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Hydrothermal Liquefaction of Agricultural and Biorefinery Residues

Final Report – CRADA #PNNL/277

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The authors acknowledge the contribution of E. L. Powers for the identification and quantification of compounds in aqueous fractions by GC-MS.

Summary

This project was performed as a Cooperative Research and Development Agreement (CRADA) with the participants: Archer-Daniels-Midland Company (ADM), ConocoPhillips (COP), and Pacific Northwest National Laboratory (PNNL). Funding from the federal government was provided by the Office of the Biomass Program within the Energy Efficiency and Renewable Energy assistant secretariat as part of the Thermochemical Conversion Platform. The three-year project was initiated in August 2007 with formal signing of the CRADA (#PNNL/277) in March 3, 2008 with subsequent amendments approved in November of 2008 and August of 2009.

This report describes the results of the work performed by PNNL and the CRADA partners ADM and ConocoPhillips. It is considered and is not available for public disclosure.

The work conducted during this project involved developing process technology at PNNL for hydrothermal liquefaction (HTL) of agricultural and biorefinery residues and catalytic hydrothermal gasification (CHG) of the aqueous byproduct from the liquefaction step. Related work performed by the partners included assessment of aqueous phase byproducts, hydroprocessing of the bio-oil product and process analysis and economic modeling of the technology.

As a part of this project three Battelle conceived three Subject Inventions and filed invention reports describing the new technology developed within the project:

Improvements to hydrothermal liquefaction	9/25/2009	16490-E
Mineral separation in hydrothermal liquefaction	10/12/2009	16525-E
Hydrothermal gasification with hydrothermal liquefaction	12/21/2009	16611-E

Task 1: Feedstock Effects

Initial tests in hydrothermal liquefaction (HTL) were performed in a micro-scale continuous-flow reactor at PNNL. The system required a clear or nearly clear feedstock because of the small orifices involved in the design. Appropriate model compounds and feedstocks were provided by ADM to PNNL for liquefaction tests.

- Model compounds were selected for the initial liquefaction tests.
- Pretreatment and fractionation of the feedstocks were evaluated by the ADM team.
- Micro-scale tests were undertaken in the existing continuous-flow reactor systems at PNNL.
- Feedstocks included agricultural and biorefinery residues and pretreated and fractionated versions thereof and were provided to PNNL by ADM.
- The incorporation of catalysts was tested at PNNL.

In parallel with the studies on feedstock effects, ADM and ConocoPhillips requested PNNL to make large samples of corn fiber and stover liquefaction oil using PNNL's current liquefaction technology. ConocoPhillips evaluated upgrading of this oil utilizing various standard refinery processes through lab scale tests.

Task 2: Process Optimization

Based on the experimental results in Task 1 and guided by the assessments in Task 5, bench-scale process optimization was undertaken at PNNL. The bench-scale tests also provided product oil in sufficient quantity for subsequent analysis and upgrading tests in Task 4.

- The bench-scale Continuous-flow Reactor System was used to optimize processing conditions for hydrothermal liquefaction, such as temperature, pressure, and residence time.
- The incorporation of alkali catalyst (sodium carbonate) was tested at PNNL

Task 3: Aqueous Product Assessment

- Detailed analysis of the aqueous phase determined composition and quantity of dissolved organic material as led by ADM with contribution from PNNL.
- Treatment or recovery of these potentially useful or valuable byproduct materials was a focus of the ADM team.
- Since the composition of the aqueous stream included only low levels of organic material, ConocoPhillips concluded that upgrading it to fuels was not reasonable.
- Following characterization of the stream, ConocoPhillips and ADM determined the best use of the stream would be as recycle to the hydrothermal liquefaction process, or hydrothermal gasification to methane which could then be used for combustion to generate high temperature steam for the process, or conversion to hydrogen to supply the hydrotreating process.
- PNNL performed bench-scale catalytic hydrothermal gasification tests to evaluate fuel gas production from the aqueous stream as a means of energy value recovery using this technology.

Task 4: Upgrading with Heteroatom Removal

Catalytic hydroprocessing of the hydrothermal liquefaction product oil was performed by Conoco-Phillips at the bench-scale. Mass balances around the process were determined and products recovered for detailed analysis for fuel applications.

- Hydroprocessing was utilized for upgrading the crude oil product.

-
- Targets for this processing included not only the oxygen heteroatoms, but also nitrogen, as well as sulfur.

ConocoPhillips sought to determine:

- Is the material suitable for directly blending into fuel?
- If not, what further treatments, including co-processing to make a material suitable for fuel in laboratory fixed bed test reactors are needed?

In addition, ConocoPhillips

- Evaluated catalytic cracking in laboratory screening reactors as an alternative upgrading option.
- Screened the fuel properties of the upgraded products.

Task 5: Techno-Economic Assessment

- Developed a baseline process model to allow techno-economic assessments.
- Utilized the model to identify the potential technical improvements that have the most significant impact on process economics.
- Permutations to the baseline model, such as the evaluation of the eliminations of catalyst and reducing gas in the liquefaction step were addressed.
- Using ADM's market information, an assessment of the scale of operation based on availability of feedstock was also undertaken. As experimental data was obtained, the model was updated throughout the life of the project.
- ConocoPhillips contributed the modeling of the upgrading portion to produce fuels.

Conclusions

Hydrothermal liquefaction can be applied to corn fiber, corn starch, or corn stover in water slurry to produce a bio-oil with 10-15% oxygen on a dry basis. Overall carbon basis yields for the several feedstocks ranged from 20% for starch, 50-55% for fiber and 30-35% for stover. The undesirable oxygen content of these HTL bio-oils is much lower than that achieved through fast pyrolysis of biomass, but at the expense of a lower bio-oil yield. The bio-oil can usually be gravity separated from the aqueous byproduct but the formation of a stable emulsion was seen during the processing of corn stover. It was thought that the mineral (ash) content of the feedstock caused this phenomenon therefore a mineral separation step prior to phase separation was developed. Only a small fraction of the biomass is converted to a gas byproduct (5-10% of the carbon) consisting mainly of carbon dioxide. The balance of the carbon is found in dissolved organics in the aqueous byproduct stream. Recycle of this aqueous stream as the solvent in the preparation of the feed slurry appears to facilitate the conversion of water soluble organics to bio-oil. Additionally, the aqueous byproduct stream can be processed via catalytic hydrothermal

gasification technology to produce fuel gas and a low biological oxygen demand (BOD) aqueous stream. The methane produced through gasification could be reformed into hydrogen and is sufficient to provide all the hydrogen required for upgrading the bio-oil to fuel.

The bio-oil product can be hydroprocessed in two stages to form hydrocarbons. Fractionation of the resulting product showed 14 wt% gasoline range, 58 wt% diesel range, and 28 wt% gas oil. The gasoline fraction had an octane value of 79 and could be used as a sub octane blending component. The diesel boiling range fraction had high aromatics content and would be suitable for distillate blending, solvent applications, or further processed via catalytic cracking. The gas oil fraction could be blended into fuel oil or further processed via catalytic cracking.

Based on the techno-economic analysis of the process the overall capital expense for a unit capable of processing 525,000 mt/year of biomass is approximately \$125 million. The annual operational expense is approximately \$72 million (including feedstock cost). Based on a yield of 42.5 gallons upgraded bio-oil per metric ton of corn stover, the minimum selling price of the bio-oil is \$4.11 per gallon (172.62/bbl). Because further refinery processing is required to incorporate the bio-oil into a final finished fuel, the bio-oil would have a refinery break-even value similar to light to medium gravity low sulfur crude oil or condensate. The current premiums for these grades of crude oil range from \$3-7 over NYMEX WTI. Thus the current price structure of the crude market does not support commercialization of this process at its current stage of development.

Currently both ADM and ConocoPhillips do not plan to conduct further research and development with this process. Significant barriers to commercialization of this technology are identified as follows:

- Low primary oil yield
- Energy consumption for grinding biomass into a slurry
- Process and product sensitivity to feedstock impurities.
- Hydrogen requirements for upgrading

Significant technical improvements addressing these barriers are needed before warranting additional evaluation of this technology.

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Introduction

The purpose of this project was to develop an understanding of hydrothermal liquefaction as applied to agricultural residue and co products produced in Archer-Daniels-Midland Company's (ADM) biorefinery operations. ADM, Pacific Northwest National Laboratory (PNNL), and ConocoPhillips Company (COP) coordinated bench-scale research efforts to generate process information to optimize the application and to allow scale-up of the technology.

Hydrothermal liquefaction of biomass with subsequent upgrading of the crude oil product provides an efficient pathway to liquid transportation fuels to displace imported petroleum. Hydrothermal processing utilizes water and/or organic solvent at medium temperatures (300–350°C) and sufficient pressure (15.9–20.7 MPa) to maintain the water in the liquid phase. The processing option is particularly applicable to wet biomass feedstocks, such as biorefinery residues.

Hydrothermal processing of biomass to liquid fuels requires expanded process development to take the technology to an industrial demonstration scale. Technical challenges associated with the technology include mixing, pressurization, transport, and pressure let down of high solid slurries, but also understanding the relationship between crude oil product properties and feedstock composition. Other challenges include optimization of the liquefaction process variables; demonstration of separation techniques; and demonstration of bio-oil upgrading processes in order to produce a product with marketable commercial value.

Feedstock Effects

Initial tests in hydrothermal liquefaction were performed in a micro-scale continuous-flow reactor at PNNL. The system required a clear or nearly clear feedstock because of the small orifices involved in the design. Appropriate model feedstocks were provided by ADM to PNNL for liquefaction tests. The results of these tests were provided in a separate report (PNNL-18644)¹.

Pretreatment and fractionation of the feedstocks was evaluated by the ADM team. A single sample of a hydrolyzed feedstock was provided to PNNL. Micro-scale processing was attempted in the continuous-flow reactor systems, which was modified for liquid product collection. The majority of the tests all ended with plugging of the feed lines in the preheating stage of unit. The high level of sulfuric acid in the product required neutralization prior to liquefaction which was accomplished by the addition of alkali. The plugging was due to alkali precipitation at the operating temperatures needed for hydrothermal liquefaction.

In parallel with the studies on feedstock effects, ADM and ConocoPhillips initially requested PNNL to make large samples of corn fiber and stover liquefaction oil using PNNL's bench-scale liquefaction reactor system. ConocoPhillips evaluated the upgrading of this oil through lab scale tests on hydrotreating and fluidized-bed catalytic cracking.

Micro-scale Process Results with Model Compounds

The process diagram for the micro-scale hydrothermal liquefaction test system is shown in **Figure 1**. A picture of the system is given in **Figure 2**. The processing system is constructed of 316 stainless steel and is designed to operate at the process conditions of up to 400°C and up to 20.7MPa.

The high-pressure metering syringe pumps from Isco were used to pump the feed solutions into the preheater/reactor component, pictured in **Figure 3**. The ¼" preheater tube operated in a downflow configuration and fed into the bottom of the ½" tubular reactor, which had an internal volume of 50 cc. Temperature was monitored by thermocouples in the feed line; shortly after the preheater, about 2 inches into the reactor; and toward the end of the reactor, about 2 inches from the outlet. The product effluent left the reactor, passed through a chiller and then drained into two liquid sample collection vessels (samplers). The samplers were operated at system pressure and were valved in and out of the process flow to alternately fill and empty them. Product gases (along with nitrogen used to prepressurize the liquid sample collection vessels) were vented from the top of the samplers through the back-pressure regulator (BPR) and measured by a wet test

¹ Elliott, DC; Rotness, LJ; Hart, TR; Neuenschwander, GG; Hydrothermal Liquefaction of Agricultural and Biorefinery Residues – Interim Report Micro-scale Tests with Model Feed stocks, PNNL, Richland Washington, August 2009, PNNL-18644.

meter (WTM). Gas samples were manually collected from the vent line and analyzed by gas chromatography.

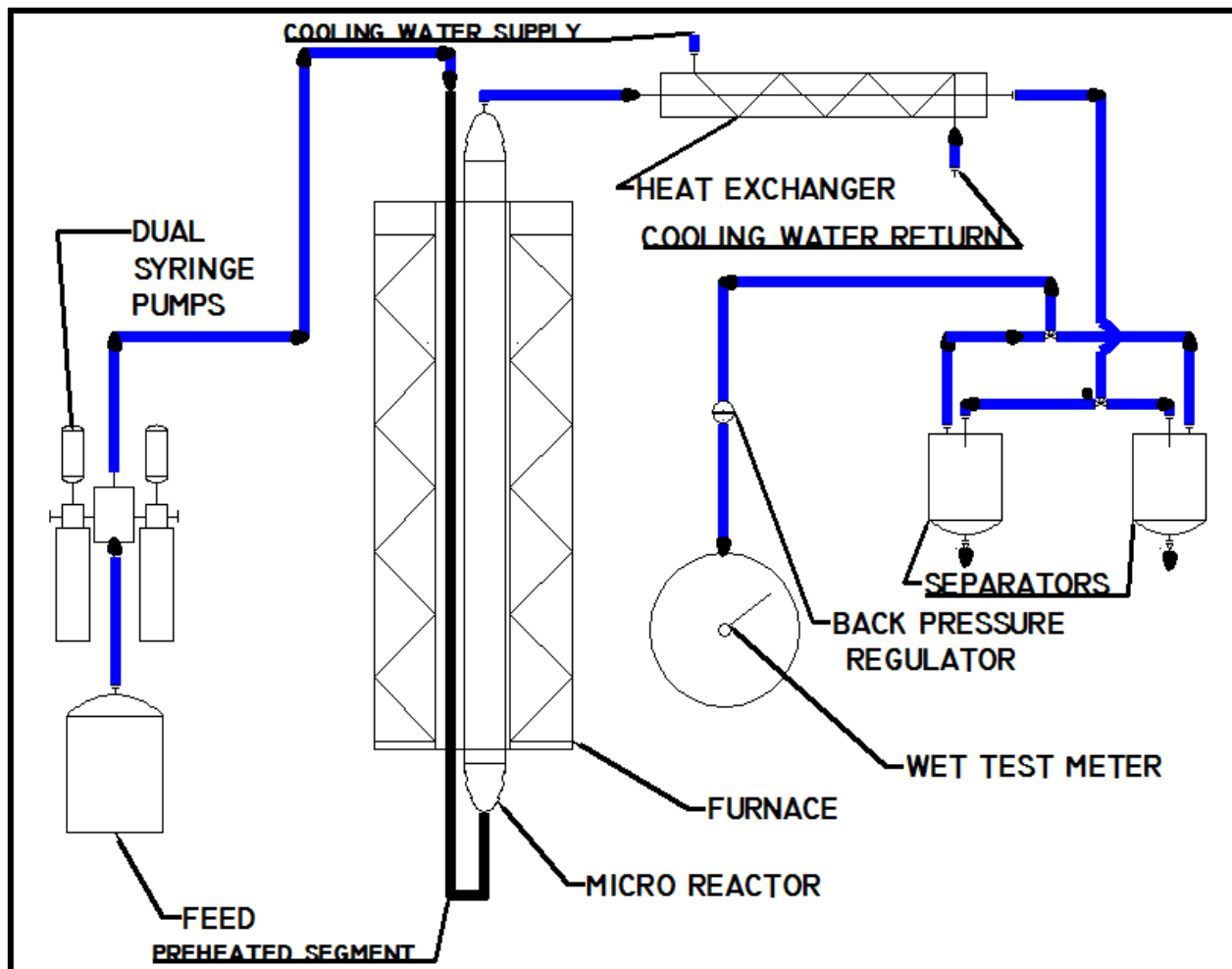


Figure 1. Process Flow Diagram of the Micro-Scale Hydrothermal Liquefaction System

In the process discussed in this report, the model feedstocks were reacted as water solutions to determine the yield of bio-oil product, which could be phase-separated from the aqueous byproduct. The bio-oil phase and the aqueous phase byproduct were recovered and separated by pouring and/or pipetting the low viscosity aqueous phase from the viscous bio-oil phase.

This microscale reactor had no internal agitation, such as a static mixer, but temperature management was viewed as adequate for the tests completed. Coking in the reactor was not found to be a major factor with these feedstocks. Other unsuccessful tests were attempted with a hydrolyzed corn fiber feedstock provided by ADM. This highly acidic material coked up immediately in the reactor and subsequent tests with neutralized (with sodium carbonate)

feedstock resulted in precipitation of solids in the preheating lines that plugged and stopped the flow.



Figure 2. Micro-scale Hydrothermal Liquefaction System



Figure 3. Preheater/Reactor

Table 1 summarizes the results of the micro-scale hydrothermal liquefaction process tests with model feedstocks. These results were all generated at 343-350°C and 20.4-21.2 MPa, with a 2.0 liter of solution per liter of reactor volume per hour liquid hourly space velocity (LHSV). All the feedstock solutions contained an added catalyst of 2 wt% Na_2CO_3 (on the total solution basis) to moderate the pH of the reactor system and maintain a near neutral processing environment. As a result, the feedstocks each had a pH of around 10, but the product aqueous phases had pH levels near 5 (7 in the isosorbide case).

Table 1. Process Results with Model Feedstocks

	dextrose	HFC syrup	sorbitol	isosorbide
Carbon conversion to oil, %	44.5*	50.9*	1.8	1.5
Carbon remaining in aqueous, %	31.6*	39.9*	59.7	70.8
Carbon conversion to gas, %	3.6*	0.5*	0.05	0.3
Carbon balance, %	89	69	62	73
Mass of recovered bio-oil, % of dry feed	20.2	15.5	0.8	0.9
Oxygen content in raw oil product, %	19.6	23.5	15.5	15.9
Oxygen content calculated to dry basis, %	13.7	15.6	7.7	10.5
pH of aqueous	4.84	4.80	5.16	6.79
Carbon content of aqueous, %	3.63	2.79	12.44	16.62
Carbon content of feed, %	12.40	8.94	14.44	17.32

* for the glucose and HFC tests, the carbon balance was normalized to 100%, while including estimated char deposit in reactor (not shown in table)

These results showed a substantial bio-oil yield for the sugar feedstocks with very little bio-oil produced from the hydrogenated sugar (sorbitol) or the dehydrated sorbitol product, isosorbide. Gas yields were low in all cases. The bio-oil product was highly oxygenated (15-24 wt% oxygen, as recovered) in all cases. However, the raw bio-oil has a significant water content which contributes to the measured oxygen. On a dry basis, the bio-oil oxygen was much lower (8-16 wt% oxygen, dry basis). In the two cases where little bio-oil was produced; most of the carbon remained dissolved in the aqueous phase.

Liquid Chromatography analysis was used to further clarify the extent of reaction of the model feedstocks. **Figure 4, Figure 5, and Figure 6** compare the feedstock with the products of the several feedstocks. The dextrose was converted in the hydrothermal processing and the remaining dissolved organics were a collection of oxygenates with acetic and glycolic acid being the most prominent (phenolics were not determined in this analysis). Essentially the same product slate was seen with the high-fructose corn (HFC) syrup. The sorbitol was converted to a significant degree into what are believed to be dehydrated sugar alcohols, sorbitans, idatan and mannitan, (misidentified as C5 sugar alcohols and lactic acid in Figure 5) with a notable yield of isosorbide also forming. Isosorbide was essentially unchanged by processing at these conditions with a small yield by hydration to sorbitol.

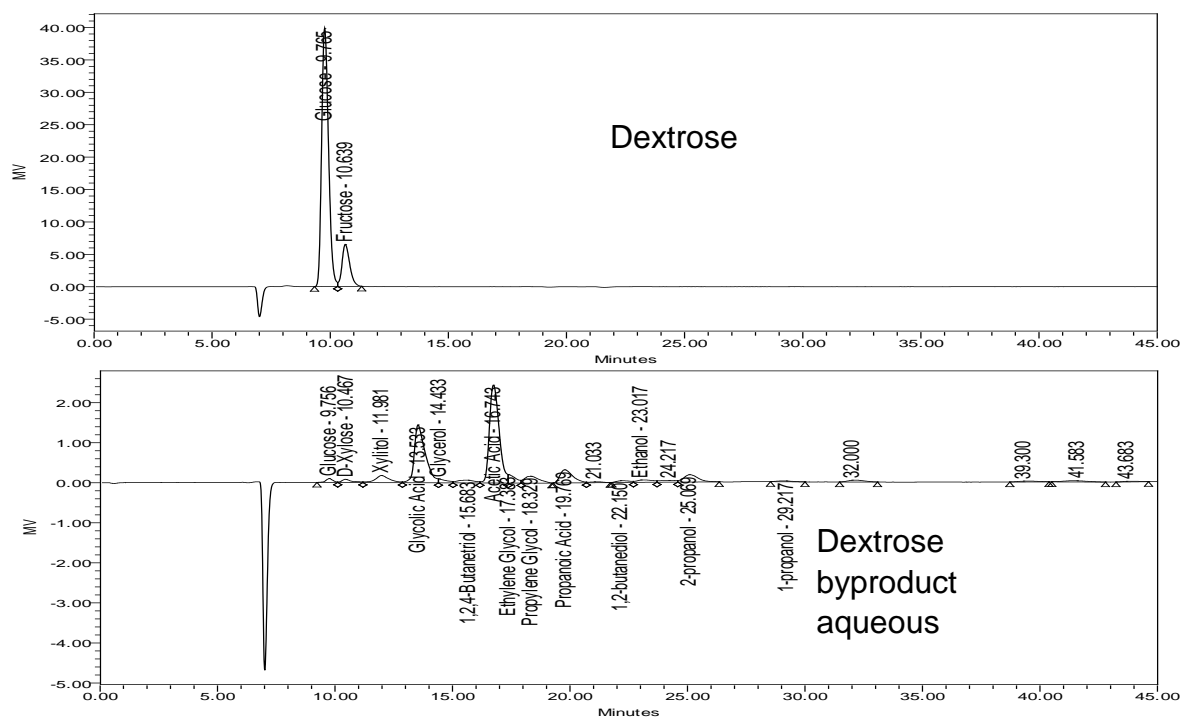


Figure 4. Liquid Chromatography of Dextrose Feedstock and Products

Subsequent tests were attempted with a biomass hydrolysate feedstock produced by ADM. The feedstock, as received, was an ultra-filtered (to remove protein), cation exchanged (to remove residual amino acids) hydrolysate produced from corn fiber. The material was determined to have a pH of 0.01. Sufficient sodium hydroxide was added to neutralize the feedstock (to a pH of 7.7) before it was processed. The sulfate content was measured by ion chromatography and found to be far outside the instrument's calibration range, of 2000 ppm, and perhaps as high as several weight percent.

These process tests were all ended prematurely with plugging in the preheater tube. Precipitation of sodium sulfate was suspected to be the cause. The small amount of bio-oil collected appeared to have a similar composition to the other bio-oils produced in this project, but no material balance or yield calculation could be obtained from the shortened runs. The aqueous byproduct carried 3.3% dissolved carbon and had a pH of 4.4. In one test, a small batch anion exchange attempt was made which raised the feedstock pH to 3.9. NaOH was then used to raise the starting pH to 7.3; however processing this feed gave the same result of a plugged preheater.

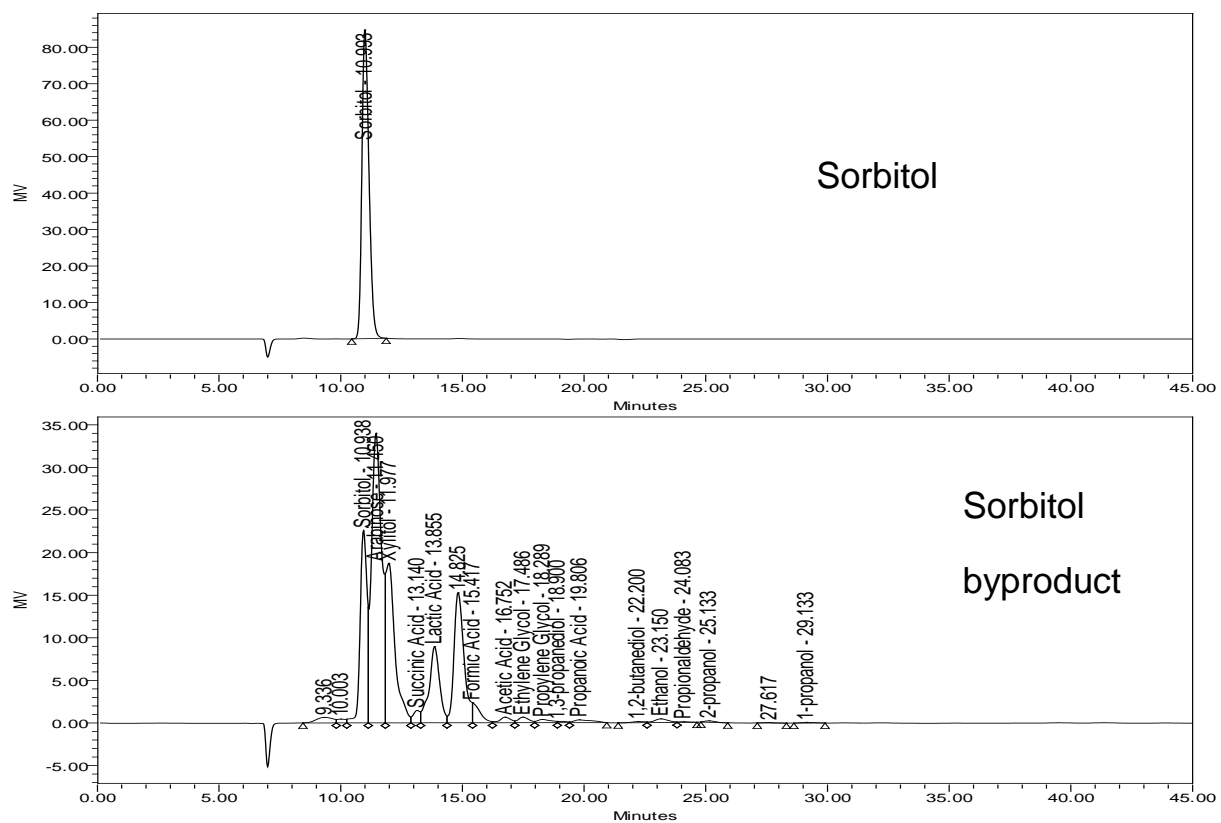


Figure 5. Liquid Chromatography of Sorbitol Feedstock and Products

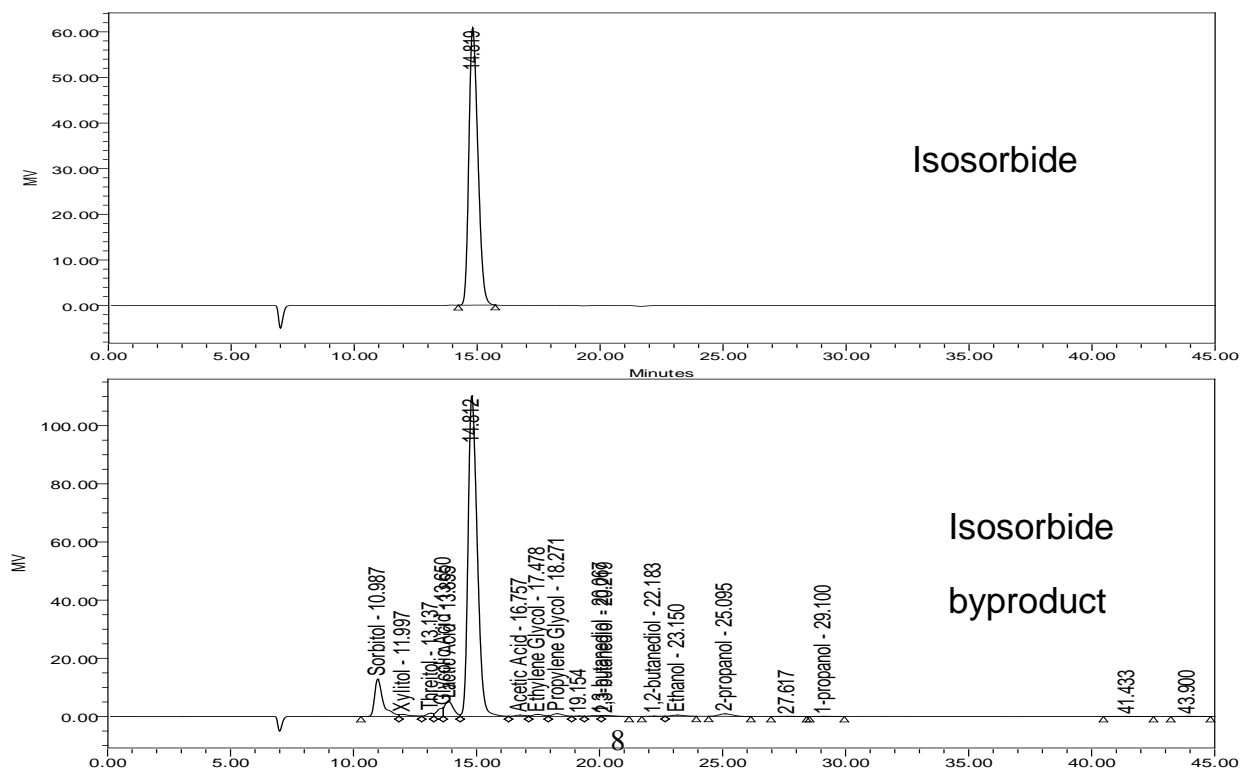


Figure 6. Liquid Chromatography of Isosorbide Feedstock and Products

These micro-scale hydrothermal liquefaction tests with model feedstocks demonstrated the principle of bio-oil formation from sugars in a pH moderated reaction system. At a temperature of 350°C and 21 MPa (pressure sufficient to maintain liquid water in the reactor system), solutions of dextrose and high-fructose corn syrup were reacted to produce a water immiscible bio-oil phase in a carbon yield of 45-50%. Minimal gas formation accompanied the reaction. A significant portion of the sugar feedstock remained dissolved in the byproduct aqueous phase. In these tests, conducted at around 30% dry solids solution, the residual yield of carbon to the aqueous phase was about 30-40%. Some coke development on the reactor wall was also seen. The processing rate was a LHSV of 2.0, which equates to a residence time of about 19 minutes based on the water density of 0.63 g/mL at the reaction conditions.

Non-sugar feedstocks did not form, to any significant degree (<2%), a separable bio-oil product. Sorbitol (a C6 sugar alcohol) was dehydrated to C6 sugar alcohol anhydrides and, isosorbide (the dianhydride). Isosorbide was almost unreactive, producing only a small yield of sorbitol, as evidenced by the HPLC result.

Process Optimization

Bench-scale process optimization was undertaken at PNNL. The bench-scale tests also provided product oil in sufficient quantity for subsequent analysis and upgrading tests in Task 4.

The bench-scale Continuous-flow Reactor System (CRS) was used to optimize processing conditions for hydrothermal liquefaction, such as temperature, pressure, and residence time.

The incorporation of alkali catalyst (sodium carbonate) was tested at PNNL

Reactor System Design

The CRS was composed of five major functional subsystems: feed pretreatment and preparation, pumping, preheater/reactor, reaction products separation, and instrumentation and control. The system was based on a throughput of 0.5-10 lb of slurry or solution per hour and was typically operated over a range of 1 to 3 liter/hour. The process flow diagram (without the pretreatment section) as initially configured is shown in **Figure 7**.

The CRS is designed for obtaining engineering data for continuous flow hydrothermal liquefaction process. The system consists of the high-pressure pump feeding system, product recovery system, data acquisition and control system, furnaces, and other equipment required to utilize the 1-liter Carberry stirred tank reactor (MAWP 6500 psi @ 800°F) and the 1-liter tubular reactor. The tubular reactor (MAWP 10,000 psi @ 72°F or approximately 7500 psi @ 400°C) can be run as a stand-alone unit or may utilize the Carberry as a stirred tank pre-heater. The CRS can be run with the removal of either of the two primary pressure vessels. The feed line, operated at ambient temperature, is ½" 316 SS tubing with 0.049" wall. All process lines at temperature of 200°C or above are ¼" 316 SS tubing with 0.065" wall). The product collection is done via two 1-liter Parr vessels.

The CRS feed system is a dual-barrel continuous-flow Isco syringe pump. After the pumps, the feed can be heated in the 1-liter stirred Carberry reactor. The feed continues to the 1-liter tubular reactor for the final process step, and then it is alternately sent to one of two PARR vessels to collect the liquids at pressure. The liquids collect in the temperature-controlled PARR vessels and gases are vented via a dome-loaded back-pressure regulator (BPR). The off gas is cooled by another chilled heat exchanger to further remove any entrained water, the liquid is accumulated in a weighed tank, and the off-gas is measured by a wet test meter and analyzed manually by a gas chromatograph. Pressure transducers on each vessel record pressures and note pressure drops due to restriction and plugging. Each vessel and most transfer lines are also monitored for temperature. Three rupture discs protect the system. A data acquisition/control system heats the furnaces and records the process parameters and offers off-normal warnings and auto-shut down.

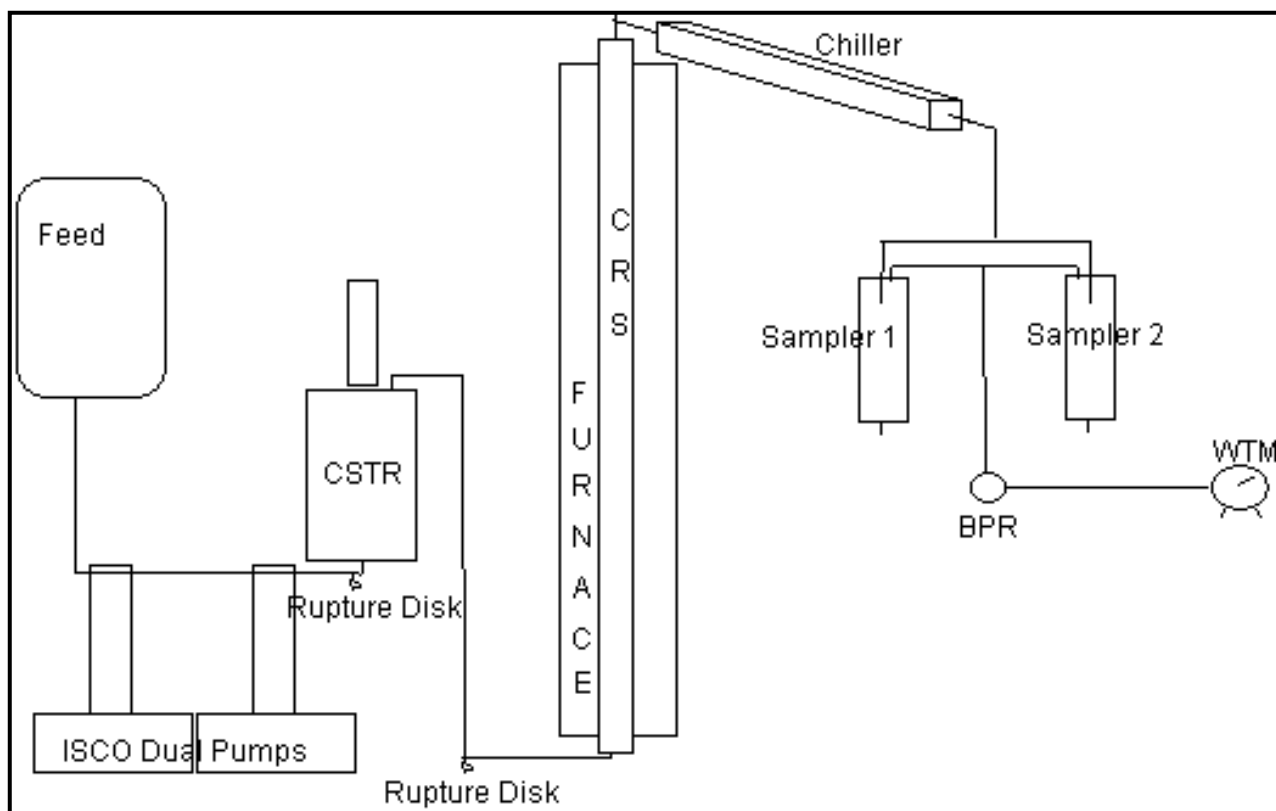


Figure 7. Initial Process Flow Schematic of the Bench-Scale Continuous-Flow Reactor System (CRS)

Feed Pretreatment and Preparation

The feedstock pretreatment and preparation method was designed to ensure a relatively homogeneous feed for the reactor. The feedstocks typically required a wet milling step in a Union Process Attrition Mill.

Pumping

The pumping subsystem was designed to operate at feed pressures up to 6000 psig and flow rates between 0.2 and 4.0 liter/hour. This system consists of a modified Isco 500D pump. The modification was the addition of a larger bore valve package in the unit that controls the feeding from one cylinder or the other. The valve package purchased consisted of four 3/8-inch air-actuated (6000 psi rated) ball valves with 3/8-inch stainless steel (SS) tubing connections installed on the Isco dual pump package. The valves and tubing were configured to fill and empty the pumps based on controller commands. We also installed oversize caps on the barrels that accommodate 3/8-inch NPT fittings. The large bore head, valve, and tubing allowed us to suction and pump the viscous slurries while still allowing the pump to operate at 3500 psi max. System piping included 0.5-inch (0.065-wall) 304 SS tubing on the outlet of the pump. Pump

inlet piping was 0.5-inch (0.035 wall) 304 SS tubing. All valves and valve trim (except the pressure-control valve) were also made of SS. Using the Isco pump, the feeding rates were measured directly by the screw drive of the positive displacement syringe pump.

Pre-Heater/Reactor

As initially tested, the preheater was a 1-liter 316 SS vessel equipped with a Carberry-type rotating basket. The preheater functioned as a continuous-flow, stirred-tank reactor (CSTR) in which the feedstock was brought to the reaction temperature.

The original reactor was a 1-inch ID X 72-inch-long 304 SS tube. The vessel had a maximum allowable working pressure of 10,000 psig at 22°C, which was derated to 5200 psig at 450°C. The vessel had bolted-closure endcaps with metal o-rings on each end. The reactor furnace was a 6-kWe resistance heater split into three separately controllable zones. The pressure was controlled with a dome-loaded diaphragm back-pressure regulator.

From our work in hydrothermal gasification we had previously learned to use an in-line system to separate precipitated solids, primarily mineral content². In the process of heat up, the organics in the biomass were pyrolyzed and liquefied while certain inorganic components, such as calcium phosphates, formed and precipitated as solids. We placed a vessel in the process line following the preheater to capture and remove the solids following heat-up to reaction temperature. The design of the separator was a simple dip leg vessel wherein the solids fell to the bottom of a vessel and the liquids passed overhead through a filter to the reactor. The solids could be removed by batch from the bottom of the vessel as they built up over time.

In later tests of hydrothermal liquefaction, we bypassed the tubular reactor and used only the CSTR as the combined preheater and reactor in line with the solids separation vessel. We included the solids removal vessel in order that the oil/water separation was more easily attained as prior experience had demonstrated. This configuration of the reactor system is depicted in **Figure 8**.

Reaction Products Separation

The liquid product collection was done via two 1-liter Parr vessels. The process effluent from the reactor was alternately sent to one of the two PARR vessels to collect the liquids at system pressure. The liquids collected in the temperature-controlled PARR vessels and gases were vented via a dome-loaded back-pressure regulator (BPR). At predetermined times the flow was

² Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G. 2008. "Catalytic Hydrothermal Gasification of Biomass for the Production of Hydrogen-Containing Feedstock (Methane)" 2nd Symposium on Hydrogen from Renewable Sources and Refinery Applications, **Prep. Pap.-Am. Chem. Soc., Div. Pet. Chem.** 53 (1), 73-74.

redirected to the second Parr vessel by process line valving so that the first vessel could be emptied while the second was filling.

Instrumentation and Control

The data acquisition and control system used in the CRS was a hybrid computer-based system employing discrete data acquisition devices and single-loop process controllers communicating to a central computer. The computer was used during experiments to monitor the process,

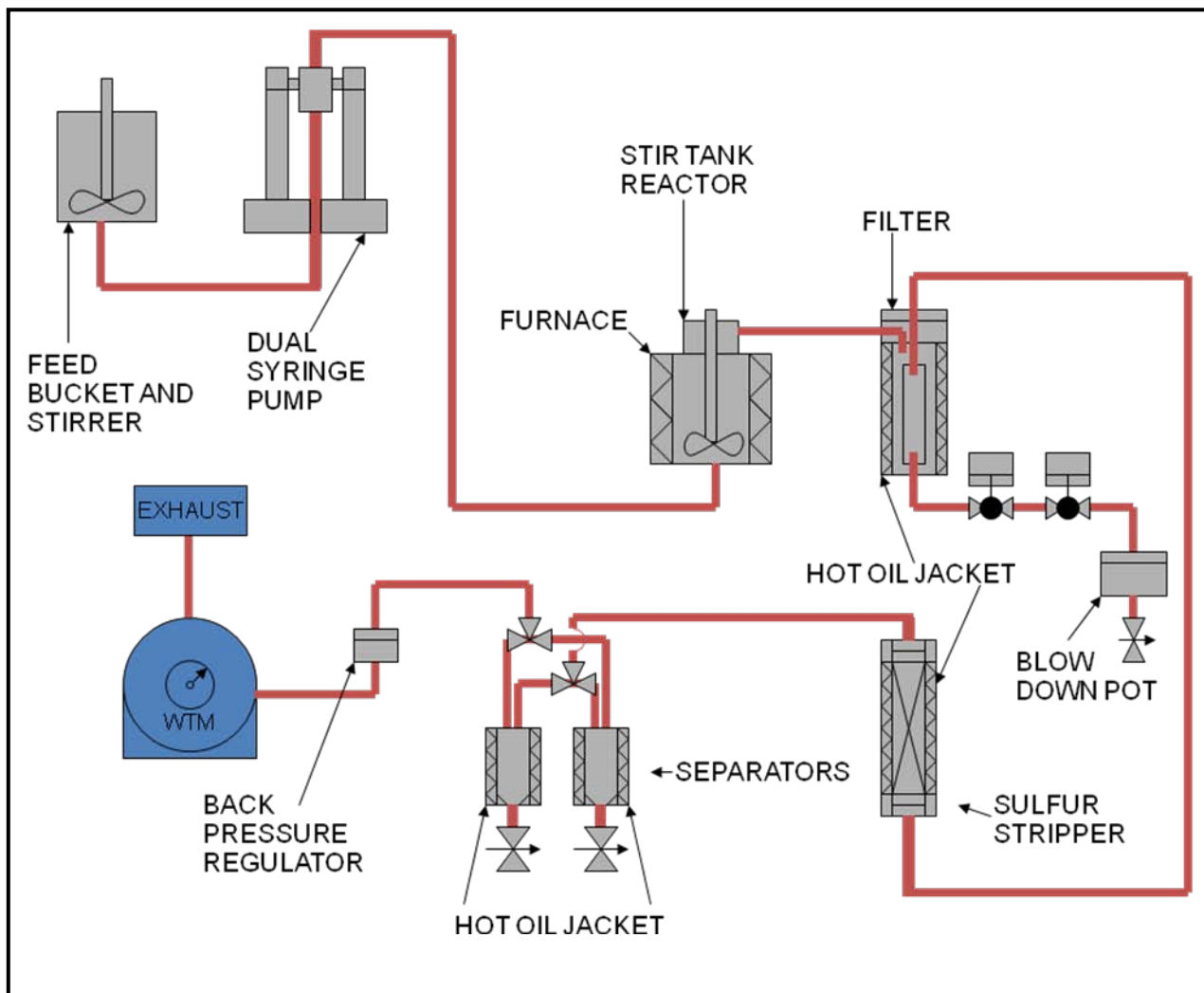


Figure 8. Hydrothermal Liquefaction System using a CSTR with a High-Pressure Solids Separator

calibrate instruments, and record data for later analysis. Labview is used to coordinate these activities. Non-control sensors such as thermocouples and pressure transducers were monitored via the data acquisition unit.

Bench-Scale Tests

A total of 23 separate process tests were performed within this project. These tests are summarized in **Table 2** and include processing corn fiber, starch and corn stover at various temperatures, flow rates and catalyst concentrations, with and without recycle of aqueous product as the solvent for the feed slurry

Table 2. Overview of Tests

Test #	feedstock	Reactor Setup	Feed rate	Temp, °C	Length of test	Catalyst
1	12.7% corn fiber	tubular	2 L/h	357	4 h – tube plug	none
2	12.7% corn fiber	CSTR & tubular	2 L/h	356	3 h – tube plug	none
3	14.7% corn fiber	CSTR & tubular	2 L/h	350	8.3 h - no plug	2% NaCarb
4	13.7% corn fiber	CSTR & tubular	2 L/h	350	7.5 h – transfer line plug	1% NaCarb
5	15.1% corn fiber	CSTR & tubular	2 L/h	350	37.8 h – transfer line plug	2% NaCarb
6	14.5% corn fiber	tubular	2 L/h	352	8.5 h – pump failed	2% NaCarb
7	8.2% corn fiber	tubular	2 & 1.5 L/h	190-340	10 h – temp out of control	2% NaCarb
8	13% corn fiber	tubular	2 & 1.5 L/h	341	9.9 h – no plug	2% NaCarb
9	13% corn fiber	tubular	2 & 1.5 L/h	330	10.2 h - no plug	2% NaCarb
10	5.3% corn stover	tubular	1.5 & 1.3 L/h	343	7 h – plug	none
11	9.6% corn stover	tubular	1.3 & 1.2 L/h	350	8.9 h – no plug	2% NaCarb
12	40% starch	tubular	1.3 L/h	351	0.9 h – feed plug	2% NaCarb
13	9% starch	tubular	1.3 L/h	352	7 h – no plug	2% NaCarb
14	8.2% starch	tubular	1.5 L/h	344	7.4 h – no plug	2% NaCarb
15	10.6% corn stover	tubular	1.5 L/h	352	22.8 h – no plug	1% NaCarb
16	10.6% corn stover	CSTR	1.5 L/h	351	10.7 h – valve fail	1% NaCarb
17	13.3% corn stover	CSTR	1.5 L/h	350	75 h – valve fail	1% NaCarb
18	10.3% corn stover	CSTR	1.5 L/h	347	14 h – filter fail	1% NaCarb
19	13.3% corn stover	CSTR	1.5 L/h	346	11.2 h – valve fail	1% NaCarb
20	10.4% corn stover	CSTR	1.2-1.8 L/h	349-327	47.1 h – no plug	1% NaCarb
21	10% corn stover with recycle	CSTR	1.5 L/h		4.8 h filter plug (residue from other)	1% NaCarb
22	10% corn stover with recycle	CSTR	1.5 L/h		30.2 h pump fail	1% NaCarb
23	12% corn stover	CSTR	1.5 L/h		88 h no plug	1% NaCarb

These tests suggest the following:

- Corn fiber can be processed effectively from 8 to 15 wt% in water; while corn stover can be processed from 5 to 13 wt%; limited testing with starch suggests processing at <10 wt% with heating to prepare pumpable slurry.
- Addition of base is required to maintain liquefaction conditions; 2 wt% of sodium carbonate facilitates corn fiber or starch; while only 1 wt% is needed for corn stover.
- A simple tubular reactor will work for hydrothermal liquefaction of corn fiber or starch, but liquefaction of corn stover requires a mineral separation step to facilitate oil/water separation in the collection system.

Corn Fiber Liquefaction

A total of nine process tests were performed using corn fiber slurries. The product yields and compositions are given in **Table 3**. The tests demonstrated bio-oil production with a significant formation of water soluble byproducts. Limited gas product was formed. Processing corn fiber slurry in a tubular reactor at nominally 350°C in the absence of pH adjustment resulted in char formation on the wall (test #1). Addition of the CSTR as a preheater before the tubular reactor did not eliminate the problem of wall coking (test #2). However, the addition of sodium carbonate to moderate the pH of the processing environment did result in no wall charring (test #3). Oxygen and moisture analysis in the product bio-oil appears faulty for this test. A subsequent test with a reduced level of sodium carbonate showed that it was not sufficient. Validation of the 2% level of sodium carbonate addition was seen in the longer term tests undertaken to produce bio-oil for subsequent hydroprocessing studies at CRADA partner, ConocoPhillips (test#5).

Table 3. Corn Fiber Liquefaction (average of data windows within test run)

	1	2	3	4	5	6	7	8	9
Oil yield, mass basis	39.67	37.8*	28.07	30.5	27.8	33.4	11.4	19.5*	20.0
Oil yield, carbon basis	68.02	61.8*	48.85	54.2	47.3	56.6	23.6	39.7*	43.6
Oil composition									
Carbon, wt%	69.31	71.51	77.0	75.9	75.2	74.3	72.7	73.2	71.4
Hydrogen, wt%	7.40	7.52	8.0	8.4	8.6	7.5	8.4	8.2	8.1
Oxygen, wt%	19.85	19.39	9.9	12.2	11.3	13.3	16.0	14.5	16.0
Oxygen, wt% dry basis	9.93	12.99	1.7	5.0	7.9	8.4	9.9	11.5	13.0
Nitrogen, wt%	2.04	1.90	2.3	3.2	3.3	3.1	2.6	2.5	2.4
Sulfur, wt%	0.33	0.21	0.27	0.30	0.30	0.30	0.30	0.24	0.24
Moisture, wt%	12.56	8.43	9.4	8.7	4.2	6.0	7.8	3.9	4.0
TAN, mg KOH/g	NA	NA	NA	NA	NA	51	58	52	50
density, g/mL	1.1	NA	NA	NA	1.079	1.067	NA	1.071	1.072
Aqueous yield, carbon basis	25.74	31.2*	30.6	30.0	33.1	34.7	72.5	55.3	46.3
pH	3.9	3.9	7.7	6.0	7.1	7.1	NA	7.7	7.7

COD	NA	30700	72000	65000	64000	70000	NA	59000	60000
Gas product yield, carbon basis	3.76	7.1	8.0	7.6	6.0	6.0	2.6	4.6*	9.2

* normalized carbon yield results

Red font indicates questionable result, likely faulty analysis

Subsequent tests used only the tubular reactor without the CSTR for preheating. Test #6 was halted because of pumping problems. Test #7 was the first test in the rebuilt system after moving to a new building. In the move process, the temperature control system lost its calibration and setup and was not functional until after a subsequent tuning session was completed. Following the tuning, lower temperature tests (tests #8 and #9) showed reduced bio-oil yields of lower quality.

Corn Starch Liquefaction

A total of three process tests were performed using corn starch slurries. The product yields and compositions are given in **Table 4** for the two successful tests. The first test with corn starch slurry (test #12) was attempted using a 40% dry starch in water slurry. Such slurry would not pump in the syringe pump and actually scoured the pump cylinder walls and seal rings and ruined the pump. The later two tests were performed with preheated starch slurry wherein the starch was “liquefied”. The tests demonstrated low levels of bio-oil production with a large amount of water soluble byproducts. Limited gas product was formed. Comparing processing corn starch slurry in a tubular reactor at 340°C and 1.3 L/h (test #13) with the lower severity test (test #14) with lower temperature, 330°C, and higher flow rate, 1.5 L/h, shows that the less severe conditions resulted in reduced bio-oil yield and the product was somewhat less deoxygenated. However, the difficulty in measuring the oxygen and moisture analysis in the product bio-oil appeared to produce inconsistent results for this test. An unrepresentative sample

Table 4. Corn Starch Liquefaction (average of data windows within test run)

	13	14
Oil yield, mass basis	10.3	5.5*
Oil yield, carbon basis	23.8	13.0*
Oil composition		
Carbon, wt%	72.2	63.9
Hydrogen, wt%	7.66	8.4
Oxygen, wt%	18.2	24.3
Oxygen, wt% dry basis	15.1	9.1
Nitrogen, wt%	0.06	1.26
Sulfur, wt%	0.02	0.01
Moisture, wt%	4.2	19.0
TAN, mg KOH/g	26	19

density, g/mL	1.08	1.04
Aqueous yield, carbon basis	66.9	81.5*
pH	7.3	7.3
COD	56000	61000
Gas product yield, carbon basis	5.0	4.4*

* normalized carbon yield results

Red font indicates questionable result, likely faulty analysis

may have also been used in the density measurement and the nitrogen analysis. The commercial starch product used had very little nitrogen (0.05-0.10 wt %). The lower density of the bio-oil does not reflect the higher oxygen content and is unlike any of the other HTL bio-oils in this project. Both bio-oil products had a low enough viscosity that they flowed at room temperature.

Corn Stover Liquefaction

A total of eleven process tests were performed using corn stover slurries. The product yields and compositions are given in **Table 5** for the successful tests. The first test with corn stover slurry (test #10) was attempted using low concentration slurry (5%) without alkali catalyst added. The test proceeded well but eventually plugged in the reactor. The next test was performed with higher concentration slurry (9.6%) with a 2% alkali catalyst added. This test ran smoothly and did not plug. The tests demonstrated significant levels of bio-oil production but with a significant amount of water soluble byproducts. Limited gas product was formed. A subsequent test with higher concentration corn stover and a 1% alkali catalyst added (test #15) performed well but there were problems with bio-oil separation from the aqueous byproduct and the significant amount of mineral precipitate formed in the process. Both the heavy bio-oil product and the mineral precipitate settle to the bottom of the condensate product and oil recovery is confounded.

Table 5. Corn Stover Liquefaction (average of data windows within test run)

	10	11	16	17	19	20a	20b	20c
Oil yield, mass basis	24.5*	17*	26.0*	15.9*	15.2	21.6*	19.1	14.6*
Oil yield, carbon basis	52.0*	38*	44.4*	30.0*	32.8	30.0*	39.9	33.4*
Oil composition								
Carbon, wt%	60.5	72.5	72.05	63.6	68.9	55.1*	68.1	69.5
Hydrogen, wt%	6.0	7.9	7.88	8.5	7.9	8.6	7.8	7.4
Oxygen, wt%	27.9	16.0	19.92	25.9	19.9	26.2	21.5	22.3
Oxygen, wt% dry basis	13.5	8.2	17.34	17.8	14.1	17.1	16.8	13.8
Nitrogen, wt%	1.11	1.2	1.35	1.06	1.15	0.92*	1.23	1.2
Sulfur, wt%	0.08	0.07	0.07	0.06	0.08	0.06	0.07	0.08

Moisture, wt%	19.05	9.6	3.61	11.3	7.74	12.6	6.62	11.2
TAN, mg KOH/g	35	32	NA	31	29	26	48	42
density, g/mL	1.09	1.10	1.04	1.08	1.094	1.073	1.066	1.109
Aqueous yield, carbon basis	37.6*	55.3*	43.9*	56.1*	56.8	53.4*	42.1	52.6
pH	3.4	7.3	4.8	5.5	4.5	5	5	5
COD	28000	56000	53000	85000	71000	58000	54000	58000
Gas product yield, carbon basis	10.6*	6.8*	5.3*	5.0*	7.8	8.0*	7.1	6.7*

* normalized carbon yield results

Red font indicates questionable result, likely faulty analysis

Subsequent tests utilized the modified process flow shown in **Figure 8** which incorporated a solids separator and high-pressure filter prior to the condensate separation and collection. By this design the mineral components in the corn stover could be separated from the products while the bio-oil water separation could be accomplished more cleanly. The CSTR served as the only reactor in this flow configuration. In test #16 the new configuration was demonstrated for a period, but then a valve failure terminated the test. The next test shown in **Table 4** (test #17) was undertaken to produce bio-oil for subsequent hydroprocessing studies at CRADA partner, ConocoPhillips. Tests 19 and 20 included a series of process parameter tests starting at 346°C and 1.5 L/h (test #19) with variations in severity with lower flowrate 1.3 L/h @ 349°C (test #20a), lower temperature 340°C and higher flow rate 1.8 L/h (test #20b), and lower temperature, 327°C @ 1.5 L/h (test #20c). It is difficult to see any consistent trends in product yield or bio-oil product quality within this range of parameter variation.

Results from tests involving recycle of the aqueous byproduct are shown in **Table 6**. Test #21 was an initial test of recycle using aqueous product from test #19; it was terminated prematurely when a pressure drop could not be cleared. On disassembly the filter was found to be plugged. It was suggested that feedstock with a high lignin content used in a prior hydrothermal gasification test was the cause. A redesigned filter assembly was put in place for the final tests. In test 22 an attempt was made to recycle the aqueous stream within the limits of the test itself by preparing subsequent feed with the aqueous stream from earlier in the run. The recycle was accomplished but was limited by the extensive time required to grind the corn stover with

Table 6. Corn Stover Liquefaction with Aqueous Recycle (average of data windows within test run)

	20b	22a	22b	22c	23a	23b	23c
Oil yield, mass basis	19.1	16.9*	18.2	18.7*	16.3*	16.0*	16.5
Oil yield, carbon basis	39.9	31.6*	37.6	42.3*	34.6*	32.7*	35.9
Oil composition							
Carbon, wt%	68.09	71.2*	68.7	73.32	67.61	67.68	71.17

Hydrogen, wt%	7.84	7.99	7.70	7.94	8.58	8.62	8.26
Oxygen, wt%	21.53	18.0	20.0	17.64	22.55	20.18	19.93
Oxygen, wt% dry basis	16.75	12.4	13.0	8.71	12.81	13.09	11.75
Nitrogen, wt%	1.23	1.35	1.39	1.46	1.19	1.05	1.30
Sulfur, wt%	0.07	0.08	0.06	0.06	0.09	0.07	0.08
moisture, wt%	6.62	7.03	9.16	9.40	12.80	9.35	10.60
ash, wt%	NA	NA	NA	NA	0.18	0.10	0.20
TAN, mg KOH/g	48	NA	NA	NA	34.8	24.4	29.7
density, g/mL	1.066	NA	NA	NA	NA	NA	NA
Aqueous yield, carbon basis	42.1	57.3*	53.6	49.8*	50.2*	53.0*	54.18
pH	5	5.05	4.7-5.4	5.04	5	5.5	5.3
COD	53700	68600	77700	82500	54000	72500	77600
Gas product yield, carbon basis	7.07	10.9*	9.3	7.3*	12.3*	8.3*	8.62
Carbon lost with solids, C basis	6.23	0.22*	0.94	0.52	2.9*	6.0*	2.63

* normalized carbon yield results

the recycled aqueous to produce pumpable slurry. Test 22a involves feedstock made with recycled aqueous from test #20 (given again in [Table 5](#) for reference). Test #22b involved recycled aqueous from test #22a, and #22c had recycle from #22b. It appears from these results that there is a trend an increasing carbon yield in the bio-oil at the expense of carbon yield in the aqueous phase, but there was also an increase in the organic loading in the aqueous byproduct. Test 23 was another extended run to produce bio-oil for subsequent hydroprocessing studies at CRADA partner, ConocoPhillips. This was an extended run to demonstrate operability of the process with some recycle. Deionized water was used for slurry preparation in the first reported phase (test #23a). Aqueous from test #17 was recycled in the second phase of the test (test #23b) and test #23a and b aqueous phase was recycled during the 23c portion of the test. The three data windows show only a slight but inconsistent trend in product yield and quality as a function of recycle but underline the inherent variability in the data generation (primarily inhomogeneous bio-oil sampling inconsistency).). Additionally, carbon lost with solids is reported for each sampling window representing the amount of carbon that was carried out with the on-line blow down of the filtered solids from the system filter. While this represents an efficiency cost, it is possible that a change in design or operation of the solids filtering could result in restoring some of this lost carbon.

Data Correlation

The data for runs 17a through 20c, all CSTR runs without recycle, were correlated in terms of the empirical expression:

$$(PROPERTY\#) = a \cdot (LHSV)^b \cdot (BMF)^c \cdot \left(\frac{T}{300}\right)^d$$

where:

PROPERTY # is Moisture Free Oil Yield, Water Solubles Yield, H/C Atomic Ratio, O/C Atomic Ratio;

LHSV is the liquid hourly space velocity in h⁻¹;

BMF is the biomass to water inlet mass fraction;and

T is temperature in °C

These correlations for Corn Stover HTL (parameter values and parity plots reported in Appendix B) were used within the experimental window of operation to show the various trends that dependent variables present in terms of the independent variables, namely Liquid Hourly Space Velocity (LHSV), Temperature (T) and Biomass Inlet Mass Fraction (BMF). All correlations are reported on a moisture free basis for the feed and the products.

Moisture Free Oil (MFO) Yield

Figure 9 shows the effect of the independent variables upon MFO yield.

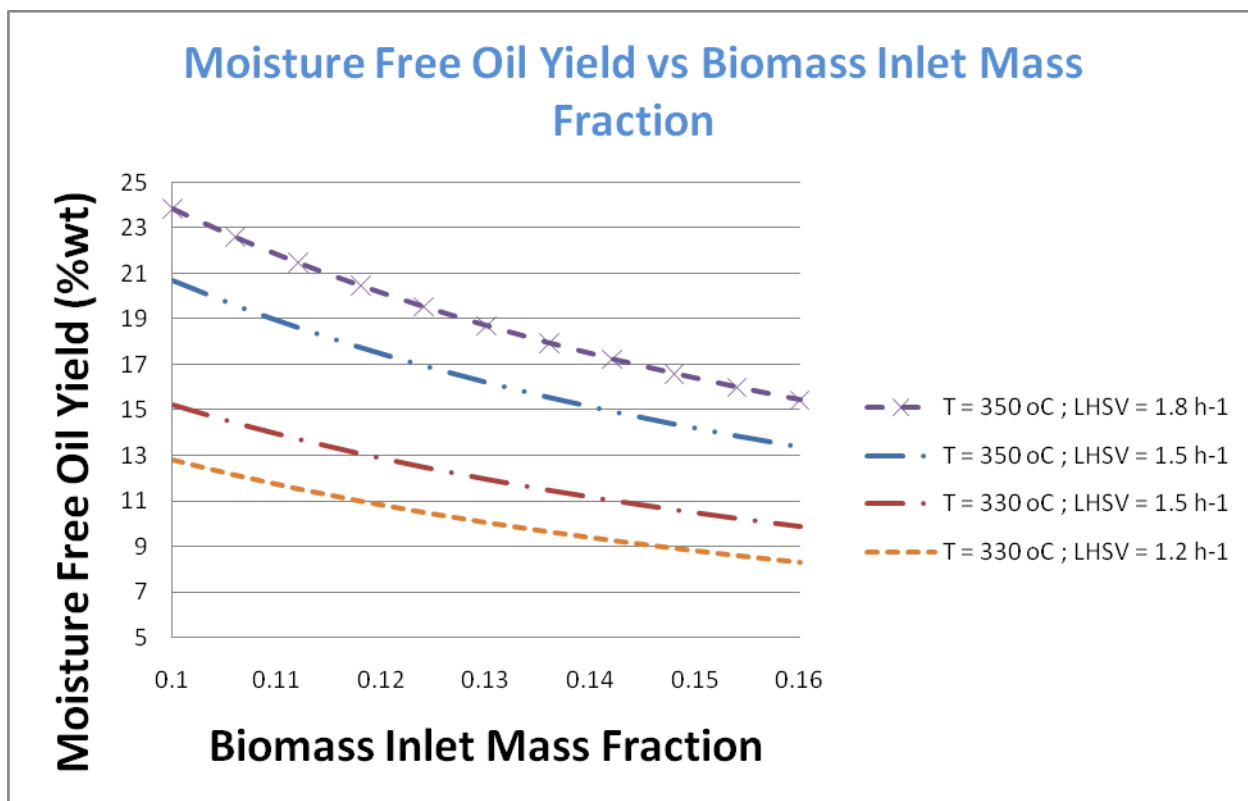


Figure 9. Moisture Free Oil Yields in terms of BMF, T and LHSV.

The MFO yield increases with temperature and LHSV, while it decreases with BMF. In this case, experimental data suggest that the maximum MFO production will benefit from processing dilute feeds, at the highest temperature and shortest residence time.

MFO H/C Atomic ratio

Figure 10 shows the effect of the independent variables upon MFO H/C atomic ratio. This demonstrates that -

The MFO H/C atomic ratio increases with temperature, decreasing BMF and LHSV. In this case, experimental data is suggesting that the maximum MFO H/C Atomic Ratio will benefit from processing dilute feeds, at the highest temperature and longest residence time.

MFO yield and its H/C atomic ratio are equally favored by processing dilute feeds and using high temperatures, but there is an opposite effect from residence time: longer times improve the MFO H/C ratio, but shorter times improve MFO yield. So, LHSV should be determined by operational and economic factors.

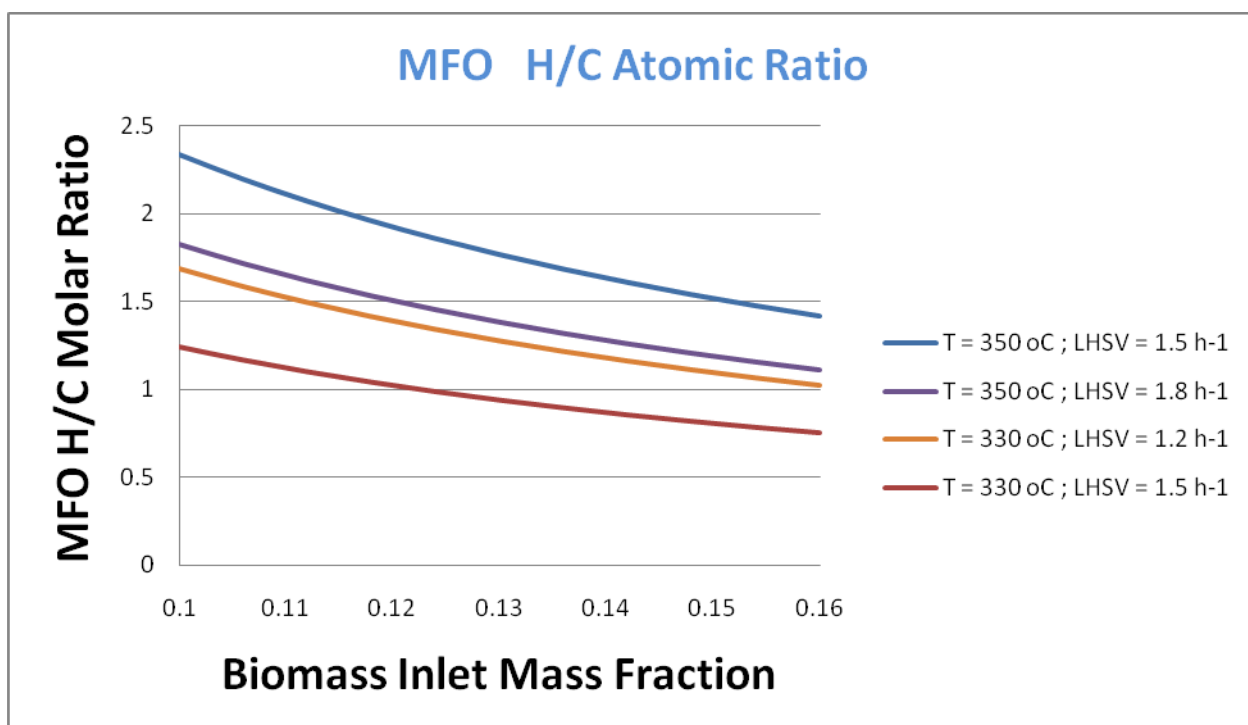


Figure 10. Moisture Free Oil H/C Atomic Ratio in terms of BMF, T and LHSV.

MFO O/C Atomic ratio

Figure 11 shows the effect of the independent variables upon MFO O/C atomic ratio.

The MFO H/C atomic ratio decreases with BMF and LHSV, while it increases with temperature. In this case, experimental data suggest that the minimum MFO O/C Atomic Ratio will benefit from processing concentrated feeds, at the lowest temperature and shortest residence time.

The MFO O/C atomic ratio optimum operating conditions are partially opposite to those that maximize MFO yield and MFO H/C atomic ratio. Because of the large impact the MFO O/C Atomic Ratio has upon the MFO HHV, it is anticipated that this parameter will override the MFO H/C Atomic Ratio maximization. There are also opposite trends for Biomass Inlet Mass Fraction and Temperature effects upon MFO yield and MFO O/C Atomic Ratio. However, short residence times favor both properties mentioned before.

There will be a trade off between MFO yield and its corresponding HHV that will dictate the final choice. This decision will be dependent also upon the downstream processing of the aqueous phase and the bio-oil upgrading.

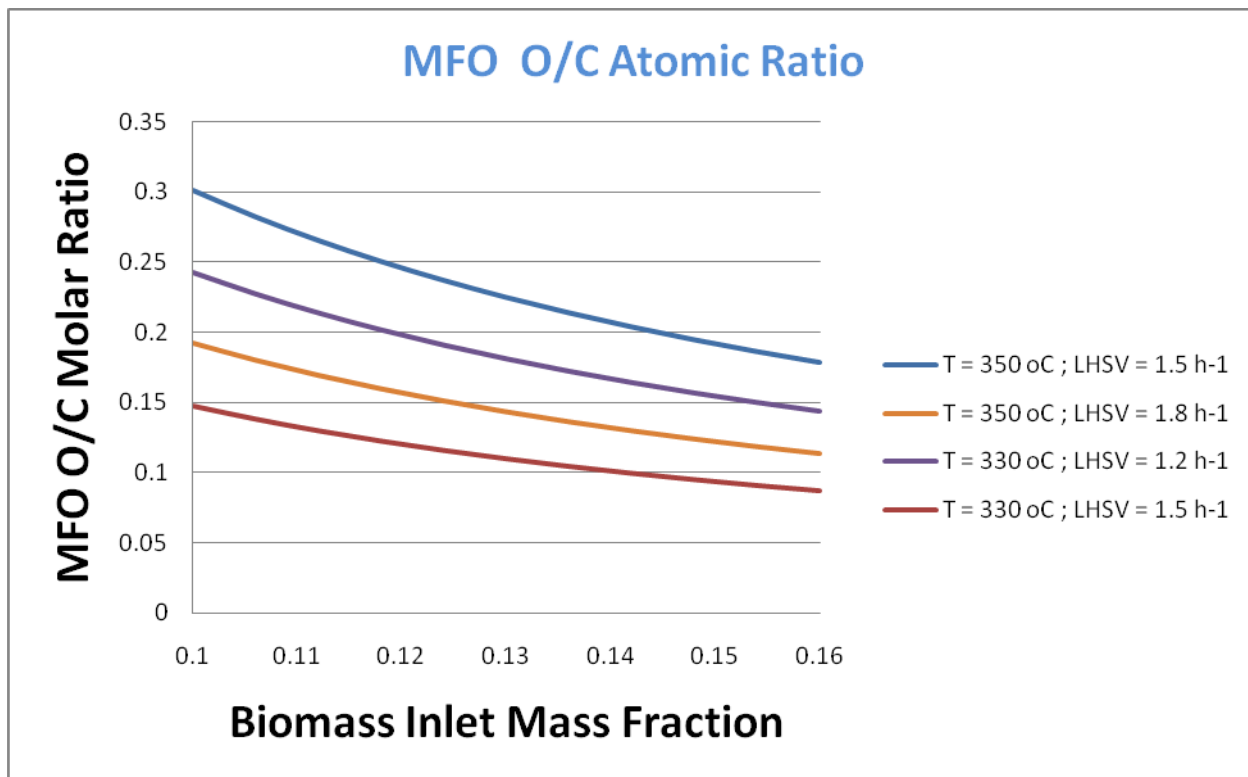


Figure 11. Moisture Free Oil O/C Atomic Ratio in terms of BMF, T and LHSV.

Water Solubles (WS) Yield

Figure 12 shows the effect of the independent variables upon WS yield. It

The WS yield decreases with temperature and BMF, but is independent of LHSV. In this case, experimental data suggest that the maximum WS production will benefit from processing dilute feeds, at the lowest temperature.

Trends for WS H/C and O/C atomic ratios are not presented due to the low number of valid data points.

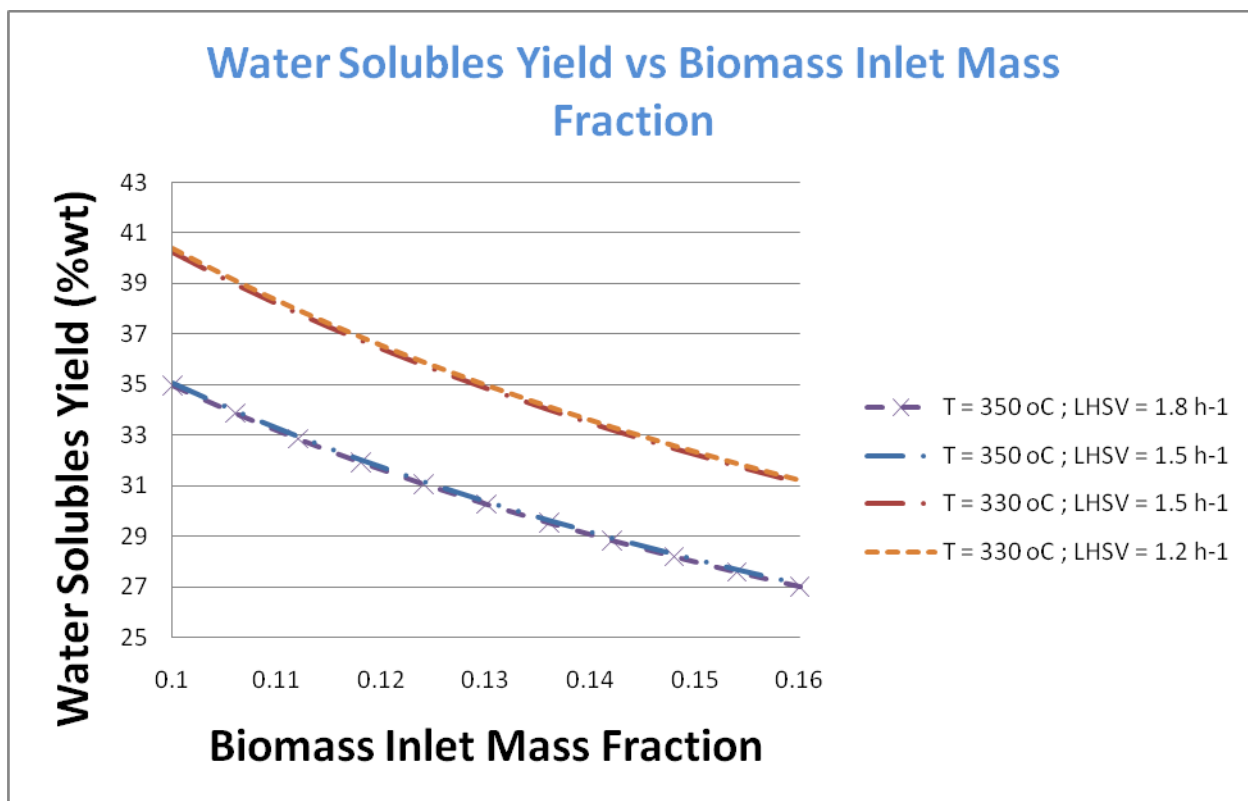


Figure 12. Water Solubles Yields in terms of BMF, T and LHSV.

Aqueous Product Assessment

Detailed analysis of the aqueous phase was undertaken to determine the composition and quantity of dissolved organic material as led by ADM with contribution from PNNL.

Treatment or recovery of these potentially useful or valuable byproduct materials was a focus of the ADM team. ConocoPhillips was involved in considering upgrading it to fuels.

Following characterization of the stream ConocoPhillips and ADM evaluated the best use of the stream. The options included stream, recycle to the hydrothermal liquefaction process, combustion to generate high temperature steam for the process, conversion to hydrogen to supply the hydrotreating process, conversion to mixed alcohols for fuels, or chemical applications. The aqueous stream analysis showed that it consisted primarily of acetic and glycolic acids (up to 2-4 wt% in some samples), with lesser amounts of acetone, other C1-C6 oxygenates, and phenols. This stream was not of interest for conversion to transportation fuels due to the low total organics concentration and high proportion of carboxylic acids. Thus, the most attractive options for monetizing this stream were determined to be: a) recycle to the liquefaction process, with the goal of further converting the dissolved organics to oil, or b) hydrothermal gasification to produce methane, which then could be converted to hydrogen through conventional steam methane reforming or burned for energy.

PNNL performed bench-scale catalytic hydrothermal gasification tests to evaluate fuel gas production from the aqueous stream as a means of energy value recovery using this

Analysis of Aqueous Product

A gas chromatography with a mass spectrometer was used to identify and quantify compounds present in the aqueous fractions of biomass samples from hydrothermal liquefaction. Samples were injected neat onto a sixty meter wax column with 0.25 mm inner diameter and 0.25 micron film thickness using a split injector ratio of 10:1. The injector was maintained at 260°C. The carrier gas was helium at a linear column flow rate of 49 cm/s. The initial oven temperature was 35°C and held for ten minutes. The oven temperature was then ramped 10°C per minute to 260°C and held for 7.5 minutes. The interface temperature was set at 260°C and the ion source was set at 230°C. The detector voltage was set to tune plus 0.7 kilovolts. Mass spectral data was collected at a scan speed of 1250 over a mass to charge range of 15-600.

The compounds present were identified using library matching of the mass spectra using both the NIST and Wiley libraries. Compounds were then quantified using the areas the total ion chromatograms and the response factors of acetic acid and butanol. Results of this analysis are presented in **Table 7**.

Table 7. Identified Components in Aqueous Byproducts from Hydrothermal Liquefaction

Feedstock		HFCS	Starch	Dextrose	Stover	Stover	Stover	Stover	Stover	Stover	Stover
Run Number		MHLT-2	LF-13	MHLT-1	LF-10	LF-11	HTL-17	HTL-19	HTL 20A	HTL 20B	HTL-20C
Molecular Formula	Family Compound	% wt	% wt	% wt	% wt	% wt	% wt	% wt	% wt	% wt	% wt
CH4O	Alcohol	0.5%		6.6%	5.7%	8.1%	20.0%	3.6%	3.5%	38.7%	1.2%
C2H4O	Aldehyde	2.8%	5.0%	2.8%	0.3%	1.8%					
C2H4O2	Acid	11.7%		1.5%	1.1%	1.2%	0.9%	9.1%	10.2%	0.1%	0.3%
C2H6O	Alcohol	2.2%		11.4%	0.1%	0.6%	11.8%	0.1%	1.3%	14.2%	0.6%
C2H6O2	Alcohol	11.2%	17.2%	1.3%			15.1%	18.4%	17.4%	2.5%	7.1%
C3H4O2	Acid				1.9%						
C3H6O	Ketone	21.9%	52.1%	1.2%	27.3%	3.6%	0.3%	7.9%	0.1%	8.2%	0.3%
C3H6O2	Alcohol						0.6%	0.2%	0.6%	1.7%	0.9%
C3H6O2	Ketone				2.1%						
C3H6O2	Acid	4.7%		1.3%	2.3%						
C3H8O	Aldehyde	1.6%	1.3%	0.2%	1.3%	0.1%					
C3H8O	Alcohol	1.8%	0.3%	4.7%	0.7%	2.8%	8.9%	8.1%	12.9%	2.4%	73.2%
C3H8O2	Alcohol						5.0%	0.9%	6.4%	0.1%	3.1%
C3H8O3	Alcohol						3.2%	1.3%	3.4%	1.3%	1.3%
C4H10O	Alcohol		4.6%	0.9%		1.6%	2.2%	2.0%	3.0%	1.9%	0.0%
C4H10O2	Alcohol		0.5%				0.3%	0.2%	0.3%	0.4%	0.2%
C4H6O2	Ketone	3.4%	16.0%	2.3%	1.4%		2.0%	0.2%	1.5%	1.2%	0.5%
C4H7NO	Ketone						0.1%	0.9%	0.9%	0.4%	0.2%
C4H8O2	Acid				0.0%	0.7%					
C4H8O2	Ketone				3.1%						
C5H10O	Ketone	2.3%		3.6%	0.4%	1.1%	0.3%	0.9%	0.6%	1.3%	0.1%
C5H10O	Alcohol				2.0%		0.4%	9.3%	7.7%	1.8%	0.3%
C5H4O2	Aldehyde				1.4%	0.2%					
C5H8O	Ketone	14.4%		16.9%	6.3%	11.4%	0.6%	0.3%	0.9%	0.6%	
C6H10O	Ketone	9.8%		1.3%	11.4%	1.2%	3.0%	0.7%	5.0%	6.5%	2.2%
C6H10O3	Acid	1.6%		0.6%	3.0%						
C6H10O4	Alcohol						4.1%	1.1%	0.5%	0.3%	0.0%
C6H6O	Alcohol				2.9%	5.5%	4.4%	7.0%	0.7%	0.9%	2.9%
C6H6O2	Alcohol	3.3%		20.7%	13.7%	1.7%	0.1%	1.9%	1.2%	1.9%	0.8%
C7H10O	Ketone	0.1%	3.1%	8.1%	0.5%	1.2%	0.1%	0.6%	0.2%	0.7%	1.1%
C7H12O	Aldehyde						13.0%	17.2%	16.3%	1.4%	0.5%
C7H8O	Alcohol						0.9%	1.1%	1.0%	0.2%	0.1%
C7H8O2	Alcohol			1.1%	0.3%	0.4%	0.8%	1.8%	0.8%	3.3%	1.5%
C7H8O2	Alcohol	5.4%		11.9%							
C8H10O	Alcohol	1.4%		1.6%	0.0%	0.8%	1.5%	3.8%	3.0%	4.4%	0.2%
C8H10O3	Alcohol				6.2%	3.5%		0.7%	0.4%	1.6%	0.6%
C8H18O	Alcohol						0.2%	0.7%	0.2%	0.9%	0.3%
C9H12O2	Alcohol				1.6%		0.3%	0.1%	0.0%	1.1%	0.4%
C10H12O4	Ketone	0.2%			3.1%	52.5%					
Total		100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

Table 7 presents the chemical analysis of the aqueous phase on a moisture free basis. Important to note is that the carbon compounds contained in this process stream only represent approximately 3-6 wt% of its mass. From the table, it can be seen that the compounds in the aqueous phase are a heterogeneous mixture of alcohols, ketones, aldehydes, and acids. The majority of water soluble compounds are alcohols (54.7%), followed by ketones (33.4%), aldehydes (6.7%), and acids (5.2%). When considering carbon number, approximately 60% of the compounds are C4 minus and the mixture has an estimated 50% boiling point of 250°F on a dry basis. Because of the dilute nature of this stream, economic recovery of the carbon

compounds will be problematic. One method, catalytic gasification, was examined and the results are presented in the next section.

Catalytic Hydrothermal Gasification

The Continuous-flow Reactor System (CRS) used in hydrothermal liquefaction was used with slight modifications in for the hydrothermal gasification. Of the five major functional subsystems: feed pretreatment and preparation, pumping, preheater/reactor, reaction products separation, and instrumentation and control, changes were required in part of the reactor system and in the product separation system while feed pretreatment was not needed. The system throughput was similar at 1 to 3 liter/hour of aqueous product. The process flow diagram is shown in **Figure 13**. The modifications implemented for handling minerals and sulfur is indicated in the diagram labeled “NEW.”

Bench-scale Test Results

A preliminary batch reactor test was performed to evaluate the aqueous byproduct from hydrothermal liquefaction as a feedstock for catalytic hydrothermal gasification (CHG). The

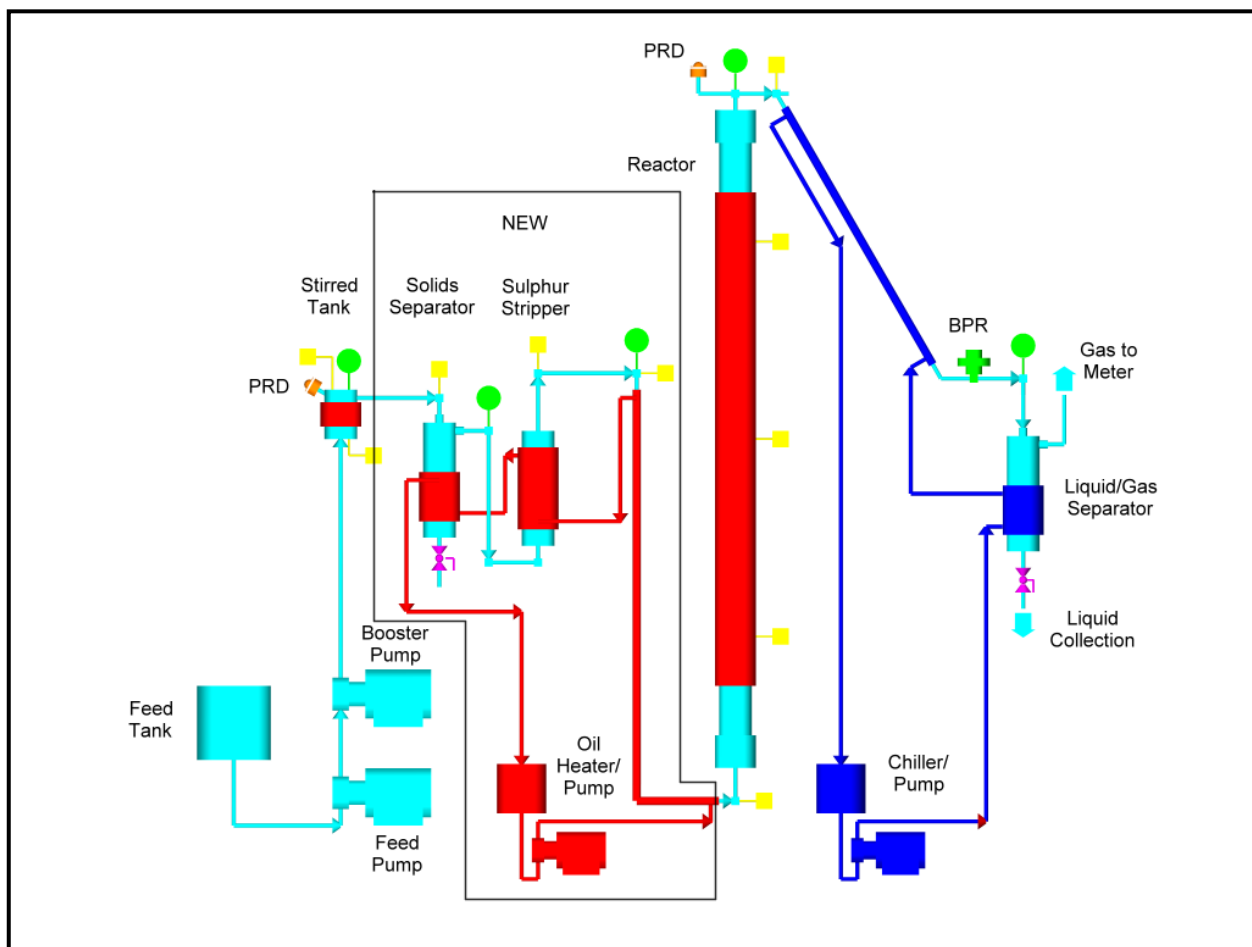


Figure 13. Schematic of the Bench-Scale Continuous-Flow Reactor System for Gasification.

aqueous stream came from test #6 which used a corn fiber feedstock. In a stirred batch reactor 261.5 g of aqueous byproduct were stirred with 35.4 g of a Ru on carbon catalyst, which had been developed and tested in other CHG applications (the catalyst had been reduced under hydrogen at 250°C overnight prior to the batch test). The test extended for 4 hours at nominally 350°C. The aqueous byproduct chemical oxygen demand (COD) was reduced from 60,300 ppm to 60 ppm. The pH of the solution increased from 7.51 to 7.98. The vented gas volume was 14.8 liters of which about 5.9 liters were the nitrogen cover gas initially left in the reactor following purge of oxygen from the system. The gas composition included 74% methane, with 12% each of carbon dioxide and hydrogen, and 1% ethane (on a nitrogen-free basis). This batch test verified that the organic contaminants left in the aqueous byproduct from hydrothermal liquefaction could be effectively gasified by CHG.

Two continuous-flow experiments were performed at bench-scale with the aqueous phase byproducts from corn stover hydrothermal liquefaction. In the tests the process was operated for 4 to 10 hours. In the first test there were plugging problems in the offgas system attributed to fine precipitate in the condensate water. In the second test, the 10-hour run was completed without stoppage although the same white precipitate (assumed to be sodium bicarbonate based on sodium analysis) was noticed in all condensate samples.

These tests, whose results are shown in **Table 8**, showed the high level of gasification achieved by this technology using the aqueous phase byproduct as the feedstock. In these tests almost all the organic material was converted to a medium-Btu gas. The gas could be used directly for process heating or further processed to generate pipeline quality natural gas substitute. Because of the low COD of the product water after gasification its reuse seems like a reasonable option and should be considered further. The recycle of the aqueous phase back to feedstock preparation for the liquefaction step would also be reasonable and has potential to reduce the cost of added alkali. The high-temperature and high-pressure separation of the bio-oil and aqueous needs to be further investigated. The solids separation prior to bio-oil separation also serves to

Table 8. CHG Process Results with Aqueous Phase Feedstock

Process Parameters	1	2	Process Results	1	2
Preheater temp, °C	324	345	gas yield, L/g aqueous feed	0.02	0.04
Tubular temp, °C	331-355-349	324-353-350	Gas Composition, vol %		
System Pressure, psig	3041	2875	methane	59.7	65.8
LHSV, L/L cat @ temp/h	2.0	1.4	carbon dioxide	39.2	31.9
Feed Composition, wt%			hydrogen	0.5	1.5
Carbon	1.8	2.8	ethane/propane	0.06	0.1
Hydrogen	10.1	11.0	carbon monoxide	0.00	0.00
Nitrogen	0.00	0.04	C conversion to gas, %	65	71
Oxygen, by dif	84.2	84.2	C conv adjust for carbonate	120	88
Sulfur	0	0.0	carbon lost with solids	0	0
ash	3.9	1.9	carbon balance	120.4	95.8
Feed COD, ppm	54000	72867	mass balance	102.6	101.6
Product COD, ppm	606	236	COD reduction	98.9	99.7

pretreat the aqueous for use in the gasification by removing insoluble minerals. The tests gave no evidence of catalyst deactivation in this application in that the COD of the effluent remained constant and the gas product composition was essentially unchanged. However, the relatively short tests only provide an initial indication and longer term catalyst lifetime tests would be required.

The direct connection of the gasification technology following liquefaction technology with an intermediate separation of the bio-oil product should be straightforward since the technologies operate at the same conditions of temperature and pressure. There would be minimal requirement for reheating or repressurizing the aqueous phase to gasification reaction conditions. **This advantage would appear to override the issue of cost for processing a dilute phase feedstock as the gas product would be essentially net production without requirement for energy use in pressuring and heating.** A detailed engineering design and economic assessment would be required to confirm this preliminary assessment.

Upgrading with Heteroatom Removal

Catalytic hydroprocessing of the hydrothermal liquefaction product oil was performed by Conoco-Phillips at the bench-scale. Mass balances around the process were determined and products recovered for detailed analysis for fuel applications.

- Hydroprocessing was utilized for upgrading the crude oil product.
- Targets for this processing included not only the oxygen heteroatoms, but also nitrogen, as well as sulfur.

ConocoPhillips sought to determine:

- Is the material suitable for directly blending into fuel?

-
- If not, what further treatments, including co-processing to make a material suitable for fuel in laboratory fixed bed test reactors are needed?

In addition, ConocoPhillips

- Evaluated catalytic cracking in laboratory screening reactors as an alternative upgrading option.
- Screened the fuel properties of the upgraded products.

Catalytic Hydroprocessing for Heteroatom Removal

The hydrothermal liquefaction oil was subjected with catalytic hydroprocessing with catalysts supplied by Albemarle. The crude liquefaction oil was not miscible with typical petroleum fractions (naphtha, distillate, etc.), therefore is not suitable for direct blending. A lab-scale, fixed-bed hydroprocessing unit was employed along with a suitable catalyst to improve the quality of the crude oil. A diagram of the unit is shown in **Figure 14**. Three catalysts were screened: a commercially available hydrotreating catalyst, KF-757, and two developmental hydrodeoxygenation catalysts designated HDO-1 and HDO-2.

Experimental Details

An aliquot of desired catalyst was charged into the reactor and converted into its active forms following a presulfiding procedure provided by the vendor. In brief, a mixture of petroleum distillate and dimethyl disulfide was combined with hydrogen gas and flowed over the catalyst while increasing the catalyst temperature. The DMDS in contact with hydrogen at elevated temperature is converted into hydrogen sulfide, H_2S , which in turn converts the catalyst from the oxide form into the active sulfide form. Following this activation procedure, ultralow sulfur diesel fuel (ULSD) was flowed through the catalyst bed to remove residual sulfur to prevent contamination during the reaction stage. Crude liquefaction oil was loaded into one of the ISCO syringe pumps and introduced into the activated catalyst bed. The pump, transfer lines leading to the reactor, and transfer lines carrying the product were heated to reduce the liquid viscosity and allow smooth flow of the reactants and products. Products were collected in a heated trap along with simultaneous analyses of the product off-gas.

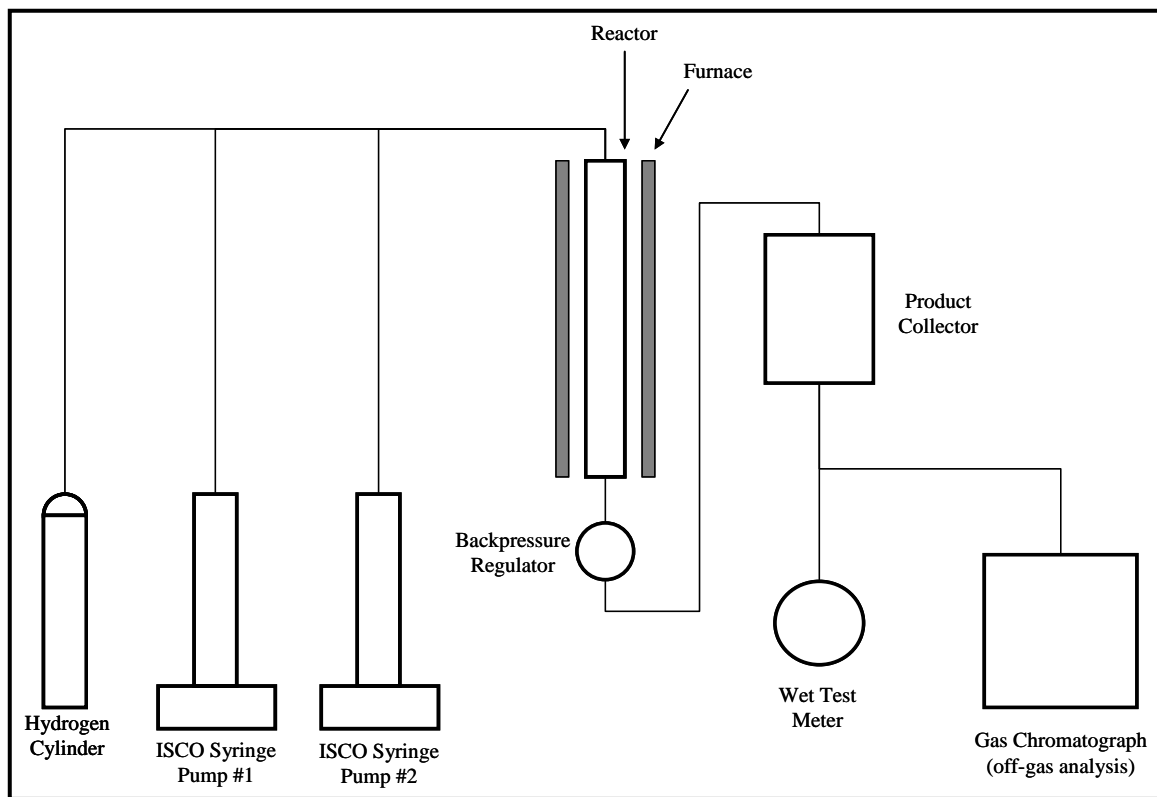


Figure 14. Diagram of Hydroprocessing Unit.

Liquefaction oil and hydroprocessed products were subjected to a standard combustion method to determine the elemental composition (CHNS, O by difference), Karl Fischer analysis for water, and total acidity number (TAN) titration with potassium hydroxide. Product improvements indicated are a decrease in the oxygen and nitrogen content, decrease in the water content, and decrease in the TAN value. If these preliminary analyses indicated significant improvement in product quality, the product was subjected to additional analyses to determine its suitability as a fuel or fuel blending component.

Process Operations

Short-duration scoping experiments were initially performed to evaluate the upgradability of the liquefaction oil. Values for reaction temperature, reaction pressure, and space velocity were determined with the scoping tests.

Following reactor parameter scoping temperatures for the hydroprocessing were selected to be 250 – 320 °C. The thermal stability of the liquefaction oil was the primary concern for determining the temperature operating envelope. Thermal degradation leads to conversion of the liquid oil into solid carbon (coke) which would plug fill the processing system and require early termination of the experimental trial. This situation must be avoided. Since the hydroprocessed

product is predicted to be more thermally stable, operation at high conversion is desirable. Conversion was maximized by operating at high pressure and low space velocity with typical values of 1200 psig and 0.13 h^{-1} .

When preliminary analysis indicated successful heteroatom removal in the $250 - 320 \text{ }^{\circ}\text{C}$ temperature window, a second stage of hydrotreating was performed on the first stage product. The increase in thermal stability induced by the first stage hydrotreating was required before the second stage hydrotreating could occur.

Summary of operation results

The sample of crude liquefaction oil used for the scoping experiments possessed the qualities given in **Table 9**.

Table 9. Properties of crude liquefaction oil

Property	Value
C, wt%	71.5
H, wt%	8.2
N, wt%	1.4
O, wt%	18.9
Total Acidity	17.3
H ₂ O, wt%	9.8

Attempts at hydrotreating this sample of liquefaction oil at $320 \text{ }^{\circ}\text{C}$ with Albemarle KF-757 resulted in formation coking of the oil inside the hydrotreating reactor. This phenomenon resulted in total plugging of the fixed bed reactor and required a shutdown of the system. No upgraded products were produced during this trial.

Attempts to avoid coke formation at $320 \text{ }^{\circ}\text{C}$ by dissolving the crude liquefaction oil in methyl-tetrahydrofuran were not successful. While the feedstock was soluble, no upgraded products were produced. All of the liquefaction oil resulted in coke formation of the catalyst surface. The addition of a high boiling solvent, diesel fuel, likewise had no effect.

A substantially lower temperature was required to avoid coke production. As the heteroatom removal would be less effective at this temperature, the space velocity was decreased to allow maximum reaction time. Properties of the crude liquefaction oil appear in the first row. The results appear in **Table 10**.

Table 10. Properties of crude and hydrotreated liquefaction oil

Hydrotreating Temperature °C	%C	%H	%N	%O	TAN mg KOH / g
---	70.44	8.32	1.45	19.79	24.61
270	81.08	9.64	1.68	7.60	15.07
280	81.35	9.25	1.79	7.61	14.95
290	82.53	9.57	1.76	6.14	18.80
300	81.79	9.58	1.71	6.92	4.36

Little oxygen removal was observed. The drop in oxygen content from the crude oil value of 19.79% to 6-7% is the result of removing the entrained water. Some improvement in total acid number was observed dropping from 24.6 mg KOH/g to 18.8 mg KOH /g at 290 °C and 4.36 mg KOH / g.

A sample of crude liquefaction oil produced with water recycle was subjected to hydrotreating with Albemarle KF-757 with similar results as shown in **Table 11**.

Table 11. Properties of crude and hydrotreated liquefaction oil

Hydrotreating Temperature °C	%C	%H	%N	%O	TAN mg KOH / g
---	71.28	8.43	1.58	18.7	30.27
270	81.11	9.70	1.80	7.39	12.02
280	81.57	9.63	1.88	6.92	7.52
290	82.78	9.97	1.87	5.38	4.49
300	84.18	10.28	1.77	3.77	3.19

Some improvement was observed, but the product is still unacceptably high in total acid number.

The final sample processed was produced during a production run. Some initial bench-top measurements indicated higher thermally stability with the crude liquefaction oil and heteroatom removal was attempted with both Albemarle HDO-1 and HDO-2 catalysts. **Table 12** shows the results from hydrotreating at 290 – 320 °C.

Table 12. Properties of crude and hydrotreated liquefaction oil using developmental catalysts

Catalyst	Hydrotreating Temperature °C	%C	%H	%N	%O	TAN mg KOH / g
	---	84.2	7.9	1.71	6.1	13.0
HDO-2	290	84.0	11.0	1.38	3.6	0.32
HDO-2	300	84.8	10.6	1.73	2.8	<0.05
HDO-2	310	85.4	10.8	1.62	2.2	<0.05
HDO-2	320	84.2	10.3	1.77	1.6	0.09
HDO-1	290	83.8	10.8	1.54	3.9	<0.05
HDO-1	300	84.9	10.9	1.49	2.8	<0.05
HDO-1	310	82.3	11.0	1.32	5.4	<0.05
HDO-1	320	85.9	11.4	1.16	1.5	<0.05

The total acid number in the upgraded product is substantially lower at 290 °C than previous trials. Acid number less than 1 remained after hydrotreating at 290 °C compared with 4.49 and 18.8 mg KOH / g using the KF-757 catalyst. Using the HDO-1 catalyst at 320 °C also appeared to remove a portion of the nitrogen heteroatom, a phenomenon not observed previously. These results, coupled with the higher apparent thermal stability, led to attempts at a second, higher temperature hydrotreating stage. The results using the products collected in the first stage hydrotreated at 350 – 380 °C appear in **Table 13**. The listed values indicated with a hydrotreating temperature range are the mean values of the properties after the first hydrotreating

Table 13. Properties of crude and hydrotreated oil using developmental catalysts after 2nd stage

Catalyst	Hydrotreating Temperature °C	%C	%H	%N	%O	TAN mg KOH / g
HDO-2	290-320	84.6	10.7	1.6	2.6	0.21
HDO-2	350	87.0	12.5	0.47	0.0	<0.05
HDO-2	365	87.5	12.1	0.29	0.1	<0.05
HDO-1	290-320	84.2	11.0	1.4	3.4	<0.05
HDO-1	350	87.4	12.6	0.00	0.1	<0.05
HDO-1	365	87.1	12.1	0.00	0.8	<0.05
HDO-1	380	87.7	12.2	0.00	0.0	<0.05

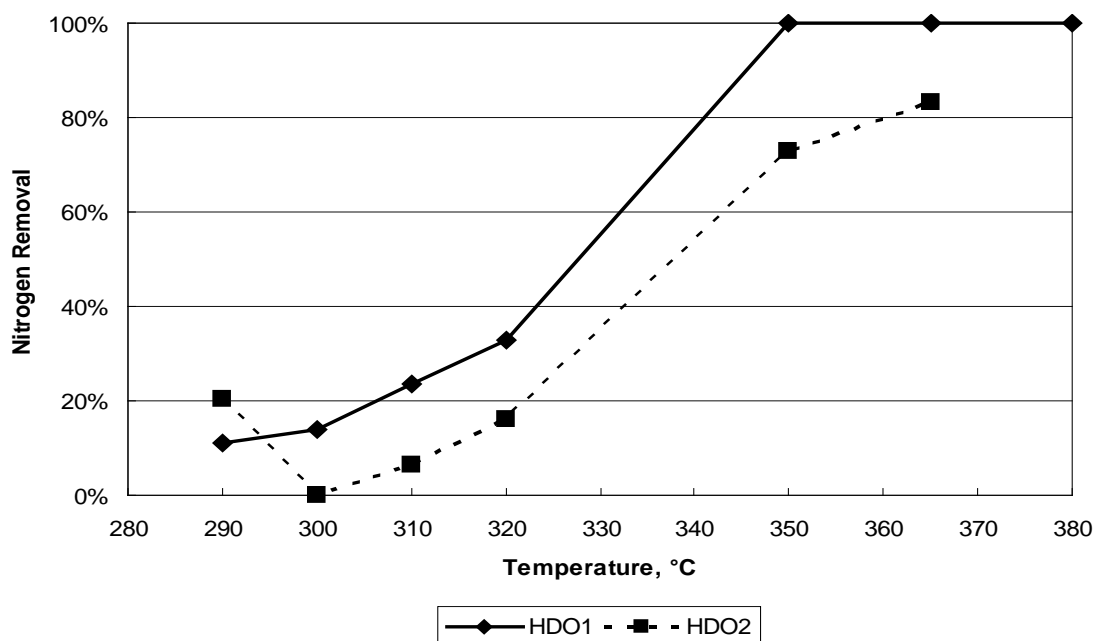


Figure 15. Apparent nitrogen removal activity as a function of hydrotreating temperature.

stage conducted within the 290-320 °C range. The products collected at 290, 300, 310, and 320 °C were combined to generate the feed for the second, higher temperature, hydrotreating stage. The preliminary analysis indicates nearly complete removal of the oxygen content and nitrogen content. HDO-1 showed higher apparent nitrogen removal activity as depicted in **Figure 15**.

The hydrotreated products from the HDO-1 trial were combined into one sample and fractionated into transportation fuel boiling ranges with the results appearing in **Table 14**.

Table 14. Boiling range composition of upgraded liquefaction oil

Fraction	Mass Percent	Silicon ppm	Nitrogen ppm
Gasoline 0-380 °F	13.7	70.7	24.4
Distillate 380-650 °F	58.3	36.5	288.9
Heavy 650-1000 °F	26.1	63.5	
Ultraheavy >1000 °F	1.8	n/a	

Each fraction was subjected to a battery of analytical assays to aid in determining the value of each fraction. Metals analyses showed only silicon as levels of all other metals were below the limit of detection, typically ~1 ppm. Trace nitrogen was about 10-fold higher in the distillate fraction than in the gasoline fraction. It can be assumed that the nitrogen content in the heavy and ultraheavy fractions was higher than the distillate, but available assays were not suitable for these samples.

Fuels and compositional properties of each fraction appear in the following **Tables 15 - 18**.

Table 15. Distillation properties of each fraction

%OFF	Gasoline	Distillate	Heavy
ibp	189.5	374.1	560.4
10%	278.0	430.7	659.8
50%	358.0	543.7	743.1
90%	411.1	654.3	854.5
fbp	474.7	782.0	999.9

Table 16. Fuel properties of liquefaction oil fractions

Property	Gasoline	Distillate	Heavy
Specific Gravity	0.827	0.973	1.157
API Gravity	39.6	14	-9.2
RVP, psi	6.173		
Cetane Index	n/a	22.48	n/a

Table 17. Results from detailed hydrocarbon analysis of gasoline fraction produced from hydrotreating liquefaction oil

Gasoline		
Group	%Wgt	%Vol
Aromatics	26.2	24.1
Paraffin	3.6	4.0
I-Paraffins	18.8	20.7
Naphthenes	22.4	23.1
Unidentified	28.9	28.1
Plus	0.1	0.1
Olefins	0.0	0.0
Oxygenates	0.0	0.0
Carbon Number	%Wgt	%Vol
C4	0.0	0.0
C5	0.0	0.0
C6	0.4	0.4
C7	1.3	1.5
C8	4.5	4.7
C9	17.0	17.5
C10	29.4	29.3
C11	13.4	13.6
C12	4.7	4.6
C13	0.2	0.2
C14	0.1	0.1
Group	RON	MON
Aromatics	24.4	25.3
Paraffin	-1.8	-1.8
I-Paraffins	15.1	15.5
Naphthenes	19.2	16.4
Unidentified	20.8	21.7
Plus	0.1	0.1
Olefins	0.0	0.0
Oxygenates	0.0	0.0
Total Linear RON = 77.81		
Total Linear MON = 77.08		
Total Calculated RON = 79.30		
Total Calculated MON = 78.76		

Table 18. Results from NOISE analysis of distillate and heavy fractions produced from hydrotreating liquefaction oil

	Distillate	Heavy
Group	%Wgt	%Wgt
Paraffin	6.97	9.72
I-Paraffins	2.85	1.85
Cycloalkanes	61.11	15.34
1-ring Aromatics	23.74	23.53
2-ring Aromatics	5.10	34.75
3-ring Aromatics	0.23	12.30
4-ring Aromatics	0.00	2.43
5-ring Aromatics	0.00	0.07
Carbon Number	%Wgt	%Wgt
5	0.00	0.00
6	0.00	0.03
7	0.00	0.00
8	0.00	0.00
9	0.01	0.00
10	0.32	0.00
11	3.70	0.02
12	10.28	0.07
13	12.74	0.09
14	13.17	0.09
15	12.63	0.10
16	12.52	0.44
17	10.37	1.64
18	10.24	4.09
19	5.59	7.40
20	3.69	10.48
21	2.23	12.13
22	1.34	12.55
23	0.70	11.51
24	0.33	9.65
25	0.11	7.24
26	0.04	5.99
27	0.00	4.29
28	0.00	3.81
29	0.00	3.03
30	0.00	1.78
31	0.00	1.15
32	0.00	0.96
33	0.00	0.57
34	0.00	0.40
35	0.00	0.25
36	0.00	0.16
37	0.00	0.04
38	0.00	0.00
39	0.00	0.00
40	0.00	0.00
average # of carbons	15.5	23.1
average # of hydrogens	27.2	36.4
average # of oxygens	0.00	0.00
average # of sulfurs	0.00	0.00
average # of nitrogens	0.00	0.00
average molecular weight	213.4	313.2
phenolic oxygen, wt%	0.00	0.00
thiophenic sulfur, wt%	0.00	0.00
carbazolic nitrogen, wt%	0.00	0.00

Evaluation of Bio-Oil for Catalytic Cracking

The bio-oil from the 1 gallon sample of corn fiber was assessed for its potential for catalytic cracking co-processing with refinery gas oil feedstock. Attempts were made to solubilize or suspend the bio-oil in gas oil for feeding into an ACE™ FCC laboratory testing reactor. Two different gas oils were used, one with a high aromatic content and one with a high aliphatic content. The samples were warmed to 40 °C in an ultrasonic bath to facilitate mixing. The bio-oil was immiscible with both gas oils at concentrations ranging from 5 wt% - 20 wt% bio-oil. In a second set of experiments, the emulsifiers, Atlox 4919 and Atlox 4912, were added to the blends at 1 wt% and 4 wt% in conjunction with warming and ultrasonication. In all cases, within a few minutes the bio-oil separated and formed a streaky film on the walls of the vessel and collected at the bottom. Because of the concern that a phase separation in the feed line to the ACE™ unit would lead to variable (and unverifiable) feed rate of bio-oil into the reactor, efforts were instead focused on hydroprocessing upgrading.

Other properties of the bio-oil that need to be considered for the FCC processing are the high nitrogen content and thermal instability. The bio-oils from corn fiber and corn stover had nitrogen contents of 4 wt% and 1.27 wt%, respectively. Higher catalyst/oil ratios would be needed to compensate for the deactivation by nitrogen. Typical inlet temperatures to the FCC reactor are in the range of 290 – 340°C. A distillation experiment with corn stover bio-oil showed that it converted to coke at 320°C, therefore one would quickly foul (coke up) the process feed preheaters prior to entering the FCCU.

Techno-Economic Assessment

- Developed a baseline process model to allow techno-economic assessments.
- Utilized the model to identify the potential technical improvements that have the most significant impact on process economics.
- Permutations to the baseline model, such as the evaluation of the eliminations of catalyst and reducing gas in the liquefaction step were addressed.
- Using ADM's market information, an assessment of the scale of operation based on availability of feedstock was also undertaken. As experimental data was obtained, the model was updated throughout the life of the project.
- ConocoPhillips contributed the modeling of the upgrading portion to produce fuels.

Hydrothermal Liquefaction: CapEx and OpEx

CapEx

The liquefaction section costs have been estimated after the paper by Goudriaan et al. (2000)³. It is assumed that the unit that has been designed in the referred document can be scaled to a 525 kton/yr biomass feed on a dry basis, with a service factor of 0.959 (350 days per year). The reference case contemplates the treatment of the waste water, so a 20% reduction in capital, electricity and external fuel was implemented for discounting this part of the process that is not employed in the present setup.

The reference has a 30 million dollar (M\$) CapEx (15% contingency) for a feedstock of 130 kton/yr (db), on 2000 US\$. This represents a 73.76M\$ investment for a 525 kton/yr feedstock today, using CEPCI Ann.Index 2000 at 394.1, and the December Preliminary Index 2009 at 524.2, along with the 0.6 scale up rule and the 20% discount because of waste water treatment not used here.

The net biocrude production has been taken from test #17a, at a 17.82%wt yield on a dry basis.

The OSBL has been calculated at 25% of the Equipment Installed Cost and is 18.44M\$. The Total Installed Cost (TIC) is 92.20M\$ for a plant processing 525 kton/yr of dry feedstock.

³ Goudriaan, F., van de Beld, B., Boerefijn, F.R., Bos, G.M., Naber, J.E., van der Wal, S. and Zeevalkink, J.A., Thermal efficiency of the HTU[®] Process for Biomass Liquefaction, in "Progress in Thermochemical Biomass Conversion", Tyrol, Austria, Sept.2000.

OpEx

Feedstock has been priced at \$60/ton (db), capital is charged at 10% (linear), and maintenance + overhead+ insurance+ taxes + royalties were taken at 6% as in the reference paper, for the sake of similarity. Labor was charged for the same number of workers per shift, at the same level as in reference, but the salaries were adjusted by inflation using inflationdata.com and the feedstock flow rate. It was taken the inflation estimated since June 2000 to January 2010 that it turned to be 25.69%.

Electricity was priced at 50.00 \$/MWh and natural gas was priced 5.00 \$/MBTU. The OpEx shown by Goudriaan et al. was used on a feedstock flow rate basis and was scaled up using the updated prices referred above and feedstock flow rate. Electricity and natural gas contributed 16.84 \$/ton and 6.21\$/ton oil product respectively. **Table 19** summarizes all the results above.

Table 19. Hydrothermal liquefaction Economics for a 525 kton/yr Dry Biomass Feed. [1 ton = 1,000 kg]

Capacity intake (kton/yr) (db)	525		
Net biocrude prod.(kton/yr)	93.56		
Installed capital(M\$)	73.76	(15% contingency)	
	M\$/yr	\$/ton prod	%
Capital charge (10%)	7.38	78.84	15.62
Feedstock (\$/dt)	31.50	336.70	66.71
Labor	1.76	18.81	3.73
Maintenance,Ovh,etc 6%	4.43	47.31	9.37
Electricity	1.58	16.84	3.34
External Fuel	0.58	6.21	1.23
TOTAL	47.22	504.71	100.00
OSBL(25% IC)	18.44		
TIC(M\$)	92.20		
\$/GJ	15.086		
\$/gal	2.121		

The HHV estimated for the Biocrude composition from test # 17a was used for calculating the OpEx on a product energy basis, as in the referred paper.

The correlation by Dermirbas⁴ was used for a dry basis composition of Biocrude of: 75.05% wt C, 7.42% wt H, 13.23% wt O and 1.41% wt N.

The OpEx can also be reported on a gallon basis, with an oil density of 1,110 kg/cm as reported in test #17a. In this case the resulting cost was 2.12 \$/gal.

Two major differences can be noticed when compared with Goudriaan et al. work: 1) feedstock has been incorporated in this work, when in the reference this input was ignored; 2) the biocrude yield in the present work (17.82%) is noticeable lower than the 37% yield reported by Goudriaan et al.

For this reason sensitivities were estimated around these two parameters that are shown in **Tables 20 and 21**.

Table 20. Operational Cost Sensitivity to Biocrude Yield at 60\$/ton Biomass

Biocrude Yield (%wt)	OpEx (k\$/ton product)	OpEx (\$/gal)
10	0.899	3.779
20	0.450	1.890
30	0.300	1.260
40	0.225	0.945

Notes: Costs on a dry basis (db). All other OpEx costs fixed as base case on a 525 kton/yr (db) biomass feed.

Table 21. Operational Costs Sensitivity to Feedstock price (\$/ton,) at 17.82% wt Biocrude Yield. All other OpEx costs fixed as base case on a 525 kton/yr (db) biomass feed.

Feedstock price (\$/ton) (db)	OpEx (k\$/ton product)	OpEx (\$/gal)
20	0.280	1.178
60	0.505	2.121
100	0.729	3.064
140	0.954	4.007

Notes: Costs on a dry basis (db). All other OpEx costs fixed as base case on a 525 kton/yr (db) biomass feed.

⁴ Demirbas, A., Calculation of higher heating values of biomass fuels, Fuel, 76, 431-434(1997).

The cost per unit mass of oil product improves with increased biocrude yield (see Table 19) at a fixed feedstock price. A four-fold bio-oil yield increase translates into a 75% OpEx reduction on a product oil basis. The feedstock price also has a significant impact upon OpEx value on a product oil basis as seen from **Table 21**.

As a reference market value, NYMEX Heating Oil Future price closed at 2.25 \$/gal on 04/23/2010. Biocrude yield improvements have the potential of greatly enhancing the HTL economics, along with the usage of the most economic feedstock.

Hydrotreating: CapEx and OpEx

The CapEx and OpEx for the dual-stage hydrotreating process have been estimated at \$58.6 Mand \$31.8 M, respectively. The estimate for the CapEx (**Table 22**) is based on January 2008 costs of equipment inflation escalated to present day. The magnitude of the process was based on 1500 dry tons per day corn stover fed to the hydrothermal liquefaction stage producing 267.3 tons per day raw oil (dry basis) with a composition of 77.2%C, 7.6%H, 13.6%O, 1.5%N, and 0.1% S. With the final product after two stages of hydrotreating having a composition of 87.8%C and 12.3%H, the total hydrogen consumption is 15.3 MM SCFD. The breakdown of the OpEx is shown in **Table 23**.

Table 22. Major Equipment for Capital Expense Estimate

Component Name	Equipment Cost	No. of items	Total Equipment Cost	Cost Factor	Total Direct Costs	% of Cost		
Charge Tank	\$ 547,300	1	\$ 547,300	2.00	\$ 1,094,600	4.1		
Feed Pump	\$ 90,400	2	\$ 180,800	4.00	\$ 723,200	2.7		
Alcohol Rxn Preheater	\$ 30,600	1	\$ 30,600	3.50	\$ 107,100	0.4		
Alcohol Rxr Rxfeed/RX exchanger	\$ 111,900	1	\$ 111,900	3.50	\$ 391,650	1.5		
Low temp reactor	\$ 1,920,000	1	\$ 1,920,000	4.00	\$ 7,680,000	28.9		
RXR Feed/Effluent Heat Exchanger	\$ 98,000	1	\$ 98,000	3.50	\$ 343,000	1.3		
Trim Heater	\$ 256,700	1	\$ 256,700	3.50	\$ 898,450	3.4		
High temp reactor	\$ 1,920,000	1	\$ 1,920,000	4.00	\$ 7,680,000	28.9		
Reactor HP Flash Column	\$ 106,900	1	\$ 106,900	4.00	\$ 427,600	1.6		
Recycle Compressor	\$ 1,323,900	1	\$ 1,323,900	2.20	\$ 2,912,580	11.0		
Reactor Cooler	\$ 924,600	1	\$ 924,600	3.50	\$ 3,236,100	12.2		
UPGRADE.DMDSPUMP	\$ 38,900	2	\$ 77,800	4.00	\$ 311,200	1.2		
Feed 2/RXR Effluent HX	\$ 32,200	1	\$ 32,200	3.50	\$ 112,700	0.4		
150# steam HX	\$ 50,300	1	\$ 50,300	3.50	\$ 176,050	0.7		
Product Storage	\$ 200,000	1	\$ 200,000	2.00	\$ 400,000	1.5		
DMDS Storage Tank	\$ 9,300	1	\$ 9,300	4.00	\$ 37,200	0.1		
Intermediate Storage Tank	\$ 241,900	1	\$ 241,900	2.00	\$ 483,800	1.8		
			\$ 8,032,200					
					TOTAL Equipment Cost	Jan-08		
					\$ 26,531,430	Total Direct Field Cost		
					\$ 13,265,715	Indirect Costs (% of DFC)	50	
					\$ 39,797,145	Total Direct and Indirect Costs		
					\$ 11,939,144	Contingency and Cost Growth Allowance	30	
			46		\$ 51,736,289	Current Costs (1st Qtr 2008)		CE Index
					\$ 51,065,509	Escalation to current costs	0.9870	532.9
					\$ 51,065,509	Total Capital Cost (Future)		
					\$ 51,065,509	Total Capital Cost (Location Adjusted)	1	Midwest
					\$ 51,000,000	Rounded Capital Cost		
					4.95	"Lang Factor" before contingency		
					6.35	"Lang Factor" after contingency		

Table 23. Estimate of Operating Expenses

	Factor		
Fixed Capital Investment			\$51,000,000
Working Capital	15%		\$7,650,000
Total Plant Investment			\$58,650,000
Operating Expenses		Units/hr	
<i>Raw Materials:</i>			
Feed to upgrader, \$/lb	0	24503	\$0
<i>Labor:</i>			
Operating Labor, \$/yr/(operator/shift)	279,552	3	\$838,656
Maintenance Labor	1.5 % FCI		\$765,000
Laboratory	20 % operating labor		\$167,731
Supervision	15 % operating labor		\$125,798
<i>Utilities:</i>			
1000# Steam, \$/Klbs	8.00	62.27	\$3,945,427
Electricity, \$/kwh	0.050	1957	\$774,972
Cooling Water, \$/Mgal circulating (20 F dT)	0.060	621.4	\$295,289
Waste water treatment, \$/Kgal	3.00	7.19	\$170,834
150# Steam credit, \$/Klbs	5	-18.365	-\$727,254
<i>Catalysts and Chemicals:</i>			
Maintenance materials	1.5 % FCI		\$765,000
General	0.5 % FCI		\$255,000
Hydrogen, 435# (from NG), \$/KSCF	2.48	637.5	\$12,521,520
Hydrogen, 435# (from offgas stream), \$/KSCF	2.67	0	\$0
HT Catalyst 1 Costs, \$/lb	20.00	128963	\$2,579,260
HT Catalyst Replacements per yr	1		
HT Catalyst 2 Costs, \$/lb	20.00	128963	\$2,579,260
Alcohol HT Catalyst Replacements per yr	1		
DMDS usage, \$/KT	2300	0.00424	\$77,236
Plant Overhead	60 % Total Labor		\$1,138,311
Insurance and Taxes	2 % FCI		\$1,020,000
Corporate	80% Total Labor		\$1,517,748
Operating Costs (Reformer for offgas)			\$3,000,000
TOTAL OPERATING COSTS			\$31,809,790
Hours on stream	7920		

Catalytic Hydrothermal Gasification: Technoeconomic Assessment

The CapEx of the catalytic hydrothermal gasification of the aqueous phase byproduct was assessed. Using the information in the PNNL study of Catalytic Hydrothermal Gasification of Lignin-Rich Biorefinery Residues and Algae⁵ a rough order of magnitude estimate was generated for gasification of the aqueous phase. The yield of aqueous phase was used from the same experiment, test #17a, as was used for the HTL CapEx estimates and the scale was adjusted from that in the report to that used in this study for HTL. The gas yields are based on test #2 in [Table 8](#). Based on a Total Equipment Cost from the report of \$14M for a plant processing 3.64 Mtonne/y, a plant of 4.93 Mtonne/yr for the HTL case would cost about \$16.8M (using a power of 0.6 to scale). In the report the Total Project Investment is given as \$52M including all the direct (installations, instrumentation and control, piping, electrical, building and services, yard improvements) costs and the indirect (engineering, construction, legal & contract fees, contingency) costs.

An important question also addressed in this assessment was the potential for hydrogen production using the gas product. Again, using the data in [Table 8](#) for gas yield and composition, and scaling to the plant size used in the HTL assessment, the yield of methane gas could be used to generate well in excess of the hydrogen requirement for the upgrading of the bio-oil to hydrocarbon fuels. The stoichiometric yield of hydrogen from the 10.5 MSCF/d methane when processed by steam reforming could generate as much as 42 MSCF/d of hydrogen compared to the requirement for hydrotreating of 15 MSCF/d. With other assumptions of reduced yield due to process efficiency, clearly there is sufficient methane produced with excess available for other process heating requirements.

Conclusions

Hydrothermal liquefaction can be applied to corn fiber, corn starch, or corn stover in water slurry to produce a bio-oil with 10-15% oxygen on a dry basis. Overall carbon basis yields for the several feedstocks ranged from 20% for starch. 50-55% for fiber and 30-35% for stover. The undesirable oxygen content of these HTL bio-oils is much lower than that achieved through fast pyrolysis of biomass, but at the expense of a lower bio-oil yield. The bio-oil can usually be gravity separated from the aqueous byproduct but the formation of a stable emulsion was seen during the processing of corn stover. It was thought that the mineral (ash) content of the feedstock caused this phenomenon therefore a mineral separation step prior to phase separation was developed. Only a small fraction of the biomass is converted to a gas byproduct (5-10% of

⁵ Elliott, DC, et al. *Catalytic Hydrothermal Gasification of Lignin-Rich Biorefinery Residues and Algae: Final Report*, PNNL-18944, Pacific Northwest National Laboratory, Richland, WA, **October 2009**.

the carbon) consisting mainly of carbon dioxide. The balance of the carbon is found in dissolved organics in the aqueous byproduct stream. Recycle of this aqueous stream as the solvent in the preparation of the feed slurry appears to facilitate the conversion of water soluble organics to bio-oil. Additionally, the aqueous byproduct stream can be processed via catalytic hydrothermal gasification technology to produce fuel gas and a low BOD aqueous stream. The methane produced through gasification could be reformed into hydrogen and is sufficient to provide all the hydrogen required for upgrading the bio-oil to fuel.

The bio-oil product can be hydroprocessed in two stages to form hydrocarbons. Fractionation of the resulting product showed 14 wt% gasoline range, 58 wt% diesel range, and 28 wt% gas oil. The gasoline fraction had an octane value of 79 and could be used as a sub octane blending component. The diesel boiling range fraction had high aromatics content and would be suitable for distillate blending, solvent applications, or further processing via catalytic cracking. The gas oil fraction could be blended into fuel oil or further processed via catalytic cracking.

Based on the techno-economic analysis of the process, the overall capital expense for a unit capable of processing 525,000 mt/year is approximately \$125 million. The annual operational expense including feedstock costs is approximately \$72 million. Based on a yield of 42.5 gallons upgraded bio-oil per metric ton of corn stover, the minimum selling price of the bio-oil is \$4.11 per gallon (\$172.62/bbl). Because further refinery processing is required to incorporate the bio-oil into a final finished fuel, the bio-oil would have a break-even value to a refiner similar to light to medium gravity low sulfur crude oil or condensate. The current premiums for these grades of crude oil range from \$3-7 over NYMEX WTI. Thus the current price structure of the crude market does not support commercialization of this process at its current stage of development.

Currently both ADM and ConocoPhillips do not plan to conduct further research and development with this process. Significant barriers to commercialization of this technology are identified as follows:

- Low primary oil yield
- Energy consumption for grinding biomass into a slurry
- Process and product sensitivity to feedstock impurities.
- Hydrogen requirements for upgrading

Significant technical improvements addressing these barriers are needed before warranting additional evaluation of this technology.

APPENIDX A
Data Sheets for Hydrothermal Liquefaction

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-1					reactor volume	1000 600	total mL mL at temperature	
Pressure	20.2 MPa 2918 psi	Reactor Temperature degrees C	158 346 357		Time	10:30-11:20			
					Date	5 Jun-08			
Total Feed	1657 cc	Feed rate	2000 cc/hr						
ground corn fiber			2020.00 g/hr						
Total Product	1697.4 g				Product oil	116.4 g/hr	sum of two phases	2036.9 g/hr	
					Product aqueous	1920.5 g/hr			
Elemental Analyses		C	H	O	density	moisture	N	S	ash
feed		46.24%	6.58%	46.55%	1.01	87.30%	2.04%	0.33%	0.89%
product oil		69.31%	7.40%	19.85%	1.14	12.56%	2.70%	0.29%	102.61%
aqueous		1.59%	11.20%	87.16%	1.0 est	97.00%	0.05%		99.55%
oxygen by difference									100.00% actual measured 84.64%
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
feed		118.61	214.55	1685.19	2018.35				
product oil		80.68	8.61	23.11					
aqueous		30.54	215.10	1673.91					
gas		4.46	0.00	11.87					
Total Products		115.67	223.70	1708.88	2048.26				
Elemental Balance		98%	104%	101%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>	101%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr	0.00 g H/hr					
Gas Out	304.8 L/hr		12.70 moles/hr						
Gas Composition			moles/hr						
volume%	C	H	O						
Hydrogen	0.00%		0.00	0.00 gH/hr					
CarbDioxide	2.92%	0.37		0.74					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00						
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00			2.94			
	2.92%								
Total Gas, C1-C4		4.46	0.00	11.87	16.33	Total gas			
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil			
		4.46	0.00	11.87	16.33	Total gas mass out			
Yields									
Oil Product Yield		101.78 g/hr	89.28 ml/hr	density, 1.14 g/ml	68.02% carbon conversion to oil				
					0.04 L/L feed				
Oil Loss in Aqueous		57.62 g/hr	57.62 ml/hr	density, est 1 g/ml	39.67% mass conversion to oil				
					0.03 L/L feed				
Gasification of Carbon	3.76%				25.74% carbon conversion to water solubles				
Hydrogen Consumption		0.00 g/hr in -	0.00 g/hr out =		0.00 g/hr consumption				
					0.00 L/hr consumption				
					0.00 L/L feed				
					0 g/g feed				
Space velocity	3.33 L/L/hr	LHSV							
Chemical Hydrogen Consumption		0.00 g/hr	0 L/L	0 nM3/tonne					
Calculation of Deoxygenation									
O content of dry product	9.93%								
O in Dry Product	10.11 g/hr								
O in Organics(H2O)	18.01 g/hr---->								
O in Dry Feed	119.41 g/hr								
Deoxygenation	76.45%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-2					CSTR volume	1000 mL		
						reactor volume	800 mL, at temp	1000 mL, total	
Pressure	20.9 MPa		CSTR Reactor	266					
	3019 psi		Tube temp,	313 bottom		Time	9:30-11:30		
			degrees C	356 top		Date	12-Jun-08		
Total Feed	4002 cc		Feed rate	2001 cc/hr					
ground corn fiber	193467	COD, ppm		2021.01 g/hr					
Total Product	4076.1 g					Product oil	52 g/hr	sum of two phases	2038
						Product aqueous	1986 g/hr		g/hr
Elemental Analyses									
		C	H	O	density	moisture	N	S	ash
feed		47.81%	5.69%	47.20%	1.01	87.28%	1.90%	0.21%	0.89%
product oil		71.51%	7.52%	19.39%	1.14	8.43%	2.80%	0.29%	103.68%
oxygen by difference		0.95%	9.16%	89.84%	1.0 est	97.00%	0.05%		101.51% actual measured
aqueous									100.00%
Material Balance		g C/hr	g H/hr	g O/hr		Total	TAN	Viscosity	
feed		122.89	212.35	1687.53		2022.77			
product oil		37.19	3.91	10.08					
aqueous		18.77	181.92	1784.22					
gas		4.27	0.00	11.38					
Total Products		60.22	185.83	1805.68		2051.73			
Elemental Balance		49%	88%	107%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>	>>>>>>>	101%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	292 L/hr		12.17 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr				
CarbDioxide	2.92%	0.36		0.71					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00						
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94		
	2.92%								
Total Gas, C1-C4		4.27	0.00	11.38	15.65	Total gas			
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil			
		4.27	0.00	11.38	15.65	Total gas mass out			
Yields									
Oil Product Yield		47.62 g/hr		41.77 ml/hr		30.26% carbon conversion to oil			
		density,		1.14 g/ml		0.02 L/L feed			
Oil Loss in Aqueous		59.58 g/hr		59.58 ml/hr		18.52% mass conversion to oil			
		density, est		1 g/ml		0.03 L/L feed			
Gasification of Carbon	3.47%					15.27% carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -		0.00 g/hr out =		0.00 g/hr consumption			
						0.00 L/hr consumption			
						0.00 L/L feed			
						0 g/g feed			
Space velocity	2.50 L/L/hr		LHSV						
Chemical Hydrogen Consumption			0.00 g/hr		0 L/L	0 nM3/tonne			
Calculation of Deoxygenation									
O content of dry product	12.99%								
O in Dry Product	6.19 g/hr								
O in Organics(H2O)	71.85 g/hr----->								
O in Dry Feed	121.33 g/hr								
Deoxygenation	35.68%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-3								
Pressure	20.5 MPa 2965 psia	CSTR Reactor Tube temp. degrees C	347 338 350	bottom top	Time Date	9:35-12:30 18-Jun-08			
Total Feed	5837 cc	Feed rate	2001 cc/hr						
ground corn fiber	10.22 pH		2021.01 g/hr						
Total Product	199.867 COD, ppm 5787.2 g	15.2 wt% Na2CO3 on dry corn fiber	6.60 wt% Na	Product oil 86.2 g/hr	sum of two phases 7.71 pH	1984.2 g/hr			
Elemental Analyses									
normalized	feed	C	H	O	density	moisture	N	S	ash
oxygen by difference	product oil	46.00%	5.60%	45.40%	1.01	85.26%	1.90%	0.21%	0.89%
	aqueous	77.65%	8.06%	9.34%	1.3	7.79%	2.01%	0.27%	100.00%
		2.21%	9.10%	88.60%	1.0 est	92.83%	0.05%		97.32% actual measured
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
	feed	137.03	209.84	1665.20	2012.07				
	product oil	66.93	6.95	8.05					
	aqueous	41.99	172.62	1681.63					
	gas	9.20	0.00	24.51					
	Total Products	118.13	179.57	1714.19	2011.89				
	Elemental Balance	86%	86%	103%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>>>>>	100%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	301.4 L/hr		12.56 moles/hr						
Gas Composition	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr				
CarbDioxide	6.10%	0.77		1.53					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00						
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.17%	0.15	0.30	0.00		2.94			
	6.27%								
	C g/hr	H g/hr	O g/hr						
Total Gas, C1-C4	9.20	0.00	24.51	33.71	Total gas				
Total Gas Oil, C5-C7	1.79	0.30	0.00	2.10	Total gas oil				
	11.00	0.30	24.51	35.81	Total gas mass out				
Yields									
Oil Product Yield	79.49 g/hr		72.26 ml/hr		48.85% carbon conversion to oil				
	density,		1.1 g/ml		0.04 L/L feed				
Oil Loss in Aqueous	136.09 g/hr		136.09 ml/hr		26.68% mass conversion to oil				
	density, est		1 g/ml		0.07 L/L feed				
Gasification of Carbon	6.71%				30.64% carbon conversion to water solubles				
Hydrogen Consumption	0.00 g/hr in -		0.00 g/hr out =		0.00 g/hr consumption				
					0.00 L/hr consumption				
					0.00 L/L feed				
					0 g/g feed				
Space velocity	2.22 L/L/hr		LHSV						
Chemical Hydrogen Consumption		0.00 g/hr		0 L/L		0 nM3/tonne			
Calculation of Deoxygenation									
O content of dry product	2.61%								
O in Dry Product	2.08 g/hr								
O in Organics(H2O)	115.48 g/hr----->								
O in Dry Feed	135.25 g/hr								
Deoxygenation	13.08%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-3								
Pressure	20.5 MPa	CSTR Reactor	347		CSTR volume	1000 mL			
	2967 psig	Tube temp.	338	bottom	reactor volume	900 mL, at temp			
		degrees C	350	top	Time	12:55-15:35			
					Date	18-Jun-08			
Total Feed	5323 cc	Feed rate	1996.1	cc/hr					
ground corn fiber	10.22 pH		2016.06	g/hr					
	199.867 COD, ppm		15.2	wt% Na2CO3 on dry corn fiber					
Total Product	5321.8 g	6.60 wt% Na		Product oil	94.9 g/hr	sum of two phases	1995.7		
				Product aqueous	1900.8 g/hr	7.77 pH			
	actual feed	47.81%	5.69%	47.20%		1.90%	0.21%		
Elemental Analyses	C	H	O	density	moisture	N	S	ash	
normalized feed	46.00%	5.60%	45.40%	1.01	85.26%	1.90%	0.21%	0.89%	100.00%
product oil	76.44%	8.01%	10.53%	1.1	11.10%	2.53%	0.27%		97.78% actual measured
oxygen by difference aqueous	2.20%	9.08%	88.70%	1.0 est	95.00%	0.05%			100.03%
Material Balance		q C/hr	q H/hr	q O/hr	Total	TAN	Viscosity		
feed	136.70	209.33	1661.12		2007.15				
product oil	72.54	7.60	9.99						
aqueous	41.77	172.59	1686.01						
gas	12.94	0.00	34.47						
Total Products	127.24	180.20	1730.48		2037.92				
Elemental Balance	93%	86%	104%						
Total Material Balance	102%								
GAS CALCULATIONS									
Gas In	0 L/hr	0.00 moles/hr	0.00 q H/hr						
Gas Out	311.5 L/hr	12.98 moles/hr							
Gas Composition		moles/hr							
volume%	C	H	O						
Hydrogen	0.00%	0.00		0.00 qH/hr					
CarbDioxide	8.30%	1.08	2.15						
CarbMonoxide	0.00%	0.00	0.00						
Methane	0.00%	0.00	0.00						
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.40%	0.36	0.73	0.00		2.94			
	8.70%								
Total Gas, C1-C4	12.94	0.00	34.47	47.41	Total gas				
Total Gas Oil, C5-C7	4.36	0.73	0.00	5.10	Total gas oil				
	17.30	0.73	34.47	52.51	Total gas mass out				
Yields									
Oil Product Yield	84.37 g/hr	76.70 ml/hr	53.06% carbon conversion to oil						
	density, g/hr	1.1 g/ml	0.04 L/L feed						
Oil Loss in Aqueous	95.04 g/hr	95.04 ml/hr	28.39% mass conversion to oil						
	density, est	1 g/ml	0.05 L/L feed						
Gasification of Carbon	9.46%		30.56% carbon conversion to water solubles						
Hydrogen Consumption	0.00 g/hr in -	0.00 g/hr out =							
			0.00 g/hr consumption						
			0.00 L/hr consumption						
			0.00 L/L feed						
			0 g/q feed						
Space velocity	2.22 L/L/hr	LHSV							
Chemical Hydrogen Consumption	0.00 g/hr	0 L/L	0 nM3/tonne						
Calculation of Deoxygenation									
O content of dry product	0.75%								
O in Dry Product	0.63 g/hr								
O in Organics(H2O)	80.89 g/hr----->								
O in Dry Feed	134.91 g/hr								
Deoxygenation	39.58%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-4								
					CSTR volume	1000 mL			
					reactor volume	900 mL, at temp	1000 mL, total		
Pressure	20.1 MPa	CSTR Reactor	349						
	2911 psig	Tube temp.	339	bottom	Time	9:35-13:25			
		degrees C	350	top	Date	19-Jun-08			
Total Feed	7667 cc	Feed rate	2000.1 cc/hr						
ground corn fiber	7.96 pH		2020.10 g/hr						
	194.933 COD, ppm	7.28 wt% Na2CO3 on dry corn fiber							
Total Product	7692.7 g	3.16 wt% Na			Product oil	69.2 g/hr	sum of two phases	2006.8	
					Product aqueous	1917.6 g/hr	5.89 pH		
	actual feed	47.81% C	5.69% H	47.20% O	density	1.90%	0.21% S	0.89% ash	103.68%
Elemental Analyses					moisture				
normalized	feed	46.00%	5.60%	45.40%	1.01	86.27%	1.90%	0.21%	0.89%
	product oil	76.20%	8.49%	12.31%	1.1	8.70%	3.16%	0.30%	100.00%
oxygen by difference	aqueous	1.99%	9.08%	88.85%	1.0 est	97.00%	0.08%		100.46%
					product moisture est.				100.00%
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
	feed	127.59	210.89	1673.31	2011.78				
	product oil	67.97	7.58	10.98					
	aqueous	38.21	174.12	1703.79					
	gas	10.49	0.00	27.95					
	Total Products	116.67	181.69	1742.73	2041.09				
	Elemental Balance	91%	86%	104%					
Total Material Balance		>>>>>>	>>>>>>>>>	>>>>>>	>>>>>>>	101%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	308.1 L/hr		12.84 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr				
CarbDioxide	6.81%	0.87		1.75					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00						
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.14%	0.13	0.25	0.00		2.94			
	6.95%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		10.49	0.00	27.95	38.45 Total gas				
Total Gas Oil, C5-C7		1.51	0.25	0.00	1.77 Total gas oil				
		12.00	0.25	27.95	40.21 Total gas mass out				
Yields									
Oil Product Yield		81.44 g/hr		74.04 ml/hr	53.28% carbon conversion to oil				
		density, g/hr		1.1 g/ml	0.04 L/L feed				
Oil Loss in Aqueous		57.53 g/hr		57.53 ml/hr	29.36% mass conversion to oil				
		density, est		1 g/ml	0.03 L/L feed				
Gasification of Carbon	8.22%				29.95% carbon conversion to water solubles				
Hydrogen Consumption		0.00 g/hr in -		0.00 g/hr out =	0.00 g/hr consumption				
					0.00 L/hr consumption				
					0.00 L/L feed				
					0 g/g feed				
Space velocity	2.22 L/L/hr	LHSV							
Chemical Hydrogen Consumption		0.00 g/hr		0 L/L	0 nM3/tonne				
Calculation of Deoxygenation									
O content of dry product	5.02%								
O in Dry Product	4.09 g/hr								
O in Organics(H2O)	50.39 g/hr----->								
O in Dry Feed	125.92 g/hr								
Deoxygenation	56.74%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-4					CSTR volume	1000 mL		
						reactor volume	900 mL, at temp	1000 mL, total	
Pressure	20.1 MPa	CSTR Reactor	349			Time	9:35-13:25		
	2911 psig	Tube temp,	339	bottom		Date	19-Jun-08		
		degrees C	350	top					
Total Feed	7667 cc	Feed rate	2000.1 cc/hr						
ground corn fiber	7.96 pH		2020.10 g/hr						
	194.933 COD, ppm	7.28 wt% Na2CO3 on dry corn fiber							
Total Product	7692.7 g	3.16 wt% Na				Product oil	89.2 g/hr	sum of two phases	2006.8
						Product aqueous	1917.6 g/hr	5.89 pH	g/hr
Elemental Analyses	actual feed	47.81%	5.69%	47.20%			1.90%	0.21%	0.89%
	C	H	O	density	moisture	N	S	ash	103.68%
normalized feed	46.00%	5.60%	45.40%	1.01	86.27%	1.90%	0.21%	0.89%	100.00%
product oil	76.20%	8.49%	12.31%	1.1	8.70%	3.16%	0.30%		100.46%
oxygen by difference aqueous	1.99%	9.08%	88.85%	1.0 est	97.00%	0.08%			100.00%
Material Balance		g C/hr	g H/hr	g O/hr		product moisture est.			
feed	127.59	210.89	1673.31		2011.78	TAN	Viscosity		
product oil	67.97	7.58	10.98						
aqueous	38.21	174.12	1703.79						
gas	10.49	0.00	27.95						
Total Products	116.67	181.69	1742.73		2041.09				
Elemental Balance	91%	86%	104%						
Total Material Balance	>>>>>>	>>>>>>>>>	>>>>>>	>>>>>>>	101%				
GAS CALCULATIONS									
Gas In	0 L/hr	0.00 moles/hr	0.00 g H/hr						
Gas Out	308.1 L/hr	12.84 moles/hr							
Gas Composition	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr				
CarbDioxide	6.81%	0.87		1.75					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00						
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.14%	0.13	0.25	0.00		2.94			
	6.95%								
	C g/hr	H g/hr	O g/hr						
Total Gas, C1-C4	10.49	0.00	27.95	38.45	Total gas				
Total Gas Oil, C5-C7	1.51	0.25	0.00	1.77	Total gas oil				
	12.00	0.25	27.95	40.21	Total gas mass out				
Yields									
Oil Product Yield	81.44 g/hr		74.04 ml/hr		53.28% carbon conversion to oil				
	density,		1.1 g/ml		0.04 L/L feed				
Oil Loss in Aqueous	57.53 g/hr		57.53 ml/hr		29.36% mass conversion to oil				
	density, est		1 g/ml		0.03 L/L feed				
Gasification of Carbon	8.22%				29.95% carbon conversion to water solubles				
Hydrogen Consumption	0.00 g/hr in -		0.00 g/hr out =		0.00 g/hr consumption				
					0.00 L/hr consumption				
					0.00 L/L feed				
					0 g/g feed				
Space velocity	2.22 L/L/hr	LHSV							
Chemical Hydrogen Consumption		0.00 g/hr	0 L/L		0 nM3/tonne				
Calculation of Deoxygenation									
O content of dry product	5.02%								
O in Dry Product	4.09 g/hr								
O in Organics(H2O)	50.39 g/hr----->								
O in Dry Feed	125.92 g/hr								
Deoxygenation	56.74%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-5					CSTR volume	1000 mL		
						reactor volume	900 mL, at temp	1000 mL, total	
Pressure	20.1 MPa	CSTR Reactor	330			Time	18:00-20:55		
	2902 psia	Tube temp,	326	bottom		Date	23-Jun-08		
		degrees C	350	top					
Total Feed	5759 cc	Feed rate	1974.5 cc/hr						
ground corn fiber	9.64 pH		1994.25 g/hr						
	185.867 COD, ppm		13.02 wt% Na2CO3 on dry corn fiber						
Total Product	5967.8 g		5.65 wt% Na			Product oil	85.54 g/hr	sum of two phases	2046.1 g/hr
						Product aqueous	1960.56 g/hr	6.78 pH	
Elemental Analyses	actual feed	47.81%	5.69%	47.20%			1.90%	0.21%	0.89%
		C	H	O	density	moisture	N	S	ash
normalized	feed	46.00%	5.60%	45.40%	1.01	84.94%	1.90%	0.21%	0.89%
	product oil	75.79%	8.61%	11.22%	1.147	3.82%	3.28%	0.33%	100.00%
oxygen by difference	aqueous	2.35%	8.61%	88.90%	1.0 est	96.00%	0.07%	0.05%	99.22%
						product moisture est.			100.02%
Material Balance		g C/hr	g H/hr	g O/hr		Total	TAN	Viscosity	
	feed	138.15	206.70	1640.38		1985.24			
	product oil	64.83	7.36	9.60					
	aqueous	45.98	169.59	1742.94					
	gas	4.53	0.08	11.37					
	Total Products	115.33	177.03	1763.91		2056.27			
	Elemental Balance	83%	86%	108%					
Total Material Balance		>>>>>>	>>>>>>>>>	>>>>>>	>>>>>>	104%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	324.3 L/hr		13.51 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr				
CarbDioxide	2.63%	0.36		0.71					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.10%	0.01	0.05						
Ethane	0.03%	0.01	0.02						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.08%	0.08	0.16	0.00		2.94			
	2.84%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		4.53	0.08	11.37	15.98 Total gas				
Total Gas Oil, C5-C7		0.94	0.16	0.00	1.10 Total gas oil				
		5.47	0.24	11.37	17.08 Total gas mass out				
Yields									
Oil Product Yield		82.27 g/hr		71.73 ml/hr		46.93% carbon conversion to oil			
		density,		1.147 g/ml		0.04 L/L feed			
Oil Loss in Aqueous		78.42 g/hr		78.42 ml/hr		27.39% mass conversion to oil			
		density, est		1 g/ml		0.04 L/L feed			
Gasification of Carbon	3.28%					33.28% carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -		0.00 g/hr out =		0.00 g/hr consumption			
						0.00 L/hr consumption			
						0.00 L/L feed			
						0 g/g feed			
Space velocity	2.19 L/L/hr		LHSV						
Chemical Hydrogen Consumption			0.00 g/hr		0 L/L		0 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	8.14%								
O in Dry Product	6.69 g/hr								
O in Organics(H2O)	69.93 g/hr----->								
O in Dry Feed	136.35 g/hr								
Deoxygenation	43.81%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-5								
Pressure	20.7 MPa	CSTR Reactor	334		CSTR volume	1000 mL			
	2986 psig	Tube temp.	305	bottom	reactor volume	700 mL, at temp			
		degrees C	350	top	Time	02:00-04:55			
					Date	24-Jun-08			
Total Feed	5796 cc	Feed rate	1987.2	cc/hr					
ground corn fiber	9.52 pH			2007.07 g/hr					
	191.133	COD, ppm	11.04	wt% Na2CO3 on dry corn fiber					
Total Product	5916.1 g	4.79 wt% Na		Product oil	90.87 g/hr	sum of two phases	2028.4		
				Product aqueous	1937.5 g/hr	7.05 pH			
	actual feed	47.81%	5.69%	47.20%		1.90%	0.21%	0.89%	103.68%
Elemental Analyses	C	H	O	density	moisture	N	S	ash	
normalized feed	46.00%	5.60%	45.40%	1.01	84.81%	1.90%	0.21%	0.89%	100.00%
product oil	75.17%	8.68%	11.45%	1.023	4.77%	3.40%	0.33%		actual measured
oxygen by difference aqueous	2.38%	8.65%	88.80%	1.0 est	96.00%	0.10%	0.05%		99.98%
Material Balance		q C/hr	q H/hr	q O/hr	Total	TAN	Viscosity		
feed	140.24	207.89	1649.80		1997.93				
product oil	68.30	7.89	10.40						
aqueous	46.11	167.59	1720.50						
gas	10.69	0.12	27.43						
Total Products	125.10	175.60	1758.33		2059.03				
Elemental Balance	89%	84%	107%						
Total Material Balance	103%								
GAS CALCULATIONS									
Gas In	0 L/hr	0.00 moles/hr	0.00 q H/hr						
Gas Out	314.4 L/hr	13.10 moles/hr							
Gas Composition		moles/hr							
volume%	C	H	O						
Hydrogen	0.00%	0.00		0.00 qH/hr					
CarbDioxide	6.54%	0.86	1.71						
CarbMonoxide	0.00%	0.00	0.00						
Methane	0.15%	0.02	0.08						
Ethane	0.05%	0.01	0.04						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.16%	0.15	0.29	0.00		2.94			
	6.90%								
	C g/hr	H g/hr	O g/hr						
Total Gas, C1-C4	10.69	0.12	27.43	38.24 Total gas					
Total Gas Oil, C5-C7	1.77	0.30	0.00	2.07 Total gas oil					
	12.46	0.42	27.43	40.30 Total gas mass out					
Yields									
Oil Product Yield	86.54 g/hr	84.59 ml/hr	48.70% carbon conversion to oil						
	density, 1.023 g/ml		0.04 L/L feed						
Oil Loss in Aqueous	77.50 g/hr	77.50 ml/hr	28.38% mass conversion to oil						
	density, est 1 g/ml		0.04 L/L feed						
Gasification of Carbon	7.62%		32.88% carbon conversion to water solubles						
Hydrogen Consumption	0.00 g/hr in -	0.00 g/hr out =							
			0.00 g/hr consumption						
			0.00 L/hr consumption						
			0.00 L/L feed						
			0 g/q feed						
Space velocity	2.84 L/L/hr	LHSV							
Chemical Hydrogen Consumption		0.00 g/hr	0 L/L	0 nM3/tonne					
Calculation of Deoxygenation									
O content of dry product	7.57%								
O in Dry Product	6.55 g/hr								
O in Organics(H2O)	67.17 g/hr----->								
O in Dry Feed	138.41 g/hr								
Deoxygenation	46.74%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-5					CSTR volume	1000 mL		
						reactor volume	750 mL, at temp	1000 mL, total	
Pressure	20.7 MPa	CSTR Reactor	335			Time	10:00-12:55		
	2985 psig	Tube temp.	309	bottom		Date	24-Jun-08		
		degrees C	350	top					
Total Feed	5865 cc	Feed rate	2010.86 cc/hr						
ground corn fiber	9.48 pH		2030.97 g/hr						
		COD, ppm	12.3	wt% Na ₂ CO ₃ on dry corn fiber					
Total Product	5961 g	5.34 wt% Na		Product oil	92.63 g/hr	sum of two phases	2043.8		
				Product aqueous	1951.2 g/hr	7.064 pH			
actual feed		47.81% C	5.69% H	47.20% O	density	moisture			
Elemental Analyses									
normalized	feed	46.00%	5.60%	45.40%	1.01	83.96%	N	1.90%	S
	product oil	74.59%	8.54%	11.33%	1.067	4.07%		0.21%	0.89%
oxygen by difference	aqueous	2.54%	6.63%	88.70%	1.0 est	96.00%		0.32%	103.68%
								0.06%	100.00%
								0.05%	100.00%
Material Balance		q C/hr	q H/hr	q O/hr	Total	TAN	Viscosity		
	feed	149.85	209.39	1661.95	2021.20				
	product oil	69.09	7.91	10.49					
	aqueous	49.56	168.78	1730.71					
	gas	9.96	0.15	25.18					
	Total Products	128.61	176.84	1766.39	2071.84				
	Elemental Balance	86%	84%	106%					
Total Material Balance		>>>>>>	>>>>>>>>>	>>>>>>	>>>>>>	103%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr	0.00 g H/hr					
Gas Out	315.8 L/hr		13.16 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr				
CarbDioxide	5.98%	0.79		1.57					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.20%	0.03	0.11						
Ethane	0.06%	0.02	0.05						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.12%	0.11	0.23	0.00		2.94			
	6.36%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		9.96	0.15	25.18	35.29 Total gas				
Total Gas Oil, C5-C7		1.37	0.23	0.00	1.60 Total gas oil				
		11.33	0.38	25.18	36.89 Total gas mass out				
Yields									
Oil Product Yield		88.86 g/hr	83.28 ml/hr	46.11% carbon conversion to oil					
		density, g/hr	1.067 g/ml	0.04 L/L feed					
Oil Loss in Aqueous		78.05 g/hr	78.05 ml/hr	27.28% mass conversion to oil					
		density, est	1 g/ml	0.04 L/L feed					
Gasification of Carbon	6.64%			33.07% carbon conversion to water solubles					
Hydrogen Consumption		0.00 g/hr in -	0.00 g/hr out =	0.00 g/hr consumption					
				0.00 L/hr consumption					
				0.00 L/L feed					
				0 g/q feed					
Space velocity	2.68 L/L/hr	LHSV							
Chemical Hydrogen Consumption		0.00 g/hr	0 L/L	0 nM3/tonne					
Calculation of Deoxygenation									
O content of dry product	8.04%								
O in Dry Product	7.14 g/hr								
O in Organics(H ₂ O)	65.69 g/hr----->								
O in Dry Feed	147.90 g/hr								
Deoxygenation	50.75%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-6								
Pressure	20.3 MPa	Reactor Temperature	231	reactor volume	1000	total mL			
	2936 psia	degrees C	351		400	mL at temperature			
Total Feed	6942 cc	Feed rate	1983 cc/hr						
ground corn fiber			2002.83 g/hr						
Total Product	7106.1 g			Product oil	95.6 g/hr	sum of two phases	2030.3		
				Product aqueous	1934.7 g/hr		g/hr		
Elemental Analyses									
normalized feed		C	H	O	density	moisture	N	S	ash
		46.00%	5.60%	45.40%	1.01	81.72%	1.90%	0.21%	0.89%
product oil		74.73%	7.30%	13.44%	1.063	6.60%	3.25%	0.32%	
aqueous		2.48%	10.40%	86.85%	1.0 est	95.00%	0.28%		
oxygen by difference									100.00%
									99.03% actual measured
									100.00%
Material Balance									
		g C/hr	g H/hr	g O/hr			TAN	Viscosity	
feed		168.41	203.97	1619.46		1991.85			
product oil		71.44	6.97	12.85					
aqueous		47.88	201.21	1680.29					
gas		7.73	0.17	17.94					
Total Products		127.06	208.35	1711.07		2046.48			
Elemental Balance		75%	102%	106%					
Total Material Balance		>>>>>>	>>>>>>>>>	>>>>>>	>>>>>>	103%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	321.1 L/hr		13.38 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr		trace		
CarbDioxide	4.19%	0.56		1.12					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace		trace		
Ethane	0.00%	0.00	0.00		trace		trace		
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.09%	0.08	0.17	0.00			2.94		
	4.28%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		6.73	0.00	17.94	24.67	Total gas			
Total Gas Oil, C5-C7		1.00	0.17	0.00	1.17	Total gas oil			
		7.73	0.17	17.94	25.84	Total gas mass out			
Yields									
Oil Product Yield		89.29 g/hr		83.68 ml/hr		42.42% carbon conversion to oil			
			density,	1.067 g/ml		0.04 L/L feed			
Oil Loss in Aqueous		96.74 g/hr		96.74 ml/hr		24.39% mass conversion to oil			
			density, est	1 g/ml		0.05 L/L feed			
Gasification of Carbon	4.00%					28.43% carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -		0.00 g/hr out =		0.00 g/hr consumption			
						0.00 L/hr consumption			
						0.00 L/L feed			
						0 g/g feed			
Space velocity	4.96 L/L/hr		LHSV						
Chemical Hydrogen Consumption			0.00 g/hr		0 L/L		0 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	8.11%								
O in Dry Product	7.24 g/hr								
O in Organics(H2O)	46.54 g/hr----->								
O in Dry Feed	166.22 g/hr								
Deoxygenation	67.64%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-6								
Pressure	20.4 MPa	Reactor Temperature	225		reactor volume	1000	total mL		
	2941 psi	degrees C	352			450	mL at temperature		
Total Feed	5809 cc	Feed rate	1936.3 cc/hr						
ground corn fiber			1955.66 g/hr						
Total Product	5889 g				Product oil	100.1 g/hr	sum of two phases	1963	
					Product aqueous	1862.9 g/hr		q/hr	
Elemental Analyses									
		C	H	O	density	measured 81.72 based on COD	N	S	ash
normalized feed		46.00%	5.60%	45.40%	1.31	85.50%	1.90%	0.21%	0.89%
product oil		73.81%	7.70%	13.20%	1.067	5.53%	3.05%	0.30%	100.00%
oxygen by difference aqueous		2.43%	11.41%	86.10%	1.0 est	97.00%	0.10%		98.06% actual measured
Material Balance									
		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
feed		130.44	203.32	1613.40	1947.16				
product oil		73.89	7.71	13.21					
aqueous		45.22	212.46	1603.96					
gas		8.73	0.15	20.87					
Total Products		127.84	220.33	1638.03	1986.20				
Elemental Balance		98%	108%	102%					
Total Material Balance		>>>>>>	>>>>>>>>>	>>>>>>>	102%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	300.7 L/hr		12.53 moles/hr						
Gas Composition									
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr	trace			
CarbDioxide	5.20%	0.65		1.30					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.09%	0.07	0.15	0.00		2.94			
	5.29%								
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr	Total gas				
Total Gas Oil, C5-C7		7.83	0.00	20.87	28.70				
		0.90	0.15	0.00	1.05	Total gas oil			
		8.73	0.15	20.87	29.75	Total gas mass out			
Yields									
Oil Product Yield		94.57 g/hr	density, 88.63 ml/hr		56.64% carbon conversion to oil				
			1.067 g/ml		0.05 L/L feed				
Oil Loss in Aqueous		55.89 g/hr	55.89 ml/hr		33.35% mass conversion to oil				
			density, est 1 g/ml		0.03 L/L feed				
Gasification of Carbon	6.00%				34.67% carbon conversion to water solubles				
Hydrogen Consumption		0.00 g/hr in -	0.00 g/hr out =		0.00 g/hr consumption				
					0.00 L/hr consumption				
					0.00 L/L feed				
					0 g/g feed				
Space velocity	4.30 L/L/hr	LHSV							
Chemical Hydrogen Consumption		0.00 g/hr	0 L/L		0 nM3/tonne				
Calculation of Deoxygenation									
O content of dry product	8.77%								
O in Dry Product	8.29 g/hr								
O in Organics(H2O)	-2.28 g/hr----->								
O in Dry Feed	128.74 g/hr								
Deoxygenation	95.33%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-7				reactor volume	1000 600	total mL mL at temperature		
Pressure	20.2 MPa 2912 psig	Reactor Temperature degrees C	151 324 339	+/-30 +/-20 +/-5	Time	21:40:00:10			
					Date	16-Sep-08			
Total Feed ground corn fiber with 2% Na2CO3	3740 cc	Feed rate	1496 1510.96	cc/hr g/hr					
Total Product	3918.9 g				Product oil Product aqueous	15.3 1552.3	g/hr g/hr	sum of two phases g/hr	1567.6
Elemental Analyses		C	H	O	density	moisture	N	S	ash
adjusted to C balance	feed	18.00%	5.80%	13.40%	1.00	91.80%	1.90%	0.21%	0.89%
normalized	product oil	72.70%	8.40%	16.00%	1.022	7.75%	2.55%	0.28%	99.93%
normalized	aqueous	2.20%	11.70%	85.70%	1.0 est	98.00%	0.43%	0.005%	100.03%
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
	feed	47.08	162.42	1297.74	1507.24				
	product oil	11.12	1.29	2.45					
	aqueous	34.15	181.62	1330.32					
	gas	1.40	0.03	3.31					
	Total Products	46.68	182.93	1336.08	1565.69				
	Elemental Balance	99%	113%	103%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>>	>>>>>>>>	104%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	230 L/hr		9.58 moles/hr						
Gas Composition		volume%	C	H	O				
						0.00 gH/hr	trace		
Hydrogen	0.00%			0.00					
CarbDioxide, est.	1.08%	0.10		0.21					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace		trace		
Ethane	0.00%	0.00	0.00		trace		trace		
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.02%	0.01	0.03	0.00			2.94		
	1.10%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		1.24	0.00	3.31	4.56 Total gas				
Total Gas Oil, C5-C7		0.16	0.03	0.00	0.19 Total gas oil				
		1.40	0.03	3.31	4.74 Total gas mass out				
Yields									
Oil Product Yield		14.11 g/hr	density, 31.05 g/hr	13.17 ml/hr	1.072 g/ml	23.63% carbon conversion to oil	0.01 L/L feed		
Oil Loss in Aqueous			density, est 31.05 g/hr	31.05 ml/hr	1 g/ml	11.39% mass conversion to oil	0.02 L/L feed		
Gasification of Carbon	2.64%					72.54% carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -		0.00 g/hr out =		0.00 g/hr consumption			
						0.00 L/hr consumption			
						0.00 L/L feed			
						0 g/g feed			
Space velocity	2.49 L/L/hr		LHSV						
Chemical Hydrogen Consumption			0.00 g/hr		0 L/L		0 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	9.88%								
O in Dry Product	1.39 g/hr								
O in Organics(H2O)	-21.90 g/hr----->								
O in Dry Feed	66.16 g/hr								
Deoxygenation	131.00%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-8	Reactor	147	reactor volume	1000	total mL			
Pressure	19.8 MPa	Temperature	340		600	mL at temperature			
	2867 psiq	degrees C	341	Time	13:17-14:55				
				Date	14-Oct-08				
Total Feed	3280 cc	Feed rate	2008 cc/hr						
ground corn fiber with 2% Na2CO3			2028.08 g/hr						
Total Product	3385 g	Product oil	37.3 g/hr	sum of two phases	2072				
		Product aqueous	2039 g/hr						
Elemental Analyses				152.4g/h organics based on COD					
normalized	feed	C	H	O	density	moisture	N	S	ash
	product oil	37.49%	6.30%	53.97%	1.01	87.98%	1.18%	0.10%	0.89%
oxygen by difference	aqueous	73.11%	7.98%	14.52%	1.070	3.85%	2.52%	0.24%	99.93%
		2.39%	10.94%	84.50%	1.0 est	93.25%	0.05%	0.005%	98.36%
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
	feed	91.39	215.37	1715.85	2022.62				
	product oil	27.27	2.98	5.41		51.95			
	aqueous	48.59	222.68	1719.58					
	gas	3.79	0.00	10.11					
	Total Products	79.65	225.66	1735.10	2040.40				
Elemental Balance		87%	105%	101%					
Total Material Balance		>>>>>>	>>>>>>>>>>>>	>>>>>>	101%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr	0.00 g H/hr					
Gas Out	307.3 L/hr		12.80 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00 gH/hr	trace			
CarbDioxide	2.47%	0.32		0.63					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00		2.94			
	2.47%								
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr	13.90	Total gas			
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil			
		3.79	0.00	10.11	13.90	Total gas mass out			
Yields									
Oil Product Yield		35.86 g/hr	density, 33.52 ml/hr	1.07 g/ml	29.84%	carbon conversion to oil			
					0.02	L/L feed			
Oil Loss in Aqueous		137.36 g/hr	density, est 137.36 ml/hr	1 g/ml	14.71%	mass conversion to oil			
					0.07	L/L feed			
Gasification of Carbon	4.15%				53.16%	carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -	0.00 g/hr out =		0.00 g/hr consumption				
					0.00 L/hr consumption				
					0.00 L/L feed				
					0 g/g feed				
Space velocity	3.35 L/L/hr	LHSV							
Chemical Hydrogen Consumption		0.00 g/hr	0 L/L		0 nM3/tonne				
Calculation of Deoxygenation									
O content of dry product	11.54%								
O in Dry Product	4.14 g/hr								
O in Organics(H2O)	32.79 g/hr----->								
O in Dry Feed	131.57 g/hr								
Deoxygenation	71.94%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-8								
					reactor volume	1000	total mL		
						600	mL at temperature		
Pressure	19.7 MPa		Reactor	166					
	2852 psiq		Temperature,	340					
			degrees C	341					
					Time	16:50-19:20			
					Date	14-Oct-08			
Total Feed	3750	cc	Feed rate	1500	cc/hr				
ground corn fiber				1515.00	g/hr				
with 2% Na2CO3									
Total Product	3797.5	g							
					Product oil	39.4	g/hr	sum of two phases	1519
					Product aqueous	1479.6	g/hr		
Elemental Analyses									
		C	H	O	density	moisture	N	S	ash
normalized feed		37.49%	6.30%	53.97%	1.07	87.06%	1.18%	0.10%	0.89%
product oil		73.20%	8.43%	14.53%	1.072	3.95%	2.57%	0.244%	99.93%
oxygen by difference aqueous		2.14%	11.18%	86.63%	1.0 est	92.25%	0.05%	0.005%	98.97%
									100.00%
Material Balance									
		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
feed		73.50	160.20	1276.91	1510.61				
product oil		28.84	3.32	5.72		52.55			
aqueous		31.66	165.38	1281.78					
gas		2.84	0.00	7.58					
Total Products		63.35	168.70	1295.08	1527.13				
Elemental Balance		86%	105%	101%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>	>>>>>>>>	101%			
GAS CALCULATIONS									
Gas In	0	L/hr	0.00	moles/hr	0.00	g H/hr			
Gas Out	230.4	L/hr	9.60	moles/hr					
Gas Composition									
	volume%	C	H	O					
Hydrogen	0.00%		0.00		0.00	gH/hr	trace		
CarbDioxide, est.	2.47%	0.24		0.47					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace		trace		
Ethane	0.00%	0.00	0.00		trace		trace		
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94		
no good GC	2.47%								
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr					
		2.84	0.00	7.58	10.42	Total gas			
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil			
		2.84	0.00	7.58	10.42	Total gas mass out			
Yields									
Oil Product Yield		37.84	g/hr	35.30	ml/hr	39.24%	carbon conversion to oil		
			density,	1.072	g/ml	0.02	L/L feed		
Oil Loss in Aqueous		114.67	g/hr	114.67	ml/hr	19.30%	mass conversion to oil		
			density, est	1	g/ml	0.08	L/L feed		
						43.08%	carbon conversion to water solubles		
Gasification of Carbon	3.87%								
Hydrogen Consumption		0.00	g/hr in -	0.00	g/hr out =	0.00	g/hr consumption		
						0.00	L/hr consumption		
						0.00	L/L feed		
						0	g/g feed		
Space velocity	2.50	L/L/hr	LHSV						
Chemical Hydrogen Consumption			0.00	g/hr	0	L/L	0	nM3/tonne	
Calculation of Deoxygenation									
O content of dry product	11.47%								
O in Dry Product	4.34	g/hr							
O in Organics(H2O)	68.51	g/hr----->							
O in Dry Feed	105.80	g/hr							
Deoxygenation	31.15%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-9								
					reactor volume	1000	total mL		
						600	mL at temperature		
Pressure	20.2 MPa		Reactor	146					
	2917 psia		Temperature	333					
			degrees C	325					
					Time	13:00-15:30			
					Date	16-Oct-08			
Total Feed	5000 cc		Feed rate	2000 cc/hr					
ground corn fiber				2020.00 g/hr					
with 2% Na2CO3									
Total Product	5061.5 g				Product oil	49.8	g/hr	sum of two phases	2024.6
					Product aqueous	1974.8	g/hr		g/hr
Elemental Analyses									
		C	H	O	density@25C	moisture	N	S	ash
normalized feed		45.02%	5.60%	45.40%	1.01	87.06%	1.90%	0.21%	0.89%
product oil		71.29%	8.11%	15.35%	1.072	3.80%	2.28%	0.24%	97.27%
oxygen by difference		2.58%	10.91%	86.45%	1.0 est	93.25%	0.05%	0.005%	100.00%
Material Balance									
		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
feed		120.24	211.77	1680.15	2012.16				
product oil		35.50	4.04	7.65		51.55			
aqueous		50.95	215.45	1707.21					
gas		6.84	0.03	18.23					
Total Products		93.30	219.51	1733.09	2045.90				
Elemental Balance		78%	104%	103%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>	102%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	303.2 L/hr		12.63 moles/hr						
Gas Composition									
	volume%	C	H	O					
Hydrogen	0.10%		0.03		0.03 gH/hr	trace			
CarbDioxide	4.51%	0.57		1.14					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00		2.94			
	4.61%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		6.84	0.00	18.23	25.08 Total gas				
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00 Total gas oil				
		6.84	0.00	18.23	25.08 Total gas mass out				
Yields									
Oil Product Yield		47.91 g/hr		44.69 ml/hr		29.53% carbon conversion to oil			
			density, ✓	1.072 g/ml		0.02 L/L feed			
Oil Loss in Aqueous		133.30 g/hr		133.30 ml/hr		18.33% mass conversion to oil			
			density, est	1 g/ml		-0.07 L/L feed			
Gasification of Carbon	5.69%					42.37% carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -		0.03 g/hr out =		-0.03 g/hr consumption			
						-0.30 L/hr consumption			
						-0.15 L/L feed			
						-1.26333E-05 g/q feed			
Space velocity	3.33 L/L/hr		LHSV						
Chemical Hydrogen Consumption			-0.02 g/hr		0 L/L		0 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	12.45%								
O in Dry Product	5.96 g/hr								
O in Organics(H2O)	70.32 g/hr----->								
O in Dry Feed	118.67 g/hr								
Deoxygenation	35.71%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-10								
					reactor volume	1000	total mL		
						500	mL at temperature		
Pressure	19.9 MPa		Reactor	162					
	2875 psig		Temperature,	329	Time	12:15-14:55			
			degrees C	345	Date	31-Dec-08			
Total Feed	3470	cc	Feed rate	1301	cc/hr				
ground corn stover				1314.01	g/hr				
Total Product	3438	g							
					Product oil	27	g/hr	sum of two phases	1289.3
					Product aqueous	1262.3	g/hr		
Elemental Analyses									
		C	H	O	density@25C	moisture	N	S	ash
feed		42.25%	5.28%	41.40%	1.1	94.74%	0.66%	0.06%	11.94%
product oil		66.32%	6.40%	25.51%	1.100	26.05%	1.28%	0.08%	0.0%
oxygen by difference		1.03%	9.73%	89.20%	1.0 est	99.00%	<0.05%	<0.005%	99.58%
									actual measured
Material Balance									
		g C/hr	g H/hr	g O/hr		Total	TAN	Viscosity	
feed		29.20	143.20	1133.95		1306.35			
product oil		17.91	1.73	6.89			36.3	solid	
aqueous		12.94	122.76	1125.97					
gas		3.65	0.03	9.44					
Total Products		34.49	124.52	1142.30		1301.31			
Elemental Balance		118%	87%	101%					
Total Material Balance		>>>>>>	>>>>>>>>	>>>>>>	>>>>>>>	100%			
GAS CALCULATIONS									
Gas In	0	L/hr		0.00	moles/hr	0.00	g H/hr		
Gas Out	210.8	L/hr		8.78	moles/hr				
Gas Composition									
	volume%	C	H	O					
Hydrogen	0.00%		0.00			0.00	gH/hr	trace	
CarbDioxide	3.36%	0.30		0.59					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.06%	0.01	0.02		trace			trace	
Ethane	0.01%	0.00	0.01						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00				2.94	
	3.44%								
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr		13.12	Total gas		
Total Gas Oil, C5-C7		3.64	0.03	9.44		0.00	Total gas oil		
		0.00	0.00	0.00		13.12	Total gas mass out		
		3.65	0.03	9.44					
Yields									
Oil Product Yield		19.97	g/hr	18.15	ml/hr	61.32%	carbon conversion to oil		
			density,	1.1	g/ml	0.01	L/L feed		
Oil Loss in Aqueous		12.62	g/hr	12.62	ml/hr	28.89%	mass conversion to oil	13%	mass yield of solids
			density, est	1	g/ml	0.01	L/L feed		plugged reactor tube
Gasification of Carbon	12.48%					44.31%	carbon conversion to water solubles		
Hydrogen Consumption		0.00	g/hr in -	0.00	g/hr out =	0.00	g/hr consumption		
						0.00	L/hr consumption		
						0.00	L/L feed		
						0	g/q feed		
Space velocity	2.60	L/L/hr	LHSV						
Chemical Hydrogen Consumption			0.00	g/hr		0	L/L	0	nM3/tonne
Calculation of Deoxygenation									
O content of dry product	3.18%	???							
O in Dry Product	0.63	g/hr							
O in Organics(H2O)	15.15	g/hr----->							
O in Dry Feed	28.61	g/hr							
Deoxygenation	44.84%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-11				reactor volume	1000 500	total mL mL at temperature		
Pressure	20.0 MPa 2884 psia	Reactor Temperature, degrees C	162 346 349		Time Date	12:35-14:35 7-Jan-09			
Total Feed	2350 cc	Feed rate	1175 cc/hr						
ground corn stover slurry w/2% sodium carbonate			1186.75 g/hr						
Total Product	2227.5 g				Product oil	18 g/hr	sum of two phases	1113.75 g/hr	
					Product aqueous	1095.75 g/hr			
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash
feed		34.02%	3.85%	42.59%	1.135	90.40%	0.72%	0.03%	18.97%
product oil		65.92%	6.83%	16.12%	1.135	7.39%	1.04%	0.06%	0.5%
oxygen by difference		1.74%	10.12%	88.10%	1.0 est	98.00%	<0.05%	<0.005%	99.96%
aqueous									
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
feed		38.75	124.64	1001.08	1164.48				
product oil		11.86	1.23	2.90		29.7 tar			
aqueous		19.07	110.84	965.36					
gas		3.27	0.07	8.68					
Total Products		34.20	112.13	976.94	1123.27				
Elemental Balance		88%	90%	98%					
Total Material Balance		>>>>>>	>>>>>>>>	>>>>>>	>>>>>>	96%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	249.5 L/hr		10.40 moles/hr						
Gas Composition			moles/hr						
volume%		C	H	O					
Hydrogen	0.31%		0.07		0.07 gH/hr	trace			
CarbDioxide	2.61%	0.27		0.54					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00		2.94			
	2.93%								
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr					
		3.27	0.00	8.68	11.95	Total gas			
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil			
		3.27	0.00	8.68	11.96	Total gas mass out			
Yields									
Oil Product Yield		16.67 g/hr		14.69 ml/hr		30.62% carbon conversion to oil			
			density,	1.135 g/ml		0.01 L/L feed			
Oil Loss in Aqueous		21.92 g/hr		21.92 ml/hr		14.63% mass conversion to oil			
			density, est	1 g/ml		0.02 L/L feed			
						49.20% carbon conversion to water solubles			
Gasification of Carbon	8.44%								
Hydrogen Consumption		0.00 g/hr in -		0.07 g/hr out =		-0.07 g/hr consumption			
						-0.78 L/hr consumption			
						-0.66 L/L feed			
						-5.53855E-05 g/g feed			
Space velocity	2.35 L/L/hr		LHSV						
Chemical Hydrogen Consumption			-0.07 g/hr		-1 L/L		-1 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	10.31%								
O in Dry Product	1.72 g/hr								
O in Organics(H2O)	10.84 g/hr----->								
O in Dry Feed	48.52 g/hr								
Deoxygenation	74.13%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-11				reactor volume	1000	total mL		
						600	mL at temperature		
Pressure	20.0 MPa		Reactor	161					
	2890 psia		Temperature	344					
			degrees C	352					
					Time	14:35-15:50			
					Date	7-Jan-09			
Total Feed	1640	cc	Feed rate	1312	cc/hr				
ground corn stover slurry				1325.12	g/hr				
w/2% sodium carbonate									
Total Product	2227.5	g							
			Product oil	23.2	g/hr	sum of two phases	1220.4		
			Product aqueous	1197.2	g/hr				
Elemental Analyses									
		C	H	O	density@25C	moisture	N	S	ash
feed		34.02%	3.85%	42.59%	1.01	90.40%	0.72%	0.03%	18.97%
product oil		72.47%	7.89%	15.98%	1.100	9.59%	1.18%	0.07%	
oxygen by difference		1.86%	10.01%	88.10%	1.0 est	98.00%	<0.05%	<0.005%	
									100.16%
									97.58%
									99.97%
Material Balance									
		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity		
feed		43.27	139.17	1117.81	1300.25				
product oil		16.81	1.83	3.71		31.6	tar		
aqueous		22.27	119.84	1054.73					
gas		1.67	0.03	4.42					
Total Products		40.75	121.70	1062.86	1225.30				
Elemental Balance		94%	87%	95%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>	>>>>>>	94%			
GAS CALCULATIONS									
Gas In	0	L/hr	0.00	moles/hr	0.00	g H/hr			
Gas Out	180	L/hr	7.50	moles/hr					
Gas Composition									
	volume%	C	H	O					
Hydrogen	0.15%		0.02		0.02	gH/hr	trace		
CarbDioxide	1.84%	0.14		0.28					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace		trace		
Ethane	0.00%	0.00	0.00		trace		trace		
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94		
	2.00%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		1.67	0.00	4.42	6.09	Total gas			
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil			
		1.67	0.00	4.42	6.09	Total gas mass out			
Yields									
Oil Product Yield	20.98	g/hr	19.07	ml/hr	38.85%	carbon conversion to oil			
		density,	1.1	g/ml	0.01	L/L feed			
Oil Loss in Aqueous	23.94	g/hr	23.94	ml/hr	16.49%	mass conversion to oil	5% mass yield of solids recovered		
		density, est	1	g/ml	0.02	L/L feed	wall deposits but no pressure drop		
Gasification of Carbon	3.85%				51.46%	carbon conversion to water solubles			
Hydrogen Consumption		0.00	g/hr in -	0.02	g/hr out =	-0.02	g/hr consumption		
						-0.28	L/hr consumption		
						-0.21	L/L feed		
						-1.76067E-05	g/q feed		
Space velocity	2.19	L/L/hr	LHSV						
Chemical Hydrogen Consumption			-0.03	g/hr	0	L/L	0	nM3/tonne	
Calculation of Deoxygenation									
O content of dry product	8.25%								
O in Dry Product	1.73	g/hr							
O in Organics(H2O)	11.84	g/hr----->							
O in Dry Feed	54.18	g/hr							
Deoxygenation	74.95%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-13				reactor volume	1000	total mL		
						600	mL at temperature		
Pressure	20.7 MPa	Reactor Temperature	232		Time	12:00-13:20			
	2988 psig	degrees C	348		Date	22-Jan-09			
Total Feed	1740 cc	Feed rate	1305 cc/hr						
corn starch slurry feed 1			1318.05 g/hr						
w/2% sodium carbonate									
Total Product	1761.5 g				Product oil	13.9 g/hr	sum of two phases	1321.16	
					Product aqueous	1307.3 g/hr			
Elemental Analyses									
		C	H	O	density@25C	moisture	N	S	ash
feed		33.15%	4.37%	50.33%		91.00%	0.08%	<0.005	21.31%
product oil		69.35%	7.74%	16.25%	1.084	4.45%	0.07%	0.02%	1.0%
aqueous		1.98%	9.83%	88.20%	1.0 est	96.00%	<0.05%	<0.005%	100.01%
oxygen by difference									actual measured
Material Balance									
		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
feed		39.32	139.63	1124.67	1303.63			60070	???
product oil		9.64	1.08	2.26		27.6		NA	
aqueous		25.82	128.51	1153.04		pH 7.29-7.41		56670	
gas		2.14	0.13	5.69					
Total Products		37.60	129.71	1160.98	1328.30				
Elemental Balance		96%	93%	103%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>>	102%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	206 L/hr		8.58 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.74%		0.13		0.13 gH/hr	trace			
CarbDioxide	2.07%		0.18	0.36					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00		2.94			
	2.81%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		2.14	0.00	5.69	7.83 Total gas				
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00 Total gas oil				
		2.14	0.00	5.69	7.83 Total gas mass out				
Yields									
Oil Product Yield		13.28 g/hr		12.25 ml/hr		24.51% carbon conversion to oil			
			density,	1.084 g/ml		0.01 L/L feed			
Oil Loss in Aqueous		52.29 g/hr		52.29 ml/hr		11.20% mass conversion to oil			
			density, est	1 g/ml		0.04 L/L feed			
Gasification of Carbon	5.45%					65.66% carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -		0.13 g/hr out =		5.45% carbon conversion to gas			
						-0.13 g/hr consumption			
						-1.52 L/hr consumption			
						-1.17 L/L feed			
						-9.73436E-05 g/g feed			
Space velocity	2.18 L/L/hr		LHSV						
Chemical Hydrogen Consumption			-0.14 g/hr		-1 L/L		-1 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	12.87%								
O in Dry Product	1.71 g/hr								
O in Organics(H2O)	37.48 g/hr----->								
O in Dry Feed	59.70 g/hr								
Deoxygenation	34.36%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-13				reactor volume	1000 600	total mL mL at temperature		
Pressure	20.7 MPa 2988 psig	Reactor Temperature, degrees C	235 355 348		Time	13:20-16:40			
					Date	22-Jan-09			
Total Feed	4350 cc	Feed rate	1305 cc/hr 1318.05 g/hr						
corn starch slurry feed 2 w/2% sodium carbonate									
Total Product	4510.5 g				Product oil Product aqueous	11.7 1341.5	g/hr g/hr	sum of two phases g/hr	1353.2
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash
feed		31.93%	4.42%	52.73%	1.077	91.00%	0.10%	<0.005	19.32%
product oil		75.14%	7.57%	20.21%	1.077	3.92%	0.05%	0.02%	1.6%
oxygen by difference		1.92%	9.88%	88.20%	1.0 est	96.00%	<0.05%	<0.005%	100.00%
aqueous									actual measured
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
feed		37.88	139.70	1127.52	1305.10			77970	
product oil		8.79	0.89	2.36		24.65		NA	
aqueous		25.79	132.51	1183.20		pH 7.32-7.37		56070	
gas		1.76	0.11	4.66					
Total Products		36.34	133.50	1190.23	1360.07				
Elemental Balance		96%	96%	106%					
Total Material Balance		>>>>>>	>>>>>>>>	>>>>>>	104%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	206 L/hr		8.58 moles/hr						
Gas Composition	volume%	C	H	O					
Hydrogen	0.62%		0.11		0.11 gH/hr	trace			
CarbDioxide	1.70%	0.15		0.29					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94		
	2.32%								
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr	6.42 Total gas				
		1.76	0.00	4.66					
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00 Total gas oil				
		1.76	0.00	4.66	6.42 Total gas mass out				
Yields									
Oil Product Yield		11.24 g/hr		10.44 ml/hr	23.21% carbon conversion to oil				
			density,	1.077 g/ml	0.01 L/L feed				
Oil Loss in Aqueous		53.66 g/hr		53.66 ml/hr	9.48% mass conversion to oil				
			density, est	1 g/ml	0.04 L/L feed				
Gasification of Carbon	4.64%				68.09% carbon conversion to water solubles				
Hydrogen Consumption		0.00 g/hr in -		0.11 g/hr out =	4.64% carbon conversion to gas				
					-0.11 g/hr consumption				
					-1.29 L/hr consumption				
					-0.99 L/L feed				
					-8.20843E-05 g/q feed				
Space velocity	2.18 L/L/hr		LHSV						
Chemical Hydrogen Consumption			-0.11 g/hr		-1 L/L		-1 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	17.41%								
O in Dry Product	1.96 g/hr								
O in Organics(H2O)	38.46 g/hr----->								
O in Dry Feed	62.55 g/hr								
Deoxygenation	35.39%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-14	Reactor	217	reactor volume	1000	total mL			
Pressure	20.0 MPa	Temperature	345		500	mL at temperature			
	2887 psiq	degrees C	344	Time	13:20:16:50				
				Date	26-Jan-09				
Total Feed	5280 cc	Feed rate	1509 cc/hr						
corn starch slurry			1524.09 g/hr						
w/2% sodium carbonate									
Total Product	1761.5 g			Product oil	6.9 g/hr	sum of two phases	1480.3		
				Product aqueous	1473.4 g/hr		g/hr		
Elemental Analyses									
		C	H	O	density@25C	moisture	N	S	ash
feed		33.59%	4.34%	46.72%	1.01	91.80%	0.05%	<0.005	20.31%
product oil		63.92%	8.41%	24.28%	1.040	19.02%	1.26%	0.01%	1.9%
aqueous		1.88%	10.51%	87.60%	1.0 est	96.00%	0.68%	<0.005%	99.99%
oxygen by difference									
Material Balance									
		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
feed		41.98	162.26	1300.66	1504.90			77070	
product oil		4.41	0.58	1.68		19.2		NA	
aqueous		27.70	154.85	1290.70		pH 7.20-7.36		61470	
gas		1.86	0.07	4.92					
Total Products		33.97	155.50	1297.30	1486.77				
Elemental Balance		81%	96%	100%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>	99%				
GAS CALCULATIONS									
Gas In		0 L/hr	0.00 moles/hr	0.00 g H/hr					
Gas Out		217.7 L/hr	9.07 moles/hr						
Gas Composition		moles/hr							
	volume%	C	H	O					
Hydrogen	0.37%		0.07		0.07 gH/hr	trace			
CarbDioxide	1.70%	0.15	0.31						
CarbMonoxide	0.00%	0.00	0.00						
Methane	0.00%	0.00	0.00	trace		trace			
Ethane	0.00%	0.00	0.00	trace		trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00						
	2.06%						2.94		
Total Gas, C1-C4		1.86 g/hr	0.00 g/hr	4.92 g/hr	6.78	Total gas			
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil			
		1.86	0.00	4.92	6.79	Total gas mass out			
Yields									
Oil Product Yield		5.59 g/hr	5.37 ml/hr	10.51%	carbon conversion to oil				
		density,	1.04 g/ml	0.00 L/L feed					
Oil Loss in Aqueous		58.94 g/hr	58.94 ml/hr	4.47%	mass conversion to oil				
		density, est	1 g/ml	0.04 L/L feed					
Gasification of Carbon	4.42%			65.98%	carbon conversion to water solubles				
Hydrogen Consumption		0.00 g/hr in -	0.07 g/hr out =	4.43%	carbon conversion to gas				
				-0.07 g/hr consumption					
				-0.80 L/hr consumption					
				-0.53 L/L feed					
Space velocity	3.02 L/L/hr	LHSV		-4.40017E-05 g/g feed					
Chemical Hydrogen Consumption		-0.07 g/hr	-1 L/L	-1 nM3/tonne					
Calculation of Deoxygenation									
O content of dry product	9.11%								
O in Dry Product	0.51 g/hr								
O in Organics(H2O)	33.40 g/hr----->								
O in Dry Feed	58.38 g/hr								
Deoxygenation	41.92%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-15								
					reactor volume	1000	total mL		
						700	mL at temperature		
Pressure	20.1 MPa		Reactor	157-173					
40-140psiq pressure drop	2900 psiq		Temperature	343-353	Time	09:45-07:15			
			degrees C	350-355	Date	2/23-24/2009			
Total Feed	32259 cc		Feed rate	1500 cc/hr					
corn stover slurry #1				1515.00 g/hr					
w/1% sodium carbonate					estimates				
Total Product	33050 g				Product oil	40 g/hr	sum of two phases	1537	
					Product aqueous	1497 g/hr		g/hr	
Elemental Analyses		C	H	O	density@25C	moisture		12.42 in CS	
estimates from LF11	feed	32.70%	3.70%	40.60%	1.0	89.40%	N	0.70%	0.03%
	product oil	72.82%	7.63%	19.99%	1.043	3.65%	S	0.03%	22.39%
oxygen by difference	aqueous	1.39%	10.28%	88.30%	1.0 est	97.00%	ash	0.05%	100.09%
									0.0%
									99.97%
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
ASH-Free Basis	feed	52.51	157.77	1267.78	1478.06	NA		91583	
	product oil	29.13	3.05	8.00		25.6		NA	
	aqueous	20.73	153.89	1321.85		pH 4.8-5.6		52000	
	gas	2.61	0.02	6.92					
	Total Products	52.47	156.96	1336.76	1546.20				
	Elemental Balance	100%	99%	105%					
Total Material Balance		>>>>>>	>>>>>>>>	>>>>>>	>>>>>>>	105%			
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	247 L/hr		10.29 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O	0.02 gH/hr				
Hydrogen	0.10%		0.02						
CarbDioxide	2.10%	0.22		0.43					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00						
Ethane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00					
	2.20%					2.94			
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		2.61	0.00	6.92	9.52 Total gas				
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00 Total gas oil				
		2.61	0.00	6.92	9.53 Total gas mass out				
Yields									
Oil Product Yield		38.54 g/hr		37.06 ml/hr		55.47% carbon conversion to oil			
			density,	1.04 g/ml		0.02 L/L feed			
Oil Loss in Aqueous		44.91 g/hr		44.91 ml/hr		24.00% mass conversion to oil			
			density, est	1 g/ml		0.03 L/L feed			
Gasification of Carbon	4.96%					39.48% carbon conversion to water solubles			
Hydrogen Consumption		0.00 g/hr in -		0.02 g/hr out =		4.97% carbon conversion to gas			
						-0.02 g/hr consumption			
						-0.25 L/hr consumption			
						-0.16 L/L feed			
						-1.37222E-05 g/g feed			
Space velocity	2.14 L/L/hr		LHSV						
Chemical Hydrogen Consumption			-0.02 g/hr		0 L/L		0 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	17.38%								
O in Dry Product	6.70 g/hr								
O in Organics(H2O)	31.10 g/hr----->								
O in Dry Feed	65.20 g/hr								
Deoxygenation	42.02%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-16				reactor volume	1000 700	total mL mL at temperature		
Pressure	19.8 MPa	CSTR	320		Time	16:30-19:45			
45 psig differential	2860 psig	CSTR filter	351 334		Date	3-Mar-09			
Total Feed	3750 cc	Feed rate	1154 cc/hr						
corn stover slurry #3			1165.54 g/hr				blowdown	10.66%	% dry solids
w/1% sodium carbonate							blowdown	125.5	g/hr
Total Product	3257.5 g				Product oil	27 g/hr	sum of two phases	1002	g/hr
Blowdown	408 g				Product aqueous	975 g/hr			
					dry blowdown	13.38 g/hr			
					density@25C		12.42 in CS		
Elemental Analyses									
estimates from LF11	feed	C	H	O	moisture	N	S	ash	
		32.80%	3.70%	40.70%	1.01	90.36%	0.70%	0.026%	22.12%
	product oil	72.05%	7.88%	19.92%	1.040	3.61%	1.35%	0.068%	0.0%
oxygen by difference	aqueous	1.96%	10.02%	88.00%	1.0 est	96.00%	<0.05	<0.005%	99.98%
not blowdown solids	dry rinsed sol	23.37%	2.74%	12.04%			0.76%	0.019%	61.00%
Material Balance									
		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
	feed	36.85	122.22	980.85	1139.92			91583	est.
	product oil	19.45	2.13	5.38				NA	
	aqueous	19.11	97.70	858.00		pH 4.5-5.0		53270	
	gas	2.29	0.04	6.09					
	blowdown	3.13	0.37	1.61					
	Total Products	43.98	100.23	871.08	1015.29				
	Elemental Balance	119%	82%	89%					
Total Material Balance		>>>>>>	>>>>>>>>>>	>>>>>>>	89%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	147.4 L/hr		6.14 moles/hr						
Gas Composition		moles/hr							
	volume%	C	H	O					
Hydrogen	0.30%		0.04		0.04 gH/hr	trace			
CarbDioxide	3.10%	0.19		0.38					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00		2.94			
	3.40%								
	C g/hr	H g/hr	O g/hr						
Total Gas, C1-C4	2.29	0.00	6.09	8.39	Total gas				
Total Gas Oil, C5-C7	0.00	0.00	0.00	0.00	Total gas oil				
	2.29	0.00	6.09	8.39	Total gas mass out				
Yields									
Oil Product Yield	26.03 g/hr		25.03 ml/hr		52.79% carbon conversion to oil				
		density,	1.04 g/ml		0.02 L/L feed				
Oil Loss in Aqueous	39.00 g/hr		39.00 ml/hr		23.16% mass conversion to oil				
		density, est	1 g/ml		0.03 L/L feed				
Gasification of Carbon	6.22%				51.85% carbon conversion to water solubles				
Hydrogen Consumption		0.00 g/hr in -	0.04 g/hr out =		6.22% carbon conversion to gas				
					-0.04 g/hr consumption				
					-0.44 L/hr consumption				
					-0.38 L/L feed				
					-3.19324E-05 g/g feed				
Space velocity	1.65 L/L/hr	LHSV							
Chemical Hydrogen Consumption		-0.49 g/hr	-5 L/L		-5 nM3/tonne				
Calculation of Deoxygenation									
O content of dry product	17.34%								
O in Dry Product	4.51 g/hr								
O in Organics(H2O)	26.00 g/hr----->								
O in Dry Feed	45.73 g/hr								
Deoxygenation	33.27%								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-17				reactor volume	1000	total mL		
						1000	mL at temperature		
Pressure	20.3 MPa	CSTR	315		Time	11:00-17:45			
45 psig differential	2936 psig	CSTR	346		Date	31-Mar-09			
		filter	334						
Total Feed	10084 cc	Feed rate	1494 cc/hr						
corn stover slurry # 1			1508.94 g/hr		215.8 tot oil				
w/1% sodium carbonate					9368 tot aq				
Total Product	9583.8 g				Product oil	32 g/hr	blowdown	20.13% % dry solids	
Blowdown	566 g				Product aqueous	1387.9 g/hr	blowdown	107.8 g/hr	
					dry blowdown	21.70 g/hr	sum of two phases	1419.9 g/hr	
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash
feed		38.61%	4.49%	38.86%	1.11	90.10%	0.66%	0.041%	19.99%
product oil		68.46%	7.75%	19.87%	1.110	8.79%	1.29%	0.097%	8.08%
aqueous		2.76%	11.05%	86.00%	1.0 est	96.00%	<0.05	<0.005%	99.80%
dry rinsed so		11.27%	1.12%	9.33%			0.20%	0.020%	78.26%
oil, dry basis		77.20%	7.63%	13.61%			1.45%	0.11%	100.19%
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
feed		57.68	159.11	1265.20	1481.98			88867	
product oil		21.91	2.48	6.36		30.4		NA	
aqueous		38.24	153.29	1193.59		pH 4.6-4.8		52868	
gas		5.79	0.08	15.39					
blowdown		2.44	0.24	2.02					
Total Products		68.37	156.09	1217.37	1441.84				
Elemental Balance		119%	98%	96%					
Ash Balance		>>>>>>	>>>>>>	>>>>>>	56.87% (without aqueous)				
Total Material Balance		>>>>>>	>>>>>>	>>>>>>	97%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	213.8 L/hr		8.91 moles/hr						
Gas Composition			moles/hr						
volume%		C	H	O					
Hydrogen	0.42%		0.07		0.08 gH/hr	trace			
CarbDioxide	5.40%	0.48		0.96					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.00%	0.00	0.00		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94		
	5.82%								
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr					
Total Gas Oil, C5-C7		5.79	0.00	15.39	21.18 Total gas				
		0.00	0.00	0.00	0.00 Total gas oil				
		5.79	0.00	15.39	21.18 Total gas mass out				
Yields									
Oil Product Yield		29.19 g/hr		26.30 ml/hr	37.98% carbon conversion to oil		32.04% C bal. adjusted		
		density,		1.11 g/ml	0.02 L/L feed				
Oil Loss in Aqueous					19.54% mass conversion to oil		16.48% C bal. adjusted		
		density, est		1 g/ml					
Gasification of Carbon	10.03%				66.29% C conversion to water soluble		55.92% C bal. adjusted		
Carbon loss in solids		2.44 g/hr			10.03% carbon conversion to gas		8.46% C bal. adjusted		
					4.24% % carbon loss in solids		3.58% C bal. adjusted		
Space velocity	1.49 L/L/hr	LHSV							
Calculation of Deoxygenation									
O content of dry product	13.22%								
O in Dry Product	3.86 g/hr								
O in Organics(H2O)	9.25 g/hr								
O in Dry Feed	58.04 g/hr								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET											
Run No.	HTL-17				reactor volume	1000	total mL				
						1000	mL at temperature				
Pressure	21.6 MPa	CSTR	320		Time	00:15:07.00					
45 psig differential	3120 psig	CSTR	345		Date	2-Apr-09					
		filter	347								
Total Feed	10130 cc	Feed rate	1500.7 cc/hr								
corn stover slurry # 7			1515.71 g/hr		225 tot oil			blowdown			
w/1% sodium carbonate					9134.5 tot aq			blowdown	87.3	20.80%	% dry solids
Total Product	9359.5 q				Product oil	33.3	g/hr	sum of two phases	1386.6		g/hr
Blowdown	589 q				Product aqueous	1363.3	g/hr				
					dry blowdown	18.16	g/hr	12.42 in CS			
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash		
feed		36.50%	4.40%	36.44%	1.01	86.75%	0.46%	0.028%	23.64%	101.44%	
product oil		63.15%	8.35%	26.57%	1.088	10.27%	1.12%	0.068%	0.0%	99.26%	
oxygen by difference		2.57%	10.13%	86.00%	1.0 est	96.00%	<0.05	<0.005%		98.70%	
aqueous		12.60%	1.16%	8.94%			0.26%	0.017%	74.22%	97.19%	
dry rinsed sol											
oil, dry basis		70.96%	8.09%	19.61%			1.26%	0.08%			
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD			
feed		73.30	156.22	1240.66	1470.19			145130			
product oil		21.03	2.78	8.85		31.31		NA			
aqueous		34.78	137.09	1163.84		pH 4.85-5.70		86760			
gas		6.18	0.12	16.27							
blowdown		2.29	0.21	1.62							
Total Products		64.27	140.20	1190.58	1395.05						
Elemental Balance		88%	90%	96%							
Ash Balance		>>>>>>	>>>>>>	>>>>>>	>>>>>>	28.39%	(without aqueous)				
Total Material Balance		>>>>>>	>>>>>>	>>>>>>	>>>>>>	95%					
GAS CALCULATIONS											
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr						
Gas Out	217.9 L/hr		9.08 moles/hr								
Gas Composition			moles/hr								
volume%		C	H	O							
Hydrogen	0.55%		0.10		0.10 gH/hr	trace					
CarbDioxide	5.60%	0.51		1.02							
CarbMonoxide	0.00%	0.00	0.00	0.00							
Methane	0.00%	0.00	0.00		trace	trace					
Ethane	0.03%	0.01	0.02		trace	trace					
Propane	0.00%	0.00	0.00								
Butanes	0.00%	0.00	0.00								
Pentanes	0.00%	0.00	0.00								
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94				
	6.18%										
		C g/hr	H g/hr	O g/hr							
Total Gas, C1-C4		6.18	0.02	16.27	22.46	Total gas					
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil					
		6.18	0.02	16.27	22.46	Total gas mass out					
Yields											
Oil Product Yield		29.88 g/hr		27.46 ml/hr		28.69% carbon conversion to oil		32.72% C bal. adjusted			
		density,	1.088 g/ml			0.02 L/L feed					
						14.88% mass conversion to oil		16.97% C bal. adjusted			
Oil Loss in Aqueous						47.45% C conversion to water soluble		54.11% C bal. adjusted			
Gasification of Carbon	8.43%					8.43% carbon conversion to gas		9.61% C bal. adjusted			
Carbon loss in solids		2.29 g/hr				3.12% % carbon loss in solids		3.56% C bal. adjusted			
Space velocity	1.50 L/L/hr	LHSV									
Chemical Hydrogen Consumption			-0.35 g/hr		-3 L/L		-3 nM3/tonne				
Calculation of Deoxygenation											
O content of dry product	19.44%										
O in Dry Product	5.81 g/hr										
O in Organics(H2O)	9.02 g/hr										
O in Dry Feed	73.18 g/hr										

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-17				reactor volume	1000	total mL		
Pressure	20.3 MPa	CSTR	319			1000	mL at temperature		
45 psig differential	2935 psig	CSTR	345		Time	06:15-10:45			
		filter	352		Date	3-Apr-09			
Total Feed	6760 cc	Feed rate	1502 cc/hr						
corn slover slurry # 7			1517.02 g/hr		131.2 tot oil			blowdown	19.02% % dry solids
w/1% sodium carbonate					6231 tot aq			blowdown	157.6 g/hr
Total Product	9583.8 g				Product oil	29.2 g/hr	sum of two phases		1413.9 g/hr
Blowdown	709 g				Product aqueous	1384.7 g/hr			
					dry blowdown	29.98 g/hr		12.42 in CS	
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash
feed	35.95%	4.40%	35.52%	1.01	86.60%	0.47%	0.013%	23.95%	100.28%
product oil	64.19%	8.71%	25.22%	1.081	12.33%	0.99%	0.048%	9.7%	99.15%
aqueous	2.79%	11.21%	86.00%	1.0 est	96.00%	<0.05%	<0.005%		100.00%
dry rinsed sol	13.96%	1.25%	9.31%			0.21%	0.014%	74.22%	98.95%
oil, dry basis	73.93%	8.44%	16.44%			1.14%	0.06%		
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
feed	73.07	156.21	1238.67		1467.95			136400	
product oil	18.74	2.54	7.36			30.91		NA	
aqueous	38.63	155.16	1190.84			pH 6.15-6.24		82600	
gas	4.74	0.09	12.60						
blowdown	4.18	0.37	2.79						
Total Products	66.30	158.16	1213.59		1438.06				
Elemental Balance	91%	101%	98%						
Ash Balance	>>>>>>	>>>>>>>>>>	>>>>>>>>>>	>>>>>>>	45.70% (without aqueous)				
Total Material Balance	>>>>>>	>>>>>>>>>>	>>>>>>>>>>	>>>>>>>	98%				
GAS CALCULATIONS									
Gas In	0 L/hr	0.00 moles/hr		0.00 g H/hr					
Gas Out	210 L/hr	8.75 moles/hr							
Gas Composition		moles/hr							
Hydrogen	0.50%								
CarbDioxide	4.50%	0.39	0.09	0.79	0.09 gH/hr	trace			
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Elthane	0.00%	0.00	0.00						
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00						
	5.00%					2.94			
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4	4.74	0.00	12.60	17.34	Total gas				
Total Gas Oil, CS-C7	0.00	0.00	0.00	0.00	Total gas oil				
	4.74	0.00	12.60	17.34	Total gas mass out				
Yields									
Oil Product Yield	25.60 g/hr	23.68 ml/hr		25.65% carbon conversion to oil	28.27% C bal. adjusted				
	density,	1.081 g/ml		0.02 L/L feed					
				12.59% mass conversion to oil	13.88% C bal. adjusted				
Oil Loss in Aqueous				52.87% C conversion to water soluble	58.27% C bal. adjusted				
Gasification of Carbon	6.48%			6.49% carbon conversion to gas	7.15% C bal. adjusted				
Carbon loss in solids	4.18 g/hr			5.72% % carbon loss in solids	6.31% C bal. adjusted				
Space velocity	1.50 L/L/hr	LHSV							
Chemical Hydrogen Consumption		-0.48 g/hr		-3 L/L		-3 nM3/tonne			
Calculation of Deoxygenation									
O content of dry product	16.26%								
O in Dry Product	4.16 g/hr								
O in Organics(H2O)	9.23 g/hr								
O in Dry Feed	72.20 g/hr								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-19				reactor volume	1000 1000	total mL mL at temperature		
Pressure	20.4 MPa 2950 psig	CSTR CSTR filter	322 346 340		Time	16:18-19:40			
					Date	28-May-09			
Total Feed	5020 cc	Feed rate	1491 cc/hr						
corn stover slurry #2			1505.91 g/hr		105.5 tot oil		blowdown	14.23%	% dry solids
w/1% sodium carbonate					4549 tot aq		blowdown	185.6	g/hr
Total Product	4654.4 q				Product oil	31.3 q/hr	sum of two phases	1382.5	g/hr
Blowdown	629 q				Product aqueous	1361.2 q/hr			
					dry blowdown	26.42 q/hr			
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash
feed		34.65%	4.66%	38.24%	1.04	87.40%	0.52%	0.032%	25.69%
product oil		68.89%	7.91%	19.89%	1.094	7.74%	1.15%	0.083%	0.0%
oxygen by difference		2.77%	10.67%	86.60%	1.0 est	96.00%	<0.05	<0.005%	100.04%
aqueous		10.61%	1.18%	12.53%			0.23%	0.019%	74.53%
dry rinsed solids									99.08%
oil, dry basis		76.39%	7.81%	14.43%			1.28%	0.09%	
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
feed		65.74	156.37	1241.18	1463.28				
product oil		21.56	2.48	6.22		28.87	>1500 cSt @ 40C		
aqueous		37.36	144.17	1170.14		4.5		71250	
gas		5.10	0.19	12.98					
blowdown		2.80	0.31	3.31					
Total Products		66.82	147.15	1192.65	1406.62				
Elemental Balance		102%	94%	96%					
Ash Balance		40.38%							(based on solids recovered and without aqueous)
Total Material Balance		96%							
GAS CALCULATIONS									
Gas In	0 L/hr	0.00 moles/hr	0.00 g H/hr						
Gas Out	217 L/hr	9.04 moles/hr							
Gas Composition		moles/hr							
Hydrogen	0.73%				0.13 gH/hr	trace			
CarbDioxide	4.49%	0.41	0.13	0.81					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.00%	0.00	0.00		trace	trace			
Ethane	0.10%	0.02	0.05		trace	trace			
Propane	0.00%	0.00	0.00						
Butanes	0.00%	0.00	0.00						
Pentanes	0.00%	0.00	0.00						
Higher HC (C7H14)	0.00%	0.00	0.00						
	5.32%					2.94			
Total Gas, C1-C4		C q/hr	H q/hr	O q/hr	18.13	Total gas			
Total Gas Oil, C5-C7		5.10	0.06	12.98	0.00	Total gas oil			
		5.10	0.06	12.98	18.13	Total gas mass out			
Yields									
Oil Product Yield		28.88 q/hr	26.41 ml/hr		32.80% carbon conversion to oil	32.27% C bal. adjusted			
		density	1.0935 q/ml		0.02 L/L feed				
					15.22% mass conversion to oil	14.97% C bal. adjusted			
Oil Loss in Aqueous					56.83% C conversion to water solubl	55.91% C bal. adjusted			
Gasification of Carbon	7.75%				7.75% carbon conversion to gas	7.63% C bal. adjusted			
Carbon loss in solids		2.80 g/hr			4.26% % carbon loss in solids	4.19% C bal. adjusted			
Space velocity	1.49 L/L/hr	LHSV							
Chemical Hydrogen Consumption		-0.47 q/hr	-4 L/L		-3 nM3/tonne				
Calculation of Deoxygenation									
O content of dry product	14.10%								
O in Dry Product	4.07 q/hr								
O in Organics(H2O)	17.12 q/hr								
O in Dry Feed	72.55 q/hr								

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET											
Run No.	HTL-20				reactor volume	1000	total mL				
						1000	mL at temperature				
Pressure	20.7 MPa		CSTR	323							
	2995 psig		CSTR	349							
			filter	342							
					Time	23:00-07:45					
					Date	6/2-3/2009					
Total Feed	11268	cc	Feed rate	1260	cc/hr						
corn stover slurry #2				1272.60	g/hr	210.5	tot oil				
w/1% sodium carbonate						10.066	tot ag				
Total Product	10276.5	g				Product oil	24.1	g/hr	blowdown	20.53%	% dry solids
Blowdown	972	g				Product aqueous	1160.4	g/hr	blowdown	111.1	g/hr
						dry blowdown	22.19	g/hr	sum of two phases	1174.5	g/hr
Elemental Analyses					density@25C	moisture			12.42 in CS		
feed	35.87%	C	H	O	1.01	89.17%	N	0.52%	S	21.42%	96.04%
product oil	43.59%		8.60%	26.15%	1.073	12.60%		0.73%	0.063%		79.13%
oxygen by difference	1.63%		10.87%	87.50%	1.0 est	96.00%		<0.05	<0.005%		100.00%
aqueous	13.55%		1.30%	13.56%				0.23%	0.014%	83.38%	112.02%
dry rinsed sol	65.52%		10.80%	22.48%				1.10%	0.09%		
oil, dry basis											
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD			
feed	49.44	133.90	1053.57		1236.90			94900			
product oil	10.51	2.07	6.30			26.04	998cSt@40C				
aqueous	18.69	125.05	1006.60			pH = 5		57533			
gas	2.80	0.12	7.06								
blowdown	3.01	0.29	3.01								
Total Products	35.01	127.53	1022.97		1185.50						
Elemental Balance		71%	95%	97%							
Ash Balance		>>>>>>	>>>>>>	>>>>>>	>>>>>>	64.42%	(solids only without liquids)				
Total Material Balance		>>>>>>	>>>>>>	>>>>>>	>>>>>>	96%					
GAS CALCULATIONS											
Gas In	0	L/hr	0.00	moles/hr	0.00	g H/hr					
Gas Out	176.5	L/hr	7.35	moles/hr							
Gas Composition		moles/hr									
volume%		C	H	O							
Hydrogen	0.50%		0.07		0.07	gH/hr	trace				
CarbDioxide	3.00%	0.22		0.44							
CarbMonoxide	0.00%	0.00	0.00	0.00							
Methane	0.10%	0.01	0.03				trace				
Ethane	0.03%	0.00	0.01				trace				
Propane	0.00%	0.00	0.00								
Butanes	0.00%	0.00	0.00								
Pentanes	0.00%	0.00	0.00								
Higher HC (C7H14)	0.00%	0.00	0.00	0.00							
	3.63%						2.94				
Total Gas, C1-C4		C g/hr	H g/hr	O g/hr							
		2.80	0.04	7.06	9.90	Total gas					
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil					
		2.80	0.04	7.06	9.90	Total gas mass out					
Yields											
Oil Product Yield		21.06	g/hr	19.62	ml/hr	21.25%	carbon conversion to oil	30.01%	C bal. adjusted		
			density,	1.07345	g/ml	0.02	L/L feed				
						15.28%	mass conversion to oil	21.58%	C bal. adjusted		
Oil Loss in Aqueous						37.81%	C conversion to water solubl	53.40%	C bal. adjusted		
Gasification of Carbon	5.66%					5.66%	carbon conversion to gas	8.00%	C bal. adjusted		
Carbon loss in solids		3.01	g/hr			6.08%	% carbon loss in solids	8.59%	C bal. adjusted		
Space velocity	1.26	L/L/hr	LHSV								
Chemical Hydrogen Consumption			-0.35	g/hr	-3	L/L		-3	nM3/tonne		
Calculation of Deoxygenation											
O content of dry product	17.10%										
O in Dry Product	3.60	g/hr									
O in Organics(H2O)	24.93	g/hr									
O in Dry Feed	46.00	g/hr									
Elliott: this calculation is skewed by the low carbon number in the oil											

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET											
Run No.	HTL-20				reactor volume	1000	total mL				
						1000	mL at temperature				
Pressure	21.1 MPa	CSTR	321		Time	09:15:45					
+/-100	3050 psig	CSTR	340		Date	3-Jun-09					
		filter	343								
Total Feed	11688	cc	Feed rate	1798	cc/hr						
corn stover slurry #3				1815.98	g/hr	254.5 tot oil		blowdown	22.38%	% dry solids	
w/1% sodium carbonate						9,728.5 tot aq		blowdown	172.2	g/hr	
Total Product	9983	q			Product oil	40.4	g/hr	sum of two phases	1661.8	g/hr	
Blowdown	861	q	#12 missing		Product aqueous	1621.4	g/hr				
					dry blowdown	38.53	g/hr	12.42 in CS			
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash		
feed	34.98%	4.61%	40.45%	1.07		89.14%	0.58%	0.040%	23.60%	104.22%	
product oil	68.09%	7.84%	21.53%	1.066		6.62%	1.23%	0.074%		98.75%	
aqueous	1.79%	10.98%	87.20%	1.0 est		96.00%	<0.05	<0.005%		99.97%	
dry rinsed so	11.15%	1.15%	11.44%				0.20%	0.016%	82.97%	106.92%	
oil, dry basis	73.91%	7.70%	16.98%				1.33%	0.08%			
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD			
feed	68.98	190.55	1517.08		1776.61			93467			
product oil	27.51	3.17	8.70			48.17	>1500 cSt@40C				
aqueous	29.02	177.95	1413.86			pH = 5		53725			
gas	4.87	0.10	12.75								
blowdown	4.29	0.44	4.41								
Total Products	65.70	181.66	1439.72		1687.07						
Elemental Balance	95%	95%	95%								
Ash Balance	>>>>>>	>>>>>>	>>>>>>	>>>>>>	68.69%	(solids only without liquids)					
Total Material Balance	>>>>>>	>>>>>>	>>>>>>	>>>>>>	95%						
GAS CALCULATIONS											
Gas In	0	L/hr	0.00	moles/hr	0.00	g H/hr					
Gas Out	251.7	L/hr	10.49	moles/hr							
Gas Composition			moles/hr								
volume%		C	H	O							
Hydrogen	0.38%		0.08		0.08	gH/hr	trace				
CarbDioxide	3.80%	0.40		0.80							
CarbMonoxide	0.00%	0.00	0.00	0.00							
Methane	0.00%	0.00	0.00		trace		trace				
Ethane	0.03%	0.01	0.02								
Propane	0.00%	0.00	0.00								
Butanes	0.00%	0.00	0.00								
Pentanes	0.00%	0.00	0.00								
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94				
	4.21%										
		C g/hr	H g/hr	O g/hr							
Total Gas, C1-C4	4.87	0.02	12.75	17.65	Total gas						
Total Gas Oil, C5-C7	0.00	0.00	0.00	0.00	Total gas oil						
	4.87	0.02	12.75	17.65	Total gas mass out						
Yields											
Oil Product Yield	37.73	g/hr	35.38	ml/hr	39.88%	carbon conversion to oil	41.87%	C bal. adjusted			
		density,	1.06624	g/ml	0.02	L/L feed					
					19.13%	mass conversion to oil	20.08%	C bal. adjusted			
Oil Loss in Aqueous					42.08%	C conversion to water soluble	44.18%	C bal. adjusted			
Gasification of Carbon	7.06%				7.07%	carbon conversion to gas	7.42%	C bal. adjusted			
Carbon loss in solids		4.29	g/hr		6.23%	% carbon loss in solids	6.54%	C bal. adjusted			
Space velocity	1.80	L/L/hr	LHSV								
Chemical Hydrogen Consumption			-0.53	g/hr	-3	L/L		-3	nM3/tonne		
Calculation of Deoxygenation											
O content of dry product	16.75%										
O in Dry Product	6.32	g/hr									
O in Organics(H2O)	30.27	g/hr									
O in Dry Feed	79.77	g/hr									

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET											
Run No.	HTL-22				reactor volume	1000 1000	total mL mL at temperature				
Pressure	20.5 MPa 296.3 psia	CSTR CSTR filter	319 349 329	inlet-bottom outlet-top	Time Date	10-15-19-15 5-Aug-09					
Total Feed	13260 cc	Feed rate	1473 cc/hr								
corn stover slurry w/HTL20 recycle water			1487.73 g/hr			296.5 g, total oil	blowdown	27.48% % dry solids			
w/1% sodium carbonate						12438 g, total aqueous	blowdown	4.83 g/hr			
Total Product	12734.5 g			Product oil		32.94 g/hr	sum of two phases	1414.94 g/hr			
Blowdown	43 g			Product aqueous		1382 g/hr					
				dry blowdown		1.33 g/hr	12.42 in CS				
Elemental Analyses		C	H	O	density@25C	moisture	N	S	ash		
feed		34.61%	4.05%	42.49%	1.01	86.15%	0.43%	0.009%	22.70%	104.26%	
product oil		60.21%	7.99%	15.20%	1.109	7.03%	1.14%	0.077%		84.61%	
aqueous		2.60%	10.11%	87.30%	1	96.00%	<0.05%			100.01%	
dry rinsed solids		10.48%	0.87%	8.70%			0.16%		79.81%	100.01%	
oil, dry basis		77.60%	9.28%	11.55%			1.47%	0.10%			
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD			
feed		71.29	152.01	1225.57	1448.87			130.467			
product oil		19.83	2.63	5.01							
aqueous		35.93	139.65	1206.49		pH = 5.05		68.610			
gas		6.83	0.21	17.35							
blowdown		0.14	0.01	0.12							
Total Products		62.73	142.50	1228.96	1434.19						
Elemental Balance		88%	94%	100%							
Ash Balance		>>>>>>	>>>>>>	>>>>>>	>>>>>>	2.26% (solids only without liquids)					
Total Material Balance		>>>>>>	>>>>>>	>>>>>>	>>>>>>	99%					
GAS CALCULATIONS											
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr						
Gas Out	209.9 L/hr		8.75 moles/hr								
Gas Composition		volume%	C	H	O						
Hydrogen	0.67%		0.12		0.12 gH/hr	trace					
CarbDioxide	6.20%	0.54		1.08							
CarbMonoxide	0.00%	0.00	0.00	0.00							
Methane	0.13%	0.01	0.05		trace	trace					
Ethane/ethylene	0.08%	0.01	0.04		trace	trace					
Propane	0.00%	0.00	0.00								
Butanes	0.00%	0.00	0.00								
Pentanes	0.00%	0.00	0.00								
Higher HC (C7H14)	0.00%	0.00	0.00	0.00			2.94				
	7.08%										
		C g/hr	H g/hr	O g/hr							
Total Gas, C1-C4		6.83	0.09	17.35	24.27 Total gas						
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00 Total gas oil						
		6.83	0.09	17.35	24.27 Total gas mass out						
Yields						27.82% carbon conversion to oil	31.61% C bal. adjusted				
Oil Product Yield		30.63 g/hr		27.61 ml/hr		0.02 L/L feed					
		density, 1.10938 g/ml				14.87% mass conversion to oil	16.89% C bal. adjusted				
Oil Loss in Aqueous						50.41% C conversion to water solubl	57.28% C bal. adjusted				
Gasification of Carbon	9.57%					9.58% carbon conversion to gas	10.88% C bal. adjusted				
Carbon loss in solids		0.14 g/hr				0.20% % carbon loss in solids	0.22% C bal. adjusted				
Space velocity	1.47 L/L/hr	LHSV									
Chemical Hydrogen Consumption			-0.14 g/hr		-1 L/L		-1 nM3/tonne				
Calculation of Deoxygenation											
O content of dry product	9.63%										
O in Dry Product	2.95 g/hr										
O in Organics(H2O)	27.18 g/hr										
O in Dry Feed	87.52 g/hr										

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET											
Run No.	HTL-23				reactor volume	1000	total mL				
						1000	mL at temperature				
Pressure	19.9 MPa	CSTR	313	inlet-bottom							
	287.7 psig	CSTR	351	outlet-top							
		filter	329								
					Time	03:00-14:15					
					Date	9-Sep-09					
Total Feed	16740	cc	Feed rate	1488	cc/hr						
corn stover slurry #3				1502.88	g/hr						
w/1% sodium carbonate						258	g, total oil	blowdown	22.41%	% dry solids	
Total Product (less 1 sample)	14718	g				14460	g, total aqueous	blowdown	65.33	g/hr	
Blowdown	735	g				24.57	g/hr	sum of two phases	1401.7	g/hr	
						1377	g/hr				
						14.64	g/hr				
Elemental Analyses		C	H	O	moisture	N	S	ash			
based on HTL22b feed	feed	66.51%	1.01%	0.55%	1.01	90.30%	0.10%	0.00%	22.41%	101.65%	
oxygen by difference	product oil	67.61%	8.58%	22.55%	1.109	12.80%	1.19%	0.086%	0.2%	100.19%	
	aqueous	1.75%	10.21%	88.00%	1	96.00%	<0.05	0.085%		99.96%	
	dry rinsed solids	9.45%	1.14%	13.67%			0.19%	0.021%	83.18%	107.64%	
	oil, dry basis	77.37%	8.17%	12.80%	feed and product densities based on earlier measurements		1.36%	0.10%			
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD			
	feed	53.19	158.43	1259.44	1471.06			113,600			
	product oil	16.61	2.11	5.54							
	aqueous	24.10	140.59	1211.76		pH = 5.0		53,950			
	gas	5.88	0.17	14.90							
	blowdown	1.38	0.17	2.00							
	Total Products	47.98	143.04	1234.20	1425.21						
Elemental Balance		90%	90%	98%							
Ash Balance		>>>>>>	>>>>>>>>	>>>>>>>>	>>>>>>>>	36.49%	(solids only without liquids)				
Total Material Balance		>>>>>>	>>>>>>>>	>>>>>>>>	>>>>>>>>	97%					
GAS CALCULATIONS											
Gas In	0	L/hr	0.00	moles/hr	0.00	g H/hr					
Gas Out	227.3	L/hr	9.47	moles/hr							
Gas Composition											
	volume%	C	H	O							
Hydrogen	0.44%		0.08		0.08	gH/hr	trace				
CarbDioxide	4.92%	0.47		0.93							
CarbMonoxide	0.00%	0.00	0.00	0.00							
Methane	0.13%	0.01	0.05		trace		trace				
Ethane/ethylene	0.06%	0.01	0.03		trace		trace				
Propane	0.00%	0.00	0.00								
Butanes	0.00%	0.00	0.00								
Pentanes	0.00%	0.00	0.00								
Higher HC (C7H14)	0.00%	0.00	0.00	0.00				2.94			
	5.55%										
		C g/hr	H g/hr	O g/hr							
Total Gas, C1-C4		5.88	0.08	14.90	20.87	Total gas					
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00	Total gas oil					
		5.88	0.09	14.90	20.87	Total gas mass out					
Yields											
Oil Product Yield		21.43	g/hr	19.31	ml/hr	31.23%	carbon conversion to oil	34.63%	C bal. adjusted		
			density,	1.10938	g/ml	0.01	L/L feed				
						14.70%	mass conversion to oil	16.30%	C bal. adjusted		
Oil Loss in Aqueous						45.30%	C conversion to water solubl	50.23%	C bal. adjusted		
Gasification of Carbon	11.06%					11.06%	carbon conversion to gas	12.26%	C bal. adjusted		
Carbon loss in solids		1.38	g/hr			2.60%	% carbon loss in solids	2.88%	C bal. adjusted		
Space velocity	1.49	L/L/hr	LHSV								
Chemical Hydrogen Consumption			-0.28	g/hr	-2	L/L		-2	nM3/tonne		
Calculation of Deoxygenation											
O content of dry product	12.81%										
O in Dry Product	2.75	g/hr									
O in Organics(H2O)	36.72	g/hr									
O in Dry Feed	54.46	g/hr									

HYDROTHERMAL LIQUEFACTION CALCULATION SHEET									
Run No.	HTL-23				reactor volume	1000 1000	total mL mL at temperature		
Pressure	20.0 MPa 2890 psia	CSTR CSTR filter	310 351 327	inlet-bottom outlet-top	Time Date	04:30-17:45 11-Sep-09			
Total Feed	19790 cc	Feed rate	1494 cc/hr						
corn stover slurry #7			1508.94 g/hr			430 g, total oil		blowdown	33.59% % dry solids
w/1% sodium carbonate						18796.5 g, total aqueous		blowdown	65.36 g/hr
Total Product	19226.5 g					Product oil	35.83 g/hr	sum of two phases	1451.1 g/hr
Blowdown	915 g					Product aqueous	1409.6 g/hr		
						dry blowdown	21.96 g/hr		
Elemental Analyses		C	H	O		moisture	N	S	ash
based on HTL22b feed	feed	78.49%	4.31%	17.14%	1.01	87.10%	0.58%	0.020%	11.89%
	product oil	71.17%	8.26%	19.93%	1.109	10.60%	1.30%	0.075%	0.2%
oxygen by difference	aqueous	2.73%	10.19%	87.10%	1	96.00%	<0.05	0.006%	100.03%
	dry rinsed solids	8.52%	1.00%	10.40%			0.17%	0.011%	84.11%
	oil, dry basis	78.79%	7.82%	11.64%			1.44%	0.08%	
					feed and product densities based on earlier measurements	estimated			ash may include significant amount of the oxygen
Material Balance		g C/hr	g H/hr	g O/hr	Total	TAN	Viscosity	COD	
	feed	71.03	155.75	1239.68	1466.46			174,200	
	product oil	25.50	2.96	7.14					
	aqueous	38.48	143.64	1227.76		pH = 5.3		77,560	
	gas	6.12	0.20	15.31					
	blowdown	1.87	0.22	2.28					
	Total Products	71.97	147.02	1252.50	1471.49				
Elemental Balance		101%	94%	101%					
Ash Balance					41.45%	(solids only without liquids)			
Total Material Balance					100%				
GAS CALCULATIONS									
Gas In	0 L/hr		0.00 moles/hr		0.00 g H/hr				
Gas Out	214.4 L/hr		8.93 moles/hr						
Gas Composition			moles/hr						
	volume%	C	H	O					
Hydrogen	0.50%		0.09		0.09 gH/hr	trace			
CarbDioxide	5.36%	0.48		0.96					
CarbMonoxide	0.00%	0.00	0.00	0.00					
Methane	0.18%	0.02		0.06		trace			
Ethane/ethylene	0.08%	0.01		0.04		trace			
Propane	0.00%	0.00		0.00					
Butanes	0.00%	0.00		0.00					
Pentanes	0.00%	0.00		0.00					
Higher HC (C7H14)	0.00%	0.00		0.00			2.94		
	6.12%								
		C g/hr	H g/hr	O g/hr					
Total Gas, C1-C4		6.12	0.11	15.31	21.54 Total gas				
Total Gas Oil, C5-C7		0.00	0.00	0.00	0.00 Total gas oil				
		6.12	0.11	15.31	21.55 Total gas mass out				
Yields									
Oil Product Yield		32.03 g/hr		28.87 ml/hr		35.90% carbon conversion to oil		35.43% C bal. adjusted	
			density,	1.10938 g/ml		0.02 L/L feed			
						16.46% mass conversion to oil		16.24% C bal. adjusted	
Oil Loss in Aqueous						54.18% C conversion to water solubi		53.47% C bal. adjusted	
Gasification of Carbon	8.62%					8.62% carbon conversion to gas		8.51% C bal. adjusted	
Carbon loss in solids		1.87 g/hr				2.63% % carbon loss in solids		2.60% C bal. adjusted	
Space velocity	1.49 L/L/hr		LHSV						
Chemical Hydrogen Consumption			-0.33 g/hr		-2 L/L		-2 nM3/tonne		
Calculation of Deoxygenation									
O content of dry product	11.75%								
O in Dry Product	3.76 g/hr								
O in Organics(H2O)	24.90 g/hr								
O in Dry Feed	72.72 g/hr								

APPENIDX B

Correlations for Corn Stover HTL Performance

Correlation Definitions

The data for runs 17a through 20c, this is for all CSTR runs without recycle, were correlated in terms of the empirical expression:

$$PROPERTY\# = a \cdot (LHSV)^b \cdot (BMF)^c \cdot \left(\frac{T}{300}\right)^d$$

where:

PROPERTY # is Moisture Free Oil Yield, Water Solubles Yield, H/C Atomic ratio, O/C Atomic Ratio

LHSV is the liquid hourly space velocity in h^{-1}

BMF is the biomass to water inlet mass fraction

T is temperature in $^{\circ}C$

- Correlations were developed based on experimental Hydrothermal Upgrading (HTU) data (series 17 through 20), on a Moisture Free Basis.
- Experimental Data fit to the equation $y = a(LHSV)^b(BMF)^c(T_{out}/300^{\circ}C)^d$ using solver application in Excel.
- Runs 17c, 19 and 20c were excluded of the Aqueous Phase correlations because of Hydrogen balance closure; however, Oxygen concentration seems to be also affected.

Correlations-Series 17 through 20

CSTR with solids separation, no recycle

Corn Stover

Oil phase

	Oil yield	wt% C	wt% H	wt% O
a	0.799720875	826.3700867	4.0477318	4.093247664

b	0.782901291	1.110112671	-0.251848595	-0.151057362
c	-0.927041409	0.96833327	-0.142373758	-0.320426642
d	5.191310295	-7.518533298	3.565760281	6.024895087
Average relative error	8.22%	5.33%	0.81%	6.90%
Correlation coefficient	0.715626111	0.862477212	0.984463039	0.715287204

Corn Stover

Aqueous phase

	Water sol. yield	wt% C	wt% H	wt% O
a	14.31367888	4.23218E+11	1.22122E+16	2.21081E-06
b	-0.018669219	0.6221798	2.221538427	-1.110382955
c	-0.548714742	7.841925287	12.64247126	-5.762025988
d	-2.331731615	-50.96627331	-74.52618053	35.29832976
Average relative error	0.01%	0.05%	0.07%	26.26%
Correlation coefficient	0.999999784	0.99999993	0.999999563	0.883712492

Range of Experimental Conditions

	LHSV	BMR	Temp (degrees C)
Minimum value	1.26	0.109877913	330
Maximum value	1.798	0.154734411	352

Corn Stover

Oil phase

	H/C Ratio	O/C Ratio
a	0.067836903	0.005750578
b	-1.358147169	-1.186200106
c	-1.060251972	-1.115042791
d	10.69267687	12.14759115
Average relative error	6.32%	0.111449813
Correlation coefficient	0.938299279	0.824830367

Corn Stover

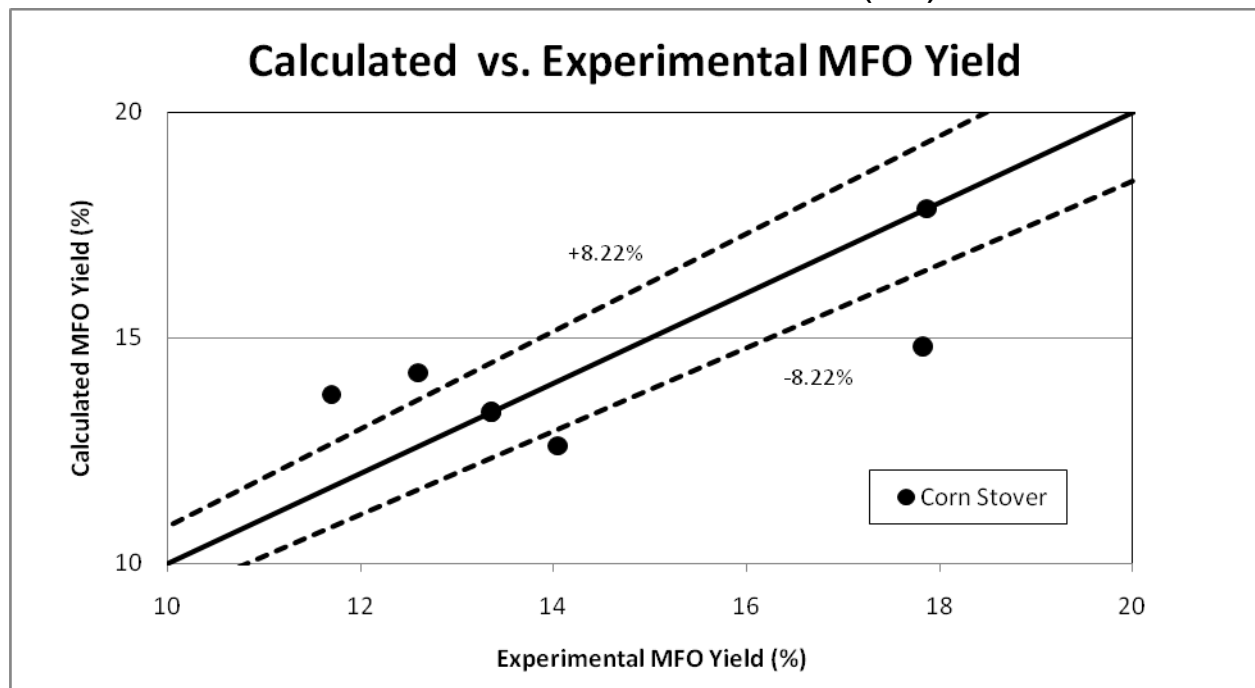
Aqueous phase

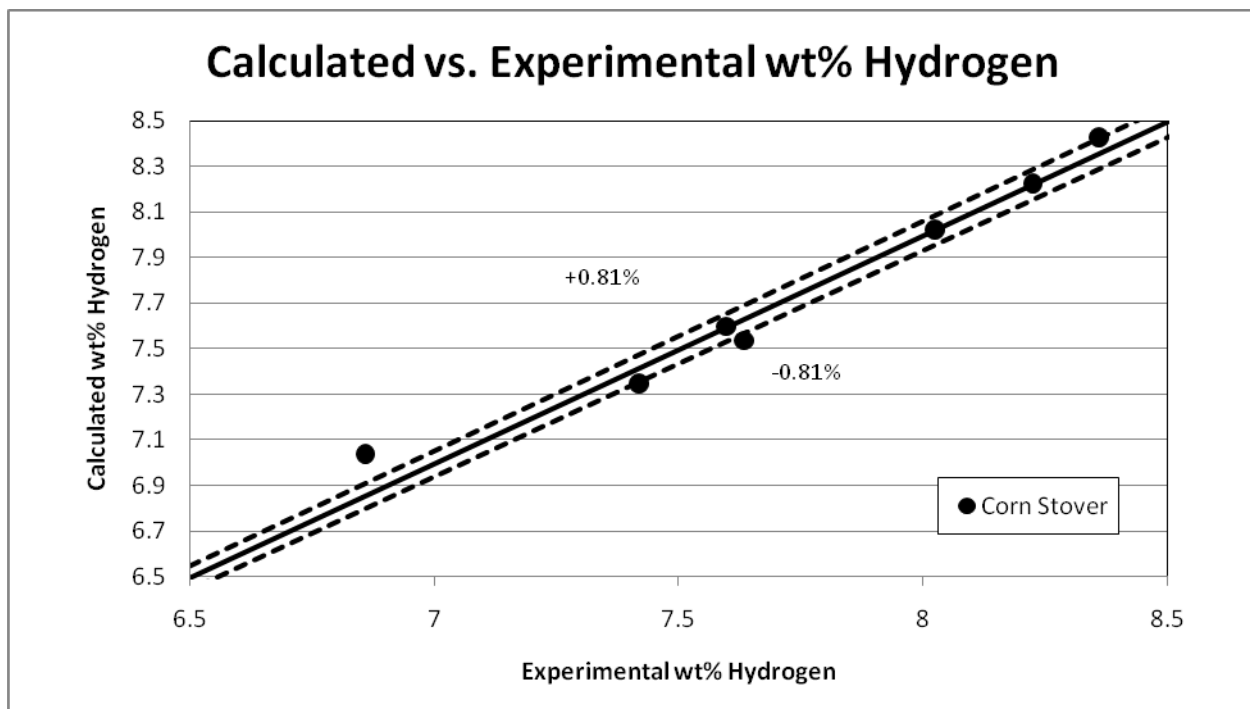
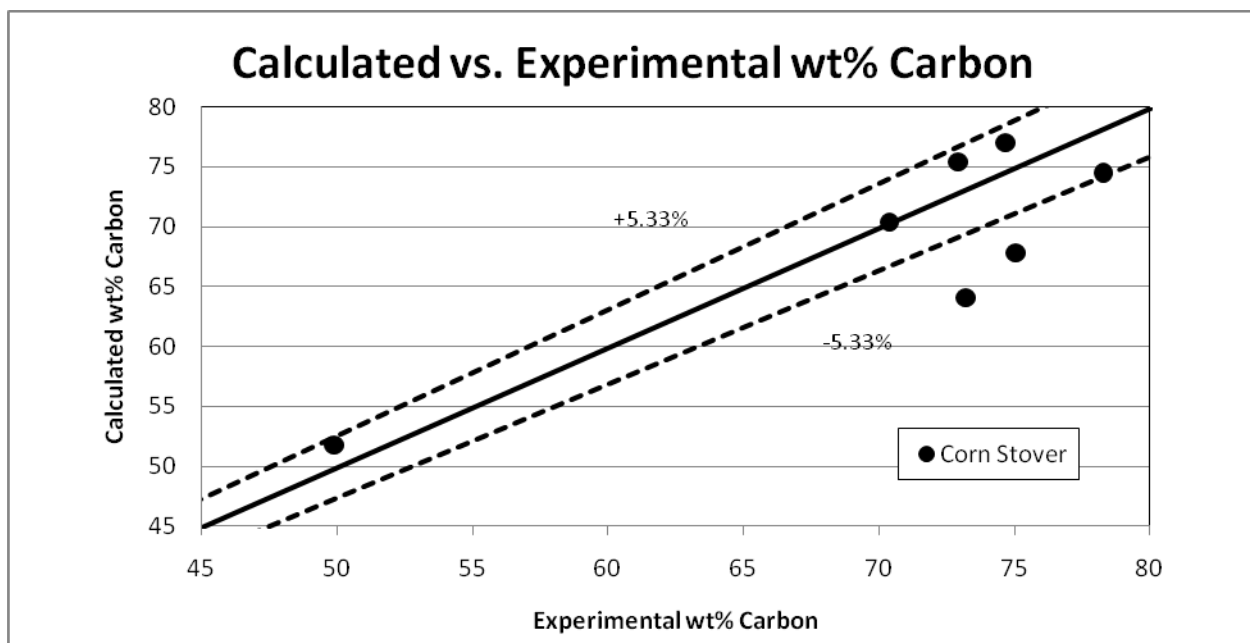
	H/C Ratio	O/C Ratio
a	342422.0312	1.3519E-05
b	1.599264989	5.802908514
c	4.799433216	-2.61179426
d	-23.55129316	14.81613352

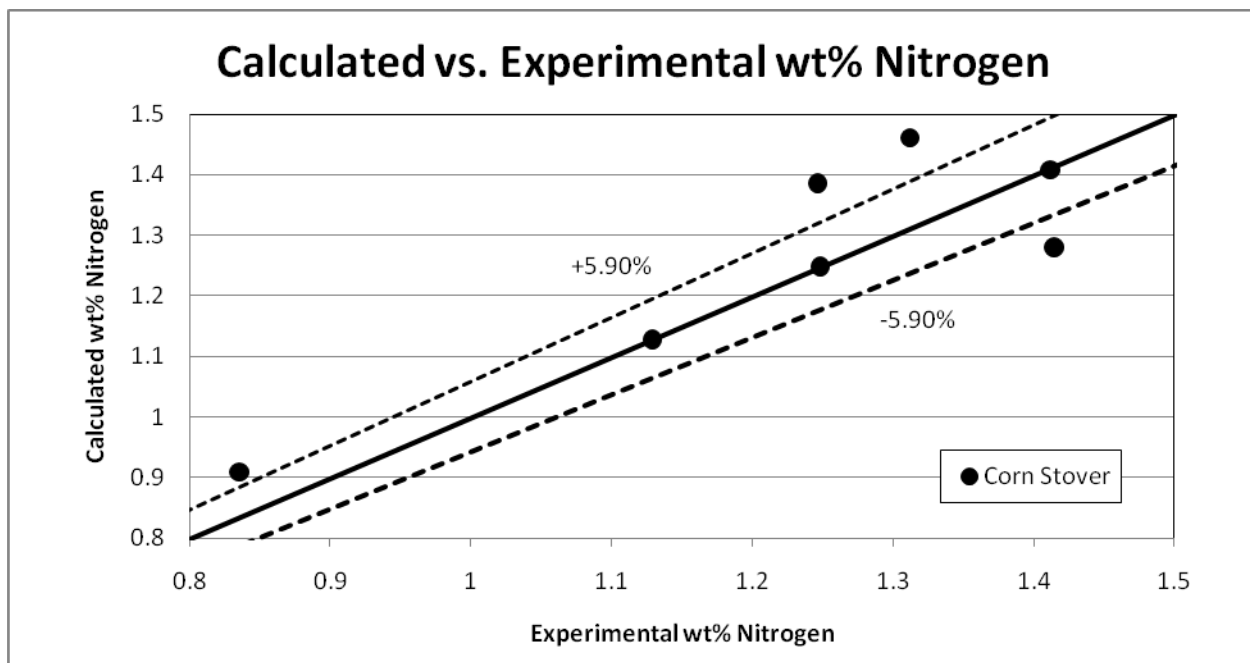
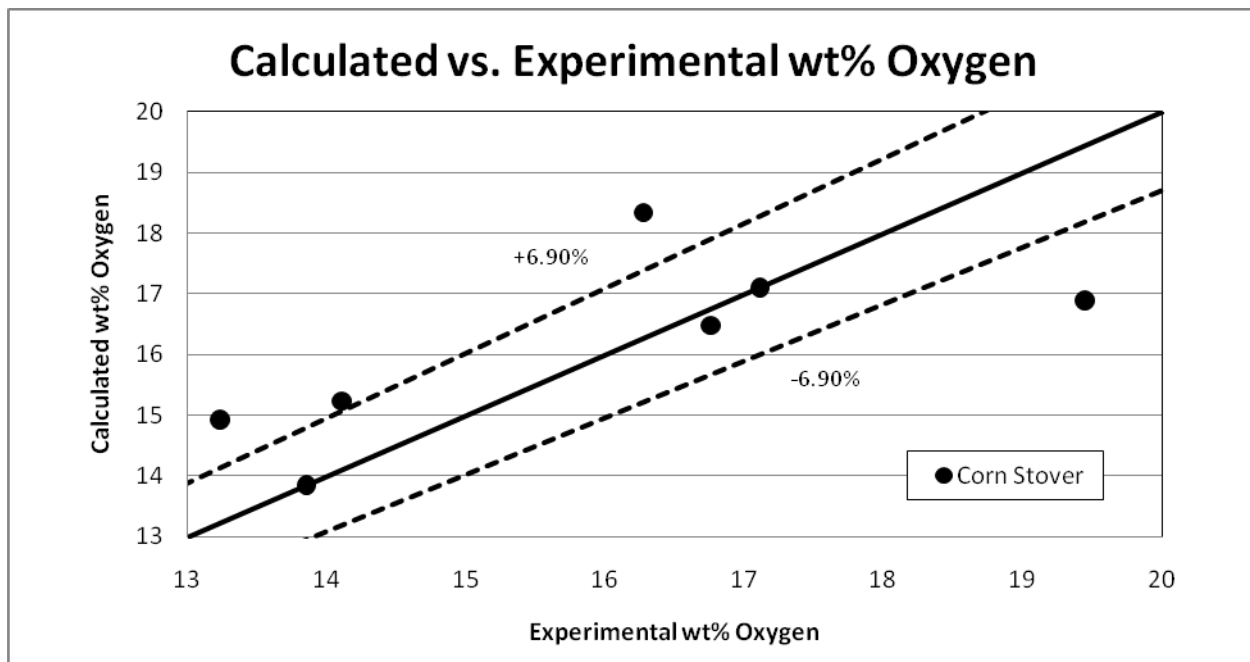
Average relative error	0.000279036	0.275986289
Correlation coefficient	0.999999577	0.199329643

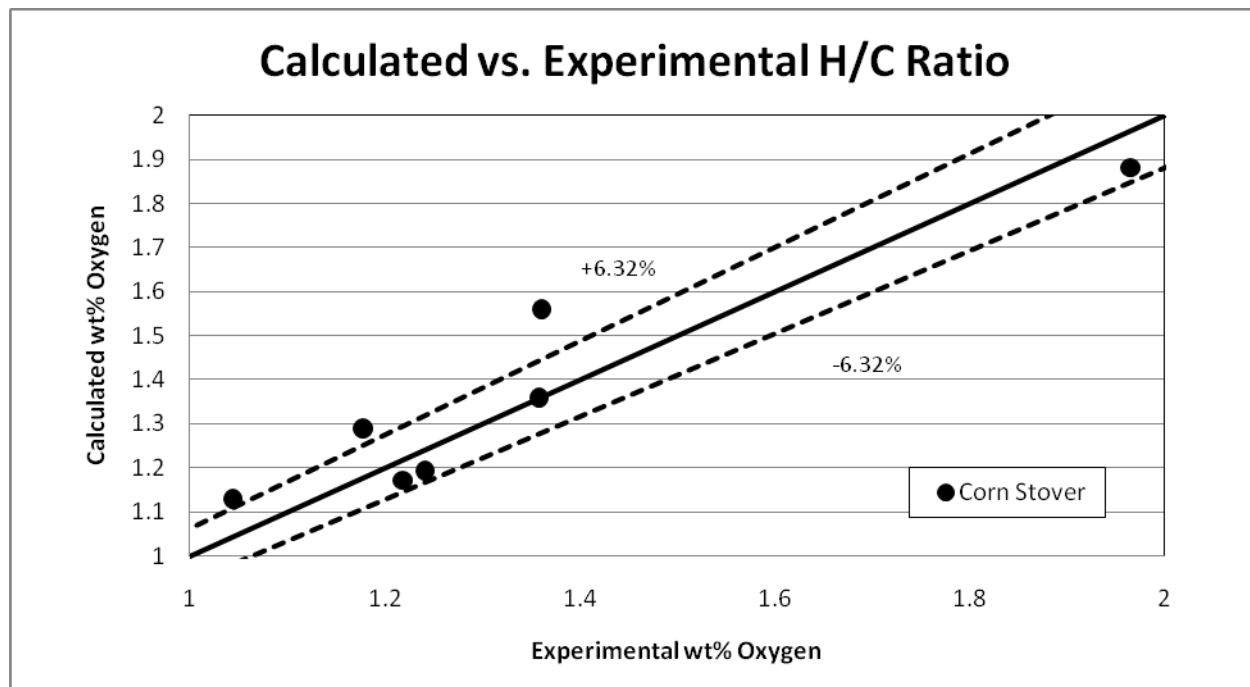
Range of Experimental Conditions	LHSV	BMR	Temp (degrees C)
Minimum value	1.26	0.109877913	330
Maximum value	1.798	0.154734411	352

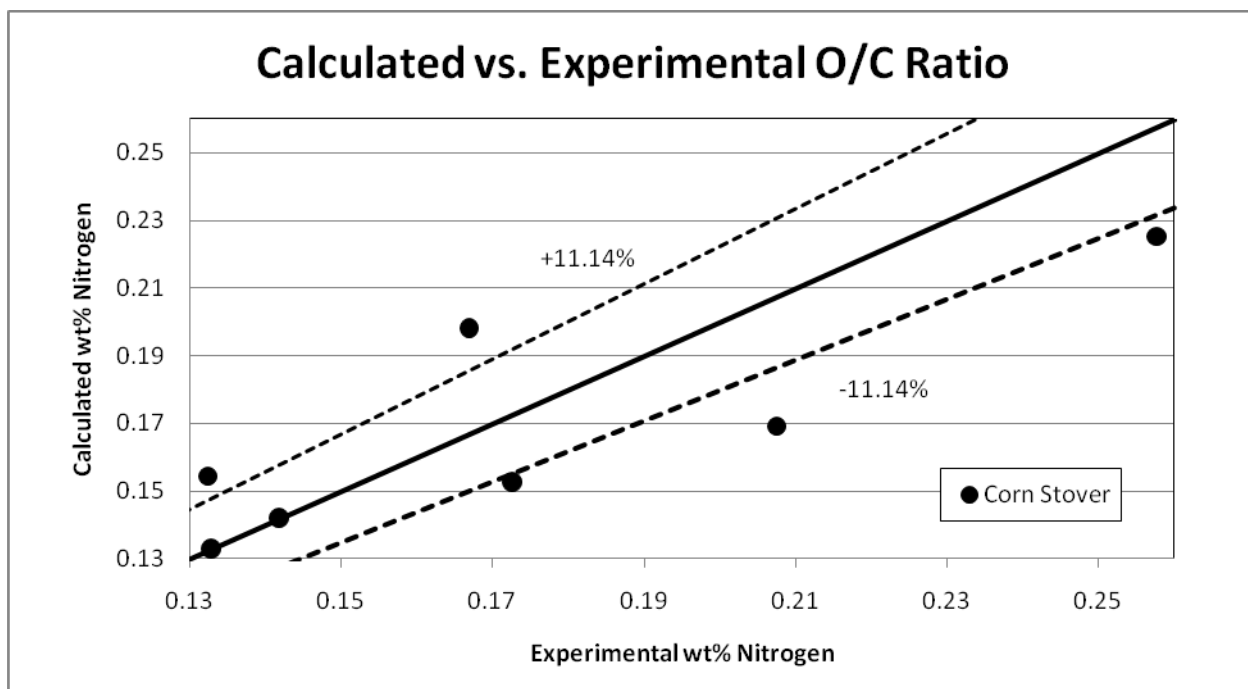
PARITY PLOTS FOR THE OIL PHASE (db)











PARITY PLOTS FOR THE AQUEOUS PHASE (db)

Runs 17c, 19 and 20c were excluded of the Aqueous Phase correlations because of Hydrogen balance closure; however, Oxygen concentration seems to be also affected.

