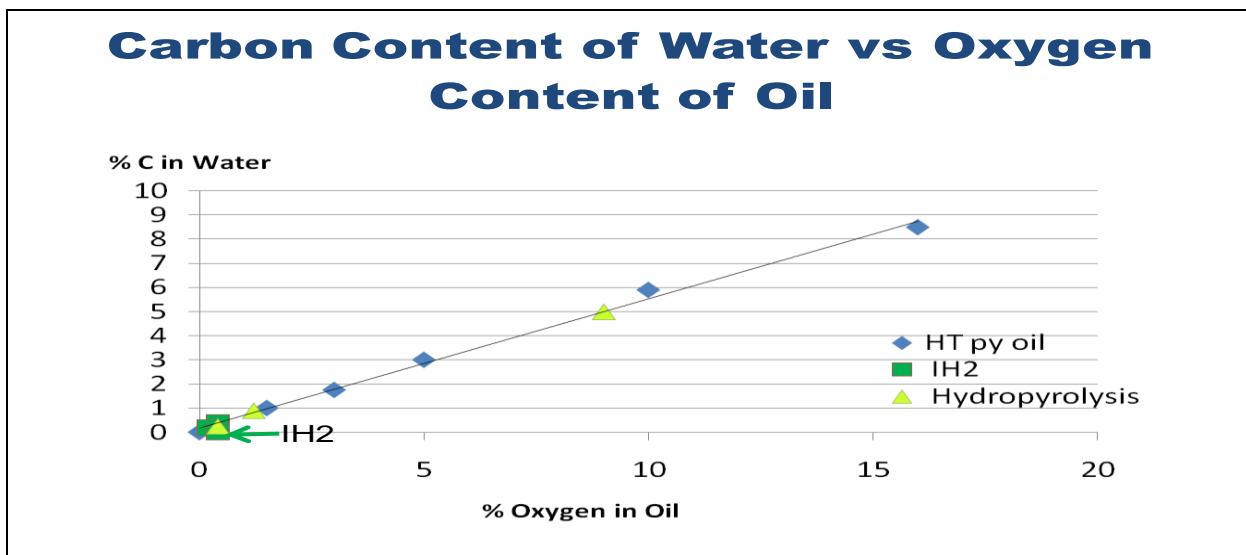


Figure 32- General Trend of %C in water vs. % Oxygen in Oil

Figure 33 shows the level of ammonia in the  $\text{IH}^2$  water and Figure 34 shows the pH of the water produced from  $\text{IH}^2$ . The  $\text{IH}^2$  water is typically 7 to 9 pH, or slightly basic, not acidic as is water produced from mild hydrotreating of pyrolysis oil.

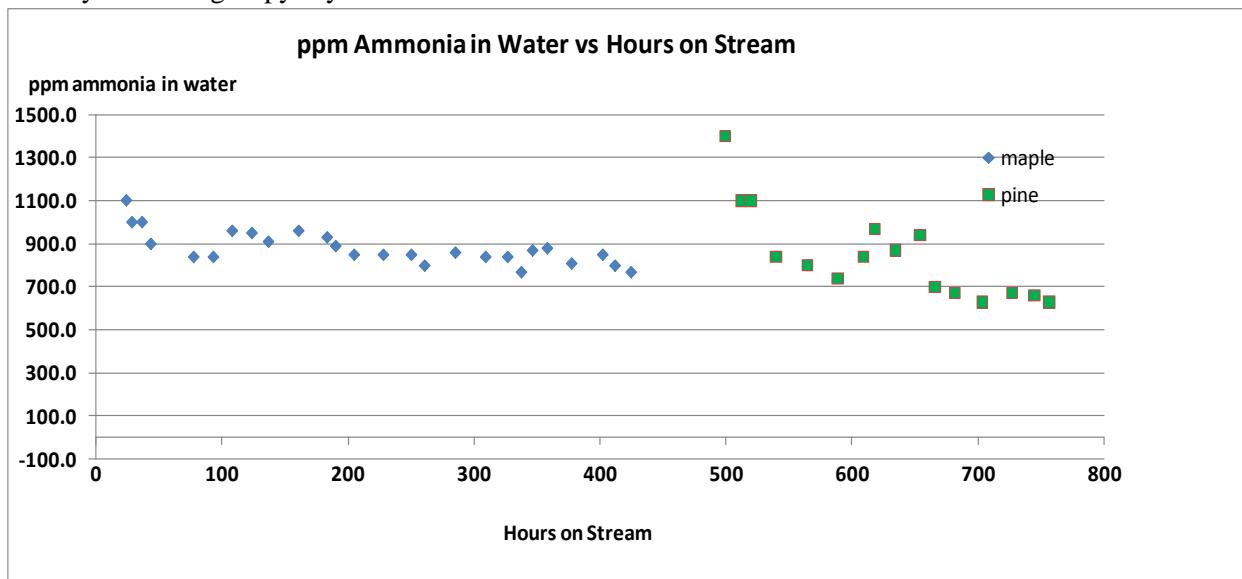


Figure 33- ppm Ammonia in Water vs. Hours on Stream

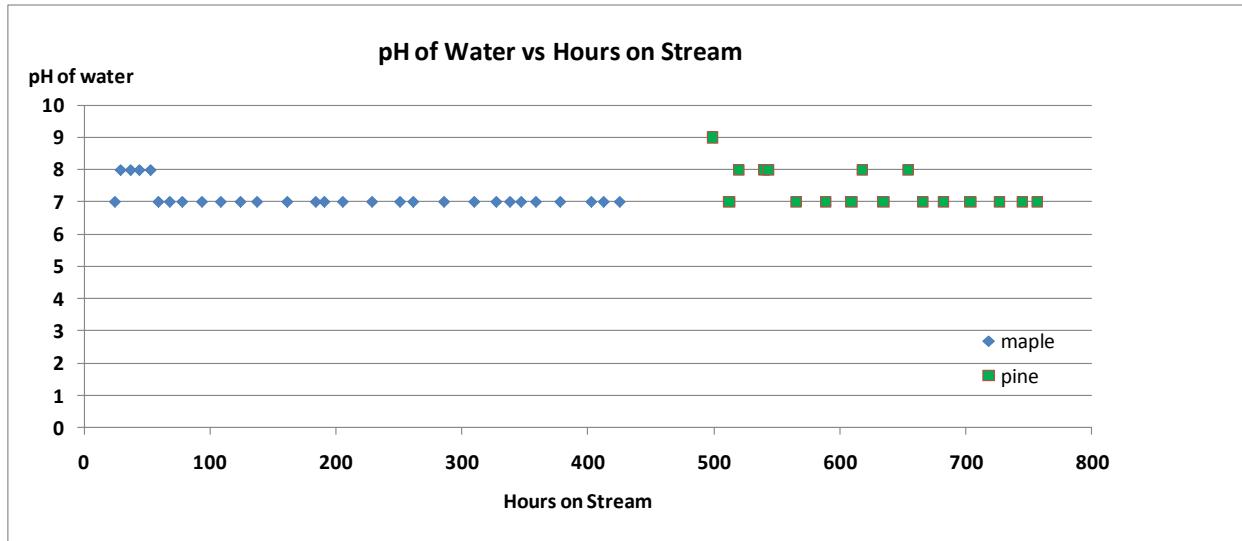


Figure 34-pH of  $\text{IH}^2$  water

More detailed analysis of the water was also completed to look for trace contaminants. This is shown in Table 8.

**Table 8- Analysis of Water for Trace Contaminants**

	Drum 1 - 6/12	Drum 2 - 7/12
pH	8.25	8.80
% organic carbon	0.16	0.66
Ammonia, ppm	1400	3209
Chloride, ppm	22	49
Carbonate, ppm	3646	6529
Sulfate, ppm	6	55
Thiosulfate, ppm	121	5
Nitrite, ppm	<5	<5
Bromide, ppm	<5	<5
Phosphate, ppm	<5	<5
Sodium, ppm	<10	<10
Potassium, ppm	<10	<10
Magnesium, ppm	<10	<10
Calcium, ppm	<10	<10

Significant amounts of carbonate are dissolved in the water which is logical because of the level of CO<sub>2</sub> in the gas product. The chloride in the water is of concern because of the potential for chloride stress corrosion cracking.

## Catalyst Analysis

The second stage catalyst was obtained from CRI Catalyst and consisted of 1.3 mm trilobes of CRI-4211. This catalyst showed no signs of significant deactivation over the course of 750 hours on stream based on the temperature profile shown in Figure 35 and the performance. The oxygen content of liquid hydrocarbon product was always below 1% over the entire 750 hours on stream. There is a clear exotherm across the hydroconversion bed of roughly 35 degrees Fahrenheit as shown in Figure 36. Sulfur is lost from the initial catalyst but it is believed that it reaches a steady state equilibrium. Low carbon levels are found on the catalyst indicating that minimal coking of the hydroconversion catalyst has occurred. Analysis of the used 2nd stage catalyst is shown in Table 9.

**Table 9- Comparison of Fresh and Used Hydroconversion Catalyst after 750 hours on Stream**

	Fresh hydroconversion catalyst-Base	Used hydroconversion catalyst- Top	Used hydroconversion catalyst Mid	Used hydroconversion catalyst Bot
% metal 1	100	84	89	86
% metal 2	100	96	106	103
% Sulfur	100	89	91	120
%Carbon	100	113	97	90
%Nitrogen	100	100	100	100
%Ash	100	105	107	106
% fixed carbon	100	47	5	118
Chloride, ppm	0	68	82	62

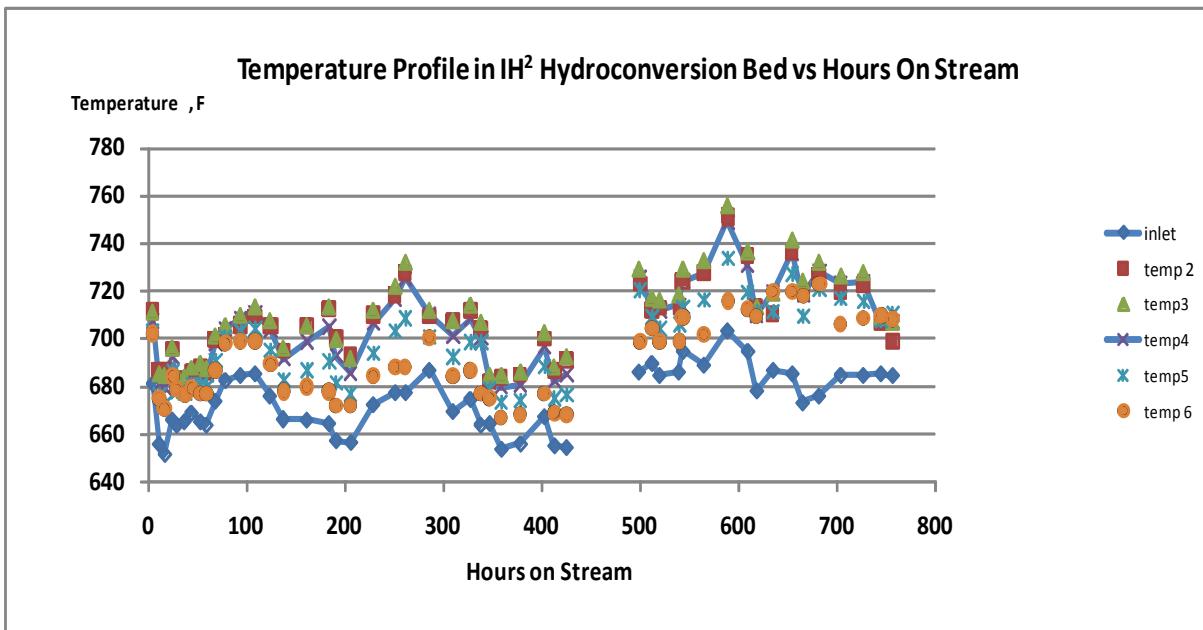


Figure 35- Temperature profile in Hydroconversion reactor over time

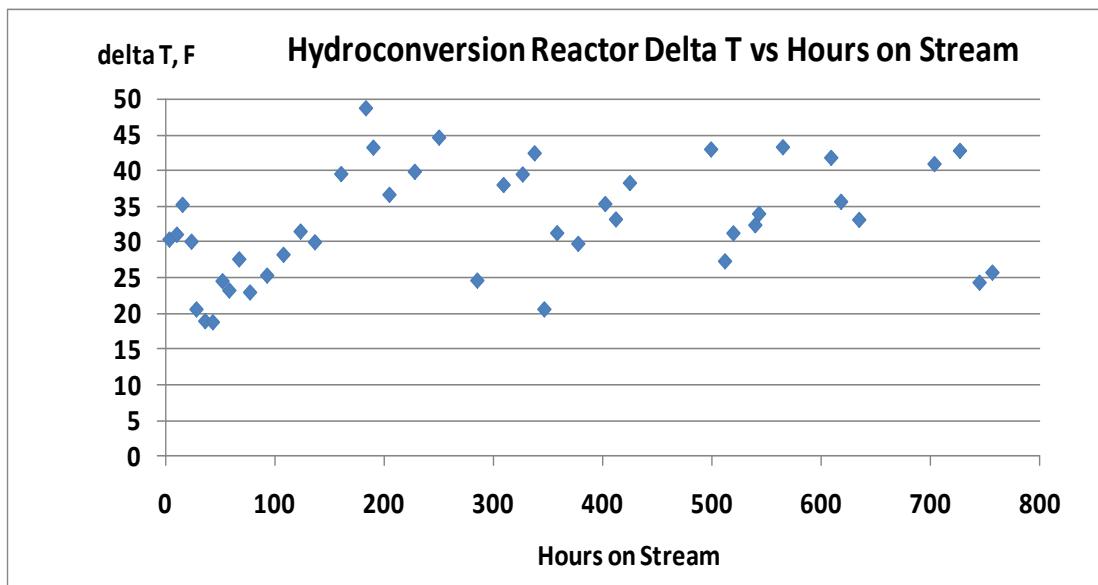


Figure 36- Hydroconversion Reactor Delta T vs. Hours on Stream

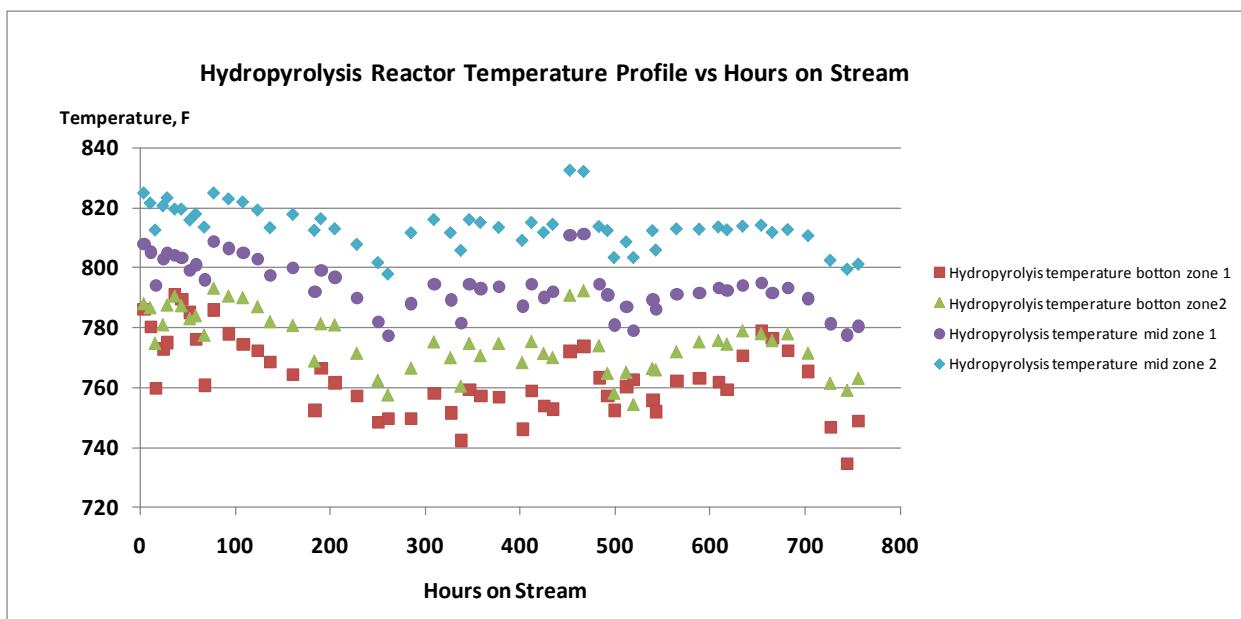
Hydropyrolysis catalyst was continually replaced to make up for catalyst losses that occurred in the hydropyrolysis reactor. Over time some char builds up in the bed but it reaches a steady state and can be separated from the catalyst by particle size. There is more carbon in the hydropyrolysis catalyst than the hydroconversion catalyst which is understandable since it was run roughly 80F hotter. When the bed was removed for analysis, there was no sign of any agglomerates or large particles in the bed. Only starting catalyst and char was found in the bed.

**Table 10- Relative Comparison of Fresh and Used Hydropyrolysis Catalyst-**

	Fresh hydropyrolysis catalyst	Used hydropyrolysis catalyst at 270 HOS	Used hydropyrolysis catalyst at 500 HOS	Used hydropyrolysis catalyst at 750 HOS
% Metal 1	100	nm*	85	76
% Metal 2	100	nm*	82	85
% Sulfur	100	88	101	79
% Carbon	100	290	206	373
% Ash	100	96	99	86
% Volatiles	100	96	77	94
Chloride, ppm	0	nm*	nm*	136

\*nm=not measured

The temperature profile in the hydropyrolysis reactor remains roughly the same with time as shown in Figure 37 and Figure 38. There is a 50 F temperature increase across the pilot plant bed despite the fluid bed system which features significant mixing of the catalyst.



**Figure 37-Hydropyrolysis Reactor Profile vs. Hours on Stream**

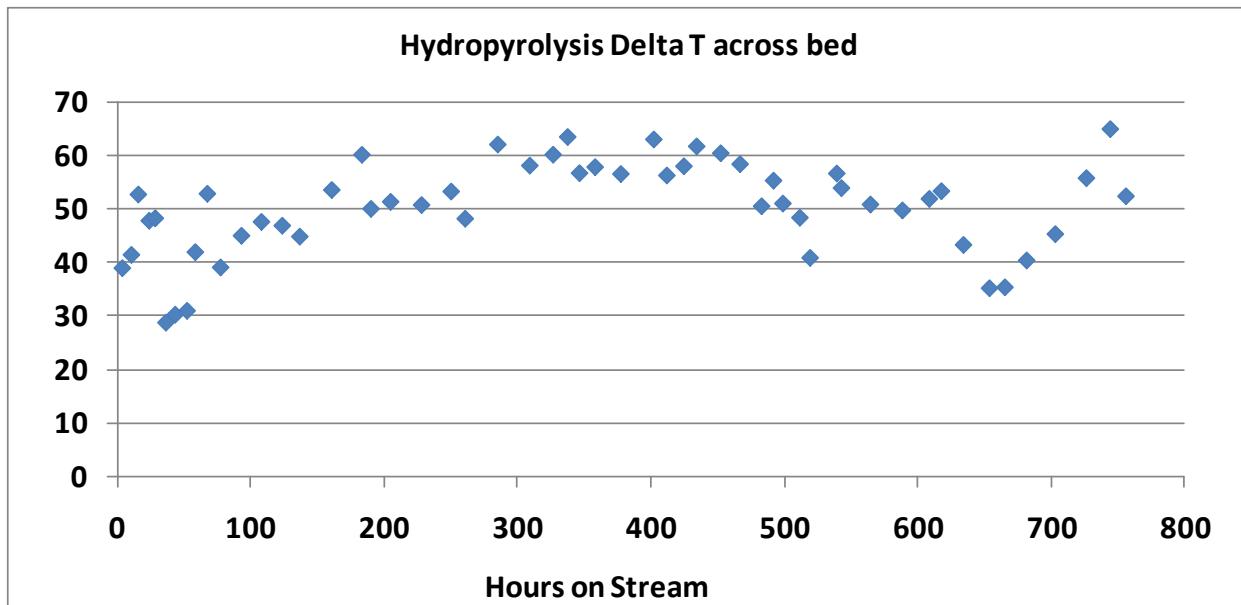


Figure 38- Hydropyrolysis Reactor Delta T, F

The goal in testing was to keep a steady level of catalyst in the hydroprocessing bed so the space velocity would remain constant at a relatively high WHSV throughout the test. However it took time to develop a methodology for accurately determining the catalyst level in the bed. Measuring pressure drop across the bed proved to be unreliable, so the best method was to measure the ash contained in the char each day and subtract out the ash from the feed. Using this methodology to calculate the catalyst in the bed, the actual/design WHSV vs. hours on stream is shown in Figure 39. This compared well to the actual level of catalyst found in the bed when the bed was shut down after 250, 500 and 750 hours on stream and samples taken for analysis. Despite these variations in WHSV, little change was seen in the final  $\text{IH}^2$  product since the hydroconversion step compensated for the variability in the hydroprocessing WHSV as designed.

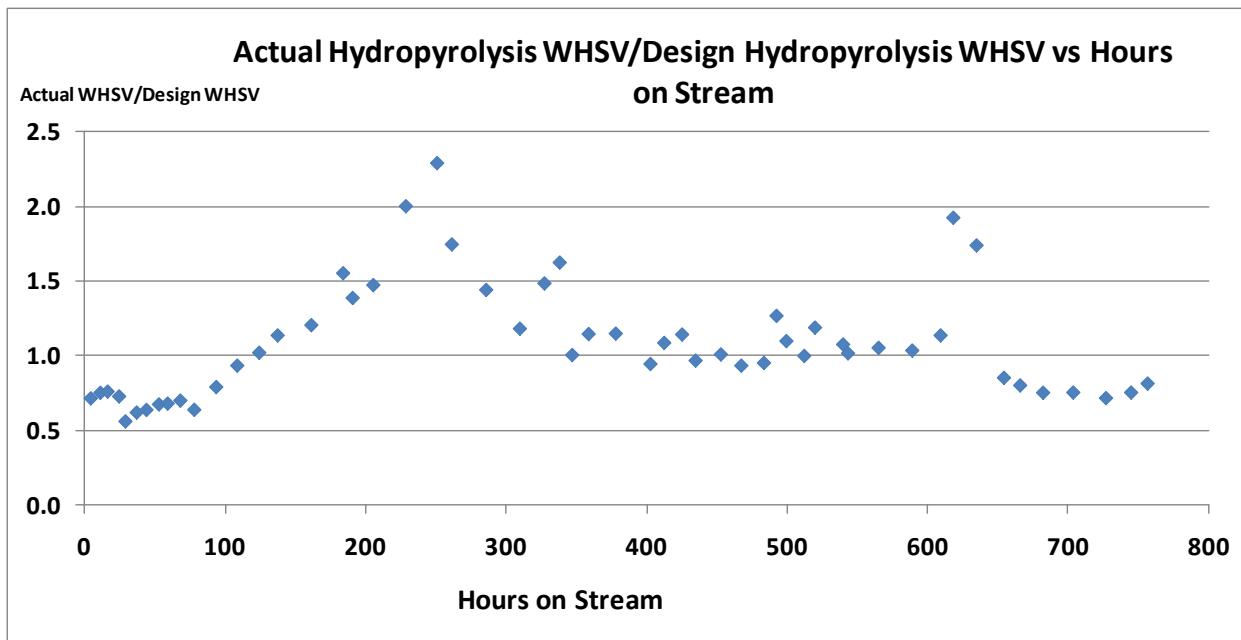
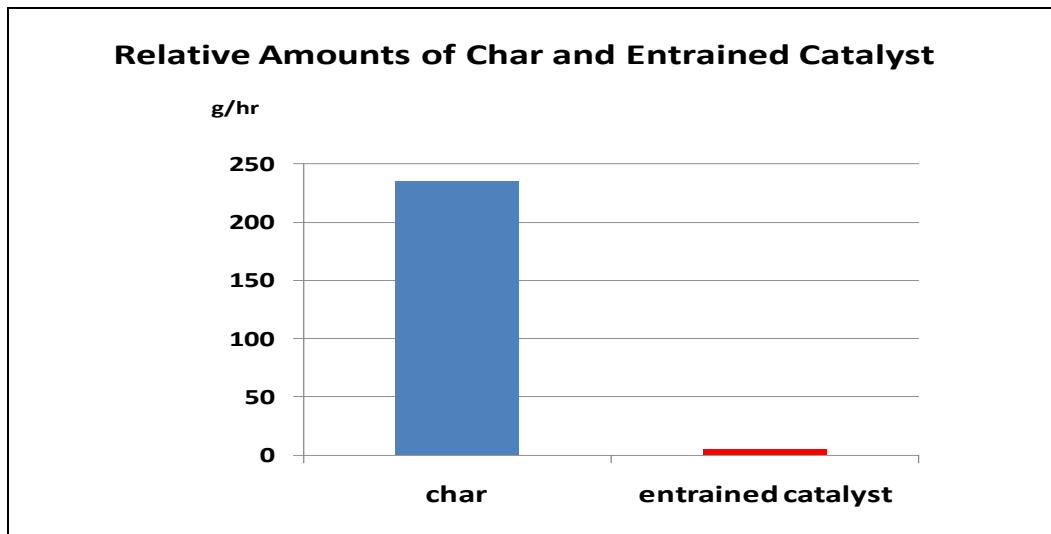


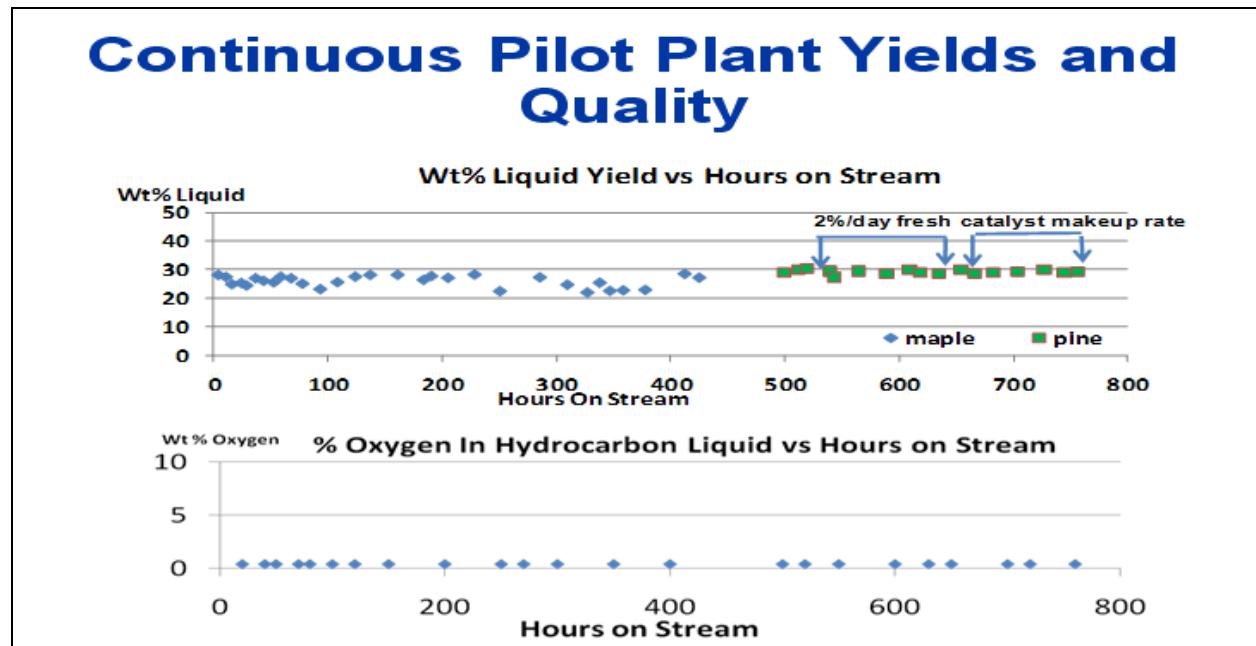
Figure 39- Hydropyrolysis Actual WHSV/Design WHSV vs. Hours on Stream

Another problem which occurred was that catalyst entrainment, although small, was more than anticipated. Relative amounts of char and entrained catalyst is shown in Figure 40.



*Figure 40- Relative amounts of Char and Entrained catalyst*

Screening of the char showed that the catalyst could be removed from the char simply by screening since the catalyst was 101 to 170% of the size of the char in size. Therefore in order to demonstrate the catalyst stability and expected replacement rate, the char was screened to recover the catalyst and this used catalyst was used to make up the excess catalyst lost to entrainment. Using this approach, a 2%/day fresh catalyst makeup rate was successfully demonstrated during the pine test as shown in Figure 41.



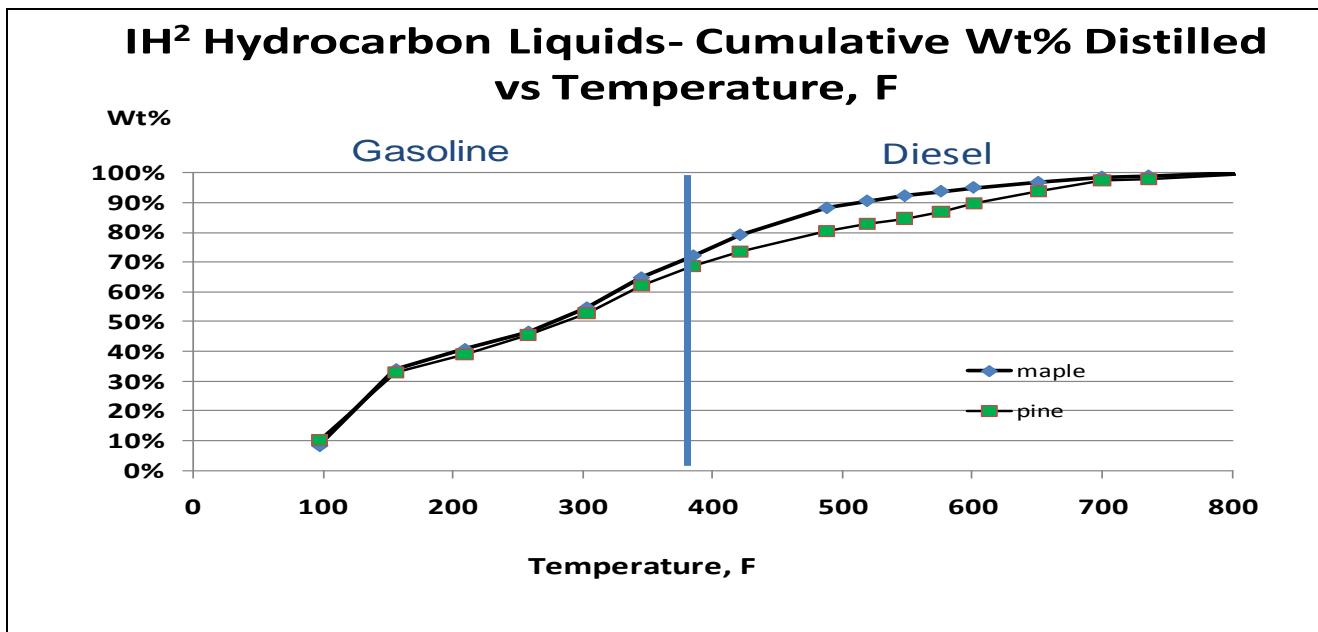
*Figure 41-Yield and quality showing demonstration of 2%/day catalyst makeup rate*

## Detailed Liquid Product Analysis/ Cost of Transportation Fuels

Detailed liquid analysis was conducted to compare the IH<sup>2</sup> products with typical petroleum hydrocarbon products and value the liquid products.

The average boiling point distribution of total hydrocarbons from maple and pine is shown in Figure 42. All the hydrocarbon product is gasoline or diesel boiling range material. Pine and maple produce very similar liquid products. Roughly 65-70% of the product is gasoline and the rest is diesel.

Figure 42- Total Hydrocarbon Liquid Product from IH<sup>2</sup>



Average elemental analysis of the hydrocarbon liquids produced from IH<sup>2</sup> testing of maple and pine is shown in Table 11. The wt% oxygen was less than the detectable limit of our direct oxygen analysis equipment which is 0.4 wt%.

Table 11-Average Elemental Analysis of IH<sup>2</sup> Total Hydrocarbon Liquids

	Total hydrocarbon product from Maple	Total Hydrocarbon Product from Pine
%C	89.05	89.16
%H	10.90	11.13
%N	<.1	<.1
%S	<.1	<.1
%O	<.4	<.4
H/C	1.47	1.50
Density,g/ml	0.802	0.811
TAN	<0.05	<0.05

In order to compare the IH<sup>2</sup> products to typical gasoline and diesel, the hydrocarbon products were distilled into cuts as shown in Table 12.

**Table 12-Wt% of IH<sup>2</sup> Fractions from Maple and Pine**

	<b>Maple, Wt%</b>	<b>Pine, Wt%</b>
Gasoline IBP-390F	72.2	
Gasoline IBP-430F		74.8
Jet 390-535	19.5	
Jet 430-535F		16.8
Heavy Diesel 535-700F	8.3	8.4
Total Diesel 390-700F	27.8	25.2

In Table 13 the analysis of the gasoline cut from IH<sup>2</sup> liquid is compared to typical fossil fuel derived gasoline. The IH<sup>2</sup> gasoline cut has excellent product quality with high octane and low sulfur.

**Table 13-Analysis of Gasoline Cut of IH<sup>2</sup> Liquid compared to Typical Fossil Gasoline**

<b>Component</b>	<b>Gasoline from maple (IBP-390F)</b>	<b>Gasoline from pine (IBP- 430F)</b>	<b>Gasoline from fossil (IBP-390F) No ethanol</b>
Wt% Carbon	87.86	87.15	86.07
Wt% Hydrogen	12.14	12.92	13.08
Wt % Oxygen	<.04	<.04	0
Wt ppm Sulfur	61	12	<30 (spec)
Wt ppm Nitrogen	<1	76	
RON (calc)	88.3	86.4	84.7
Bromine Number	0	8.3	9.4
H/C molar ratio	1.66	1.78	1.83
Benzene		0.87	1.0(max)
Density g/ml	.761	.790	.77(max)
Chloride ppm	<5	<0.3	-

The hydrocarbon liquids from pine appeared to be very close to drop in gasoline and meets the sulfur and the benzene specifications but should have been cut at 390F, like the maple, instead of 430F so that it would meet the density specification. It is believed that the slight differences between the maple and pine gasoline sulfur is not the result of the feedstock difference but rather the result of the fact that the 2nd stage for the pine was run at 20F higher temperature for the specific purpose of reducing sulfur.

Comparison of the distillation of the gasoline cut of typical petroleum and IH<sup>2</sup> gasoline is shown in Figure 43. IH<sup>2</sup> gasoline has a continuous boiling point distribution similar to petroleum gasoline and meets all gasoline boiling point specifications. As shown in Figure 44, IH<sup>2</sup> gasoline contains the same types of components as petroleum gasoline but has fewer olefins and more naphthenes.

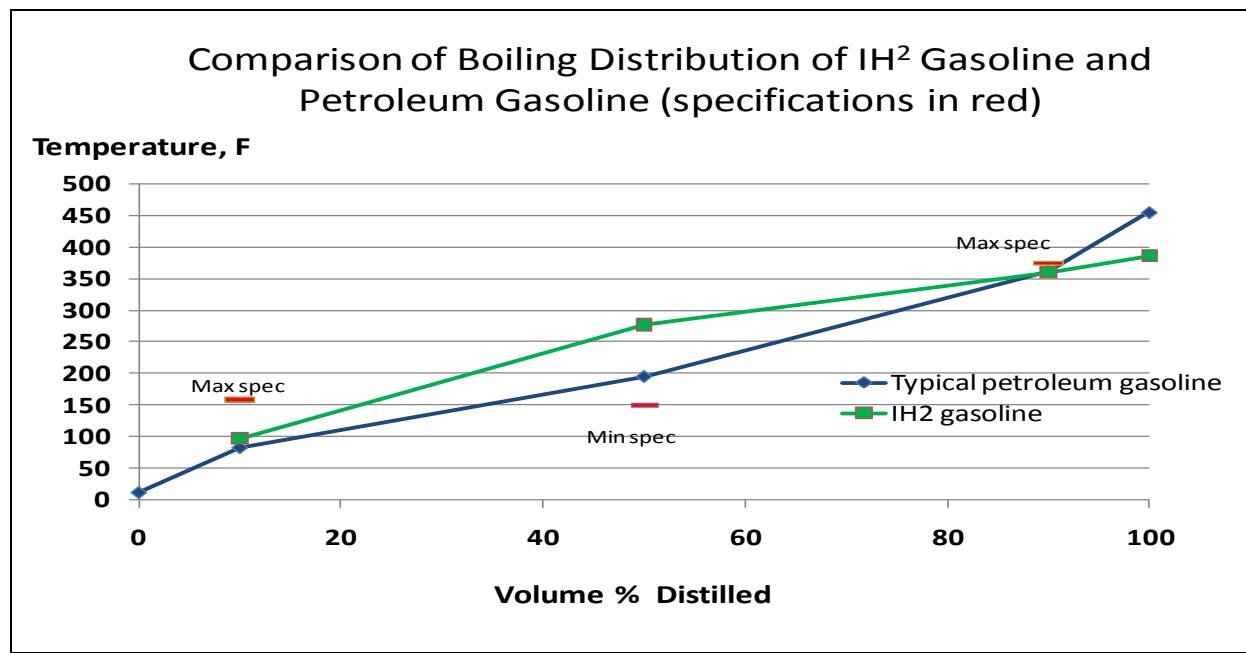


Figure 43- Comparison of the Boiling Point distribution of IH<sup>2</sup> Gasoline from wood with typical Petroleum derived Gasoline

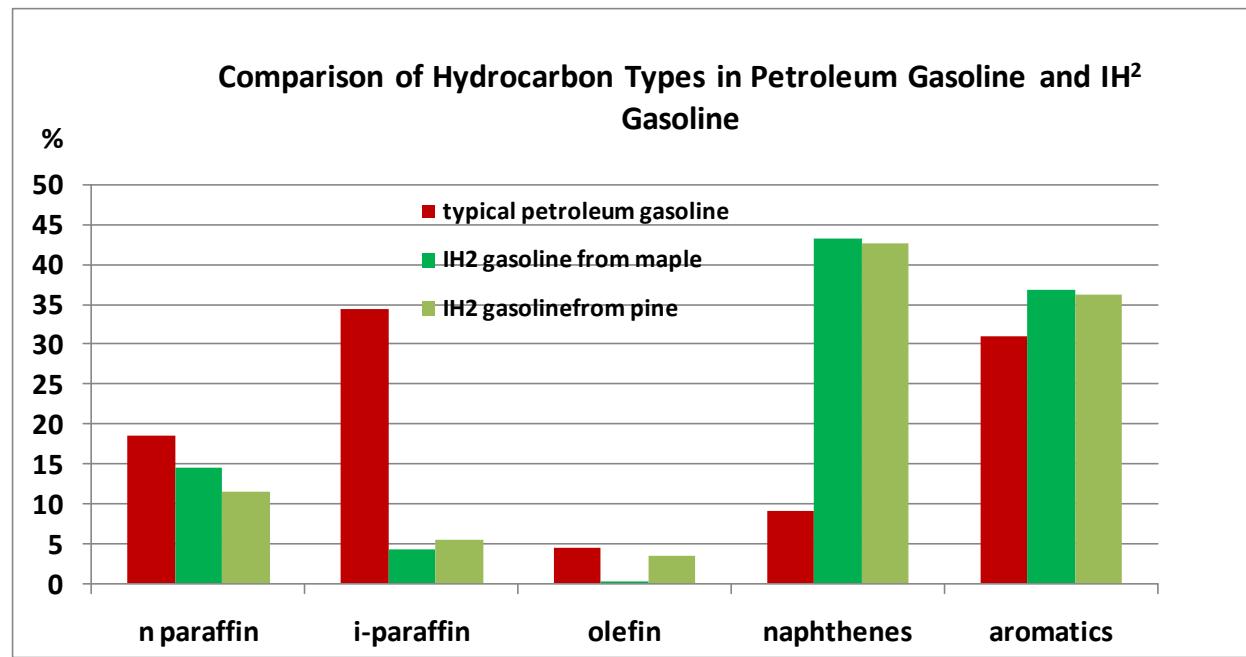


Figure 44- Comparison of Hydrocarbon Types for Typical Petroleum Gasoline and IH<sup>2</sup> Gasoline derived from wood

Additional specification comparisons for the IH<sup>2</sup> gasoline from wood to ASTM D4814-10b are shown in Table 14. The IH<sup>2</sup> gasoline from wood meets all the specifications except copper strip corrosion.

**Table 14- Comparison of IH<sup>2</sup>-50 Gasoline from Wood with ASTM D4814-10b Gasoline Specifications**

	Test method	ASTM D4814-10b specification	IH <sup>2</sup> gasoline from wood
Distillation T 10,C max	ASTM D86	70	51
Distillation T 50 C max	ASTM D86	121	89
Distillation T 90 C max	ASTM D86	190	173
Distillation FBP C max	ASTM D86	225	195
Distillation Residue, vol % max	ASTM D86	2	1
Oxidative stability(induction period ) min	ASTM D 525	240	960+
Copper strip corrosion, 3hr @50C merit class	ASTM D 130	1	<b>2A</b>
RVP at 37.8C(100F) kPa,max	ASTM D5191	103	67.4
Sulfur ppm, max	ASTM D 5453	80	40

Based on these analyses it is concluded that IH<sup>2</sup> gasoline is an excellent blending component for gasoline and is close to a R-100 drop in fuel if cut properly. Its value is 100% of that of wholesale gasoline which is essentially \$2.30-\$2.50/gal or \$810-880/ton. This includes no credits for being an advanced biofuel.

Analysis of IH<sup>2</sup> diesel from wood and algae is compared to petroleum derived diesel and petroleum derived light cycle oil (LCO) in Table 15.

**Table 15- IH<sup>2</sup> Diesel Properties compared to Petroleum Derived Diesel**

Component	IH <sup>2</sup> Diesel from maple (390-700)	IH <sup>2</sup> Diesel from pine (430-700F)	IH <sup>2</sup> Diesel from algae from earlier semi continuous testing (430F-700F)	Typical Diesel from fossil (400-700F)	Typical LCO from Fossil fuel (400-700F)
Wt% Carbon	89.75	89.81	86.11	86.1	87.93
Wt% Hydrogen	10.23	10.19	12.86	13.9	9.45
Wt % Oxygen	nil	nil	nil	nil-	Nil
Wt ppm Sulfur	30	20	46	15(max)	2.6
Wt ppm Nitrogen	170	202	9630		250
Density, g/ml	.936	.952	.851	.820-.845 typical	.960
Cetane Index(D-4737)	27	27	51	40(min)	24
H/C molar ratio	1.37	1.36	1.79	1.94	1.29
Aromatics	83wt%	nm	nm	35 vol%	82wt%
Chloride ppm	<.5ppm	<.5ppm	nm	nil	nil

IH<sup>2</sup> diesel is very close to meeting the diesel sulfur specification. The diesel sulfur specification for IH<sup>2</sup> diesel could likely be achieved by a slight increase in the pressure on the IH<sup>2</sup> pilot plant or a change in catalyst. However there is too much aromatics in the IH<sup>2</sup> diesel from wood and therefore too low a cetane number in IH<sup>2</sup> diesel from wood to meet the U.S. diesel cetane requirements. IH<sup>2</sup> diesel produced from algae in the small semi continuous bench unit is included in Table 15 for comparison as well, to show that the composition of the IH<sup>2</sup> diesel is highly dependent on the type of feed used. IH<sup>2</sup> diesel produced from algae has high cetane number and high H/C ratio.

However the IH<sup>2</sup> diesel compares favorably to petroleum derived light cycle oil (LCO) since IH<sup>2</sup> diesel has similar aromatics content but much less sulfur content than typical LCO. In some

petroleum refineries, LCO is upgraded by adding it to a hydrocracker. However in many petroleum refineries, LCO is simply blended into diesel, especially if the LCO meets the sulfur specification for diesel. This is possible because many US refineries are processing more light sweet crude, using oil produced from tight shale formations, which produces high cetane diesel product. This results in cetane give away in the U.S. which means that in the U.S. low sulfur LCO can be readily blended with diesel. In Europe, LCO is more difficult to blend away since they don't process as much light sweet crude and their diesel cetane requirement is 50 minimum.

Given this background, a conservative estimate for the value of IH<sup>2</sup> diesel is that it is \$2-4/bbl ( \$.05-.10/gal) less valuable than ULSD ( ultra low sulfur diesel) and has a similar value to LCO<sup>(6)</sup>. This puts IH<sup>2</sup> diesel value at \$2.2-2.45/gallon or \$615-\$685/ton. This valuation includes no renewable fuel credit.

The overall value of IH<sup>2</sup> combined liquids are therefore \$752-821/ton or \$2.30-\$2.51/gal. A \$1.0/ gal tax credit would increase IH<sup>2</sup> fuels product still further. The value of IH<sup>2</sup> fuel is summarized in Table 16.

**Table 16- Value of IH<sup>2</sup> Gasoline and Diesel Blending Components-( not including tax credit)**

	Value of petroleum derived Gasoline	Value of IH <sup>2</sup> gasoline	Value of petroleum derived diesel	Value of petroleum derived LCO	Value of IH <sup>2</sup> Diesel Blending component	Value of Total IH <sup>2</sup> Hydrocarbon Liquids
\$/gal	2.30-2.50	2.30-2.50	2.30-2.50	2.20-2.45	2.20-2.45	2.30-2.51
\$/ton	810-880	810-880	723-786	615-685	615-685	752-821

Jet Fuel is a light subset of diesel fuel derived by cutting the diesel fuel at 535F. A comparison of jet fuel specification and IH<sup>2</sup> jet fuel from wood is shown in Table 17.

**Table 17-Comparison of IH<sup>2</sup> Jet Properties from Wood Feed with Jet Specifications in ASTM 1655-11b**

	Test method	ASTM D1655-11b specification	IH <sup>2</sup> jet from wood
Total acidity,mg KOH/g max	ASTM D 3242	0.1	0.029
Sulfur, wt%, max	ASTM D 2622	0.3	0.0022
Sulfur mercaptan wt% max	ASTM D3227	0.003	0.0016
Flash point, C min	ASTM D 56	38	82
Freeze point, C , max	ASTM D 2386	-40	-70
Viscosity at -20C,cst, max	ASTM D 445	8	7.9
Existent Gum,mg/100ml, max	ASTM D 381	7	4
Conductivity pS/m, min	ASTM D 2625	-47	80
Distillation T10, C , max	ASTM D 86	205	217
Distillation FBP, C , max	ASTM D 86	300	274
Total aromatics, vol%, max	ASTM D1319	25	92.2
Density,at 15C kg/m3, max	ASTM D4052	840	919
Net Heat combustion,MJ/kg, min	ASTM D3338	42.8	41.6
Smoke point mm,min	ASTM D1322	18	3.5
Naphthalenes,vol%,max	ASTM D1840	3	8.44
Copper Strip Corrosion,max	ASTM D 130	1	3A
Filter Pressure drop,mm Hg, max	ASTM D3241	25	75.7

The jet cut from IH<sup>2</sup> diesel from wood has too many aromatics to pass many of the jet point specifications related to aromatic content such as aromatics, smoke point, and net heat of combustion. However the IH<sup>2</sup> jet from wood could be a blending component for Fischer Tropsh produced jet fuels which don't have enough aromatics or further upgraded in a refinery based diesel hydrotreater.

The IH<sup>2</sup> heavy diesel cut from wood boiling between 535-700F was also analyzed and compared to ASTM D-975-11. The heavy diesel cut passed most of the specifications except those related to aromaticity and cetane. The viscosity spec for the IH<sup>2</sup> diesel could be met by adjusting the cut point, to include more low boiling material. The cetane number or maximum aromatic specification could be met by refinery diesel hydrotreating to provide aromatic saturation.

**Table 18- Heavy Diesel Cut (535-700F) Comparison to Diesel Specifications**

	Test method	No 2 – D S15 specification	IH <sup>2</sup> heavy diesel from wood
Sulfur ,ppm max	ASTM D 5453	15	9
Distillation, T90 max	ASTM D 86	338	341
Flash Point, C min	ASTM D 93	52	156
Carbon residue ,wt% max	ASTM D 524	0.35	0.25
Water and sediment, vol % max	ASTM D2709	0.05	<0.005
Ash wt% max	ASTM D482	0.01	<0.001
Lubricity@ 60C, micron max	ASTM D6079	520	330
Copper strip corrosion, 3 hr @ 50C max	ASTM D130	No3	1A
Cetane Index, min	ASTM D976	40	<b>25</b>
Viscosity @ 40C, cSt, max	ASTM D 445	4.1	<b>7.6</b>

It should be noted that based on earlier small scale semi- continuous testing IH<sup>2</sup> liquids produced from algae, would meet cetane and aromatic specifications.

## Corrosion Testing

The IH<sup>2</sup> pilot plant is constructed primarily of 316 stainless steel. The final IH<sup>2</sup> product has low TAN and therefore minimal corrosion is expected. Although intermediate stages have higher acid number, there is no intermediate condensation of products between hydropyrolysis and hydroconversion stages in IH<sup>2</sup> which is beneficial for metallurgy and catalyst. However all biomass contains some chloride which can lead to chloride stress corrosion cracking. According to the literature, chloride stress corrosion cracking is particularly a problem where water is condensed.

In order to determine if any corrosion has occurred in our IH<sup>2</sup> pilot plant, Mistras<sup>(7)</sup> was contracted to visually inspect key areas in the IH<sup>2</sup> pilot plant after more than 750 hours on stream. Mistras has over 40 years in corrosion inspection experience in oil refineries and skilled corrosion inspectors who take pictures and visually inspect equipment. Mistras inspected

- 1 The hydropyrolysis reactor
- 2 The hydroconversion reactor
- 3 The product recovery heat exchanger inlet
- 4 The product recovery tank

Forty three pictures of the inside of the equipment were taken and studied by Mistras corrosion experts. No signs of corrosion were noted on the hydropyrolysis reactor, the hydroconversion reactor, or the product recovery heat exchanger. The product recovery tank showed very minor corrosion on one weld. No signs of chloride stress corrosion cracking were found in any location. Typical corrosion inspection pictures taken by Mistras are shown in Figure 45-Figure 48.



Figure 45- Mistras Picture of Inside of Hydropyrolysis Reactor



Figure 46- Mistras picture of Inside of Hydroconversion Reactor



Figure 47- Mistras Picture of inlet to Heat Exchanger



*Figure 48-Mistras picture of pipe weld area near inlet/outlet tee on top of product Collection vessel showing minor pitting at weld*

## Future Operational Improvements

One section which was not successfully automated was the 2 hot filters. The hot filters were designed to be switched back and forth, blown back, automatically dumped and then be placed back on line. Instead it was found that the blow back system was improperly designed and never correctly cleared the filter candles, ultimately required periodically depressuring the offline filter section and manually scraping the filter candles to remove fines before the filter could be brought back on-line. This problem added unwanted complexity to the operation.

The filter operation was directly affected by the efficiency of the cyclone. The variability in the cyclone efficiency, shown in Figure 49, was believed to be primarily due to problems associated with putting a stirrer down the exit of the cyclone which could periodically clog or back up. The pine had high fines in the feed which may have contributed to the problem as well. An improved design of the cyclone should improve the filter operation by reducing the load from the filter and will be implemented during the next turnaround.

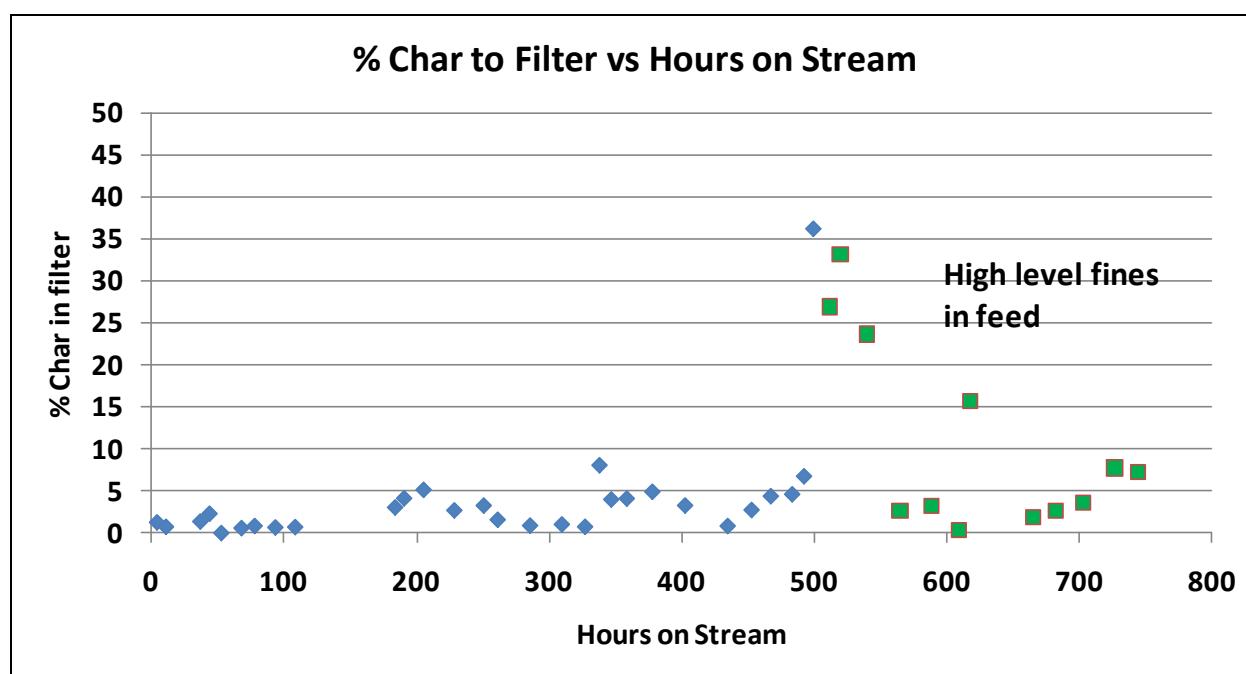


Figure 49- % Char to Filter vs. Hours on Stream

A planned pilot plant improvement is to add an additional cyclone to the pilot plant and upgrade the efficiency of the cyclones to reduce the load from the filters. This should make them last longer before maintenance is required. Additionally we expect to test the use of particle traps instead of filters which should greatly improve operability if successful. If the filter is required, an improved blowback system and automated char removal system for the filter section will be designed and implemented.

Another operability problem which occurred was excessive entrainment of the catalyst with the char. This was the result of inadequate hydrolysis reactor design. The IH<sup>2</sup> reactor in the 50kg/day pilot plant is a straight pipe. Typically a disengagement zone in a fluidized bed reactor is used to reduce entrainment. It is anticipated that adding a properly designed disengagement zone will reduce catalyst entrainment. Cold flow modeling using a Plexiglas system will be used to verify the new reactor design.

## Future Work

More continuous testing with wood, cornstover, and lemma feeds is recommended to provide additional information on catalyst life and stability using a variety of feedstocks. Additional testing is also needed to more closely study the first hydrolysis stage alone and obtain a better understanding of the effect of process variables in hydrolysis. The hydrolysis step is the key step in the IH<sup>2</sup> process and is also the most complex since the biomass must devolatilize and be deoxygenated while the char is continuously separated from the catalyst. Modeling this step to assist in reactor design is a key to successful scale up of the process.

Further R&D work to gather information on the effect of particle sizes is also needed. All the results reported here were for biomass feeds of less than 500 micron. Small scale batch testing in the mini bench IH<sup>2</sup> proof of principle unit indicated that the biomass particle size will have no significant effect on yields or product quality for particle sizes smaller than 3.3mm. But this batch test was conducted at long char residence times where the catalyst is not continuously separated from the char as is needed in a commercial plant. Large 3.3 mm particle sizes must be tested in the continuous IH<sup>2</sup> pilot plant where catalyst and char are continually separated to determine if residence time requirements in the hydrolysis 1<sup>st</sup> stage are effected by particle size.

It should be noted that the IH<sup>2</sup> process has not been optimized and significant improvements would likely result from additional R&D.

The construction of a demonstration unit in the scale of 1-10 ton/day size is recommended to provide further confidence and reduce risk for scale up to full commercial size.

## Conclusions

Gas Technology Institute has developed a new breakthrough catalytic technology, IH<sup>2</sup>, for thermochemically converting biomass directly into gasoline, and diesel fuels and/or high quality blend stocks. Initial testing has demonstrated and validated the conceptual and technical basis of this process. Larger scale 50 kg/day continuous testing has shown the operability and practicality of the IH<sup>2</sup> process over a 750+ hour test campaign. The construction and testing of a demonstration scale IH<sup>2</sup> unit of 1-10 ton per day is recommended to demonstrate the IH<sup>2</sup> process scale up and speed commercialization.

The IH<sup>2</sup> process has excellent LCA and technoeconomics. The LCA, for wood and agricultural residues, previously completed by MTU, had shown that hydrocarbon fuel products from the IH<sup>2</sup> process reduce GHGs by greater than 90% compared to the comparable fossil fuels. The technoeconomic analysis, previously completed by NREL show the low capital cost for the IH<sup>2</sup> technology and the capability to make gasoline and diesel at less than \$2.00/gallon using the IH<sup>2</sup> process.

The IH<sup>2</sup> technology, when fully commercialized, will be a game-changing technology, by reducing U.S. dependence on foreign crude, reducing greenhouse gas emissions, creating U.S. jobs and producing high quality and low-priced transportation fuels from U.S. grown biomass resources.

## References

- (1) Ringer,M., Putsche V., Scahill,J., “Large Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis”, NREL Technical Report Nov. 2006, p6
- (2) Marker, T., Roberts, M., Linck, M., Felix,L., Ortiz-Toral, P., Wangerow J., Final DOE Technical Report DOE DE-EE0002873 “Biomass to Gasoline and Diesel using Integrated Hydropyrolysis plus Hydroconversion”, Dec 28,2012.
- (3) Marker, T., Felix, L., Linck, M., Roberts, M., Integrated Hydropyrolysis and Hydroconversion (IH<sup>2</sup>) 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, July 2012, Vol 31, Number 2.
- (4) Press Release “DynaMotive Announces Completion of Successful Industrial Tests on Char by Leading US Briquette Manufacturer; Long-Term Supply Agreement Planned”, December 10, 2001
- (5) Elliott D.C.,”Historical Developments in Hydroprocessing Bio-oils”, Energy and Fuels, 2007, p1805
- (6) Thakkar,V.P., Abdo, S. F., Gembicki,V.A., Mc Gehee, J.F., “LCO Upgrading A Novel Approach for Greater Value Added and Improved Returns”, Petroleum Technology Quarterly v10(4): 41-49, 2005
- (7) <http://www.mistrasgroup.com/services/applications/refinery.aspx>