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Pyrolysis Oil to Gasoline-Final Report

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Pyrolysis Oil to Gasoline-Final Report

Battelle
As operator of Pacific Northwest National Laboratory ("PNNL")
Under its U.S. Department of Energy Contract
No. DE-AC05-76RLO 1830 (hereinafter "Battelle" or "Contractor")

And
Midwest Research Institute
As operator of the National Renewable Energy Laboratory ("NREL")
Under is U.S. Department of Energy Contract
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And

UOP LLC

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Executive Summary

The use of sustainable lignocellulosic biomass can provide an alternative source of liquid hydrocarbon fuels without impacting the food supply. Fast pyrolysis and subsequent catalytic hydroprocessing can produce infrastructure compatible fuels from lignocellulosic feedstocks. Recent results in the CRADA project involving UOP LLC, PNNL and NREL have demonstrated an economically viable process in laboratory scale tests.

Introduction

Biofuel production is expanding worldwide because of increasing petroleum prices, government mandates and incentives/commitments to green-house gas reduction. Today's biofuels are produced almost exclusively from food based sources.

The future widespread use of biofuels will largely depend on:

- The availability of a sustainable supply of non-food based renewable feedstock.
- The development of new technology to produce fuels from the unique composition of these highly oxygenated feedstocks.

Availability of non-food based feedstock

A feasibility study conducted by the U.S. Depts. of Agriculture and Energy concluded that the U.S. has the potential to produce a billion dry tons of biomass per year. The large scale availability of ligno-cellulosic biomass could potentially supply a high percentage of future liquid transportation fuels (see figure below) when commercial conversion processes become available. (Purvin&Gertz; USDA FSA Circulars)

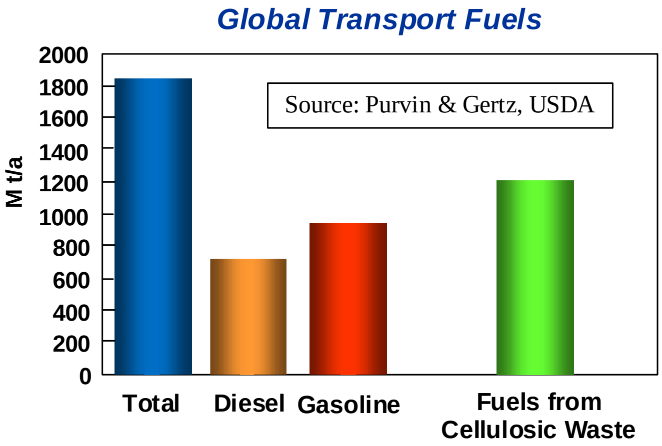

Figure 1 Global Transport Fuel Potential

Development of conversion technology

In 2006, a collaboration between UOP and the national labs, Pacific Northwest National Laboratory and National Renewable Energy Laboratory was established to identify practical processing options. The focus of this study was on a processing route for producing biofuels from forest and agro-wastes by first converting the biomass to fast pyrolysis oil and then upgrading the fast pyrolysis oil to transportation fuels.

The objective is to produce fuel that is indistinguishable from petroleum-based fuel to take advantage of existing transportation and distribution infrastructure.

Process Description

The first step is the fast pyrolysis of the lignocellulosic biomass. This is a thermochemical process with the potential to convert the large volumes of cellulosic biomass available in the U.S. and globally into liquid fuels.

A solid biomass feedstock is injected into a fluidized bed with high heat transfer capability for short contact times followed by separating char and then quenching to condense a liquid bio-oil in 50-75% yields, with gas and char forming the balance. This bio-oil contains the thermally cracked molecular fragments of the original cellulose, hemi-cellulose, and lignin fractions comprising the original biomass. It also contains a high percentage of water, often as high as 30% as well as significant organic oxygen remaining in the thermally cracked fragments.

In the second step, the pyrolysis oil is converted to a fuel by hydroprocessing. This, in itself, is a 2-step process. The first step greatly reduces the oxygen content, which significantly improves the thermal stability. The stabilized oil is then further hydrodeoxygenated to produce a hydrocarbon fuel with properties similar to petroleum based hydrocarbon fuels.

Hydroprocessing of the fast pyrolysis oil typically yields a product in which 20% is gasoline range hydrocarbons and another 20% is in the diesel range. The remaining 60% is mostly light ends, CO_2 and water.

The table below shows the composition of the gasoline range product. The (RON+MON)/2 of this cut was about 90.

Hydroprocessed bio-oil (from mixed wood)			*Gasoline*
	Min	*Max*	*Typical*
Paraffin, wt%	5.2	9.5	9
Iso-Paraffin, wt%	16.7	24.9	35
Olefin, wt%	0.6	0.9	4
Naphthene, wt%	39.6	55.0	7
Aromatic, wt%	9.9	34.6	38
Oxygenate, wt%		0.8	7

Table 1 Comparison of Fuel Properties 1

The economics for producing gasoline range and diesel range fuels from pyrolysis oil are shown in the next table, assuming $25/bbl pyrolysis oil cost and $100/bbl fuel value (based on the average December 2007 gasoline price). The tables show that this process can make a fungible fuel that meets the current DOE state of technology.

	Wood	*Corn Stover*	*DOE Bioethanol*	
			2007	*2012 Goal*
Cost $/gal, Hydrocarbon	2.50	2.82	-	-
Cost $/gal, Ethanol equivalent	1.55	1.74	2.43	1.36
Gallons of ethanol equivalent/ton biomass	120	87	71.9	89.7
% Carbon recovery	44	36	27.5	34.5

All cases based on 2007$, $46/ton biomass, $100/bbl fuel value ($2.38/gallon), 10% ROI

Table 2 Cost Estimates for the Production of Naphtha, Diesel and Fuel Oil Product from Pyrolysis Oils

Conceptual Pyrolysis Oil based Refinery

A proposed refining scheme is shown below. In this case several distributed pyrolysis units could supply a central bio-refinery for conversion to fungible transportation fuels.

Processing of fast pyrolysis oil requires more development, e.g. improved stability, to enable large scale commercially viable operations. In the long term, however, fast pyrolysis oil production can be increased to exploit the large amount of sustainable cellulosic biomass available.

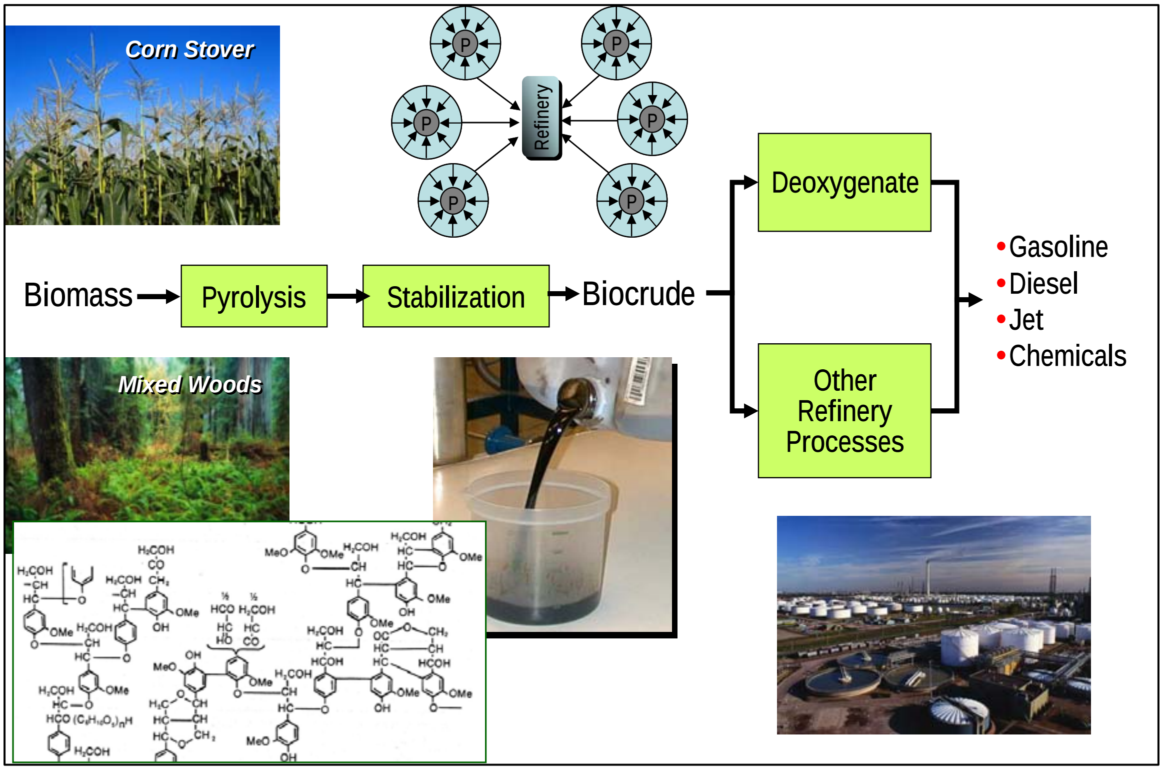

Figure 2 Proposed Refining Scheme

Study Goals and Basis

In the DOE report “Opportunities for Biorenewables in Oil Refineries,” refined pyrolysis oils were shown to have the potential to replace a significant portion of transportation fuels (60%). This thermal processing route can effectively utilize a vast majority of the 1 billion tons of biomass projected to be available in the United States, including those feedstocks unsuitable for fermentation. The pyrolysis pathway therefore provides the opportunity for increasing the impact of biofuels while leveraging existing processing and distribution systems.

In 2005, UOP, MRI and Battelle performed proof-of-principle experiments that indicated that pyrolytic lignin could be converted to gasoline with reasonable H2 consumption using mild hydrotreating followed by hydrocracking. A key finding was that mild hydrotreating conditions promote decarboxylation which significantly reduces the hydrogen consumption. The economics of this process are attractive when the price of crude oil increases (3 year payback for $50/bbl crude) or the price of pyrolysis oil decreases.

The desired outcome of this CRADA is to provide a foundation for development of an economically viable process for upgrading pyrolysis oil to gasoline. The purpose of this phase is to gain a fundamental understanding of the process sensitivity to pyrolysis oil feed properties. At the end of this project recommendations for a standard pyrolysis feed will be made and initial feed standards will be defined. The output of this analysis will be used in a stage gate development process to help decide whether further commercial development will proceed.

The project plan includes a series of analysis, research, development, and design efforts targeted at assessing the potential for the production of gasoline from pyrolysis oil derived from a diverse range of biomass feedstocks.

Barriers Addressed:

The primary barriers being addressed are technical issues related to the utilization of pyrolysis oil for transportation fuels. For pyrolysis oils to be widely accepted as a feedstock for transportation fuels an economically viable catalytic conversion process is required. In addition, a standard for pyrolysis oil feeds is highly desirable.

Rationale:

In the DOE report “Opportunities for Biorenewables in Oil Refineries,” (Marinangeli, 2006)refined pyrolysis oils were shown to have the potential to replace a significant portion of transportation fuels. This thermal processing route can effectively utilize a vast majority of the 1.3 billion tons of biomass projected to be available in the United States, including those feedstocks unsuitable for fermentation. The pyrolysis pathway therefore provides the opportunity for increasing the impact of biofuels while leveraging existing processing and distribution systems. The short term option produces gasoline and refinery fuel, while longer term advanced thermal conversion configurations may have the potential to produce both gasoline and ethanol. The project supports the 30 x 30 goal of replacement of 30% of 2005 gasoline with renewable fuels by 2030 and supports the $1.07 goal ($2005) by investigating alternative higher value uses of lignin rich streams in a biochemical biorefinery.

Fast Pyrolysis

NREL Thermochemical Pilot Development Unit (TCPDU)

A process flow diagram of the TCPDU, configured for pyrolysis, is shown in Figure 1. The feeding system consists of a loss-in-weight feeder with a 0.450-m^3 hopper (200 kg capacity). Pelletized biomass is metered into a crusher that grinds the material to minus 2.3 mm particle size. The material passes through a pair of rotary valves that isolate the process from the feeding system, into an eductor where hot nitrogen (100°C) is used to feed biomass into the pyrolysis reactor at a rate from 5 to 25 kg/hr.

An entrained flow reactor is used in pyrolysis experiments. The reactor is a 26-meter (85 ft) long by 3.81-cm (1.5 inch diameter tube with 11 independently controlled electrically heated zones used to raise the product temperature to a maximum of 950˚C. For pyrolysis experiments the nominal reactor temperature is varied between 500 and 600°C. The volume of the thermal cracker is approximately 0.028m^3 (1.0 ft^3).

The products then enter two cyclone separators in series with 10.2 cm (4 inch) and 7.6 cm (3 inch) diameter barrels, respectively. The solids removed in these cyclones are collected in char pots below the cyclones. The char pots are emptied periodically into an intermediate vessel where the char is cooled using nitrogen gas. The cooling vessel is operated like a lock hopper. Once the char has cooled, it is transferred from the intermediate vessel into a bag for further analysis or disposal. The products leaving the cyclones moves quickly through the remaining 3.81 cm (1.5") diameter pipe to the scrubber system. The volume of the piping between the cyclones and the condensation system is about 7.08 liters (0.25 ft^3). Heated sample ports are available in this section of pipe for removing process gas or vapors, and directing it to on-line analytical equipment for compositional analysis.

The scrubber operation consists of a conical vessel (25.4 cm to 5.08 cm taper) for mixing hot gases with cooling liquid followed by a 25.4 cm (10 inch) diameter vessel with nozzles in the top to spray in cooling liquid. The liquid flow rate is about 113.6 liters/minute (30 gallon per minute). This is sufficiently high to keep the cooling liquid from heating up significantly as it contacts the hot gases and vapors entering the scrubber vessels. The scrubbing liquid passes through nominal 25-micron filters then to a heat exchanger to remove heat from the cooling liquid. A phase separator after the heat exchanger allows the water and water soluble materials to drain out to the settling tank with the scrubbing liquid recirculating through the top of the separator back to the first scrubber vessel. Dodecane is re-circulated in the scrubbing loop as the cooling liquid, so over time hydrocarbon compounds such as benzene and naphthalene accumulate.

Condensed steam from the reactor is pumped from the middle phase of the settling tank through a series of filters and into a stripping column where light hydrocarbons are removed by nitrogen. The stripped gases and nitrogen are directed to the thermal oxidizer for destruction. Entrained particles or droplets exiting the scrubber vessels are removed by nominal 2-micron filters. Remaining aerosols are also removed at this point. Typically, an insignificant quantity of liquid is removed from this vessel during operation. However, this is dependent on the feedstock and mass flow rate through the system. Process pressure is about 68.9 kPag (10 psig). Unless the process gas is to be used for some other purpose, it is sent to a thermal oxidizer where it is combusted at 650°C.

Extensive analytical instrumentation is available for determining gas composition at the exit of the scrubbing system. With steam and other condensable vapors removed from the product gas stream compositions can be measured with three on-line, continuous, non-dispersive infrared (NDIR) chemical analyzers to monitor CO, CO_2, and CH_4; a thermal conductivity H_2 analyzer; a paramagnetic O_2 analyzer; a four channel, rapid analysis gas chromatograph that cycles every 2 minutes for measuring permanent gases and hydrocarbons up to C4; and a transportable molecular beam mass spectrometer (TMBMS) for continuous, real-time monitoring of all gas phase products with particular emphasis on tars and heteroatom products**.**

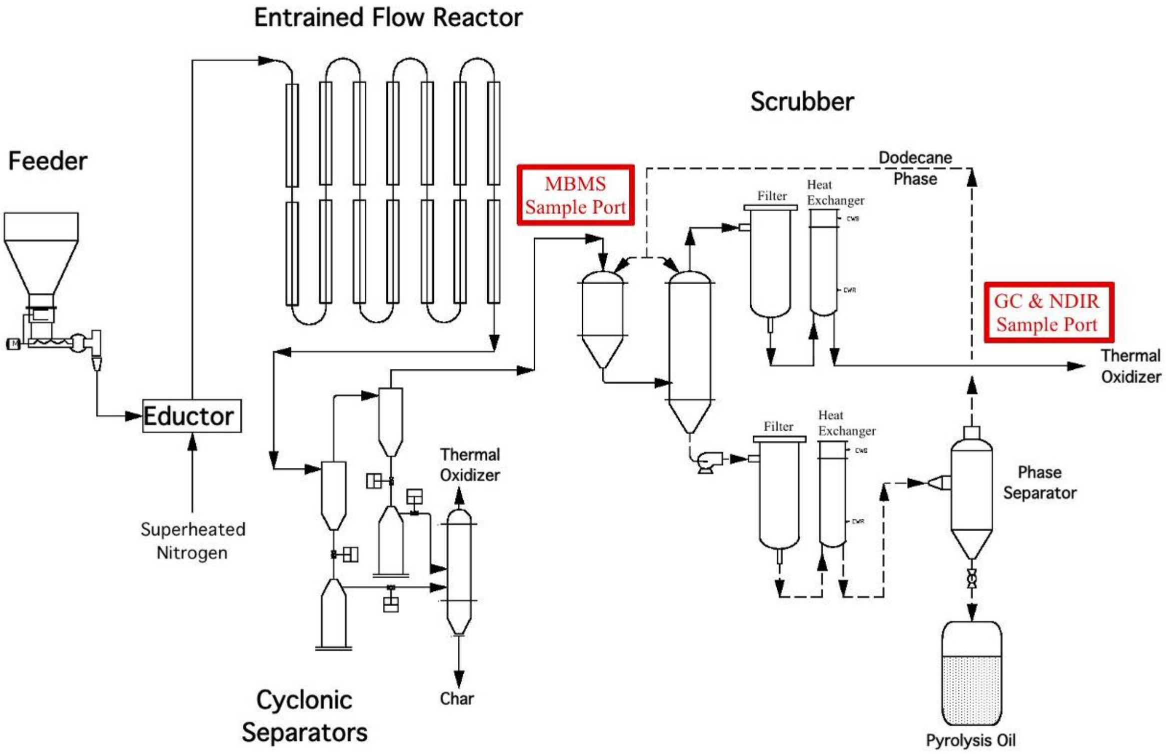

Figure 3 : NREL Thermochemical Process Development Unit, Configured for Entrained Flow Pyrolysis

Oil Production Campaign One

NREL performed three (3) pyrolysis experiments in the TCPDU to produce substantial quantities of pyrolysis oil as feed for hydrotreating and hydrocracking experiments at UOP and PNNL. Two of the experiments were performed using corn stover feedstock, and one experiment was performed using mixed wood feed (normally referred to as Vermont mixed wood). Woody materials and corn stover are abundant, available resources (each potentially available in quantities in excess of 250 million tons annually(Perlack, 2005)) that can have significant impact on biofuels production. Analyses were performed to characterize both the biomass feed and the product pyrolysis oil. Material balance data were collected and summarized for use in technoeconomic analyses. Samples of the oil produced were shipped to UOP and PNNL for additional analyses and upgrading experiments. Feed and char analyses included ultimate analysis, proximate analysis, ash component analysis, and heating value. Oil analyses included ultimate analysis, water content, ash component analysis, density, and pH. NREL also performed some limited on-line molecular beam mass spectrometry analysis to investigate compound identification.

An analysis of the feeds used is given in Table 3; a summary of the tests and material balances achieved is given in Tables 2 – 4.

Table 3: Feed Analyses Bio-Oil Production, Campaign One

Proximate, Ultimate, and Elemental Ash Analyses for Feeds

	DDGs	Corn Stover 1	Corn Stover 2	Mixed Wood
Proximate Analysis (wt% as received)				
Moisture		**5.83**	**5.78**	**4.26**
Ash		**10.29**	**10.69**	**0.55**
Volatile Matter		**68.54**	**67.35**	**82.96**
Fixed C		**15.34**	**16.18**	**12.23**
HHV (Btu/lb)		**6919**	**6824**	**8098**
Ultimate Analysis (wt% as received)				
C		**43.85**	**44.00**	**49.58**
H		**4.60**	**4.68**	**5.54**
N		**0.74**	**0.68**	**0.23**
O (by difference)		**34.39**	**33.90**	**39.83**
S		**0.08**	**0.08**	**0.01**
Cl		**0.22**	**0.19**	**0.00**
H/C		**1.25**	**1.27**	**1.33**
Elemental Ash Analysis (wt% of ash as oxide)				
SiO_2		**66.45**	**66.11**	**17.64**
Al_2O_3		**4.85**	**5.23**	**5.05**
TiO_2		**0.04**	**0.13**	**0.27**
Fe_2O_3		**0.96**	**0.94**	**2.64**
CaO		**4.00**	**3.80**	**26.60**
MgO		**1.58**	**1.63**	**4.33**
Na_2O		**0.99**	**1.04**	**1.77**
K_2O		**14.80**	**14.60**	**15.90**
P_2O_5		**2.87**	**2.75**	**2.56**
SO_3		**0.82**	**0.80**	**1.70**
Cl		**1.53**	**1.51**	
CO_2		**0.70**	**0.94**	

Table 4a. : Campaign One ,Test Summary Information

	Corn Stover 1	Mixed Wood	Corn Stover 2
Conditions			
Temperature, (deg C)	480	480	460
Est Residence Time (sec)	1.6	1.6	1.6
Nominal Feed Rate (kg/hr)	20.0	20.0	20.0
Nitrogen Carrier Rate (kg/hr)	20.0	20.0	20.0
Nominal Test Duration (hr)	10.1	8.5	15.2
Results			
Total Feed (kg / %)	202.8	175.8	303.3
Pyrolysis Liquids (kg)	107.3	123.2	143.7
Est % Aq	85.0		
Char (kg)	51.4	20.5	75.0
Gas(kg)	33.8	32.3	50.3
Water in Gas (Psat=24 mmHg, Pt=620 mmHg)	7.8	6.5	6.3
Overall Material Balance, wt %	98.7	103.8	90.8
Char	25.3	11.7	24.7
Oil	52.9	70.1	47.4
Wet Gas	20.5	22.1	18.7
C	95.7	99.3	104.2
H	90.3	96.8	92.8
O	104.9	109.8	96.9
Ash	94.6	134.4	89.3

Table 4b. Test One Summary Information (cont.)

	Corn Stover	Mixed Wood	Corn Stover 2
Feed			
Amount, kg	202.8	175.8	303.3
C, wt %	42.29	49.58	42.29
H	4.91	5.54	4.91
N	0.74	0.23	0.74
O	33.40	39.83	33.40
Ash	10.47	0.55	10.47
H2O	8.08	4.26	8.08
Oil			
Amount, kg	107.3	123.2	143.7
Percent Aqueous	85.00	-	
Organic			
Amount, kg	16.1	123.2	143.7
C, wt %	55.38	44.94	51.19
H	7.18	6.92	7.61
N	1.39	0.18	0.77
S			0.08
O	36.05	47.96	40.20
Ash	0.20	<0.05	0.15
Aqueous			
Amount, kg	91.21		
C, wt %	35.94		
H	7.85		
N	0.87		
O	55.34		
Ash	0.24		
H2O			

Table 4c. Campaign One Test Summary Information (cont.)

	Corn Stover	Mixed Wood	Corn Stover 2
Char			
Amount, kg	51.4	20.5	75.0
C, wt %	55.47	89.10	57.82
H	2.14	1.88	2.41
N	0.70	0.14	0.72
S			0.01
O	3.04	2.76	1.78
Ash	38.59	6.34	37.26
Gas			
Amount, kg	33.8	32.3	50.3
Ave Composition, mole% (Dry, N2, He Free)			
H2	-	-	-
CO	35.39	53.13	28.20
CO2	55.30	32.20	65.90
CH4	4.40	8.72	3.60
Acetylene	1.86	1.50	-
Ethylene	1.44	2.68	1.20
Ethane	0.11	0.08	-
Propylene	0.72	1.07	0.40
Propane	-	-	-
1-Butylene	0.57	0.52	0.70
2-t-Butylene	0.22	0.11	-
2-c-Butylene	-	-	-
Total	100.00	100.00	100.00
Benzene (ppmv)	7.34	-	-

Oil Production Campaign Two

Over a four week period in February and March 2008 150 gallons of pyrolysis oil were produced in NREL's TCPDU at three reactor temperatures; the most pyrolysis oil ever produced in this facility in one month. Most of the oil was produced for the joint CRADA project with UOP/NREL/PNNL and will be used as the feedstock for catalytically upgrading produced oil to make gasoline/diesel products. The additional oil will be held in reserve to provide uniform pyrolysis oil for use in upcoming pyrolysis solicitations. Usually used for steam gasification experiments (700°C to 950°C), the TCPDU reactor and downstream equipment presented different challenges when running at pyrolysis conditions (500°C to 600°C).

At the lowest temperature the oil yield was 57%, char yield was 13%, and light gas yield (carbon monoxide, carbon dioxide, etc.) was 24%; 95% of mass was accounted for in the mass balance. As expected, oil yield decreased with increasing temperature to 40% at the highest temperature. Qualitatively, the low-temperature oil was dark brown and thick, while the higher temperature oil was thinner and lighter brown. A significant amount of process and analytical data and product samples were collected during the course of the experiments,

A run summary and analysis of the feed is given in Table 5; pyrolysis oils analyses are given in Table 6; and gas analyses and char analyses are given in Table 7.

Temperature	500 ^{o}C			550 ^{o}C		600 ^{o}C	
Yields	kg		wt %	kg	wt %	kg	wt%
Feed	622.40		100.00	360.80	100.00	465.70	100.00
Oil	322.27		51.78	177.59	49.22	185.09	39.74
Gas	228.50		36.71	152.45	42.25	271.11	58.22
Char	73.95		11.88	36.71	10.17	42.13	9.05
Other Liquids	8.54		1.37	9.18	2.54	7.99	1.72
Product			101.74		104.19		108.72
Carbon			95.16		98.76		94.62
Hydrogen			111.17		113.81		115.50
Feed Analysis							
Moisture	5.23	+/-	0.27				
Ash	0.48		0.04				
Volatile Matter	81.39		1.31				
Fixed C	12.91		1.12				
HHV (Btu/lb)	7,879		65				
Ultimate Analysis (wt% as received)							
C	47.51	+/-	0.92				
H	5.24		0.09				
N	0.28		0.13				
O (by difference)	41.05		1.02				
S	0.21		0.13				
Cl	0.01		0.00				
Elemental Ash Analysis (wt% of ash as oxide)							
SiO_2	3.44	+/-	0.86				
Al_2O_3	0.39		0.23				
TiO_2	0.02		0.02				
Fe_2O_3	0.64		0.13				
CaO	41.66		3.29				
MgO	1.98		0.16				
Na_2O	0.37		0.18				
K_2O	20.40		1.25				
P_2O_5	2.62		0.25				
SO_3	1.51		0.66				
Cl	0.05		0.03				

Table 5. Campaign Two, Oak Pyrolysis, Yields and Feed Composition

Temperature	500 °C	550 °C	600 °C	
Oil				
Ultimate, As Received, wt%				
Water	24.6	25.3	42.8	
Ash	0.064	0.028	0.065	
C	42.76	42.83	29.82	
H	4.65	4.71	3.31	
N	0.01	0.01	0.01	
S	0.019	0.009	0.018	
O	27.91	27.12	23.99	
Dry Oil, wt %				
C	56.75	57.35	52.18	
H	6.17	6.31	5.79	
N	0.01	0.01	0.01	
S	0.03	0.01	0.03	
O	37.04	36.32	41.98	
Molar Ratio, C = 1				
C	1.0000	1.0000	1.0000	
H	1.2957	1.3103	1.3225	
N	0.0002	0.0001	0.0002	
S	0.0002	0.0001	0.0002	
O	0.4899	0.4753	0.6039	
Metals, mg/kg				
Ti	5.9	5.5	6.0	SW846-6010B
Fe	26	23	42	ASTM D3682
Ca	316	242	311	ASTM D3682
Mg	39.6	36.5	35.6	ASTM D3682
Na	839	425	345	ASTM D3682
K	111	84.7	138	ASTM D3682
P	<10	<10	<10	SM 4500-P M-C

Table 6. Campaign Two, Oak Pyrolysis, Pyrolysis Oil Analysis

Temperature	500 °C			550 °C			600 °C		
Gas Composition (mol%, N2, He free)									
H2	0.35	+/-	0.80	2.19	+/-	0.78	6.46	+/-	0.15
CO	37.10		4.02	44.84		3.82	51.30		0.16
CO2	19.23		1.49	13.86		0.55	10.07		0.12
CH4	10.01		0.66	10.13		0.52	10.92		0.06
C2H6	0.00		0.00	0.00		0.00	0.00		0.00
C2H4	2.22		0.21	2.73		0.19	3.44		0.04
C2H2	1.10		0.16	1.26		0.12	1.50		0.03
C3H8	0.00		0.00	0.00		0.00	0.23		0.02
C3H6	0.86		0.14	1.08		0.13	1.31		0.02
1-C4H8	0.43		0.05	0.52		0.07	0.63		0.03
2-cis-C4H8	0.10		0.04	0.11		0.09	0.14		0.03
2-trans-C4H8	0.14		0.02	0.16		0.09	0.12		0.02
H2O	28.46		3.53	23.12		5.27	13.88		0.19
	100.00			100.00			100.00		
Char									
Proximate Analysis (wt% as received)									
Moisture	0.02			0.01			0.01		
Ash	4.38			3.79			4.59		
Volatile Matter	23.25			21.66			19.11		
Fixed C	72.36			75.55			76.30		
HHV (Btu/lb)	13,115			13,178			13,514		
Ultimate Analysis (wt% as received)									
C	82.64			83.07			84.44		
H	2.73			2.80			2.56		
N	0.29			0.22			0.41		
O (by difference)	9.93			10.12			7.99		
S	0.02			0.01			0.01		
Cl	0.01			0.01			0.01		
Elemental Ash Analysis (wt% of ash as oxide)									
SiO2	5.99			3.07			3.06		
Al2O3	0.52			0.64			0.46		
TiO2	0.04			0.06			0.04		
Fe2O3	1.15			0.60			0.63		
CaO	38.27			39.17			40.37		
MgO	4.50			1.80			2.12		
Na2O	0.56			0.30			0.44		
K2O	17.55			18.90			19.63		
P2O5	2.22			2.27			2.13		
SO3	0.90			0.86			1.32		
Cl	0.05			0.11			0.02		

Table 7. Campaign Two, Oak Pyrolysis, Gas and Char Analysis

Accelerated aging test of bio-oil

Accelerated aging testing was performed according to the procedure described in the pyrolysis oil stabilization solicitation (USDOE,2008) on two samples of bio-oil produced by fast pyrolysis of oak at 500 ºC and 550ºC using the NREL entrained flow reactor system. Approximately 1 kg sample of each bio-oil was taken for the tests from a corresponding drum after vigorous stirring. Six 90 to 100g samples of each bio-oil enclosed in 100 mL screw-cap bottles were placed in a convection oven at 90°C for 24 hours. Three samples of each bio-oil were removed from the oven after 8 hours and three remaining after 24 hours. The weight loss of the samples was less than 0.4 g (<0.5%) except for one sample (550°C/90°C/8 h) that was not used in further measurements. After the high-temperature storage, the samples were placed in a refrigerator for a few days until viscosities measurements were performed. The initial bio-oil samples as well as the bio-oil produced at 500°C and stored at 90°C for 8 hours looked homogeneous while the other three samples (500°C/90°C/24 h, 550°C/90°C/8h, and 550°C/90°C/24h) despite vigorous shaking clearly remained two-phase liquids.

The viscosity of single-phase bio-oil samples was measured using a Brooksfield Digital Viscometer Model LVTD. The precision of the measurement is estimated at ±5%, which mostly results from potential variations in the liquid temperature. Viscosities were measured at 25°C and 40°C in duplicate for each sample stored at 90ºC for 0, 8, and for 24 hours. The average viscosity as well as the standard deviation for the set of bio-oil samples stored at the same conditions was calculated. The results are shown in Table 8.

Temperature/time	Avg. viscosity, cP
500°C/0 h	56
500°C/8 h	93
550°C/0 h	50

Table 8. Viscosity at 40°C of Bio-Oil Samples Aged at 90°C

The average rate of viscosity increase for the bio-oil produced at 500°C was 4.6 cP/h during the first eight hours of storage at 90°C. The performed tests showed that the accelerated storage conditions were too severe for a quantitative assessment of bio-oil stability measured as the viscosity increase per time unit. Phase separation occurred in the bio-oil produced at 550°C after less than 8 hours at 90°C and in the bio-oil produced at 500°C after less than 24 hours. For better quantitative observation of the changes in bio-oil properties (viscosity), we decided to lower the storage temperature to 50°C and measure viscosity of the samples as a function of aging time. Table 9 summarizes the results of viscosity measurements performed at 40°C.

Pyrolysis temperature, °C	500°C	550°C
Time of storage, hrs	Viscosity measured at 40°C, cP	
0	56	50
8	57	51

24	57	55
72	85	65
96	107	85

Table 9. Viscosity at 40°C of Bio-Oil Samples Aged at 50°C

Notable is that the viscosity of bio-oil produced at 500°C changed very little during 24 hours of storage at 50°C then it increased at an accelerated rate. The viscosity of bio-oil almost doubled after four days of storage at 50°C. The bio-oil produced at 550°C had slightly lower viscosity that increased at a somewhat lower rate. The viscosity change on storage is well represented as a quadratic function of time as shown in Figure 2.

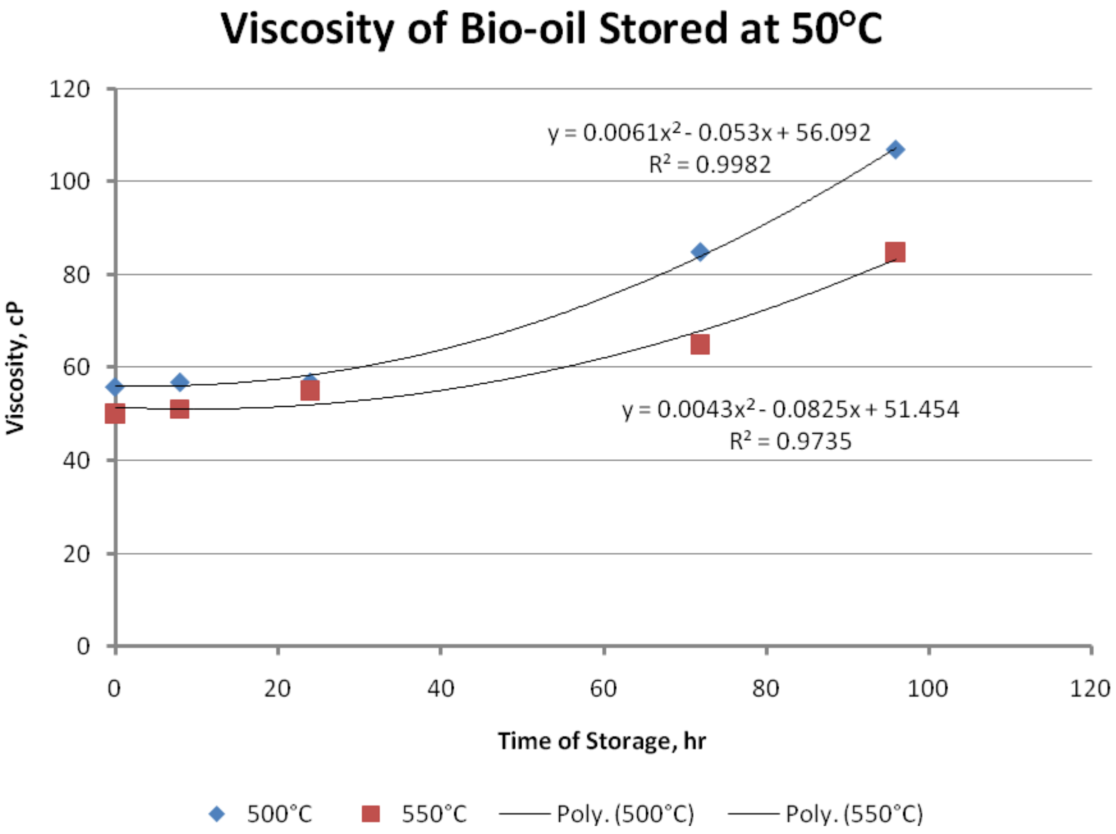

Figure 4. Viscosity of Bio-oil stored at 50 ^{o}C

The presented data show that an accelerated (less than a day) aging test for bio-oil based on the viscosity increase should be carried out at a temperature higher than 50°C but lower than 90°C. If a 4-day aging test is acceptable, then the existing procedure seems appropriate.

Stabilization by Hydrotreating

Purpose:

The desired outcome of the project was to provide a foundation for development of an economically viable process for upgrading pyrolysis oil to refinery feedstock. The purpose of this phase was to gain a fundamental understanding of the process sensitivity to pyrolysis oil feed properties.

Approach:

This project, extending from FY06 to FY09, built on proof-of-principle experiments performed on heavy phase bio-oil (“pyrolytic lignin”) in the FY05 DOE project titled, “Opportunities for Biorenewables in Oil Refineries,” in which the parties to this CRADA participated. Process optimization and catalyst stability testing is required for the hydrotreating and hydrocracking steps.

Within the project, there were these objectives and tasks requiring PNNL to perform hydroprocessing on bio-oil samples provided by NREL:

1. Optimize the conversion of the pyrolysis oils using mild hydrotreating.
2. Optimize the conversion of the hydrotreated product to gasoline by hydrocracking.

Hydrotreating Experiments

It was envisioned that the bulk of the catalytic processing would be carried out on pyrolysis oil derived from wood. Preliminary process conditions identified in the FY05 DOE project were verified and optimized using pyrolysis oil derived from a mixed wood feedstock. Initial targets were set as Liquid Hourly Space Velocity (LHSV) of 1 and pressure less than 1700 psig. Product quality was too low at these targets and more useful product resulted using around 0.25 LHSV and 2000 psig. Catalysts from both Battelle and UOP were tested in a bench-scale, fixed-bed reactor to hydrogenate the bio-oil and produce a partially upgraded bio-oil suitable to processing at more severe hydrocracking conditions as would be typically found in a petroleum refinery. Once suitable test conditions and catalyst stability were determined, other pyrolysis oil feedstocks were evaluated. These tests were continued over a period of time sufficient to achieve steady state operation and allow product samples to be recovered for analysis. Analyses included ultimate analysis (C, H, N, O, S), moisture, viscosity, density, acid number and GC-MS analyses for characterizing chemical class composition. Water addition prior to hydrotreating was evaluated as a phase splitting mechanism to produce feed oil, which was more highly concentrated in lignin such that production of higher yields of liquid products was expected. Based on these tests optimum processing conditions were chosen and extended runs performed (nominally 100 hr) to evaluate catalyst lifetime and to produce sufficient product to feed the subsequent hydrocracking processing step. Samples of each hydrotreated feed were sent to UOP for analyses after the end of each campaign.

Hydrocracking Experiments

The hydrotreated products from the previous task were used as feedstocks for catalytic hydrocracking tests to evaluate the partially upgraded bio-oil as a refinery feedstock. The baseline processing conditions were developed in concert with UOP and UOP supplied the hydrocracking catalyst. Steady-state operations were evaluated in a continuous-flow regime. Process conditions were optimized to produce a product with low oxygen content and a low acid number. Products were produced for subsequent analysis by UOP for typical refinery product parameters including distillation, PONA, octane measurements and elemental analyses. PNNL completed GC-MS analysis for comparison of the hydrocracked products with the hydrotreated products and the bio-oil feedstocks, as well as ultimate analysis (C, H, N, O, S), moisture, viscosity, density and acid number.

Experimental:

Facilities The hydrotreating and hydrocracking experiments were undertaken in the bench-scale hydrotreater system in the Chemical Engineering Laboratory at PNNL. That system included a fixed-bed catalytic reactor with required feeding and product recovery components. The bio-oil was fed by a high-pressure metering syringe pump. Hydrogen was introduced into the reactor via high-pressure lines and mass flow controller from a gas cylinder manifold. The products were cooled and collected in a dual cylinder sampling system with the uncondensed gases sampled, measured and vented. The recovered liquid products were phase separated, weighed and sampled for further analysis. Manually recovered gas samples were analyzed by gas chromatography. A schematic drawing of the reactor system is shown below in **Figure 6**.

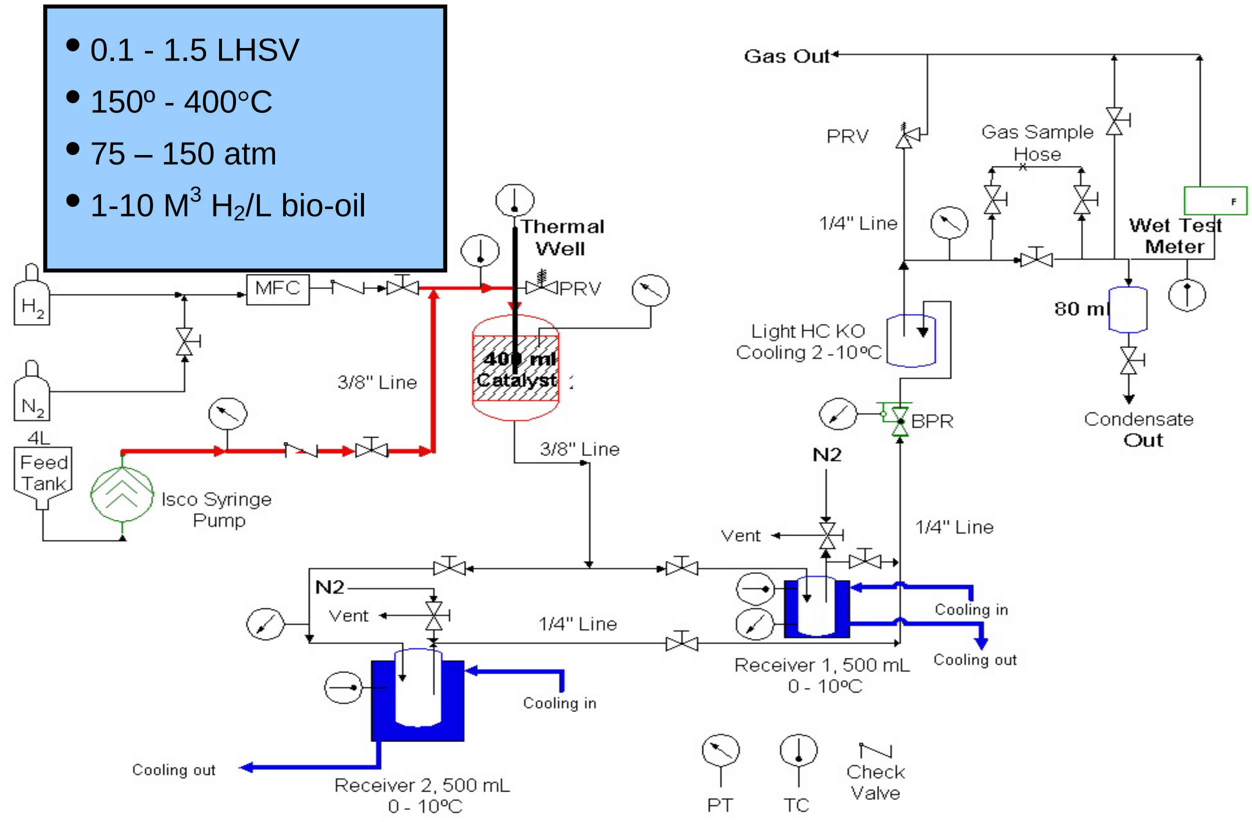

Figure 6. Schematic of bench-scale hydrotreater at PNNL

Hydrotreating Experiments A palladium on carbon catalyst was used (sometimes in combination with other catalysts in a layered bed) in a bench-scale, fixed-bed reactor to hydrogenate the bio-oil and produce a partially upgraded bio-oil suitable to processing at more severe hydrocracking conditions as would be typically found in a petroleum refinery. The Pd/C catalyst was identified in earlier experimentation and subsequently patented for use in bio-oil upgrading (see attached U.S. patent #7,425,657). The starting conditions were 340°C, 2000 psig, and a 0.28 Liquid Hourly Space Velocity (LHSV). The bio-oils were processed at a range of conditions: at higher and lower temperature (310°C and 375°C) and LHSV (0.18 and 1.12) in order to determine process sensitivities. These tests were continued over a period of time sufficient to achieve steady state operation and allow product samples to be recovered for analysis. Analyses included ultimate analysis (C, H, N, O, S), moisture, viscosity, density, acid number and GC-MS analyses for characterizing chemical class composition. Following these tests the optimum processing conditions of 340°C and 0.28 LHSV were used in extended runs performed to evaluate catalyst lifetime and to produce sufficient product to feed the subsequent hydrocracking processing step.

Coking of bio-oil was identified as a significant problem in extended operation of the hydrotreatment, often in combination with corrosion of the reactor wall. Use of the layered catalyst beds was an attempt to place a more active catalyst in the coking zone. Attempts to decouple the corrosion and coking were made by:

1) use of a corrosion-resistant (coated) reactor for hydrotreating, and
2) acquisition of a Hastelloy™
3) reactor for corrosion-free hydrotreating tests

Hydrotreating Experimental Summary

Data sheets covering the several data windows within each of these tests will be published electronically. The data sheets list the detailed analytical results and calculations of the process results.

Initial tests of mixed wood bio-oil feedstock in a 1.5" ID X 15" L 304 Stainless Steel reactor

HT88

Using the mixed wood feedstock a single Pd/C catalyst bed (355 ml bed of a 6/8 mesh Pd/C)
was used in four successive days of operation, each 8 to 10 hours on stream at 340-360°C set point. ICP analysis of the feed (numbers in ppm) showed S 210, K 78, Ni 58, Na 40, Ca 37, and Al 31 with Mg 22, and others below 10 are Fe, P, Zn, Cu, Zr, Ti, Mn, Co, Cd, Cr, and Si is undetectable. Operating temperature setpoints of 345° and 360°C were used throughout. The LHSV used was 0.28 to 0.7 with an acetone wash at the end of each day. During these tests there was evidence of a build up of a pressure drop. Time on stream for the four days amounted to 9:09h on day 1, 8:20h on day 2, 8:15h on day 3,and 8:38h on day 4 for a 34.6 hr total.
On the 5th day operating at 360°C but LHSV of 1.12 a very high pressure drop developed and even after reducing the LHSV to 0.85, there was still a high pressure drop. After 5 hr total test time, the run was stopped and the catalyst bed washed with acetone. These tests are summarized in the Table 6.

A restart on the 6th day, operating at 375°C and LHSV o f 0.85, found there was still a high pressure drop, so the run was stopped and the catalyst bed washed with acetone. A restart on the 7th day found that even at the beginning operating conditions of 345°C and LHSV o f 0.28 there still was a high pressure drop, so the test was stopped and the catalyst bed washed with acetone.

Upon opening the reactor after cooldown, it was found that the top 3" were filled with coke. A screen on top of the catalyst bed was imbedded in ¼" dark brown "burnt" oil (coke). The balance of the catalyst bed (about 3/4) looked the same as before the test. ICP analysis of catalyst bed samples showed the expected Pd catalytic metal (8920 to 15700 ppm) but also a high level of sulfur (1420 at the inlet down to 190 ppm at the bottom), along with nickel (3650 to 58 ppm), iron (862 to 1450 ppm) and chromium (45 to 297 ppm). Some of the nickel was attributed to the feedstock, as was a bit of iron and chromium. However, analysis

of a coke sample recovered from the spaces between catalyst particles, which was low in Pd (46 ppm) and
S (244 ppm), showed clearly that the reactor wall metals were an important component in the coke with 6400 ppm Ni, 4930 ppm Fe, 448 ppm Cr, and even 261 ppm Mo, which was not found in the feedstock. Magnesium was the next largest component in the coke (399 ppm) but was found less in the catalyst (130 to 210 ppm). Al, Zn, Si, and K were all found at 100-500 ppm in the samples with no clear concentration in either the coke or the catalyst. Cu, Co, and Mn were found at around 100 ppm or less and were slightly concentrated in the coke. Na and P were not found in the bed samples. In the various samples, the sulfur concentration better correlated with that of the reactor metal, Ni, than the Pd catalyst.

	1	2	3	4	5
bed temperature, ^{o}C	349	345	359	368	363‡
reactor pressure, psig	1976	1976	1924	1941	2024‡
LHSV, hr-1	0.28	0.70	0.70	0.28	0.85
WHSV, hr-1	0.66	1.66	1.66	0.66	1.99
mass balance %	94	98	98	100	102
product yield, g/g	0.62*	0.74	0.74*	0.72	0.79
H_2 consumption, l/l	245	106	127	262	106
deoxygenation, %	66.77*	47.30	50.33*	56.56	45.12
O %, dry product	10.03	20.82	19.64	16.21	19.79
C %, aqueous	11.20	13.09	12.35	10.85	12.14

*normalized to 100% mass balance
‡average point – large temperature profile and significant pressure drop

Table 10. Initial Hydrotreatment Tests with Mixed Wood Bio-oil

HT89
An experiment to restart with the used HT88 catalyst produced lower quality oil, so it was stopped after 10:13h. There was no significant restriction, but a little bit of coke was found on the catalyst about 2” into reactor.

HT90, 91, 92
A new Pd/C catalyst bed was used in three successive runs of operation in the 9 L/D reactor. Each lasted from 30 to 40 hours on stream at a 340°C set point and an LHSV of 0.28 until a noticeable pressure drop developed. Front bed additions of Ru/C catalyst did not resolve the coking problem. The product oil from these tests was used as the feedstock for the first set of hydrocracking tests for mixed wood oil.

- In HT90, a new Pd/C catalyst bed made up of both small (-20 mesh) and large (6/8 mesh) particle size catalyst was used. The test was on line for 31 hr until the beginning of a noticeable pressure drop. After 9 hr more of operation with increasing pressure drop, the test was shutdown. An acetone wash was attempted but did not clear the restriction. Again the top 3”of the reactor were filled with coke and the top screen was imbedded in ¼” dark brown “burnt” oil (coke). As before, the balance of bed (3/4) looked OK.
- In HT 91, the catalyst bed consisted of 86% new Pd/C with 14% used Pd/C from HT90. An active hydrogenation catalyst, Ru/C, was added on top of the Pd/C on top (1.5-2”) and no screen or open space was used at the front end of the bed. A 31 hr test was completed until the start of a noticeable restriction. After 20 hr more of operation with increasing pressure drop, the test was shutdown. An acetone wash was attempted but did not clear the restriction.
- In HT 92, a new Pd/C catalyst bed with the used Ru/C from HT91 on top was tried to keep the front end hotter. After 37.5 hr a noticeable restriction developed and after 4 hr more the feed was stopped. An acetone wash of the reactor bed was accomplished. Upon opening the reactor, coke was found at 3” into the catalyst bed, at the start of Pd/C portion of the bed. The balance of the bed (about 3/4) looked similar to fresh catalyst.

Mixed wood bio-oil feedstock tests in a 1” ID X 32.1” L reactor

A reactor vessel with a higher L to D ratio was used in subsequent hydrotreating tests with mixed wood bio-oil. The vessel was rotated end for end after the hydrocracking test with sulfided feedstocks because of noticeable corrosion of the reactor walls at the front end of the tube. By rotating the reactor, the non-corroded end was placed into the zone where the corrosion occurred so that the corrosion could be monitored for further development.

HT102, 103

A new catalyst bed consisting of an extremely edge-coated Pd on C particles (catalyst synthesis number PNNL-58959-167-1) was used in two successive runs of 6 and 10 hours on stream at a 340°C set point and an LHSV of 0.25 until noticeable pressure drop developed. Front catalyst bed additions of Ru/TiO_2 catalyst did not resolve the coking problem.

- In HT 102 fresh Pd/C with 5” of Ru/TiO_2 on top was used with corrosion test coupons.

At 6.2 hr a noticeable restriction developed and after 1 hr more the feed was stopped. An acetone wash cleared the catalyst bed, but coke was found at the start of the Pd/C bed; the balance of the bed (about 3/4) looked OK. Analysis of a coke sample showed the highest levels of Fe (666 ppm) and Ni (584 ppm) with Pd (254 ppm) and S (261 ppm), as well as Si, Al, Cr, Na and K at 308, 240, 185, 176, and 120 ppm, respectively. Corrosion products from the coupons were suspected as catalyzing the formation of coke, so the test was repeated without the coupons.

- In HT 103, with the same catalyst and no coupons a noticeable restriction developed only 10.25 hr from the start. After 1.1 hr more with increasing pressure drop the feed was stopped and an acetone wash was attempted without success. Upon opening the reactor a similar scene was found. There was coke starting at 1” into the reactor and continuing through the Ru to 1” into start of Pd/C bed. Again the balance of bed looked like the original catalyst. Analysis of a coke sample showed Ru at 333 ppm and Ti at 611 ppm with some Pd (49 ppm), but no S was found. Fe (202 ppm) and Ni (73 ppm) were still significant components as were Al, K, and Na at 91, 93, and 159 ppm, respectively.

HT104

Based on a concern that the extremely edge-coated Pd on C catalyst might be the cause of the short time to coke formation, a new Pd/C catalyst bed (PNNL synthesis - like Engelhard 864A-3-260-21) with 5” Ru/ TiO_2 on top was tested. After 11.5 hours at a 340°C set point and an LHSV of 0.25, a noticeable pressure drop developed. Bio-oil feed was continued for 2.1hr more, then shutdown. The catalyst bed was washed with acetone. The disassembled reactor showed the typical plugged portion, which was removed for analysis. Analysis of a coke sample showed high levels of Ru (521 ppm) and Ti (975 ppm) with some Pd (166 ppm) and S (399 ppm). The major components were Fe (1180 ppm) and Ni (1680 ppm). As in HT 102, Al, Si, Na, Cr, and K were found at 377, 321, 203, 183, and 100 ppm, respectively; but also Cu (110 ppm) and Mg (101 ppm).

It was concluded that the front bed replacement of the Pd/C catalyst by Ru/TiO_2 catalyst did not resolve the coking problem. It also became clear that the time lapse until a pressure drop became evident was a direct function of the cross-sectional area of the reactor, such that the smaller reactor tube was plugged more quickly than the larger bore. The result was attributed to a corrosion product catalyzed reaction, initiated at the reactor wall, which built a solid coke formation out to the center of the reactor with time on stream.

HT105

In order to displace the carbon support from the coking zone, the Pd/C bed from HT104 was used to refill the bottom portion (250cc) of the reactor with front bed of 12-13” (155cc) of Pd/SiC balls. In this test at a 340°C set point and an LHSV of 0.25, the noticeable pressure drop developed after only 6.7 hours on stream. After 0.4 hr more on stream the test was shutdown and the reactor bed washed with acetone. In this test there was loose catalyst at the front of the bed but coke at 1” into the reactor. The bottom of bed (27”) came out easily and looked as originally. In between there was coke at about the same place as the several previous runs. Analysis of a coke sample from the SiC balls showed some Ru (36 ppm) and Ti (200 ppm) with little Pd (0.1 ppm) and no S was found. The other major components were Fe (166 ppm) and Ni (109 ppm). Like HT 103, Al and Na were found at 61 and 157 ppm, respectively, but no K was detected. The front bed of Pd/SiC catalyst did not affect the outcome of plugging at the front heat-up zone. The Pd/SiC balls seemed softer after the run, suggesting that SiC may not be a good support for acidic, hydrothermal systems.

HT106

A final run was attempted to produce sufficient product oil for subsequent hydrocracking tests. The Pd/C bed (300cc) from the previous test was used with some (120cc) new Pd/C catalyst.

By operating at lower temperature, a 310°C set point, the test was kept on line for 28.75 hours at an LHSV of 0.24 until there was a noticeable pressure drop. The pressure drop continued to build over another 7.2 hours until the test was ended. With an acetone wash the restriction went away, but when restarted with bio-oil feedstock the restriction was found to be still in place.

After an acetone wash and cooldown the reactor was opened to find loose catalyst at front but coke at 4" into reactor. The bottom of bed (28") came out easily and looked OK. In between was a hard coke plug, ¾" by 1". Analysis of a coke plug sample showed the highest levels of Fe (2960 ppm) and Ni (3100 ppm) with Pd (5740 ppm) and S (914 ppm). Also Si, Al, Cr, Na and K at 549, 633, 111, 112, and 222 ppm, respectively; but also Zn (674 ppm) and Mg (576 ppm).

The sulfur concentration correlated better with the reactor metal, Ni, than with Pd catalyst in the five samples.

Mixed wood bio-oil feedstock tests in reactors constructed of special materials

HT113

The 1" ID X 32.1" L 304 stainless steel reactor was coated by the Silcosteel™ process to evaluate corrosion effects. A new batch of Pd/C catalyst was used for 27.6 hours on stream at 347°C (340°C set point) with an LHSV of 0.21 with a noticeable pressure drop causing the test to be terminated. Catalyst deactivation was noted throughout the test. Pressure drop built for an additional 1.5 hours until the run was ended. The reactor was acetone washed and cooled.

Upon opening, the catalyst poured out of the bottom and middle portions of the reactor tube; a restriction was found only in the top 3" of reactor. From 1" to 3" in, the catalyst was encased in a hard coke which had to be chipped out. The Silcosteel coating seemed unaffected, but some residual scratches were noted where the catalyst plug was chipped out.

Analysis of a coke plug sample showed the usual high levels of Fe (2250 ppm) and Ni (5520 ppm) with Pd (7880 ppm) and S (4700 ppm). Also Si, Al, Cr, Na and K at 1630, 686, negligible (14.5), 226, and 156 ppm, respectively; but also Zn (748 ppm) and Mg (265 ppm) as well as additional findings of Ca (689ppm) and P (462ppm). Of these elements found in the coke, all are also present in the catalyst bed at similar levels, except S (2130-3400ppm) and Ni (423-827 ppm), as well as Ca and P, which were found at much lower levels.

The sulfur concentration correlated better with Ni than with Pd. SEM/EDS analysis confirmed the association, although there was sulfur with the Pd as well, at a molar ratio of 0.2 or less.

A longer run time was achieved at normal temperature operation with the coated reactor, but the trace elements found in the coke seemed to suggest that corrosion was still an important factor in its formation.

HT115

In this test the silcosteel coated reactor was reused after placement of a Hastelloy liner in the front end of the tube as further protection against corrosion. The catalyst bed was composed of 98% reused HT113 Pd/C catalyst with 2% new (460cc PNNL cat) with the mixed wood bio-oil feedstock part sulfide added**.** The test extended for 24.9 hours on stream at 342°C (340°C set point) with the LHSV of 0.22. Catalyst deactivation was noted throughout based on increasing density and viscosity of the oil product, at which point a noticeable pressure drop developed. The pressure drop continued building until after another 2 hours the run was ended. The reactor system was acetone washed and cooled.

Upon opening, lightly oil coated catalyst was found at the front of the bed, but there was coked catalyst at 1 to 3" into reactor. The bottom of bed (28") came out easily and appeared as at the beginning of the test. There was no obvious corrosion of the liner.

Similar to HT113, a longer run time was achieved with the Hasteloy liner as with the silcosteel treating alone, but, in the end, the same coking problem developed.

HT118

In a third attempt to address the corrosion issue a new 1" ID X 32.1" long reactor made of Hastelloy C-276 was used. A catalyst bed of 2.5%Pd/C composed of 76% HT112 used cat and 24% used HT116 cat (450cc PNNL cat) was used with the mixed wood bio-oil feedstock with sulfide added. The test was on stream only 14.6 hours at 304-344°C and LHSV of 0.18. The catalyst remained active throughout, but a noticeable pressure drop developed. There were heating difficulties with new reactor configuration, which confused any conclusions. The test was shutdown and acetone washed. A hard coke deposit was found in the front end as typically seen; there was no sign of corrosion.

Corn stover bio-oil feedstock tests in a 1" ID X 32.1" L 304 SS reactor

Using the corn stover light phase feedstock a 2.5% Pd/C catalyst bed, with front bed additions of Ru/C and Pd/ZrO_2 catalysts, was used in 2 successive runs, at 340°C set point, LHSV of 0.27 to 0.42 in the new long reactor. The Ru and Pd catalysts were added at the front end of the reactor in an attempt to preempt the coke formation with more active catalysts, less susceptible to coke formation. These tests provided the hydrotreated bio-oil feedstock for future hydrocracking tests. ICP analysis of the feed showed 436 ppm S, 460 ppm K, 68 ppm Na, and 120 ppm Ca; with 64 ppm Mg, 32 ppm Al, 40 ppm Ni, 17 ppm Fe, and 13 ppm P.

HT96

Used Pd/C from HT92 (300cc) and fresh (70cc) formed the main bed and a "pretreating bed" of Ru/C (C3610) (30cc) was the top 2.3" followed by a second "pretreating bed" of 2.3" Pd/ZrO_2 1/8" tablets. There was no screen or gap at the top of the reactor. The test was on line for 34.5h (plus 41.5 hr from HT92) until a noticeable pressure drop developed. The pressure drop continued building for another 2.5 hours until the run was ended. The reactor was acetone washed and cooled.

Upon opening was found hard coke in the inlet to reactor and extending about 1" into catalyst bed. The bottom of the catalyst bed (22") came out easily and looked unchanged. In between was a partially coked catalyst, which could be "coaxed" out by hand with a couple inches of drill bit work. Insulation placed on top of the reactor in this first test in the 1 X 32 reactor was removed for subsequent tests.

HT97

Used Pd/C from HT96 (330cc) and (25cc) fresh catalyst was used with "pre-treating beds" of Ru/C (C3610) 3.1" (40cc) on top followed by 2.3" Pd/ZrO_2 1/8" tablets. There was no screen or gap at the top. The test was on line for 66.9h (plus 78.5 hr from HT92 and HT96) until a noticeable pressure drop developed. The pressure drop continued building for another 3.8 hours until the run was ended. The reactor was acetone washed and water washed.

Upon opening it was found that with the cooler front end of the reactor, there was loose catalyst at the front but coke was found at 1" into the reactor. The bottom of the bed (27") came out easily and looks unchanged; in between, 4" had to be chipped out.

ICP analysis of samples from the used catalyst bed showed high levels of sulfur (2760-5010 ppm) and iron (958-1760 ppm) throughout the first part of the catalyst bed. Three samples were analyzed; one from the top 1", one lower still in the Ru/C bed and one lower into the Pd/ZrO_2 catalyst bed. In the first inch before the plug there was a high level of alkali (484 ppm Na and 551 ppm K) while in the later samples the total alkali (Na+K) ranged from 714 to 543 ppm. The nickel, calcium and aluminum contents (409, 1610, 92, ppm respectively, in the sample in front of the plug) were much higher in the second sample (5620, 6330, 908 ppm) where the plugging was first found. The phosphorus content trended with the calcium but at a much lower level (100 to 1212 ppm). Mg, Zn, and Si were all found at an elevated level in the third sample (270, 250, 475 ppm). Other elements were fairly consistent through the three samples. These results suggest that there was metal sulfide formation and reactor wall corrosion, along with other bio-oil mineral deposition.

The corn stover heavy phase feedstock was tested with Pd/C catalyst and front end "pretreating beds" of Ru/TiO_2 and Pd/ZrO_2. This test provided hydrotreated bio-oil feedstock for a future hydrocracking test. ICP analysis of the feed showed a high sulfur level of 1190 ppm with 243 ppm K, 140 ppm Ca, 139 ppm Al, and 105 ppm Si; with 89 ppm Zn, 58 ppm Mg, 42 ppm Na, 64 ppm Ni, 46 ppm Fe, 29 ppm P.

HT98

A Pd/C catalyst bed (340cc), reused HT97, with 40cc new and front end pre-treatment beds of Ru/TiO_2 (Degussa H7709) (35cc) and Pd/ZrO_2 (30cc) catalysts were used. The test was on stream 51.3 hours (plus 149.2 hr from HT92, 96, 97) at 340°C set point, LHSV of 0.26 to 0.20 with no noticeable pressure drop. This appeared to be an important development that the test could go so long without plugging. The test was shutdown and the reactor acetone washed and cooled.

Upon opening there was found loose catalyst in Pd/C portion, for the most part, with a small plug piece (1/2" x 1/2") recovered. The Ru/TiO_2 and Pd/ZrO_2 portions were very lightly coked. There was minor wall coating at inlet, leaving it 90% open. This bio-oil appeared to be less susceptible to coking.

ICP analysis of samples from the used catalyst bed showed high levels of sulfur (364-1910 ppm) throughout the catalyst bed. Four samples were analyzed; one from the top 1", one lower with the Ru/C bed mixed with Pd/ZrO_2, one lower into the Pd/ZrO_2 catalyst bed and a final sample from the bottom primarily composed of the Pd/C but also some of the upper beds. In the first inch before the plug the bed was fairly clean (except the S at 691 ppm) with 168 ppm Ca, 149 ppm Ni, 146 ppm Fe, and 102 ppm K, as the major contaminants. In the Ru bed the sulfur concentration actually dropped to 364 ppm with higher levels of Na (852 ppm), Ni (724 ppm), Mg (619 ppm), Al (516 ppm), K (487 ppm), Fe (236 ppm), and Ca (233 ppm). The high level of Na continued into the next sample. The other major elements (Fe, Si, Al, K, S, Zn) were found at significantly higher levels (7000 to 1000 ppm) in both of the last two samples. Ca and Mg (as well as Cu and Mn only at lower levels) were also high (but <1000) in the last two samples. The phosphorus content trended with the calcium but at a much lower level (186-68 ppm). Other elements are fairly consistent through the three samples. These results also suggest that there was metal sulfide formation and reactor wall corrosion, along with other bio-oil mineral deposition.

The second corn stover single phase feedstock (bulk middle phase minus bottom tar and top dodecane) was tested with the Pd/C catalyst at 340°C set point, LHSV of 0.26 to 0.20 in two different tests. These tests produced hydrotreated bio-oil feedstock for future hydrocracking tests. Pretreatment beds of either Ru/TiO_2 or Pd/ZrO_2 were used. ICP analysis of the feed showed less sulfur, 518 ppm, with the other usual biomass components, K 407 ppm, Na 235 ppm, and Ca 89 ppm; with Mg 47 ppm, Al 32 ppm, Ni 24 ppm, and Fe 14 ppm.

HT99

Reused Pd/C catalyst bed from HT98 (380cc) with about 30cc makeup of fresh Pd/C catalyst and front bed additions of Ru/TiO_2 (Degussa H7709) (30cc) and Pd/ZrO_2 (30cc) catalysts (5" total) was tested with this feedstock.

The test operated for 32.2 hours (plus 200.5 hr from HT92, 96, 97, 98) on stream until a noticeable pressure drop developed. The pressure drop continued building for another 2.75 hours until the run was ended. The reactor was acetone washed and cooled.

Upon opening, loose catalyst was found at the front of the bed, but coke formed at 1" into the Ru/TiO_2. The bottom of the catalyst bed came out easily appeared unchanged; the in between 2-3" (including all the Pd/ZrO_2) had to be chipped out. There was material adhering to the reactor walls. Catalyst pieces were stuck together with brown dust. ICP analysis of the plug showed (in addition to the Ru and Ti catalyst) 7280 ppm Ni, 3350 ppm S, 1900 ppm Fe, 1500 ppm Ca, 834 ppm Cr, 368 ppm Al, 233 ppm Cu, 224 ppm P, 115 ppm K, 69 ppm Na, 65 ppm Co, 48 ppm Si, 44 ppm Mg, 33 ppm Mn, and 11 ppm Mo, with Zn and Cd at <5 ppm. These analyses suggested that there was significant deposit of metal sulfides (Ni_3S_2 heazlewoodite was identified by XRD). Corrosion of reactor wall metals (noted upon disassembly) was suggested by the Ni, Fe, Cr, and Mo in the coke deposits. Calcium (from the feed) formation of $CaNi_4O_8$ was identified by XRD while formation of insoluble Ca phosphate was also likely at these conditions. Soluble forms of K and Na must have moved through the plugged portion of the bed. SEM EDS analysis showed high levels of associated sulfur and nickel on the edges of the Ru/TiO_2 catalyst with surface crusts also showing particles of Fe, Ni, Cr and Mn. Crystallites of Fe phosphate and aluminum phosphate were also seen. There was no indication of the sulfur associated with the ruthenium.

Analysis of the brown powder around the Pd/ZrO_2 catalyst pellets gave results similar to the earlier corn stover except for much higher levels of alkali (apparently from the feed), Na 1140 ppm and K 709 ppm, as well as Co 333 ppm and Mg 258 ppm. Other elements were at levels of 1/3rd to 1/10th of the levels found in the plug; 988 ppm Ni, S 301 ppm, 691 ppm Fe, 567 ppm Ca, Cr 28 ppm, 100 ppm Al, 93 ppm Cu, 47 ppm P, no Si, and 27 ppm Mn. The same $CaNi_4O_8$ was found by XRD but the nickel sulfide form was Ni_3S_4 polydymite. These results suggest metal sulfide formation and reactor wall corrosion with other bio-oil mineral deposition.

HT100

The catalyst bed for this test was reused Pd/C catalyst from HT99 (380cc) with about 30cc makeup fresh catalyst. A larger front end “pretreatment bed” of Ru/TiO_2 (Degussa H7709) (5” total) was used to eliminate Pd and carbon granule support effects.

The test was on stream for 33.3 hours (plus 235.5 hr from HT 92, 96, 97, 98, 99) until a noticeable pressure drop developed. The pressure drop continued building for another 1.3 hours until the bio-oil feed was shutdown and the reactor was acetone washed and cooled.

Upon opening the inlet opening was found to be 20% restricted by yellowish solids. The top 1” was chipped out including reddish solids dust. The next 2” was coked and had to be chipped out. The last 2” of Ru/TiO_2 was not coked. The bottom of the catalyst bed (Pd/C) came out easily and appeared unchanged. ICP analysis of samples from the used catalyst bed showed high levels of sulfur (1040-1760 ppm) throughout the first 5” of the catalyst bed. Three samples were analyzed; one from the top 1”, one at 1-3” inches in and one at 3-5” into the catalyst bed. In the first inch before the plug there was a high level of alkali (1310 ppm Na and 1020 ppm K) while in the later samples the total alkali (Na+K) was only 825-665 ppm. The nickel and calcium contents, 7620 and 2780 ppm, respectively, were much higher in the second sample where the plugging was found. Iron was also higher (2280 ppm) in that sample but not so dramatically as the nickel. The phosphorus content (34-153 ppm) trended with the calcium but at a much lower level. Other elements were fairly consistent through the three samples. XRD analysis of the top 1" sample showed only the $CaNi_4O_8$ compound in addition to the titania phases. A deposit at the inlet to the reactor included heazlewoodite, violarite ($FeNi_2S_4$), magnesium hydrogen phosphate hydrate, alumina, and iron titanium, while the material was mostly amorphous. These results suggested metal sulfide formation and reactor wall corrosion with other bio-oil mineral deposition.

Corn stover bio-oil, heavy phase hydroprocessing in the 1" ID X 32.1" L Hastelloy reactor

HT120

In this test the corn stover heavy phase was retested to further investigate the earlier finding of less susceptibility to coking. A fresh 2.5% Pd/C catalyst bed (395cc PNNL cat) was used without a "pretreatment" bed. Heavy Corn Stover phase feedstock (4/06) was processed without sulfide added.

The test was on stream 68.5 hours at 343°C and a LHSV of 0.25 until a pressure drop over the reactor bed was detected. Catalyst deactivation was noted throughout the run. The oil feed was shutdown at 71.5 hr and the reactor was acetone washed and cooled. Upon opening the same type of plugging was found suggesting that the heavy phase was not immune to the plugging problem.

Hot-Filtered Poplar bio-oil in the 1" ID X 32.1" L reactor (304 SS after use with sulfided feedstocks in hydrocracking tests)

A single test was performed with a sample of the hot-filtered poplar wood fast pyrolysis bio-oil from the NREL ablative cyclone reactor. The bio-oil (M2-R8) had been in refrigerated storage at NREL since 1996. ICP analysis of the feed showed 66 ppm sulfur (however, 0.15 wt% was reported by direct S analysis), 46 ppm Zn, 34 ppm Na, 34 ppm Fe, and 15 ppm Ca; with 9 ppm K, 4 ppm Ni, 4 ppm Cu, 2 ppm Mg, 2 ppm Al, 2 ppm Zr, and others below 1 ppm are Mn, Ti, Co, and Cd; with Si, P, Mo, Cr undetectable.

HT108

The catalyst bed was composed of Pd/C (293 cc), used (HT106), with some (140 cc) of new Pd/C catalyst (PNNL-like Engelhard 864A-3-260-21). The test was operated at a 340°C set point and a LHSV of 0.23.

The test was on stream for 47 hours (plus 36 hr more for the catalyst from HT106) until noticeable pressure drop developed. The bio-oil feed was shutdown and the reactor was acetone washed and cooled.

Upon opening the reactor, loose catalyst was found at the front of the bed with brown fines, but a conglomerated coke bed was found at 1" into the reactor. The bottom of bed (28") came out easily and appeared unchanged. In between was 3" of coked catalyst which had to be chipped out including a ½" intact plug. The temperatures during the test in the coked zone ranged from 190°C at 1" from the front end of the reactor to 315°C at 4" into the reactor. A much longer operating period was achieved than with mixed wood bio-oil, but in this test there was a cooler (uninsulated) front end of the reactor tube. In all cases, the agglomerated catalyst plug formed at the point of the feed bio-oil reaching about 300°C.

ICP analysis of samples from the used catalyst bed showed significant levels of sulfur (515-794 ppm) throughout the catalyst bed. Four samples were analyzed; one from the top 1", one lower in the plug zone, one lower below the plug and a final sample from the bottom primarily composed of the Pd/C. In the first inch before the plug the bed contained (in addition to S) 4020 ppm Fe, 1560 ppm Zn, 738 ppm Ni, 556 ppm K, and 453 ppm Al as the major contaminants. There were lesser amounts of Si, Na, Ca, Cu, and Mg. Others (P, Co, Ti, Mn, Cr) were present at <30 ppm. In the plug material, lower levels (1190 ppm Fe, 741 ppm Ni, 616 ppm Zn, 601 ppm Al, 552 ppm K) of the elements are found, apparently due to dilution by carbon coke deposit. Sodium was found at much higher levels in the lower portions of the bed (3430-1020 ppm). The major elements found at significant levels in both of the last two samples were Fe (1540-2350 ppm), Al (777-1510 ppm), K (742-1730 ppm), Zn (338-2380 ppm), Si (426-868 ppm), Ca (603-461 ppm), and Mg (220-263 ppm). The phosphorus content trended at a much lower level (46-133 ppm). Other elements were consistently low (<100 ppm) through the four samples.

The plug material was examined in more detail with SEM/EDS. These images showed a well-dispersed palladium metal catalyst on the highly porous carbon structure. Some of the images suggested that iron (or nickel, or zinc to a lesser degree) was associated with the palladium metal (at levels less than 10%), but there was little evidence of sulfur associated with the Pd. There was some evidence of zinc and sulfur association, as well as some iron-zinc-sulfur structure on the edge of a catalyst pellet. Some large silicon-containing structures were also seen, but may have been relics of the carbon catalyst support structure formation. These results also suggested metal sulfide formation and bio-oil mineral deposition.

Kentucky Oak Bio-oil in the 1" ID X 32.1" L Hastelloy reactor

HT119

This test was performed primarily with the Kentucky Oak bio-oil feedstock produced in the NREL reactor operated at nominally 500°C. Later in the run some of the mixed wood bio-oil feedstock with sulfide added was also processed. A bed of 2.5% Pd/C was composed of 97% used catalyst (HT118) and the balance used from HT116 for a total bed of 423cc of catalyst synthesized at PNNL.

The test was on stream for 10.1 hours at 346°C and LHSV of 0.24 when a pressure drop was first noted. The catalyst was active throughout. The bio-oil feed was shutdown at 12.65 hr and the reactor was acetone washed and cooled. Upon opening the reactor the earlier type of plugging was noted with no sign of corrosion.

Conversion of Stabilized Oil

Conversion Experiments The hydrotreated products from some of the previous tests were used as feedstocks for catalytic hydrocracking tests to evaluate the partially upgraded bio-oil as a refinery feedstock. The baseline processing conditions developed in concert with UOP were near conventional conditions: 400°C, 2000 psig, and 0.4 LHSV using a conventional hydrocracking catalyst. Steady-state operations were evaluated in a continuous-flow regime. Products were produced for subsequent analysis by UOP for typical refinery product parameters including distillation and PONA. PNNL completed GC-MS analysis for comparison of the hydrocracked products with the hydrotreated products and the bio-oil feedstocks, as well as ultimate analysis (C, H, N, O, S), moisture, viscosity, density and acid number.

Experimental Summary

Data sheets covering the several data windows within each of these tests are included in appendix A of this report. The data sheets list the detailed analytical results and calculations of the process results.

Tests of hydrotreated mixed wood bio-oil feedstock in a 1.5” ID X 15” L 304 SS reactor

Using the hydrotreated mixed wood feedstock produced in HT90-HT92 two UOP catalysts for hysrocracking and hydrotreating were tested in their presulfided forms. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. These tests were not very useful and later in the project additional tests were made with the hydrotreated mixed wood bio-oil with much better results.

HT93

Attempts to process the hydrotreated bio-oil over the UOP Hydrocracking catalyst were made at three different temperatures (328-384°C) on four different days. The tests lasted for 3-8 hours on stream and in all cases the product contained heavy, insoluble solids which plugged the product collection system. The process pressure was 1500 psig, and a LHSV of 0.28-0.14 was used. Because of the difficulty to collect the heavy (incompletely reacted portion) of the product oil, the mass balance of these tests was poor (54-61%). The fluid portion of the product oil was a low density (0.81-0.85 g/ml) mostly hydrocarbon product (5-5.4% oxygen). The solid portion of the product contained 15.8-17.8% oxygen.

HT94-95

Attempts to process the hydrotreated bio-oil over the UOP hydrotreating catalyst were made at a range of temperatures (318-429°C) on two different days. The same catalyst bed was used in both tests. The tests lasted for 6.5 and 10 hours on stream and in both cases the product contained heavy, insoluble solids which plugged the product collection system. The process pressure was 1500 psig, and a LHSV of 0.24-0.36 was used. Because of the difficulty to collect the heavy (incompletely reacted portion) of the product oil, the mass balance of these tests was poor (59-78%). The fluid portion of the product oil was a low density (0.77-0.90 g/ml) mostly hydrocarbon product (3.4-6.5% oxygen).

Tests of hydrotreated corn stover bio-oil feedstocks in a 1” ID X 32.1” L 304 SS reactor
Using the hydrotreated corn stover bio-oil feedstocks produced in HT96-HT100, UOP hydrotreating catalyst was tested in its presulfided form. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. This test provided much better results for hydrocracking of hydrotreated bio-oil.

<u>HT101</u>
An extended run with hydrotreated bio-oil products from all three corn stover bio-oils, the light and heavy phases of the original corn stover bio-oil received in 2006 and the new corn stover (single phase) received in 2008. Using a single catalyst bed, testing of all three feedstocks was completed over an 80 hour on-stream period including 6 hours off-line at one point with a pump breakdown. The process temperature setpoint was 390°C with bed temperatures ranging from 399°C to 410°C for LHSV ranging from 0.13 to 0.25. No heavy, insoluble solids were produced and there were no problems with plugging in the product collection system. The process pressure was 1500 psig. Because there was no difficulty in collecting the product oil, the mass balance of these tests were good (91-99%). The product oil was a low density (0.78-0.87 g/ml) mostly hydrocarbon product (0.42-0.95% oxygen). Catalyst deactivation was not easily measured as the process parameters and feedstock were varied over the test. The offgas stream contained 10 to 15 ppm hydrogen sulfide throughout the test.

Tests of hydrotreated mixed wood bio-oil feedstocks in a 1” ID X 32.1” L 304 SS reactor
Using the hydrotreated mixed wood bio-oil feedstocks produced in HT102-HT106, UOP hydrotreating catalyst was tested in its presulfided form. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. This test provided much better results for hydrocracking of hydrotreated mixed wood bio-oil than seen in earlier tests.

<u>HT107</u>
A run was made with hydrotreated bio-oil products from the four mixed wood bio-oil hydrotreating tests. Using a single catalyst bed, testing of all three feedstocks was completed over a 25.5 hour on-stream period. The process temperature setpoint was 390°C with bed temperatures ranging from 394 to 405°C for LHSV ranging from 0.12 to 0.23. No heavy, insoluble solids were produced and there were no problems with plugging in the product collection system. The process pressure was 1500 psig. Because there was no difficulty in collecting the product oil, the mass balance of these tests were good (85-103%). The product oil was a

low density (0.77-0.86 g/ml) mostly hydrocarbon product (0.35-0.54% oxygen). Evidence of catalyst deactivation was seen by the increase in product oil density over time from an initial level of 0.77 to 0.81 at low space velocity and from 0.83 to 0.86 at the higher space velocity.

Tests of hydrotreated hot-filtered poplar bio-oil feedstocks in a 1” ID X 32.1” L 304 SS reactor

Using the hydrotreated hot-filtered poplar bio-oil feedstocks produced in HT108, UOP hydrotreating catalyst was tested in its presulfided form. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. This test provided much better results for hydrocracking of hydrotreated bio-oil.

HT110

A run with hydrotreated bio-oil product from the hot-filtered poplar run at NREL in 1996 was made using a catalyst bed composed of the used catalyst from HT101 with makeup of fresh catalyst from UOP. The test was on stream for 27.5 hour (plus the 80 hr on stream from HT101) with a process temperature setpoint of 390°C. The bed temperatures ranged from 394°C to 408°C for LHSV ranging from 0.12 to 0.24. The process pressure was 1500 psig. The mass balances of these tests were good (95-102%). The product oil was a low density (0.84-0.87 g/ml) mostly hydrocarbon product (0.27-0.32% oxygen). Evidence of catalyst deactivation was less dramatic in this test (apparently due to the extended period on line for the catalyst), but an increase in product oil density over time was still measureable from an initial level of 0.84 to 0.85 at low space velocity and from 0.86 to 0.87 at the higher space velocity.

Non-isothermal tests using 1.5” ID X 32.1” L (2-stage) reactor

The non-isothermal reactor configuration allowed both hydrotreating at low temperature and hydrocracking at high temperature to be accomplished in a single pass through a fixed bed reactor. By this arrangement the product oil was a mostly hydrocarbon product such that there was little organic contamination of the byproduct water phase. The 2-stage reactor could be filled with two different catalysts to accomplish somewhat different chemistries in the two temperature ranges or could be filled entirely with a single catalyst, which had activity at both temperature ranges. Typically, a palladium on carbon catalyst was used in combination with UOP hydrotreating catalyst in a layered bed. In the non-isothermal configuration, the bio-oils were processed at a low temperature of 250°C and a higher temperature of 380°C. LHSV in the range of 0.2 was used. These tests were continued over a period of time sufficient to achieve steady state operation and allow product samples to be recovered for analysis. The original reactor was constructed of 304 SS.

Experimental Summary Data sheets covering the several data windows within each of these tests are included in appendix A of this report. The data sheets list the detailed analytical results and calculations of the process results.

Non-isothermal Hydroprocessing of Bio-oil in a 304SS Reactor

HT109

A previously used bed of sulfided CoMo on alumina catalyst was used in processing the hot-filtered poplar wood bio-oil feedstock without added sulfide. The test was on stream for 101.7 hours at 230-240° in the top (front) bed and 430-440°C in the lower portion of the reactor. The LHSV of 0.14 was used throughout while no noticeable pressure drop developed. At that point the feed oil was shutdown and the reactor bed acetone washed, cooled and disassembled. Some “hard-packed” catalyst (lightly coked) was found at 2 to 9” into the catalyst bed, effectively the heatup and low temperature zone where temperatures ranged from 200-245°C. Also there was about 1” of “charred” catalyst at 10” from the bottom, which was effectively the hot spot of the catalyst bed where the maximum heating from the exothermic reaction was found.

HT111

A front bed (390 cc) of fresh Pd/C and a back bed (210 cc new and 310 cc HT110) of UOP hydrotreating presulfided catalyst were used with the mixed wood bio-oil feedstock without sulfide addition (dodecane quench liquid separated from the top of the bio-oil prior to the test). The test started up without problem. A less dense orange liquid phase was recovered over yellow water product (a dark green oil sample was recovered when contaminated with residual left in the second separator). Less than 10 ppm H_2S was measured in the offgas, but it could be smelled in the reactor room.

The test was on stream for 32.8 hours at 255°C and 420°C (set point of hot oil heater at 380°C with a range of exothermic heating from 435°C down to 412°C in the hottest point of the catalyst bed over the duration of the test) with an LHSV of 0.14 overall without development of noticeable pressure drop. The product oil became more viscous and brown as the exotherm waned and the lower bed peak temperature dropped to 410°C, so the oil heater set point was increased to 390°C at 19 h TOS. There appeared to be improved product quality, but some solids adhered to the bottle wall. The lower bed temperature increased back to 420°C. At 25 hr on stream, 150 ppm sulfide was added to the feedstock. The top zone oil heater set point was increased by 15°C, but no exotherm change was noted. The product remained a viscous emulsion (mousse) with some brown oil separating to the top. Attempts to centrifuge the mousses provided little separation of the emulsion.

When the catalyst became deactivated, the feed oil was shutdown and the reactor bed acetone washed, cooled, and disassembled. The front 4 to 5” of the removed bed was composed of little brown particles interspersed with catalyst. Some lightly coked catalyst was found about 5” into the Pd/C catalyst bed, at about the point of maximum heating in the upper bed from the exothermic reaction. The top bed was mostly loose catalyst; other than the small amount of coke, the rest of Pd/C catalyst poured out.

The coke had 0.5% each of Pd and Ni. The sulfur content was at 0.5 mole per mole of Ni, i.e. Ni_2S. Fe was found at half the amount of the Ni. Mo was found at ¼ of the Fe. Al, Si and P were present, but the amounts in the several samples were inconsistent. Also, some wall sliver/castes of coke were recovered at the front end of the bed. These contained half the Pd but were highly enriched (11% of total) in Ni and S in the same ratio as the coke. There was a high level of Cu, with no apparent explanation. The caste was also slightly enriched in Fe, twice the Pd, rather than half the Pd, as in the coke found among the catalyst granules. The caste was also enriched with Mo in the same ratio. There was more Si and P but less Al compared to the coke.

The lower portion of the top bed had a more reasonable Pd content of 0.7%. It also had significant Fe, Al, K and Ca. The sulfur content was half of that in the coke, but the Ni content was also much lower. The sulfur content was higher in the top of the bed and the nickel was somewhat higher but well below the level found in the coke. Al and Fe were also high in the front of the bed as was Mo. The K and Ca were not so high.

UOP hydrotreating catalyst was “coaxed” out; maybe it wouldn’t pour because it was damp. It was very lightly coked. Small area of clumping about 2” into hot stage (at 12” from the bottom). In this coked catalyst the Mo and Al were reduced to 60-65% while the Ni remained at the same level as measured in the fresh catalyst. A large deposit of Fe was present; but the S level was only at 70% of that in the fresh catalyst. The material was also enriched in Cr, K, Na, Ca, Mg, Zn and Mn. It contained 14.4% carbon. The used, but loose, catalyst in the bottom of the bed (mostly loose catalyst) had a 19.3% carbon content and the components were all diluted to 80 to 85% of the fresh catalyst amount, except for some enrichment (but much less than the charred catalyst) in Fe, K, Na, and Ca.

HT112

Fresh 2.5% Pd/C catalyst (470 cc PNNL catalyst) and a presulfided UOP hydrotreating catalyst(500 cc) were used as the low- and high-temperature beds, respectively. The bulk (top) phase from the 2nd corn stover bio-oil was used as feedstock, without sulfide added.

The test was on stream 87.3 hours at 245°C and 395-415°C with a LHSV of 0.14 overall. The catalysts remained active and no noticeable pressure drop developed; the test was stopped when we ran out of feed. At that point the system was shutdown, acetone washed and cooled. We noticed a unique problem of white deposits forming and plugging in the overhead condenser following the liquid product collection system. Incomplete analysis suggested that this material may be an ammonium carbonate type mineral. No significant elemental content was found by ICP (81 ppm Mo, 18 ppm Na, 16 ppm Fe, and 7 ppm Zn with 1 to 3 ppm of Al, Cu, Ni, Cr, and Pd).

HT116

Fresh 2.5% Pd/C, with 7% of used HT112 catalyst (485 cc total PNNL catalyst) and a presulfided UOP hydrocracking catalyst (480 cc) were used as the low- and high-temperature beds, respectively. The Kentucky oak 500°C bio-oil feedstock was tested without sulfide added.

The test was on stream for 60.1 hours at 257° and 415-420°C with a LHSV of 0.14. Catalysts deactivation was noted throughout. An emulsion product resulted by the end of the test, but no noticeable pressure drop developed. The reactor was shutdown, acetone washed and cooled. Upon opening the reactor a tenacious coke deposit was found in the front end at the same point of significant evidence of corrosion.

HT117

Fresh 2.5% Pd/C with 12% of used HT116 catalyst (465 cc total PNNL catalyst) and a presulfided UOP hydrotreating catalyst (515 cc) were used as the low- and high-temperature beds, respectively. The Kentucky oak 550°C bio-oil was used as feedstock with sulfide added because of catalyst deactivation in HT116.

The test was on stream for 27.2 hours at 257° and 414-422°C with a LHSV of 0.14 overall. Catalyst deactivation was noted throughout, but a rather sudden onset of formation of the emulsion product triggered the end of the run even though there was no noticeable pressure drop. The test was shutdown, acetone washed and cooled. Upon opening the reactor some coke deposit was found in the front end, as in earlier runs. It was noted that it was difficult to detect any incremental increase in corrosion of the reactor wall.

Non-isothermal Hydroprocessing of Mixed Wood bio-oil in a Hastelloy Reactor

HT121

For this test a Hastelloy 276 reactor tube (1" ID X 32.1" L) was used. Fresh 2.5%Pd/C catalyst (200 cc PNNL catalyst) and a presulfided UOP hydrotreating catalyst (210 cc) were used as the low- and high-temperature beds, respectively. The feedstock tested was the mixed wood bio-oil feedstock with sulfide added.

The test was on stream for 78 hours 252°C and 401-388°C with a LHSV of 0.29 in each bed (LHSV 0.14 overall). It appeared that the catalysts deactivated throughout; an emulsion product resulted by the end of the test. Noticeable pressure drop developed so the feed oil was shutdown at 80.6 h and the reactor acetone washed and cooled. When the reactor was opened, an intact coke deposit was found at 1.5-4" in from the front end of the reactor. There was no evidence of corrosion.

HT122

The HT121 test was repeated with a catalyst bed composed entirely of presulfided UOP hydrotreating catalyst (443 cc). The test extended 41.75 hours on stream at 262°C and 382-385°C with a LHSV of 0.14. Some catalyst deactivation was evident throughout. A noticeable pressure drop developed and the reactor was shutdown at 47.8 hr, acetone washed and cooled. An intact coke deposit was found at 1.5-3” in from the front end of the reactor. There was no evidence of corrosion.

HT123

Fresh 2.5% Pd/C catalyst (230 cc PNNL catalyst #59893-55-1) and presulfided UOP hydrotreating catalyst (210 cc) were used as the low- and high-temperature beds, respectively. A heavy phase was separated from the mixed wood bio-oil feedstock by water addition and was used as the feedstock with sulfide added.

The test extended 45.2 hours on stream at 252° and 401-396°C with a LHSV of 0.26 and 0.29 in the low- and high-temperature bed, respectively (0.14 overall). Catalyst deactivation was evident through the first 30 hr (density increasing from 0.79 g/mL to 0.88 g/mL), but nearly stable after that. A noticeable pressure drop developed, and the reactor was shutdown at 48.2 h, acetone washed and cooled. Upon opening the reactor an intact coke deposit was found 2-4” in from the front end and the balance of the catalyst bed poured out.

In the non-isothermal tests involving both UOP hydrocracking catalyst and PNNL hydrotreating catalyst, catalyst deactivation was evident based on increasing density of the oil product and its color. However, almost invariably the hydrotreating bed eventually coked and plugged while the hydrocracking catalyst had much less coke formation evident.

Expt #	database number	date	catalyst	feed stock	reactor configuration	time to plug (@ 340°C)	feed to plug
HT88	HT1-9	7/10-18/06	Pd/C	mixed wood	1.5” X 15” 1.77 sq in	38 h (intermediate washing)	4.6 liter
HT90		9/19-20/06	Pd/C	mixed wood	1.5” X 15” 1.77 sq in	31 h	3.32 liter
HT91	HT10	9/25-26/06	Pd/C w/Ru/C	mixed wood	1.5” X 15” 1.77 sq in	31 h	3.1 liter
HT92	HT11	9/27-29/06	Pd/C w/Ru/C	mixed wood	1.5” X 15” 1.77 sq in	37.5 h	3.75 liter
HT102		5/21-22/07	Pd/C w/Ru/TiO_2	mixed wood	1” X 32” 0.79 sq in	6.2 h	0.64 liter
HT103	HT12	5/22-23/07	Pd/C w/Ru/TiO_2	mixed wood	1” X 32” 0.79 sq in	10.2 h	1.04 liter
HT104		5/24/07	Pd/C w/Ru/TiO_2	mixed wood	1” X 32” 0.79 sq in	11.5 h	0.96 liter
HT105	HT12	5/25/07	Pd/C w/Pd/SiC	mixed wood	1” X 32” 0.79 sq in	6.7 h	0.66 liter
HT106	HT13-14	6/12-14/07	Pd/C	mixed wood	1” X 32” 0.79 sq in	28.8 h (@310°C)	3.42 liter
HT113	HT65-67	1/28-29/08	Pd/C	mixed wood	w /Silcosteel-CR	27.6 h	2.91 liter
HT115	HT68-70	5/5-6/08	Pd/C	mixed wood part	w/Silcosteel-CR with Hastelloy	24.9 h	2.69 liter

				sulfided	liner		
HT118	HT80	9/2-3/08	Pd/C	mixed wood sulfided	Hastelloy	14.6 h	1.25 liter
HT108	HT51-53	8/13-15/07	Pd/C	hot-filtered wood	1” X 32” 0.79 sq in	47 h	4.46 liter
HT96	HT21-23	12/13-14/06	Pd/C w/Ru/C & Pd/ZrO_2	corn stover light	1” X 32” 0.79 sq in	34.5 h (insulated at top)	3.65 liter
HT97	HT24-29	1/23-25/07	Pd/C w/Ru/C & Pd/ZrO_2	corn stover light	1” X 32” 0.79 sq in	66.9 h	7.41 liter
HT98	HT31-35	1/29-2/1/07	Pd/C w/Ru/TiO_2 & Pd/ZrO_2	corn stover heavy	1” X 32” 0.79 sq in	51.3 h with no pressure drop	4.25 liter
HT99	HT41-44	3/19-20/07	Pd/C w/Ru/TiO_2 & Pd/ZrO_2	new corn stover	1” X 32” 0.79 sq in	32.2 h	2.92 liter
HT100	HT45-48	3/21-22/07	Pd/C w/Ru/TiO_2	new corn stover	1” X 32” 0.79 sq in	33.3 h	3.2 liters
HT120	HT82-83	10/27-30/08	Pd/C	corn stover heavy	Hastelloy 0.79 sq in	68.5 h	7.14 liter
HT119	HT81	9/4/08	Pd/C	KY Oak 500°C sulfided	Hastelloy 0.79 sq in	10.1 h	1.26 liter
HYDROCRACKING							
HT93	HC1-2		UOP Hydro crack	HT mixed wood	1.5” X 15” 1.77 sq in	6.6 + 5.3 h outlet plugs	
HT94	HC3-4		UOP Hydrotreat	HT mixed wood	1.5” X 15” 1.77 sq in	7.7 h day’s end	
HT95	HC5-6		UOP Hydrotreat	HT mixed wood	1.5” X 15” 1.77 sq in	6.5 h out of feed	
HT101	HC7-12		UOP Hydrotreat	HT corn stover phases	1” X 32” 0.79 sq in	64.1 h out of feed	4.65 liters
HT107	HC13-16		UOP Hydrotreat	HT mixed wood	1” X 32” 0.79 sq in	25.7 h out of feed	1.56 liters
HT110	HC17-19		UOP Hydrotreat	HT hot-filtered	1” X 32” 0.79 sq in	26.4 h out of feed	1.84 liters
NON-ISOTHERMAL							
HT109	HT54-59 HC20-25	8/20-24/07	CoMoS	hot-filtered wood	1.5” X 15” 1.77 sq in	101.7 h with no pressure drop, but catalyst is coked	13.73 liters
HT111	HT61-62 HC26-27	11/5-7/07	Pd/C & UOP Hydrotreat	mixed wood	1.5” X 15” 1.77 sq in	32.8 h with no pressure drop but catalyst deactivated	4.44 liter
HT112	HT63-64 HC28-29	11/13-16/07	Pd/C & UOP	new corn stover	1.5” X 15” 1.77 sq in	87.3 h with no pressure drop,	11.54 liters

			Hydrotreat			maintained catalyst activity	
HT116	HT71-74 HC30-33	6/30-7/2/08	Pd/C & UOP Hydro crack	KY Oak 500°C	1.5” X 15” 1.77 sq in	60.1 h with no pressure drop but catalyst deactivated	8.07 liter
HT117	HT76-79 HC35-38	7/7-8/08	Pd/C & UOP Hydrotreating	KY Oak 550°C sulfided	1.5” X 15” 1.77 sq in	27.2 h with no pressure drop but catalyst deactivated	3.66 liter
HT121		12/8-11/08	Pd/C & UOP Hydrotreating	mixed wood with sulfide	1” X 32” Hastelloy	78 h until pressure drop and catalyst deactivated	4.13 liter
HT122		12/15-17/08	Pd/C & UOP Hydrotreating	mixed wood with sulfide	1” X 32” Hastelloy	41.8 h until pressure drop with some catalyst deactivation	2.84 liter
HT123		2/3-5/09	Pd/C & UOP Hydrotreating	mixed wood, heavy phase with sulfide	1” X 32” Hastelloy	45 until pressure drop and deactivated catalyst stabilized	3.14 liter

Table 11. Hydroprocessing Test Summary

Discussion of Results

Feedstock Descriptions

The bio-oil feedstocks for these hydroprocessing tests were provided by the National Renewable Energy Laboratory through the joint CRADA with UOP and PNNL. The bio-oils were produced as described in the related portion of this report. The bio-oil feedstocks were shipped from NREL to PNNL at various times through the project. The bio-oils were stored in well-sealed containers in closed cabinets. The bio-oils were of various ages at the time of hydrotreatment depending on the progress in the research project.

The bio-oils represented several biomass types. A mixed wood feedstock was used to produce the bulk of the bio-oil. Corn stover was pyrolyzed at two different times and at two different conditions. The original corn stove bio-oil was phase separated as received into a light (more hydrophilic) phase and a heavy (more hydrophobic) phase, which were tested separately. The second corn stover bio-oil was received in essentially one phase. However, over time a dodecane (quenching solvent) layer was recovered off the top of this bio-oil and a heavy phase began to separate as well. Oak-derived bio-oils produced at three different temperatures were also received and tested. Finally, we also tested a poplar wood derived bio-oil which had been produced in 1996 using a hot-vapor filtration method at NREL.

In order to calculate elemental balances around our hydroprocessing experiments, these bio-oils were analyzed (Columbia Analytical Services) for carbon, hydrogen, nitrogen, and oxygen, and in most cases sulfur. The range of the analyses (as they were performed numerous times throughout the project) is presented in **Table 13**. These analyses show a range of products dependent on the biomass feedstock but also on the phase stability or the pyrolysis temperature. They also show the variability of the analytical result due to the inhomogeneity of the bio-oil. The oxygen entry for the single set of data for the Oak 550°C appears to be an error based on the lack of closure to 100% and in comparison to the other two oak bio-oils. The light phases are a more water soluble material and have a higher moisture content and lower carbon content. The nitrogen content is highly dependent on the biomass feedstock. The corn stover produced a much higher nitrogen content bio-oil. Sulfur levels are typically lower than nitrogen, often by an order of magnitude. The poplar bio-oil is the single exception. **Table 14** shows these analyses corrected to a moisture-free basis. The higher carbon content of the wood bio-oils is evident as underlined by the lower hydrogen to carbon atomic ratio. The temperature trend in the oak bio-oils is also noticeable with lower H/C ratios at higher temperature

biomass	**carbon**	**hydrogen**	**oxygen**	**nitrogen**	**sulfur (as received)**	**sulfur (sulfided)**
mixed wood	45.00, 47.74 51.12, 44.04 41.88, 43.98	7.28, 7.38 7.20, 7.70 7.04, 6.87	41.09, 46.09 47.64, 46.64 44.90, 45.00	0.16, 0.16 0.16, 0.16, 0.16, 0.18, 0.16	0.028	0.033, 0.032, 0.026
mixed wood heavy phase	56.08	6.90	39.60	0.46	NA	0.036
corn stover light phase	31.22, 26.08	8.17, 9.37	57.77, 52.92	0.87, 0.27	0.046	NA
corn stover heavy phase	55.75, 52.46, 50.02	6.36, 7.62, 7.24	43.45, 32.68, 35.87	0.92, 1.32, 1.12	0.170, 0.16	NA
2nd corn stover	30.42, 33.77	7.44, 8.77	56.34, 54.51	0.68, 0.63	0.048, 0.076	NA
oak 500°C	42.50	7.16	49.74	0.12	0.008	NA
oak 550°C	37.48	7.37	28.20(?)	<0.05	NA	0.020
oak 600°C light phase	26.47	7.78	60.85	0.19	0.008	NA
oak 600°C heavy phase	59.58	6.54	32.11	0.33	0.024	NA
poplar	46.50, 46.20	7.05, 6.94	40.88, 42.33	<0.05, 0.05	0.16, 0.149	NA

Table 13. Elemental Analysis of Bio-oil Feedstocks

biomass	H/C	carbon	hydrogen	oxygen	nitrogen
mixed wood	1.28	57.7	6.2	33.7	0.2
mixed wood heavy phase	0.94	73.2	5.8	25.3	0.6
corn stover light phase	1.76	48.8	7.2	31.8	1.0
corn stover heavy phase	1.20	62.6	6.3	27.7	1.3
2nd corn stover	1.48	50.6	6.3	36.2	1.0
oak 500°C	1.27	55.4	5.9	37.9	0.2
oak 550°C	1.06	58.6	5.2	10.4(?)	0.0
oak 600°C light phase	1.65	41.8	5.8	44.8	0.0
oak 600°C heavy phase	1.03	68.0	5.9	24.1	0.4
poplar (hot-filtered)	1.26	56.9	6.0	30.9	0.0

Table 14. Elemental Composition of Bio-oils on a Moisture-Free Basis

We also performed density measurements to facilitate mass balances and moisture analyses to better understand the elemental compositions. Total Acid Number and viscosity were also analyzed in most cases. These analyses are shown in **Table 15.** These analyses show that the lighter phases, of course, have lower densities; and also are less viscous. They contain a much higher level of dissolved water (moisture). The acid numbers are extremely high compared to the experience with petroleum feedstocks. The high level of oxygenates include organic acids but also phenolics, which would also be included in this analysis. The pyrolytic lignin number is the residual water insolubles determined by aggressive stirring of the bio-oil into water. It is believed to represent lignin-derived polymeric structure, which has not been effectively pyrolyzed.

biomass	density	TAN	viscosity	moisture	pyrolytic lignin
mixed wood	1.177@25°C	117, 111.4, 200.2, 150.8	36.6 @40°C, 39.5@40°C	22.45, 19.6, 20.71, 21.1	22.31
mixed wood heavy phase	1.211	87.2	NA	22.63	NA
corn stover light phase	1.087@25°C	133.3	4.4@40°C	41.94, 40.61	5.37
corn stover heavy phase	1.154@25°C	107.8, 140.67, 195.6	409@40°C	16.4, 15.82, 15.24	57.5
2nd corn stover	1.16	134.6, 125.27	NA	38.56, 34.44	NA
oak 500°C	1.21	166.9	NA	23.29	NA
oak 550°C	1.19	111.1	NA	36.0	NA
oak 600°C	1.11	40.7	NA	36.6	NA

light phase					
oak 600°C heavy phase	NA	131.4	NA	12.4	NA
poplar	1.166@25°C	172.8, 199.4	49.1@40°C,	18.68, 18.34	NA

Table 15. Bio-oil Properties

Trace element analysis was performed by inductively-coupled plasma/optical emission spectroscopy (ICP-OES) on most of the bio-oils. The results are shown in **Table 16**. These results show that the bio-oils carried most of the elements expected to be found in the biomass feedstock. The ag residue (corn stover) bio-oil, with a higher loading of ash, resulted in a bio-oil with a higher level of most of these elements compared to the wood-derived bio-oils. A notable exception to the biomass-derived scenario was the high level of nickel found in the mixed wood and corn stover bio-oils. The poplar bio-oil had a significantly reduced level of contaminants as a result of the hot-filtration vapor cleanup step applied in the earlier test. The low sulfur content found by ICP in the hot-filtered poplar bio-oil was at odds with the direct total sulfur analysis by thermal method. The relatively higher zinc and iron contents became noticeable in the catalyst bed plug analysis described later. It was reasonable to assume that the iron and zinc are corrosion products from the reactor systems used in its production/collection. Similarly, the high nickel content is also likely resulting from the processing system rather than derived from the biomass feedstock.

element	mixed wood	corn stover light phase	corn stover heavy phase	2nd corn stover	poplar, hot-filtered	oak, 500°C	oak, 550°C
Sulfur	210.0	436.0	1190.0	518.0	65.6	93	127
Potassium	78.0	460.0	243.0	407.0	8.7	113	99
Calcium	36.9	120.0	140.0	89.4	14.6	161	115
Sodium	40.4	68.3	41.9	235.0	34.3	96	85
Magnesium	22.2	63.7	57.7	46.7	2.4	14	9
Nickel	58.1	40.5	64.2	24.3	3.9	5	6
Aluminum	31.0	31.8	139.0	31.5	1.8	8	6
Iron	8.0	17.5	46.3	13.6	34.0	15	27
Phosphorus	8.0	12.9	29.1	2.9	ND	28	16
Zinc	7.0	8.2	88.5	0.4	46.2	22	30
Silicon	ND	9.4	105.0	3.9	ND	18	17
Copper	4.2	1.5	5.1	1.0	4.5	15	31
Manganese	0.3	1.2	1.9	1.0	0.4	2	2
Titanium	0.5	0.1	2.4	0.7	0.5	1	2
Zirconium	0.7	0.1	0.1	0.6	1.8	0.4	0.8
Cadmium	0.07	0.05	0.19	0.19	0.12	ND	1
Cobalt	0.16	0.06	0.08	0.003	0.01	20	ND
Chromium	0.07	ND	1.3	ND	ND	2	3
Molybdenum	ND	ND	0.4	ND	ND	2	2

Table 16. Trace Element Analysis of Bio-oils, mg/L

4.2 Hydrotreating Process Results

In the hydrotreating process development effort the testing focused on the low-temperature processing using the palladium on carbon catalyst, which was recently patented by Battelle. Comparisons can be made between the several biomass feedstock bio-oils to determine an effect of feedstock. Some process optimization was also performed around process temperature and residence time, as measured by liquid hourly space velocity.

The effect of feedstock was not dramatic in terms of yield structure, hydrogen consumption, or relative strength of the exothermic reaction, as the fast pyrolysis process tended to produce a relatively similar bio-oil from all biomasses. That being said, there were important differences in the composition of the bio-oils which were reflected in the hydrotreatment processing results. In making these comparisons we were forced to ignore the potential effect of the front end bed of a pretreatment catalyst used in several of the corn stover bio-oil tests. As related in section 4.3, the differences did not appear to be large and could be reasonably ignored in this comparison. Process results with the several feedstocks at 340°C, 2000 psig and 0.14-0.25 LHSV (with large excess hydrogen flow, 10,000 SCF/bbl) are given in Table 17.

bio-oil	**oil yield, g/g dry feed**	**aqueous yield, g/g wet feed**	**gas yield, g/g carbon feed**	**Hydrogen consumption, liter/liter feed**	**Relative exotherm versus setpoint**
mixed wood	0.62	0.48	0.062	205	+6°C
corn stover light phase	0.45	0.68	0.071	82	+0°C
corn stover heavy phase	0.78	0.31	0.073	128	+3°C
2nd corn stover	0.45	0.61	0.066	76	+3°C
poplar	0.59	0.46	0.060	252	+2°C

Table 17. Feedstock Effect on Hydrotreating Process Results

These results showed that a higher oil product yield was obtained from the whole bio-oil or the heavy phase, when adjusted to the amount of dry organic material fed. Similarly, the light phase resulted in less oil product and a larger aqueous phase (primarily because of the larger fraction of water in the feedstock). Gas generation was relatively low in all cases. A moderate bed heating suggested an exothermic reaction. The results support the view that the second corn stover bio-oil was more similar to the light phase of the 1st corn stover bio-oil.

The effect of process parameters can be evaluated for the mixed wood bio-oil feedstock using the Pd/C catalyst. All tests were performed at nominally 2000 psig with a large excess flow of hydrogen (10,000 scf/bbl) with results shown in Table 18. At higher temperature the gas yield increases as does the hydrogen consumption and the oil yield decreases. The oxygen content appears to hit a "sweet spot" at a set point of 340°C in the reactor bed. Higher temperature operation did not reduce the oxygen content of the product oil further and the product actually had more oxygen. At higher flow rate (lower residence time) the remaining oxygen content of the product oil is higher and the hydrogen consumption is reduced. It appeared that the hydrocarbon portion of the oil was reduced by cracking to gas rather than increased hydrodeoxygenation of the oil.

parameter	oil yield, g/g dry feed	oxygen content dry basis	aqueous yield, g/g wet feed	gas yield, g/g carbon feed	Hydrogen consumption, liter/liter feed	Relative exotherm versus setpoint
Temp., °C						
310	0.75	11.6	0.35	0.037		+5°C
340	0.62	10.2	0.48	0.062	205	+6°C
360	0.56	16.2	0.47	0.109	262	+8°C
LHSV, L/L/hr						
0.25	0.62	10.2	0.48	0.062	205	+6°C
0.70	0.62	20.8	0.41	0.076	106	+5°C

Table 18. Process Parameter Effects on Hydroprocessing Results

4.2.1 Hydrotreating Product Composition

The chemical composition of the biomass feedstock and the derived bio-oil product from a specific biomass remained evident in the composition of the hydrotreated bio-oil products as shown in Table 19. The composition of the bio-oils is similar for all feedstocks. The relatively clean (low nitrogen and sulfur) mixed wood and oak wood bio-oils was translated into relatively clean hydrotreated products.

bio-oil source	H/C (dry)	C	H	O	N	S	moisture
mixed wood	1.43	75.5	9.4	12.3	0.6	0.02	2.7
corn stover light phase	1.28	76.2	8.5	15.5	2.4	NA	2.6
corn stover heavy phase	1.40	76.2	9.4	12.7	2.0	0.06	3.5
2nd corn stover	1.53	77.1	10.2	11.9	2.3	NA	2.9
oak (500C)	1.35	74.2	9.0	14.5	0.1	0.01	5.7
poplar (hot-filtered)	1.33	73.1	8.6	17.9	0.2	0.16	3.5

340°C, 2000 psig, 0.25 LHSV

Table 19. Composition of Hydrotreated Bio-oils.

The several tests with different front end (pre-treatment) catalyst beds had remarkedly little effect on the final product composition. A summary of the different products is presented in Table 20. In all these tests the main catalyst bed, comprising 85 to 90% of the reactor volume was the 2.5 wt% Pd on carbon catalyst. Variations in the product are derived primarily from the differences in the feedstock tested.

bio-oil source	catalyst	C	H	O	N	S	Moisture	TAN	viscosity	density g/mL
mixed wood	Pd/C only	72.8	8.6	18.9	0.4	NA	4.2	74	657 cSt @ 100°C	1.06
mixed wood	Ru/C	71.7	9.0	19.4	0.4	NA	4.0	79	1367 cSt @ 100 °C	1.05
mixed wood	Pd/SiC	75.5	9.4	12.3	0.6	0.02	2.7	49	NA	1.02
corn stover light phase	Ru/C & Pd/ZrO_2	76.2	8.5	15.5	2.4	NA	2.6	54	36 cPs @ 80°C	1.02
corn stover heavy phase	Ru/TiO_2 & Pd/ZrO_2	76.2	9.4	12.7	2.0	0.06	3.5	46	NA	1.05
2nd corn stover	Ru/TiO_2 & Pd/ZrO_2	77.1	10.2	11.9	2.3	NA	2.9	60	NA	1.04
2nd corn stover	Ru/TiO_2	77.6	10.6	11.8	1.8	NA	3.3	52	NA	1.04

340°C, 2000 psig, 0.25 LHSV

Table 20. Composition of Hydrotreated Products using different Pre-treatment catalysts

In all the 1st stage hydrotreating tests a 2-phase product was produced. In addition to the oil products described above, there was also a separate aqueous phase product. The aqueous phase was typically contaminated with the soluble portion of the product oil. In addition to the dissolved carbon found in the water, the nitrogen and sulfur residues from the feedstock were also found. As shown by the data plotted in **Figure 7,** the amount of dissolved carbon as a straight-line function of the amount of oxygen remaining in the product oil in the range of hydrotreated products tested. Apparently the relationship changes as the oxygen content is reduced to lower levels, so that the carbon dissolved in the water will approach zero when the product oil approaches a pure hydrocarbon product.

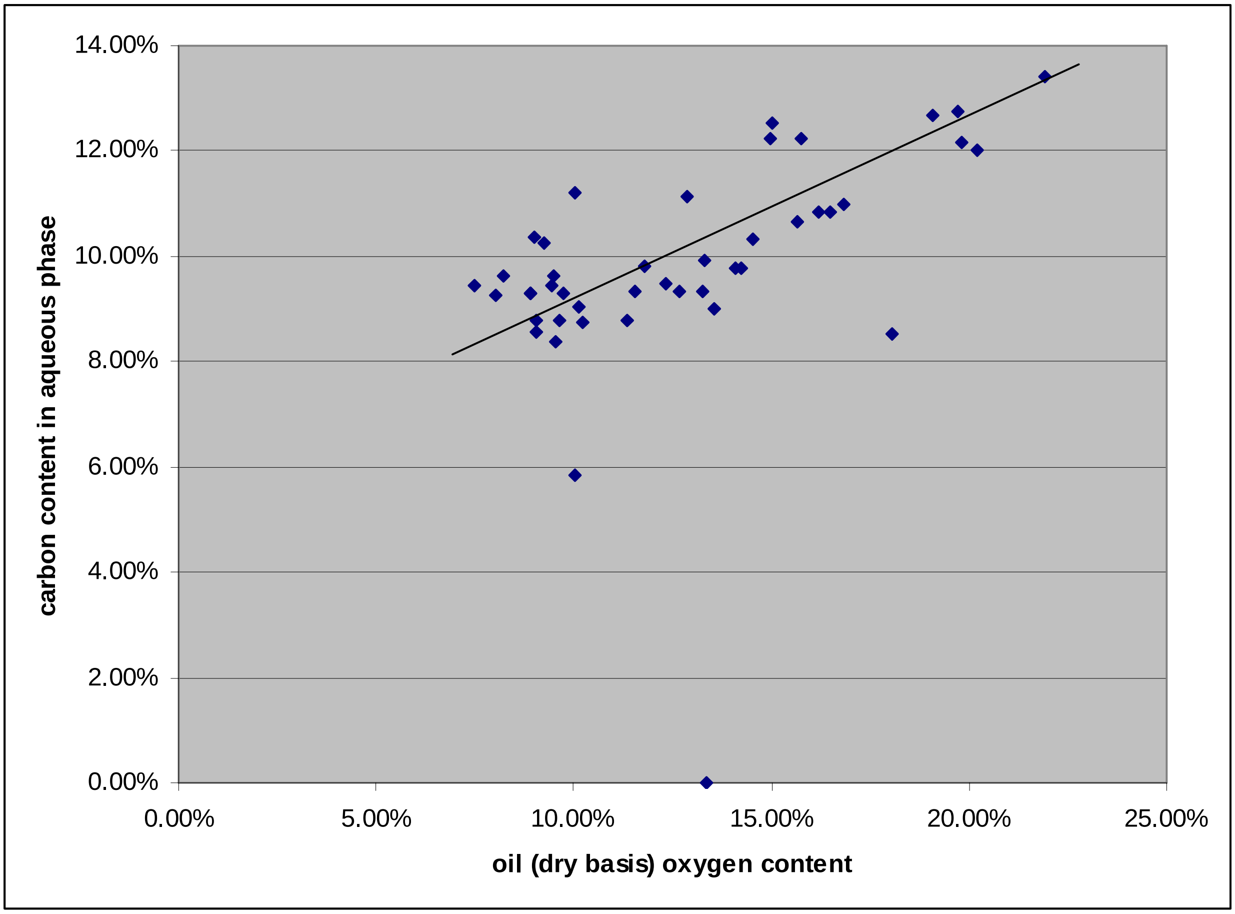

Figure 7. Dissolved carbon in byproduct water versus the residual oxygen in the product oil

As shown in **Figure 8** there is a limited relationship between the nitrogen content of the product oil and the nitrogen content of the aqueous byproduct. The nitrogen resides primarily in the oil product with the amount in the aqueous byproduct being lower by an order of magnitude or more. The nitrogen content of the oil phase seems to define an upper limit for the nitrogen in the aqueous phase; however, there are a large number of products which have significantly lower nitrogen contents in the aqueous phase than would be predicted based on the oil composition.

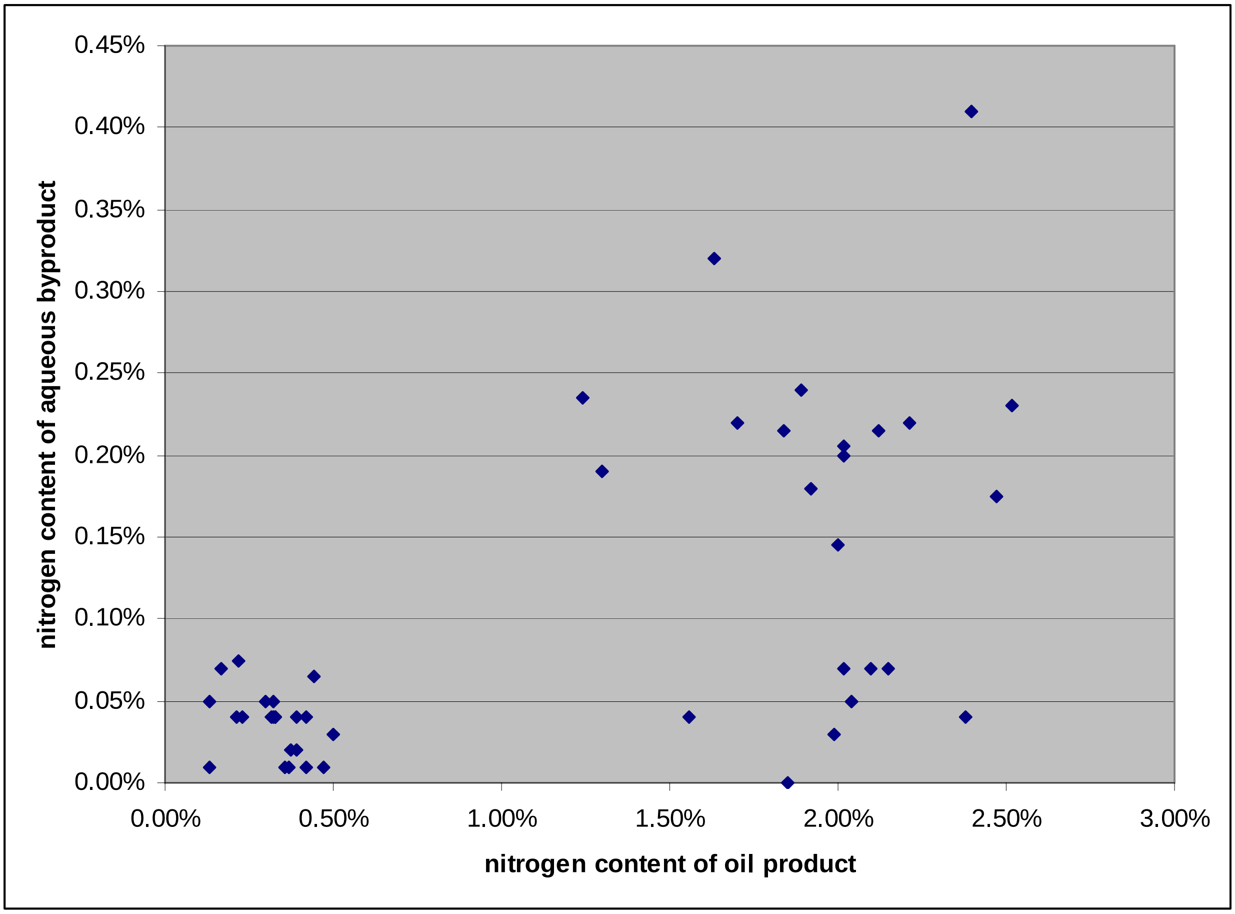

Figure 8. Relationship of nitrogen contents in oil product relative to the aqueous byproduct

The gas products from the hydrotreating tests were minimal in amount and typically the same composition. The main gas collected was hydrogen, as there was a great excess of hydrogen added to the reactor system to maintain a high partial pressure and facilitate its mass transfer. Because of the operational procedures for the bench-scale reactor, and specifically the liquid product collectors, the gas product recovered from the vent was diluted with nitrogen gas. The nitrogen was present in the reactor portion but was used to repressurize the collectors to reaction pressure prior to their being rotated into use and going “on stream.” The main product gas was carbon dioxide with a smaller amount of methane. In the higher temperature tests carbon monoxide was also found as were larger amounts of other hydrocarbon gases including ethane and propane. On a nitrogen-free basis the product gas was typically 96 to 98% hydrogen with 1 to 4 percent carbon dioxide, less than 1 percent methane, and less than 0.1% of ethane or propane and higher hydrocarbon gases.

Many of the products were analyzed by gas chromatography (GC) to better understand the specific component composition of the bio-oils and products. A GC equipped with a mass selective detector (MSD) was used to identify specific components. A GC equipped with a flame ionization detector (FID) was used to quantify the components. The GC FID served as a better base for quantitation because of the more uniform response of the various types of components in the bio-oil. The relative response for any given functional type varied from another functional type by +/-30% for those quantified in this study. As a result, the table of quantities shown below should be taken as approximate, as all components were not individually quantified, but a representative standard was used for all components. Clearly the trends in the data were evident. The chromatographs were quite complex and with the wide range of polarity among the various component types, not easily resolved in all cases.

Table 21. provides data on product oils from hydrotreating the mixed wood bio-oil (in the Silcosteel-CR coated reactor). The data listed under Feed 1 and Feed 2 represented two samples of the mixed wood bio-oil and demonstrated the range of variation in the analyses. O1, O2 and O3 are data for three different hydrotreated products from a single test (HT113). The show a trend of catalyst deactivation wherein the O1 sample has a larger fraction of actual alkane hydrocarbon products and less residual intermediate alkylphenolic and alkylguaiacolic products. In addition to these component groups found in the wood-derived bio-oils, alkylated pyrolles were found at low levels in the corn stover derived bio-oils. In the nomenclature used in Table 11, total alkanes includes all cyclic and acyclic alkanes, and complex guaiacols includes compounds that are guaiacol structures containing ring-substituents having carbonyl or olefin structures.

component group	Feed 1	O1	Feed 2	O2	O3
unsaturated ketones/aldehydes	3.37%	0.98%	4.46%	0.00%	0.39%
carbonyls (hydroxyketones, aldehydes)	9.27%	3.27%	9.36%	0.00%	0.00%
Total alkanes	0.00%	9.86%	0.00%	4.45%	3.18%
saturated guaiacols(diol,ones)	0.00%	0.15%	0.00%	0.29%	0.71%
phenol and alkyl phenols	10.27%	13.86%	6.83%	18.55%	26.67%
alcohols & diols	3.50%	4.62%	9.31%	5.29%	1.94%
HDO aromatics	0.00%	0.81%	0.00%	0.87%	0.27%
Total saturated ketones	1.13%	21.00%	0.96%	25.08%	17.68%
Total acids & esters	19.78%	23.43%	41.81%	25.21%	25.68%
Total furans & furanones	8.50%	1.09%	3.01%	2.19%	1.52%
Total tetrahydrofurans	3.18%	3.26%	2.88%	4.65%	2.35%
Complex guaiacols	26.40%	9.49%	8.34%	4.57%	7.70%
guaiacol and alkyl guaiacols	7.77%	5.00%	6.71%	5.41%	6.70%
unknowns	6.83%	3.17%	6.32%	3.44%	5.21%
TOTAL	100.00%	100.00%	100.00%	100.00%	100.00%

Table 21. Hydrotreating Product Oil Chemical Components

Hydrotreater Reactor Plugging

Over the life of the project, plugging in the front end of the catalyst bed, effectively in the heat up zone, became recognized as a critical limitation to the hydroprocessing of bio-oil. The tendency toward polymer formation (identified as thermal instability of the bio-oil) in the catalyst bed resulted in the buildup of pressure drop over time. After shutdown of the experiment a solid plug of “coke” encrusted catalyst particles that had formed in a portion of the catalyst bed could be recovered for analysis. Several options to eliminate the coking were addressed in the research, including:

- lower temperatures in the 1st stage,
- different catalysts,
- the effects of different biomass sources,
- elimination of reactor wall corrosion products, and
- removal of instability-causing components by phase separation of the bio-oil.

In earlier hydrotreating studies at PNNL[1] at lower temperature, 180 to 240°C, no evidence of coke formation in the hydrotreater catalyst bed was noted. As described earlier, the initial tests within this project were performed over four days at 340°C to 370°C but were only extended from 8-10 hours on stream before shutdown and the catalyst bed washed with acetone. In these tests no plugging was noted through 35 hr of operation until the 5th day when a much higher flow rate was attempted. After 5 hr of operation this bed had become unrecoverably plugged. Subsequent tests of 30 to 40 hours at 340°C similarly resulted in plugged catalyst beds. The time of plugging was noted when there was a change in pressure drop (>5 psig) over the catalyst bed. The “total flow until plugging” is the amount of bio-oil fed to the reactor system from the introduction of bio-oil until the time of plugging. Following those tests an attempt was made at 315°C. In this test the plug took longer to form and upon opening the reactor the plug was found further into the catalyst bed, essentially at the same point of heat up, where the bio-oil was passing through the range of 300°C. Other tests performed in the non-isothermal configuration involved a 1st stage catalyst bed at only 250°C. As shown in **Figure 9**, in these lower temperature tests the plugging in the catalyst bed was delayed even further. Several of these tests were not pursued to the point of plugging, therefore the trend indicated in the figure is at least as steep as shown and potentially much more so (as indicated by the arrows). However, these times on stream are exceptionally short relative to conventional operations in petroleum processing.

The results presented in **Figure 9** include an additional normalization based on cross-sectional area of the reactor. This correction is required because the reactor initially used has a 1.5 inch internal diameter while later reactors had an internal diameter of 1.0 inch. The reactors were of different lengths such that the volumes of the catalyst beds were the same. Since the plug required sufficient

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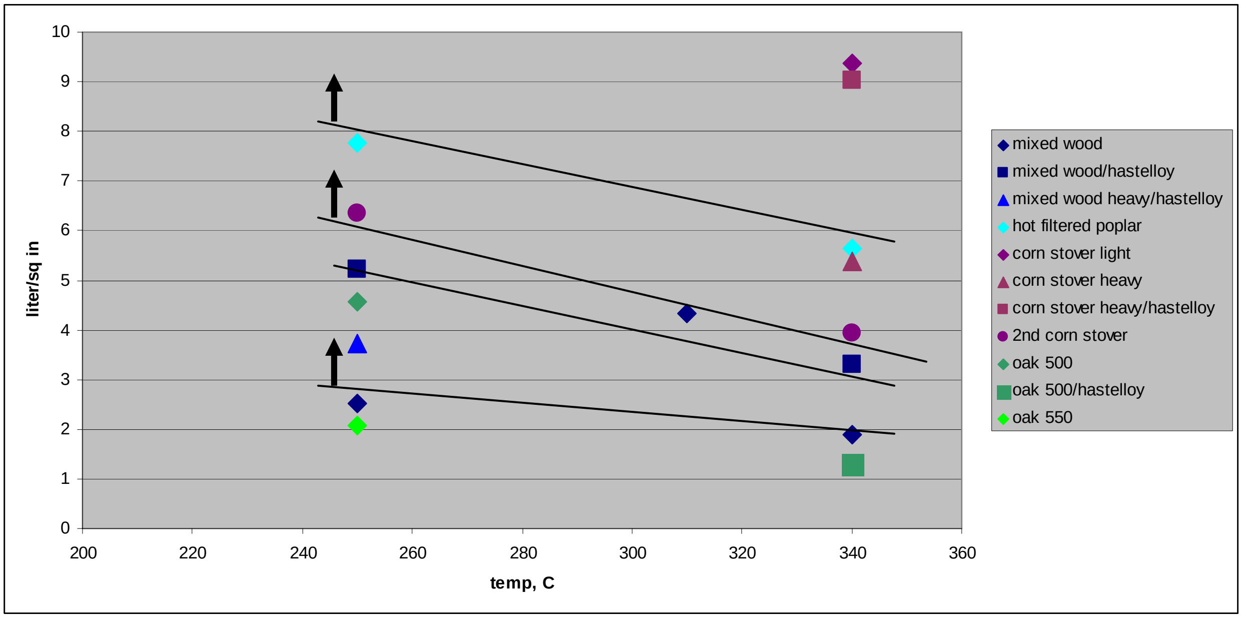
[1] Elliott, D.C.; Neuenschwander, G.G.; Hart, T.R.; Hu, J.; Solana, A.E.; Cao, C. 2006. “Hydrogenation of Bio-Oil for Chemical and Fuel Production.” In: **Science in Thermal and Chemical Biomass Conversion**, A. V. Bridgwater and D. G. B. Boocock, eds., pp. 1536-1546, CPL Press, Newbury Berks, UK.

mass to seal the cross sectional area, different masses of plug material were required in the two reactors. Therefore, using the same volumetric flow in each reactor to maintain the same space velocity, the “time to plugging” was dependent on the cross sectional area.



Tests at nominally 2000 psig with flow rate (LHSV) of about 0.25 liter bio-oil per liter of catalyst bed per hour

Figure 9. Temperature effect on total flow until plugging

We have considered the effect of feedstock composition on the plugging issue. In all cases at 340°C the plug eventually formed. The time on stream to development of a pressure drop suggested some differences in comparing the several feedstocks. The wood bio-oils (mixed wood or oak) resulted in coke formation more quickly than the corn stover bio-oils. The relevant results, corrected for cross sectional area of the reactor are presented in **Figure 9**.

The catalyst bed was typically Pd on carbon granules in the feedstock comparison tests, performed at 340°C. In the tests presented in **Table 22** there was an alternate material in the front end of the bed, which, as described earlier, appeared to have little effect on the coking issue. The “time to plugging” is the time of operation of the reactor system from the introduction of bio-oil until a noticeable change in pressure drop (>5 psig) over the catalyst bed was noted. The amount of oil feed over the time to plugging was then corrected for cross sectional area of the reactor for comparison purposes. From these results it is apparent that the alternative catalysts had only a minor effect on the plugging compared to the much larger effect due to feedstock composition differences between mixed wood and corn stover.

bio-oil	**time to plugging**	**volume oil fed**	**liter/sq in**
mixed wood, Pd/C only	31 hr	3.32 liter	1.88
mixed wood, Ru/C in front of Pd/C	31-37.5 hr	3.10-3.75 liter	1.75-2.12
mixed wood, Ru/TiO_2 in front of Pd/C	10.2-11.5 hr	1.04-0.96 liter	1.32-1.22
mixed wood, Pd/SiC instead of Pd/C	6.7 hr	0.66 liter	0.84
corn stover light phase, Pd/ZrO_2	66.9 hr	7.41 liter	9.38
2nd corn stover with Ru/TiO_2 and Pd/ZrO_2 in front of Pd/C	32.2 hr	2.92 liter	3.70
2nd corn stover with Ru/TiO_2 in front of Pd/C	33.3 hr	3.3 liter	4.18

Table 22. Bio-oil processed with several catalyst front end beds

Corrosion of the reactor wall and the thermowell had been previously noted as a result of hydrotreating tests. The corrosion noted in these tests appeared to be associated with the zone of coke formation, i.e., toward the front end of the reactor and in the zone where the bio-oil is reaching the reaction temperature. Of course, this is the region most exposed to the bio-oil in its most acidic “primary” form before it has reacted and been “stabilized.” The composition of the coke was examined in detail in an electron microscope. Imaging of the catalyst pellets encrusted in coke provided information about the elemental composition of the coke. Early on it was recognized that the metals with significant presence in the coke were nickel and iron, metals also found in the reactor wall, along with sulfur. As a result of the corrosion and the apparent link to coke formation, alternate materials were tested for the reactor wall. The 304 stainless steel was given a corrosion resistant coating in a commercial method called Silcosteel-CR. In another test, the reactor was fitted with a Hastelloy liner. In this case, all fittings and tubing on the feed side were also replaced with Hastelloy units. The feed pump was not replaced as it was fabricated from nitronic 50, which is a high-nickel alloy similar to Hastelloy. Finally, a Hastelloy reactor was put into operation. Comparative results for these test are given in **Table 23.** The first three tests strongly suggest that a corrosion-based mechanism might be linked to the coke formation. However, even with corrosion resistant construction, the coke formation still occurred and was only delayed. The last test seems to imply that addition of sulfur into the reaction environment will facilitate coke formation to such a degree that the advantage of a corrosion-resistant alloy construction is over-ridden.

reactor material	time to plugging	volume oil fed	liter/sq in
304 SS (1.77 sq in cross sectional reactor)	31 hr	3.32 liter	1.88
Silcosteel-CR-coated 304SS	27.6 hr	2.76 liter	3.49
Hastelloy-liner in 304SS	24.9 hr	2.49 liter	3.59-4.14
Hastelloy C-276 (sulfided bio-oil)	14.6 hr	1.19 liter	1.51

Table 23. Mixed wood bio-oil processed in reactors of different materials of construction

Analysis of Plug Material from Heat-up zone of Hydrotreating

Samples of the coke encrusted catalyst bed ("plug") were analyzed in several tests with electron microscopy (SEM) with electron dispersive spectroscopy (EDS). With these results the catalyst particle structures can be evaluated and elemental composition of deposits can be ascertained.

Oak 500°C bio-oil w/Pd-C catalyst (HT116)

The electron micrograph (**Figure 9**) at right shows a cross section of the plug with several catalyst pellets visible. The particle at center left showed evidence of surface coating while the particle in the upper middle seemed to be coating free. This sample was from a non-isothermal hydroprocessing test wherein the Pd catalyst was operated at about 250°C.

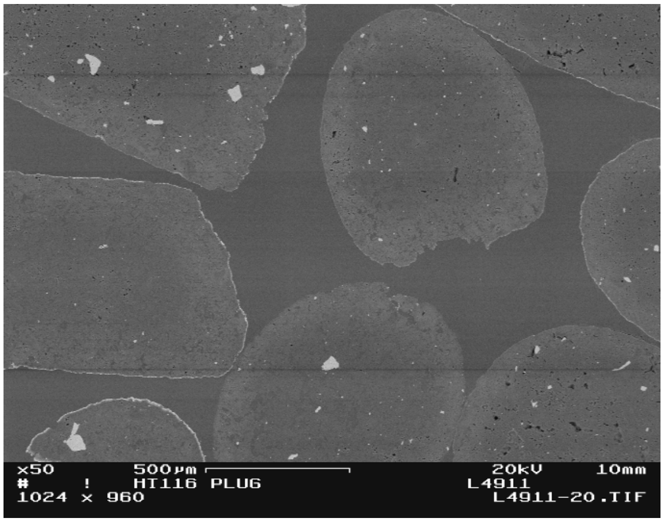


Figure 9 SEM of plug & catalyst

The EDS analysis of the coating free catalyst (**Figure 10-**higher resolution SEM at left) provided the profile of elements along a pathway over the catalyst particle from the edge toward the center of the particle. Carbon, being the catalyst support, was the major element throughout. The palladium composition across the particle suggested a strongly surface-impregnated (edge-coated) catalyst. Sulfur was found throughout the catalyst particle. The spectroscopy along line is shown in the four graphs below. Analysis of the light colored spot showed that it was a silicon rich inclusion.

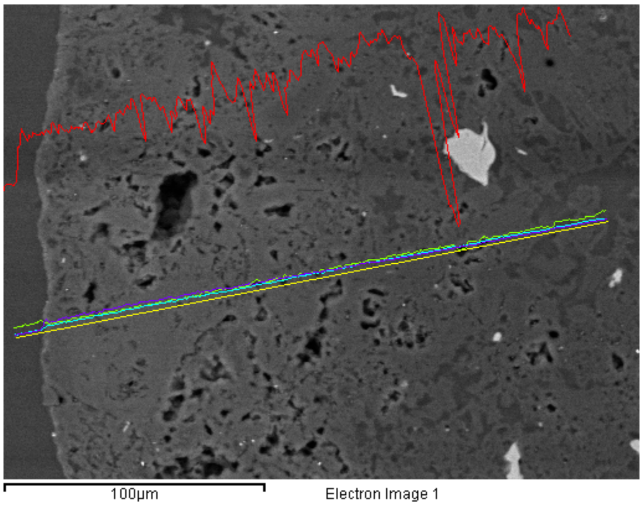


Figure 10a-EDS of catalyst particle from plug region

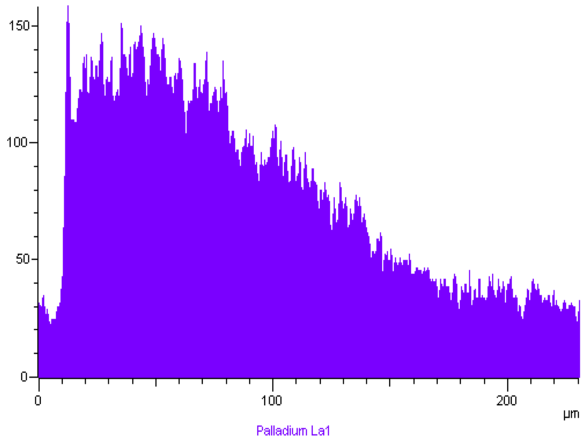


Figure 10b-Pd EDS of catalyst particle from plug region

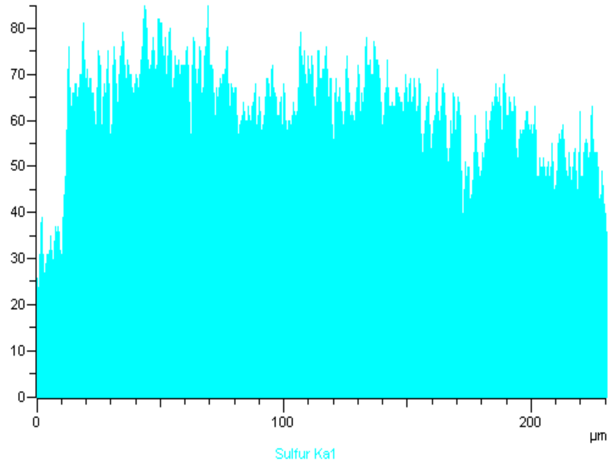


Figure 10c- S EDS of catalyst particle from plug region

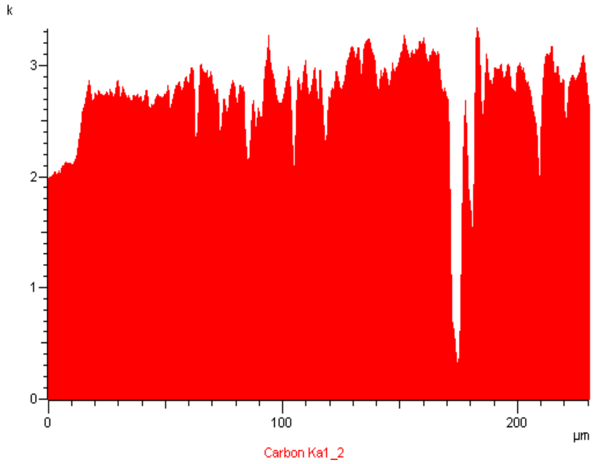


Figure 10d- C EDS of catalyst particle from plug region

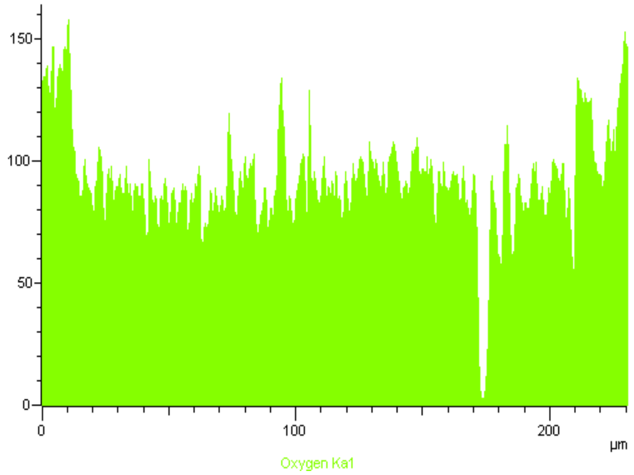


Figure 10e-O EDS of catalyst particle from plug region

An analysis of the coated particle, shown at left in a higher resolution SEM (**Figure 11**), provided similar results. Again, the Pd profile demonstrated an edge-coated catalyst while the sulfur was distributed throughout the catalyst particle. In this case, it appeared that the Pd may have migrated to the surface in conjunction with the sulfur. The reason for the visible edge-crusting was apparently a highly associated Pd and S mixture/ compound. This bright edge-crust also had iron and nickel associated with it in most cases.

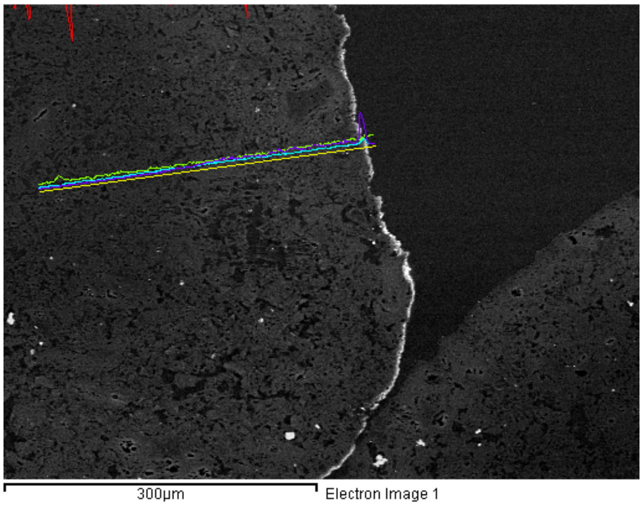


Figure 11a-HREDS of catalyst particle from plug region

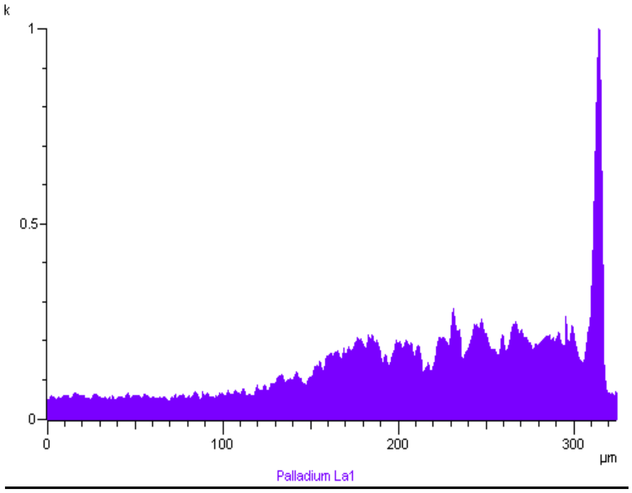


Figure 11b-Palladium HREDS of catalyst particle from plug region

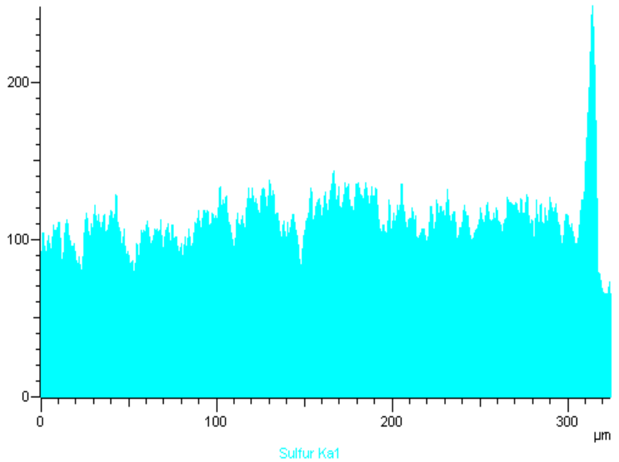


Figure 11c-Sulfur HREDS of catalyst particle from plug region

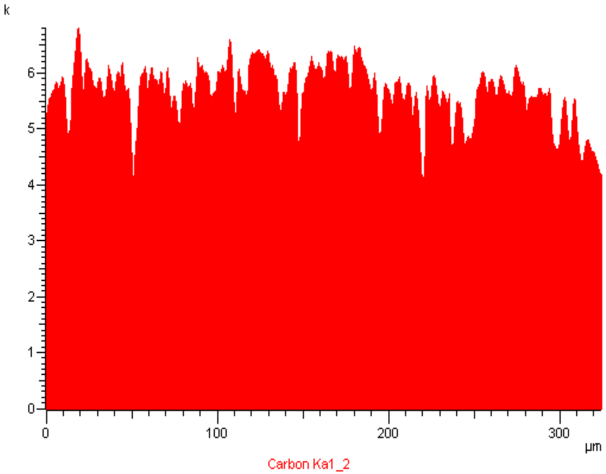


Figure 11d- Carbon HREDS of catalyst particle from plug region

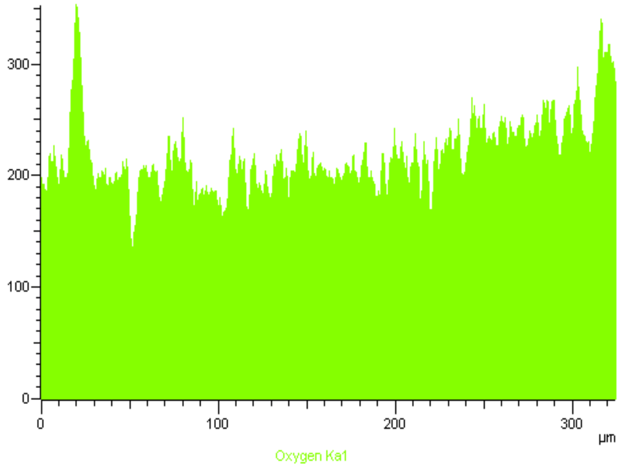


Figure 11e-Oxygen HREDS of catalyst particle from plug region

Table 24 provides the bulk elemental analysis a sample of the fresh Pd on carbon catalyst and 3 portions of the catalyst bed used to hydrotreat oak 500°C bio-oil. The fresh catalyst sample contains primarily palladium with a significant component of silicon and sulfur. In the sample of the top of the catalyst bed, although it is not coked catalyst, there is already a significant increase in the nickel, iron, chromium and molybdenum, all suggesting corrosion product deposits from the stainless steel system components (in red font). Calcium, copper, zinc and cobalt are also significantly elevated. In the second portion, which contains the coked material, the same changes are noted. The elements are largely diluted by carbon deposition. Below the coke plug the catalyst contained lesser amounts of contaminants except for iron.

Analyte Name	Fresh Pd/C 59893-43-1	HT116 Top	HT116 Plug	HT 116 Mid Cat
Al 396.153	305.0	134.0	90.9	160.0
Mo 202.031	5.9	513.0	727.0	425.0
Pd 340.458	12900.0	4790.0	3750.0	8630.0
S 180.669	3050.0	2410.0	1920.0	1460.0
Ni 231.604	9.6	2670.0	3370.0	176.0
Si 251.611	3520.0	2550.0	1900.0	1080.0
Fe 238.204	170.0	557.0	452.0	923.0
Cr 267.716	4.1	56.1	94.9	42.1
Ca 317.933	151.0	717.0	364.0	132.0
P 178.221	45.3	65.2	82.7	65.4
Co 228.616	0.6	9.7	6.9	22.8
Cu 327.393	41.0	219.0	259.0	121.0
Na 589.592	558.0	117.0	41.4	56.8
K 766.490	55.8	92.8	40.7	111.0
Mg 285.213	165.0	80.3	45.0	37.3
Mn 257.610	6.7	7.4	7.6	4.0
Pb 220.353	158.0	84.9	62.7	104.0
Ti 334.903	449.0	170.0	118.0	153.0
Zn 206.200	4.3	24.3	14.4	15.7

Table 24. Bulk Analysis of the HT116 catalyst

Oak 500°C bio-oil with Pd-C catalyst from the Hastelloy reactor (HT119)

In this plug sample, shown by SEM back-scatter at left, the catalyst particles appeared to have the same bright edging in most cases.

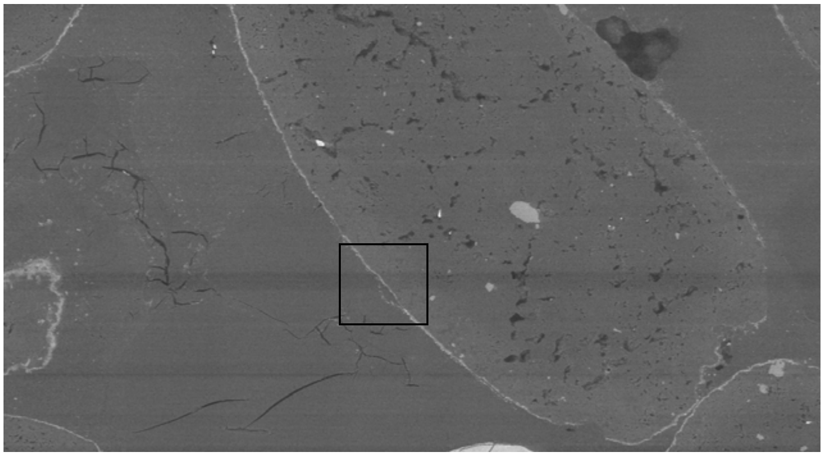


Figure 13a SEM back-scatter of catalyst & plug from oak oil

An image of increased magnification of the pellet edge (indicated by the rectangle drawn on the image at left) is shown below.

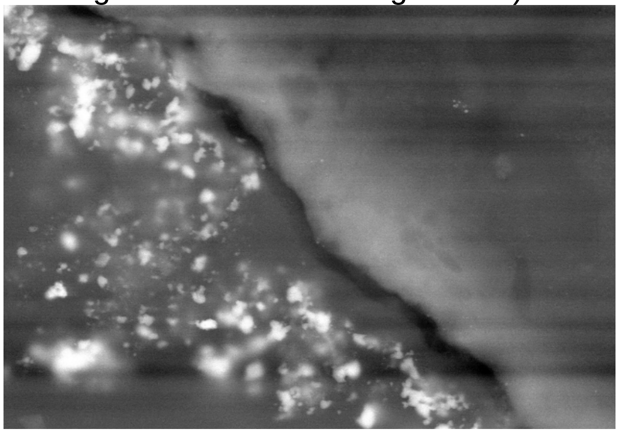


Figure 13b Higher Resolution SEM back-scatter of catalyst & plug from oak oil

The colorized version below can be used to visualize the elemental distribution in the image. In this case the palladium is shown in blue, while nickel and sulfur show as green and yellow

In another image shown below the edge of a catalyst particle is visible with bright particulates next to it. Using the scanning technique, the distribution of elements was traced across the image. With these spectra, shown below, it was clear to see the edge-coated palladium with the bright spot of nickel and sulfur. There was also

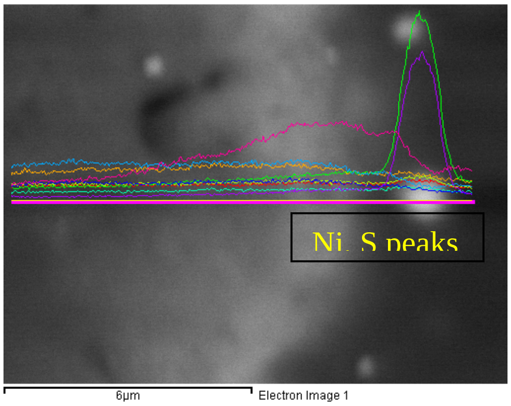


Figure 13c-Ni, S distribution of catalyst particle from plug region

evidence of calcium, phosphorus and aluminum enrichment in the spot, while it was deficient in iron and chromium.

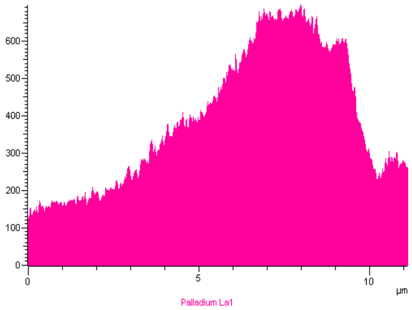


Figure 13d-Palladium HREDS of catalyst particle from plug region

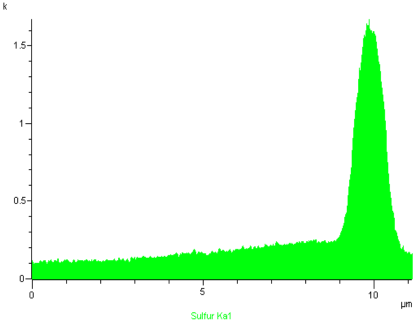


Figure 13e-Sulfur HREDS of catalyst particle from plug region

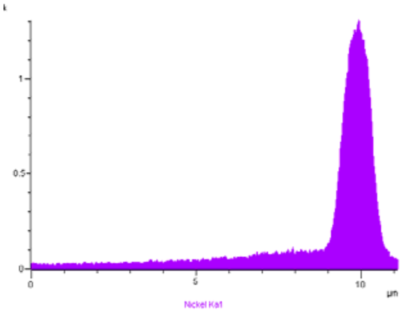


Figure 13f-Nickel HREDS of catalyst particle from plug region

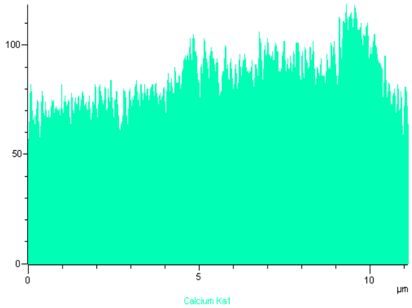


Figure 13g-Calcium HREDS of catalyst particle from plug region

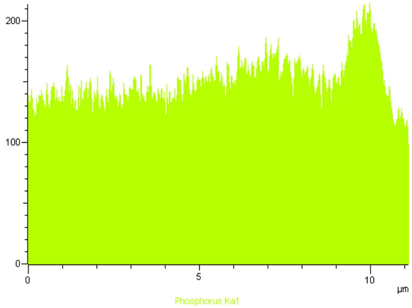


Figure 13h-Phosphorus HREDS of catalyst particle from plug region

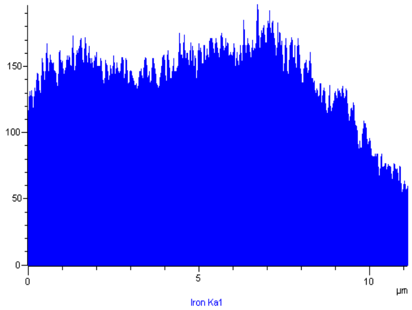


Figure 13i-Iron HREDS of catalyst particle from plug region

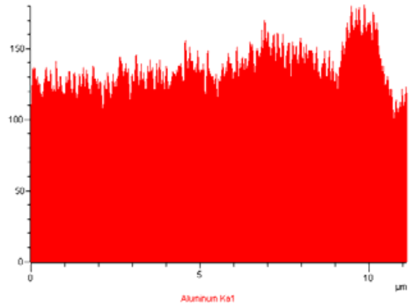


Figure 13j-Aluminum HREDS of catalyst particle from plug region

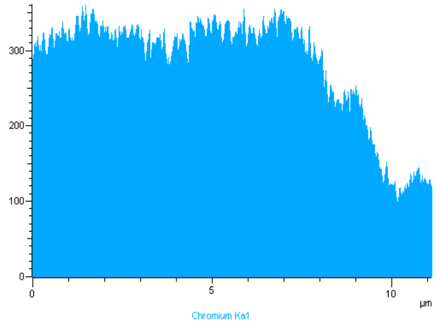


Figure 13k-Chromium HREDS of catalyst particle from plug region

Mixed Wood bio-oil with Pd-C Catalyst from Silcosteel CR lined 304SS reactor

The Silcosteel lining appeared to have little effect on the catalyst materials in the plug. As seen in this SEM image the catalyst particles had the bright edging seen before. Analysis of this material showed the same palladium on carbon dispersed catalytic formulation, but the edge material had significant clusters of nickel and sulfur and others of primarily palladium but also zinc, nickel and iron along with some sulfur. The spots within the catalyst pellet appeared to be the same silicon and oxygen material (silica deposits).

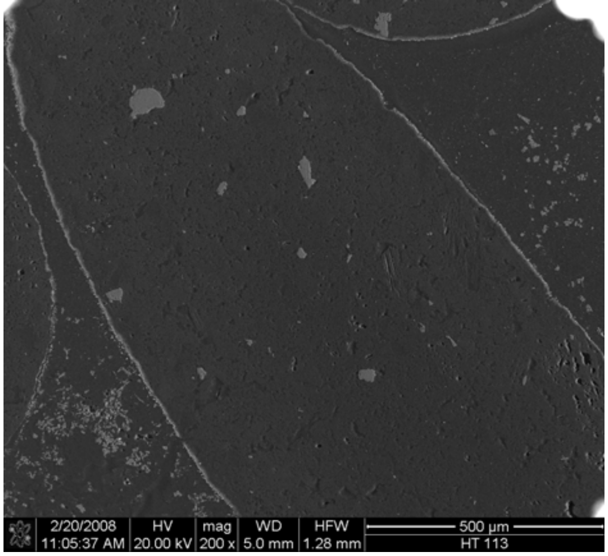


Figure 14: SEM of Pd-C Catalyst& Plug from mixed wood bio-oil in Silcosteel CR lined 304SS reactor

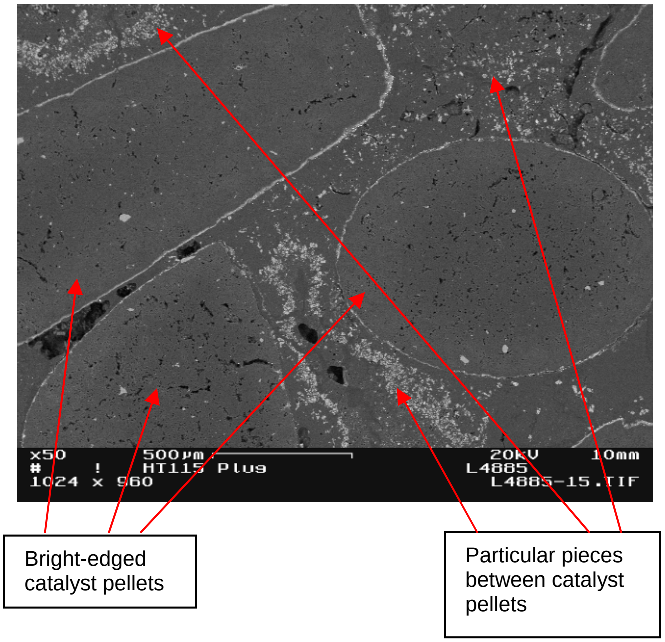


Figure 15: SEM of Several Pd-C Catalyst Particles and plug in lined reactor with Hastelloy insert

<u>Mixed wood bio-oil with Pd-C catalyst from SilcosteelCR lined 304SS reactor with a Hastelloy liner insert</u>

This plug also looked very much like others. In this SEM, several catalyst pellets can be seen as well as some particular material which has formed in the space between pellets within the coke matrix. The EDS analysis showed that the particular material was composed of iron and about half the amount of nickel, with lesser amounts of zinc and magnesium. As found with the other mixed wood bio-oil feedstock test discussed above, the bright edging contained zinc as well as nickel and iron. The palladium was also present in the bright edging along with sulfur. A portion of the bright edging is shown below in the SEM and the colorized form to show nickel/sulfur particles decorating the finely dispersed palladium.

Table 25 provides the bulk elemental analysis of 4 portions of the catalyst bed used to hydrotreated mixed wood bio-oil in the 304 SS reactor. The top portion of the bed is relatively coke free and contains primarily palladium catalyst although nickel has also been deposited. In the second portion, which contains the coked material, nickel and iron dominate with magnesium and chromium also elevated. The elements are largely diluted by carbon deposition. Below the coke plug the catalyst is mostly free of contaminant except for iron.

Analyte Name	HT88 Top	HT88 Char	HT88 Mid	HT88 Bottom
Pd	8920	46.2	15700	10900
S	1420	244	881	190
Ni	3650	6400	585	58.1
Fe	862	4930	1710	1450
Mg	130	399	157	210
Cr	45	448	175	297
Mo	184	261	156	123
Al	207	193	257	328
Zn	195	149	512	274
Si	141	124	389	129
K	115	208	273	429
Cu	67	110	42	64
Co	16	27	13	12
Mn	4	33	14	17
Ti	22	4	23	15
Ca	30	ND	8	ND

Table 25. Trace Element Analysis in Hydrotreating Mixed Wood Bio-oil, ppm

Sulfided mixed wood bio-oil with Pd-C catalyst from the Hastelloy reactor (HT121)

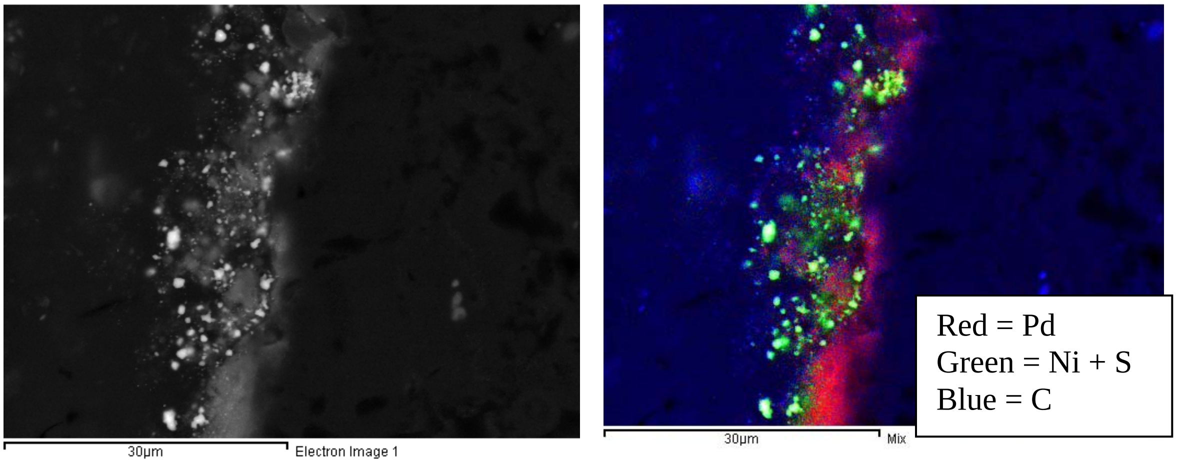


Figure 16: SEM of Sulfided mixed wood bio-oil with Pd-C catalyst from the Hastelloy reactor (HT121)

This sample is from a non-isothermal hydroprocessing test such that the Pd catalyst bed was operated at 250°C. Examination of this catalyst showed essentially the same things:

- carbon catalyst particles and carbon matrix between the particles;
- catalyst particles contain small silica particles;
- palladium is primarily edge-coated;
- sulfur is found throughout the catalyst;
- bright edging is composed of nickel/sulfur particles or palladium with iron, nickel and sulfur;
- in the mixed wood bio-oil tests, zinc is also found in the palladium bright edging and zinc/sulfur particles are also found in the bright edging.

Sulfided mixed wood bio-oil with UOP Hydrotreating catalyst from the Hastelloy reactor (HT122)

This sample is from a non-isothermal hydroprocessing test such that the Pd catalyst bed was operated at 250°C. The only difference in this test was the use of the UOP Hydrotreating catalyst in the hydrotreating zone. The analysis of the catalyst showed similar results. Although the bulk catalyst was an alumina support, sulfur was present throughout. Since molybdenum and sulfur can not be distinguished in this method, molybdenum might have been, and was expected to be, present throughout. There was a range of 25 to 28 wt% carbon found in the catalyst particles. Nickel was found at about 2 to 3.5%. The pieces of particulate visible in the coke matrix were the nickel/iron material (except this time it was nickel with half the amount of iron) with slightly more magnesium than zinc. There were also phosphorus particles near the edge of the catalyst pieces. There was a bright edge to the catalyst that seemed to be mostly nickel/sulfur, but the presence of molybdenum was also possible. The nickel was highly concentrated at the edge of the catalyst particles.

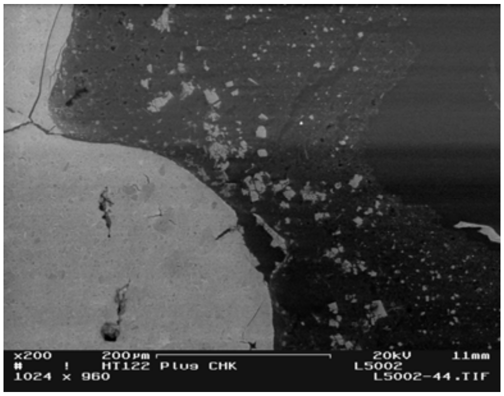


Figure 17: Sulfided mixed wood bio-oil with UOP Hydrotreating catalyst from the Hastelloy reactor (HT122)

Corn stover bio-oil with Ru on TiO_2 catalyst in 304 SS reactor

The coked catalyst sample was analyzed at two main sites, the edge of the coke from the sidewall of the reactor (as shown at right in B&W and colorized) and along the edge of a catalyst pellet, as shown below. The coke along the reactor wall contained significant metal both as a nickel/sulfur crust and as distinct nickel, iron, chromium pieces imbedded in the crust and coke, as indicated in the colorized version. Also identified in the coke were crystalline formations of iron and phosphorus, aluminum and phosphorus, barium and sulfur and calcium (possibly as carbonate).

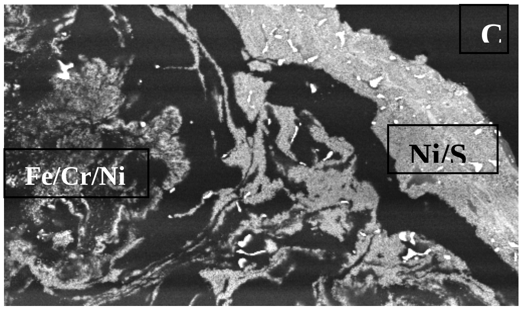


Figure 18 SEM of Catalyst and Plug with Ru/TiO2 catalyst in 304 SS reactor

The analysis of the catalyst pellet edge (shown in Figure 19) showed a similar deposit formation with this ruthenium on rutile titania as was seen earlier with the other catalysts. The nickel/sulfur crust highlighted the catalyst edge. The elemental mapping also showed that the ruthenium was concentrated near the edge of the titania extrudate.

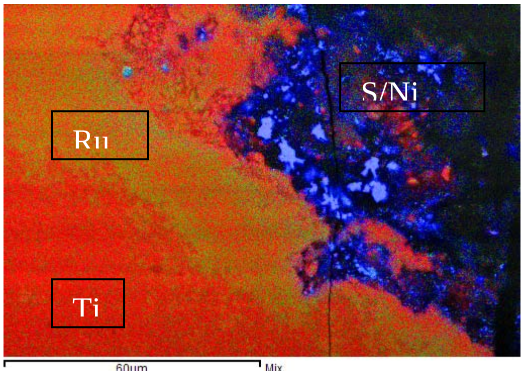


Figure19: HREDS Analysis of Catalyst and Plug with Ru/TiO2 catalyst in 304 SS reactor

Table 26 provides the bulk elemental analysis of three portions of the front end of the catalyst bed. The first 1 inch is free of coke; the section from 1-3 inches is the coke plug material; and the section from 3-5 inches is coke free again. The titania and ruthenium are the catalyst. The low recovery of titania is a function of the sample preparation. This analysis clearly shows the deposit of nickel, iron, calcium, chromium, copper and phosphorus along with an elevated level of sulfur. The elevated level of iron and chromium carry into the portion of the bed following the plug as well.

Analyte Name	Top 1	Top 1-3	Top 3-5	inches from top
Ti 334.903	366	638	644	
Ru 240.272	14700	11700	14400	
S 180.669	1320	3930	1250	
Ni 231.604	414	7620	395	
Fe 238.204	900	2280	2310	
Ca 317.933	492	2780	257	
Na 589.592	315	266	148	
K 766.490	194	186	197	
Al 396.153	144	106	74	
Si 251.611	257	95	126	
Cr 267.716	74	716	330	
Cu 327.393	47	263	43	
Zr 343.823	21	5	6	
P 178.221	4	92	-18	
Mg 285.213	36	38	78	
Zn 206.200	1	-2	-3	
	titania pellets	plug	titania pellets	

Table 26. Trace Element Analysis in Hydrotreating 2^{nd} Corn Stover Bio

Hot-filtered poplar bio-oil with Pd on carbon catalyst in 304 SS reactor

The SEM images (**Figure 20** in low and high resolution) showed the highly porous carbon structure which was decorated with heavy element (bright) particles. Analysis of these particles confirmed that they were primarily palladium, with lesser amounts (1/10th) of iron and less of zinc. Different from the other tests, edge analysis showed a lack of nickel or sulfur.

The relationship of the bio-oil sulfur content relative to the coke deposit composition seems to be important. Although the poplar bio-oil was found to have relatively high sulfur content compared to the other bio-oils by the thermal method, the ICP analysis showed that its sulfur content was much lower than for the other bio-oils. Similarly, the poplar bio-oil was low in nickel, yet had notable iron and zinc content. These differences were also reflected in the deposits on the catalyst in the coked region of the bed. The higher nickel content in the mixed wood and corn stover bio-oils may be a significant factor in the deposit formations in those tests, irrespective of the reactor metal of construction. Alternatively, although the Hastelloy metal components were visibly more resistant to pitting corrosion, the high nickel content may have actually contributed to the deposit formation. Hastelloy metal components are considered to be more resistant to corrosion by acids, but the high nickel content may have actually contributed to the deposit formation through a more uniform corrosion mechanism.

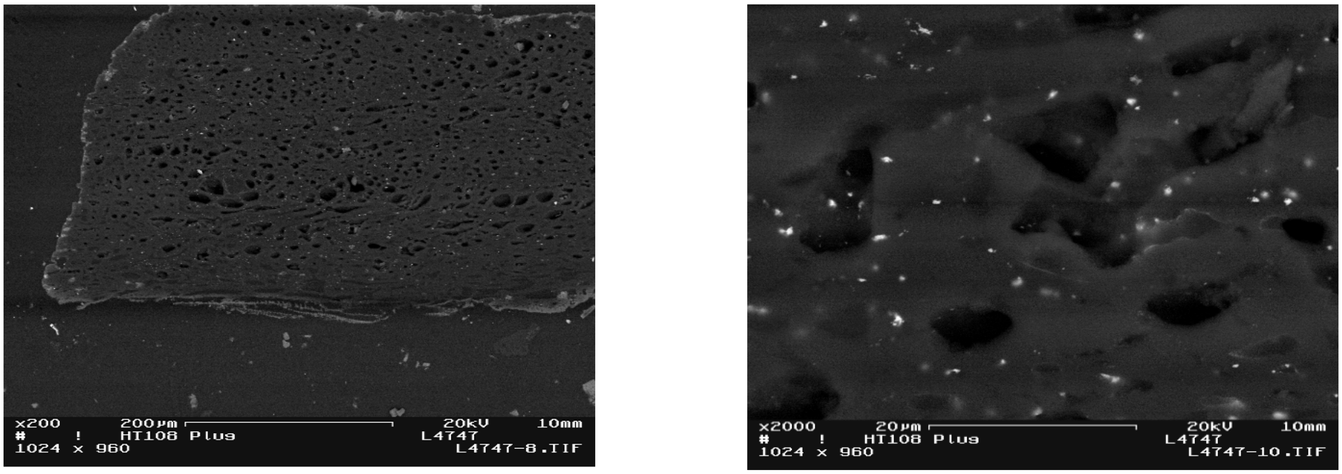


Figure 20: Low (L) and High (R) resolution SEM of catalyst and plug from Hot-filtered poplar bio-oil with Pd on carbon catalyst in 304 SS reactor

4.6 Hydrocracking Process Results

The hydrocracking tests were performed with the UOP Hydrotreating catalyst from UOP in its sulfided form as received from UOP. By using the hydrotreated bio-oil as the feedstock it was possible to perform the tests at lower pressure and higher temperature than the hydrotreating of the as-produced bio-oil. In these tests the yield structure was highly biased toward the oil layer as opposed to the high water yields in the hydrotreating tests. The splits ranged from 2-3 times as much oil with the wood bio-oil, which contained 8% moisture, to 4-6 times as much oil with the hot-filtered poplar bio-oil, which contained less than 3% moisture.

These results from **Table 27** showed a consistently higher oil product yield. Gas generation was substantially more in all cases and was primarily hydrocarbons rather than carbon dioxide. A significant bed heating suggested a strongly exothermic reaction. The hydrogen consumption was much higher in the hydrocracking step than in the hydrotreating step.

bio-oil	**oil yield, g/g dry feed**	**aqueous yield, g/g wet feed**	**gas yield, g/g carbon feed**	**Hydrogen consumption, liter/liter feed**	**Relative exotherm versus setpoint**
mixed wood	0.61	0.24	0.087	290	+16°C
corn stover light phase	0.74	0.13	0.100	550	+12°C
corn stover heavy phase	0.82	0.14	0.077	510	+17°C
2nd corn stover	0.81	0.14	0.090	490	+20°C
poplar	0.80	0.17	0.116	430	+17°C

405°C, 1500 psig, 0.2 LHSV

Table 27. Feedstock Effect on Hydrocracking Process Results

4.7 Effect of Feedstock in Hydrocracking

The initial conclusion drawn from the results of the hydrocracking tests, as shown in **Table 28**, was that the final products were even more similar than the bio-oil products regardless of the original biomass feedstock. In all five cases tested, high quality hydrocarbon products could be produced after appropriate processing conditions were identified.

bio-oil source	**C**	**H**	**O**	**N**	**S**	**moisture**	**density**	**TAN**
mixed wood	86.6	12.9	0.4	<0.06	0.01	0.01	0.85	2.5
corn stover light phase	86.6	12.5	0.8	<0.1	<0.01	0.01	0.81	0.5
corn stover heavy phase	87.6	12.1	0.4	0.6	<0.01	0.14	0.86	1.5
2nd corn stover	86.8	12.2	0.6	0.5	<0.01	0.15	0.87	2.7
hot-filtered poplar	87.4	12.0	0.3	0.2	0.01	0.06	0.87	2.0

405°C, 1500 psig, 0.2 LHSV

Table 28. Composition of Hydrocracked Products

Many of the products from hydrocracking were also analyzed by GC to better understand the specific component composition of the bio-oils and products. The same system of GC-MSD, to identify specific components, and GC-FID, to quantify the components, was used. The relative response for the hydrocarbon products was much more uniform; as a result, the table of quantities shown below should be more accurate. However, a single representative standard was used for all components. Again, the trends in the data were evident. The chromatographs were less complex and more easily resolved.

Table 29. provides data on product oils from hydrocracking the hydrotreated mixed wood bio-oil. The data listed under Feed 1 are comparable to the products of mixed wood bio-oil hydrotreating given in Table 11. O1, O2, O3, and O4 are data for four different hydrocracked products from a single test (HT107). The data demonstrate consistent catalyst activity throughout the test. The products are essentially all hydrocarbons, largely cyclic in nature (naphthenes and aromatics). The unknowns are higher molecular weight material, for the most part, and may represent oxygenated components.

Component Groups	**O1**	**O2**	**O3**	**O4**	**Feed 1**
component group	0.00%	0.00%	0.00%	0.00%	0.00%
unsaturated ketones/aldehydes	0.00%	0.00%	0.00%	0.00%	0.00%
carbonyls (hydroxyketones, aldehydes)	70.77%	67.88%	69.67%	71.63%	4.22%
Total alkanes	0.00%	0.00%	0.00%	0.00%	0.00%
saturated guaiacols(diol,ones)	0.00%	0.00%	0.00%	0.00%	15.68%
phenol and alkyl phenols	0.00%	0.00%	0.00%	0.00%	22.67%
alcohols & diols	12.02%	14.05%	11.53%	12.82%	10.51%
HDO aromatics	0.00%	0.00%	0.00%	0.00%	12.84%
Total saturated ketones	0.00%	0.00%	0.00%	0.00%	11.89%
Total acids & esters	0.00%	0.00%	0.00%	0.00%	0.00%
Total furans & furanones	0.00%	0.00%	0.00%	0.00%	3.28%
Total tetrahydrofurans	0.00%	0.00%	0.00%	0.00%	0.00%
Complex guaiacols	0.00%	0.00%	0.00%	0.00%	18.91%
guaiacol and alkyl guaiacols	11.72%	13.62%	13.18%	10.32%	0.00%
unknowns	5.49%	4.45%	5.62%	5.24%	0.00%
TOTAL	100.00%	100.00%	100.00%	100.00%	100.00%

Table 29. Hydrocracking Product Oil Chemical Components

4.8 Catalyst Coking in Hydrocracking

There was little evidence of catalyst coking in these tests. No pressure drop developed over the reactor and the tests were terminated voluntarily when the feedstock was exhausted. Other than a slight crust of coke at the very top (1/8”) of the reactor in the quiescent zone around the edge there were no coke deposits in the catalyst bed.

4.9 Non-Isothermal Process Results

The non-isothermal hydroprocessing tests were performed to test a low-temperature first step in combination with a high-temperature second step without product phase separation between steps. Bio-oil was used as the feedstock. In these tests the yield structure was highly biased toward the aqueous layer with the combination of the high water yields at low temperature and further hydrodeoxygenation and water formation at higher temperature without intermediate water separation. The splits ranged from 1.2 to 1.6 times as much aqueous phase as oil phase, except up to 3 with the corn stover bio-oil, which contained significantly more water.

These results from **Table 30** showed a consistently higher aqueous product yield but the carbon loss is low as the carbon content in the aqueous phase is less than 0.5% in all cases except the hot-filtered poplar. Gas generation was substantially more in all cases and was primarily hydrocarbons along with carbon dioxide. A very significant bed heating suggested a very strongly exothermic reaction in the lower, high-temperature bed. The hydrogen consumption was very high as a combination of utilization in both the hydrocracking step and the hydrotreating step.

bio-oil	**oil yield, g/g dry feed**	**aqueous yield, g/g wet feed**	**gas yield, g/g carbon feed**	**Hydrogen consumption, liter/liter feed**	**Relative exotherm versus setpoint**
mixed wood	0.50	0.48	0.192	710	+32°C
oak, 500°C	0.54	0.44	0.320	640	+45°C
oak, 550°C	0.53	0.52	0.290	655	+39°C
2nd corn stover	0.37	0.64	0.323	490	+26°C
hot-filtered poplar	0.48	0.46	0.259	630	+60°C

250-410°C, 2000 psig, 0.15 LHSV

Table 30. Feedstock Effect on Non-isothermal Processing Results

4.10 Effect of Feedstock in Non-isothermal Tests

A conclusion similar to that recognized in the hydrocracking tests was that the final products were uniform, as shown in **Table 31,** despite the variation in the source of the bio-oil or the original biomass feedstock. In all cases tested, except the hot-filtered poplar, high quality hydrocarbon products could be produced in this once-through process. The lower quality product with the hot-filtered bio-oil was attributed to a lower activity catalyst (even though it exhibited the largest exotherm).

bio-oil source	**C**	**H**	**O**	**N**	**S**	**moisture**	**densit**	**TAN**

							y	
mixed wood	87.7	11.6	0.6	<0.05	0.01	0.07	0.84	1.6
oak, 500°C	87.7	11.7	0.3	0.05	0.06	0.04	0.84	0.8
oak, 550°C	86.9	12.5	0.2	0.06	0.005	0.002	0.82	0.1
2nd corn stover	87.4	11.9	0.4	0.40	0.005	0.06	0.84	2.5
hot-filtered poplar	85.2	10.2	4.9	0.14	0.19	0.51	0.92	6.1

250-410°C, 2000 psig, 0.15 LHSV

Table 31. Composition of Non-isothermal Hydroprocessed Products

4.11 Effect of Catalyst in Non-isothermal Tests

With two exceptions, in the tests listed in **Table 29**, the catalysts used were a Pd/C granule in the low-temperature bed and the UOP Hydrotreating hydrocracking catalyst (pre-sulfided) in the high-temperature bed. The exceptions were the use of a CoMo/alumina catalyst for the entire bed with the hot-filtered poplar bio-oil and the use of the HC-43 (presulfided) in place of the UOP Hydrotreating in the 500°C oak test. How the CoMo catalyst could have had the largest exotherm, reacted a large amount of hydrogen, produced a large amount of hydrocarbon gases, yet produced such an inferior oil product in terms of deoxygenation was unexplained. The use of the UOP Hydrocracking instead of the UOP Hydrotreating was indistinguishable by these data.

4.12 Catalyst Coking in Non-isothermal Tests

Plugging was not an issue in these tests. The lower temperature in the front bed seemed to retard the coke formation. No pressure drop build up was noted in these tests even though the bio-oil throughput ranged up to 7.8 liters per square inch of cross section of the reactor in the case of the hot-filtered poplar bio-oil. The mixed wood bio-oil was processed up to 2.5 L/in^2 without plugging (compared to 0.8 to 2.1 with plugging at 340°C in a 304SS reactor) and the corn stover test reached 6.3 L/in^2 (compared to 3.7-4.2 with plugging at 340°C). These differences suggest the value of operation at lower temperature to avoid plugging. The two oak tests extended for 3.6 and 2.1 L/in^2 for the 500°C bio-oil and 550°C bio-oil, respectively. Although no pressure drop developed in processing the 500°C oak bio-oil, in fact, a plug was found in the catalyst bed following the test. Apparently the test was near to being ended with a plug formation.

However, in subsequent tests in the Hastelloy reactor the coke formation problem became evident again. Two tests of mixed wood bio-oil and a third with the heavy phase separated from the mixed wood bio-oil by water addition all ended when a significant pressure drop developed. These three tests all produced quality products early on, but, as seen in **Table 32,** showed signs of deactivation over time and eventually plugged. Note that in all three of these cases the wood derived bio-oil carried the added sulfiding agent ditertbutyldisulfide. These tests are also different from those in Table 16 in that they were performed in the reactor with the smaller cross-sectional area. These mixed wood bio-oil tests achieved from 3.59 to 5.23 L/in^2 before significant pressure drop was noted. These numbers are better than the Hastelloy result in Table 12 for operation at 340°C (1.5 L/in^2), underscoring the value of operation at lower temperature and the thermal instability of bio-oil.

bio-oil source	C	H	O	N	S	moisture	density	TAN
mixed wood, sulfided	87.4	12.1	0.3	<0.05	<0.005	0.011	0.85	0.07
mixed wood sulfided	87.6	11.8	0.3	<0.05	<0.005	0.023	0.87	0.09
mixed wood, heavy phase, sulfided	87.4	12.2	0.5	0.565	<0.005	0.105	0.88	<0.1

250-390°C, 2000 psig, 0.14 LHSV

Table 32. Composition of Non-isothermal Hydroprocessed Products from Hastelloy Reactor

Overall Assessment

Hydrotreating followed by hydrocracking can be applied to bio-oil to produce hydrocarbon products. Table 23 provides some relevant data for three feedstocks. The first step of hydrotreating bio-oil produces a viscous bio-oil product with a reduced amount of oxygen and dissolved water. A separate aqueous phase is also produced which carries a portion of the hydrotreated bio-oil as dissolved organic. Gas production, primarily as carbon dioxide, results in a noticeable byproduct stream with relatively low hydrogen consumption. The second step of hydrocracking the hydrotreated bio-oil produces a nearly oxygen-free hydrocarbon product. There is additional aqueous byproduct which carries very little organic material. Gas production is up to twice that resulting from hydrotreating and it contains significant hydrocarbon components. The hydrogen consumption is much higher in hydrocracking ranging from 40% higher to over 6 times higher in the three cases presented here.

The results of the consecutive step operation (HT/HC total in Table 23) can be compared to our non-isothermal operation in which the two steps are operated in a two-stage reactor without intermediate product recovery and separation. In non-isothermal operation the overall oil product yield is higher by 4% to 35%. The byproduct water product is reduced, as is the loss of dissolved organic, because the aqueous product is very low in organic contamination. The overall gas yield is higher by 2 to 3 times, but much of this gas is hydrocarbon material that can be reused in hydrogen production. The reduced loss of organic in the aqueous phase and the higher gas yield suggests that the low-molecular weight oxygenates in the water are being gasified by reaction with hydrogen in the hydrocracking step; at the same time some are converted to hydrocarbon liquids. In the non-isothermal case the hydrogen consumption is higher by 25 to 84%.

Table 23. Comparative Yields of Two-stage Processing versus Non-isothermal Processing

		Hydro-treating	Hydro-cracking	HT/HC total	Non-isothermal
Mixed Wood	dry oil yield, g/g	0.62	0.61	0.37	0.50
	aqueous yield, g/g	0.48	0.24	0.63	0.48
	C gas g/g	0.062	0.087	0.116	0.192

	H_2 consumption, L/L	205	290	385	710
2nd Corn Stover	dry oil yield, g/g	0.45	0.81	0.35	0.37
	aqueous yield, g/g	0.61	0.14	0.67	0.64
	C gas g/g	0.066	0.090	0.106	0.323
	H_2 consumption, L/L	76	490	296	490
Hot-filtered poplar	dry oil yield, g/g	0.59	0.80	0.46	0.48
	aqueous yield, g/g	0.46	0.17	0.56	0.46
	C gas g/g	0.060	0.116	0.128	0.259
	H_2 consumption, L/L	252	430	506	630

Database Development

As part of this CRADA project, PNNL developed an ACCESS Database to collect the process data for all portions of this project. It included biomass feed analyses (ultimate, proximate, ash composition, and heating value), pyrolysis oil analyses (ultimate analysis, water content, ash component analysis, density, pH, and compound classification), and pyrolysis oil production material balance data based on input from NREL as well as some product analyses performed by PNNL. The Database also included similar tables related to hydrotreating experiments as well as for the hydrocracking experiments. Tables included process parameters and product analyses, including oil and aqueous phases and gaseous products. The tables were also included for the non-isothermal processing experiments; however, for those experiments there was no recovery of hydrotreated products. As a result, there were no data entries in the tables for hydrotreated oil products, hydrotreated aqueous products or hydrotreated gas products for those tests which were non-isothermal in nature. The product analyses for the non-isothermal tests were recorded in hydrocracking products tables. In addition, the gas calculations and mass balances were recorded on the hydrocracking process table and not the hydrotreating process table.

Analyses and Characterization

Various analytical methods were employed at UOP to determine the properties of fuels derived from hydroconverted pyrolysis oils. Gas chromatography was a major technique used in the compositional characterization of bio-derived fuels. Other ancillary techniques that determined elemental compositions of the oils were also employed.

Gas chromatographic methods

Simulated Distillation, D2887

This method is used for petroleum fractions or products that have a final boiling point of 538°C. Boiling range distributions obtained by this test method are essentially equivalent to those obtained by true boiling point (TBP) distillation (i.e. Test Method D 2892). D2887 was used in determining the boiling range distribution of components in hydroconverted pyrolysis oil, as well as in the gasoline and diesel fractions from the spinning band distillation of the hydroconverted pyrolysis oil.

Detailed Hydrocarbon Analysis (DHA)

This method is useful in the determination of hydrocarbon groups and prediction of some physical properties of reformulated gasoline, e.g. Density, RON/MON, etc. The analysis uses a high resolution capillary GC column, which can provide a detailed analysis, specifying individual compounds. This method was used in characterizing the composition of hydroconverted pyrolysis oils, as well as gasoline and diesel fractions obtained from the spinning band distillation of the hydroconverted pyrolysis oils.

Paraffins, Isoparaffins, Olefins, Naphthenes, Aromatics (PIONA)

PIONA is another analysis that can provide information on the hydrocarbon composition of reformulated gasoline. Unlike the DHA, it does not provide identification of individual hydrocarbon compounds. It yields group type separation of n-paraffins, isoparaffins, naphthenes, olefins, and aromatics by carbon number distribution. While this method was originally designed for use on FCC gasoline, it was used in the compositional characterization of the gasoline fraction from the hydroconverted pyrolysis oil, derived from spinning band distillation.

GC x GC FID

This is a relatively newer technique that utilizes 2 gas chromatographic columns of differing selectivities, in the separation of components in complex mixtures, such as hydroconverted pyrolysis oils. The method is applicable to naphtha to VGO range fractions. The components are separated from one another on the basis of two properties: boiling point and polarity. Their respective locations on a contour plot gives information on which molecular types they belong to, i.e. paraffins, olefins, naphthenes, aromatics, as well their carbon numbers. This analysis is quantitative since a Flame Ionization Detector (FID) is used. A variant of this method is being developed at UOP, to specifically quantitate oxygenated components in partially deoxygenated pyrolysis oils.

Elemental analysis

Percent Total Oxygen

This technique uses high temperature pyrolysis which converts oxygen contained in the sample to carbon monoxide. The carbon monoxide produced is detected by a Thermal Conductivity Detector (TCD), and its concentration is related to the total oxygen in the sample. This method was used in the determination of oxygen content in hydroconverted pyrolysis oil, which is a measure of the degree of deoxygenation.

Total Sulfur, XRF

This technique uses high energy X-ray bombardment of the sample to produce fluorescence radiation. The resultant characteristic emission line from a specific element, e.g. sulfur, is isolated by means of a WDXRF spectrometer. The signal from the characteristic photon is detected and integrated and the measured intensity is related to elemental composition by the use of a calibration procedure. This technique was used in measuring sulfur, associated with the catalyst being used in the hydrotreatment of raw pyrolysis oils.

Total Chloride

The hydrocarbon sample to be analyzed is injected onto a quartz boat, which is sent into a furnace in a pyrohydrolytic environment. The products of combustion are HCl and Cl2. The resultant gases are absorbed in an aqueous solution which is injected into a Ion Chromatograph, where the chloride species are detected and measured. This method was used in the evaluation of raw and processed pyrolysis oil, to determine the levels of chloride, associated with corrosion in process equipment.

Carbon, Hydrogen, Nitrogen (CHN)

This technique employs combustion of a sample in the presence of oxygen. Catalysts aid in the formation of CO from carbon, H2O from hydrogen.

The oxides of nitrogen formed in the combustion are reduced to diatomic nitrogen via a different catalyst. All products formed are separated by gas chromatography and detected by a Thermal Conductivity Detector.

Carbonyl Number

Known as UOP 624, this method is a spectrophotometric determination of the carbonyl number, present as ketone or aldehyde carbonyl, and defined as "milligrams of carbonyl function per liter of sample using acetophenone as the standard.". The typical analysis range for carbonyl number is 0.1 to 100 mg/L carbonyl. The sample must be colorless. This method was used in determining degree of decarboxylation of hydroconverted pyrolysis oil, particularly in the evaluation of the gasoline fractions from spinning band distillation.

Physical methods

Specific Gravity, API Gravity

ASTM D4052 was used in determining the specific gravity and API gravity of raw and hydroconverted pyrolysis oils, as well as for gasoline and diesel fractions generated from spinning band distillation.

Cetane Number

Measurement of the cetane number of the diesel fraction obtained by spinning band distillation of hydroconverted pyrolysis oil was done by ASTM D6890, Derived Cetane Number. This automated test method measures the ignition delay and utilizes a constant volume combustion chamber with direct fuel injection into heated, compressed air. The minimum volume required for this test is 35 mL.

Spinning Band Distillation

A form of distillation which involves the use of a rotating helical spinning band to create a high number of theoretical plates. The spinning band forces rising vapors to be in close contact with the condensate. This intimate contact between the two phases enhances a good separation between components in a mixture. This was used in fractionating hydroconverted pyrolysis oils into gasoline, diesel, and bottoms fractions.

Database Development

As part of this CRADA project, PNNL developed an ACCESS Database to collect the process data for all portions of this project. It included biomass feed analyses (ultimate, proximate, ash composition, and heating value), pyrolysis oil analyses (ultimate analysis, water content, ash component analysis, density, pH, and compound classification), and pyrolysis oil production material balance data based on input from NREL as well as some product analyses performed by PNNL. The Database also included similar tables related to hydrotreating experiments and hydrocracking experiments. Tables included process parameters and product analyses, including oil and aqueous phases and gaseous products. . The tables were also included for the non-isothermal processing experiments; however, for those experiments there was no recovery of hydrotreated products. As a result, there were no data entries in the tables for hydrotreated oil products, hydrotreated aqueous products or hydrotreated gas products for those tests which were non-isothermal in nature. The product analyses for the non-isothermal tests were recorded in hydrocracking products tables. In addition, the gas calculations and mass balances were recorded on the hydrocracking process table and not the hydrotreating process table. The Database is included as Appendix B to this report.

These appendices will be provided in electronic form as files on a CD.

Process Data Sheets from Hydrotreating, Hydrocracking and Non-isothermal Hydroprocessing Confidential Submission to DOE

Database Tables for Pyrolysis, Hydrotreating and Hydrocracking Confidential Submission to DOE

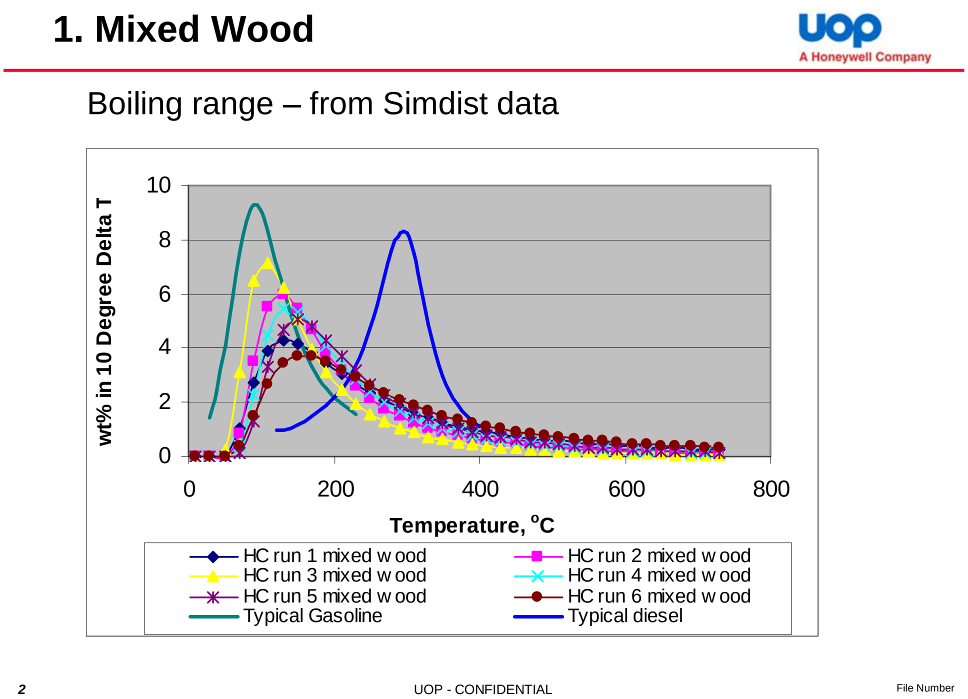
Summary Tables and Plots The limited amount of hydrotreated pyrolysis oil produced per run has made it difficult to follow a particular bio feedstock from pyrolysis all the way to the final hydrocracked product. Nevertheless, an attempt has been made below to do this for the 3 different feedstocks: Mixed Wood (**Table 33**), Corn Stover (**Table 34**), and Poplar (**Table 35**). Where more that one run was used, ranges are indicated for conditions and product properties.

1. Mixed Wood

	Pyrolysis, 1 run	Hydrotreating, 1 run	Hydrocracking, 6 runs	
	NREL:	PNNL:	PNNL:	
	(2006)	Catalyst: Pd/C	UOP HC/UOP HT	
Temp, °C	480	342	359-429	
Pressure, psig	res time =1.6sec	1900	1525-1570	
LHSV	N2 carrier	0.28	0.14-0.36	
	Yields:	Yields:	Yields:	
	Pyrolysis oil: 70wt%	HT oil: 66 vol%	HC oil: >95%	
	Aqueous phase: -	Aqueous phase: 48wt%		
	Char: 12wt%	(10%C)		
	Gas: 15wt%			
	Py oil analysis:	HT oil analysis:	HC oil analysis:	
N, wt %	0.18	0.37	0.03-0.71	
O, wt %	48.0	20.1	3.5-6.3 (0.2-1)	
S, wt %	-	-	19-64 ppm	
Density, g/ml	-	1.06	0.77-0.90	
TAN, mg KOH/g oil	-	85.0	-	
H/C (mol)	1.85	1.49	1.74-1.84	
ICP, wt%				
				PIONA-Oxy
alkanes			8-22	paraffines: 5-10%
cyclic alkanes			64-79	iso-paraffins: 15-25%
hydroaromatics			3.9-27.2	olefins: 0.5-1%
phenols			0.13-0.42	naphthenes: 40-55%
alcohols/diols			0	aromatics: 10-30%
ketones			0	oxygenates: 0.1-0.8%
acids/esters			0 (0.2)	
tetrahydrofurans			0	calc MON=75
guaiacols and syringols			0 (0.6)	calc RON=82

Table 33-Summary of Mixed Wood Bio-Oil Runs

A simulated boiling point analysis was done on the final hydrocracked product. The figure below includes a comparison with typical gasoline and diesel boiling ranges. It shows that the mixed wood product has a boiling range similar to gasoline, although some higher boiling components are present as well.



1. Mixed Wood

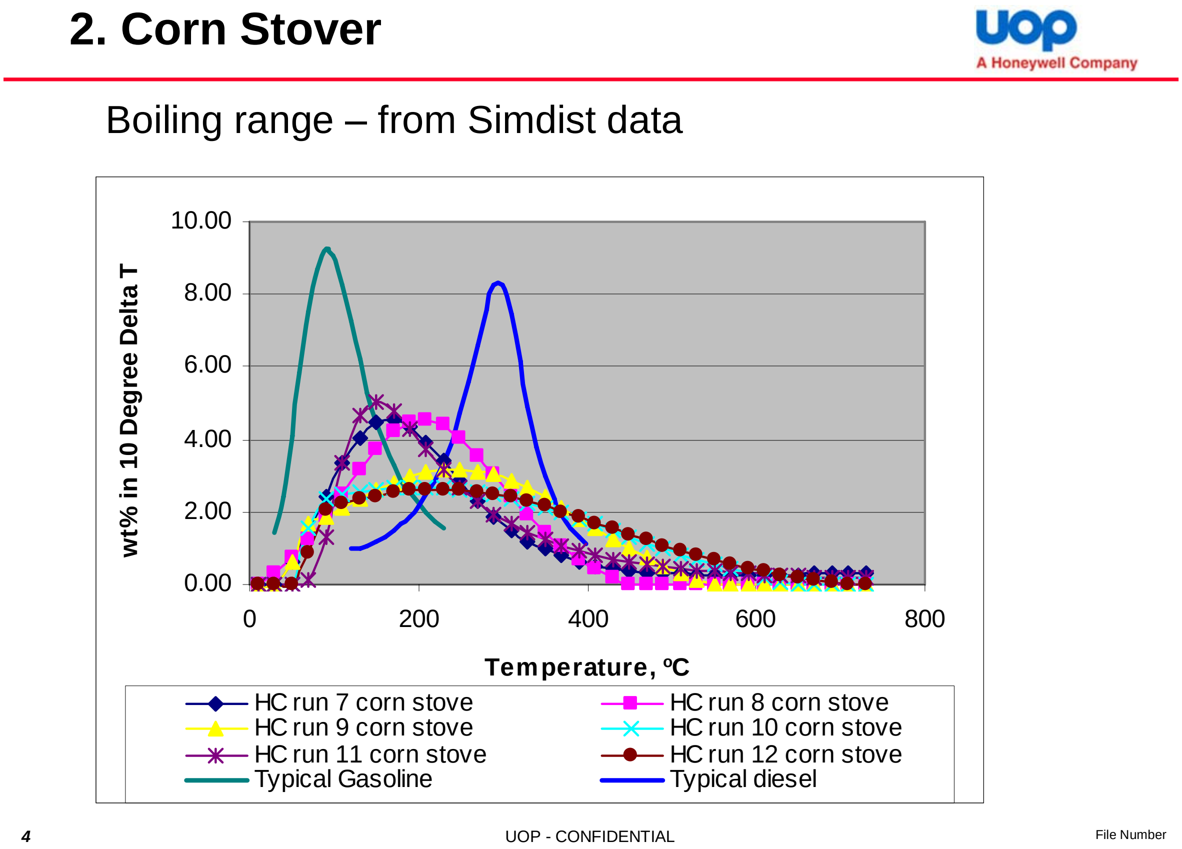
Boiling range – from Simdist data

Figure 21: Simulated Distillation of Mixed Wood Products

2. Corn Stover

	Pyrolysis, 2 runs	Hydrotreating, 3 runs	Hydrocracking, 6 runs	
	NREL:	PNNL:	PNNL:	
	(2006)	Catalyst: Pd/C	UOP Hydroprocessing	
Temp, °C	480	339-343	399-410	
Pressure, psig	res time =1.6sec	1933-1944	1508-1542	
LHSV	N2 carrier	0.26-0.28	0.13-0.25	
	Yields:	Yields:	Yields:	
	Pyrolysis oil: 8/47 wt%	HT oil: 35-55 vol%	HC oil: >95%	
	Aqueous liq: 45/- wt%	Aqueous liq: 60-75 wt%		
	Char: 25 wt%	(9%C, 0.2%N)		
	Gas: 13 wt%			
	Py oil analysis:	HT oil analysis:	HC oil analysis:	
N, wt %	0.8/1.4	1.3-2.0	0.03-0.61	
O, wt %	36/40	9.5-11.4	0.42-0.95 (0-0.6)	
S, wt %	-/0.1	0.03-0.04	8-28 ppm	
Density, g/ml	-	1.02-1.04	0.78-0.87	
TAN, mg KOH/g oil	-	51-57	0.5-1.6	
H/C (mol)	1.55/1.78	1.51-1.61	1.66-1.96	
ICP, wt%				
				PIONA-Oxy
alkanes			8.7-12.4	paraffins: 8-11%
cyclic alkanes			57-67	iso-paraffins: 15-17%
hydroaromatics			18-28	olefins: 0.2-0.3%
phenols			0.14-0.71	naphthenes: 40-55%
alcohols/diols			0	aromatics: 16-35-30%
ketones			0	oxygenates: 0%
acids/esters			0	
tetrahydrofurans			-	Calc MON=75
guaiacols and syringols			0	Calc RON=84

Table 34 - Summary of Corn Stover Bio-Oil Runs



2. Corn Stover

A Honeywell Company

Boiling range – from Simdist data

4 UOP - CONFIDENTIAL File Number

Figure 22: Simulated Distillation of Corn Stover Products

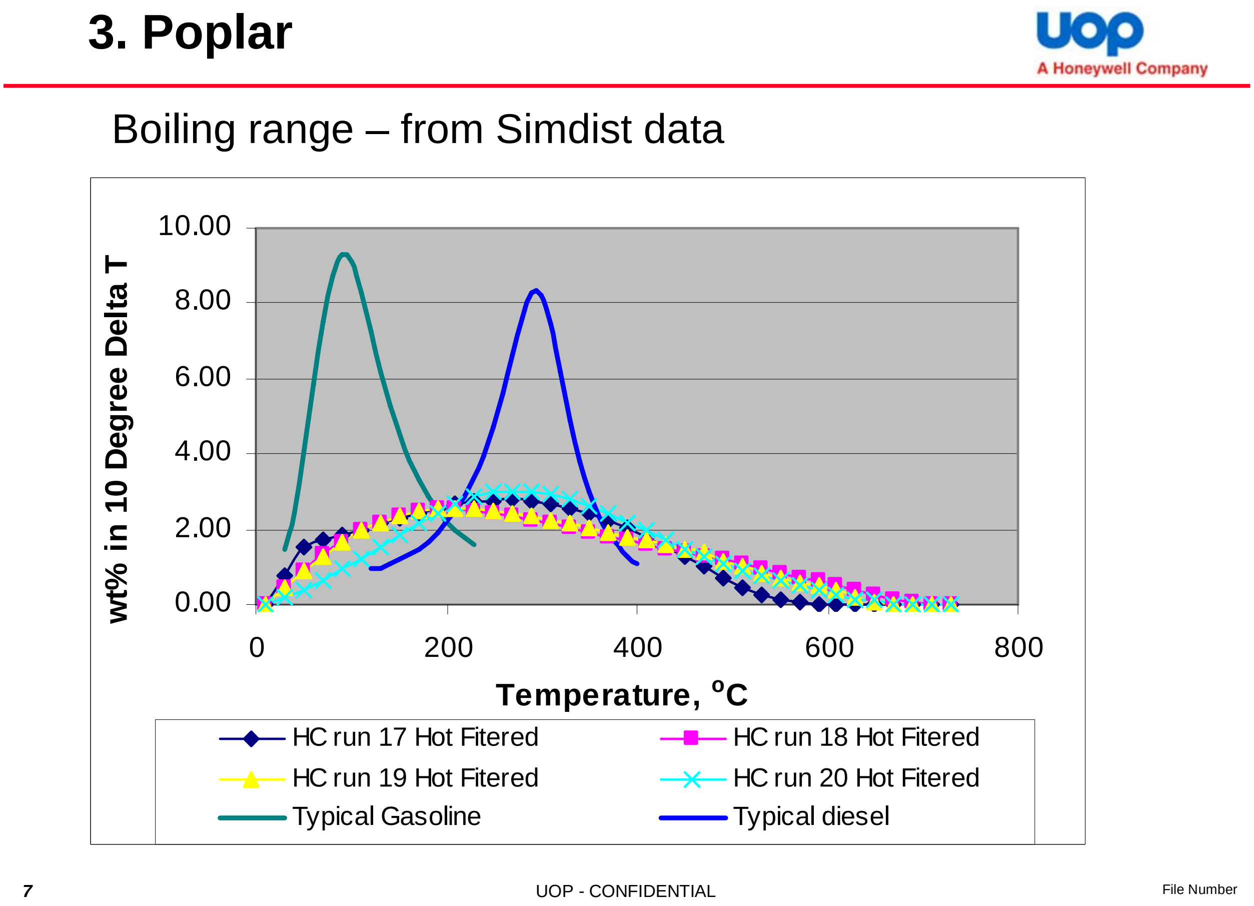
2. Poplar

	Pyrolysis, 1 run	Hydrotreating, 2 runs	Hydrocracking, 4 runs
	NREL: (1996) T=480C? t=1.6 sec N2 carrier	PNNL: Catalyst: Pd/C T=342/237* ~1950 psig LHSV=0.23 / 0.14*	PNNL: UOP Hydroprocessing T=394-408/445* 1486-1505/1975* LHSV=0.12-0.24
	Yields: Pyrolysis oil: NA Char: NA Gas: NA Aqueous phase: NA	Yields: HT oil: 0.69 vol% Aqueous phase: NA	Yields: HC oil: NA
	Py oil analysis:	HT oil analysis:	HC oil analysis:
N, wt %		0.23	0.07-0.29/0.12*
O, wt %		17.2	0.3/4.8*
S, wt %		0.17	1-20 ppm
Density, g/ml		1.05	0.85-0.87/0.92*
TAN, mg KOH/g oil		57.0	1.8-2.0/4.0*
H/C (mol)		1.40	1.65/1.41*

alkanes		-	8-10
cyclic alkanes		-	77-79/46*
hydroaromatics		0.0	11-14/4*
phenols		15.7	0.22/40.3*
alcohols/diols		22.7	0
saturated ketones		14.3	-
acids/esters		25.1	0
tetrahydrofurans		3.3	-
guaiacols and syringols		18.9	0

* = dual bed

Table 35-Summary of Poplar Bio-Oil Runs



3. Poplar

Boiling range – from Simdist data

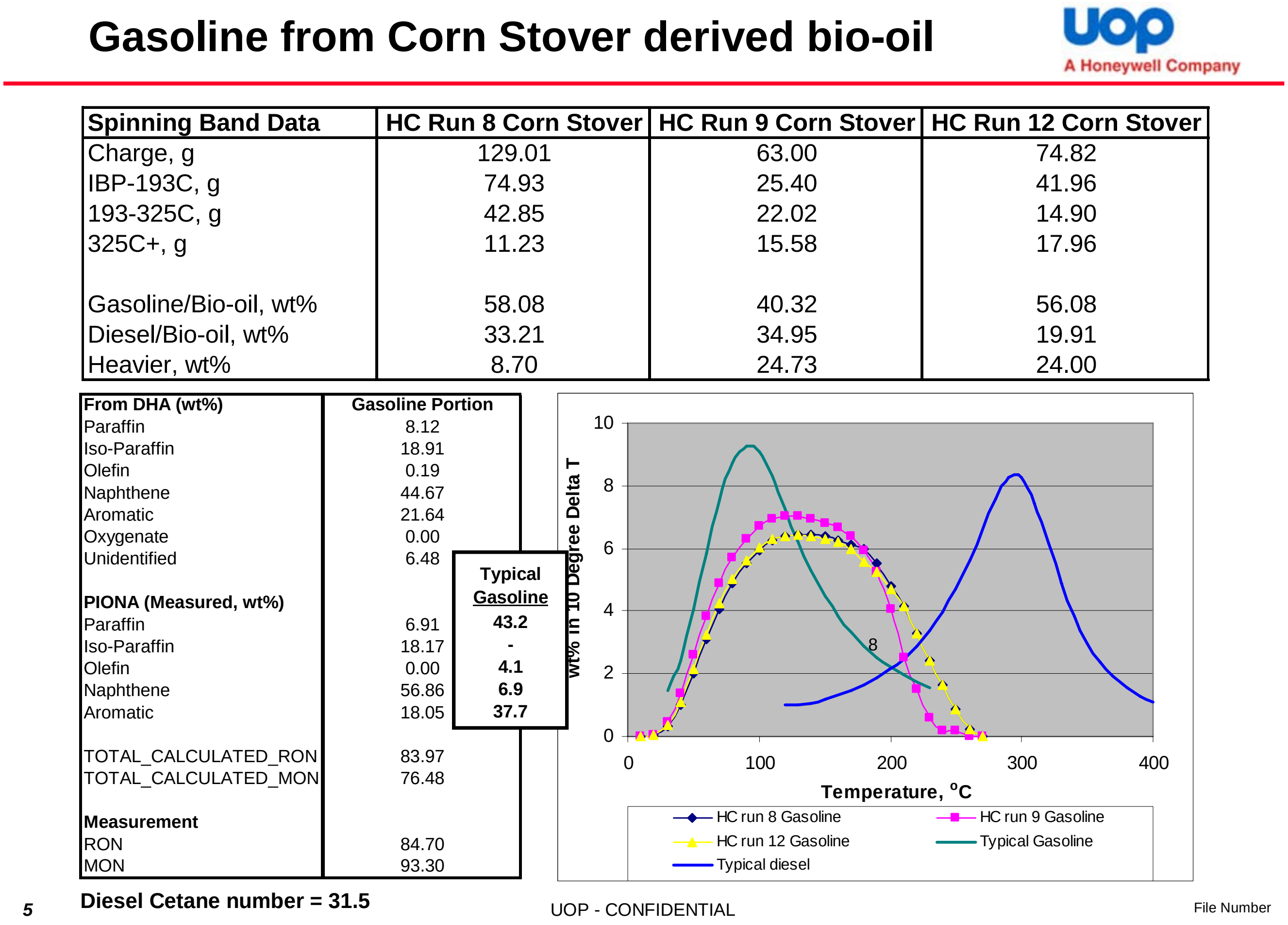
7 UOP - CONFIDENTIAL File Number

Figure 23: Simulated Distillation of Poplar Product

For all 3 feedstocks we see a significant reduction in oxygen level across each processing step. Only phenols are left in the final hydrocracked product. During the hydrocracking step the density goes down and the H/C ratio goes up, indicative of the reduction in size of the hydrocarbon components in this reaction.

As mentioned above for the case of the mixed wood, the final hydrocracked product boils mainly in the gasoline range. The corn stover and poplar products, however, show a wider boiling range distribution and a significant fraction boils in the diesel (and even heavier) range.

Comparison of Fuels from Mixed Wood, Corn Stover and Poplar In the case of the corn stover product, for 3 hydrocracking runs the final product was separated in a gasoline fraction and a diesel fraction by spinning band distillation. The details are shown below in **Figures 24.**. The gasoline fraction has lower total paraffin content, lower aromatics content and much higher naphthene content than typical gasoline. Calculated RON and MON for this case were 84 and 76.5 respectively. The diesel fraction had a cetane number of 31.5.



Gasoline from Corn Stover derived bio-oil

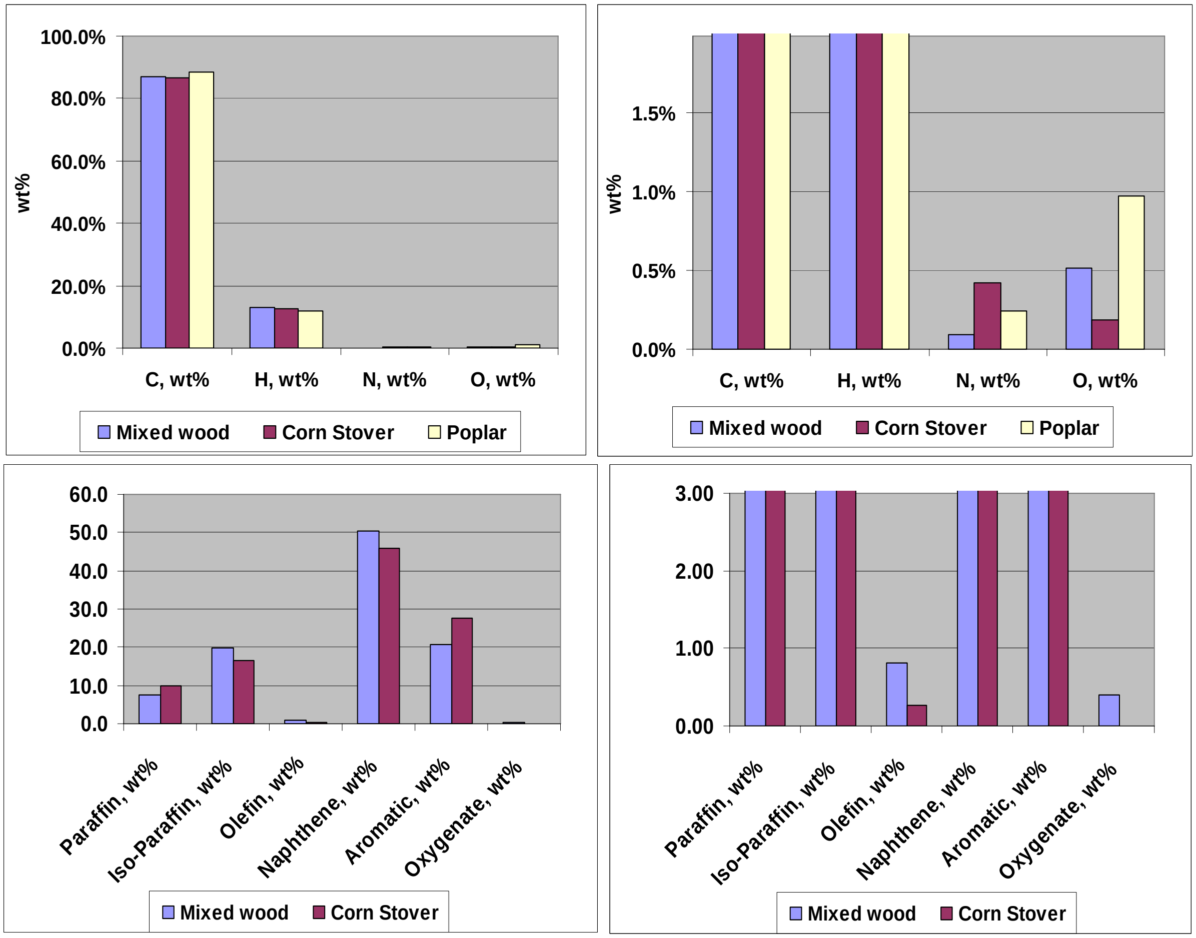
Spinning Band Data	HC Run 8 Corn Stover	HC Run 9 Corn Stover	HC Run 12 Corn Stover
Charge, g	129.01	63.00	74.82
IBP-193C, g	74.93	25.40	41.96
193-325C, g	42.85	22.02	14.90
325C+, g	11.23	15.58	17.96
Gasoline/Bio-oil, wt%	58.08	40.32	56.08
Diesel/Bio-oil, wt%	33.21	34.95	19.91
Heavier, wt%	8.70	24.73	24.00

From DHA (wt%)	Gasoline Portion	Typical Gasoline
Paraffin	8.12	
Iso-Paraffin	18.91	
Olefin	0.19	
Naphthene	44.67	
Aromatic	21.64	
Oxygenate	0.00	
Unidentified	6.48	
PIONA (Measured, wt%)		
Paraffin	6.91	43.2
Iso-Paraffin	18.17	-
Olefin	0.00	4.1
Naphthene	56.86	6.9
Aromatic	18.05	37.7
TOTAL_CALCULATED_RON	83.97	
TOTAL_CALCULATED_MON	76.48	
Measurement		
RON	84.70	
MON	93.30	

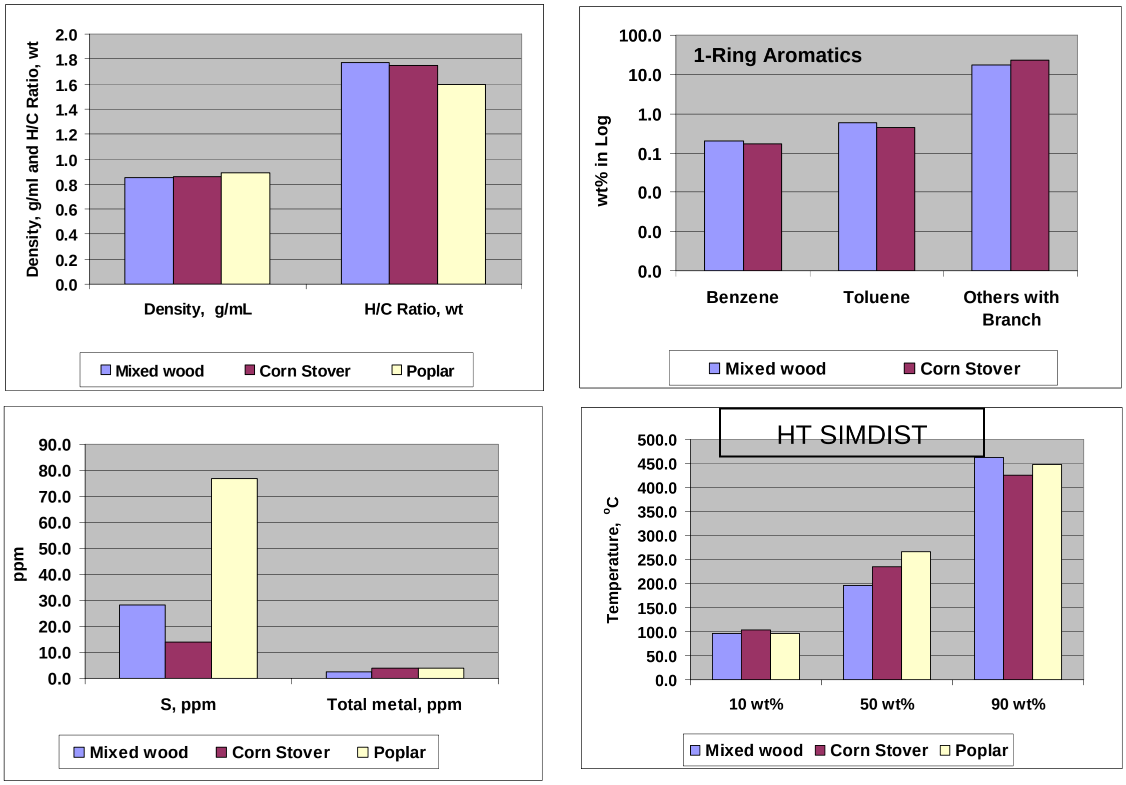
Diesel Cetane number = 31.5

Figure 24: Summary of Corn Stover Runs

In the **Figures 25 a-h** below, the products of the 3 feedstocks are compared in a number of additional properties. Most properties – elemental composition, density, hydrocarbon types, boiling range (simdist) – turn out to be quite similar for the different feed sources.



Figures 25 a-d Chemical Analysis of Product from Three Types of Biomass



Figures 25 e-h Physical & Chemical Analysis of Products from Three Types of Biomass

Inspection of a number of product properties suggests that density and H/C ratio are good indicators of hydrocracking severity/efficiency. The density was shown to increase consistently with time on stream**(Figure 26 a,b).** This suggests that the catalysts are deactivating during the hydrocracking phase. It also complicates the data analysis.

Density, H/C
measure of
hydrocracking
efficiency?

Density increase
during HC run
→ deactivation

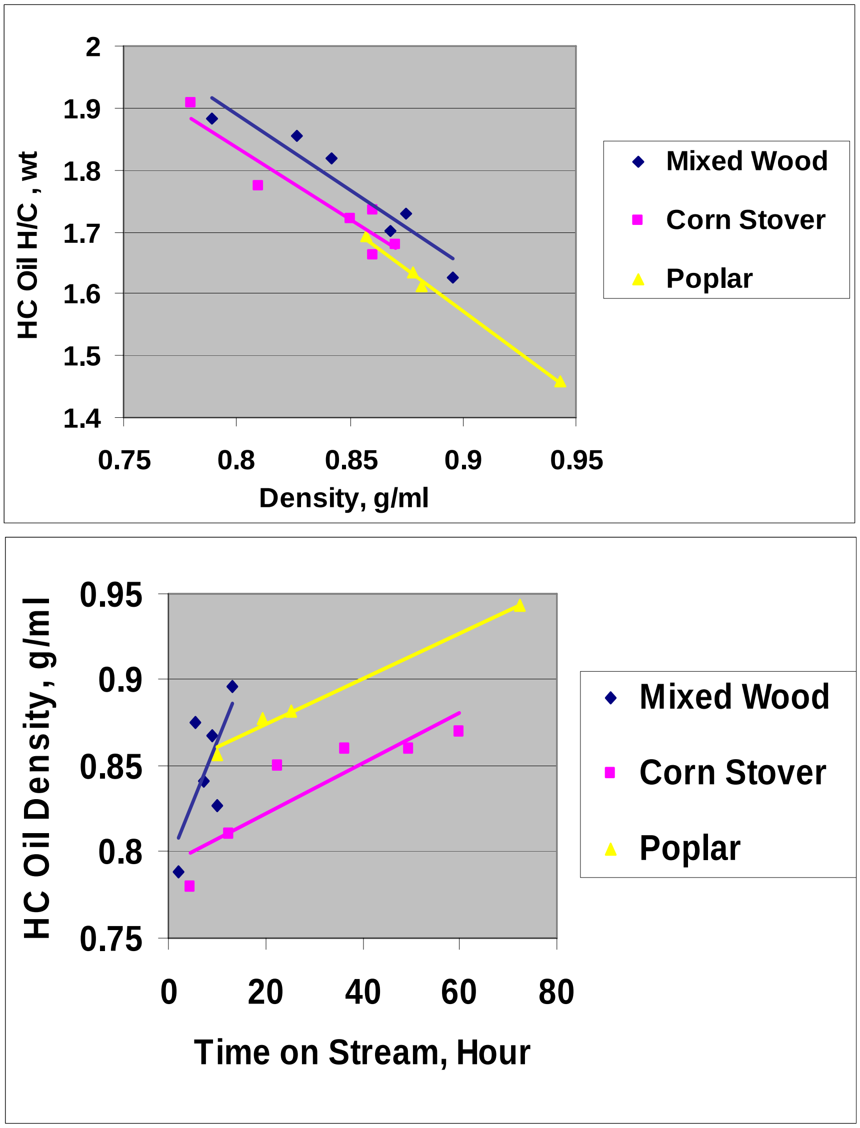


Figure 26 a. H/C ratio as a function of density b. Density as a function of time on stream.

Life Cycle Assessment

A life cycle assessment (LCA) totaling environmental flows was done on a corn stover pyrolysis process, from the production of the feedstock to end use in a vehicle. This LCA model is by no means an exact accounting of environmental and energy flows in a corn stover pyrolysis process. When using this LCA model, it is important to consider the assumptions, detailed in this report, used to arrive at these numbers. Life cycle inventory data for corn stover production and stover transportation come from a previous LCA performed on a corn stover E85 ethanol process (Sheehan, et al. 2000). The data for pyrolysis and refining processes in the LCA model are based on data from runs by UOP and analysis by UOP, Pacific Northwest National Laboratory (PNNL), or the National Renewable Energy Laboratory (NREL). The pyrolysis process flow is derived from NREL milestone report FY04-545 (Putsche 2004). Emissions from heaters and combustors are estimated from the Environmental Protection Agency's *AP-42 Air Pollutant Emissions Factors* (EPA 2007). Emissions from the use of fuel in vehicles are calculated from EPA emissions data from test cars (EPA 2000). Resource inputs and emissions outputs for some steps in the LCA are taken from standard modules in the TEAM LCA software package database (ECOBILAN 2003).

The bulk of carbon dioxide emissions from fossil fuel sources occurs during the production of the corn stover. When compared to a corn stover process producing E85 ethanol, the LCA model shows fossil fuel carbon dioxide emissions, electricity input, and raw corn stover input favor the pyrolysis process on a per vehicle mile traveled basis. When compared to an unleaded gasoline life cycle, the pyrolysis LCA is favorable from oil use and fossil fuel carbon dioxide emissions perspectives.

Scope

The objective of this LCA model is to track emissions through the life cycle of corn stover from corn production to end use. The processes included are stover production, stover transportation, stover pyrolysis, transportation to refinery, refining, fuel distribution, and fuel use **(Figure 27)** . Material flows from processes are tracked from “cradle to grave”—from the natural resource acquisition to eventual emission or disposal. While emissions from the processes are included, emissions from production of capital goods are not. For example, emissions from production and use of diesel fuel in tractors are included, but the emissions from the manufacture of the tractor are not.

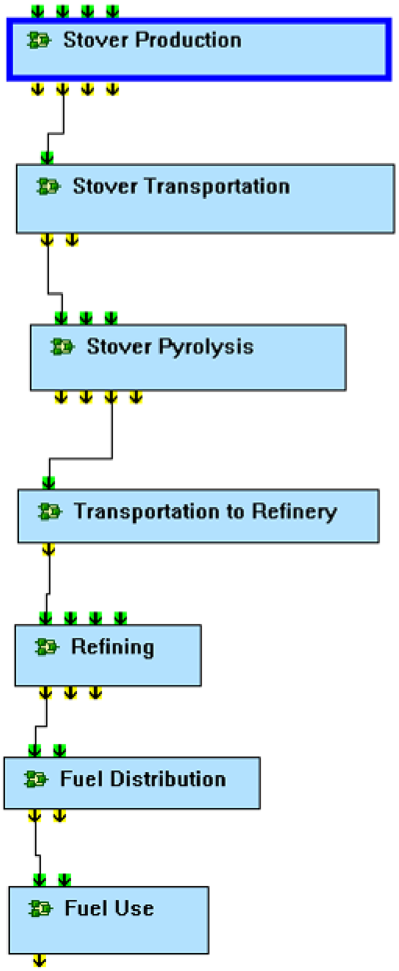


Figure 27. Processes in Corn Stover Pyrolysis Production of Gasoline and Diesel

Methods

The software for this LCA is ECOBILAN's TEAM 4.0 (ECOBILAN 2003). TEAM includes a stock database, called DEAM, of emissions from various processes. The production of electricity and manufacture of hydrogen gas are two of the DEAM modules used in this model.

Material and energy data come from or are derived from several sources. Pyrolysis and refining material balance data are from experiments run by UOP and analyzed by UOP, PNNL, or NREL (CRADA 2007). The pyrolysis process design is based on an NREL Aspen Plus^{TM} model for wood pyrolysis (Putsche 2004). Several modules are taken from an NREL LCA on corn stover production of E85 ethanol (Sheehan, et al. 2000). Emissions data for heaters and combustors are based on the Environmental Protection Agency's AP-42 Air Pollutant Emissions Factors (EPA 2007).

Processes Modeled

Stover Production

The stover production LCA is unchanged from the previous NREL model for corn stover production of E85 ethanol (Sheehan, et al. 2000). The output of this process is raw corn stover, and the inputs include fertilizer, diesel oil, tractor lube oil, and crop information from Iowa counties.

Stover Transportation

The stover transportation LCA is also based on the 2000 NREL model. In that model, distances from each Iowa County to appropriately located ethanol plants are tabulated. This model assumes that a JCB tractor with wagon will transport the stover to the ethanol plant, which likely overestimates the fuel use and emissions. For the pyrolysis model, the stover transportation LCA was simplified to assume that stover travels an average of 33 miles, based on a 50 mile collection radius (Aden, et al. 2002). With this modification, sensitivity to varying distance from farms to pyrolysis plants could be analyzed.

Stover Pyrolysis

The stover pyrolysis process is based on the 2004 Aspen Plus model for wood pyrolysis (Putsche 2004). Figure 4 shows the steps in stover pyrolysis, with block names corresponding to the Aspen Plus model names. Because life cycle assessment is only concerned with mass and energy flowing into or out of the process, the LCA model is not concerned with recycle streams and does not include the level of unit operation detail found in an Aspen Plus model process design.

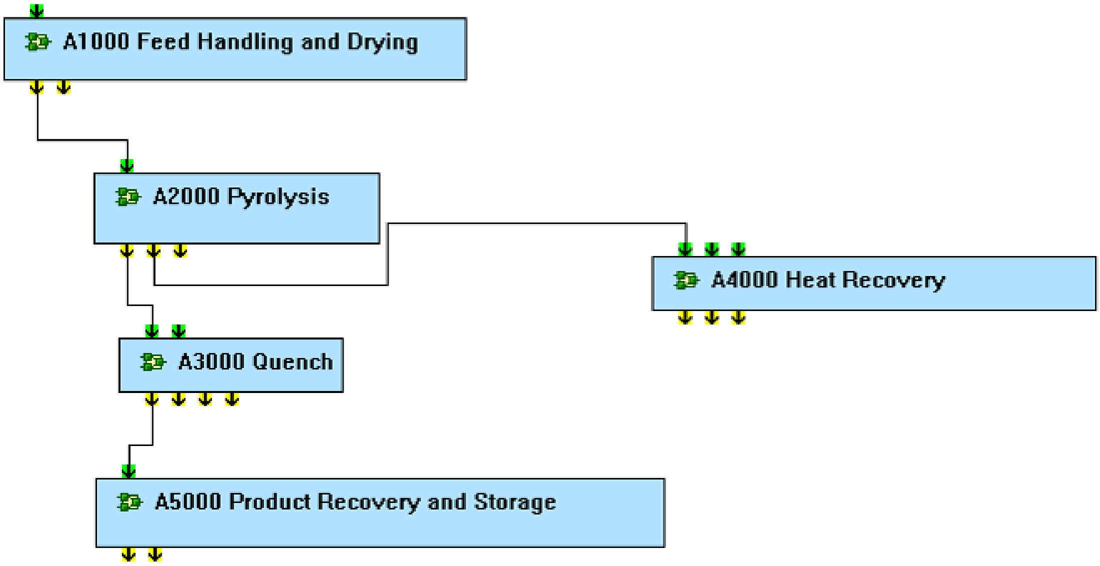


Figure 28. Stover Pyrolysis Process

Feed Handling and Drying

“A1000 Feed Handling and Drying” includes a dryer to remove moisture from the corn stover. Because the water content of the corn stover is included as part of the data from UOP’s pyrolysis step, the water removed is not accounted for in this drying step, but instead, in the “A2000 Pyrolysis” step. The purpose of this drying step in the LCA is to tally the emissions from operating a dryer. The emissions from the dryer are taken from AP-42 emissions for a particleboard, softwood, direct wood-fired, rotary dryer with a multiclone particulate matter emission control device, based on mass of the softwood. In this case, the mass of the raw corn stover was used. The energy necessary for drying is not accounted for in this step, but included in a net electricity term in the “A3000 Quench” step. The largest emission from this step is particulates.

Pyrolysis

The actual pyrolysis step of converting corn stover into pyrolysis oil is represented by “A2000 Pyrolysis.” The pyrolysis unit converts the raw corn stover to pyrolysis oil, char, and gas. Conversion data for the pyrolysis unit are taken from UOP pyrolysis run 2, which provided a better overall mass balance than run 3. In the Aspen Plus model, the char combustor in “A4000 Heat Recovery” combusts the carbon monoxide produced in the pyrolysis unit. As a result, CO is not listed as an emission in this step. In addition, although the char combustor in the Aspen Plus model has ash as an input and output, in the LCA, ash is separated out at the pyrolysis unit as “Waste: Slags and Ash.” The energy needed for pyrolysis is also not considered in this step but included in a net electricity term in the “A3000 Quench” step. The largest emission in this step is CO_2 from biomass sources.

Heat Recovery

Heat recovery includes inputs and outputs from the char and gas combustor and a rotary filter. Incoming char and carbon monoxide is mixed with air to produce CO_2 and water. Carbon dioxide produced from combustion is calculated assuming that all the carbon in the char (55%) is combusted. The water produced from combustion is calculated by scaling the water output from the Aspen Plus wood pyrolysis model by the ratio of CO_2 output in the LCA corn stover pyrolysis to CO_2 in the Aspen Plus model. In addition to the products of combustion, there are emissions from the combustion process. These emissions are once again calculated from AP-42 emission factors for wood residue combustion in boilers with a fabric filter particulate matter control device. The energy recovered from combustion is included in the net electricity term in the “A3000 Quench” step.

The rotary filter requires a quench water stream. This amount of circulated water is calculated by scaling the water required from the Aspen Plus wood pyrolysis model by the ratio of the corn stover mass to the wood mass. The water needed as an input is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

Quench

The quench includes the net electricity generated from the char combustor minus the energy needed for pyrolysis and other unit operations. The inventory for this step includes the input water needed to replenish the 3% blowdown in the steam recycle loop (based on the Aspen Plus model) and the output water in the blowdown stream.

Product Recovery and Storage

The product recovery and storage step includes the cooling water to cool the product to 20°C. This water is taken and outputted without wastewater treatment. The water needed as an input is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

Transportation to Refinery

For the pyrolysis oil to be transported to the refinery, the oil is assumed to be transported by rail, 300 miles away to refineries in the Chicago area. The emissions and resources in the process are calculated using two DEAM modules for diesel oil production and rail transport (**Figure 29**).

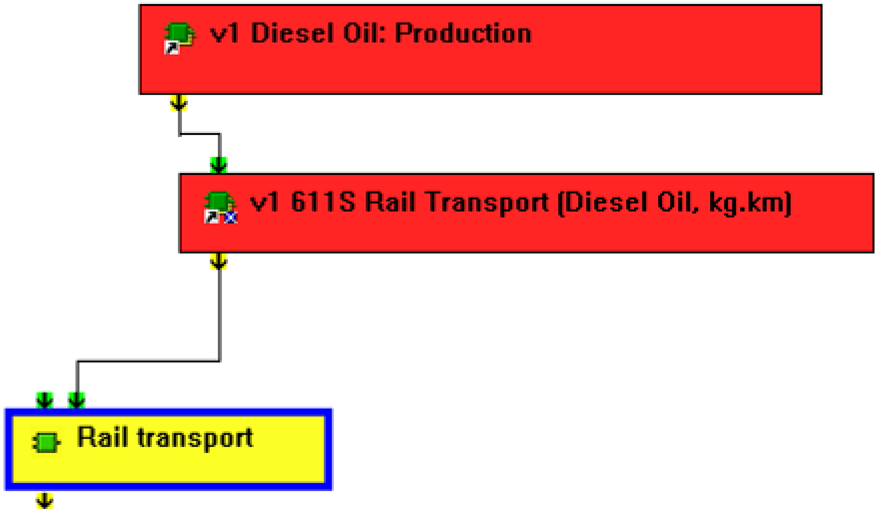


Figure 29. Transportation to Refinery Modules

Refining

The refining step includes upgrading of the pyrolysis oil and then separation of the refinery products (**Figure 30**).

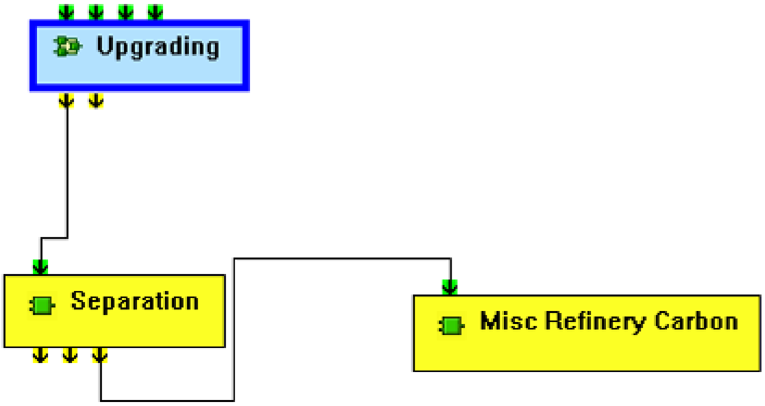


Figure 30. Refining Modules

Upgrading the pyrolysis oil into gasoline and diesel requires hydrotreating and hydrocracking. The modules needed for refining are shown in **Figure 31**.

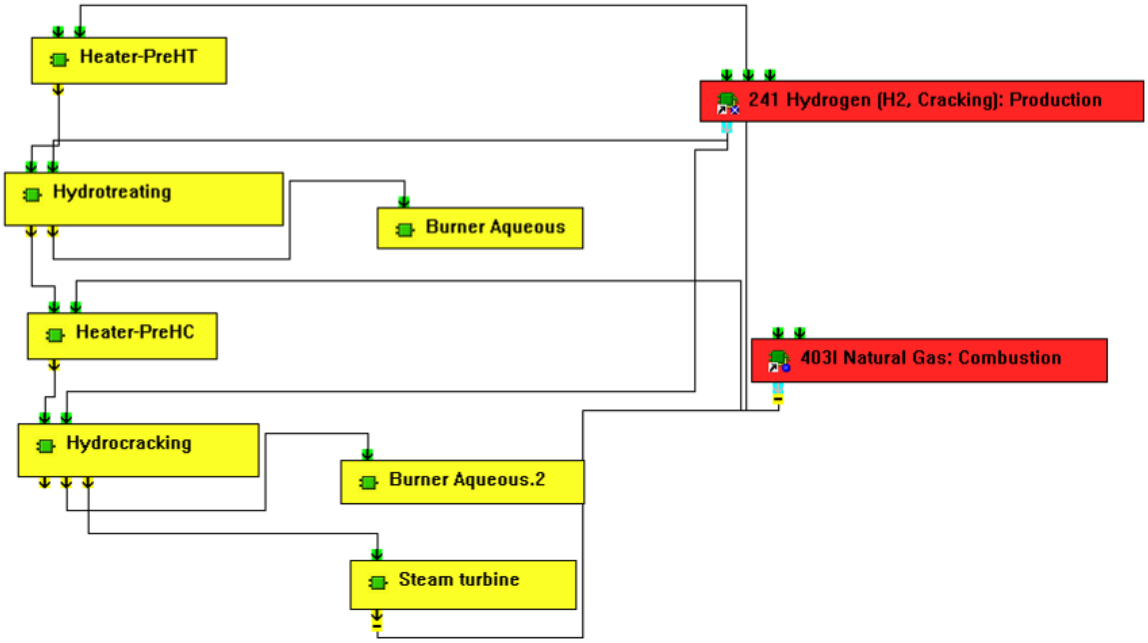


Figure 31. Upgrading Modules

Hydrotreating

For the hydrotreating process design, two generic process configurations published in Hydrocarbon Processing's Refining Processes 2004 Handbook are used. One is by CB&I Howe-Baker Process and Technology (**Figure 32**), and the other is by UOP LLC(**Figure 33**). Fuel energy, electricity, and cooling water data are averaged from these two processes for input into the LCA model. The water used is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

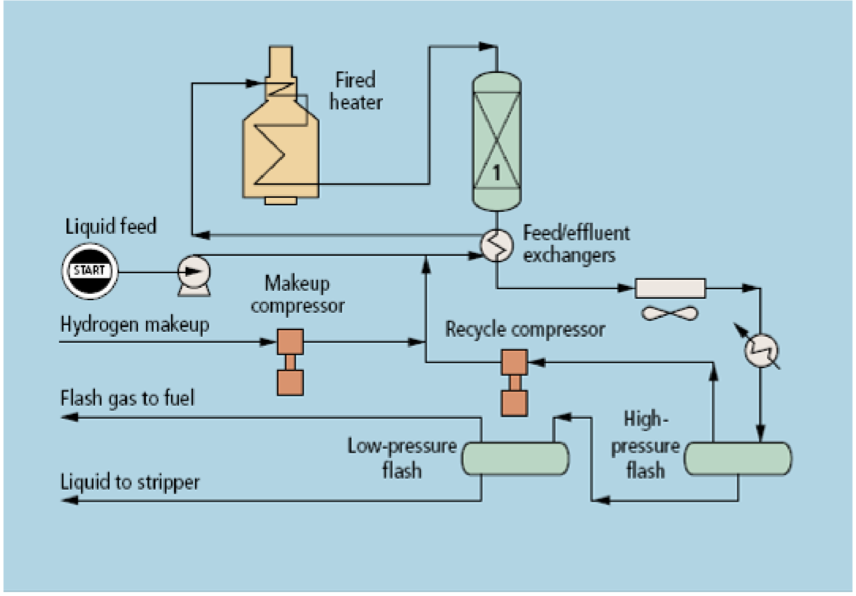


Figure 32: CB&I Howe-Baker Process and Technology Hydrotreating Process Design (Hydrocarbon Processing 2004)

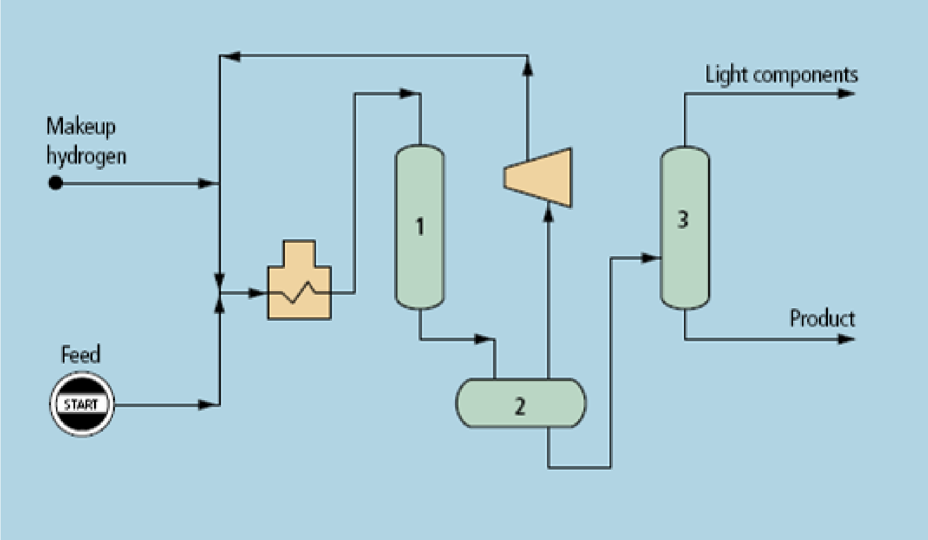


Figure 33. UOP LLC hydrotreating Process Design (Hydrocarbon Processing 2004)

The fuel energy needed for the heater in the hydrotreating process is determined from the fuel energy data from Hydrocarbon Processing's Refining Processes 2004 Handbook. This energy is supplied by natural gas combustion, which has its life cycle inventory represented by a DEAM module.

The products of hydrotreating are based on UOP hydrotreating run 32 (CRADA 2007). This run had an oil yield of 0.79 l/l and was selected in order to help the overall LCA carbon balance. The pyrolysis oil density in the calculations is 1.16 g/ml. The required input hydrogen is based on the hydrogen consumption data rather than the overall hydrogen feed, since it was assumed the hydrogen would be recycled in the final process. The difference in the sulfur content in the pyrolysis oil and the hydrotreated oil is assumed to leave as hydrogen sulfide. The aqueous material goes to an aqueous burner. Because energy data are not available from the burning of the aqueous material, the burner only generates CO_2 based on the carbon percentage of the aqueous material and polluted water.

Hydrocracking

The hydrocracking inputs and outputs are based on four process designs from Hydrocarbon Processing's Refining Processes 2004 Handbook. These are by Axens, ExxonMobil, Chevron Lummus Global(CLG) LLC, and UOP LLC. Fuel energy, steam, water, and electricity data are averaged among the processes for which data are available. The most used process designs are the ones by ExxonMobil and CLG. The water used is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

The energy for the heater ("Heater-PreHC")in the hydrocracking process is determined from the fuel energy data from Hydrocarbon Processing's Refining Processes 2004 Handbook. Natural gas combustion supplies the energy for this heater.

The hydrogen input is based on hydrogen consumption data, and the emissions from the production of hydrogen are tracked using a DEAM module. The output of the hydrocracking process is based on hydrocracking run 10 (CRADA 2007). This run, with an oil yield of 0.98 l/l was selected to help the overall LCA carbon balance.

The steam output from the hydrocracking process is used to generate electricity. The electricity is calculated from scaling the electricity from a steam turbine in the Aspen Plus wood pyrolysis model by the ratio of the mass of steam in each process. This electricity output is used to offset some of the natural gas combustion needed by the hydrocracking heater.

As with hydrotreating, hydrocracking produces an aqueous byproduct, which may be burnt. In the LCA model, this aqueous portion does not produce energy or electricity, only carbon dioxide and polluted water waste.

Separation

The resulting hydrocracked oil is separated into gasoline, diesel, and miscellaneous refinery product cuts. From the distillation curve for HT-101 (0935-1135), the gasoline cut is taken as the fraction (0.684) with a boiling point below 330°C, the diesel cut is the fraction (0.296) with a boiling point between 330°C and 600°C, and miscellaneous refinery products are the remaining fraction (0.020) (CRADA 2007).

From analysis of the hydrocracked oil, the carbon weight percent is 87%. The "Misc Refinery Carbon" module accounts for the carbon unaccounted for after considering the carbon emissions from the end use of diesel and gasoline. This carbon is emitted as carbon dioxide. The mass of carbon needed to make up the difference is currently greater than the mass of the miscellaneous refinery products. This suggests that the emissions from the gasoline and diesel cuts should have more CO_2 output.

Fuel Distribution

The gasoline and diesel oil is distributed from refineries to bulk storage terminals to retail outlets(**Figure 34**). The LCA modeling of this stage is taken from the previous E85 ethanol LCA TEAM model, with the assumption that diesel oil is transported the same way as gasoline . The model assumes that only rail and pipeline are used to transport the gas and diesel from refineries to bulk storage terminals and only trucks are used to transport the fuel to retail outlets. Barge and tanker are not used in this LCA model.

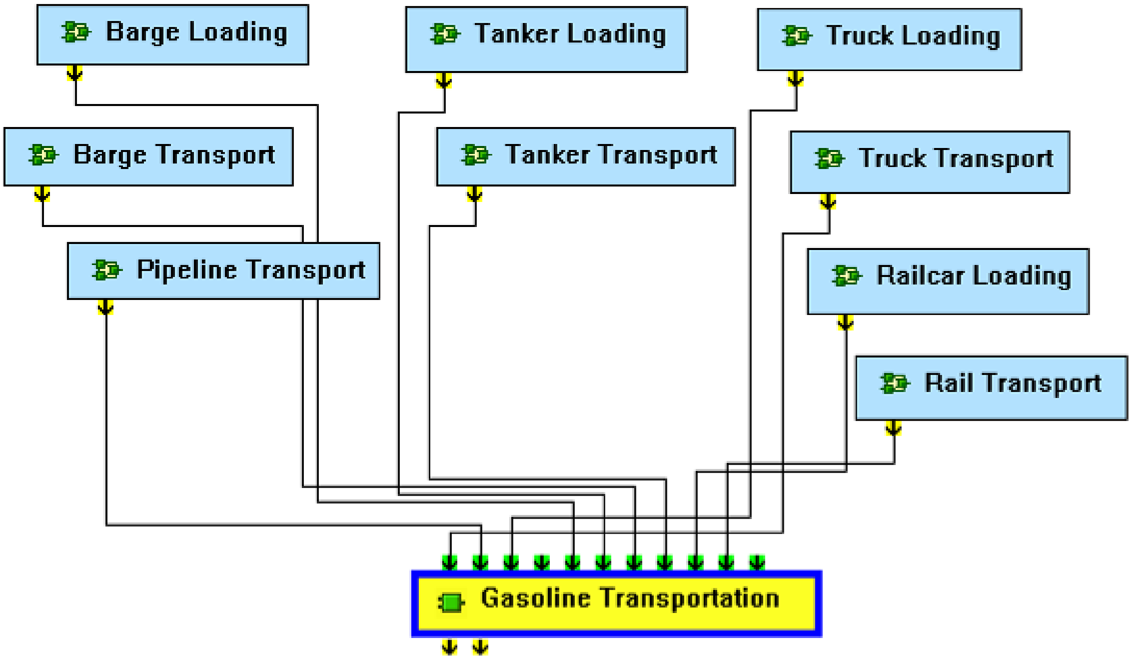


Figure 34. Fuel Distribution (not all modes of transportation are used)

Fuel Use

Emissions and fuel economy for gasoline use are based on the corn stover E85 ethanol LCA model. In that model, the vehicle basis is a 2000 Ford Taurus flexible fuel vehicle. Emissions from diesel are based mainly on tailpipe emission data for a 2000 Volkswagen Jetta diesel vehicle (EPA 2000). For sulfur dioxide and non-methane hydrocarbon emissions from the diesel vehicle, data were taken from a DEAM module for diesel fuel use in a truck, which overestimates these emissions. Diesel fuel economy is taken as 33% better than gasoline (U.S. DOE 2007).

Results

Inputs

The total fossil fuel and water used in this pyrolysis process is shown in Table 36. The breakdown of the fossil fuel inputs is shown in **Figure 35**. The largest fossil fuel use comes from the production of the stover. The second largest impact is in the refining (hydrotreating and hydrocracking), from both the steam reformation of methane and the natural gas needed for heaters.

	g/mile
(r) Coal (in ground)	4.6
(r) Natural Gas (in ground)	16.1
(r) Oil (in ground)	9.7
Water Used (total)	148.9

Table 36. Total Fossil Fuel and Water Input

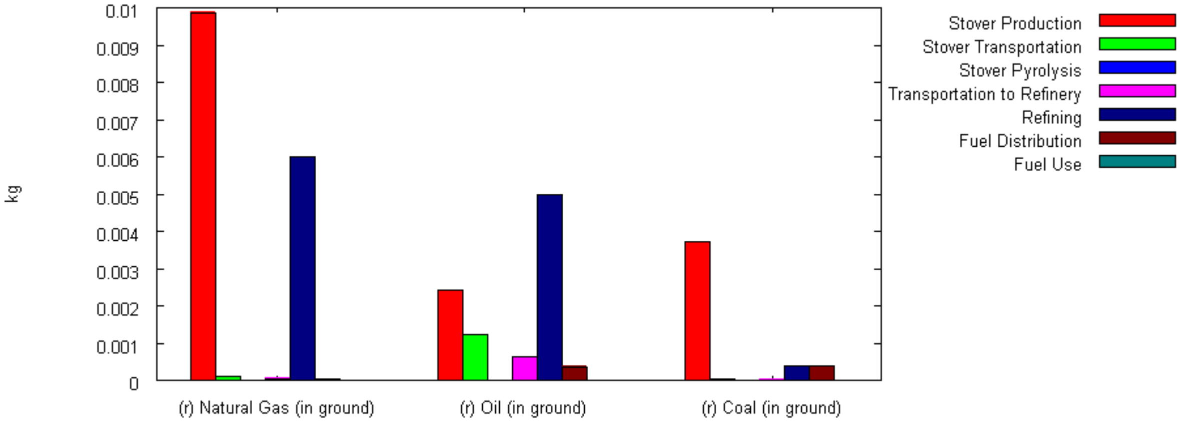


Figure 35. Fossil Fuel Inputs

Water use is dominated by stover production (**Figure 36**). Cooling water constitutes most of the water needed in the pyrolysis and refining steps. Stover production consumes the most electricity, followed by refining (**Figure 37)**. The pyrolysis step, through the char combustor, produces electricity.

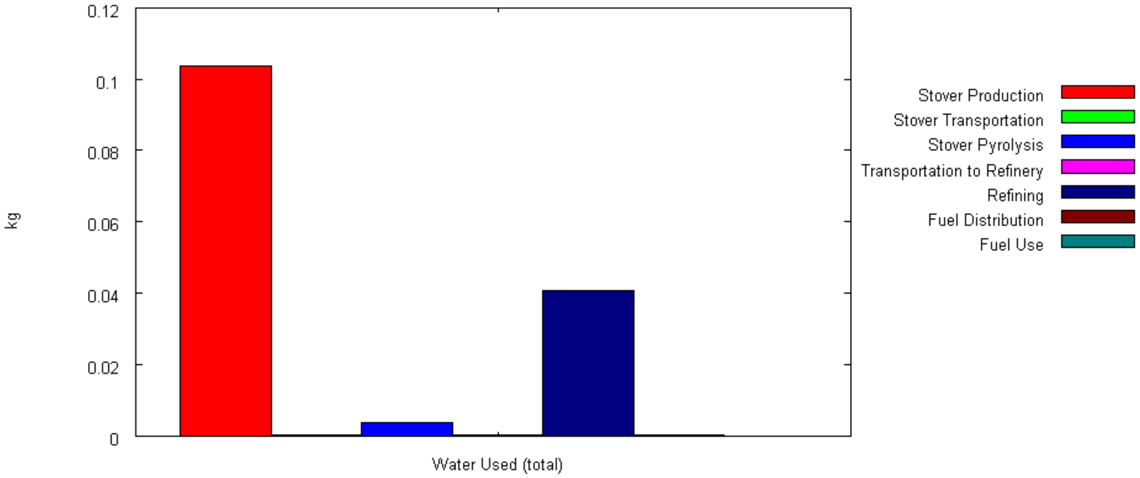


Figure 36. Water Use

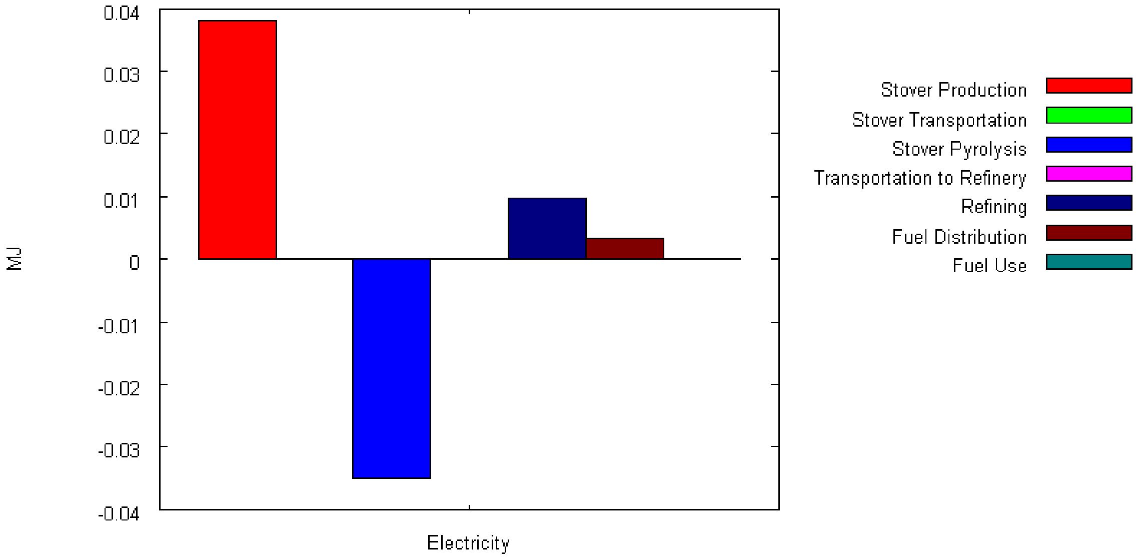


Figure 37. Electricity Use

Outputs

As a greenhouse gas, carbon dioxide emissions are of particular interest in this LCA. Carbon dioxide emissions should be split into emissions from fossil fuel sources and emissions from biomass sources. Because corn takes in carbon dioxide from the atmosphere in the corn plant's lifetime, the release of this biomass carbon dioxide back into the atmosphere is not as deleterious as releasing carbon dioxide sequestered in fossil sources for millions of years.

The total emissions of three main greenhouse gases—carbon dioxide, methane, and nitrous oxide—are shown in Table 11. One column shows the total mass in grams of the emission. The other column is adjusted by the 100-year global warming potential of each gas to report a CO_2 equivalent mass (methane has a GWP of 23, and nitrous oxide has a GWP of 296) (IPCC 2001).

	g/mile	g/mile, CO_2 equivalent
(a) Carbon Dioxide (CO_2, fossil)	47	47
(a) Methane (CH_4)	0.93	21
(a) Nitrous Oxide (N_2O)	0.26	77

Table 37. Total Emissions from Main Greenhouse Gases

As shown in **Figure 38**, the biomass carbon dioxide is negative during the stover production step, denoting an intake of carbon dioxide. This biomass carbon dioxide is released over the pyrolysis, refining, and fuel use steps. Some of the original biomass carbon dioxide intake is released as other hydrocarbon sources, such as carbon monoxide or methane. It is more appropriate to look at the biomass carbon, rather than just carbon dioxide. However, because carbon dioxide still constitutes the bulk of the biomass carbon emissions, the results do not change much when considering all carbon sources (**Figure 38**). In this LCA, the carbon balance is 93% satisfied.

Although the production of corn stover takes in carbon dioxide from the atmosphere, the corn stover also requires a large amount of fossil carbon to fertilize, grow, and harvest (**Figure 39**). The refining step also results in fossil carbon dioxide emissions. Since the electricity needed for the hydrotreating and hydrocracking heaters are calculated based off of traditional petrochemical processes, the actual natural gas combustion used for refining of corn stover pyrolysis oil may be significantly different. As calculated in this report, this impact of the refining heaters on carbon dioxide emissions is minimal. The hydrotreating heater's electricity demand results in 0.3 g of CO_2 emissions, constituting 0.5% of the total carbon dioxide emissions. The hydrocracking process net natural gas combustion demand (heater demand minus electricity from steam output) results in 0.6 g of CO_2 emissions, constituting 1% of the total carbon dioxide emissions. The transportation steps have a lesser fossil carbon dioxide output, with the stover transportation step the largest emitter because the mode of transportation (tractor) is the least efficient.

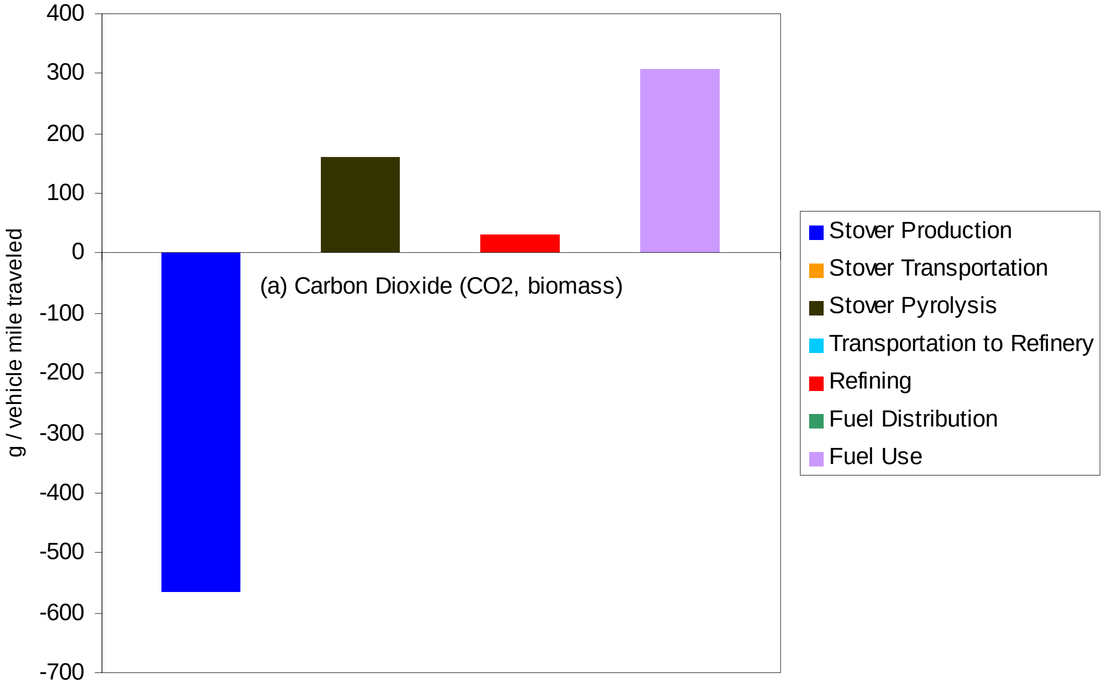


Figure 38. Carbon dioxide emissions from biomass sources

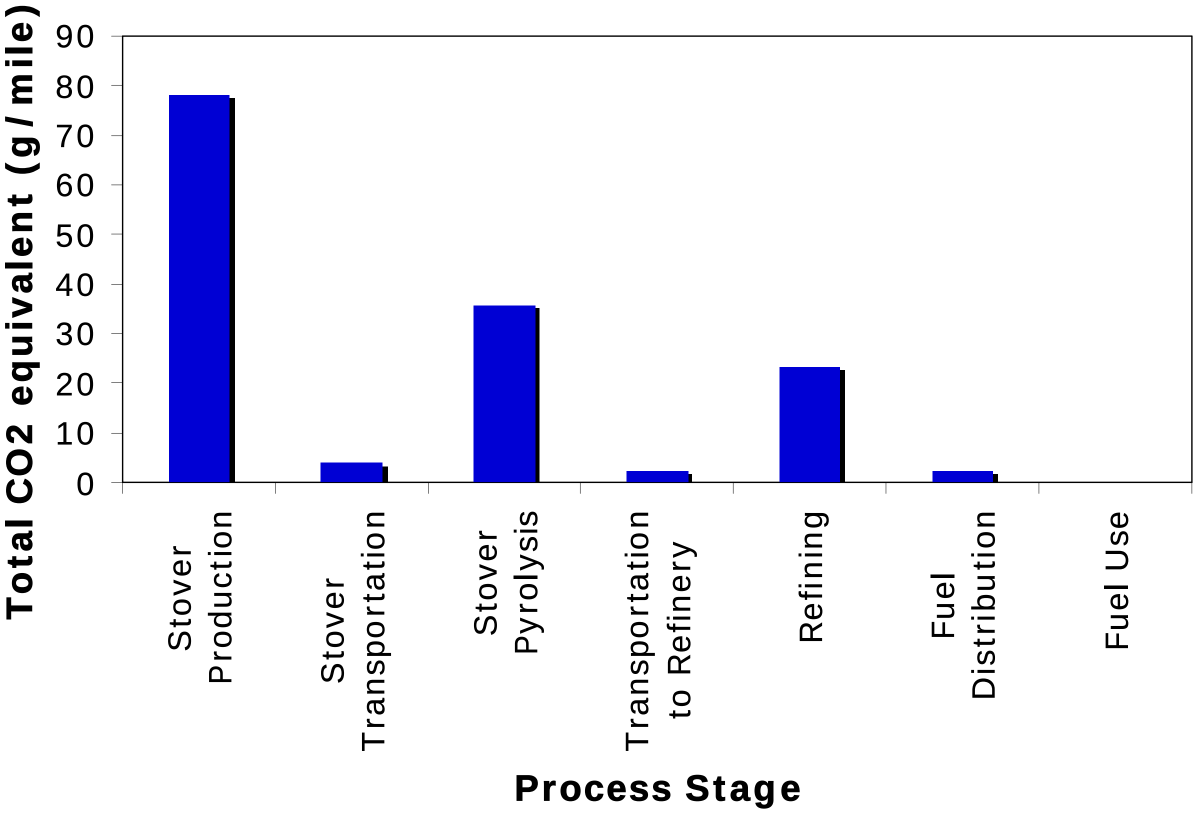


Figure 39. Carbon dioxide emissions from fossil fuel sources

Some of the carbon dioxide emitted to the atmosphere comes from sequestered carbon in the soil. This carbon dioxide is released only in the stover production stage (**Figure 10**). The total carbon dioxide emissions from all sources is shown in **Figure 41**.

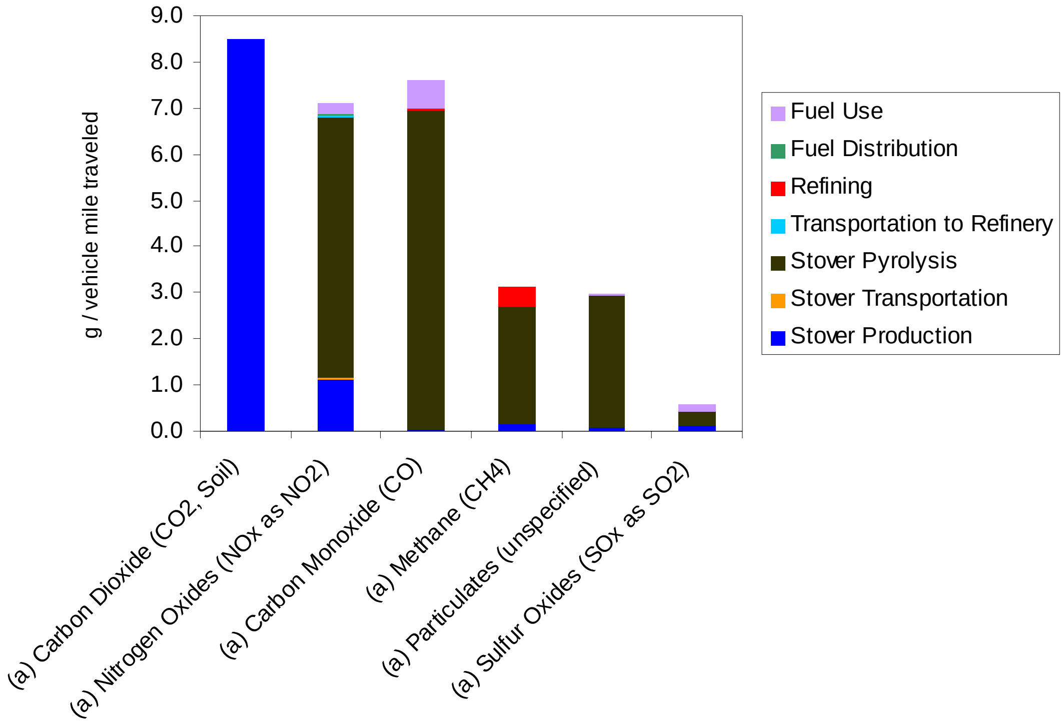


Figure 10. Carbon dioxide from soil and other gaseous emissions

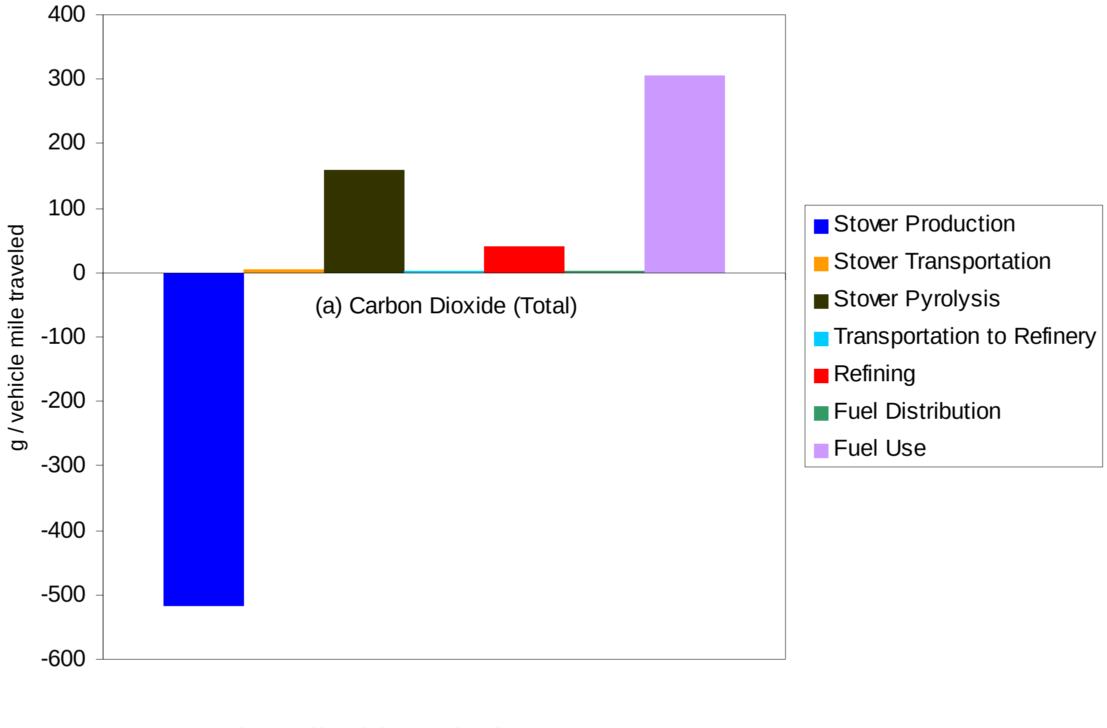


Figure 41. Total carbon dioxide emissions

As seen in **Figure 10**, the nitrogen oxide emissions are high, with most of the emissions coming from the pyrolysis step, specifically the char combustor. Nitrogen oxides are air pollutants, but have not been characterized with a global warming potential by the IPCC. These emissions can be reduced with different assumptions and NO_x emission control. NO_x emissions at the combustor can be reduced by 80% using selective catalytic reduction (Cooper 2004). This would require addition of ammonia gas to reduce NO_x to nitrogen and water (**Figure 42**). Additional sources of NO_x emission reduction include taking the best NO_x emission data from the AP-42 source for external combustion, taking the best Volkswagen Jetta NO_x tailpipe emission data, and taking the actual Volkswagen Jetta fuel economy improvement over the Ford Taurus FFV. The results of all these scenarios are shown in 38. If all the factors were taken as best case, the NO_x level would be 74% less than the base case, with 54% of the NO_x emissions coming from stover production. The NO_x emissions in the stover production process come from the assumption that 5% of the nitrogen in the fertilizer will be volatized as NO_x (Sheehan, et al. 2000). The disadvantage of the catalytic reduction is that the production of ammonia results in increased CO_2 emissions. Adding the catalytic reduction alone will increase the CO_2 emissions by 48 g or 82%. If all factors are added together, the CO_2 emissions increase is 12 g or 20%.

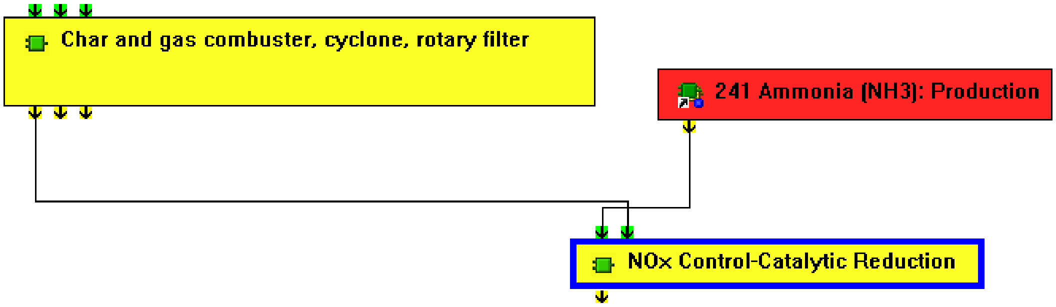


Figure 42. Catalytic reduction of NO_x emissions

Factor	Original value	Low NO_x value	% change in parameter	NO_x level [g]	% change in NO_x
Original	-	-	-	7.101	-
Best combustor emissions	0.49	0.187	-61.8%	3.675	-48.2%
Catalytic reduction (fraction NO_x remaining)	1	0.2	-80.0%	2.813	-60.4%

Best VW Jetta emission	0.625	0.53	-15.2%	7.066	-0.5%
VW Jetta diesel efficiency over gasoline	1.33	1.66	24.8%	6.563	-7.6%
Combine all				1.882	-73.5%

Table 38. NO$_x$ reduction scenarios

The waste streams are shown in **Figure 43**. The waste total from the stover pyrolysis is due to the ash. The high metals emissions are mainly the result of emissions from diesel oil production (**Figure 44**).

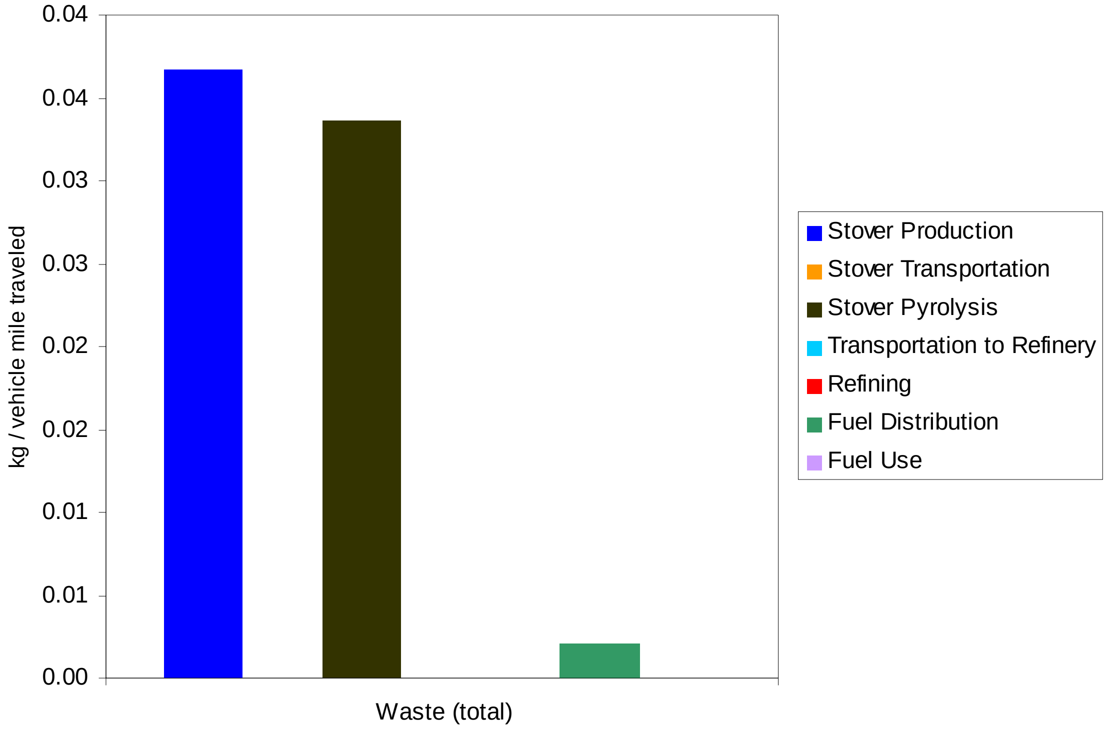


Figure 43. Waste

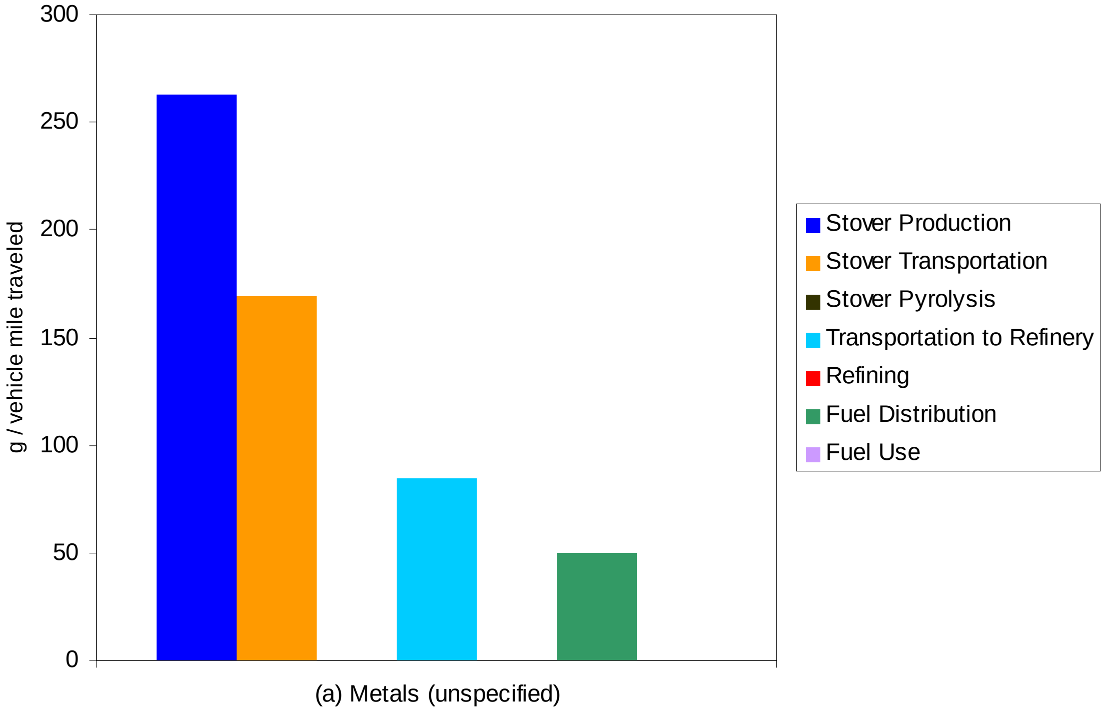


Figure 44. Metals

Comparison with Ethanol and Gasoline Life Cycles

Inputs and outputs were compared with two other transportation fuel life cycle assessments. One comparison was with the biochemical conversion of corn stover to create ethanol in an E85 process. The original LCA model is modified by removing an unleaded gasoline avoided impact module and the model is corrected to account for the 15% moisture in the corn stover. The other comparison is with the life cycle assessment of unleaded gasoline. The LCA of unleaded gasoline is taken from parts of the analysis for production of E85 ethanol from corn stover (Sheehan, et al. 2000).

The unleaded gasoline LCA consists of the production, transportation, and distribution of unleaded gasoline, denoted in **Figure 45** as “Unleaded Gasoline,” and the use of gasoline in the vehicle, denoted in **Figure 45** as “Gasoline Use.” The production, both domestic and foreign, transportation, and distribution of gasoline is shown in more detail in **Figure 46** and is explained in greater detail in Corn Stover Life Cycle Analysis (Sheehan, et al. 2000). The emissions from gasoline use are based on EPA tailpipe emissions for a 2000 Ford Taurus flexible fuel vehicle using only gasoline for 50,000 miles.

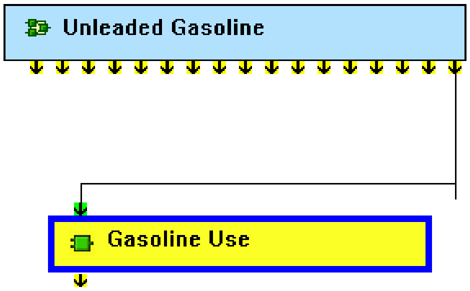


Figure 45. Unleaded gasoline LCA

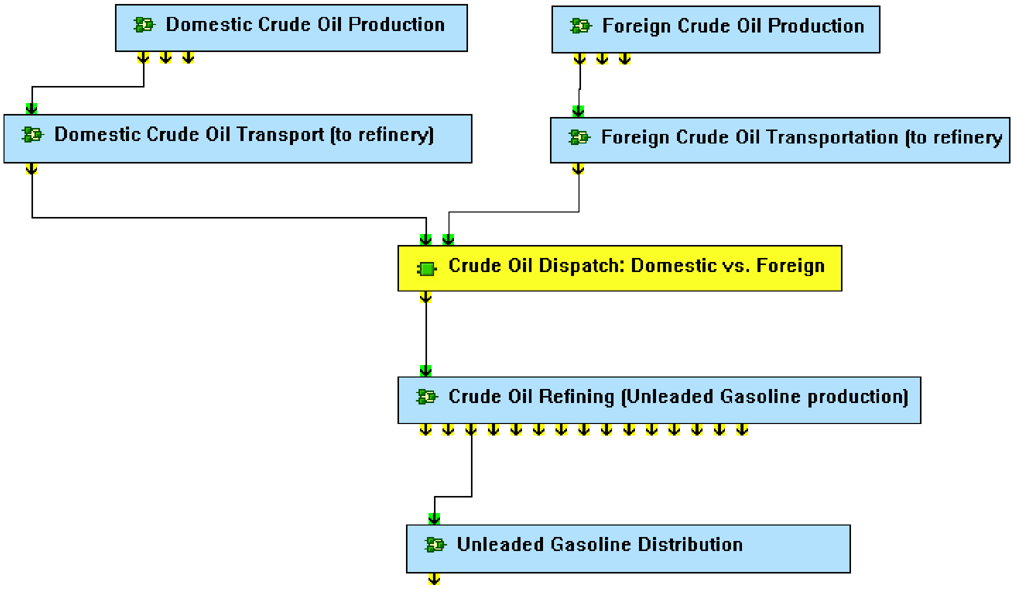


Figure 46. Production and distribution of unleaded gasoline

Figure 47 shows a comparison of various inputs for the three processes. The coal and natural gas usage for pyrolysis and ethanol are greater than or equal to usage for gasoline, but both pyrolysis and ethanol processes consume considerably less oil. As seen in **Figure 48**, the pyrolysis process uses more water than the gasoline process but less water than the ethanol process. In general, the pyrolysis process requires fewer resources than the ethanol process. This can be attributed directly to the smaller amount of corn stover and cropland needed in the pyrolysis case (**Figure 49** and **Figure 50**). The electricity used in the pyrolysis process is less than what is used in both the ethanol and gasoline processes (**Figure 51**). Although electricity and corn stover are used in these processes, they are technically not inputs because the life cycle assessment takes into account the natural resources needed to produce electricity and corn stover.

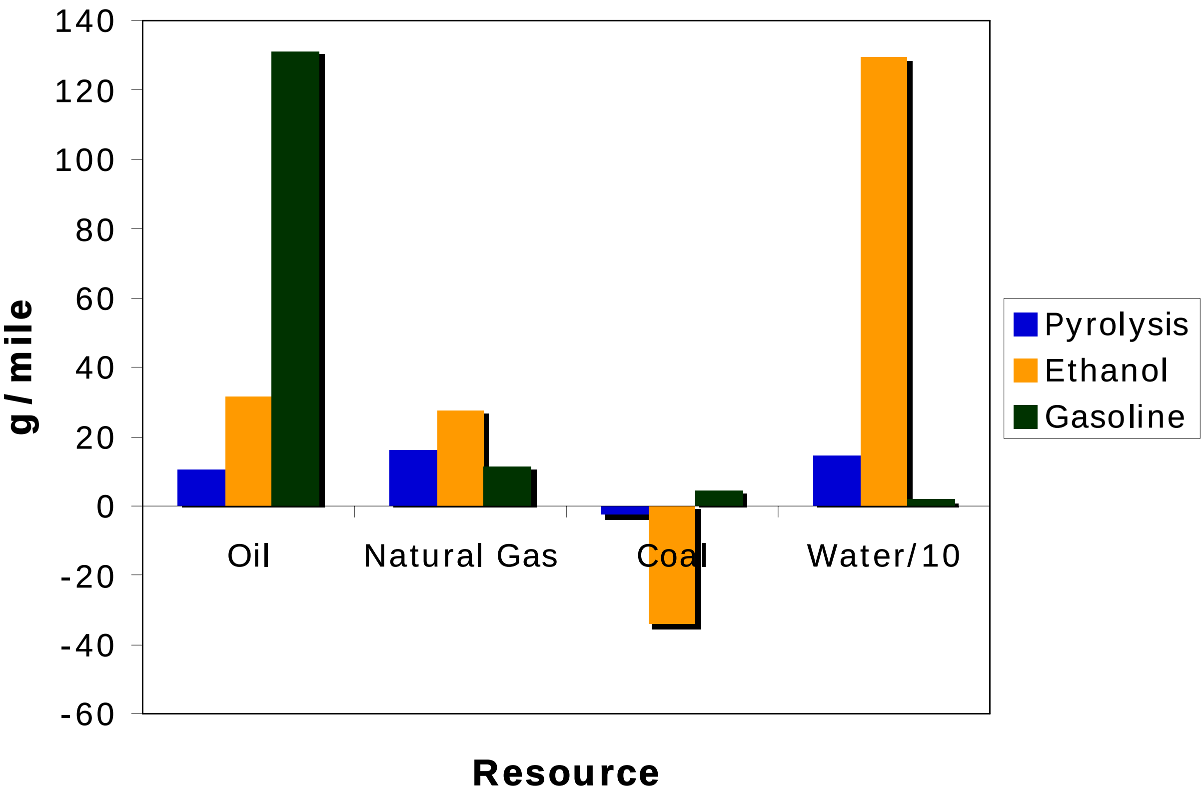


Figure 47. Comparison of various inputs

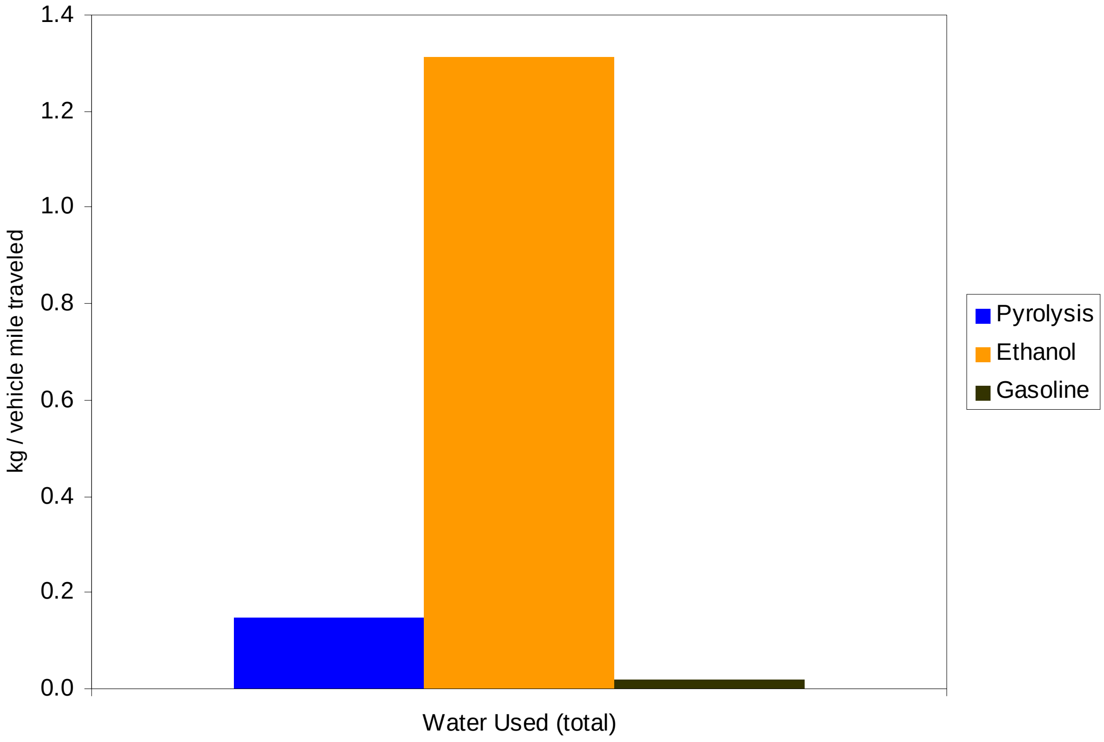


Figure 48. Water usage comparison

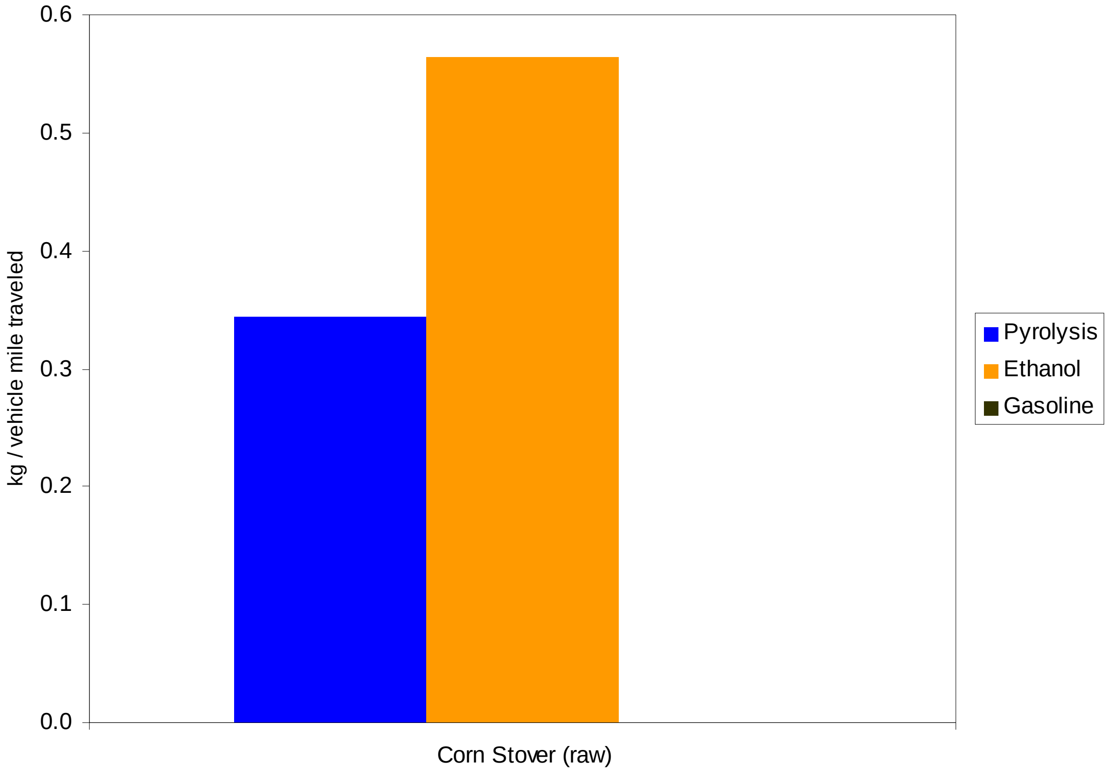


Figure 49. Corn stover input comparison

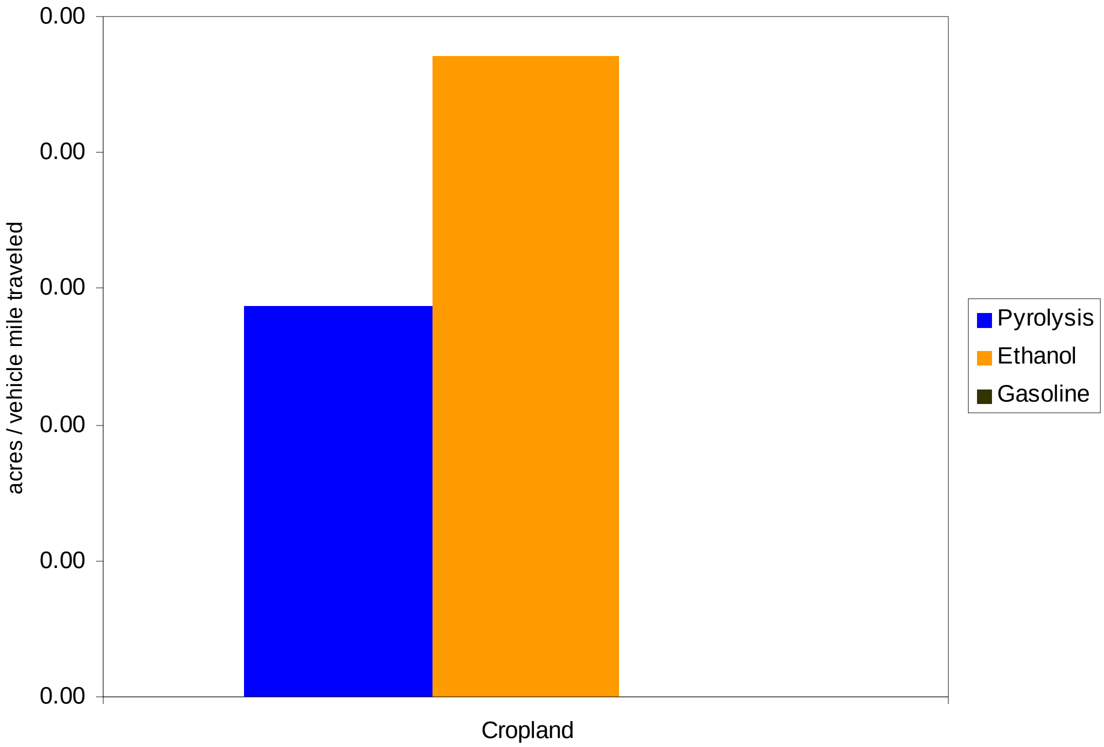


Figure 50. Cropland comparison

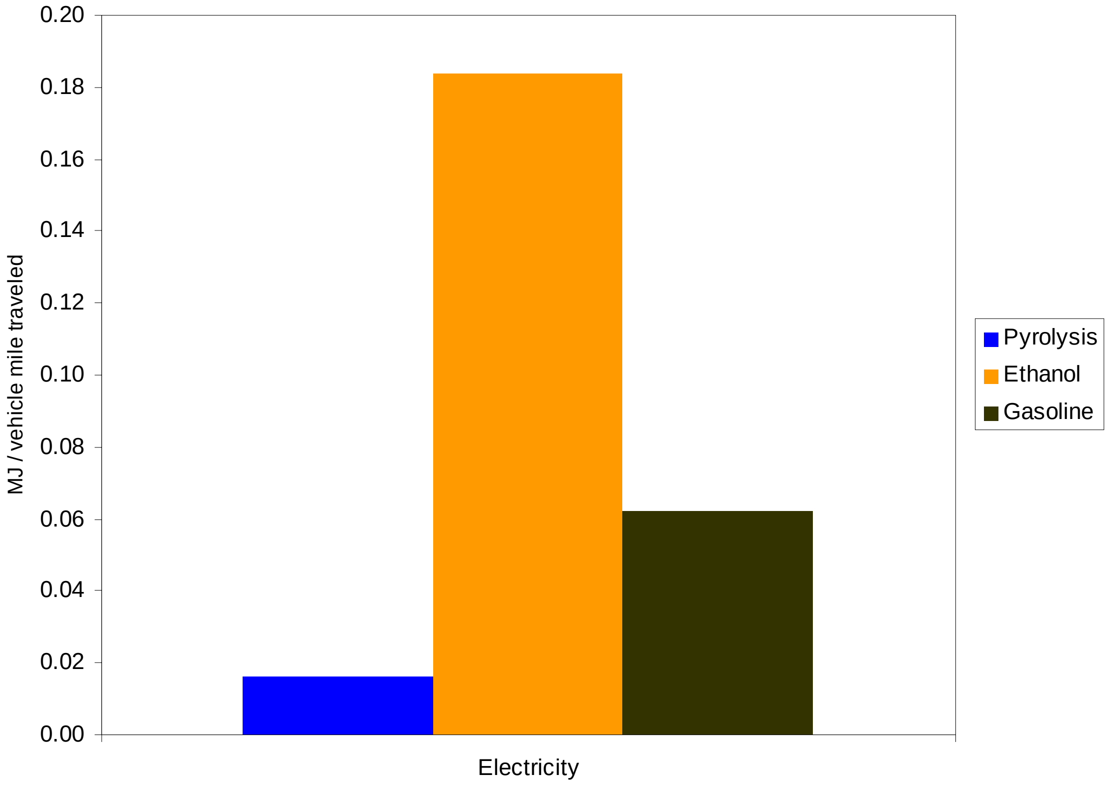


Figure 51. Electricity input comparison

Pyrolysis has more carbon dioxide emission from fossil fuel sources than ethanol, but less emission than gasoline. There is a net decrease in carbon dioxide emission from biomass sources for both pyrolysis and ethanol. The sum of the carbon dioxide released to the atmosphere from fossil, biomass, and soil sources is shown in **Figure 52**. Both the pyrolysis and ethanol processes emit less total carbon dioxide than the unleaded gasoline process.

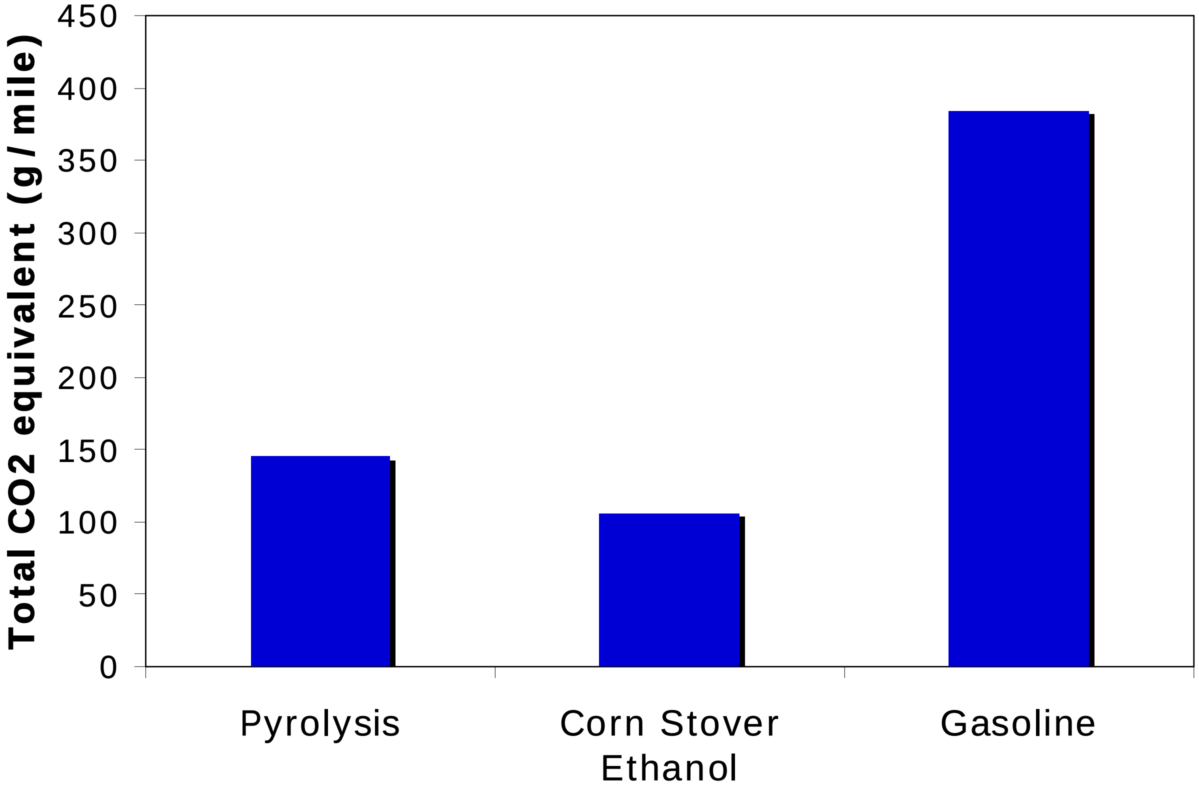


Figure 52. Total carbon dioxide equivalent output comparison

In **Figure 53**, various output flows with amounts in the gram range are shown. Pyrolysis has higher flows than E85 ethanol and gasoline in many flows, including carbon monoxide, nitrogen oxides, methane, and particulates.

Figure 54 shows water and waste output streams. The “Water (unspecified)” flow denotes water that does not need to be treated. The “Water: Chemically Polluted” flow is water that would need to be sent to a wastewater treatment center. Pyrolysis produces more wastewater than the E85 ethanol process in part because the water used for enzyme production eventually becomes solid waste. The gasoline process has the highest “Water: Chemically Polluted” output flow.

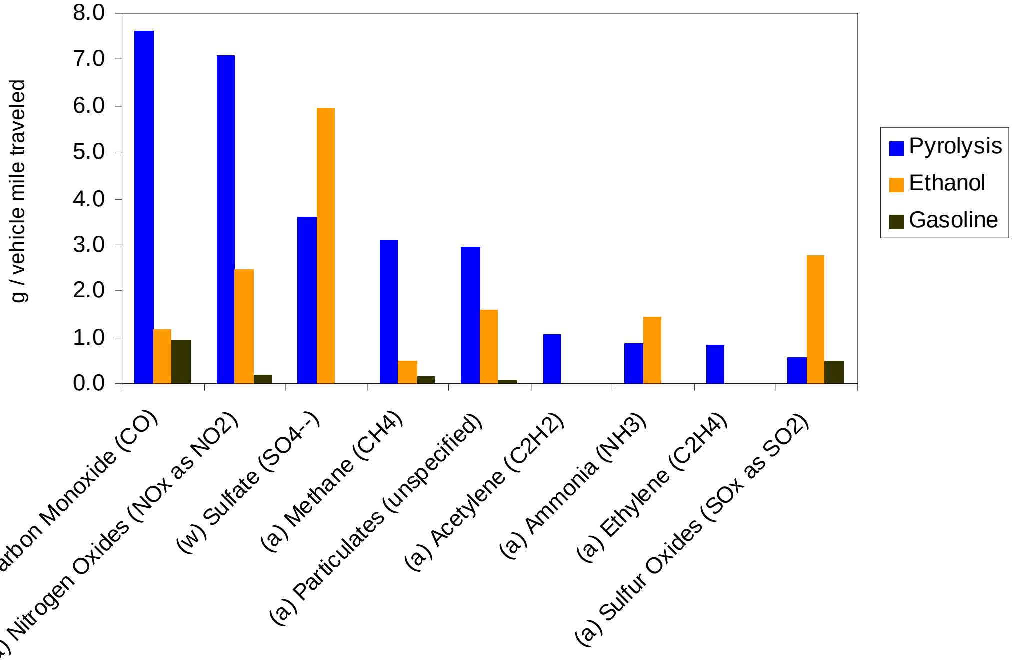


Figure 53. Various output flows comparison

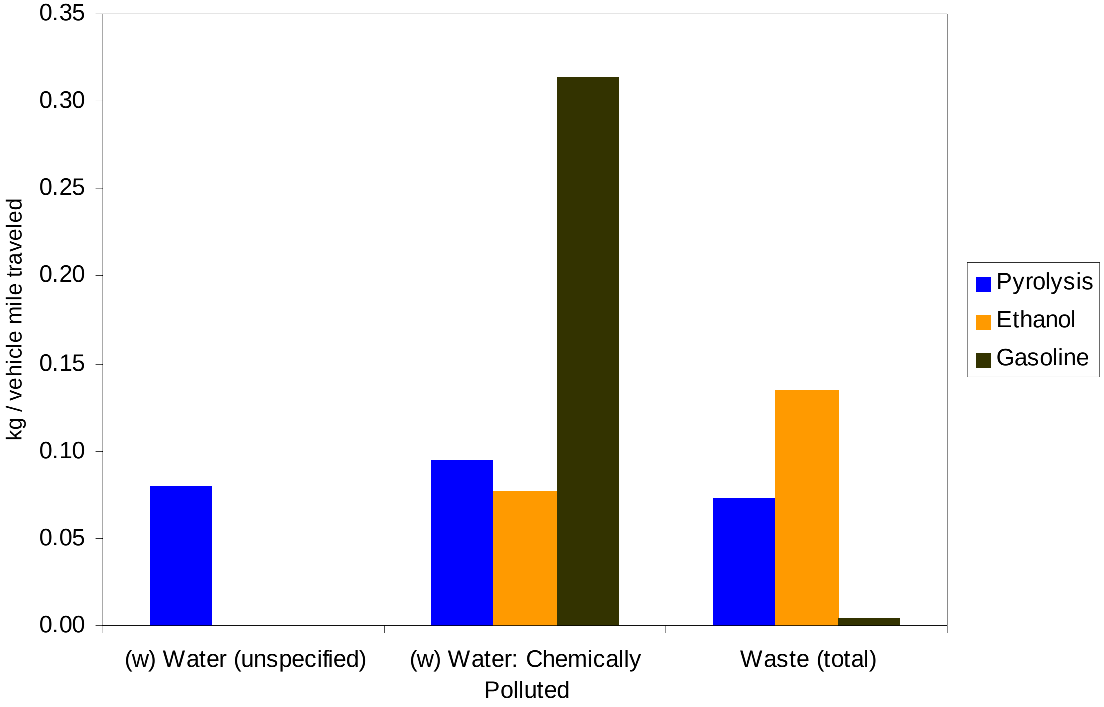


Figure 54. Waste comparison

A comparison of the three main greenhouse emissions and NO_x and SO_x air emissions is shown in **Table 39**. Fossil carbon dioxide emissions are noticeably lower in the pyrolysis and ethanol life cycles than in the unleaded gasoline life cycle. Methane, nitrous oxide, and nitrogen oxides, however, are higher in the pyrolysis life cycle. Methane and nitrous oxide have higher global warming potentials than carbon dioxide, but the increase in these emissions is more than offset by the reduction in CO_2. The production of nitrogen oxides, namely NO_2, is higher in pyrolysis than unleaded gasoline, even under the most aggressive NO_x emission control scenarios. Additional decreases in NO_x in pyrolysis could come from reductions in fertilizer use or reductions in emissions of NO_x below the 5% assumption used in the LCA.

Greenhouse Gas Emission	Units	Pyrolysis	Corn Stover Ethanol	Gasoline
Carbon dioxide (fossil)	g/mile	39	48	380
Carbon dioxide (soil)	g/mile	8.0	12	
Methane	g/mile	0.93	0.22	0.13
Nitrous oxide	g/mile	0.26	0.14	0.005
Total CO_2 equivalent	g/mile	145	106	384

Table 39. Comparison of air emissions from pyrolysis and gasoline LCAs.

Summary

A life cycle assessment of the corn stover pyrolysis process was done, using data from a previous LCA on corn stover E85 ethanol process (Sheehan, et al. 2000), a wood pyrolysis AspenPlus model (Putsche 2004), data from pyrolysis, hydrotreating, and hydrocracking runs by UOP, and EPA emissions factors (EPA 2007). Most carbon dioxide coming from fossil fuel sources are emitted during the production of corn stover. The corn stover pyrolysis produces fewer greenhouse gas emissions than a corn stover ethanol process and an unleaded gasoline process. While pyrolysis and ethanol processes consume less oil than the gasoline process, they both consume equal or more coal and natural gas. The pyrolysis process requires more water than the gasoline process, but less than the ethanol process. Much of the water required occurs during the production of corn stover. Although the pyrolysis process consumes fewer resources and emits less greenhouse gases than the ethanol process, this LCA also shows that the production of corn stover is a particularly resource intensive step, with most of the carbon dioxide from fossil fuel sources and the water required coming in this step.

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U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy. U.S. Environmental Protection Agency. 2007. *Fuel Economy Guide.* Gaithersburg, MD: Office of Energy Efficiency and Renewable Energy. http://www.fueleconomy.gov/feg/FEG2007.pdf.

Proposed Flowscheme

The UOP Hydrocracking flowscheme shown in **Figure 33** will be the basis for the economic analysis

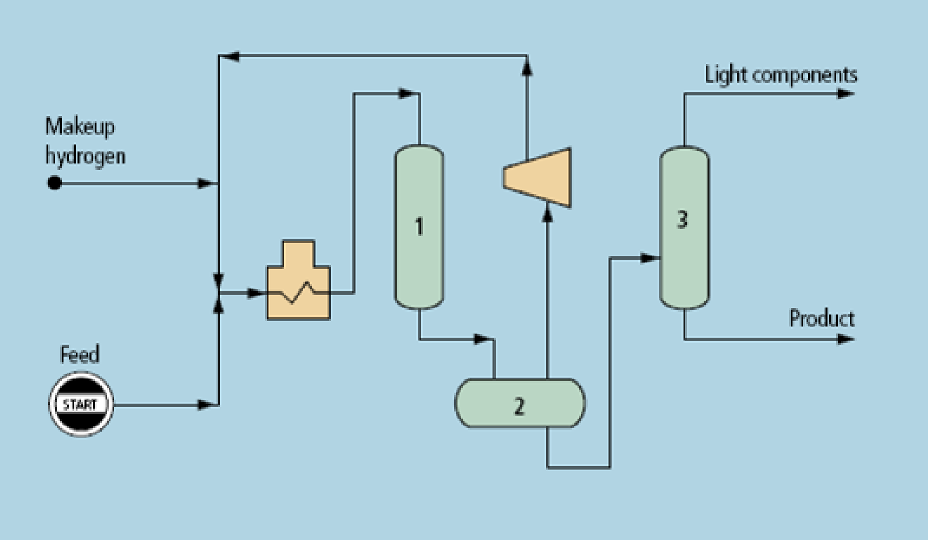


Figure 33. UOP LLC hydrotreating Process Design (Hydrocarbon Processing 2004)

Economic Analysis

Basis:

The prices used in the study were derived from the UOP standard price set for 2008 which were slightly adjusted, as requested by NREL and PNNL, to be consistent with a $100/bbl gasoline price which is needed for comparison with other DOE projects. NREL provided the biomass price of $46/ton and NREL also provided the pyrolysis oil price of $25/bbl which they calculated based on their economic analysis of the costs of production of pyrolysis oil including capital charges. NREL's standard pyrolysis oil price is based on a pyrolysis unit processing 2000t/d of biomass. Their standard pyrolysis unit design includes capital costs for the feed preparation, pyrolysis, fluid bed combustion of the char and generation of electricity from the char combustion.

Table 41- Pyrolysis Oil to Gasoline Price Basis

CRADA Price structure

Pyrolysis Oil	$25/bbl
Biomass Feedstock	$46/ton
Gasoline	$100/bbl
Diesel	$100/bbl
VGO(650-1000 F)	$76/bbl
H2	2100/MT
Fuel gas	$410/MT

Table 41 shows the price structure used in the CRADA economics.

Yields and material balances for the pyrolysis oil section were based on NREL results which show 70% yield of pyrolysis oil from wood biomass. These yields are typical for pyrolysis oil from wood reported in the literature. Yields and material balances for the pyrolysis oil upgrading section were based on PNNL results which were generated in the CRADA. Doug Elliot reviewed the data used in the study and picked the most representative results as the basis for the economic study.

The material balance used in the economics is shown in **Table 42.**

Table 42 – Pyrolysis Oil Upgrading Material Balances

Material Balance T/d

	Wood feed	Corn stover feed
Feedstock	2000	2000
Pyrolysis oil	1400(7160bpd)	946(5130bpd)
H2 required	39 (2.8%)	22.7(2.4%)
gasoline	280(2073bpd)	194(1400bpd)
diesel	168(1249bpd)	117(844bpd)
VGO	58(428bpd)	40(289bpd)
Total products	506(3748bpd)	350(2534bpd)

Table 42-Pyrolysis Oil Upgrading Material Balances

The landmass requirements for feeding a 2000T/d pyrolysis oil plant are large but not outrageous. A 2000t/d pyrolysis unit could be fed from a biomass circle of 12 miles diameter if wood or switch grass are used as the basis. Algae would require a much smaller landmass of only 5.3miles diameter. This comparison is shown in **Table 43**.

Landmass Requirements for a Pyrolysis Unit

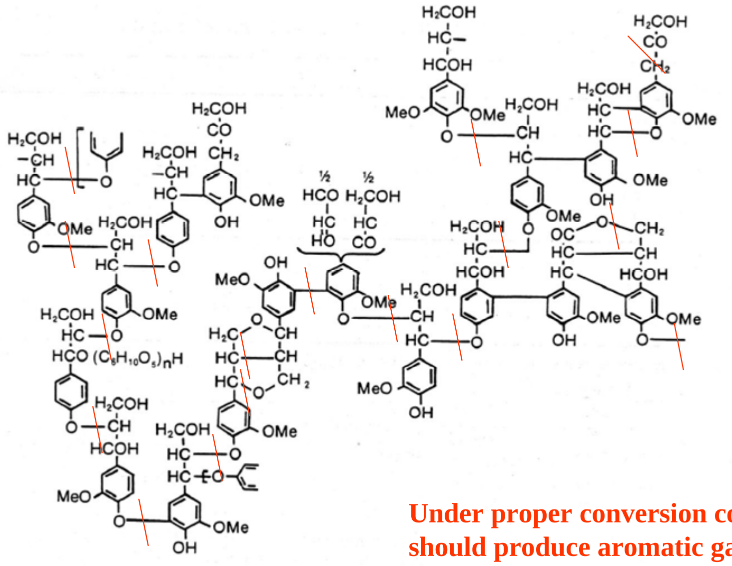
Size of Pyrolysis unit t/d	Biomass yield/acre/yr	Square miles of biomass(acres)	Biomass Circle diameter miles	Bpd of pyrolysis oil	Bpd of finished HC products
2000	10(wood, switch grass)	112(72,000)	12	7160	4000
2000	5 (wood, switchgrass)	224(144,000)	17	7160	4000
2000	50(algae)	22.4(14,400)	5.3	7160	4000
1000	10(wood, switch grass)	56(36,000)	8.5	3580	2000
1000	5 (wood, switchgrass)	112(72,000)	12	3580	2000
1000	50(algae)	11.2(7200)	3.8	3580	2000
500	10(wood, switch grass)	28(18,000)	6.0	1790	1000
500	5 (wood, switchgrass)	56(36,000)	8.5	1790	1000
500	50(algae)	5.6(3600)	2.7	1790	1000

Table 42- Landmass requirements to feed a Pyrolysis Unit

Pyrolysis oil conversion using hydroconversion, which has been done as part of the CRADA with PNNL and NREL, has primarily been done with a PNNL catalyst of Pd-C in the first stage and UOP Hydrotreating catalyst in the second stage. Although PNNL has referred to the first stage as hydrotreating and the second stage as hydrocracking, this terminology is misleading since in both stages the oxygen is being removed and the molecules are breaking where the oxygen linkages are removed not because C-C linkages are broken. In standard terminology, heteroatom removal is typically called hydrotreating whereas the breakage of C-C bonds is typically called hydrocracking.

When the oxygen is removed from pyrolysis oils the molecules naturally fall apart to make gasoline(55%), diesel(33%) and VGO(11%) since so many oxygen linkages are present. The effect of oxygen removal is depicted for a typical lignin molecule in **Figure 48**. Because there is so much oxygen in biomass when the oxygen is removed the pieces left will be small.

Typical Structure of Lignin-Hydrocarbon part



Under proper conversion conditions should produce aromatic gasoline

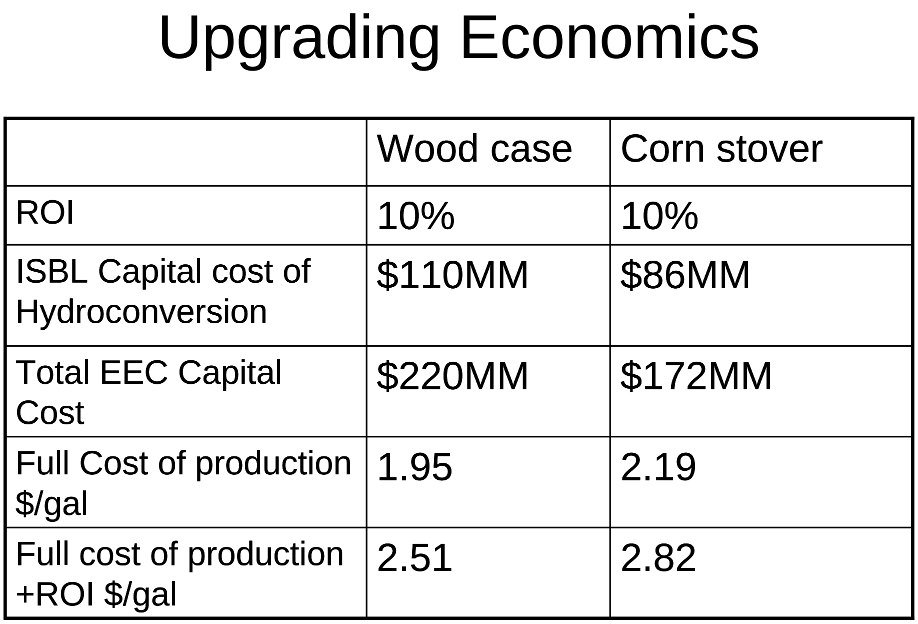
Figure 3-10: Representative Structure of Coniferous Lignin

Figure 48- Biomaterial Cracking when Oxygen is Removed

Economics for Gasoline and Diesel Production:

The economics for upgrading the pyrolysis oil to gasoline are shown in **Tables 44 and 45**. ISBL capital cost for the hydroconversion step were taken as $110MM for upgrading 7160 bpd of pyrolysis oil. These capital costs assume that 1 step upgrading could be done with a NiMo catalyst in a fixed bed unit. If upgrading must be done in a slurry bed or ebullated bed design it will increases capital costs. The capital costs do not include a H2 plant and instead it is assumed that H2 is purchased and fuel gas is sold. An alternative case would use the fuel gas to produce H2 and build a H2 plant. If a H2 plant is built, capital charges would increase and H2 feed costs would decrease but the economics should be equivalent.

Table 34- Pyrolysis Oil Upgrading Economics

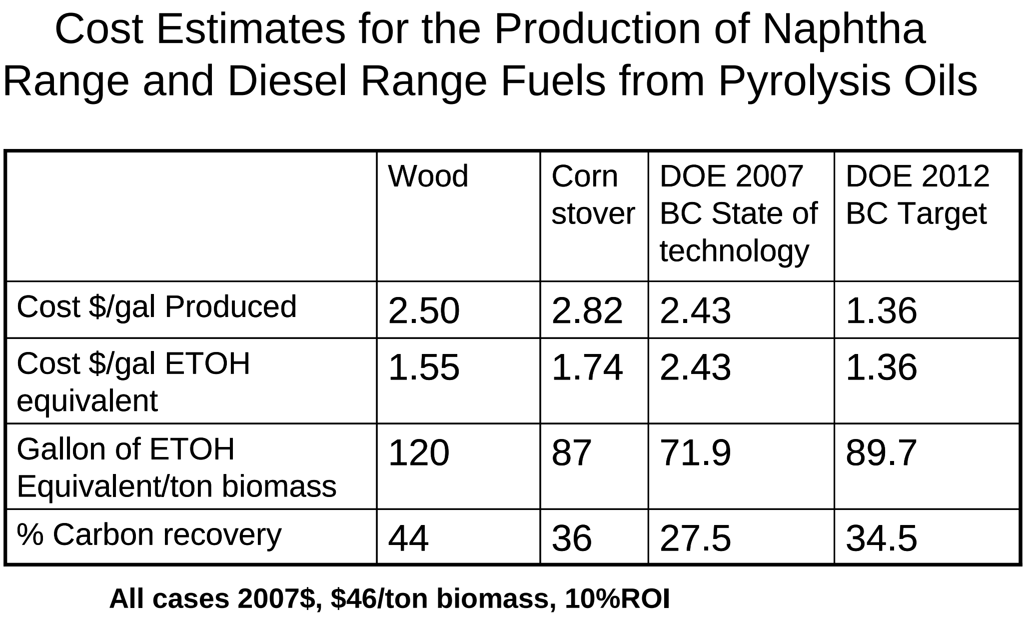


Upgrading Economics

	Wood case	Corn stover
ROI	10%	10%
ISBL Capital cost of Hydroconversion	$110MM	$86MM
Total EEC Capital Cost	$220MM	$172MM
Full Cost of production $/gal	1.95	2.19
Full cost of production +ROI $/gal	2.51	2.82

Table 44-Pyrolysis Oil Upgrading Economics

Table 44-$/gallon costs of Bio-Gasoline and Green Diesel produced from Pyrolysis Oil Upgrading



Cost Estimates for the Production of Naphtha Range and Diesel Range Fuels from Pyrolysis Oils

	Wood	Corn stover	DOE 2007 BC State of technology	DOE 2012 BC Target
Cost $/gal Produced	2.50	2.82	2.43	1.36
Cost $/gal ETOH equivalent	1.55	1.74	2.43	1.36
Gallon of ETOH Equivalent/ton biomass	120	87	71.9	89.7
% Carbon recovery	44	36	27.5	34.5

All cases 2007$, $46/ton biomass, 10%ROI

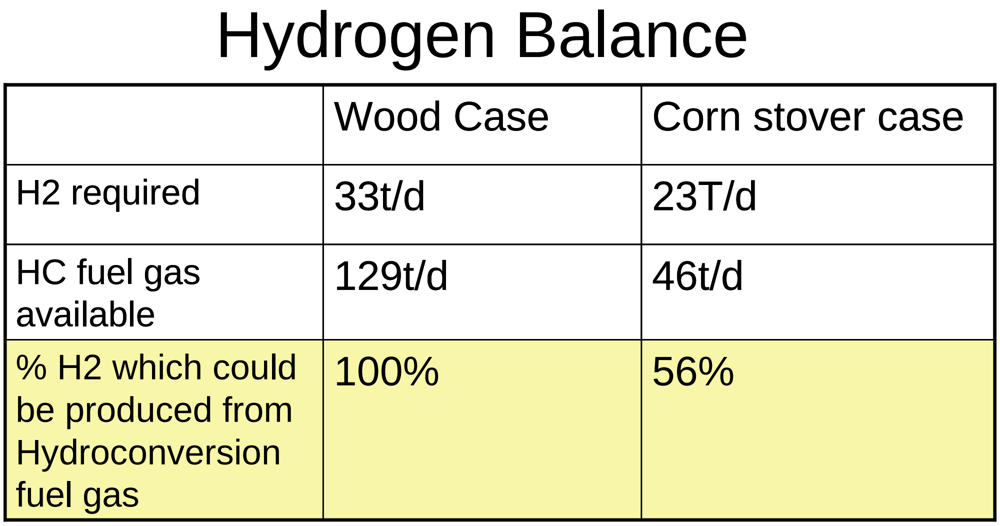
Table 45-$/gallon costs of Bio-Gasoline and Green Diesel produced from Pyrolysis Oil Upgrading

The H2 required for the upgrading is based on the H2 requirements measured at PNNL. Many paper studies have assumed that all the oxygen in the pyrolysis oil is removed as water which results in much higher H2 requirements. In reality (based on the PNNL data) much of oxygen is removed as CO2 and much of the

H2 needed for upgrading is produced in situ from the water gas shift reaction of CO with water to make CO2 and H2.

Analysis of the H2 required and the fuel gas produced shows that all of the H2 required for upgrading can be produced from the fuel gas byproduct made in the upgrading. For the case of wood, all of the H2 required could be produced from the fuel gas and for the case of corn stover, 56% of the H2 required could be produced from byproduct fuel gas. This is shown in **Table 46**.

Table 45- Hydrogen Balance for Pyrolysis Oil Upgrading



Hydrogen Balance

	Wood Case	Corn stover case
H2 required	33t/d	23T/d
HC fuel gas available	129t/d	46t/d
% H2 which could be produced from Hydroconversion fuel gas	100%	56%

Table 46- Hydrogen Balance for Pyrolysis Oil Upgrading

Economics of Fuel Oil Production:

Pyrolysis oil is a fuel oil with very low heating value, high acidity and poor stability. In order to better market this fuel oil, it is believed that stability should be improved. Stability typically means that the viscosity and phases do not change over time (solids don’t fall out and no separate phases are formed upon standing). Literature data has shown that pyrolysis oil stability is good once metals are removed through hot filtering. It is believed that alkali metals in pyrolysis oil catalyze polymerization reactions which lead to viscosity increases and solids formation. Therefore it is likely that metals removal can result in the production of stable pyrolysis oil. Removal of metals will also be needed for hydrotreating applications in fixed beds since it has been shown that high alkali metals will plug fixed beds and deactivate hydroconversion catalyst.

Metals removal of 100’s of ppm metals with hydroconversion catalyst would cause plugging in a fixed bed but could be done in an ebullated bed or slurry bed system but would add catalyst and equipment cost. **Table 47** shows the costs and size of the hydroconversion catalyst needed to remove large quantities of metals for a 2 year life.

Table 46- Metals Removal using Hydroconversion Catalyst

Removal of Metals from Pyrolysis oils using Hydroconversion Catalyst

	Typical Hydroconversion Guard Bed	Wood pyrolysis oil	Corn stover
Metals, ppm	10	100,250 Avg 175	640,987,522 Avg 524
Guard bed size,ft3 for 6500bpd feed	671	15266	45708
Guard bed section dimension	7.5ft length x 10.7 ft diameter	172 ft length x 10.7 ft diameter	511 ft length X 10.7 ft diameter
Catalyst cost, $MM	.2	4.6	11.4

Table 47-Metals Removal using Hydroconversion Catalyst

Reduction of TAN (total acid number) naturally occurs when hydroconversion is done since oxygen is removed, however experimental work at PNNL has shown that TAN number is not reduced to less than 5 (where standard metallurgy could be used) until almost all of the oxygen is removed from the pyrolysis oil. This data is shown in **Figure 49**.

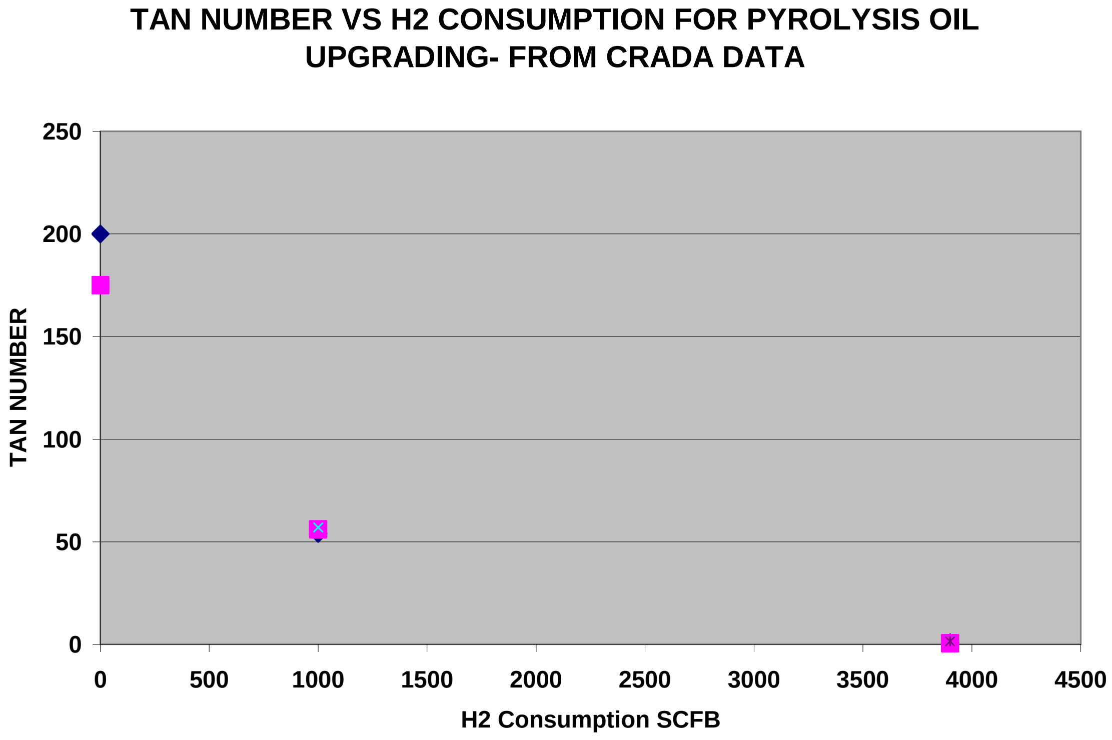
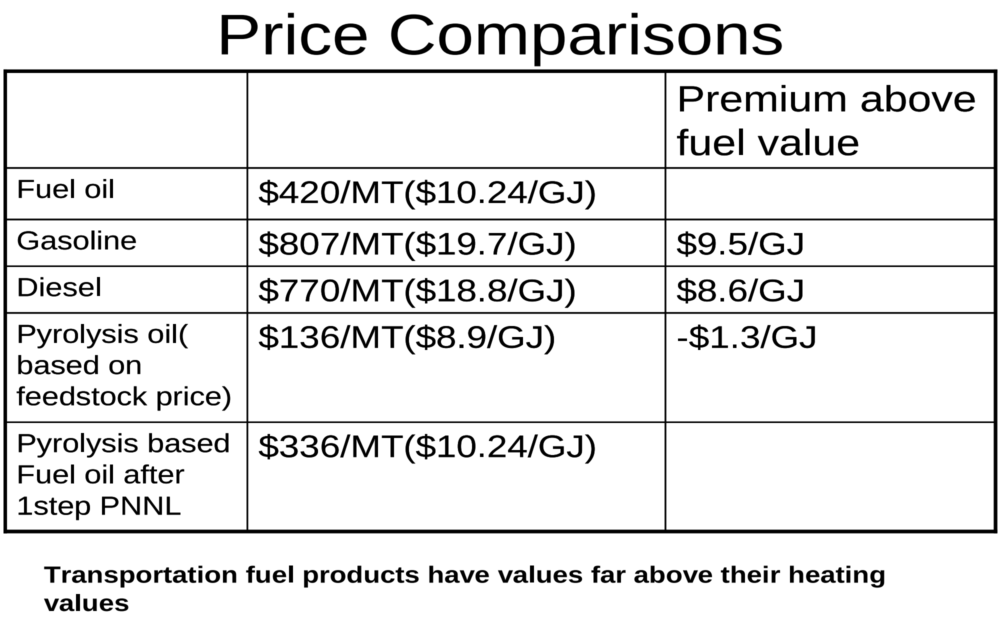


Figure 49- TAN Number vs H2 Consumption

The economics of upgrading pyrolysis oil to fuel oil are a function of the value of the fuel oil. At best pyrolysis based fuel oil would have a value equivalent to its heating value. Gasoline and diesel fuels have values significantly above their heating value as shown in **Table 48**.



Price Comparisons

		Premium above fuel value
Fuel oil	\$420/MT(\$10.24/GJ)	
Gasoline	\$807/MT(\$19.7/GJ)	\$9.5/GJ
Diesel	\$770/MT(\$18.8/GJ)	\$8.6/GJ
Pyrolysis oil(based on feedstock price)	\$136/MT(\$8.9/GJ)	-\$1.3/GJ
Pyrolysis based Fuel oil after 1step PNNL	\$336/MT(\$10.24/GJ)	

Transportation fuel products have values far above their heating values

Table 47- Price comparisons of Fuel Oil with Gasoline and Diesel

The low value of pyrolysis fuel oil provides very little incentive for upgrading through hydroconversion to make a fuel oil product. **Table 49** compares the economics of stabilizing pyrolysis oil by metals removal to make fuel oil versus partial hydrotreating to make a stable fuel oil versus full hydroconversion to make gasoline and diesel. Stabilizing the pyrolysis oil by doing a simple metals removal step such as hot filtering, assuming that significant yield loss does not occur, would be quite valuable and have 0.6years to payback. Fully upgrading pyrolysis oil to make gasoline and diesel has 3.8 years to payback and is also attractive. However partially hydrotreating pyrolysis oil to make a stable fuel oil, using the first step of the PNNL process, would cost a lot and produce a low valued product.

Table 48- Economics for Upgrading Pyrolysis Oil

Simple Economics for Upgrading Pyrolysis oil from 2000t/d Wood

	Partially Hydrotreating	Stabilizing	Full HT
Cost of Feed	$62MM/yr	$62MM/yr	$62MM/yr
Cost of H2	$11MM/yr	-	$23MM/yr
Utilities	$1MM/yr	-	$2MM/yr
Value of Product	$75.5MM/yr	$70MM/yr	$150MM/yr
Incentive to Produce	$2.5MM/yr	$8MM	$63MM/yr
Capital Cost	$120MM	$5MM	$240MM
Years to payback	48	.6	3.8

Table 49- Economics for Upgrading Pyrolsis Oil

Economics Summary:

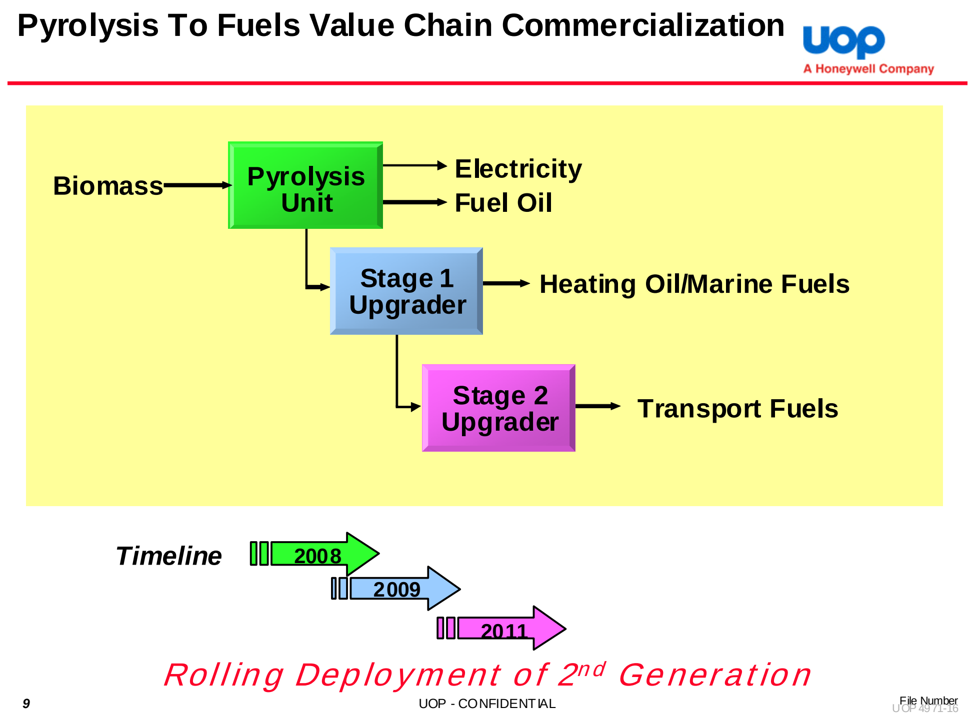
Upgrading pyrolysis oil to make a stabilized fuel oil through a simple metals removal step (or other low capital cost treatments) has excellent economics. Upgrading pyrolysis oil to gasoline and diesel has good economics. Upgrading pyrolysis oil by partial hydroconversion to fuel oil has extremely poor economics and is not recommended unless it could be done extremely cheaply, and the water-hydrocarbon separation problems could somehow be eliminated.

Path to Commercialization

Commercializing this technology value chain may actually be less of a challenge than some alternates. The critical differentiator is that the pyrolysis technology is commercially available already, meaning that reliable capex and opex data can be provided, and small commercial / demonstration units can be visited. These critical elements mitigate much of the risk associated with investment in new technology.

Downstream of the pyrolysis oil unit, whilst stabilization and upgrading is as yet commercially unproven, the concepts and equipment are well understood within the refining sector. Companies which can demonstrate significant experience in the adjacent hydroprocessing sector of the oil refining industry, should be able to successfully bridge the gap between research and commercial offering for pyrolysis upgrading based upon hydroprocessing.

The difference in technology maturity between the upstream [pyrolysis oil] and downstream [stabilizing/upgrading] units lends itself to a potential strategy of rolling investment and commercialization**(Figure 50)**.



Pyrolysis To Fuels Value Chain Commercialization

uop
A Honeywell Company

Biomass
Pyrolysis Unit
Electricity
Fuel Oil
Stage 1 Upgrader
Heating Oil/Marine Fuels
Stage 2 Upgrader
Transport Fuels

Timeline
2008
2009
2011

Rolling Deployment of 2nd Generation

9
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File Number
UOP 4971-16

Figure 50 Rolling Deployment of 2nd Generation Technology

In this rolling commercialization strategy, potential clients will be able to build pyrolysis oil units early, enabling them to gain experience in operation and biomass logistics whilst the research on downstream unit technology is completed. The immediate use of pyrolysis oil for thermal or power applications means that the pyrolysis unit can provide significant value in its early years. Under a Cap and Trade structure or GHG limited world, using the pyrolysis oil to substitute for fossil-derived fuel oils will enable users to move into compliance early. As the downstream technologies become available, without a significant increase in GHG, the product slate is changed from thermal to transport, possibly also with the addition of further pyrolysis capacity.

Without a need to have the pyrolysis units in the same location as the Upgrading unit, we would also see early opportunity in deploying pyrolysis within industries that don't yet have a direct interest in transport fuels. Examples of these maybe the utilities, cement, or paper and pulp industries. As pyrolysis oil production capacity grows, and as the Upgrading technology is rolled out, these incumbent pyrolysis oil producers will then find alternate outlets for their oil, slowly creating a market for pyrolysis oil as a traded commodity. In turn, as supply increases, refiners who might not otherwise invest in the entire value chain, may consider Upgrader investments using oil produced by others.

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Appendix

Life Cycle Inventory Tables

Appendix: Inventory Tables

Table A1. Life Cycle Inventory (LCI) inputs, sorted by amount, restricted to mass greater than 1 mg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution
Nitrogen (N_2)	kg	0.771419	0	0	0.771419	0	0	0
Oxygen (O_2)	kg	0.192855	0	0	0.192855	0	0	0
(r) Phosphate Rock (in ground)	kg	1.71E-02	1.71E-02	0	0	0	1.65E-09	0
(r) Natural Gas (in ground)	kg	1.61E-02	9.88E-03	1.07E-04	0	5.33E-05	6.01E-03	3.46E-05
(r) Oil (in ground)	kg	9.66E-03	2.42E-03	1.24E-03	0	6.21E-04	5.00E-03	3.74E-04
(r) Potassium Chloride (KCl, as K_2O, in ground)	kg	5.32E-03	5.32E-03	0	0	0	9.6E-09	0
(r) Coal (in ground)	kg	4.58E-03	3.73E-03	3.88E-05	0	1.94E-05	3.88E-04	3.98E-04
(r) Limestone ($CaCO_3$, in ground)	kg	3.43E-04	2.96E-04	7.35E-06	0	3.67E-06	4.16E-06	3.27E-05
(r) Sodium Chloride (NaCl, in ground or in sea)	kg	3.15E-05	2.94E-05	1.36E-10	0	0	2.04E-06	1.88E-10
Raw Materials (unspecified)	kg	2.16E-05	2.16E-05	0	0	0	0	0
(r) Iron (Fe, ore)	kg	1.80E-05	1.28E-05	0	0	0	5.17E-06	0
(r) Lignite (in ground)	kg	1.30E-05	1.21E-05	0	0	0	9.14E-07	0
(r) Pyrite (FeS_2, ore)	kg	7.87E-06	6.94E-06	0	0	0	9.24E-07	0
Biomass (unspecified)	kg	7.18E-06	0	0	0	0	7.18E-06	0
(r) Barium Sulfate ($BaSO_4$, in ground)	kg	4.33E-06	4.33E-06	0	0	0	0	0

(r) Sulfur (S, in ground)	kg	3.25E-06	3.25E-06	0	0	0	0	0
Peat	kg	2.57E-06	0	0	0	0	2.57E-06	0
(r) Bentonite (Al2O3.4SiO2.H2O, in ground)	kg	1.52E-06	4.09E-07	0	0	0	1.11E-06	0
(r) Clay (in ground)	kg	1.21E-06	8.11E-07	0	0	0	3.99E-07	0
Cropland	acres	1.44E-04	1.44E-04	0	0	0	0	0
Land Use (II -> IV)	m2a	1.87E-10	1.87E-10	0	0	0	0	0
Land Use (II -> III)	m2a	1.54E-10	1.54E-10	0	0	0	0	0
Land Use (III -> IV)	m2a	2.12E-13	2.12E-13	0	0	0	0	0
Water Used (total)	liter	0.148896	0.103642	2.86E-04	3.87E-03	8.64E-05	0.0407917	2.16E-04
Water: Public Network	liter	0.116291	0.0862705	0	3.87E-03	0	0.0261464	0
Water: Unspecified Origin	liter	1.87E-02	1.50E-02	1.13E-04	0	0	3.46E-03	1.65E-04
Water: Sea	liter	6.65E-03	0	0	0	0	6.65E-03	0
Water: River	liter	4.54E-03	0	0	0	0	4.54E-03	0
Water: Well	liter	3.78E-09	0	0	0	0	3.78E-09	0

Table A2. LCI air emission outputs, sorted by amount, mass greater than 1 μg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
Nitrogen (N2)	g	7.71E+02	0	0	7.71E+02	0	0	0	0
(a) Metals (unspecified)	g	5.67E+02	2.63E+02	1.69E+02	0	8.48E+01	3.78E-06	5.00E+01	0
(a) Carbon Dioxide (CO2, fossil)	g	5.79E+01	3.92E+01	4.13E+00	0	2.09E+00	1.03E+01	2.21E+00	0
Oxygen (O2)	g	3.96E+01	0	0	3.96E+01	0	0	0	0
(a) Carbon Dioxide (CO2, Soil)	g	8.50E+00	8.50E+00	0	0	0	0	0	0
(a) Carbon Monoxide (CO)	g	7.62E+00	3.23E-02	1.40E-02	6.90E+00	6.97E-03	5.22E-02	4.55E-03	0.606798
(a) Nitrogen Oxides (NOx as NO2)	g	7.10E+00	1.12E+00	3.89E-02	5.64E+00	3.45E-02	1.44E-02	1.68E-02	0.241008
(a) Methane (CH4)	g	3.13E+00	1.61E-01	1.49E-03	2.52E+00	7.51E-04	4.39E-01	2.17E-03	0
(a) Particulates (unspecified)	g	2.97E+00	7.80E-02	8.83E-04	2.86181	4.41E-04	4.71E-03	2.62E-03	0.020092
(a) Acetylene (C2H2)	g	1.07E+00	9.42E-12	0	1.07E+00	0	0	0	0
(a) Ammonia (NH3)	g	8.79E-01	8.79E-01	2.89E-08	0	2.65E-09	3.79E-06	2.44E-07	0
(a) Ethylene (C2H4)	g	8.27E-01	1.30E-03	0	8.25E-01	0	1.73E-04	0	0
(a) Sulfur Oxides (SOx as SO2)	g	5.67E-01	1.24E-01	6.09E-03	2.83E-01	3.04E-03	0	5.33E-03	0.145635
(a) Propylene (CH2CHCH3)	g	4.13E-01	4.12E-07	0	4.13E-01	0	5.64E-09	0	0
(a) Butene (1-CH3CH2CHCH2)	g	3.27E-01	2.14E-07	0	3.27E-01	0	3.86E-09	0	0
(a) Ethane (C2H6)	g	3.10E-01	4.47E-04	8.42E-09	6.56E-02	0	2.44E-01	2.20E-08	0
(a) Propane (C3H8)	g	2.80E-01	1.27E-04	1.81E-11	1.55E-01	0	1.25E-01	3.43E-09	0
(a) Nitrous Oxide (N2O)	g	2.55E-01	1.07E-01	4.11E-04	1.47E-01	2.23E-05	5.54E-06	2.35E-04	0
(a) Hydrogen Sulfide (H2S)	g	2.31E-01	5.97E-05	9.11E-06	0	4.54E-06	2.31E-01	2.74E-06	0
(a) Hydrocarbons (except methane)	g	2.09E-01	9.56E-03	3.02E-03	0	1.04E-04	1.00E-02	7.70E-04	0.185893
(a) VOC (Volatile Organic Compounds)	g	1.92E-01	0	0	1.92E-01	0	9.83E-05	0	0
(a) Hydrocarbons (unspecified)	g	1.73E-01	7.78E-03	1.64E-03	0	2.42E-03	3.71E-02	7.95E-02	0.044214
(a) Butene (2-CH3CHCHCH3)	g	1.26E-01	0	0	1.26E-01	0	0	0	0
(a) C10 alkanes (unspecified)	g	1.15E-01	0	0	1.15E-01	0	0	0	0
(a) Butane (C4H10)	g	5.11E-02	1.52E-07	5.71E-09	0	0	5.11E-02	1.49E-08	0
(a) Formaldehyde (CH2O)	g	2.42E-02	1.75E-05	3.74E-06	2.41E-02	1.86E-06	1.43E-06	1.20E-06	0.000127
(a) Benzaldehyde (C6H5CHO)	g	2.06E-02	1.28E-12	0	2.06E-02	0	1.70E-13	0	0
(a) Aldehyde (unspecified)	g	1.91E-02	1.77E-04	1.44E-07	1.89E-02	6.41E-08	3.79E-06	1.98E-05	0
(a) Methanol (CH3OH)	g	1.89E-02	1.36E-08	0	1.89E-02	0	1.81E-09	0	0
(a) Pentane (C5H12)	g	1.79E-02	1.38E-04	7.06E-09	0	0	1.78E-02	1.85E-08	0
(a) Acetone (CH3COCH3)	g	1.44E-02	1.90E-08	0	1.44E-02	0	2.53E-09	0	0
(a) Sulphur Oxides (SOx as SO2)	g	1.38E-02	0	0	0	0	1.38E-02	0	0
(a) Particulates (PM 10)	g	9.88E-03	3.14E-03	4.68E-03	0	8.45E-04	0	1.21E-03	0
(a) Organic Matter (unspecified)	g	3.47E-03	4.43E-04	1.36E-06	0	2.93E-07	3.02E-03	3.75E-06	0
(a) Hydrogen Chloride (HCl)	g	2.65E-03	2.21E-03	2.08E-05	0	1.04E-05	1.67E-04	2.38E-04	0
(a) Acetaldehyde (CH3CHO)	g	2.24E-03	1.10E-06	4.14E-11	2.24E-03	0	1.50E-08	1.10E-07	0
(a) Crotonaldehyde (C4H6O)	g	1.72E-03	0	0	1.72E-03	0	0	0	0
(a) Alkane (unspecified)	g	3.51E-04	3.10E-04	0	0	0	4.05E-05	0	0
(a) Hydrogen Fluoride (HF)	g	3.38E-04	2.97E-04	2.61E-06	0	1.30E-06	7.61E-06	2.97E-05	0
(a) Butane (n-C4H10)	g	1.15E-04	1.03E-04	0	0	0	1.16E-05	0	0
(a) Benzene (C6H6)	g	6.04E-05	5.31E-05	4.34E-07	0	1.39E-07	5.70E-06	1.03E-06	0
(a) Aromatic Hydrocarbons (unspecified)	g	3.42E-05	3.92E-06	5.70E-13	0	0	3.02E-05	7.88E-13	0
(a) Hydrogen (H2)	g	3.02E-05	4.07E-17	0	0	0	3.02E-05	0	0

(a) Toluene (C6H5CH3)	g	2.59E-05	2.30E-05	4.04E-11	0	0	2.86E-06	4.78E-08	0
(a) Magnesium (Mg)	g	2.13E-05	1.91E-05	7.99E-10	0	0	1.76E-08	2.12E-06	0
(a) Acetic Acid (CH3COOH)	g	1.82E-05	1.60E-05	0	0	0	2.14E-06	0	0
(a) Lead (Pb)	g	1.12E-05	7.05E-06	1.34E-10	0	0	3.79E-06	3.36E-07	0
(a) Zinc (Zn)	g	1.02E-05	6.35E-06	1.09E-10	0	0	3.83E-06	5.11E-09	0
(a) Chromium (Cr III, Cr VI)	g	9.46E-06	5.11E-06	2.30E-10	0	0	3.78E-06	5.67E-07	0
(a) Hydrogen Sulphide (H2S)	g	9.24E-06	0	0	0	0	9.24E-06	0	0
(a) Chlorinated Matter (unspecified, as Cl)	g	7.70E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Chlorine (Cl2)	g	7.70E-06	3.93E-06	5.78E-14	0	0	3.78E-06	2.59E-13	0
(a) Mercaptans	g	7.70E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Arsenic (As)	g	7.19E-06	3.07E-06	1.51E-10	0	0	3.78E-06	3.39E-07	0
(a) Manganese (Mn)	g	6.97E-06	6.26E-06	2.42E-10	0	0	7.93E-08	6.32E-07	0
(a) Nickel (Ni)	g	6.52E-06	6.04E-06	1.32E-09	0	0	1.45E-08	4.65E-07	0
(a) Vanadium (V)	g	5.04E-06	5.01E-06	2.87E-09	0	0	1.25E-08	1.06E-08	0
(a) Polycyclic Aromatic Hydrocarbons (PAH, unspecified)	g	5.00E-06	1.07E-06	6.34E-16	0	0	3.92E-06	8.76E-16	0
(a) Cyanide (CN-)	g	4.81E-06	4.32E-06	1.82E-10	0	0	4.50E-10	4.82E-07	0
(a) Hexane (C6H14)	g	4.29E-06	4.22E-06	4.90E-09	0	0	3.75E-08	2.57E-08	0
(a) Fluorides (F-)	g	4.02E-06	4.01E-06	4.12E-11	0	1.35E-15	0	9.24E-09	0
(a) Cadmium (Cd)	g	4.01E-06	2.09E-07	8.79E-12	0	0	3.78E-06	2.20E-08	0
(a) Mercury (Hg)	g	4.01E-06	2.11E-07	9.43E-12	0	0	3.78E-06	2.11E-08	0
(a) Copper (Cu)	g	3.84E-06	5.58E-08	1.69E-11	0	0	3.78E-06	3.77E-10	0
(a) Antimony (Sb)	g	3.82E-06	3.90E-08	6.83E-12	0	0	3.78E-06	4.36E-09	0
(a) Asbestos	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Carbon Disulphide (CS2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Fluorine (F2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Halogenated Hydrocarbons (unspecified)	g	3.78E-06	4.93E-17	3.17E-18	0	0	3.78E-06	4.38E-18	0
(a) Hydrogen Cyanide (HCN)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Sulphuric Acid (H2SO4)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Selenium (Se)	g	2.55E-06	2.30E-06	1.01E-10	0	0	5.03E-09	2.51E-07	0
(a) Potassium (K)	g	2.51E-06	2.22E-06	0	0	0	2.95E-07	0	0
(a) Heptane (C7H16)	g	2.00E-06	1.98E-06	0	0	0	1.79E-08	0	0
(a) Sodium (Na)	g	1.90E-06	1.89E-06	1.09E-09	0	0	7.57E-09	2.00E-09	0
(a) Iron (Fe)	g	1.72E-06	1.60E-06	4.10E-10	0	0	1.23E-07	7.52E-10	0
(a) Benzyl Chloride (C7H7Cl)	g	1.34E-06	1.21E-06	5.09E-11	0	0	0	1.35E-07	0
(a) Silicon (Si)	g	1.21E-06	1.10E-06	1.84E-10	0	0	1.08E-07	3.37E-10	0
(a) Isophorone	g	1.11E-06	1.00E-06	4.21E-11	0	0	0	1.12E-07	0
(a) Calcium (Ca)	g	1.10E-06	1.01E-06	1.84E-10	0	0	9.31E-08	3.37E-10	0
(a) Methyl Chloride (CH3Cl)	g	1.02E-06	9.16E-07	3.85E-11	0	0	0	1.02E-07	0

Table A3. LCI of water outputs, sorted by amount, above 1 μg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(w) Water: Chemically Polluted	liter	9.44E-02	5.18E-03	3.08E-03	0	1.54E-03	8.37E-02	9.24E-04	0
(w) Water (unspecified)	liter	7.97E-02	9.90E-09	0	4.01E-02	0	3.97E-02	0	0
(w) Sulfate (SO4--)	g	3.62E+00	3.62E+00	9.68E-10	0	0	0	1.20E-07	0
(w) Dissolved Matter (unspecified)	g	1.88E-01	8.71E-02	5.60E-02	0	2.80E-02	9.20E-05	1.65E-02	0
(w) Acids (H+)	g	1.86E-01	1.86E-01	1.01E-12	0	0	1.51E-05	4.57E-12	0
(w) Sodium (Na+)	g	8.50E-02	4.08E-02	2.30E-02	0	1.15E-02	2.83E-03	6.89E-03	0
(w) Chlorides (Cl-)	g	6.91E-02	3.64E-02	1.78E-02	0	8.90E-03	6.41E-04	5.35E-03	0
(w) COD (Chemical Oxygen Demand)	g	2.51E-02	1.13E-02	7.05E-03	0	3.52E-03	1.21E-03	2.10E-03	0
(w) Suspended Matter (unspecified)	g	2.07E-02	1.28E-02	3.78E-03	0	1.89E-03	1.12E-03	1.13E-03	0
(w) BOD5 (Biochemical Oxygen Demand)	g	3.74E-03	1.94E-03	8.34E-04	0	4.16E-04	2.95E-04	2.48E-04	0
(w) Sulphate (SO4--)	g	3.17E-03	0	0	0	0	3.17E-03	0	0
(w) Oils (unspecified)	g	1.71E-03	7.83E-04	4.13E-04	0	2.06E-04	1.81E-04	1.23E-04	0
(w) TOC (Total Organic Carbon)	g	1.20E-03	7.01E-04	9.50E-12	0	0	5.00E-04	1.31E-11	0
(w) Barytes	g	8.88E-04	7.84E-04	0	0	0	1.04E-04	0	0
(w) Calcium (Ca++)	g	6.01E-04	5.65E-04	0	0	0	3.57E-05	0	0
(w) Ammonia (NH4+, NH3, as N)	g	4.31E-04	2.06E-04	1.22E-04	0	6.09E-05	5.97E-06	3.65E-05	0
(w) Carbonates (CO3--, HCO3-, CO2, as C)	g	2.87E-04	0	0	0	0	2.87E-04	0	0
(w) Metals (unspecified)	g	1.97E-04	5.94E-05	3.45E-05	0	1.72E-05	7.56E-05	1.03E-05	0
(w) Chlorinated Matter (unspecified, as Cl)	g	1.41E-04	1.25E-04	0	0	0	1.66E-05	0	0
(w) Hydrocarbons (unspecified)	g	1.36E-04	5.77E-06	1.15E-06	0	5.73E-07	1.29E-04	3.45E-07	0
(w) Strontium (Sr II)	g	6.78E-05	6.36E-05	0	0	0	4.13E-06	0	0
(w) Phenol (C6H5OH)	g	6.76E-05	3.12E-05	1.60E-05	0	8.00E-06	7.64E-06	4.77E-06	0
(w) Potassium (K+)	g	6.71E-05	6.12E-05	0	0	0	5.97E-06	0	0
(w) Organic Dissolved Matter (unspecified)	g	5.68E-05	3.92E-06	0	0	0	5.29E-05	0	0
(w) Nitrate (NO3-)	g	5.50E-05	9.51E-06	6.58E-10	0	0	4.54E-05	1.33E-07	0
(w) Dissolved Organic Carbon (DOC)	g	5.00E-05	4.41E-05	0	0	0	5.87E-06	0	0
(w) Triethylene Glycol (C6H14O4)	g	5.00E-05	4.41E-05	0	0	0	5.87E-06	0	0
(w) Saponifiable Oils and Fats	g	4.94E-05	4.94E-05	0	0	0	0	0	0
(w) Nitrogenous Matter (unspecified, as N)	g	4.67E-05	8.76E-06	1.71E-13	0	0	3.79E-05	2.36E-13	0
(w) Iron (Fe++, Fe3+)	g	3.84E-05	3.12E-05	2.73E-10	0	1.35E-10	7.24E-06	1.17E-09	0
(w) Magnesium (Mg++)	g	3.78E-05	3.10E-05	0	0	0	6.78E-06	0	0
(w) Barium (Ba++)	g	2.99E-05	2.94E-05	3.04E-12	0	0	5.38E-07	4.20E-12	0
(w) Aluminum (Al3+)	g	2.68E-05	2.68E-05	1.54E-09	0	0	0	2.13E-09	0
(w) Fluorides (F-)	g	2.18E-05	1.62E-05	1.39E-07	0	6.96E-08	4.71E-06	6.02E-07	0
(w) Salts (unspecified)	g	1.74E-05	1.54E-05	1.75E-08	0	0	2.01E-06	2.42E-08	0
(w) Aluminium (Al3+)	g	1.11E-05	0	0	0	0	1.11E-05	0	0
(w) Aromatic Hydrocarbons (unspecified)	g	1.02E-05	9.64E-06	9.50E-13	0	0	5.81E-07	1.31E-12	0
(w) Xylene (C6H4(CH3)2)	g	1.00E-05	9.97E-06	0	0	0	5.90E-08	0	0
(w) Lead (Pb++, Pb4+)	g	8.11E-06	4.28E-06	1.27E-14	0	0	3.83E-06	1.75E-14	0
(w) Cyanide (CN-)	g	7.78E-06	4.00E-06	4.43E-15	0	0	3.78E-06	6.13E-15	0
(w) Organic Dissolved Matter (chlorinated)	g	7.70E-06	3.92E-06	0	0	0	3.78E-06	0	0
(w) Manganese (Mn II, Mn IV, Mn VII)	g	4.99E-06	1.13E-06	0	0	0	3.86E-06	0	0

(w) Zinc (Zn++)	g	4.97E-06	1.05E-06	1.27E-13	0	0	3.91E-06	3.76E-13	0
(w) Nickel (Ni++, Ni3+)	g	3.96E-06	1.62E-07	6.34E-15	0	0	3.80E-06	8.76E-15	0
(w) Copper (Cu+, Cu++)	g	3.94E-06	1.42E-07	6.34E-14	0	0	3.80E-06	8.76E-14	0
(w) Arsenic (As3+, As5+)	g	3.84E-06	5.71E-08	0	0	0	3.79E-06	0	0
(w) AOX (Adsorbable Organic Halogens)	g	3.80E-06	2.22E-08	4.05E-15	0	0	3.78E-06	5.60E-15	0
(w) Cadmium (Cd++)	g	3.79E-06	8.62E-09	3.17E-15	0	0	3.78E-06	4.38E-15	0
(w) Bromates (BrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chlorates (ClO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chlorine (Cl2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chromites (CrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Mercury (Hg+, Hg++)	g	3.78E-06	4.21E-11	1.46E-17	0	0	3.78E-06	2.01E-17	0
(w) Organic Matter (unspecified)	g	3.78E-06	1.16E-10	2.68E-12	0	0	3.78E-06	1.20E-11	0
(w) Sulphide (S--)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) VOC (Volatile Organic Compounds)	g	3.54E-06	3.54E-06	0	0	0	0	0	0
(w) Alkane (unspecified)	g	2.01E-06	1.93E-06	0	0	0	8.14E-08	0	0
(w) Benzene (C6H6)	g	2.01E-06	1.93E-06	9.62E-17	0	4.82E-17	8.17E-08	2.84E-17	0
(w) Phosphates (PO4 3-, HPO4--, H2PO4-, H3PO4, as P)	g	2.01E-06	3.21E-07	6.31E-12	0	0	1.69E-06	8.75E-12	0
(w) Toluene (C6H5CH3)	g	1.72E-06	1.65E-06	1.39E-13	0	0	7.36E-08	1.93E-13	0
(w) Titanium (Ti3+, Ti4+)	g	1.63E-06	1.44E-06	0	0	0	1.92E-07	0	0
(w) Iode (I-)	g	1.02E-06	1.02E-06	0	0	0	5.07E-10	0	0

Table A4. LCI of solid, waste, recovered matter outputs, sorted by amount, above 1 μg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(s) Calcium (Ca)	g	2.50E-04	2.21E-04	0	0	0	2.94E-05	0	0
(s) Carbon (C)	g	1.88E-04	1.66E-04	0	0	0	2.21E-05	0	0
(s) Iron (Fe)	g	1.25E-04	1.10E-04	0	0	0	1.47E-05	0	0
(s) Aluminum (Al)	g	5.53E-05	5.53E-05	0	0	0	0	0	0
(s) Sulfur (S)	g	3.31E-05	3.31E-05	0	0	0	0	0	0
(s) Phosphorus (P)	g	3.13E-06	2.77E-06	0	0	0	3.68E-07	0	0
(s) Manganese (Mn)	g	2.50E-06	2.21E-06	0	0	0	2.94E-07	0	0
Waste (total)	kg	7.24E-02	3.67E-02	2.20E-05	3.36E-02	1.06E-05	4.12E-05	2.04E-03	0
Waste: Slags and Ash (unspecified)	kg	5.26E-02	1.70E-02	7.14E-07	3.36E-02	0	2.19E-05	0.00189783	0
Waste: Mineral (inert)	kg	1.84E-02	1.84E-02	2.81E-11	0	0	4.76E-06	3.89E-11	0
Waste (unspecified)	kg	9.75E-04	8.76E-04	3.62E-08	0	0	3.02E-06	9.61E-05	0
Waste: FGD Sludge	kg	6.10E-05	5.49E-05	2.30E-09	0	0	0	6.12E-06	0
Waste (municipal and industrial)	kg	6.01E-05	2.91E-05	1.85E-05	0	9.27E-06	-2.24E-06	5.48E-06	0
Waste (hazardous)	kg	1.47E-05	4.41E-06	2.71E-06	0	1.35E-06	5.37E-06	8.07E-07	0
Waste: Non Toxic Chemicals (unspecified)	kg	7.50E-06	1.73E-07	6.59E-12	0	0	7.33E-06	9.11E-12	0
Waste (unspecified, to incineration)	kg	1.39E-06	3.36E-07	1.42E-10	0	0	1.06E-06	2.61E-10	0
Waste: Low Radioactive (class A)	kg	6.18E-08	6.18E-08	0	0	0	0	0	0
Waste: Non Mineral (inert)	kg	1.99E-08	1.99E-08	0	0	0	0	0	0
Waste: Radioactive (unspecified)	kg	9.86E-09	9.86E-09	0	0	0	0	0	0
Waste (tailings)	kg	3.78E-09	0	0	0	0	3.78E-09	0	0
Waste: Bauxite Residues (red mud)	kg	2.35E-09	2.04E-09	1.31E-10	0	0	0	1.81E-10	0
Recovered Matter (total)	kg	2.17E-04	1.96E-04	7.34E-09	0	0	1.44E-06	1.95E-05	0
Recovered Matter: Ash	kg	1.94E-04	1.75E-04	7.34E-09	0	0	0	1.95E-05	0
Recovered Matter (unspecified)	kg	2.28E-05	2.14E-05	0	0	0	1.44E-06	0	0

Table A5: All Life Cycle Inventory (LCI) Inputs

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution
(r) Barium Sulfate (BaSO4, in ground)	kg	4.33E-06	4.33E-06	0	0	0	0	0
(r) Barium Sulphate (BaSO4, in ground)	kg	5.80E-07	0	0	0	0	5.80E-07	0
(r) Bauxite (Al2O3, ore)	kg	1.28E-07	2.67E-08	4.83E-10	0	0	1.00E-07	6.67E-10
(r) Bentonite (Al2O3.4SiO2.H2O, in ground)	kg	1.52E-06	4.09E-07	0	0	0	1.11E-06	0
(r) Calcium Sulfate (CaSO4, ore)	kg	5.46E-10	5.46E-10	0	0	0	0	0
(r) Calcium Sulphate (CaSO4, ore)	kg	1.06E-07	0	0	0	0	1.06E-07	0
(r) Chromium (Cr, ore)	kg	4.72E-09	8.33E-10	0	0	0	3.89E-09	0
(r) Clay (in ground)	kg	1.21E-06	8.11E-07	0	0	0	3.99E-07	0
(r) Coal (in ground)	kg	4.58E-03	3.73E-03	3.88E-05	0	1.94E-05	3.88E-04	3.98E-04
(r) Copper (Cu, ore)	kg	4.80E-09	4.24E-09	0	0	0	5.64E-10	0
(r) Dolomite (CaCO3.MgCO3, in ground)	kg	4.54E-08	0	0	0	0	4.54E-08	0
(r) Feldspar (ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Fluorspar (CaF2, ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Granite (in ground)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Gravel (unspecified)	kg	8.97E-08	7.46E-08	0	0	0	1.51E-08	0
(r) Iron (Fe, ore)	kg	1.80E-05	1.28E-05	0	0	0	5.17E-06	0
(r) Iron Sulfate (FeSO4, ore)	kg	3.39E-14	3.39E-14	0	0	0	0	0
(r) Lead (Pb, ore)	kg	5.28E-09	1.32E-09	0	0	0	3.96E-09	0
(r) Lignite (in ground)	kg	1.30E-05	1.21E-05	0	0	0	9.14E-07	0
(r) Limestone (CaCO3, in ground)	kg	3.43E-04	2.96E-04	7.35E-06	0	3.67E-06	4.16E-06	3.27E-05
(r) Manganese (Mn, ore)	kg	5.5E-10	4.85E-10	0	0	0	6.46E-11	0
(r) Mercury (Hg, ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Natural Gas (in ground)	kg	1.61E-02	9.88E-03	1.07E-04	0	5.33E-05	6.01E-03	3.46E-05
(r) Nickel (Ni, ore)	kg	4.1E-09	2.82E-10	0	0	0	3.82E-09	0
(r) Oil (in ground)	kg	9.66E-03	2.42E-03	1.24E-03	0	6.21E-04	5.00E-03	3.74E-04
(r) Olivine ((Mg,Fe)2SiO4, ore)	kg	3.02E-08	0	0	0	0	3.02E-08	0
(r) Perlite (SiO2, ore)	kg	9.44E-07	4.38E-07	2.82E-07	0	1.41E-07	0	8.32E-08
(r) Phosphate Rock (in ground)	kg	1.71E-02	1.71E-02	0	0	0	1.65E-09	0
(r) Potassium Chloride (KCl, as K2O, in ground)	kg	5.32E-03	5.32E-03	0	0	0	9.6E-09	0
(r) Pyrite (FeS2, ore)	kg	7.87E-06	6.94E-06	0	0	0	9.24E-07	0
(r) Sand (in ground)	kg	7.72E-07	1.35E-07	2.96E-10	0	0	6.37E-07	4.09E-10
(r) Silver (Ag, ore)	kg	2.38E-11	2.1E-11	0	0	0	2.8E-12	0
(r) Sodium Chloride (NaCl, in ground or in sea)	kg	3.15E-05	2.94E-05	1.36E-10	0	0	2.04E-06	1.88E-10
(r) Sulfur (S, in ground)	kg	3.25E-06	3.25E-06	0	0	0	0	0
(r) Sulphur (S, in ground)	kg	7.50E-07	0	0	0	0	7.50E-07	0
(r) Talcum (4SiO2.3MgO.H2O, ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Titanium (Ti, ore)	kg	2.27E-09	0	0	0	0	2.27E-09	0
(r) Uranium (U, ore)	kg	1.29E-07	5.44E-08	9.24E-10	0	4.61E-10	6.93E-08	3.99E-09
(r) Zinc (Zn, ore)	kg	3.81E-09	3.08E-11	0	0	0	3.78E-09	0
Biomass (unspecified)	kg	7.18E-06	0	0	0	0	7.18E-06	0
Cropland	acres	1.44E-04	1.44E-04	0	0	0	0	0
Diesel Oil	kg	5.93E-02	0	0	0	0	0	2.97E-02
Explosive (unspecified)	kg	4E-13	4E-13	0	0	0	0	0
Ferromanganese (Fe, Mn, C)	kg	3.78E-09	0	0	0	0	3.78E-09	0
Iron Scrap	kg	4.14E-08	4.14E-08	0	0	0	0	0
Land Use (II -> III)	m2a	1.54E-10	1.54E-10	0	0	0	0	0
Land Use (II -> IV)	m2a	1.87E-10	1.87E-10	0	0	0	0	0
Land Use (III -> IV)	m2a	2.12E-13	2.12E-13	0	0	0	0	0
Nitrogen (N2)	kg	0.771419	0	0	0.771419	0	0	0
Oxygen (O2)	kg	0.192855	0	0	0.192855	0	0	0
Peat	kg	2.57E-06	0	0	0	0	2.57E-06	0
Raw Materials (unspecified)	kg	2.16E-05	2.16E-05	0	0	0	0	0
Steel	kg	3.96E-08	3.96E-08	0	0	0	0	0
Water Used (total)	liter	0.148896	0.103642	2.86E-04	3.87E-03	8.64E-05	0.0407917	2.16E-04
Water: Public Network	liter	0.116291	0.0862705	0	3.87E-03	0	0.0261464	0
Water: River	litre	4.54E-03	0	0	0	0	4.54E-03	0
Water: Sea	litre	6.65E-03	0	0	0	0	6.65E-03	0
Water: Unspecified Origin	liter	1.87E-02	1.50E-02	1.13E-04	0	0	3.46E-03	1.65E-04
Water: Well	litre	3.78E-09	0	0	0	0	3.78E-09	0

Wood	kg	1.76E-07	1.52E-07	0	0	0	2.40E-08	0

Table A6: LCI outputs above 1 μg, air emissions A-M

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(a) Acetaldehyde (CH3CHO)	g	0.002237	1.1E-06	4.14E-11	0.002235	0	1.5E-08	1.1E-07	0
(a) Acetic Acid (CH3COOH)	g	1.82E-05	0.000016	0	0	0	2.14E-06	0	0
(a) Acetone (CH3COCH3)	g	0.014445	1.9E-08	0	0.014445	0	2.53E-09	0	0
(a) Acetylene (C2H2)	g	1.06614	9.42E-12	0	1.06614	0	0	0	0
(a) Aldehyde (unspecified)	g	0.019116	0.000177	1.44E-07	0.018915	6.41E-08	3.79E-06	1.98E-05	0
(a) Alkane (unspecified)	g	0.000351	0.00031	0	0	0	4.05E-05	0	0
(a) Ammonia (NH3)	g	0.8793	0.879296	2.89E-08	0	2.65E-09	3.79E-06	2.44E-07	0
(a) Antimony (Sb)	g	3.82E-06	3.9E-08	6.83E-12	0	0	3.78E-06	4.36E-09	0
(a) Aromatic Hydrocarbons (unspecified)	g	3.42E-05	3.92E-06	5.7E-13	0	0	3.02E-05	7.88E-13	0
(a) Arsenic (As)	g	7.19E-06	3.07E-06	1.51E-10	0	0	3.78E-06	3.39E-07	0
(a) Asbestos	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Benzaldehyde (C6H5CHO)	g	0.020635	1.28E-12	0	0.020635	0	1.7E-13	0	0
(a) Benzene (C6H6)	g	6.04E-05	5.31E-05	4.34E-07	0	1.39E-07	5.7E-06	1.03E-06	0
(a) Benzyl Chloride (C7H7Cl)	g	1.34E-06	1.21E-06	5.09E-11	0	0	0	1.35E-07	0
(a) Butane (C4H10)	g	0.051061	1.52E-07	5.71E-09	0	0	0.051061	1.49E-08	0
(a) Butane (n-C4H10)	g	0.000115	0.000103	0	0	0	1.16E-05	0	0
(a) Butene (1-CH3CH2CHCH2)	g	0.32672	2.14E-07	0	0.32672	0	3.86E-09	0	0
(a) Butene (2-CH3CHCHCH3)	g	0.126102	0	0	0.126102	0	0	0	0
(a) C10 alkanes (unspecified)	g	0.114524	0	0	0.114524	0	0	0	0
(a) Cadmium (Cd)	g	4.01E-06	2.09E-07	8.79E-12	0	0	3.78E-06	2.2E-08	0
(a) Calcium (Ca)	g	1.1E-06	1.01E-06	1.84E-10	0	0	9.31E-08	3.37E-10	0
(a) Carbon Dioxide (CO2, fossil)	g	57.9034	39.1612	4.13153	0	2.08922	10.3152	2.20619	0
(a) Carbon Dioxide (CO2, Soil)	g	8.50212	8.50212	0	0	0	0	0	0
(a) Carbon Disulphide (CS2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Carbon Monoxide (CO)	g	7.61673	0.032253	0.014013	6.89991	0.006973	0.052225	0.004553	0.606798
(a) Chlorinated Matter (unspecified, as Cl)	g	7.7E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Chlorine (Cl2)	g	7.7E-06	3.93E-06	5.78E-14	0	0	3.78E-06	2.59E-13	0
(a) Chromium (Cr III, Cr VI)	g	9.46E-06	5.11E-06	2.3E-10	0	0	3.78E-06	5.67E-07	0
(a) Copper (Cu)	g	3.84E-06	5.58E-08	1.69E-11	0	0	3.78E-06	3.77E-10	0
(a) Crotonaldehyde (C4H6O)	g	0.00172	0	0	0.00172	0	0	0	0
(a) Cyanide (CN-)	g	4.81E-06	4.32E-06	1.82E-10	0	0	4.5E-10	4.82E-07	0
(a) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Ethane (C2H6)	g	0.309908	0.000447	8.42E-09	0.065631	0	0.24383	2.2E-08	0
(a) Ethylene (C2H4)	g	0.826871	0.0013	0	0.825398	0	0.000173	0	0
(a) Fluorides (F-)	g	4.02E-06	4.01E-06	4.12E-11	0	1.35E-15	0	9.24E-09	0
(a) Fluorine (F2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Formaldehyde (CH2O)	g	0.024227	1.75E-05	3.74E-06	0.024074	1.86E-06	1.43E-06	1.2E-06	0.000127
(a) Halogenated Hydrocarbons (unspecified)	g	3.78E-06	4.93E-17	3.17E-18	0	0	3.78E-06	4.38E-18	0
(a) Heptane (C7H16)	g	0.000002	1.98E-06	0	0	0	1.79E-08	0	0
(a) Hexane (C6H14)	g	4.29E-06	4.22E-06	4.9E-09	0	0	3.75E-08	2.57E-08	0
(a) Hydrocarbons (except methane)	g	0.209355	0.009555	0.003017	0	0.000104	0.010015	0.00077	0.185893
(a) Hydrocarbons (unspecified)	g	0.172597	0.007777	0.001635	0	0.002422	0.037072	0.079476	0.044214

(a) Hydrogen (H2)	g	3.02E-05	4.07E-17	0	0	0	3.02E-05	0	0
(a) Hydrogen Chloride (HCl)	g	0.002646	0.002211	2.08E-05	0	1.04E-05	0.000167	0.000238	0
(a) Hydrogen Cyanide (HCN)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Hydrogen Fluoride (HF)	g	0.000338	0.000297	2.61E-06	0	1.3E-06	7.61E-06	2.97E-05	0
(a) Hydrogen Sulfide (H2S)	g	0.23092	5.97E-05	9.11E-06	0	4.54E-06	0.230844	2.74E-06	0
(a) Hydrogen Sulphide (H2S)	g	9.24E-06	0	0	0	0	9.24E-06	0	0
(a) Iron (Fe)	g	1.72E-06	1.6E-06	4.1E-10	0	0	1.23E-07	7.52E-10	0
(a) Isophorone	g	1.11E-06	0.000001	4.21E-11	0	0	0	1.12E-07	0
(a) Lead (Pb)	g	1.12E-05	7.05E-06	1.34E-10	0	0	3.79E-06	3.36E-07	0
(a) Magnesium (Mg)	g	2.13E-05	1.91E-05	7.99E-10	0	0	1.76E-08	2.12E-06	0
(a) Manganese (Mn)	g	6.97E-06	6.26E-06	2.42E-10	0	0	7.93E-08	6.32E-07	0
(a) Mercaptans	g	7.7E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Mercury (Hg)	g	4.01E-06	2.11E-07	9.43E-12	0	0	3.78E-06	2.11E-08	0
(a) Metals (unspecified)	g	567.098	263.037	169.339	0	84.7659	3.78E-06	49.9562	0
(a) Methane (CH4)	g	3.12652	0.161389	0.001489	2.52205	0.000751	0.43867	0.002169	0
(a) Methanol (CH3OH)	g	0.018915	1.36E-08	0	0.018915	0	1.81E-09	0	0
(a) Methyl Chloride (CH3Cl)	g	1.02E-06	9.16E-07	3.85E-11	0	0	0	1.02E-07	0

Table A7: LCI outputs above 1μg, air emissions N-Z, solid outputs, and water emissions A-L

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(a) Nickel (Ni)	g	6.52E-06	6.04E-06	1.32E-09	0	0	1.45E-08	4.65E-07	0
(a) Nitrogen Oxides (NOx as NO2)	g	7.10081	1.11613	0.038865	5.63917	0.034462	0.014385	0.016796	0.241008
(a) Nitrous Oxide (N2O)	g	0.254547	0.106909	0.000411	0.146965	2.23E-05	5.54E-06	0.000235	0
(a) Organic Matter (unspecified)	g	0.003472	0.000443	1.36E-06	0	2.93E-07	0.003024	3.75E-06	0
(a) Particulates (PM 10)	g	0.009879	0.003137	0.004683	0	0.000845	0	0.001215	0
(a) Particulates (unspecified)	g	2.96859	0.078034	0.000883	2.86181	0.000441	0.004708	0.002623	0.020092
(a) Pentane (C5H12)	g	0.017916	0.000138	7.06E-09	0	0	0.017778	1.85E-08	0
(a) Polycyclic Aromatic Hydrocarbons (PAH, unspecified)	g	0.000005	1.07E-06	6.34E-16	0	0	3.92E-06	8.76E-16	0
(a) Potassium (K)	g	2.51E-06	2.22E-06	0	0	0	2.95E-07	0	0
(a) Propane (C3H8)	g	0.279602	0.000127	1.81E-11	0.154762	0	0.124713	3.43E-09	0
(a) Propylene (CH2CHCH3)	g	0.412699	4.12E-07	0	0.412699	0	5.64E-09	0	0
(a) Selenium (Se)	g	2.55E-06	2.3E-06	1.01E-10	0	0	5.03E-09	2.51E-07	0
(a) Silicon (Si)	g	1.21E-06	1.1E-06	1.84E-10	0	0	1.08E-07	3.37E-10	0
(a) Sodium (Na)	g	1.9E-06	1.89E-06	1.09E-09	0	0	7.57E-09	2E-09	0
(a) Sulfur Oxides (SOx as SO2)	g	0.566833	0.12411	0.006092	0.282624	0.003041	0	0.005331	0.145635
(a) Sulphur Oxides (SOx as SO2)	g	0.013812	0	0	0	0	0.013812	0	0
(a) Sulphuric Acid (H2SO4)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Toluene (C6H5CH3)	g	2.59E-05	0.000023	4.04E-11	0	0	2.86E-06	4.78E-08	0
(a) Vanadium (V)	g	5.04E-06	5.01E-06	2.87E-09	0	0	1.25E-08	1.06E-08	0
(a) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) VOC (Volatile Organic Compounds)	g	0.192283	0	0	0.192184	0	9.83E-05	0	0
(a) Zinc (Zn)	g	1.02E-05	6.35E-06	1.09E-10	0	0	3.83E-06	5.11E-09	0
(s) Aluminum (Al)	g	5.53E-05	5.53E-05	0	0	0	0	0	0
(s) Calcium (Ca)	g	0.00025	0.000221	0	0	0	2.94E-05	0	0
(s) Carbon (C)	g	0.000188	0.000166	0	0	0	2.21E-05	0	0
(s) Iron (Fe)	g	0.000125	0.00011	0	0	0	1.47E-05	0	0
(s) Manganese (Mn)	g	2.5E-06	2.21E-06	0	0	0	2.94E-07	0	0
(s) Phosphorus (P)	g	3.13E-06	2.77E-06	0	0	0	3.68E-07	0	0
(s) Sulfur (S)	g	3.31E-05	3.31E-05	0	0	0	0	0	0
(w) Acids (H+)	g	0.185864	0.185848	1.01E-12	0	0	1.51E-05	4.57E-12	0
(w) Alkane (unspecified)	g	2.01E-06	1.93E-06	0	0	0	8.14E-08	0	0
(w) Aluminium (Al3+)	g	1.11E-05	0	0	0	0	1.11E-05	0	0
(w) Aluminum (Al3+)	g	2.68E-05	2.68E-05	1.54E-09	0	0	0	2.13E-09	0
(w) Ammonia (NH4+, NH3, as N)	g	0.000431	0.000206	0.000122	0	6.09E-05	5.97E-06	3.65E-05	0
(w) AOX (Adsorbable Organic Halogens)	g	3.8E-06	2.22E-08	4.05E-15	0	0	3.78E-06	5.6E-15	0
(w) Aromatic Hydrocarbons (unspecified)	g	1.02E-05	9.64E-06	9.5E-13	0	0	5.81E-07	1.31E-12	0
(w) Arsenic (As3+, As5+)	g	3.84E-06	5.71E-08	0	0	0	3.79E-06	0	0
(w) Barium (Ba++)	g	2.99E-05	2.94E-05	3.04E-12	0	0	5.38E-07	4.2E-12	0
(w) Barytes	g	0.000888	0.000784	0	0	0	0.000104	0	0
(w) Benzene (C6H6)	g	2.01E-06	1.93E-06	9.62E-17	0	4.82E-17	8.17E-08	2.84E-17	0
(w) BOD5 (Biochemical Oxygen Demand)	g	0.003736	0.001943	0.000834	0	0.000416	0.000295	0.000248	0
(w) Bromates (BrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0

(w) Cadmium (Cd++)	g	3.79E-06	8.62E-09	3.17E-15	0	0	3.78E-06	4.38E-15	0
(w) Calcium (Ca++)	g	0.000601	0.000565	0	0	0	3.57E-05	0	0
(w) Carbonates (CO3--, HCO3-, CO2, as C)	g	0.000287	0	0	0	0	0.000287	0	0
(w) Chlorates (ClO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chlorides (Cl-)	g	0.06911	0.036387	0.017834	0	0.008898	0.000641	0.005351	0
(w) Chlorinated Matter (unspecified, as Cl)	g	0.000141	0.000125	0	0	0	1.66E-05	0	0
(w) Chlorine (Cl2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chromites (CrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) COD (Chemical Oxygen Demand)	g	0.025139	0.01125	0.007053	0	0.003522	0.001215	0.002099	0
(w) Copper (Cu+, Cu++)	g	3.94E-06	1.42E-07	6.34E-14	0	0	3.8E-06	8.76E-14	0
(w) Cyanide (CN-)	g	7.78E-06	0.000004	4.43E-15	0	0	3.78E-06	6.13E-15	0
(w) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Dissolved Matter (unspecified)	g	0.187815	0.087147	0.056007	0	0.028035	0.000092	0.016534	0
(w) Dissolved Organic Carbon (DOC)	g	0.00005	4.41E-05	0	0	0	5.87E-06	0	0
(w) Fluorides (F-)	g	2.18E-05	1.62E-05	1.39E-07	0	6.96E-08	4.71E-06	6.02E-07	0
(w) Hydrocarbons (unspecified)	g	0.000136	5.77E-06	1.15E-06	0	5.73E-07	0.000129	3.45E-07	0
(w) Iode (I-)	g	1.02E-06	1.02E-06	0	0	0	5.07E-10	0	0
(w) Iron (Fe++, Fe3+)	g	3.84E-05	3.12E-05	2.73E-10	0	1.35E-10	7.24E-06	1.17E-09	0
(w) Lead (Pb++, Pb4+)	g	8.11E-06	4.28E-06	1.27E-14	0	0	3.83E-06	1.75E-14	0

Table A8: LCI outputs above 1μg, water emissions M-Z, waste, miscellaneous, carbon/electrocity/stover reminders

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(w) Magnesium (Mg++)	g	3.78E-05	0.000031	0	0	0	6.78E-06	0	0
(w) Manganese (Mn II, Mn IV, Mn VII)	g	4.99E-06	1.13E-06	0	0	0	3.86E-06	0	0
(w) Mercury (Hg+, Hg++)	g	3.78E-06	4.21E-11	1.46E-17	0	0	3.78E-06	2.01E-17	0
(w) Metals (unspecified)	g	0.000197	5.94E-05	3.45E-05	0	1.72E-05	7.56E-05	1.03E-05	0
(w) Nickel (Ni++, Ni3+)	g	3.96E-06	1.62E-07	6.34E-15	0	0	3.8E-06	8.76E-15	0
(w) Nitrate (NO3-)	g	0.000055	9.51E-06	6.58E-10	0	0	4.54E-05	1.33E-07	0
(w) Nitrogenous Matter (unspecified, as N)	g	4.67E-05	8.76E-06	1.71E-13	0	0	3.79E-05	2.36E-13	0
(w) Oils (unspecified)	g	0.001706	0.000783	0.000413	0	0.000206	0.000181	0.000123	0
(w) Organic Dissolved Matter (chlorinated)	g	7.7E-06	3.92E-06	0	0	0	3.78E-06	0	0
(w) Organic Dissolved Matter (unspecified)	g	5.68E-05	3.92E-06	0	0	0	5.29E-05	0	0
(w) Organic Matter (unspecified)	g	3.78E-06	1.16E-10	2.68E-12	0	0	3.78E-06	1.2E-11	0
(w) Phenol (C6H5OH)	g	6.76E-05	3.12E-05	0.000016	0	0.000008	7.64E-06	4.77E-06	0
(w) Phosphates (PO4 3-, HPO4--, H2PO4-, H3PO4, as P)	g	2.01E-06	3.21E-07	6.31E-12	0	0	1.69E-06	8.75E-12	0
(w) Potassium (K+)	g	6.71E-05	6.12E-05	0	0	0	5.97E-06	0	0
(w) Salts (unspecified)	g	1.74E-05	1.54E-05	1.75E-08	0	0	2.01E-06	2.42E-08	0
(w) Saponifiable Oils and Fats	g	4.94E-05	4.94E-05	0	0	0	0	0	0
(w) Sodium (Na+)	g	0.084965	0.040822	0.022964	0	0.011457	0.002831	0.006891	0
(w) Strontium (Sr II)	g	6.78E-05	6.36E-05	0	0	0	4.13E-06	0	0
(w) Sulfate (SO4--)	g	3.6179	3.6179	9.68E-10	0	0	0	1.2E-07	0
(w) Sulphate (SO4--)	g	0.003175	0	0	0	0	0.003175	0	0
(w) Sulphide (S--)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Suspended Matter (unspecified)	g	0.02071	0.01279	0.003783	0	0.001889	0.001122	0.001126	0
(w) Titanium (Ti3+, Ti4+)	g	1.63E-06	1.44E-06	0	0	0	1.92E-07	0	0
(w) TOC (Total Organic Carbon)	g	0.0012	0.000701	9.5E-12	0	0	0.0005	1.31E-11	0
(w) Toluene (C6H5CH3)	g	1.72E-06	1.65E-06	1.39E-13	0	0	7.36E-08	1.93E-13	0
(w) Triethylene Glycol (C6H14O4)	g	0.00005	4.41E-05	0	0	0	5.87E-06	0	0
(w) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) VOC (Volatile Organic Compounds)	g	3.54E-06	3.54E-06	0	0	0	0	0	0
(w) Water (unspecified)	liter	0.079711	9.9E-09	0	0.040058	0	0.039654	0	0
(w) Water: Chemically Polluted	liter	0.094402	0.00518	0.003084	0	0.001539	0.083674	0.000924	0
(w) Xylene (C6H4(CH3)2)	g	0.00001	9.97E-06	0	0	0	5.9E-08	0	0
(w) Zinc (Zn++)	g	4.97E-06	1.05E-06	1.27E-13	0	0	3.91E-06	3.76E-13	0
(wr) Radium (Ra226)	kBq	1.01E-06	1.01E-06	0	0	0	0	0	0
(wr) Radium (Ra228)	kBq	1.01E-06	1.01E-06	0	0	0	0	0	0
(wr) Thorium (Th228)	kBq	2.03E-06	2.03E-06	0	0	0	0	0	0
Farmland	acres	0.000144	0.000144	0	0	0	0	0	0
Nitrogen (N2)	kg	0.771419	0	0	0.771419	0	0	0	0
Oxygen (O2)	kg	0.039588	0	0	0.039588	0	0	0	0
Recovered Matter (total)	kg	0.000217	0.000196	7.34E-09	0	0	1.44E-06	1.95E-05	0
Recovered Matter (unspecified)	kg	2.28E-05	2.14E-05	0	0	0	1.44E-06	0	0
Recovered Matter: Ash	kg	0.000194	0.000175	7.34E-09	0	0	0	1.95E-05	0
Waste (hazardous)	kg	1.47E-05	4.41E-06	2.71E-06	0	1.35E-06	5.37E-06	8.07E-07	0

Waste (municipal and industrial)	kg	6.01E-05	2.91E-05	1.85E-05	0	9.27E-06	-2.2E-06	5.48E-06	0
Waste (total)	kg	0.072405	0.036653	0.000022	0.033637	1.06E-05	4.12E-05	0.002041	0
Waste (unspecified)	kg	0.000975	0.000876	3.62E-08	0	0	3.02E-06	9.61E-05	0
Waste (unspecified, to incineration)	kg	1.39E-06	3.36E-07	1.42E-10	0	0	1.06E-06	2.61E-10	0
Waste: FGD Sludge	kg	0.000061	5.49E-05	2.3E-09	0	0	0	6.12E-06	0
Waste: Mineral (inert)	kg	0.018379	0.018374	2.81E-11	0	0	4.76E-06	3.89E-11	0
Waste: Non Toxic Chemicals (unspecified)	kg	7.5E-06	1.73E-07	6.59E-12	0	0	7.33E-06	9.11E-12	0
Waste: Slags and Ash (unspecified)	kg	0.052564	0.017006	7.14E-07	0.033637	0	2.19E-05	0.001898	0
Corn Stover (raw)	kg	0.343916	0	0	0.343916	0	0	0	0
Electricity	MJ elec	0.016042	0.038064	0	-0.03502	0	0.009756	0.003241	0

Database Contents-to be stored electronically. A confidential copy will be given to DOE.

Economic Calculations

ECONOMICS FOR PYROLYSIS OIL UPGRADING

Assumes $100/bbl gasoline

	T/day	density	bbl/d	l/l	$/ton	$/gal	$MM	$MM/yr	SCFB	SCFD	% C	Carbon recover
Type of feed	**Mixed Wood**											
Size of Pyrolysis unit	2000										49.58	
Cost of Pyrolysis Unit						**0.51**						
Yield of Pyrolysis oil	0.7											
Amount of Pyrlysis oil	1400	1.18	7463.299			**0.59**		67.5033			45.7	0.64521
Hydrogen for HT	16.0454			157	**2100**			12.2988	932.1204			
Yield from HT	0.485											
Amount of Feed to HC	679	1.06	4029.477								75.4	0.5163
Hydrogen for HC	16.83864684			292	**2100**			12.90682	1733.625			
Total H2	32.88404684							25.20562	2665.746	9.992938		
Total methane required for H2	118.2879383										**75**	
Total cost								92.70892				
Yield from HCK	0.746											
Yield Oil T/D Case 2	506.534	0.85	3748.647								86.8	0.4433
Overall yields	0.253267											
Final product sample #	HC16											
% diesel boiling range	0.333		1248.299			**2.38**		45.5447				
% Gasoline boiling range	0.553		2073.002			**2.38**		75.63429				
% VGO range	0.114		427.3457			1.8		11.79218				
Total prodcut value			3748.647					132.9712				
Total Incentive								40.26225				
Fuel gas from HT	51.17											
Fuel Gas from HCK	78.085											
Total HC available	129.255											
Hydrotreating conditions												
LHSV	0.22											
Pressure	2025											
Temp C	342											
Catalyst	Pd/C											
Cost of HT per annual gallon	0.169602087						19.40458					
Utilities for HT	1252.2048	0.07						0.701235				
Hydrocracking conditions												
LHSV	0.25											
Pressure	1515											
Temp C	405											
Catalyst	NiMo											
Cost of HCK	0.508806262						31.42992					
Utilities of HCK	1257.408651	0.07						0.704149				
Total capital							50.8345					
	T/day	density	bbl/d	l/l	$/ton	$/gal	$MM	$MM/yr	SCFB	SCFD		

Type of feed	**New Corn Stover**														
Size of Pyrolysis unit	2000										42.29		845.8		907.14713
Cost of Pyrolysis Unit						**0.51**									
Yield of Pyrolysis oil	0.473														
Amount of Pyrlysis oil	946	1.16	5130.007			**0.59**		46.39938			33.77	0.3777066	319.4642		
Hydrogen for HT	4.281596			62	**2100**			3.281843	368.0985						
Yield from HT	0.466														
Amount of Feed to HC	440.836	1.04	2666.42								76	0.3961165	335.0354		
Hydrogen for HC	18.45774047			493	**2100**			14.14786	2926.977						
Total H2	22.73933647							17.4297	3295.075	8.349781					
Total methane required for H2	81.79617436										**75**		61.34713		
Toatl Cost of feeds								63.82908							
Yield from HCK	0.795														
Yield Oil T/D Case 2	350.46462	0.87	2534.018								86.8	0.3596634	304.2033	0.359663	0.3353406
Overall yields	0.17523231														
Final product sample #	HC12 in database		5/11/07 02:50-10:20												
Gas from HT	43.516														
Gas from HCK	37.47106														
fr diesel boiling range	**0.333**		843.8281			**2.38**		30.78741							
fr Gasoline boiling range	**0.553**		1401.312			**2.38**		51.12743							
fr VGO range	**0.114**		288.8781			1.8		7.971302							
Total product			2534.018					81.91484							
total incentive								18.08576							
Fuel gas from HT	8.26804														
Fuel Gas from HCK	37.47106														
Total HC available	45.7391														
Hydrotreating conditions		kw													
LHSV	0.26														
Pressure	1944														
Temp C	343														
Catalyst	Pd/C														
Cost of HT per annual gallon	0.169602087						13.33802								
Utilities for HT-kw	339.9026262	**0.07**						0.190345							
Cost of Catalyst															
Hydrocracking conditions															
LHSV	0.25														
Pressure	1533														
Temp C	410														
Catalyst	NiMo-S														
Cost of HCK per annual gallon	0.508806262						20.79808								
Utilities of HCK-kw	1404.818819	**0.07**						0.786699							
Total Capital							34.13609								

MIXED WOOD CASE

HT fuel gas	vol%	MW	wt	wt%
Co2	55	44	2420	0.57062
CO	0.5	32	16	0.003773
c1	24	16	384	0.090545
c2	4	32	128	0.030182
c3	2.5	44	110	0.025937
c4	0.5	58	29	0.006838
c5	0.5	72	36	0.008489
c6+	13	86	1118	0.263617
			4241	1
sum Hydrocarbons				0.42938

Corn Stover case

HT fuel gas	vol%	MW	wt	wt%
Co2	75	44	3300	0.812408
CO	0	32	0	0
c1	14	16	224	0.055145
c2	6	32	192	0.047267
c3	2	44	88	0.021664
c4	0	58	0	0
c5	0	72	0	0
c6+	3	86	258	0.063516
			4062	1
sum Hydrocarbons				0.187592

Pyrolysis Oil to Gasoline-Final Report

Cooperative Research and Development Agreement

CRADA No. PNNL/259 between

Battelle
As operator of Pacific Northwest National Laboratory ("PNNL")
Under its U.S. Department of Energy Contract
No. DE-AC05-76RLO 1830 (hereinafter "Battelle" or "Contractor")

And
Midwest Research Institute
As operator of the National Renewable Energy Laboratory ("NREL")
Under is U.S. Department of Energy Contract
No. DE-AC36-99GO10337 (hereinafter "MRI" or "Contractor")

And

UOP LLC

Richard Marinangeli (UOP), Edwin Boldingh (UOP), Stella Cabanban (UOP)
Zhihao Fei (UOP), Graham Ellis (UOP)
Rich Bain (NREL), David Hsu (NREL)
Doug Elliott (PNNL)

Executive Summary

The use of sustainable lignocellulosic biomass can provide an alternative source of liquid hydrocarbon fuels without impacting the food supply. Fast pyrolysis and subsequent catalytic hydroprocessing can produce infrastructure compatible fuels from lignocellulosic feedstocks. Recent results in the CRADA project involving UOP LLC, PNNL and NREL have demonstrated an economically viable process in laboratory scale tests.

Introduction

Biofuel production is expanding worldwide because of increasing petroleum prices, government mandates and incentives/commitments to green-house gas reduction. Today's biofuels are produced almost exclusively from food based sources.

The future widespread use of biofuels will largely depend on:

- The availability of a sustainable supply of non-food based renewable feedstock.
- The development of new technology to produce fuels from the unique composition of these highly oxygenated feedstocks.

Availability of non-food based feedstock

A feasibility study conducted by the U.S. Depts. of Agriculture and Energy concluded that the U.S. has the potential to produce a billion dry tons of biomass per year. The large scale availability of ligno-cellulosic biomass could potentially supply a high percentage of future liquid transportation fuels (see figure below) when commercial conversion processes become available. (Purvin&Gertz; USDA FSA Circulars)

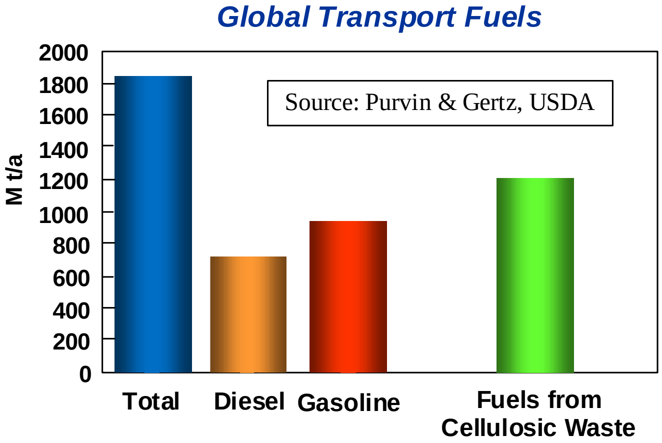

Figure 1 Global Transport Fuel Potential

Development of conversion technology

In 2006, a collaboration between UOP and the national labs, Pacific Northwest National Laboratory and National Renewable Energy Laboratory was established to identify practical processing options. The focus of this study was on a processing route for producing biofuels from forest and agro-wastes by first converting the biomass to fast pyrolysis oil and then upgrading the fast pyrolysis oil to transportation fuels.

The objective is to produce fuel that is indistinguishable from petroleum-based fuel to take advantage of existing transportation and distribution infrastructure.

Process Description

The first step is the fast pyrolysis of the lignocellulosic biomass. This is a thermochemical process with the potential to convert the large volumes of cellulosic biomass available in the U.S. and globally into liquid fuels.

A solid biomass feedstock is injected into a fluidized bed with high heat transfer capability for short contact times followed by separating char and then quenching to condense a liquid bio-oil in 50-75% yields, with gas and char forming the balance. This bio-oil contains the thermally cracked molecular fragments of the original cellulose, hemi-cellulose, and lignin fractions comprising the original biomass. It also contains a high percentage of water, often as high as 30% as well as significant organic oxygen remaining in the thermally cracked fragments.

In the second step, the pyrolysis oil is converted to a fuel by hydroprocessing. This, in itself, is a 2-step process. The first step greatly reduces the oxygen content, which significantly improves the thermal stability. The stabilized oil is then further hydrodeoxygenated to produce a hydrocarbon fuel with properties similar to petroleum based hydrocarbon fuels.

Hydroprocessing of the fast pyrolysis oil typically yields a product in which 20% is gasoline range hydrocarbons and another 20% is in the diesel range. The remaining 60% is mostly light ends, CO_2 and water.

The table below shows the composition of the gasoline range product. The (RON+MON)/2 of this cut was about 90.

Hydroprocessed bio-oil (from mixed wood)			*Gasoline*
	Min	*Max*	*Typical*
Paraffin, wt%	5.2	9.5	9
Iso-Paraffin, wt%	16.7	24.9	35
Olefin, wt%	0.6	0.9	4
Naphthene, wt%	39.6	55.0	7
Aromatic, wt%	9.9	34.6	38
Oxygenate, wt%		0.8	7

Table 1 Comparison of Fuel Properties 1

The economics for producing gasoline range and diesel range fuels from pyrolysis oil are shown in the next table, assuming $25/bbl pyrolysis oil cost and $100/bbl fuel value (based on the average December 2007 gasoline price). The tables show that this process can make a fungible fuel that meets the current DOE state of technology.

	Wood	*Corn Stover*	*DOE Bioethanol*	
			2007	*2012 Goal*
Cost \$/gal, Hydrocarbon	2.50	2.82	-	-
Cost \$/gal, Ethanol equivalent	1.55	1.74	2.43	1.36
Gallons of ethanol equivalent/ton biomass	120	87	71.9	89.7
% Carbon recovery	44	36	27.5	34.5

All cases based on 2007\$, \$46/ton biomass, \$100/bbl fuel value (\$2.38/gallon), 10% ROI

Table 2 Cost Estimates for the Production of Naphtha, Diesel and Fuel Oil Product from Pyrolysis Oils

Conceptual Pyrolysis Oil based Refinery

A proposed refining scheme is shown below. In this case several distributed pyrolysis units could supply a central bio-refinery for conversion to fungible transportation fuels.

Processing of fast pyrolysis oil requires more development, e.g. improved stability, to enable large scale commercially viable operations. In the long term, however, fast pyrolysis oil production can be increased to exploit the large amount of sustainable cellulosic biomass available.

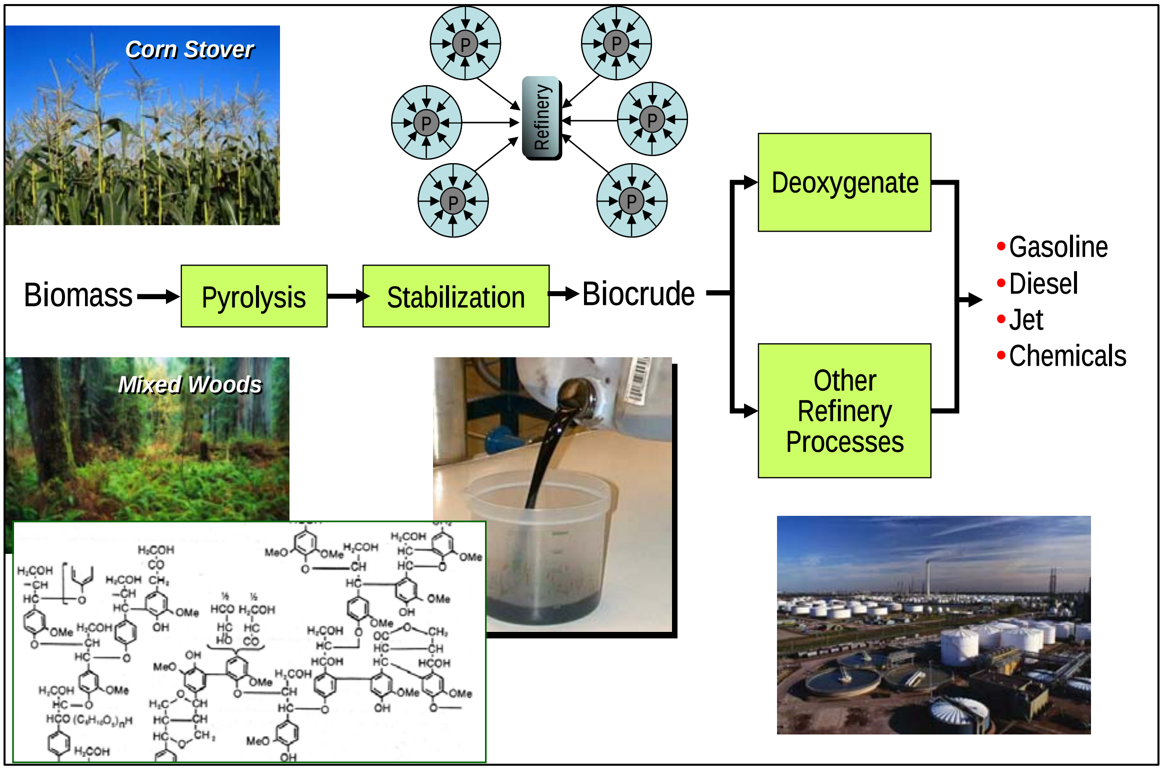

Figure 2 Proposed Refining Scheme

Study Goals and Basis

In the DOE report "Opportunities for Biorenewables in Oil Refineries," refined pyrolysis oils were shown to have the potential to replace a significant portion of transportation fuels (60%). This thermal processing route can effectively utilize a vast majority of the 1 billion tons of biomass projected to be available in the United States, including those feedstocks unsuitable for fermentation. The pyrolysis pathway therefore provides the opportunity for increasing the impact of biofuels while leveraging existing processing and distribution systems.

In 2005, UOP, MRI and Battelle performed proof-of-principle experiments that indicated that pyrolytic lignin could be converted to gasoline with reasonable H2 consumption using mild hydrotreating followed by hydrocracking. A key finding was that mild hydrotreating conditions promote decarboxylation which significantly reduces the hydrogen consumption. The economics of this process are attractive when the price of crude oil increases (3 year payback for $50/bbl crude) or the price of pyrolysis oil decreases.

The desired outcome of this CRADA is to provide a foundation for development of an economically viable process for upgrading pyrolysis oil to gasoline. The purpose of this phase is to gain a fundamental understanding of the process sensitivity to pyrolysis oil feed properties. At the end of this project recommendations for a standard pyrolysis feed will be made and initial feed standards will be defined. The output of this analysis will be used in a stage gate development process to help decide whether further commercial development will proceed.

The project plan includes a series of analysis, research, development, and design efforts targeted at assessing the potential for the production of gasoline from pyrolysis oil derived from a diverse range of biomass feedstocks.

Barriers Addressed:

The primary barriers being addressed are technical issues related to the utilization of pyrolysis oil for transportation fuels. For pyrolysis oils to be widely accepted as a feedstock for transportation fuels an economically viable catalytic conversion process is required. In addition, a standard for pyrolysis oil feeds is highly desirable.

Rationale:

In the DOE report "Opportunities for Biorenewables in Oil Refineries," (Marinangeli, 2006)refined pyrolysis oils were shown to have the potential to replace a significant portion of transportation fuels. This thermal processing route can effectively utilize a vast majority of the 1.3 billion tons of biomass projected to be available in the United States, including those feedstocks unsuitable for fermentation. The pyrolysis pathway therefore provides the opportunity for increasing the impact of biofuels while leveraging existing processing and distribution systems. The short term option produces gasoline and refinery fuel, while longer term advanced thermal conversion configurations may have the potential to produce both gasoline and ethanol. The project supports the 30 x 30 goal of replacement of 30% of 2005 gasoline with renewable fuels by 2030 and supports the $1.07 goal ($2005) by investigating alternative higher value uses of lignin rich streams in a biochemical biorefinery.

Fast Pyrolysis

NREL Thermochemical Pilot Development Unit (TCPDU)

A process flow diagram of the TCPDU, configured for pyrolysis, is shown in Figure 1. The feeding system consists of a loss-in-weight feeder with a 0.450-m^3 hopper (200 kg capacity). Pelletized biomass is metered into a crusher that grinds the material to minus 2.3 mm particle size. The material passes through a pair of rotary valves that isolate the process from the feeding system, into an eductor where hot nitrogen (100°C) is used to feed biomass into the pyrolysis reactor at a rate from 5 to 25 kg/hr.

An entrained flow reactor is used in pyrolysis experiments. The reactor is a 26-meter (85 ft) long by 3.81-cm (1.5 inch diameter tube with 11 independently controlled electrically heated zones used to raise the product temperature to a maximum of 950˚C. For pyrolysis experiments the nominal reactor temperature is varied between 500 and 600°C. The volume of the thermal cracker is approximately 0.028m^3 (1.0 ft^3).

The products then enter two cyclone separators in series with 10.2 cm (4 inch) and 7.6 cm (3 inch) diameter barrels, respectively. The solids removed in these cyclones are collected in char pots below the cyclones. The char pots are emptied periodically into an intermediate vessel where the char is cooled using nitrogen gas. The cooling vessel is operated like a lock hopper. Once the char has cooled, it is transferred from the intermediate vessel into a bag for further analysis or disposal. The products leaving the cyclones moves quickly through the remaining 3.81 cm (1.5”) diameter pipe to the scrubber system. The volume of the piping between the cyclones and the condensation system is about 7.08 liters (0.25 ft^3). Heated sample ports are available in this section of pipe for removing process gas or vapors, and directing it to on-line analytical equipment for compositional analysis.

The scrubber operation consists of a conical vessel (25.4 cm to 5.08 cm taper) for mixing hot gases with cooling liquid followed by a 25.4 cm (10 inch) diameter vessel with nozzles in the top to spray in cooling liquid. The liquid flow rate is about 113.6 liters/minute (30 gallon per minute). This is sufficiently high to keep the cooling liquid from heating up significantly as it contacts the hot gases and vapors entering the scrubber vessels. The scrubbing liquid passes through nominal 25-micron filters then to a heat exchanger to remove heat from the cooling liquid. A phase separator after the heat exchanger allows the water and water soluble materials to drain out to the settling tank with the scrubbing liquid recirculating through the top of the separator back to the first scrubber vessel. Dodecane is re-circulated in the scrubbing loop as the cooling liquid, so over time hydrocarbon compounds such as benzene and naphthalene accumulate.

Condensed steam from the reactor is pumped from the middle phase of the settling tank through a series of filters and into a stripping column where light hydrocarbons are removed by nitrogen. The stripped gases and nitrogen are directed to the thermal oxidizer for destruction. Entrained particles or droplets exiting the scrubber vessels are removed by nominal 2-micron filters. Remaining aerosols are also removed at this point. Typically, an insignificant quantity of liquid is removed from this vessel during operation. However, this is dependent on the feedstock and mass flow rate through the system. Process pressure is about 68.9 kPag (10 psig). Unless the process gas is to be used for some other purpose, it is sent to a thermal oxidizer where it is combusted at 650°C.

Extensive analytical instrumentation is available for determining gas composition at the exit of the scrubbing system. With steam and other condensable vapors removed from the product gas stream compositions can be measured with three on-line, continuous, non-dispersive infrared (NDIR) chemical analyzers to monitor CO, CO_2, and CH_4; a thermal conductivity H_2 analyzer; a paramagnetic O_2 analyzer; a four channel, rapid analysis gas chromatograph that cycles every 2 minutes for measuring permanent gases and hydrocarbons up to C4; and a transportable molecular beam mass spectrometer (TMBMS) for continuous, real-time monitoring of all gas phase products with particular emphasis on tars and heteroatom products**.**

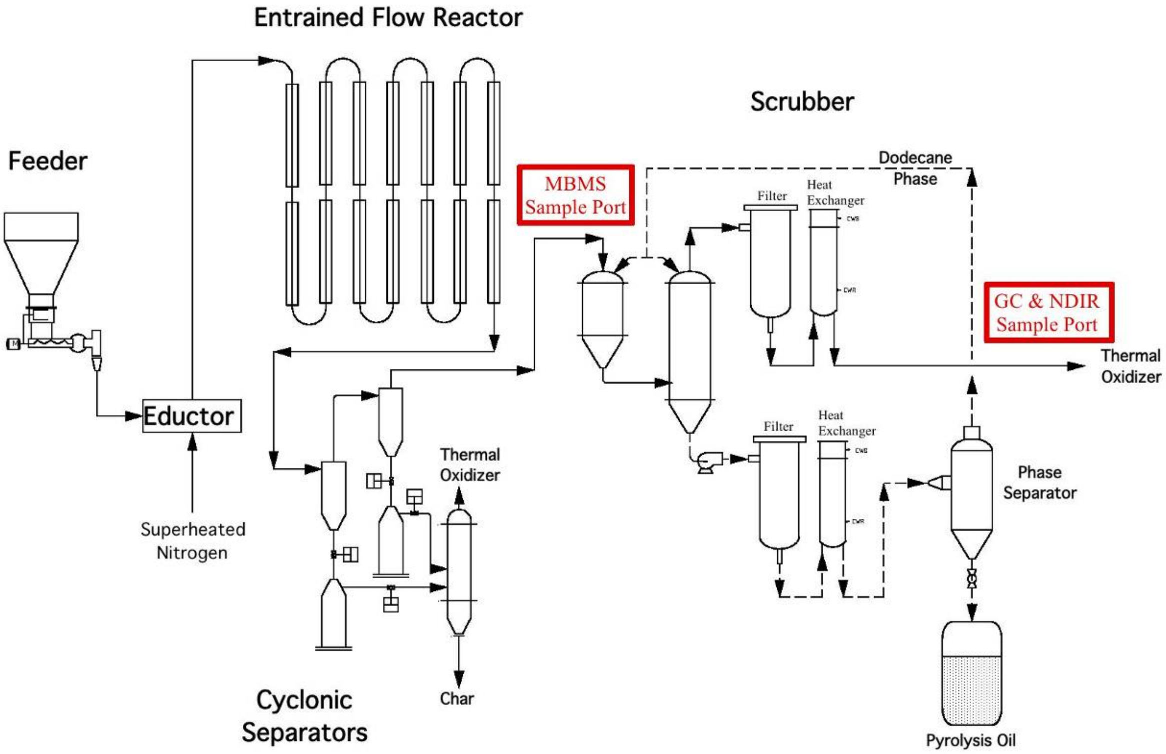

Figure 3 : NREL Thermochemical Process Development Unit, Configured for Entrained Flow Pyrolysis

Oil Production Campaign One

NREL performed three (3) pyrolysis experiments in the TCPDU to produce substantial quantities of pyrolysis oil as feed for hydrotreating and hydrocracking experiments at UOP and PNNL. Two of the experiments were performed using corn stover feedstock, and one experiment was performed using mixed wood feed (normally referred to as Vermont mixed wood). Woody materials and corn stover are abundant, available resources (each potentially available in quantities in excess of 250 million tons annually(Perlack, 2005)) that can have significant impact on biofuels production. Analyses were performed to characterize both the biomass feed and the product pyrolysis oil. Material balance data were collected and summarized for use in technoeconomic analyses. Samples of the oil produced were shipped to UOP and PNNL for additional analyses and upgrading experiments. Feed and char analyses included ultimate analysis, proximate analysis, ash component analysis, and heating value. Oil analyses included ultimate analysis, water content, ash component analysis, density, and pH. NREL also performed some limited on-line molecular beam mass spectrometry analysis to investigate compound identification.

An analysis of the feeds used is given in Table 3; a summary of the tests and material balances achieved is given in Tables 2 – 4.

Table 3: Feed Analyses Bio-Oil Production, Campaign One

Proximate, Ultimate, and Elemental Ash Analyses for Feeds

	DDGs	Corn Stover 1	Corn Stover 2	Mixed Wood
Proximate Analysis (wt% as received)				
Moisture		**5.83**	**5.78**	**4.26**
Ash		**10.29**	**10.69**	**0.55**
Volatile Matter		**68.54**	**67.35**	**82.96**
Fixed C		**15.34**	**16.18**	**12.23**
HHV (Btu/lb)		**6919**	**6824**	**8098**
Ultimate Analysis (wt% as received)				
C		**43.85**	**44.00**	**49.58**
H		**4.60**	**4.68**	**5.54**
N		**0.74**	**0.68**	**0.23**
O (by difference)		**34.39**	**33.90**	**39.83**
S		**0.08**	**0.08**	**0.01**
Cl		**0.22**	**0.19**	**0.00**
H/C		**1.25**	**1.27**	**1.33**
Elemental Ash Analysis (wt% of ash as oxide)				
SiO_2		**66.45**	**66.11**	**17.64**
Al_2O_3		**4.85**	**5.23**	**5.05**
TiO_2		**0.04**	**0.13**	**0.27**
Fe_2O_3		**0.96**	**0.94**	**2.64**
CaO		**4.00**	**3.80**	**26.60**
MgO		**1.58**	**1.63**	**4.33**
Na_2O		**0.99**	**1.04**	**1.77**
K_2O		**14.80**	**14.60**	**15.90**
P_2O_5		**2.87**	**2.75**	**2.56**
SO_3		**0.82**	**0.80**	**1.70**
Cl		**1.53**	**1.51**	
CO_2		**0.70**	**0.94**	

Table 4a. : Campaign One ,Test Summary Information

	Corn Stover 1	Mixed Wood	Corn Stover 2
Conditions			
Temperature, (deg C)	480	480	460
Est Residence Time (sec)	1.6	1.6	1.6
Nominal Feed Rate (kg/hr)	20.0	20.0	20.0
Nitrogen Carrier Rate (kg/hr)	20.0	20.0	20.0
Nominal Test Duration (hr)	10.1	8.5	15.2
Results			
Total Feed (kg / %)	202.8	175.8	303.3
Pyrolysis Liquids (kg)	107.3	123.2	143.7
Est % Aq	85.0		
Char (kg)	51.4	20.5	75.0
Gas(kg)	33.8	32.3	50.3
Water in Gas (Psat=24 mmHg, Pt=620 mmHg)	7.8	6.5	6.3
Overall Material Balance, wt %	98.7	103.8	90.8
Char	25.3	11.7	24.7
Oil	52.9	70.1	47.4
Wet Gas	20.5	22.1	18.7
C	95.7	99.3	104.2
H	90.3	96.8	92.8
O	104.9	109.8	96.9
Ash	94.6	134.4	89.3

Table 4b. Test One Summary Information (cont.)

	Corn Stover	Mixed Wood	Corn Stover 2
Feed			
Amount, kg	202.8	175.8	303.3
C, wt %	42.29	49.58	42.29
H	4.91	5.54	4.91
N	0.74	0.23	0.74
O	33.40	39.83	33.40
Ash	10.47	0.55	10.47
H2O	8.08	4.26	8.08
Oil			
Amount, kg	107.3	123.2	143.7
Percent Aqueous	85.00	-	
Organic			
Amount, kg	16.1	123.2	143.7
C, wt %	55.38	44.94	51.19
H	7.18	6.92	7.61
N	1.39	0.18	0.77
S			0.08
O	36.05	47.96	40.20
Ash	0.20	<0.05	0.15
Aqueous			
Amount, kg	91.21		
C, wt %	35.94		
H	7.85		
N	0.87		
O	55.34		
Ash	0.24		
H2O			

Table 4c. Campaign One Test Summary Information (cont.)

	Corn Stover	Mixed Wood	Corn Stover 2
Char			
Amount, kg	51.4	20.5	75.0
C, wt %	55.47	89.10	57.82
H	2.14	1.88	2.41
N	0.70	0.14	0.72
S			0.01
O	3.04	2.76	1.78
Ash	38.59	6.34	37.26
Gas			
Amount, kg	33.8	32.3	50.3
Ave Composition, mole% (Dry, N2, He Free)			
H2	-	-	-
CO	35.39	53.13	28.20
CO2	55.30	32.20	65.90
CH4	4.40	8.72	3.60
Acetylene	1.86	1.50	-
Ethylene	1.44	2.68	1.20
Ethane	0.11	0.08	-
Propylene	0.72	1.07	0.40
Propane	-	-	-
1-Butylene	0.57	0.52	0.70
2-t-Butylene	0.22	0.11	-
2-c-Butylene	-	-	-
Total	100.00	100.00	100.00
Benzene (ppmv)	7.34	-	-

Oil Production Campaign Two

Over a four week period in February and March 2008 150 gallons of pyrolysis oil were produced in NREL's TCPDU at three reactor temperatures; the most pyrolysis oil ever produced in this facility in one month. Most of the oil was produced for the joint CRADA project with UOP/NREL/PNNL and will be used as the feedstock for catalytically upgrading produced oil to make gasoline/diesel products. The additional oil will be held in reserve to provide uniform pyrolysis oil for use in upcoming pyrolysis solicitations. Usually used for steam gasification experiments (700°C to 950°C), the TCPDU reactor and downstream equipment presented different challenges when running at pyrolysis conditions (500°C to 600°C).

At the lowest temperature the oil yield was 57%, char yield was 13%, and light gas yield (carbon monoxide, carbon dioxide, etc.) was 24%; 95% of mass was accounted for in the mass balance. As expected, oil yield decreased with increasing temperature to 40% at the highest temperature. Qualitatively, the low-temperature oil was dark brown and thick, while the higher temperature oil was thinner and lighter brown. A significant amount of process and analytical data and product samples were collected during the course of the experiments,

A run summary and analysis of the feed is given in Table 5; pyrolysis oils analyses are given in Table 6; and gas analyses and char analyses are given in Table 7.

Temperature	500 ^{o}C			550 ^{o}C		600 ^{o}C	
Yields	kg		wt %	kg	wt %	kg	wt%
Feed	622.40		100.00	360.80	100.00	465.70	100.00
Oil	322.27		51.78	177.59	49.22	185.09	39.74
Gas	228.50		36.71	152.45	42.25	271.11	58.22
Char	73.95		11.88	36.71	10.17	42.13	9.05
Other Liquids	8.54		1.37	9.18	2.54	7.99	1.72
Product			101.74		104.19		108.72
Carbon			95.16		98.76		94.62
Hydrogen			111.17		113.81		115.50
Feed Analysis							
Moisture	5.23	+/-	0.27				
Ash	0.48		0.04				
Volatile Matter	81.39		1.31				
Fixed C	12.91		1.12				
HHV (Btu/lb)	7,879		65				
Ultimate Analysis (wt% as received)							
C	47.51	+/-	0.92				
H	5.24		0.09				
N	0.28		0.13				
O (by difference)	41.05		1.02				
S	0.21		0.13				
Cl	0.01		0.00				
Elemental Ash Analysis (wt% of ash as oxide)							
SiO_2	3.44	+/-	0.86				
Al_2O_3	0.39		0.23				
TiO_2	0.02		0.02				
Fe_2O_3	0.64		0.13				
CaO	41.66		3.29				
MgO	1.98		0.16				
Na_2O	0.37		0.18				
K_2O	20.40		1.25				
P_2O_5	2.62		0.25				
SO_3	1.51		0.66				
Cl	0.05		0.03				

Table 5. Campaign Two, Oak Pyrolysis, Yields and Feed Composition

Temperature	500 °C	550 °C	600 °C	
Oil				
Ultimate, As Received, wt%				
Water	24.6	25.3	42.8	
Ash	0.064	0.028	0.065	
C	42.76	42.83	29.82	
H	4.65	4.71	3.31	
N	0.01	0.01	0.01	
S	0.019	0.009	0.018	
O	27.91	27.12	23.99	
Dry Oil, wt %				
C	56.75	57.35	52.18	
H	6.17	6.31	5.79	
N	0.01	0.01	0.01	
S	0.03	0.01	0.03	
O	37.04	36.32	41.98	
Molar Ratio, C = 1				
C	1.0000	1.0000	1.0000	
H	1.2957	1.3103	1.3225	
N	0.0002	0.0001	0.0002	
S	0.0002	0.0001	0.0002	
O	0.4899	0.4753	0.6039	
Metals, mg/kg				
Ti	5.9	5.5	6.0	SW846-6010B
Fe	26	23	42	ASTM D3682
Ca	316	242	311	ASTM D3682
Mg	39.6	36.5	35.6	ASTM D3682
Na	839	425	345	ASTM D3682
K	111	84.7	138	ASTM D3682
P	<10	<10	<10	SM 4500-P M-C

Table 6. Campaign Two, Oak Pyrolysis, Pyrolysis Oil Analysis

Temperature	500 ^{o}C			550 ^{o}C			600 ^{o}C		
Gas Composition (mol%, N2, He free)									
H2	0.35	+/-	0.80	2.19	+/-	0.78	6.46	+/-	0.15
CO	37.10		4.02	44.84		3.82	51.30		0.16
CO2	19.23		1.49	13.86		0.55	10.07		0.12
CH4	10.01		0.66	10.13		0.52	10.92		0.06
C2H6	0.00		0.00	0.00		0.00	0.00		0.00
C2H4	2.22		0.21	2.73		0.19	3.44		0.04
C2H2	1.10		0.16	1.26		0.12	1.50		0.03
C3H8	0.00		0.00	0.00		0.00	0.23		0.02
C3H6	0.86		0.14	1.08		0.13	1.31		0.02
1-C4H8	0.43		0.05	0.52		0.07	0.63		0.03
2-cis-C4H8	0.10		0.04	0.11		0.09	0.14		0.03
2-trans-C4H8	0.14		0.02	0.16		0.09	0.12		0.02
H2O	28.46		3.53	23.12		5.27	13.88		0.19
	100.00			100.00			100.00		
Char									
Proximate Analysis (wt% as received)									
Moisture	0.02			0.01			0.01		
Ash	4.38			3.79			4.59		
Volatile Matter	23.25			21.66			19.11		
Fixed C	72.36			75.55			76.30		
HHV (Btu/lb)	13,115			13,178			13,514		
Ultimate Analysis (wt% as received)									
C	82.64			83.07			84.44		
H	2.73			2.80			2.56		
N	0.29			0.22			0.41		
O (by difference)	9.93			10.12			7.99		
S	0.02			0.01			0.01		
Cl	0.01			0.01			0.01		
Elemental Ash Analysis (wt% of ash as oxide)									
SiO2	5.99			3.07			3.06		
Al2O3	0.52			0.64			0.46		
TiO2	0.04			0.06			0.04		
Fe2O3	1.15			0.60			0.63		
CaO	38.27			39.17			40.37		
MgO	4.50			1.80			2.12		
Na2O	0.56			0.30			0.44		
K2O	17.55			18.90			19.63		
P2O5	2.22			2.27			2.13		
SO3	0.90			0.86			1.32		
Cl	0.05			0.11			0.02		

Table 7. Campaign Two, Oak Pyrolysis, Gas and Char Analysis

Accelerated aging test of bio-oil

Accelerated aging testing was performed according to the procedure described in the pyrolysis oil stabilization solicitation (USDOE,2008) on two samples of bio-oil produced by fast pyrolysis of oak at 500 ºC and 550ºC using the NREL entrained flow reactor system. Approximately 1 kg sample of each bio-oil was taken for the tests from a corresponding drum after vigorous stirring. Six 90 to 100g samples of each bio-oil enclosed in 100 mL screw-cap bottles were placed in a convection oven at 90°C for 24 hours. Three samples of each bio-oil were removed from the oven after 8 hours and three remaining after 24 hours. The weight loss of the samples was less than 0.4 g (<0.5%) except for one sample (550°C/90°C/8 h) that was not used in further measurements. After the high-temperature storage, the samples were placed in a refrigerator for a few days until viscosities measurements were performed. The initial bio-oil samples as well as the bio-oil produced at 500°C and stored at 90°C for 8 hours looked homogeneous while the other three samples (500°C/90°C/24 h, 550°C/90°C/8h, and 550°C/90°C/24h) despite vigorous shaking clearly remained two-phase liquids.

The viscosity of single-phase bio-oil samples was measured using a Brooksfield Digital Viscometer Model LVTD. The precision of the measurement is estimated at ±5%, which mostly results from potential variations in the liquid temperature. Viscosities were measured at 25°C and 40°C in duplicate for each sample stored at 90ºC for 0, 8, and for 24 hours. The average viscosity as well as the standard deviation for the set of bio-oil samples stored at the same conditions was calculated. The results are shown in Table 8.

Temperature/time	Avg. viscosity, cP
500°C/0 h	56
500°C/8 h	93
550°C/0 h	50

Table 8. Viscosity at 40°C of Bio-Oil Samples Aged at 90°C

The average rate of viscosity increase for the bio-oil produced at 500°C was 4.6 cP/h during the first eight hours of storage at 90°C. The performed tests showed that the accelerated storage conditions were too severe for a quantitative assessment of bio-oil stability measured as the viscosity increase per time unit. Phase separation occurred in the bio-oil produced at 550°C after less than 8 hours at 90°C and in the bio-oil produced at 500°C after less than 24 hours. For better quantitative observation of the changes in bio-oil properties (viscosity), we decided to lower the storage temperature to 50°C and measure viscosity of the samples as a function of aging time. Table 9 summarizes the results of viscosity measurements performed at 40°C.

Pyrolysis temperature, °C	500°C	550°C
Time of storage, hrs	Viscosity measured at 40°C, cP	
0	56	50
8	57	51

24	57	55
72	85	65
96	107	85

Table 9. Viscosity at 40°C of Bio-Oil Samples Aged at 50°C

Notable is that the viscosity of bio-oil produced at 500°C changed very little during 24 hours of storage at 50°C then it increased at an accelerated rate. The viscosity of bio-oil almost doubled after four days of storage at 50°C. The bio-oil produced at 550°C had slightly lower viscosity that increased at a somewhat lower rate. The viscosity change on storage is well represented as a quadratic function of time as shown in Figure 2.

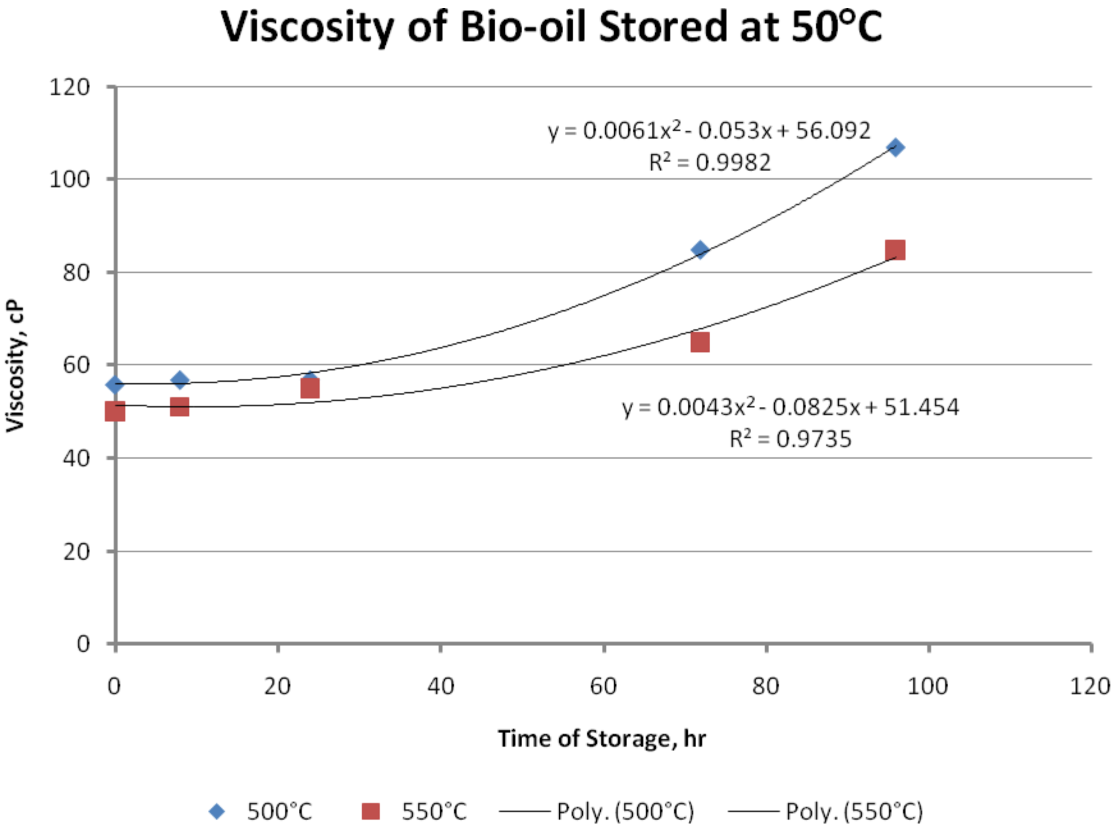

Figure 4. Viscosity of Bio-oil stored at 50 ^{o}C

The presented data show that an accelerated (less than a day) aging test for bio-oil based on the viscosity increase should be carried out at a temperature higher than 50°C but lower than 90°C. If a 4-day aging test is acceptable, then the existing procedure seems appropriate.

Stabilization by Hydrotreating

Purpose:

The desired outcome of the project was to provide a foundation for development of an economically viable process for upgrading pyrolysis oil to refinery feedstock. The purpose of this phase was to gain a fundamental understanding of the process sensitivity to pyrolysis oil feed properties.

Approach:

This project, extending from FY06 to FY09, built on proof-of-principle experiments performed on heavy phase bio-oil ("pyrolytic lignin") in the FY05 DOE project titled, "Opportunities for Biorenewables in Oil Refineries," in which the parties to this CRADA participated. Process optimization and catalyst stability testing is required for the hydrotreating and hydrocracking steps.

Within the project, there were these objectives and tasks requiring PNNL to perform hydroprocessing on bio-oil samples provided by NREL:

1. Optimize the conversion of the pyrolysis oils using mild hydrotreating.
2. Optimize the conversion of the hydrotreated product to gasoline by hydrocracking.

Hydrotreating Experiments

It was envisioned that the bulk of the catalytic processing would be carried out on pyrolysis oil derived from wood. Preliminary process conditions identified in the FY05 DOE project were verified and optimized using pyrolysis oil derived from a mixed wood feedstock. Initial targets were set as Liquid Hourly Space Velocity (LHSV) of 1 and pressure less than 1700 psig. Product quality was too low at these targets and more useful product resulted using around 0.25 LHSV and 2000 psig. Catalysts from both Battelle and UOP were tested in a bench-scale, fixed-bed reactor to hydrogenate the bio-oil and produce a partially upgraded bio-oil suitable to processing at more severe hydrocracking conditions as would be typically found in a petroleum refinery. Once suitable test conditions and catalyst stability were determined, other pyrolysis oil feedstocks were evaluated. These tests were continued over a period of time sufficient to achieve steady state operation and allow product samples to be recovered for analysis. Analyses included ultimate analysis (C, H, N, O, S), moisture, viscosity, density, acid number and GC-MS analyses for characterizing chemical class composition. Water addition prior to hydrotreating was evaluated as a phase splitting mechanism to produce feed oil, which was more highly concentrated in lignin such that production of higher yields of liquid products was expected. Based on these tests optimum processing conditions were chosen and extended runs performed (nominally 100 hr) to evaluate catalyst lifetime and to produce sufficient product to feed the subsequent hydrocracking processing step. Samples of each hydrotreated feed were sent to UOP for analyses after the end of each campaign.

Hydrocracking Experiments

The hydrotreated products from the previous task were used as feedstocks for catalytic hydrocracking tests to evaluate the partially upgraded bio-oil as a refinery feedstock. The baseline processing conditions were developed in concert with UOP and UOP supplied the hydrocracking catalyst. Steady-state operations were evaluated in a continuous-flow regime. Process conditions were optimized to produce a product with low oxygen content and a low acid number. Products were produced for subsequent analysis by UOP for typical refinery product parameters including distillation, PONA, octane measurements and elemental analyses. PNNL completed GC-MS analysis for comparison of the hydrocracked products with the hydrotreated products and the bio-oil feedstocks, as well as ultimate analysis (C, H, N, O, S), moisture, viscosity, density and acid number.

Experimental:

<u>Facilities</u> The hydrotreating and hydrocracking experiments were undertaken in the bench-scale hydrotreater system in the Chemical Engineering Laboratory at PNNL. That system included a fixed-bed catalytic reactor with required feeding and product recovery components. The bio-oil was fed by a high-pressure metering syringe pump. Hydrogen was introduced into the reactor via high-pressure lines and mass flow controller from a gas cylinder manifold. The products were cooled and collected in a dual cylinder sampling system with the uncondensed gases sampled, measured and vented. The recovered liquid products were phase separated, weighed and sampled for further analysis. Manually recovered gas samples were analyzed by gas chromatography. A schematic drawing of the reactor system is shown below in **Figure 6**.

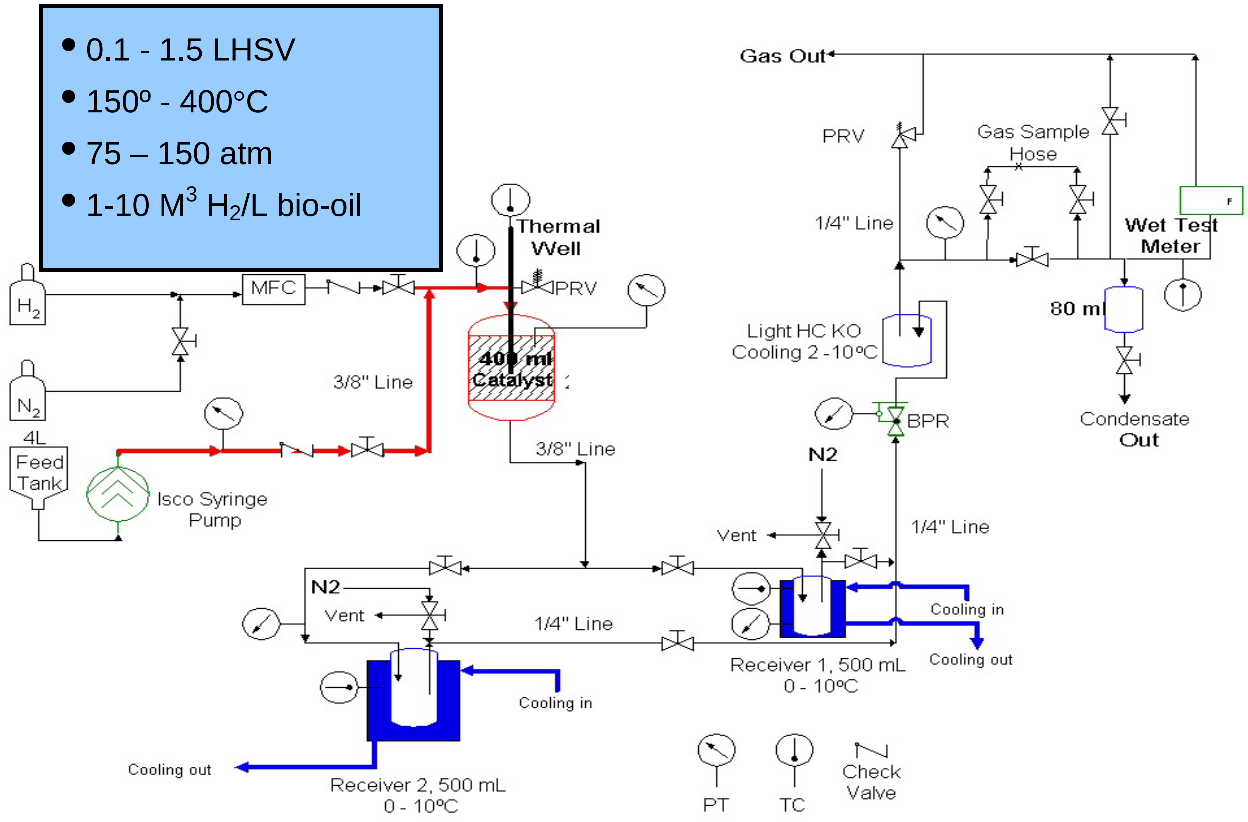

Figure 6. Schematic of bench-scale hydrotreater at PNNL

Hydrotreating Experiments A palladium on carbon catalyst was used (sometimes in combination with other catalysts in a layered bed) in a bench-scale, fixed-bed reactor to hydrogenate the bio-oil and produce a partially upgraded bio-oil suitable to processing at more severe hydrocracking conditions as would be typically found in a petroleum refinery. The Pd/C catalyst was identified in earlier experimentation and subsequently patented for use in bio-oil upgrading (see attached U.S. patent #7,425,657). The starting conditions were 340°C, 2000 psig, and a 0.28 Liquid Hourly Space Velocity (LHSV). The bio-oils were processed at a range of conditions: at higher and lower temperature (310°C and 375°C) and LHSV (0.18 and 1.12) in order to determine process sensitivities. These tests were continued over a period of time sufficient to achieve steady state operation and allow product samples to be recovered for analysis. Analyses included ultimate analysis (C, H, N, O, S), moisture, viscosity, density, acid number and GC-MS analyses for characterizing chemical class composition. Following these tests the optimum processing conditions of 340°C and 0.28 LHSV were used in extended runs performed to evaluate catalyst lifetime and to produce sufficient product to feed the subsequent hydrocracking processing step.

Coking of bio-oil was identified as a significant problem in extended operation of the hydrotreatment, often in combination with corrosion of the reactor wall. Use of the layered catalyst beds was an attempt to place a more active catalyst in the coking zone. Attempts to decouple the corrosion and coking were made by:

1) use of a corrosion-resistant (coated) reactor for hydrotreating, and
2) acquisition of a Hastelloy™
3) reactor for corrosion-free hydrotreating tests

Hydrotreating Experimental Summary

Data sheets covering the several data windows within each of these tests will be published electronically. The data sheets list the detailed analytical results and calculations of the process results.

Initial tests of mixed wood bio-oil feedstock in a 1.5" ID X 15" L 304 Stainless Steel reactor

<u>HT88</u>

Using the mixed wood feedstock a single Pd/C catalyst bed (355 ml bed of a 6/8 mesh Pd/C)
was used in four successive days of operation, each 8 to 10 hours on stream at 340-360°C set point. ICP analysis of the feed (numbers in ppm) showed S 210, K 78, Ni 58, Na 40, Ca 37, and Al 31 with Mg 22, and others below 10 are Fe, P, Zn, Cu, Zr, Ti, Mn, Co, Cd, Cr, and Si is undetectable. Operating temperature setpoints of 345° and 360°C were used throughout. The LHSV used was 0.28 to 0.7 with an acetone wash at the end of each day. During these tests there was evidence of a build up of a pressure drop. Time on stream for the four days amounted to 9:09h on day 1, 8:20h on day 2, 8:15h on day 3,and 8:38h on day 4 for a 34.6 hr total.
On the 5th day operating at 360°C but LHSV of 1.12 a very high pressure drop developed and even after reducing the LHSV to 0.85, there was still a high pressure drop. After 5 hr total test time, the run was stopped and the catalyst bed washed with acetone. These tests are summarized in the Table 6.

A restart on the 6th day, operating at 375°C and LHSV o f 0.85, found there was still a high pressure drop, so the run was stopped and the catalyst bed washed with acetone. A restart on the 7th day found that even at the beginning operating conditions of 345°C and LHSV o f 0.28 there still was a high pressure drop, so the test was stopped and the catalyst bed washed with acetone.

Upon opening the reactor after cooldown, it was found that the top 3" were filled with coke. A screen on top of the catalyst bed was imbedded in ¼" dark brown "burnt" oil (coke). The balance of the catalyst bed (about 3/4) looked the same as before the test. ICP analysis of catalyst bed samples showed the expected Pd catalytic metal (8920 to 15700 ppm) but also a high level of sulfur (1420 at the inlet down to 190 ppm at the bottom), along with nickel (3650 to 58 ppm), iron (862 to 1450 ppm) and chromium (45 to 297 ppm). Some of the nickel was attributed to the feedstock, as was a bit of iron and chromium. However, analysis

of a coke sample recovered from the spaces between catalyst particles, which was low in Pd (46 ppm) and
S (244 ppm), showed clearly that the reactor wall metals were an important component in the coke with 6400 ppm Ni, 4930 ppm Fe, 448 ppm Cr, and even 261 ppm Mo, which was not found in the feedstock. Magnesium was the next largest component in the coke (399 ppm) but was found less in the catalyst (130 to 210 ppm). Al, Zn, Si, and K were all found at 100-500 ppm in the samples with no clear concentration in either the coke or the catalyst. Cu, Co, and Mn were found at around 100 ppm or less and were slightly concentrated in the coke. Na and P were not found in the bed samples. In the various samples, the sulfur concentration better correlated with that of the reactor metal, Ni, than the Pd catalyst.

	1	2	3	4	5
bed temperature, °C	349	345	359	368	363‡
reactor pressure, psig	1976	1976	1924	1941	2024‡
LHSV, hr-1	0.28	0.70	0.70	0.28	0.85
WHSV, hr-1	0.66	1.66	1.66	0.66	1.99
mass balance %	94	98	98	100	102
product yield, g/g	0.62*	0.74	0.74*	0.72	0.79
H_2 consumption, l/l	245	106	127	262	106
deoxygenation, %	66.77*	47.30	50.33*	56.56	45.12
O %, dry product	10.03	20.82	19.64	16.21	19.79
C %, aqueous	11.20	13.09	12.35	10.85	12.14

*normalized to 100% mass balance
‡average point – large temperature profile and significant pressure drop

Table 10. Initial Hydrotreatment Tests with Mixed Wood Bio-oil

HT89

An experiment to restart with the used HT88 catalyst produced lower quality oil, so it was stopped after 10:13h. There was no significant restriction, but a little bit of coke was found on the catalyst about 2" into reactor.

HT90, 91, 92

A new Pd/C catalyst bed was used in three successive runs of operation in the 9 L/D reactor. Each lasted from 30 to 40 hours on stream at a 340°C set point and an LHSV of 0.28 until a noticeable pressure drop developed. Front bed additions of Ru/C catalyst did not resolve the coking problem. The product oil from these tests was used as the feedstock for the first set of hydrocracking tests for mixed wood oil.

- In HT90, a new Pd/C catalyst bed made up of both small (-20 mesh) and large (6/8 mesh) particle size catalyst was used. The test was on line for 31 hr until the beginning of a noticeable pressure drop. After 9 hr more of operation with increasing pressure drop, the test was shutdown. An acetone wash was attempted but did not clear the restriction. Again the top 3”of the reactor were filled with coke and the top screen was imbedded in ¼” dark brown “burnt” oil (coke). As before, the balance of bed (3/4) looked OK.
- In HT 91, the catalyst bed consisted of 86% new Pd/C with 14% used Pd/C from HT90. An active hydrogenation catalyst, Ru/C, was added on top of the Pd/C on top (1.5-2”) and no screen or open space was used at the front end of the bed. A 31 hr test was completed until the start of a noticeable restriction. After 20 hr more of operation with increasing pressure drop, the test was shutdown. An acetone wash was attempted but did not clear the restriction.
- In HT 92, a new Pd/C catalyst bed with the used Ru/C from HT91 on top was tried to keep the front end hotter. After 37.5 hr a noticeable restriction developed and after 4 hr more the feed was stopped. An acetone wash of the reactor bed was accomplished. Upon opening the reactor, coke was found at 3” into the catalyst bed, at the start of Pd/C portion of the bed. The balance of the bed (about 3/4) looked similar to fresh catalyst.

Mixed wood bio-oil feedstock tests in a 1” ID X 32.1” L reactor

A reactor vessel with a higher L to D ratio was used in subsequent hydrotreating tests with mixed wood bio-oil. The vessel was rotated end for end after the hydrocracking test with sulfided feedstocks because of noticeable corrosion of the reactor walls at the front end of the tube. By rotating the reactor, the non-corroded end was placed into the zone where the corrosion occurred so that the corrosion could be monitored for further development.

<u>HT102, 103</u>

A new catalyst bed consisting of an extremely edge-coated Pd on C particles (catalyst synthesis number PNNL-58959-167-1) was used in two successive runs of 6 and 10 hours on stream at a 340°C set point and an LHSV of 0.25 until noticeable pressure drop developed. Front catalyst bed additions of Ru/TiO_2 catalyst did not resolve the coking problem.

- In HT 102 fresh Pd/C with 5” of Ru/TiO_2 on top was used with corrosion test coupons.

At 6.2 hr a noticeable restriction developed and after 1 hr more the feed was stopped. An acetone wash cleared the catalyst bed, but coke was found at the start of the Pd/C bed; the balance of the bed (about 3/4) looked OK. Analysis of a coke sample showed the highest levels of Fe (666 ppm) and Ni (584 ppm) with Pd (254 ppm) and S (261 ppm), as well as Si, Al, Cr, Na and K at 308, 240, 185, 176, and 120 ppm, respectively. Corrosion products from the coupons were suspected as catalyzing the formation of coke, so the test was repeated without the coupons.

- In HT 103, with the same catalyst and no coupons a noticeable restriction developed only 10.25 hr from the start. After 1.1 hr more with increasing pressure drop the feed was stopped and an acetone wash was attempted without success. Upon opening the reactor a similar scene was found. There was coke starting at 1” into the reactor and continuing through the Ru to 1” into start of Pd/C bed. Again the balance of bed looked like the original catalyst. Analysis of a coke sample showed Ru at 333 ppm and Ti at 611 ppm with some Pd (49 ppm), but no S was found. Fe (202 ppm) and Ni (73 ppm) were still significant components as were Al, K, and Na at 91, 93, and 159 ppm, respectively.

HT104

Based on a concern that the extremely edge-coated Pd on C catalyst might be the cause of the short time to coke formation, a new Pd/C catalyst bed (PNNL synthesis - like Engelhard 864A-3-260-21) with 5” Ru/ TiO_2 on top was tested. After 11.5 hours at a 340°C set point and an LHSV of 0.25, a noticeable pressure drop developed. Bio-oil feed was continued for 2.1hr more, then shutdown. The catalyst bed was washed with acetone. The disassembled reactor showed the typical plugged portion, which was removed for analysis. Analysis of a coke sample showed high levels of Ru (521 ppm) and Ti (975 ppm) with some Pd (166 ppm) and S (399 ppm). The major components were Fe (1180 ppm) and Ni (1680 ppm). As in HT 102, Al, Si, Na, Cr, and K were found at 377, 321, 203, 183, and 100 ppm, respectively; but also Cu (110 ppm) and Mg (101 ppm).

It was concluded that the front bed replacement of the Pd/C catalyst by Ru/TiO_2 catalyst did not resolve the coking problem. It also became clear that the time lapse until a pressure drop became evident was a direct function of the cross-sectional area of the reactor, such that the smaller reactor tube was plugged more quickly than the larger bore. The result was attributed to a corrosion product catalyzed reaction, initiated at the reactor wall, which built a solid coke formation out to the center of the reactor with time on stream.

HT105

In order to displace the carbon support from the coking zone, the Pd/C bed from HT104 was used to refill the bottom portion (250cc) of the reactor with front bed of 12-13” (155cc) of Pd/SiC balls. In this test at a 340°C set point and an LHSV of 0.25, the noticeable pressure drop developed after only 6.7 hours on stream. After 0.4 hr more on stream the test was shutdown and the reactor bed washed with acetone. In this test there was loose catalyst at the front of the bed but coke at 1” into the reactor. The bottom of bed (27”) came out easily and looked as originally. In between there was coke at about the same place as the several previous runs. Analysis of a coke sample from the SiC balls showed some Ru (36 ppm) and Ti (200 ppm) with little Pd (0.1 ppm) and no S was found. The other major components were Fe (166 ppm) and Ni (109 ppm). Like HT 103, Al and Na were found at 61 and 157 ppm, respectively, but no K was detected. The front bed of Pd/SiC catalyst did not affect the outcome of plugging at the front heat-up zone. The Pd/SiC balls seemed softer after the run, suggesting that SiC may not be a good support for acidic, hydrothermal systems.

HT106

A final run was attempted to produce sufficient product oil for subsequent hydrocracking tests. The Pd/C bed (300cc) from the previous test was used with some (120cc) new Pd/C catalyst.

By operating at lower temperature, a 310°C set point, the test was kept on line for 28.75 hours at an LHSV of 0.24 until there was a noticeable pressure drop. The pressure drop continued to build over another 7.2 hours until the test was ended. With an acetone wash the restriction went away, but when restarted with bio-oil feedstock the restriction was found to be still in place.

After an acetone wash and cooldown the reactor was opened to find loose catalyst at front but coke at 4" into reactor. The bottom of bed (28") came out easily and looked OK. In between was a hard coke plug, ¾" by 1". Analysis of a coke plug sample showed the highest levels of Fe (2960 ppm) and Ni (3100 ppm) with Pd (5740 ppm) and S (914 ppm). Also Si, Al, Cr, Na and K at 549, 633, 111, 112, and 222 ppm, respectively; but also Zn (674 ppm) and Mg (576 ppm).

The sulfur concentration correlated better with the reactor metal, Ni, than with Pd catalyst in the five samples.

Mixed wood bio-oil feedstock tests in reactors constructed of special materials

HT113

The 1" ID X 32.1" L 304 stainless steel reactor was coated by the Silcosteel™ process to evaluate corrosion effects. A new batch of Pd/C catalyst was used for 27.6 hours on stream at 347°C (340°C set point) with an LHSV of 0.21 with a noticeable pressure drop causing the test to be terminated. Catalyst deactivation was noted throughout the test. Pressure drop built for an additional 1.5 hours until the run was ended. The reactor was acetone washed and cooled.

Upon opening, the catalyst poured out of the bottom and middle portions of the reactor tube; a restriction was found only in the top 3" of reactor. From 1" to 3" in, the catalyst was encased in a hard coke which had to be chipped out. The Silcosteel coating seemed unaffected, but some residual scratches were noted where the catalyst plug was chipped out.

Analysis of a coke plug sample showed the usual high levels of Fe (2250 ppm) and Ni (5520 ppm) with Pd (7880 ppm) and S (4700 ppm). Also Si, Al, Cr, Na and K at 1630, 686, negligible (14.5), 226, and 156 ppm, respectively; but also Zn (748 ppm) and Mg (265 ppm) as well as additional findings of Ca (689ppm) and P (462ppm). Of these elements found in the coke, all are also present in the catalyst bed at similar levels, except S (2130-3400ppm) and Ni (423-827 ppm), as well as Ca and P, which were found at much lower levels.

The sulfur concentration correlated better with Ni than with Pd. SEM/EDS analysis confirmed the association, although there was sulfur with the Pd as well, at a molar ratio of 0.2 or less.

A longer run time was achieved at normal temperature operation with the coated reactor, but the trace elements found in the coke seemed to suggest that corrosion was still an important factor in its formation.

HT115

In this test the silcosteel coated reactor was reused after placement of a Hastelloy liner in the front end of the tube as further protection against corrosion. The catalyst bed was composed of 98% reused HT113 Pd/C catalyst with 2% new (460cc PNNL cat) with the mixed wood bio-oil feedstock part sulfide added**.** The test extended for 24.9 hours on stream at 342°C (340°C set point) with the LHSV of 0.22. Catalyst deactivation was noted throughout based on increasing density and viscosity of the oil product, at which point a noticeable pressure drop developed. The pressure drop continued building until after another 2 hours the run was ended. The reactor system was acetone washed and cooled.

Upon opening, lightly oil coated catalyst was found at the front of the bed, but there was coked catalyst at 1 to 3" into reactor. The bottom of bed (28") came out easily and appeared as at the beginning of the test. There was no obvious corrosion of the liner.

Similar to HT113, a longer run time was achieved with the Hasteloy liner as with the silcosteel treating alone, but, in the end, the same coking problem developed.

HT118

In a third attempt to address the corrosion issue a new 1" ID X 32.1" long reactor made of Hastelloy C-276 was used. A catalyst bed of 2.5%Pd/C composed of 76% HT112 used cat and 24% used HT116 cat (450cc PNNL cat) was used with the mixed wood bio-oil feedstock with sulfide added. The test was on stream only 14.6 hours at 304-344°C and LHSV of 0.18. The catalyst remained active throughout, but a noticeable pressure drop developed. There were heating difficulties with new reactor configuration, which confused any conclusions. The test was shutdown and acetone washed. A hard coke deposit was found in the front end as typically seen; there was no sign of corrosion.

Corn stover bio-oil feedstock tests in a 1" ID X 32.1" L 304 SS reactor

Using the corn stover light phase feedstock a 2.5% Pd/C catalyst bed, with front bed additions of Ru/C and Pd/ZrO_2 catalysts, was used in 2 successive runs, at 340°C set point, LHSV of 0.27 to 0.42 in the new long reactor. The Ru and Pd catalysts were added at the front end of the reactor in an attempt to preempt the coke formation with more active catalysts, less susceptible to coke formation. These tests provided the hydrotreated bio-oil feedstock for future hydrocracking tests. ICP analysis of the feed showed 436 ppm S, 460 ppm K, 68 ppm Na, and 120 ppm Ca; with 64 ppm Mg, 32 ppm Al, 40 ppm Ni, 17 ppm Fe, and 13 ppm P.

HT96

Used Pd/C from HT92 (300cc) and fresh (70cc) formed the main bed and a "pretreating bed" of Ru/C (C3610) (30cc) was the top 2.3" followed by a second "pretreating bed" of 2.3" Pd/ZrO_2 1/8" tablets. There was no screen or gap at the top of the reactor. The test was on line for 34.5h (plus 41.5 hr from HT92) until a noticeable pressure drop developed. The pressure drop continued building for another 2.5 hours until the run was ended. The reactor was acetone washed and cooled.

Upon opening was found hard coke in the inlet to reactor and extending about 1” into catalyst bed. The bottom of the catalyst bed (22”) came out easily and looked unchanged. In between was a partially coked catalyst, which could be “coaxed” out by hand with a couple inches of drill bit work. Insulation placed on top of the reactor in this first test in the 1 X 32 reactor was removed for subsequent tests.

HT97

Used Pd/C from HT96 (330cc) and (25cc) fresh catalyst was used with “pre-treating beds” of Ru/C (C3610) 3.1” (40cc) on top followed by 2.3” Pd/ZrO_2 1/8” tablets. There was no screen or gap at the top. The test was on line for 66.9h (plus 78.5 hr from HT92 and HT96) until a noticeable pressure drop developed. The pressure drop continued building for another 3.8 hours until the run was ended. The reactor was acetone washed and water washed.

Upon opening it was found that with the cooler front end of the reactor, there was loose catalyst at the front but coke was found at 1” into the reactor. The bottom of the bed (27”) came out easily and looks unchanged; in between, 4” had to be chipped out.

ICP analysis of samples from the used catalyst bed showed high levels of sulfur (2760-5010 ppm) and iron (958-1760 ppm) throughout the first part of the catalyst bed. Three samples were analyzed; one from the top 1”, one lower still in the Ru/C bed and one lower into the Pd/ZrO_2 catalyst bed. In the first inch before the plug there was a high level of alkali (484 ppm Na and 551 ppm K) while in the later samples the total alkali (Na+K) ranged from 714 to 543 ppm. The nickel, calcium and aluminum contents (409, 1610, 92, ppm respectively, in the sample in front of the plug) were much higher in the second sample (5620, 6330, 908 ppm) where the plugging was first found. The phosphorus content trended with the calcium but at a much lower level (100 to 1212 ppm). Mg, Zn, and Si were all found at an elevated level in the third sample (270, 250, 475 ppm). Other elements were fairly consistent through the three samples. These results suggest that there was metal sulfide formation and reactor wall corrosion, along with other bio-oil mineral deposition.

The corn stover heavy phase feedstock was tested with Pd/C catalyst and front end “pretreating beds” of Ru/TiO_2 and Pd/ZrO_2. This test provided hydrotreated bio-oil feedstock for a future hydrocracking test. ICP analysis of the feed showed a high sulfur level of 1190 ppm with 243 ppm K, 140 ppm Ca, 139 ppm Al, and 105 ppm Si; with 89 ppm Zn, 58 ppm Mg, 42 ppm Na, 64 ppm Ni, 46 ppm Fe, 29 ppm P.

HT98

A Pd/C catalyst bed (340cc), reused HT97, with 40cc new and front end pre-treatment beds of Ru/TiO_2 (Degussa H7709) (35cc) and Pd/ZrO_2 (30cc) catalysts were used. The test was on stream 51.3 hours (plus 149.2 hr from HT92, 96, 97) at 340°C set point, LHSV of 0.26 to 0.20 with no noticeable pressure drop. This appeared to be an important development that the test could go so long without plugging. The test was shutdown and the reactor acetone washed and cooled.

Upon opening there was found loose catalyst in Pd/C portion, for the most part, with a small plug piece (1/2” x 1/2”) recovered. The Ru/TiO_2 and Pd/ZrO_2 portions were very lightly coked. There was minor wall coating at inlet, leaving it 90% open. This bio-oil appeared to be less susceptible to coking.

ICP analysis of samples from the used catalyst bed showed high levels of sulfur (364-1910 ppm) throughout the catalyst bed. Four samples were analyzed; one from the top 1”, one lower with the Ru/C bed mixed with Pd/ZrO_2, one lower into the Pd/ZrO_2 catalyst bed and a final sample from the bottom primarily composed of the Pd/C but also some of the upper beds. In the first inch before the plug the bed was fairly clean (except the S at 691 ppm) with 168 ppm Ca, 149 ppm Ni, 146 ppm Fe, and 102 ppm K, as the major contaminants. In the Ru bed the sulfur concentration actually dropped to 364 ppm with higher levels of Na (852 ppm), Ni (724 ppm), Mg (619 ppm), Al (516 ppm), K (487 ppm), Fe (236 ppm), and Ca (233 ppm). The high level of Na continued into the next sample. The other major elements (Fe, Si, Al, K, S, Zn) were found at significantly higher levels (7000 to 1000 ppm) in both of the last two samples. Ca and Mg (as well as Cu and Mn only at lower levels) were also high (but <1000) in the last two samples. The phosphorus content trended with the calcium but at a much lower level (186-68 ppm). Other elements are fairly consistent through the three samples. These results also suggest that there was metal sulfide formation and reactor wall corrosion, along with other bio-oil mineral deposition.

The second corn stover single phase feedstock (bulk middle phase minus bottom tar and top dodecane) was tested with the Pd/C catalyst at 340°C set point, LHSV of 0.26 to 0.20 in two different tests. These tests produced hydrotreated bio-oil feedstock for future hydrocracking tests. Pretreatment beds of either Ru/TiO_2 or Pd/ZrO_2 were used. ICP analysis of the feed showed less sulfur, 518 ppm, with the other usual biomass components, K 407 ppm, Na 235 ppm, and Ca 89 ppm; with Mg 47 ppm, Al 32 ppm, Ni 24 ppm, and Fe 14 ppm.

<u>HT99</u>

Reused Pd/C catalyst bed from HT98 (380cc) with about 30cc makeup of fresh Pd/C catalyst and front bed additions of Ru/TiO_2 (Degussa H7709) (30cc) and Pd/ZrO_2 (30cc) catalysts (5” total) was tested with this feedstock.

The test operated for 32.2 hours (plus 200.5 hr from HT92, 96, 97, 98) on stream until a noticeable pressure drop developed. The pressure drop continued building for another 2.75 hours until the run was ended. The reactor was acetone washed and cooled.

Upon opening, loose catalyst was found at the front of the bed, but coke formed at 1” into the Ru/TiO_2. The bottom of the catalyst bed came out easily appeared unchanged; the in between 2-3” (including all the Pd/ZrO_2) had to be chipped out. There was material adhering to the reactor walls. Catalyst pieces were stuck together with brown dust. ICP analysis of the plug showed (in addition to the Ru and Ti catalyst) 7280 ppm Ni, 3350 ppm S, 1900 ppm Fe, 1500 ppm Ca, 834 ppm Cr, 368 ppm Al, 233 ppm Cu, 224 ppm P, 115 ppm K, 69 ppm Na, 65 ppm Co, 48 ppm Si, 44 ppm Mg, 33 ppm Mn, and 11 ppm Mo, with Zn and Cd at <5 ppm. These analyses suggested that there was significant deposit of metal sulfides (Ni_3S_2 heazlewoodite was identified by XRD). Corrosion of reactor wall metals (noted upon disassembly) was suggested by the Ni, Fe, Cr, and Mo in the coke deposits. Calcium (from the feed) formation of $CaNi_4O_8$ was identified by XRD while formation of insoluble Ca phosphate was also likely at these conditions. Soluble forms of K and Na must have moved through the plugged portion of the bed. SEM EDS analysis showed high levels of associated sulfur and nickel on the edges of the Ru/TiO_2 catalyst with surface crusts also showing particles of Fe, Ni, Cr and Mn. Crystallites of Fe phosphate and aluminum phosphate were also seen. There was no indication of the sulfur associated with the ruthenium.

Analysis of the brown powder around the Pd/ZrO_2 catalyst pellets gave results similar to the earlier corn stover except for much higher levels of alkali (apparently from the feed), Na 1140 ppm and K 709 ppm, as well as Co 333 ppm and Mg 258 ppm. Other elements were at levels of 1/3rd to 1/10th of the levels found in the plug; 988 ppm Ni, S 301 ppm, 691 ppm Fe, 567 ppm Ca, Cr 28 ppm, 100 ppm Al, 93 ppm Cu, 47 ppm P, no Si, and 27 ppm Mn. The same $CaNi_4O_8$ was found by XRD but the nickel sulfide form was Ni_3S_4 polydymite. These results suggest metal sulfide formation and reactor wall corrosion with other bio-oil mineral deposition.

HT100

The catalyst bed for this test was reused Pd/C catalyst from HT99 (380cc) with about 30cc makeup fresh catalyst. A larger front end “pretreatment bed” of Ru/TiO_2 (Degussa H7709) (5” total) was used to eliminate Pd and carbon granule support effects.

The test was on stream for 33.3 hours (plus 235.5 hr from HT 92, 96, 97, 98, 99) until a noticeable pressure drop developed. The pressure drop continued building for another 1.3 hours until the bio-oil feed was shutdown and the reactor was acetone washed and cooled.

Upon opening the inlet opening was found to be 20% restricted by yellowish solids. The top 1” was chipped out including reddish solids dust. The next 2” was coked and had to be chipped out. The last 2” of Ru/TiO_2 was not coked. The bottom of the catalyst bed (Pd/C) came out easily and appeared unchanged. ICP analysis of samples from the used catalyst bed showed high levels of sulfur (1040-1760 ppm) throughout the first 5” of the catalyst bed. Three samples were analyzed; one from the top 1”, one at 1-3” inches in and one at 3-5” into the catalyst bed. In the first inch before the plug there was a high level of alkali (1310 ppm Na and 1020 ppm K) while in the later samples the total alkali (Na+K) was only 825-665 ppm. The nickel and calcium contents, 7620 and 2780 ppm, respectively, were much higher in the second sample where the plugging was found. Iron was also higher (2280 ppm) in that sample but not so dramatically as the nickel. The phosphorus content (34-153 ppm) trended with the calcium but at a much lower level. Other elements were fairly consistent through the three samples. XRD analysis of the top 1” sample showed only the $CaNi_4O_8$ compound in addition to the titania phases. A deposit at the inlet to the reactor included heazlewoodite, violarite ($FeNi_2S_4$), magnesium hydrogen phosphate hydrate, alumina, and iron titanium, while the material was mostly amorphous. These results suggested metal sulfide formation and reactor wall corrosion with other bio-oil mineral deposition.

Corn stover bio-oil, heavy phase hydroprocessing in the 1” ID X 32.1” L Hastelloy reactor

HT120

In this test the corn stover heavy phase was retested to further investigate the earlier finding of less susceptibility to coking. A fresh 2.5% Pd/C catalyst bed (395cc PNNL cat) was used without a “pretreatment” bed. Heavy Corn Stover phase feedstock (4/06) was processed without sulfide added.

The test was on stream 68.5 hours at 343°C and a LHSV of 0.25 until a pressure drop over the reactor bed was detected. Catalyst deactivation was noted throughout the run. The oil feed was shutdown at 71.5 hr and the reactor was acetone washed and cooled. Upon opening the same type of plugging was found suggesting that the heavy phase was not immune to the plugging problem.

Hot-Filtered Poplar bio-oil in the 1” ID X 32.1” L reactor (304 SS after use with sulfided feedstocks in hydrocracking tests)

A single test was performed with a sample of the hot-filtered poplar wood fast pyrolysis bio-oil from the NREL ablative cyclone reactor. The bio-oil (M2-R8) had been in refrigerated storage at NREL since 1996. ICP analysis of the feed showed 66 ppm sulfur (however, 0.15 wt% was reported by direct S analysis), 46 ppm Zn, 34 ppm Na, 34 ppm Fe, and 15 ppm Ca; with 9 ppm K, 4 ppm Ni, 4 ppm Cu, 2 ppm Mg, 2 ppm Al, 2 ppm Zr, and others below 1 ppm are Mn, Ti, Co, and Cd; with Si, P, Mo, Cr undetectable.

HT108

The catalyst bed was composed of Pd/C (293 cc), used (HT106), with some (140 cc) of new Pd/C catalyst (PNNL-like Engelhard 864A-3-260-21). The test was operated at a 340°C set point and a LHSV of 0.23.

The test was on stream for 47 hours (plus 36 hr more for the catalyst from HT106) until noticeable pressure drop developed. The bio-oil feed was shutdown and the reactor was acetone washed and cooled.

Upon opening the reactor, loose catalyst was found at the front of the bed with brown fines, but a conglomerated coke bed was found at 1” into the reactor. The bottom of bed (28”) came out easily and appeared unchanged. In between was 3” of coked catalyst which had to be chipped out including a ½” intact plug. The temperatures during the test in the coked zone ranged from 190°C at 1” from the front end of the reactor to 315°C at 4” into the reactor. A much longer operating period was achieved than with mixed wood bio-oil, but in this test there was a cooler (uninsulated) front end of the reactor tube. In all cases, the agglomerated catalyst plug formed at the point of the feed bio-oil reaching about 300°C.

ICP analysis of samples from the used catalyst bed showed significant levels of sulfur (515-794 ppm) throughout the catalyst bed. Four samples were analyzed; one from the top 1", one lower in the plug zone, one lower below the plug and a final sample from the bottom primarily composed of the Pd/C. In the first inch before the plug the bed contained (in addition to S) 4020 ppm Fe, 1560 ppm Zn, 738 ppm Ni, 556 ppm K, and 453 ppm Al as the major contaminants. There were lesser amounts of Si, Na, Ca, Cu, and Mg. Others (P, Co, Ti, Mn, Cr) were present at <30 ppm. In the plug material, lower levels (1190 ppm Fe, 741 ppm Ni, 616 ppm Zn, 601 ppm Al, 552 ppm K) of the elements are found, apparently due to dilution by carbon coke deposit. Sodium was found at much higher levels in the lower portions of the bed (3430-1020 ppm). The major elements found at significant levels in both of the last two samples were Fe (1540-2350 ppm), Al (777-1510 ppm), K (742-1730 ppm), Zn (338-2380 ppm), Si (426-868 ppm), Ca (603-461 ppm), and Mg (220-263 ppm). The phosphorus content trended at a much lower level (46-133 ppm). Other elements were consistently low (<100 ppm) through the four samples.

The plug material was examined in more detail with SEM/EDS. These images showed a well-dispersed palladium metal catalyst on the highly porous carbon structure. Some of the images suggested that iron (or nickel, or zinc to a lesser degree) was associated with the palladium metal (at levels less than 10%), but there was little evidence of sulfur associated with the Pd. There was some evidence of zinc and sulfur association, as well as some iron-zinc-sulfur structure on the edge of a catalyst pellet. Some large silicon-containing structures were also seen, but may have been relics of the carbon catalyst support structure formation. These results also suggested metal sulfide formation and bio-oil mineral deposition.

Kentucky Oak Bio-oil in the 1" ID X 32.1" L Hastelloy reactor

HT119

This test was performed primarily with the Kentucky Oak bio-oil feedstock produced in the NREL reactor operated at nominally 500°C. Later in the run some of the mixed wood bio-oil feedstock with sulfide added was also processed. A bed of 2.5% Pd/C was composed of 97% used catalyst (HT118) and the balance used from HT116 for a total bed of 423cc of catalyst synthesized at PNNL.

The test was on stream for 10.1 hours at 346°C and LHSV of 0.24 when a pressure drop was first noted. The catalyst was active throughout. The bio-oil feed was shutdown at 12.65 hr and the reactor was acetone washed and cooled. Upon opening the reactor the earlier type of plugging was noted with no sign of corrosion.

Conversion of Stabilized Oil

Conversion Experiments The hydrotreated products from some of the previous tests were used as feedstocks for catalytic hydrocracking tests to evaluate the partially upgraded bio-oil as a refinery feedstock. The baseline processing conditions developed in concert with UOP were near conventional conditions: 400°C, 2000 psig, and 0.4 LHSV using a conventional hydrocracking catalyst. Steady-state operations were evaluated in a continuous-flow regime. Products were produced for subsequent analysis by UOP for typical refinery product parameters including distillation and PONA. PNNL completed GC-MS analysis for comparison of the hydrocracked products with the hydrotreated products and the bio-oil feedstocks, as well as ultimate analysis (C, H, N, O, S), moisture, viscosity, density and acid number.

Experimental Summary

Data sheets covering the several data windows within each of these tests are included in appendix A of this report. The data sheets list the detailed analytical results and calculations of the process results.

Tests of hydrotreated mixed wood bio-oil feedstock in a 1.5" ID X 15" L 304 SS reactor

Using the hydrotreated mixed wood feedstock produced in HT90-HT92 two UOP catalysts for hysrocracking and hydrotreating were tested in their presulfided forms. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. These tests were not very useful and later in the project additional tests were made with the hydrotreated mixed wood bio-oil with much better results.

HT93

Attempts to process the hydrotreated bio-oil over the UOP Hydrocracking catalyst were made at three different temperatures (328-384°C) on four different days. The tests lasted for 3-8 hours on stream and in all cases the product contained heavy, insoluble solids which plugged the product collection system. The process pressure was 1500 psig, and a LHSV of 0.28-0.14 was used. Because of the difficulty to collect the heavy (incompletely reacted portion) of the product oil, the mass balance of these tests was poor (54-61%). The fluid portion of the product oil was a low density (0.81-0.85 g/ml) mostly hydrocarbon product (5-5.4% oxygen). The solid portion of the product contained 15.8-17.8% oxygen.

HT94-95

Attempts to process the hydrotreated bio-oil over the UOP hydrotreating catalyst were made at a range of temperatures (318-429°C) on two different days. The same catalyst bed was used in both tests. The tests lasted for 6.5 and 10 hours on stream and in both cases the product contained heavy, insoluble solids which plugged the product collection system. The process pressure was 1500 psig, and a LHSV of 0.24-0.36 was used. Because of the difficulty to collect the heavy (incompletely reacted portion) of the product oil, the mass balance of these tests was poor (59-78%). The fluid portion of the product oil was a low density (0.77-0.90 g/ml) mostly hydrocarbon product (3.4-6.5% oxygen).

Tests of hydrotreated corn stover bio-oil feedstocks in a 1” ID X 32.1” L 304 SS reactor

Using the hydrotreated corn stover bio-oil feedstocks produced in HT96-HT100, UOP hydrotreating catalyst was tested in its presulfided form. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. This test provided much better results for hydrocracking of hydrotreated bio-oil.

<u>HT101</u>

An extended run with hydrotreated bio-oil products from all three corn stover bio-oils, the light and heavy phases of the original corn stover bio-oil received in 2006 and the new corn stover (single phase) received in 2008. Using a single catalyst bed, testing of all three feedstocks was completed over an 80 hour on-stream period including 6 hours off-line at one point with a pump breakdown. The process temperature setpoint was 390°C with bed temperatures ranging from 399°C to 410°C for LHSV ranging from 0.13 to 0.25. No heavy, insoluble solids were produced and there were no problems with plugging in the product collection system. The process pressure was 1500 psig. Because there was no difficulty in collecting the product oil, the mass balance of these tests were good (91-99%). The product oil was a low density (0.78-0.87 g/ml) mostly hydrocarbon product (0.42-0.95% oxygen). Catalyst deactivation was not easily measured as the process parameters and feedstock were varied over the test. The offgas stream contained 10 to 15 ppm hydrogen sulfide throughout the test.

Tests of hydrotreated mixed wood bio-oil feedstocks in a 1” ID X 32.1” L 304 SS reactor

Using the hydrotreated mixed wood bio-oil feedstocks produced in HT102-HT106, UOP hydrotreating catalyst was tested in its presulfided form. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. This test provided much better results for hydrocracking of hydrotreated mixed wood bio-oil than seen in earlier tests.

<u>HT107</u>

A run was made with hydrotreated bio-oil products from the four mixed wood bio-oil hydrotreating tests. Using a single catalyst bed, testing of all three feedstocks was completed over a 25.5 hour on-stream period. The process temperature setpoint was 390°C with bed temperatures ranging from 394 to 405°C for LHSV ranging from 0.12 to 0.23. No heavy, insoluble solids were produced and there were no problems with plugging in the product collection system. The process pressure was 1500 psig. Because there was no difficulty in collecting the product oil, the mass balance of these tests were good (85-103%). The product oil was a low density (0.77-0.86 g/ml) mostly hydrocarbon product (0.35-0.54% oxygen). Evidence of catalyst deactivation was seen by the increase in product oil density over time from an initial level of 0.77 to 0.81 at low space velocity and from 0.83 to 0.86 at the higher space velocity.

Tests of hydrotreated hot-filtered poplar bio-oil feedstocks in a 1” ID X 32.1” L 304 SS reactor

Using the hydrotreated hot-filtered poplar bio-oil feedstocks produced in HT108, UOP hydrotreating catalyst was tested in its presulfided form. The hydrotreated bio-oil feedstock was sulfided to a level of 100 ppm by the addition of di-tert-butyl-disulfide. This test provided much better results for hydrocracking of hydrotreated bio-oil.

HT110

A run with hydrotreated bio-oil product from the hot-filtered poplar run at NREL in 1996 was made using a catalyst bed composed of the used catalyst from HT101 with makeup of fresh catalyst from UOP. The test was on stream for 27.5 hour (plus the 80 hr on stream from HT101) with a process temperature setpoint of 390°C. The bed temperatures ranged from 394°C to 408°C for LHSV ranging from 0.12 to 0.24. The process pressure was 1500 psig. The mass balances of these tests were good (95-102%). The product oil was a low density (0.84-0.87 g/ml) mostly hydrocarbon product (0.27-0.32% oxygen). Evidence of catalyst deactivation was less dramatic in this test (apparently due to the extended period on line for the catalyst), but an increase in product oil density over time was still measureable from an initial level of 0.84 to 0.85 at low space velocity and from 0.86 to 0.87 at the higher space velocity.

Non-isothermal tests using 1.5” ID X 32.1” L (2-stage) reactor

The non-isothermal reactor configuration allowed both hydrotreating at low temperature and hydrocracking at high temperature to be accomplished in a single pass through a fixed bed reactor. By this arrangement the product oil was a mostly hydrocarbon product such that there was little organic contamination of the byproduct water phase. The 2-stage reactor could be filled with two different catalysts to accomplish somewhat different chemistries in the two temperature ranges or could be filled entirely with a single catalyst, which had activity at both temperature ranges. Typically, a palladium on carbon catalyst was used in combination with UOP hydrotreating catalyst in a layered bed. In the non-isothermal configuration, the bio-oils were processed at a low temperature of 250°C and a higher temperature of 380°C. LHSV in the range of 0.2 was used. These tests were continued over a period of time sufficient to achieve steady state operation and allow product samples to be recovered for analysis. The original reactor was constructed of 304 SS.

Experimental Summary Data sheets covering the several data windows within each of these tests are included in appendix A of this report. The data sheets list the detailed analytical results and calculations of the process results.

Non-isothermal Hydroprocessing of Bio-oil in a 304SS Reactor

HT109

A previously used bed of sulfided CoMo on alumina catalyst was used in processing the hot-filtered poplar wood bio-oil feedstock without added sulfide. The test was on stream for 101.7 hours at 230-240° in the top (front) bed and 430-440°C in the lower portion of the reactor. The LHSV of 0.14 was used throughout while no noticeable pressure drop developed. At that point the feed oil was shutdown and the reactor bed acetone washed, cooled and disassembled. Some "hard-packed" catalyst (lightly coked) was found at 2 to 9" into the catalyst bed, effectively the heatup and low temperature zone where temperatures ranged from 200-245°C. Also there was about 1" of "charred" catalyst at 10" from the bottom, which was effectively the hot spot of the catalyst bed where the maximum heating from the exothermic reaction was found.

HT111

A front bed (390 cc) of fresh Pd/C and a back bed (210 cc new and 310 cc HT110) of UOP hydrotreating presulfided catalyst were used with the mixed wood bio-oil feedstock without sulfide addition (dodecane quench liquid separated from the top of the bio-oil prior to the test). The test started up without problem. A less dense orange liquid phase was recovered over yellow water product (a dark green oil sample was recovered when contaminated with residual left in the second separator). Less than 10 ppm H_2S was measured in the offgas, but it could be smelled in the reactor room.

The test was on stream for 32.8 hours at 255°C and 420°C (set point of hot oil heater at 380°C with a range of exothermic heating from 435°C down to 412°C in the hottest point of the catalyst bed over the duration of the test) with an LHSV of 0.14 overall without development of noticeable pressure drop. The product oil became more viscous and brown as the exotherm waned and the lower bed peak temperature dropped to 410°C, so the oil heater set point was increased to 390°C at 19 h TOS. There appeared to be improved product quality, but some solids adhered to the bottle wall. The lower bed temperature increased back to 420°C. At 25 hr on stream, 150 ppm sulfide was added to the feedstock. The top zone oil heater set point was increased by 15°C, but no exotherm change was noted. The product remained a viscous emulsion (mousse) with some brown oil separating to the top. Attempts to centrifuge the mousses provided little separation of the emulsion.

When the catalyst became deactivated, the feed oil was shutdown and the reactor bed acetone washed, cooled, and disassembled. The front 4 to 5" of the removed bed was composed of little brown particles interspersed with catalyst. Some lightly coked catalyst was found about 5" into the Pd/C catalyst bed, at about the point of maximum heating in the upper bed from the exothermic reaction. The top bed was mostly loose catalyst; other than the small amount of coke, the rest of Pd/C catalyst poured out.

The coke had 0.5% each of Pd and Ni. The sulfur content was at 0.5 mole per mole of Ni, i.e. Ni_2S. Fe was found at half the amount of the Ni. Mo was found at ¼ of the Fe. Al, Si and P were present, but the amounts in the several samples were inconsistent. Also, some wall sliver/castes of coke were recovered at the front end of the bed. These contained half the Pd but were highly enriched (11% of total) in Ni and S in the same ratio as the coke. There was a high level of Cu, with no apparent explanation. The caste was also slightly enriched in Fe, twice the Pd, rather than half the Pd, as in the coke found among the catalyst granules. The caste was also enriched with Mo in the same ratio. There was more Si and P but less Al compared to the coke.

The lower portion of the top bed had a more reasonable Pd content of 0.7%. It also had significant Fe, Al, K and Ca. The sulfur content was half of that in the coke, but the Ni content was also much lower. The sulfur content was higher in the top of the bed and the nickel was somewhat higher but well below the level found in the coke. Al and Fe were also high in the front of the bed as was Mo. The K and Ca were not so high.

UOP hydrotreating catalyst was “coaxed” out; maybe it wouldn’t pour because it was damp. It was very lightly coked. Small area of clumping about 2” into hot stage (at 12” from the bottom). In this coked catalyst the Mo and Al were reduced to 60-65% while the Ni remained at the same level as measured in the fresh catalyst. A large deposit of Fe was present; but the S level was only at 70% of that in the fresh catalyst. The material was also enriched in Cr, K, Na, Ca, Mg, Zn and Mn. It contained 14.4% carbon. The used, but loose, catalyst in the bottom of the bed (mostly loose catalyst) had a 19.3% carbon content and the components were all diluted to 80 to 85% of the fresh catalyst amount, except for some enrichment (but much less than the charred catalyst) in Fe, K, Na, and Ca.

HT112

Fresh 2.5% Pd/C catalyst (470 cc PNNL catalyst) and a presulfided UOP hydrotreating catalyst(500 cc) were used as the low- and high-temperature beds, respectively. The bulk (top) phase from the 2nd corn stover bio-oil was used as feedstock, without sulfide added.

The test was on stream 87.3 hours at 245°C and 395-415°C with a LHSV of 0.14 overall. The catalysts remained active and no noticeable pressure drop developed; the test was stopped when we ran out of feed. At that point the system was shutdown, acetone washed and cooled. We noticed a unique problem of white deposits forming and plugging in the overhead condenser following the liquid product collection system. Incomplete analysis suggested that this material may be an ammonium carbonate type mineral. No significant elemental content was found by ICP (81 ppm Mo, 18 ppm Na, 16 ppm Fe, and 7 ppm Zn with 1 to 3 ppm of Al, Cu, Ni, Cr, and Pd).

HT116

Fresh 2.5% Pd/C, with 7% of used HT112 catalyst (485 cc total PNNL catalyst) and a presulfided UOP hydrocracking catalyst (480 cc) were used as the low- and high-temperature beds, respectively. The Kentucky oak 500°C bio-oil feedstock was tested without sulfide added.

The test was on stream for 60.1 hours at 257° and 415-420°C with a LHSV of 0.14. Catalysts deactivation was noted throughout. An emulsion product resulted by the end of the test, but no noticeable pressure drop developed. The reactor was shutdown, acetone washed and cooled. Upon opening the reactor a tenacious coke deposit was found in the front end at the same point of significant evidence of corrosion.

HT117

Fresh 2.5% Pd/C with 12% of used HT116 catalyst (465 cc total PNNL catalyst) and a presulfided UOP hydrotreating catalyst (515 cc) were used as the low- and high-temperature beds, respectively. The Kentucky oak 550°C bio-oil was used as feedstock with sulfide added because of catalyst deactivation in HT116.

The test was on stream for 27.2 hours at 257° and 414-422°C with a LHSV of 0.14 overall. Catalyst deactivation was noted throughout, but a rather sudden onset of formation of the emulsion product triggered the end of the run even though there was no noticeable pressure drop. The test was shutdown, acetone washed and cooled. Upon opening the reactor some coke deposit was found in the front end, as in earlier runs. It was noted that it was difficult to detect any incremental increase in corrosion of the reactor wall.

Non-isothermal Hydroprocessing of Mixed Wood bio-oil in a Hastelloy Reactor

HT121

For this test a Hastelloy 276 reactor tube (1” ID X 32.1” L) was used. Fresh 2.5%Pd/C catalyst (200 cc PNNL catalyst) and a presulfided UOP hydrotreating catalyst (210 cc) were used as the low- and high-temperature beds, respectively. The feedstock tested was the mixed wood bio-oil feedstock with sulfide added.

The test was on stream for 78 hours 252°C and 401-388°C with a LHSV of 0.29 in each bed (LHSV 0.14 overall). It appeared that the catalysts deactivated throughout; an emulsion product resulted by the end of the test. Noticeable pressure drop developed so the feed oil was shutdown at 80.6 h and the reactor acetone washed and cooled. When the reactor was opened, an intact coke deposit was found at 1.5-4” in from the front end of the reactor. There was no evidence of corrosion.

HT122

The HT121 test was repeated with a catalyst bed composed entirely of presulfided UOP hydrotreating catalyst (443 cc). The test extended 41.75 hours on stream at 262°C and 382-385°C with a LHSV of 0.14. Some catalyst deactivation was evident throughout. A noticeable pressure drop developed and the reactor was shutdown at 47.8 hr, acetone washed and cooled. An intact coke deposit was found at 1.5-3” in from the front end of the reactor. There was no evidence of corrosion.

HT123

Fresh 2.5% Pd/C catalyst (230 cc PNNL catalyst #59893-55-1) and presulfided UOP hydrotreating catalyst (210 cc) were used as the low- and high-temperature beds, respectively. A heavy phase was separated from the mixed wood bio-oil feedstock by water addition and was used as the feedstock with sulfide added.

The test extended 45.2 hours on stream at 252° and 401-396°C with a LHSV of 0.26 and 0.29 in the low- and high-temperature bed, respectively (0.14 overall). Catalyst deactivation was evident through the first 30 hr (density increasing from 0.79 g/mL to 0.88 g/mL), but nearly stable after that. A noticeable pressure drop developed, and the reactor was shutdown at 48.2 h, acetone washed and cooled. Upon opening the reactor an intact coke deposit was found 2-4” in from the front end and the balance of the catalyst bed poured out.

In the non-isothermal tests involving both UOP hydrocracking catalyst and PNNL hydrotreating catalyst, catalyst deactivation was evident based on increasing density of the oil product and its color. However, almost invariably the hydrotreating bed eventually coked and plugged while the hydrocracking catalyst had much less coke formation evident.

Expt #	database number	date	catalyst	feed stock	reactor configuration	time to plug (@ 340°C)	feed to plug
HT88	HT1-9	7/10-18/06	Pd/C	mixed wood	1.5” X 15” 1.77 sq in	38 h (intermediate washing)	4.6 liter
HT90		9/19-20/06	Pd/C	mixed wood	1.5” X 15” 1.77 sq in	31 h	3.32 liter
HT91	HT10	9/25-26/06	Pd/C w/Ru/C	mixed wood	1.5” X 15” 1.77 sq in	31 h	3.1 liter
HT92	HT11	9/27-29/06	Pd/C w/Ru/C	mixed wood	1.5” X 15” 1.77 sq in	37.5 h	3.75 liter
HT102		5/21-22/07	Pd/C w/Ru/TiO_2	mixed wood	1” X 32” 0.79 sq in	6.2 h	0.64 liter
HT103	HT12	5/22-23/07	Pd/C w/Ru/TiO_2	mixed wood	1” X 32” 0.79 sq in	10.2 h	1.04 liter
HT104		5/24/07	Pd/C w/Ru/TiO_2	mixed wood	1” X 32” 0.79 sq in	11.5 h	0.96 liter
HT105	HT12	5/25/07	Pd/C w/Pd/SiC	mixed wood	1” X 32” 0.79 sq in	6.7 h	0.66 liter
HT106	HT13-14	6/12-14/07	Pd/C	mixed wood	1” X 32” 0.79 sq in	28.8 h (@310°C)	3.42 liter
HT113	HT65-67	1/28-29/08	Pd/C	mixed wood	w /Silcosteel-CR	27.6 h	2.91 liter
HT115	HT68-70	5/5-6/08	Pd/C	mixed wood part	w/Silcosteel-CR with Hastelloy	24.9 h	2.69 liter

				sulfided	liner		
HT118	HT80	9/2-3/08	Pd/C	mixed wood sulfided	Hastelloy	14.6 h	1.25 liter
HT108	HT51-53	8/13-15/07	Pd/C	hot-filtered wood	1" X 32" 0.79 sq in	47 h	4.46 liter
HT96	HT21-23	12/13-14/06	Pd/C w/Ru/C & Pd/ZrO$_2$	corn stover light	1" X 32" 0.79 sq in	34.5 h (insulated at top)	3.65 liter
HT97	HT24-29	1/23-25/07	Pd/C w/Ru/C & Pd/ZrO$_2$	corn stover light	1" X 32" 0.79 sq in	66.9 h	7.41 liter
HT98	HT31-35	1/29-2/1/07	Pd/C w/Ru/TiO$_2$ & Pd/ZrO$_2$	corn stover heavy	1" X 32" 0.79 sq in	51.3 h with no pressure drop	4.25 liter
HT99	HT41-44	3/19-20/07	Pd/C w/Ru/TiO$_2$ & Pd/ZrO$_2$	new corn stover	1" X 32" 0.79 sq in	32.2 h	2.92 liter
HT100	HT45-48	3/21-22/07	Pd/C w/Ru/TiO$_2$	new corn stover	1" X 32" 0.79 sq in	33.3 h	3.2 liters
HT120	HT82-83	10/27-30/08	Pd/C	corn stover heavy	Hastelloy 0.79 sq in	68.5 h	7.14 liter
HT119	HT81	9/4/08	Pd/C	KY Oak 500°C sulfided	Hastelloy 0.79 sq in	10.1 h	1.26 liter
HYDROCRACKING							
HT93	HC1-2		UOP Hydro crack	HT mixed wood	1.5" X 15" 1.77 sq in	6.6 + 5.3 h outlet plugs	
HT94	HC3-4		UOP Hydrotreat	HT mixed wood	1.5" X 15" 1.77 sq in	7.7 h day's end	
HT95	HC5-6		UOP Hydrotreat	HT mixed wood	1.5" X 15" 1.77 sq in	6.5 h out of feed	
HT101	HC7-12		UOP Hydrotreat	HT corn stover phases	1" X 32" 0.79 sq in	64.1 h out of feed	4.65 liters
HT107	HC13-16		UOP Hydrotreat	HT mixed wood	1" X 32" 0.79 sq in	25.7 h out of feed	1.56 liters
HT110	HC17-19		UOP Hydrotreat	HT hot-filtered	1" X 32" 0.79 sq in	26.4 h out of feed	1.84 liters
NON-ISOTHERMAL							
HT109	HT54-59 HC20-25	8/20-24/07	CoMoS	hot-filtered wood	1.5" X 15" 1.77 sq in	101.7 h with no pressure drop, but catalyst is coked	13.73 liters
HT111	HT61-62 HC26-27	11/5-7/07	Pd/C & UOP Hydrotreat	mixed wood	1.5" X 15" 1.77 sq in	32.8 h with no pressure drop but catalyst deactivated	4.44 liter
HT112	HT63-64 HC28-29	11/13-16/07	Pd/C & UOP	new corn stover	1.5" X 15" 1.77 sq in	87.3 h with no pressure drop,	11.54 liters

			Hydrotreat			maintained catalyst activity	
HT116	HT71-74 HC30-33	6/30-7/2/08	Pd/C & UOP Hydro crack	KY Oak 500°C	1.5” X 15” 1.77 sq in	60.1 h with no pressure drop but catalyst deactivated	8.07 liter
HT117	HT76-79 HC35-38	7/7-8/08	Pd/C & UOP Hydrotreating	KY Oak 550°C sulfided	1.5” X 15” 1.77 sq in	27.2 h with no pressure drop but catalyst deactivated	3.66 liter
HT121		12/8-11/08	Pd/C & UOP Hydrotreating	mixed wood with sulfide	1” X 32” Hastelloy	78 h until pressure drop and catalyst deactivated	4.13 liter
HT122		12/15-17/08	Pd/C & UOP Hydrotreating	mixed wood with sulfide	1” X 32” Hastelloy	41.8 h until pressure drop with some catalyst deactivation	2.84 liter
HT123		2/3-5/09	Pd/C & UOP Hydrotreating	mixed wood, heavy phase with sulfide	1” X 32” Hastelloy	45 until pressure drop and deactivated catalyst stabilized	3.14 liter

Table 11. Hydroprocessing Test Summary

Discussion of Results

Feedstock Descriptions

The bio-oil feedstocks for these hydroprocessing tests were provided by the National Renewable Energy Laboratory through the joint CRADA with UOP and PNNL. The bio-oils were produced as described in the related portion of this report. The bio-oil feedstocks were shipped from NREL to PNNL at various times through the project. The bio-oils were stored in well-sealed containers in closed cabinets. The bio-oils were of various ages at the time of hydrotreatment depending on the progress in the research project.

The bio-oils represented several biomass types. A mixed wood feedstock was used to produce the bulk of the bio-oil. Corn stover was pyrolyzed at two different times and at two different conditions. The original corn stove bio-oil was phase separated as received into a light (more hydrophilic) phase and a heavy (more hydrophobic) phase, which were tested separately. The second corn stover bio-oil was received in essentially one phase. However, over time a dodecane (quenching solvent) layer was recovered off the top of this bio-oil and a heavy phase began to separate as well. Oak-derived bio-oils produced at three different temperatures were also received and tested. Finally, we also tested a poplar wood derived bio-oil which had been produced in 1996 using a hot-vapor filtration method at NREL.

In order to calculate elemental balances around our hydroprocessing experiments, these bio-oils were analyzed (Columbia Analytical Services) for carbon, hydrogen, nitrogen, and oxygen, and in most cases sulfur. The range of the analyses (as they were performed numerous times throughout the project) is presented in **Table 13**. These analyses show a range of products dependent on the biomass feedstock but also on the phase stability or the pyrolysis temperature. They also show the variability of the analytical result due to the inhomogeneity of the bio-oil. The oxygen entry for the single set of data for the Oak 550°C appears to be an error based on the lack of closure to 100% and in comparison to the other two oak bio-oils. The light phases are a more water soluble material and have a higher moisture content and lower carbon content. The nitrogen content is highly dependent on the biomass feedstock. The corn stover produced a much higher nitrogen content bio-oil. Sulfur levels are typically lower than nitrogen, often by an order of magnitude. The poplar bio-oil is the single exception. **Table 14** shows these analyses corrected to a moisture-free basis. The higher carbon content of the wood bio-oils is evident as underlined by the lower hydrogen to carbon atomic ratio. The temperature trend in the oak bio-oils is also noticeable with lower H/C ratios at higher temperature

biomass	**carbon**	**hydrogen**	**oxygen**	**nitrogen**	**sulfur (as received)**	**sulfur (sulfided)**
mixed wood	45.00, 47.74 51.12, 44.04 41.88, 43.98	7.28, 7.38 7.20, 7.70 7.04, 6.87	41.09, 46.09 47.64, 46.64 44.90, 45.00	0.16, 0.16 0.16, 0.16, 0.16, 0.18, 0.16	0.028	0.033, 0.032, 0.026
mixed wood heavy phase	56.08	6.90	39.60	0.46	NA	0.036
corn stover light phase	31.22, 26.08	8.17, 9.37	57.77, 52.92	0.87, 0.27	0.046	NA
corn stover heavy phase	55.75, 52.46, 50.02	6.36, 7.62, 7.24	43.45, 32.68, 35.87	0.92, 1.32, 1.12	0.170, 0.16	NA
2nd corn stover	30.42, 33.77	7.44, 8.77	56.34, 54.51	0.68, 0.63	0.048, 0.076	NA
oak 500°C	42.50	7.16	49.74	0.12	0.008	NA
oak 550°C	37.48	7.37	28.20(?)	<0.05	NA	0.020
oak 600°C light phase	26.47	7.78	60.85	0.19	0.008	NA
oak 600°C heavy phase	59.58	6.54	32.11	0.33	0.024	NA
poplar	46.50, 46.20	7.05, 6.94	40.88, 42.33	<0.05, 0.05	0.16, 0.149	NA

Table 13. Elemental Analysis of Bio-oil Feedstocks

biomass	H/C	carbon	hydrogen	oxygen	nitrogen
mixed wood	1.28	57.7	6.2	33.7	0.2
mixed wood heavy phase	0.94	73.2	5.8	25.3	0.6
corn stover light phase	1.76	48.8	7.2	31.8	1.0
corn stover heavy phase	1.20	62.6	6.3	27.7	1.3
2nd corn stover	1.48	50.6	6.3	36.2	1.0
oak 500°C	1.27	55.4	5.9	37.9	0.2
oak 550°C	1.06	58.6	5.2	10.4(?)	0.0
oak 600°C light phase	1.65	41.8	5.8	44.8	0.0
oak 600°C heavy phase	1.03	68.0	5.9	24.1	0.4
poplar (hot-filtered)	1.26	56.9	6.0	30.9	0.0

Table 14. Elemental Composition of Bio-oils on a Moisture-Free Basis

We also performed density measurements to facilitate mass balances and moisture analyses to better understand the elemental compositions. Total Acid Number and viscosity were also analyzed in most cases. These analyses are shown in **Table 15.** These analyses show that the lighter phases, of course, have lower densities; and also are less viscous. They contain a much higher level of dissolved water (moisture). The acid numbers are extremely high compared to the experience with petroleum feedstocks. The high level of oxygenates include organic acids but also phenolics, which would also be included in this analysis. The pyrolytic lignin number is the residual water insolubles determined by aggressive stirring of the bio-oil into water. It is believed to represent lignin-derived polymeric structure, which has not been effectively pyrolyzed.

biomass	density	TAN	viscosity	moisture	pyrolytic lignin
mixed wood	1.177@25°C	117, 111.4, 200.2, 150.8	36.6 @40°C, 39.5@40°C	22.45, 19.6, 20.71, 21.1	22.31
mixed wood heavy phase	1.211	87.2	NA	22.63	NA
corn stover light phase	1.087@25°C	133.3	4.4@40°C	41.94, 40.61	5.37
corn stover heavy phase	1.154@25°C	107.8, 140.67, 195.6	409@40°C	16.4, 15.82, 15.24	57.5
2nd corn stover	1.16	134.6, 125.27	NA	38.56, 34.44	NA
oak 500°C	1.21	166.9	NA	23.29	NA
oak 550°C	1.19	111.1	NA	36.0	NA
oak 600°C	1.11	40.7	NA	36.6	NA

light phase					
oak 600°C heavy phase	NA	131.4	NA	12.4	NA
poplar	1.166@25°C	172.8, 199.4	49.1@40°C,	18.68, 18.34	NA

Table 15. Bio-oil Properties

Trace element analysis was performed by inductively-coupled plasma/optical emission spectroscopy (ICP-OES) on most of the bio-oils. The results are shown in **Table 16**. These results show that the bio-oils carried most of the elements expected to be found in the biomass feedstock. The ag residue (corn stover) bio-oil, with a higher loading of ash, resulted in a bio-oil with a higher level of most of these elements compared to the wood-derived bio-oils. A notable exception to the biomass-derived scenario was the high level of nickel found in the mixed wood and corn stover bio-oils. The poplar bio-oil had a significantly reduced level of contaminants as a result of the hot-filtration vapor cleanup step applied in the earlier test. The low sulfur content found by ICP in the hot-filtered poplar bio-oil was at odds with the direct total sulfur analysis by thermal method. The relatively higher zinc and iron contents became noticeable in the catalyst bed plug analysis described later. It was reasonable to assume that the iron and zinc are corrosion products from the reactor systems used in its production/collection. Similarly, the high nickel content is also likely resulting from the processing system rather than derived from the biomass feedstock.

element	mixed wood	corn stover light phase	corn stover heavy phase	2nd corn stover	poplar, hot-filtered	oak, 500°C	oak, 550°C
Sulfur	210.0	436.0	1190.0	518.0	65.6	93	127
Potassium	78.0	460.0	243.0	407.0	8.7	113	99
Calcium	36.9	120.0	140.0	89.4	14.6	161	115
Sodium	40.4	68.3	41.9	235.0	34.3	96	85
Magnesium	22.2	63.7	57.7	46.7	2.4	14	9
Nickel	58.1	40.5	64.2	24.3	3.9	5	6
Aluminum	31.0	31.8	139.0	31.5	1.8	8	6
Iron	8.0	17.5	46.3	13.6	34.0	15	27
Phosphorus	8.0	12.9	29.1	2.9	ND	28	16
Zinc	7.0	8.2	88.5	0.4	46.2	22	30
Silicon	ND	9.4	105.0	3.9	ND	18	17
Copper	4.2	1.5	5.1	1.0	4.5	15	31
Manganese	0.3	1.2	1.9	1.0	0.4	2	2
Titanium	0.5	0.1	2.4	0.7	0.5	1	2
Zirconium	0.7	0.1	0.1	0.6	1.8	0.4	0.8
Cadmium	0.07	0.05	0.19	0.19	0.12	ND	1
Cobalt	0.16	0.06	0.08	0.003	0.01	20	ND
Chromium	0.07	ND	1.3	ND	ND	2	3
Molybdenum	ND	ND	0.4	ND	ND	2	2

Table 16. Trace Element Analysis of Bio-oils, mg/L

4.2 Hydrotreating Process Results

In the hydrotreating process development effort the testing focused on the low-temperature processing using the palladium on carbon catalyst, which was recently patented by Battelle. Comparisons can be made between the several biomass feedstock bio-oils to determine an effect of feedstock. Some process optimization was also performed around process temperature and residence time, as measured by liquid hourly space velocity.

The effect of feedstock was not dramatic in terms of yield structure, hydrogen consumption, or relative strength of the exothermic reaction, as the fast pyrolysis process tended to produce a relatively similar bio-oil from all biomasses. That being said, there were important differences in the composition of the bio-oils which were reflected in the hydrotreatment processing results. In making these comparisons we were forced to ignore the potential effect of the front end bed of a pretreatment catalyst used in several of the corn stover bio-oil tests. As related in section 4.3, the differences did not appear to be large and could be reasonably ignored in this comparison. Process results with the several feedstocks at 340°C, 2000 psig and 0.14-0.25 LHSV (with large excess hydrogen flow, 10,000 SCF/bbl) are given in Table 17.

bio-oil	**oil yield, g/g dry feed**	**aqueous yield, g/g wet feed**	**gas yield, g/g carbon feed**	**Hydrogen consumption, liter/liter feed**	**Relative exotherm versus setpoint**
mixed wood	0.62	0.48	0.062	205	+6°C
corn stover light phase	0.45	0.68	0.071	82	+0°C
corn stover heavy phase	0.78	0.31	0.073	128	+3°C
2nd corn stover	0.45	0.61	0.066	76	+3°C
poplar	0.59	0.46	0.060	252	+2°C

Table 17. Feedstock Effect on Hydrotreating Process Results

These results showed that a higher oil product yield was obtained from the whole bio-oil or the heavy phase, when adjusted to the amount of dry organic material fed. Similarly, the light phase resulted in less oil product and a larger aqueous phase (primarily because of the larger fraction of water in the feedstock). Gas generation was relatively low in all cases. A moderate bed heating suggested an exothermic reaction. The results support the view that the second corn stover bio-oil was more similar to the light phase of the 1st corn stover bio-oil.

The effect of process parameters can be evaluated for the mixed wood bio-oil feedstock using the Pd/C catalyst. All tests were performed at nominally 2000 psig with a large excess flow of hydrogen (10,000 scf/bbl) with results shown in Table 18. At higher temperature the gas yield increases as does the hydrogen consumption and the oil yield decreases. The oxygen content appears to hit a "sweet spot" at a set point of 340°C in the reactor bed. Higher temperature operation did not reduce the oxygen content of the product oil further and the product actually had more oxygen. At higher flow rate (lower residence time) the remaining oxygen content of the product oil is higher and the hydrogen consumption is reduced. It appeared that the hydrocarbon portion of the oil was reduced by cracking to gas rather than increased hydrodeoxygenation of the oil.

parameter	oil yield, g/g dry feed	oxygen content dry basis	aqueous yield, g/g wet feed	gas yield, g/g carbon feed	Hydrogen consumption, liter/liter feed	Relative exotherm versus setpoint
Temp., °C						
310	0.75	11.6	0.35	0.037		+5°C
340	0.62	10.2	0.48	0.062	205	+6°C
360	0.56	16.2	0.47	0.109	262	+8°C
LHSV, L/L/hr						
0.25	0.62	10.2	0.48	0.062	205	+6°C
0.70	0.62	20.8	0.41	0.076	106	+5°C

Table 18. Process Parameter Effects on Hydroprocessing Results

4.2.1 Hydrotreating Product Composition

The chemical composition of the biomass feedstock and the derived bio-oil product from a specific biomass remained evident in the composition of the hydrotreated bio-oil products as shown in Table 19. The composition of the bio-oils is similar for all feedstocks. The relatively clean (low nitrogen and sulfur) mixed wood and oak wood bio-oils was translated into relatively clean hydrotreated products.

bio-oil source	H/C (dry)	C	H	O	N	S	moisture
mixed wood	1.43	75.5	9.4	12.3	0.6	0.02	2.7
corn stover light phase	1.28	76.2	8.5	15.5	2.4	NA	2.6
corn stover heavy phase	1.40	76.2	9.4	12.7	2.0	0.06	3.5
2nd corn stover	1.53	77.1	10.2	11.9	2.3	NA	2.9
oak (500C)	1.35	74.2	9.0	14.5	0.1	0.01	5.7
poplar (hot-filtered)	1.33	73.1	8.6	17.9	0.2	0.16	3.5

340°C, 2000 psig, 0.25 LHSV

Table 19. Composition of Hydrotreated Bio-oils.

The several tests with different front end (pre-treatment) catalyst beds had remarkedly little effect on the final product composition. A summary of the different products is presented in Table 20. In all these tests the main catalyst bed, comprising 85 to 90% of the reactor volume was the 2.5 wt% Pd on carbon catalyst. Variations in the product are derived primarily from the differences in the feedstock tested.

bio-oil source	catalyst	C	H	O	N	S	Moisture	TAN	viscosity	density g/mL
mixed wood	Pd/C only	72.8	8.6	18.9	0.4	NA	4.2	74	657 cSt @ 100°C	1.06
mixed wood	Ru/C	71.7	9.0	19.4	0.4	NA	4.0	79	1367 cSt @ 100 °C	1.05
mixed wood	Pd/SiC	75.5	9.4	12.3	0.6	0.02	2.7	49	NA	1.02
corn stover light phase	Ru/C & Pd/ZrO_2	76.2	8.5	15.5	2.4	NA	2.6	54	36 cPs @ 80°C	1.02
corn stover heavy phase	Ru/TiO_2 & Pd/ZrO_2	76.2	9.4	12.7	2.0	0.06	3.5	46	NA	1.05
2nd corn stover	Ru/TiO_2 & Pd/ZrO_2	77.1	10.2	11.9	2.3	NA	2.9	60	NA	1.04
2nd corn stover	Ru/TiO_2	77.6	10.6	11.8	1.8	NA	3.3	52	NA	1.04

340°C, 2000 psig, 0.25 LHSV

Table 20. Composition of Hydrotreated Products using different Pre-treatment catalysts

In all the 1st stage hydrotreating tests a 2-phase product was produced. In addition to the oil products described above, there was also a separate aqueous phase product. The aqueous phase was typically contaminated with the soluble portion of the product oil. In addition to the dissolved carbon found in the water, the nitrogen and sulfur residues from the feedstock were also found. As shown by the data plotted in **Figure 7,** the amount of dissolved carbon as a straight-line function of the amount of oxygen remaining in the product oil in the range of hydrotreated products tested. Apparently the relationship changes as the oxygen content is reduced to lower levels, so that the carbon dissolved in the water will approach zero when the product oil approaches a pure hydrocarbon product.

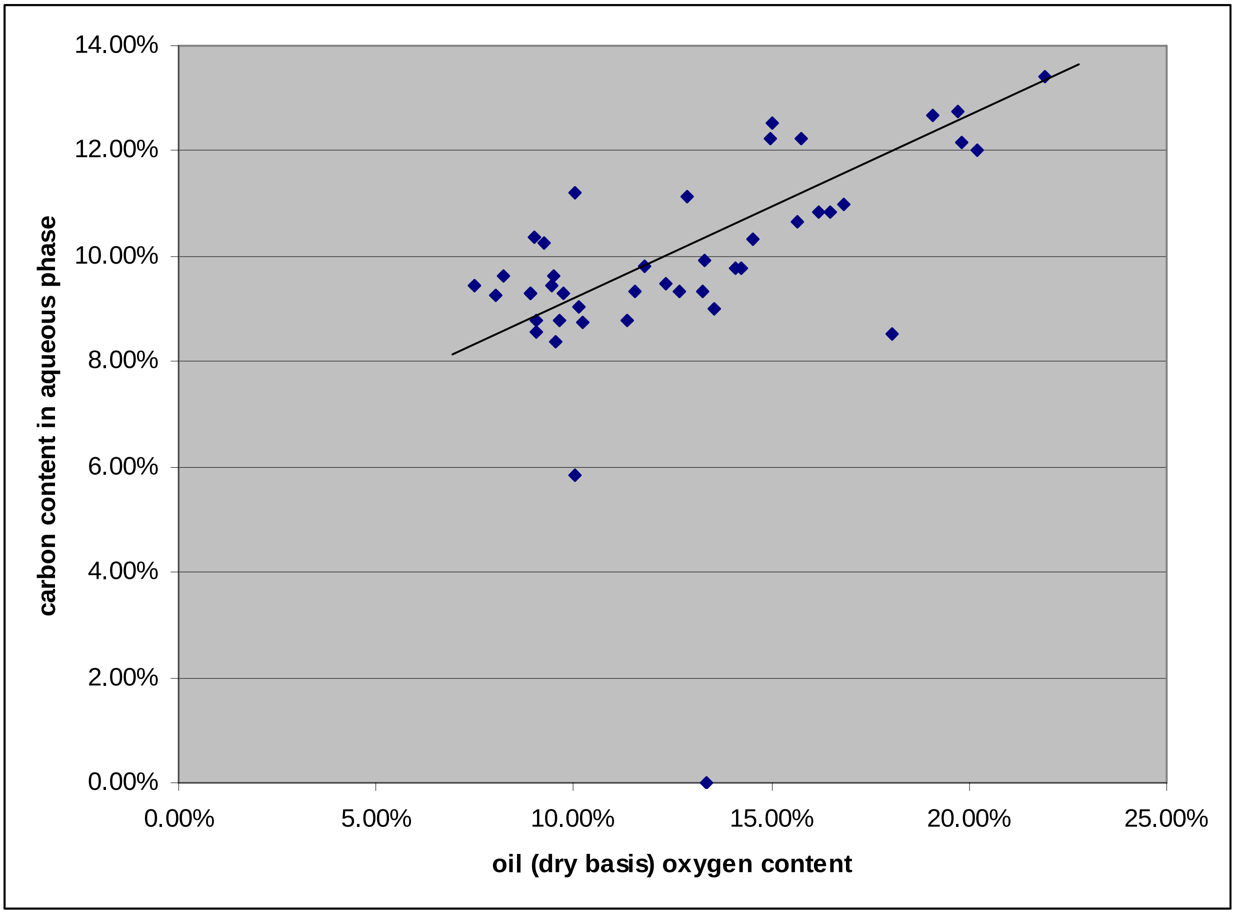

Figure 7. Dissolved carbon in byproduct water versus the residual oxygen in the product oil

As shown in **Figure 8** there is a limited relationship between the nitrogen content of the product oil and the nitrogen content of the aqueous byproduct. The nitrogen resides primarily in the oil product with the amount in the aqueous byproduct being lower by an order of magnitude or more. The nitrogen content of the oil phase seems to define an upper limit for the nitrogen in the aqueous phase; however, there are a large number of products which have significantly lower nitrogen contents in the aqueous phase than would be predicted based on the oil composition.

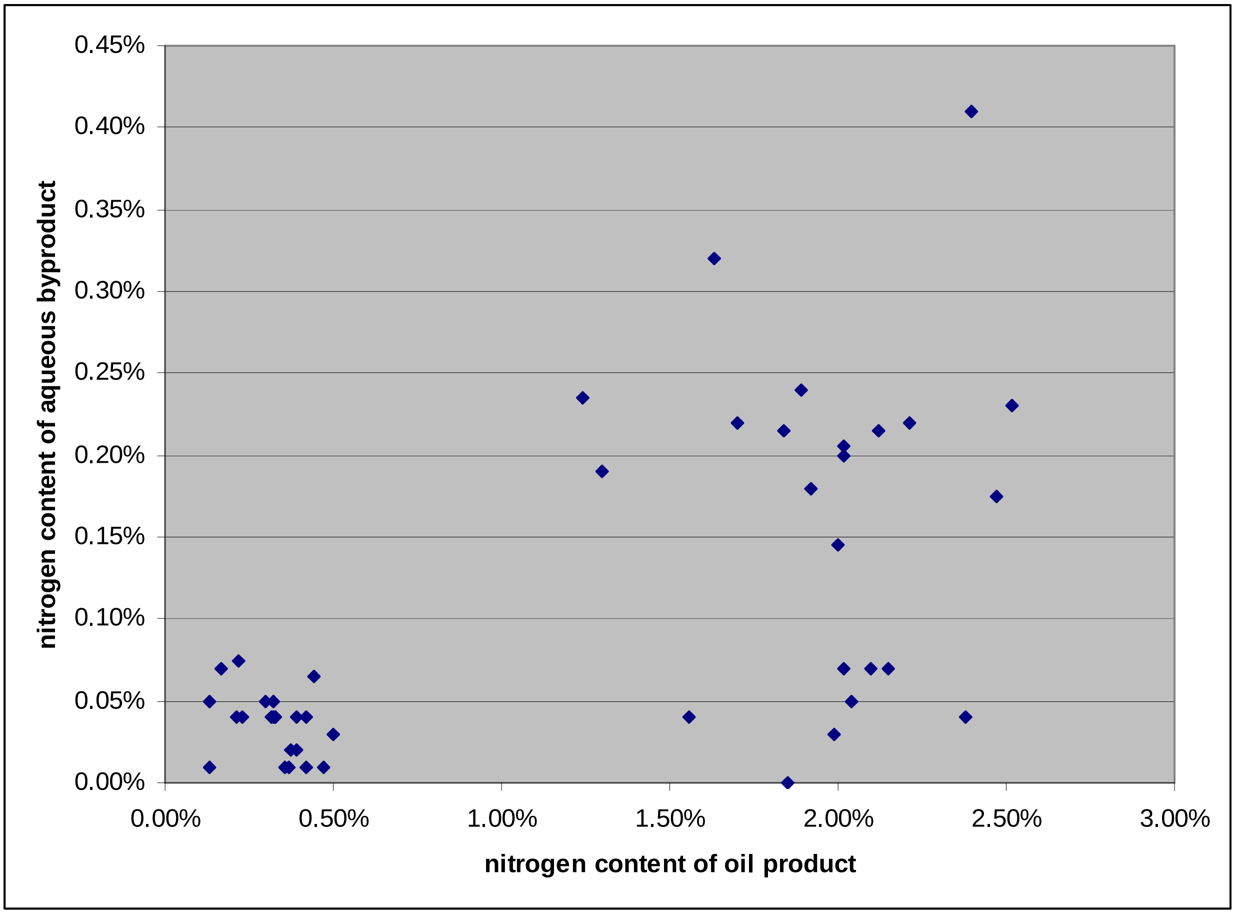

Figure 8. Relationship of nitrogen contents in oil product relative to the aqueous byproduct

The gas products from the hydrotreating tests were minimal in amount and typically the same composition. The main gas collected was hydrogen, as there was a great excess of hydrogen added to the reactor system to maintain a high partial pressure and facilitate its mass transfer. Because of the operational procedures for the bench-scale reactor, and specifically the liquid product collectors, the gas product recovered from the vent was diluted with nitrogen gas. The nitrogen was present in the reactor portion but was used to repressurize the collectors to reaction pressure prior to their being rotated into use and going “on stream.” The main product gas was carbon dioxide with a smaller amount of methane. In the higher temperature tests carbon monoxide was also found as were larger amounts of other hydrocarbon gases including ethane and propane. On a nitrogen-free basis the product gas was typically 96 to 98% hydrogen with 1 to 4 percent carbon dioxide, less than 1 percent methane, and less than 0.1% of ethane or propane and higher hydrocarbon gases.

Many of the products were analyzed by gas chromatography (GC) to better understand the specific component composition of the bio-oils and products. A GC equipped with a mass selective detector (MSD) was used to identify specific components. A GC equipped with a flame ionization detector (FID) was used to quantify the components. The GC FID served as a better base for quantitation because of the more uniform response of the various types of components in the bio-oil. The relative response for any given functional type varied from another functional type by +/-30% for those quantified in this study. As a result, the table of quantities shown below should be taken as approximate, as all components were not individually quantified, but a representative standard was used for all components. Clearly the trends in the data were evident. The chromatographs were quite complex and with the wide range of polarity among the various component types, not easily resolved in all cases.

Table 21. provides data on product oils from hydrotreating the mixed wood bio-oil (in the Silcosteel-CR coated reactor). The data listed under Feed 1 and Feed 2 represented two samples of the mixed wood bio-oil and demonstrated the range of variation in the analyses. O1, O2 and O3 are data for three different hydrotreated products from a single test (HT113). The show a trend of catalyst deactivation wherein the O1 sample has a larger fraction of actual alkane hydrocarbon products and less residual intermediate alkylphenolic and alkylguaiacolic products. In addition to these component groups found in the wood-derived bio-oils, alkylated pyrolles were found at low levels in the corn stover derived bio-oils. In the nomenclature used in Table 11, total alkanes includes all cyclic and acyclic alkanes, and complex guaiacols includes compounds that are guaiacol structures containing ring-substituents having carbonyl or olefin structures.

component group	Feed 1	O1	Feed 2	O2	O3
unsaturated ketones/aldehydes	3.37%	0.98%	4.46%	0.00%	0.39%
carbonyls (hydroxyketones, aldehydes)	9.27%	3.27%	9.36%	0.00%	0.00%
Total alkanes	0.00%	9.86%	0.00%	4.45%	3.18%
saturated guaiacols(diol,ones)	0.00%	0.15%	0.00%	0.29%	0.71%
phenol and alkyl phenols	10.27%	13.86%	6.83%	18.55%	26.67%
alcohols & diols	3.50%	4.62%	9.31%	5.29%	1.94%
HDO aromatics	0.00%	0.81%	0.00%	0.87%	0.27%
Total saturated ketones	1.13%	21.00%	0.96%	25.08%	17.68%
Total acids & esters	19.78%	23.43%	41.81%	25.21%	25.68%
Total furans & furanones	8.50%	1.09%	3.01%	2.19%	1.52%
Total tetrahydrofurans	3.18%	3.26%	2.88%	4.65%	2.35%
Complex guaiacols	26.40%	9.49%	8.34%	4.57%	7.70%
guaiacol and alkyl guaiacols	7.77%	5.00%	6.71%	5.41%	6.70%
unknowns	6.83%	3.17%	6.32%	3.44%	5.21%
TOTAL	100.00%	100.00%	100.00%	100.00%	100.00%

Table 21. Hydrotreating Product Oil Chemical Components

Hydrotreater Reactor Plugging

Over the life of the project, plugging in the front end of the catalyst bed, effectively in the heat up zone, became recognized as a critical limitation to the hydroprocessing of bio-oil. The tendency toward polymer formation (identified as thermal instability of the bio-oil) in the catalyst bed resulted in the buildup of pressure drop over time. After shutdown of the experiment a solid plug of “coke” encrusted catalyst particles that had formed in a portion of the catalyst bed could be recovered for analysis. Several options to eliminate the coking were addressed in the research, including:

- lower temperatures in the 1st stage,
- different catalysts,
- the effects of different biomass sources,
- elimination of reactor wall corrosion products, and
- removal of instability-causing components by phase separation of the bio-oil.

In earlier hydrotreating studies at PNNL[1] at lower temperature, 180 to 240°C, no evidence of coke formation in the hydrotreater catalyst bed was noted. As described earlier, the initial tests within this project were performed over four days at 340°C to 370°C but were only extended from 8-10 hours on stream before shutdown and the catalyst bed washed with acetone. In these tests no plugging was noted through 35 hr of operation until the 5th day when a much higher flow rate was attempted. After 5 hr of operation this bed had become unrecoverably plugged. Subsequent tests of 30 to 40 hours at 340°C similarly resulted in plugged catalyst beds. The time of plugging was noted when there was a change in pressure drop (>5 psig) over the catalyst bed. The “total flow until plugging” is the amount of bio-oil fed to the reactor system from the introduction of bio-oil until the time of plugging. Following those tests an attempt was made at 315°C. In this test the plug took longer to form and upon opening the reactor the plug was found further into the catalyst bed, essentially at the same point of heat up, where the bio-oil was passing through the range of 300°C. Other tests performed in the non-isothermal configuration involved a 1st stage catalyst bed at only 250°C. As shown in **Figure 9**, in these lower temperature tests the plugging in the catalyst bed was delayed even further. Several of these tests were not pursued to the point of plugging, therefore the trend indicated in the figure is at least as steep as shown and potentially much more so (as indicated by the arrows). However, these times on stream are exceptionally short relative to conventional operations in petroleum processing.

The results presented in **Figure 9** include an additional normalization based on cross-sectional area of the reactor. This correction is required because the reactor initially used has a 1.5 inch internal diameter while later reactors had an internal diameter of 1.0 inch. The reactors were of different lengths such that the volumes of the catalyst beds were the same. Since the plug required sufficient

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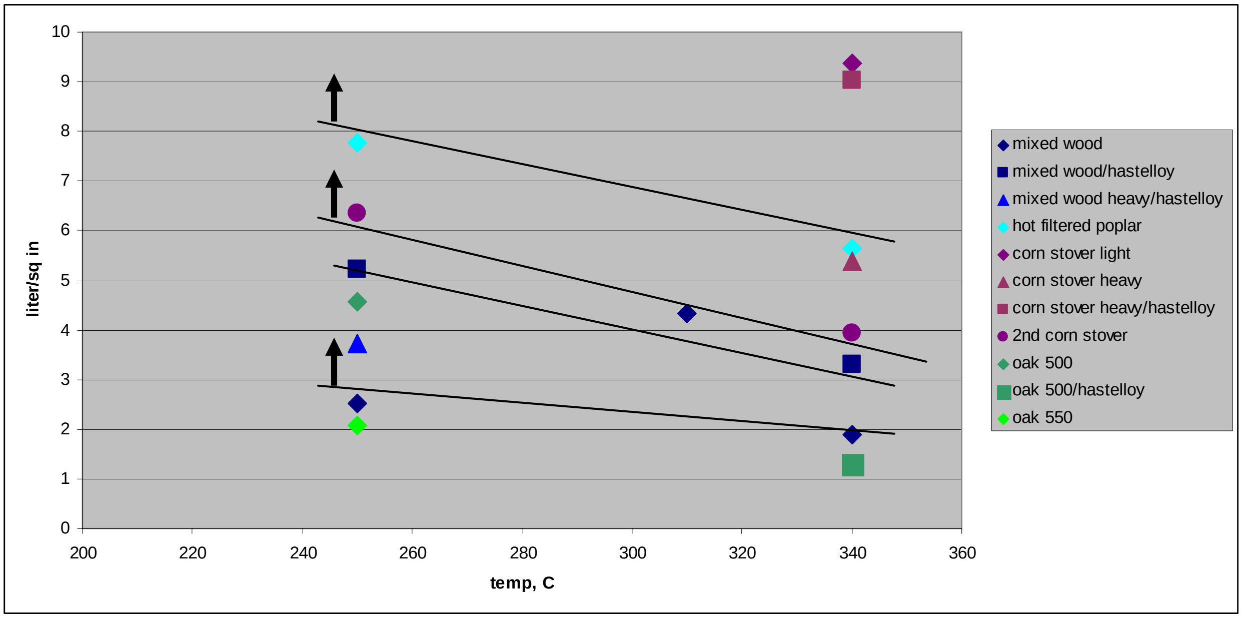
[1] Elliott, D.C.; Neuenschwander, G.G.; Hart, T.R.; Hu, J.; Solana, A.E.; Cao, C. 2006. “Hydrogenation of Bio-Oil for Chemical and Fuel Production.” In: **Science in Thermal and Chemical Biomass Conversion**, A. V. Bridgwater and D. G. B. Boocock, eds., pp. 1536-1546, CPL Press, Newbury Berks, UK.

mass to seal the cross sectional area, different masses of plug material were required in the two reactors. Therefore, using the same volumetric flow in each reactor to maintain the same space velocity, the "time to plugging" was dependent on the cross sectional area.



Tests at nominally 2000 psig with flow rate (LHSV) of about 0.25 liter bio-oil per liter of catalyst bed per hour

Figure 9. Temperature effect on total flow until plugging

We have considered the effect of feedstock composition on the plugging issue. In all cases at 340°C the plug eventually formed. The time on stream to development of a pressure drop suggested some differences in comparing the several feedstocks. The wood bio-oils (mixed wood or oak) resulted in coke formation more quickly than the corn stover bio-oils. The relevant results, corrected for cross sectional area of the reactor are presented in **Figure 9**.

The catalyst bed was typically Pd on carbon granules in the feedstock comparison tests, performed at 340°C. In the tests presented in **Table 22** there was an alternate material in the front end of the bed, which, as described earlier, appeared to have little effect on the coking issue. The "time to plugging" is the time of operation of the reactor system from the introduction of bio-oil until a noticeable change in pressure drop (>5 psig) over the catalyst bed was noted. The amount of oil feed over the time to plugging was then corrected for cross sectional area of the reactor for comparison purposes. From these results it is apparent that the alternative catalysts had only a minor effect on the plugging compared to the much larger effect due to feedstock composition differences between mixed wood and corn stover.

bio-oil	**time to plugging**	**volume oil fed**	**liter/sq in**
mixed wood, Pd/C only	31 hr	3.32 liter	1.88
mixed wood, Ru/C in front of Pd/C	31-37.5 hr	3.10-3.75 liter	1.75-2.12
mixed wood, Ru/TiO_2 in front of Pd/C	10.2-11.5 hr	1.04-0.96 liter	1.32-1.22
mixed wood, Pd/SiC instead of Pd/C	6.7 hr	0.66 liter	0.84
corn stover light phase, Pd/ZrO_2	66.9 hr	7.41 liter	9.38
2nd corn stover with Ru/TiO_2 and Pd/ZrO_2 in front of Pd/C	32.2 hr	2.92 liter	3.70
2nd corn stover with Ru/TiO_2 in front of Pd/C	33.3 hr	3.3 liter	4.18

Table 22. Bio-oil processed with several catalyst front end beds

Corrosion of the reactor wall and the thermowell had been previously noted as a result of hydrotreating tests. The corrosion noted in these tests appeared to be associated with the zone of coke formation, i.e., toward the front end of the reactor and in the zone where the bio-oil is reaching the reaction temperature. Of course, this is the region most exposed to the bio-oil in its most acidic "primary" form before it has reacted and been "stabilized." The composition of the coke was examined in detail in an electron microscope. Imaging of the catalyst pellets encrusted in coke provided information about the elemental composition of the coke. Early on it was recognized that the metals with significant presence in the coke were nickel and iron, metals also found in the reactor wall, along with sulfur. As a result of the corrosion and the apparent link to coke formation, alternate materials were tested for the reactor wall. The 304 stainless steel was given a corrosion resistant coating in a commercial method called Silcosteel-CR. In another test, the reactor was fitted with a Hastelloy liner. In this case, all fittings and tubing on the feed side were also replaced with Hastelloy units. The feed pump was not replaced as it was fabricated from nitronic 50, which is a high-nickel alloy similar to Hastelloy. Finally, a Hastelloy reactor was put into operation. Comparative results for these test are given in **Table 23.** The first three tests strongly suggest that a corrosion-based mechanism might be linked to the coke formation. However, even with corrosion resistant construction, the coke formation still occurred and was only delayed. The last test seems to imply that addition of sulfur into the reaction environment will facilitate coke formation to such a degree that the advantage of a corrosion-resistant alloy construction is over-ridden.

reactor material	time to plugging	volume oil fed	liter/sq in
304 SS (1.77 sq in cross sectional reactor)	31 hr	3.32 liter	1.88
Silcosteel-CR-coated 304SS	27.6 hr	2.76 liter	3.49
Hastelloy-liner in 304SS	24.9 hr	2.49 liter	3.59-4.14
Hastelloy C-276 (sulfided bio-oil)	14.6 hr	1.19 liter	1.51

Table 23. Mixed wood bio-oil processed in reactors of different materials of construction

Analysis of Plug Material from Heat-up zone of Hydrotreating

Samples of the coke encrusted catalyst bed ("plug") were analyzed in several tests with electron microscopy (SEM) with electron dispersive spectroscopy (EDS). With these results the catalyst particle structures can be evaluated and elemental composition of deposits can be ascertained.

Oak 500°C bio-oil w/Pd-C catalyst (HT116)

The electron micrograph (**Figure 9**) at right shows a cross section of the plug with several catalyst pellets visible. The particle at center left showed evidence of surface coating while the particle in the upper middle seemed to be coating free. This sample was from a non-isothermal hydroprocessing test wherein the Pd catalyst was operated at about 250°C.

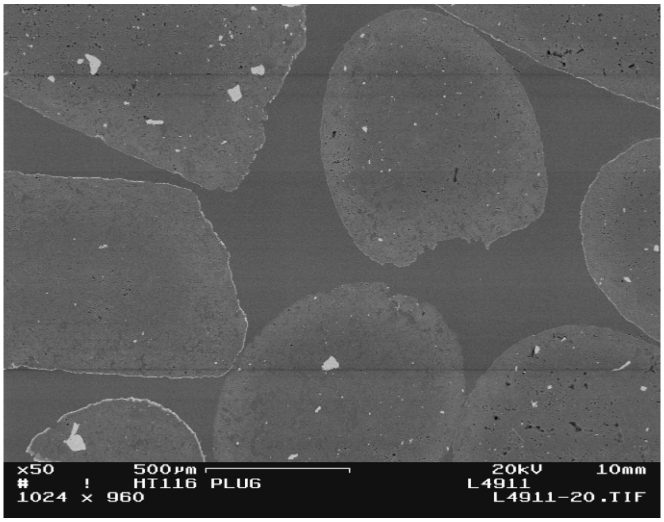


Figure 9 SEM of plug & catalyst

The EDS analysis of the coating free catalyst (**Figure 10-**higher resolution SEM at left) provided the profile of elements along a pathway over the catalyst particle from the edge toward the center of the particle. Carbon, being the catalyst support, was the major element throughout. The palladium composition across the particle suggested a strongly surface-impregnated (edge-coated) catalyst. Sulfur was found throughout the catalyst particle. The spectroscopy along line is shown in the four graphs below. Analysis of the light colored spot showed that it was a silicon rich inclusion.

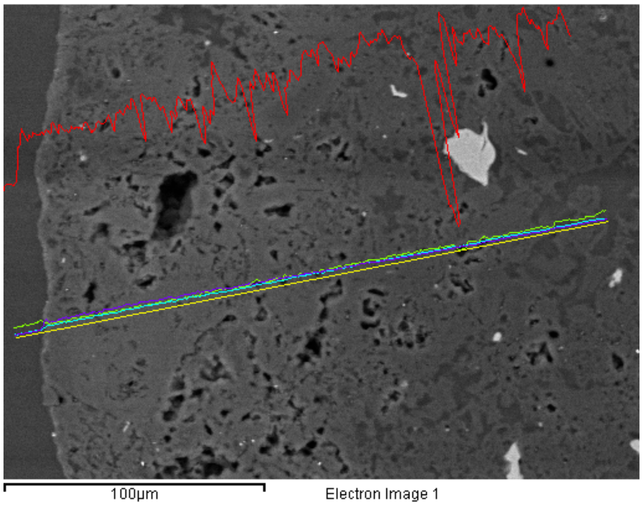


Figure 10a-EDS of catalyst particle from plug region

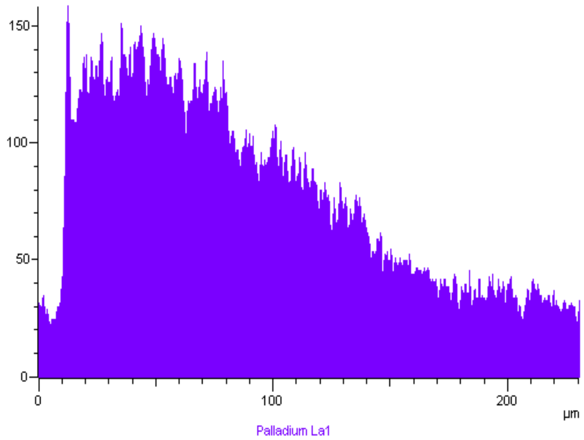


Figure 10b-Pd EDS of catalyst particle from plug region

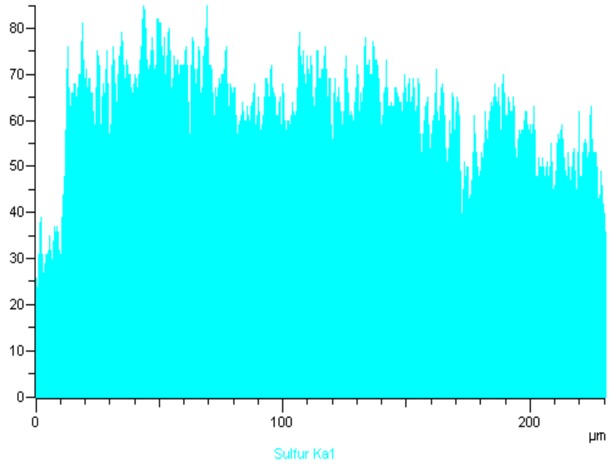


Figure 10c- S EDS of catalyst particle from plug region

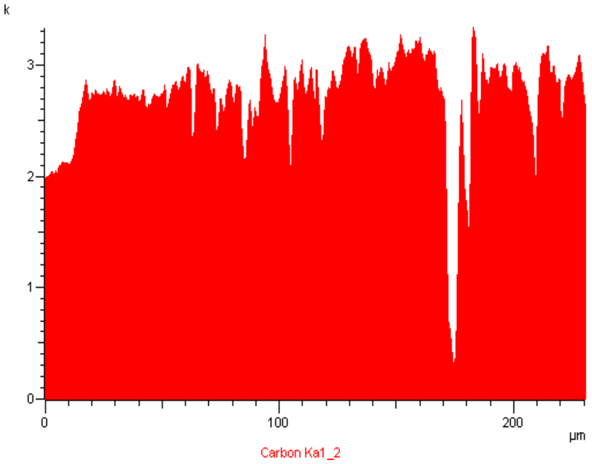


Figure 10d- C EDS of catalyst particle from plug region

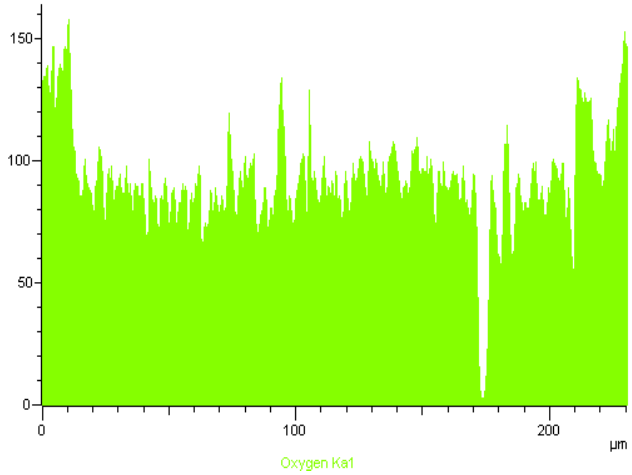


Figure 10e-O EDS of catalyst particle from plug region

An analysis of the coated particle, shown at left in a higher resolution SEM (**Figure 11**), provided similar results. Again, the Pd profile demonstrated an edge-coated catalyst while the sulfur was distributed throughout the catalyst particle. In this case, it appeared that the Pd may have migrated to the surface in conjunction with the sulfur. The reason for the visible edge-crusting was apparently a highly associated Pd and S mixture/ compound. This bright edge-crust also had iron and nickel associated with it in most cases.

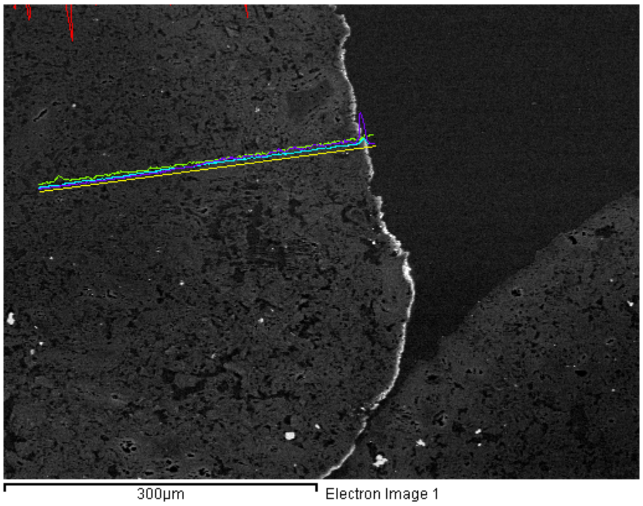


Figure 11a-HREDS of catalyst particle from plug region

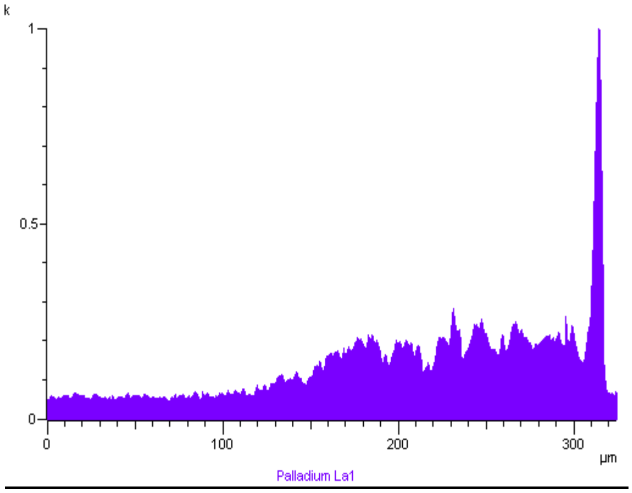


Figure 11b-Palladium HREDS of catalyst particle from plug region

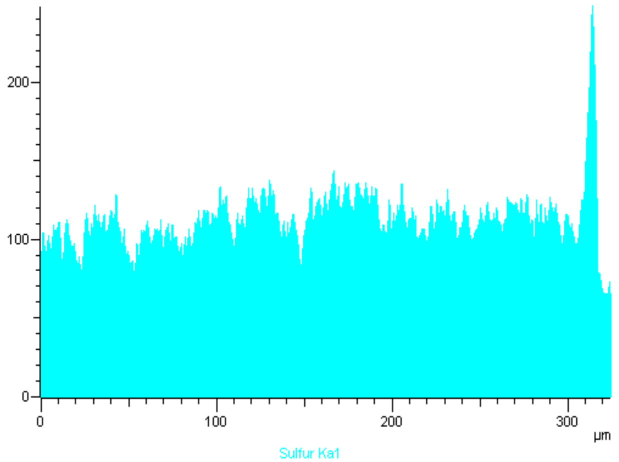


Figure 11c-Sulfur HREDS of catalyst particle from plug region

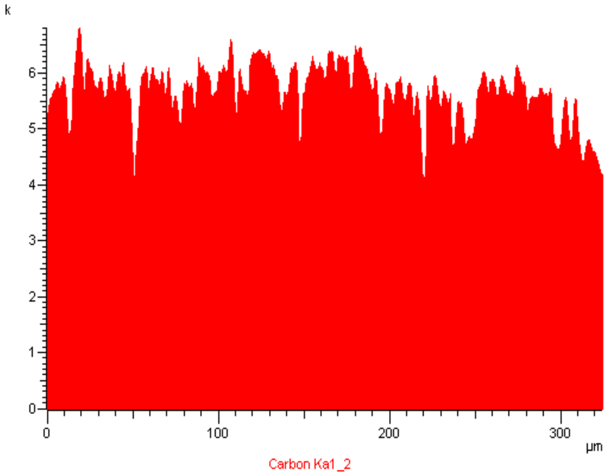


Figure 11d- Carbon HREDS of catalyst particle from plug region

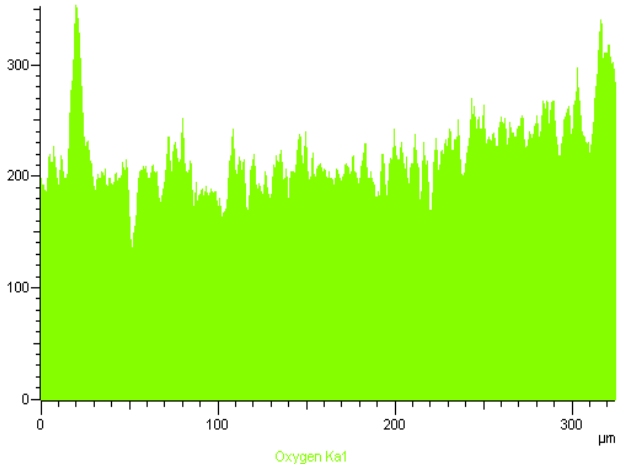


Figure 11e-Oxygen HREDS of catalyst particle from plug region

Table 24 provides the bulk elemental analysis a sample of the fresh Pd on carbon catalyst and 3 portions of the catalyst bed used to hydrotreat oak 500°C bio-oil. The fresh catalyst sample contains primarily palladium with a significant component of silicon and sulfur. In the sample of the top of the catalyst bed, although it is not coked catalyst, there is already a significant increase in the nickel, iron, chromium and molybdenum, all suggesting corrosion product deposits from the stainless steel system components (in red font). Calcium, copper, zinc and cobalt are also significantly elevated. In the second portion, which contains the coked material, the same changes are noted. The elements are largely diluted by carbon deposition. Below the coke plug the catalyst contained lesser amounts of contaminants except for iron.

Analyte Name	Fresh Pd/C 59893-43-1	HT116 Top	HT116 Plug	HT 116 Mid Cat
Al 396.153	305.0	134.0	90.9	160.0
Mo 202.031	5.9	513.0	727.0	425.0
Pd 340.458	12900.0	4790.0	3750.0	8630.0
S 180.669	3050.0	2410.0	1920.0	1460.0
Ni 231.604	9.6	2670.0	3370.0	176.0
Si 251.611	3520.0	2550.0	1900.0	1080.0
Fe 238.204	170.0	557.0	452.0	923.0
Cr 267.716	4.1	56.1	94.9	42.1
Ca 317.933	151.0	717.0	364.0	132.0
P 178.221	45.3	65.2	82.7	65.4
Co 228.616	0.6	9.7	6.9	22.8
Cu 327.393	41.0	219.0	259.0	121.0
Na 589.592	558.0	117.0	41.4	56.8
K 766.490	55.8	92.8	40.7	111.0
Mg 285.213	165.0	80.3	45.0	37.3
Mn 257.610	6.7	7.4	7.6	4.0
Pb 220.353	158.0	84.9	62.7	104.0
Ti 334.903	449.0	170.0	118.0	153.0
Zn 206.200	4.3	24.3	14.4	15.7

Table 24. Bulk Analysis of the HT116 catalyst

Oak 500°C bio-oil with Pd-C catalyst from the Hastelloy reactor (HT119)

In this plug sample, shown by SEM back-scatter at left, the catalyst particles appeared to have the same bright edging in most cases.

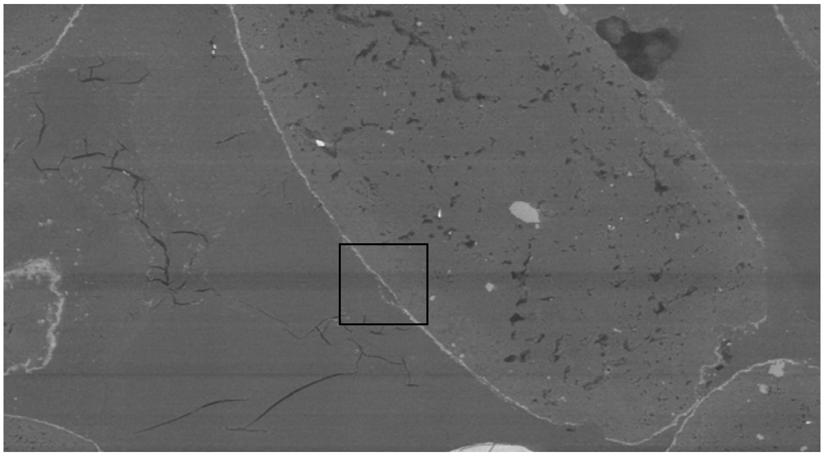


Figure 13a SEM back-scatter of catalyst & plug from oak oil

An image of increased magnification of the pellet edge (indicated by the rectangle drawn on the image at left) is shown below.

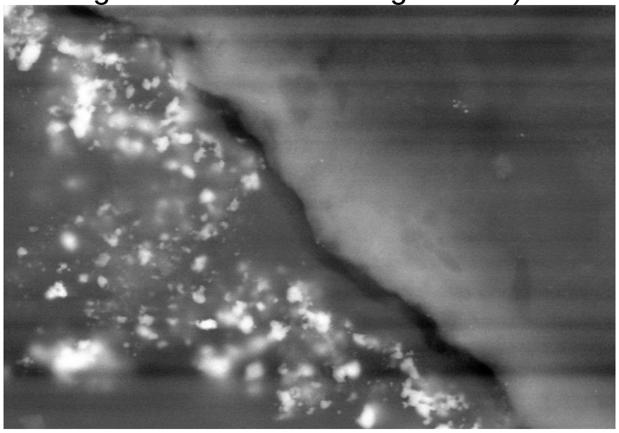


Figure 13b Higher Resolution SEM back-scatter of catalyst & plug from oak oil

The colorized version below can be used to visualize the elemental distribution in the image. In this case the palladium is shown in blue, while nickel and sulfur show as green and yellow
In another image shown below the edge of a catalyst particle is visible with bright particulates next to it. Using the scanning technique, the distribution of elements was traced across the image. With these spectra, shown below, it was clear to see the edge-coated palladium with the bright spot of nickel and sulfur. There was also

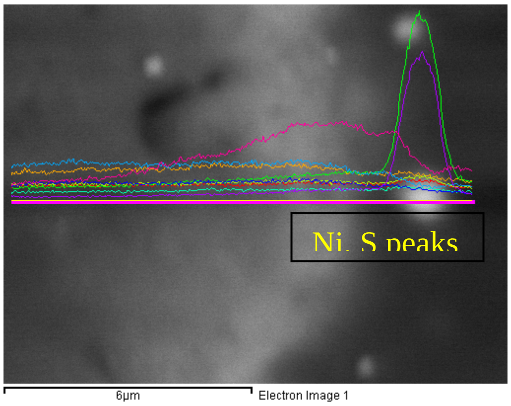


Figure 13c-Ni, S distribution of catalyst particle from plug region

evidence of calcium, phosphorus and aluminum enrichment in the spot, while it was deficient in iron and chromium.

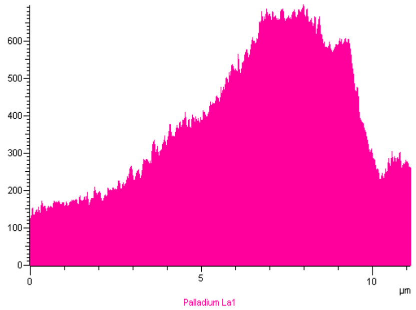


Figure 13d-Palladium HREDS of catalyst particle from plug region

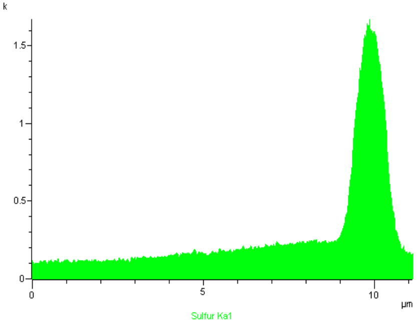


Figure 13e-Sulfur HREDS of catalyst particle from plug region

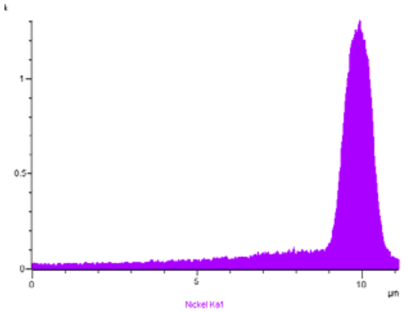


Figure 13f-Nickel HREDS of catalyst particle from plug region

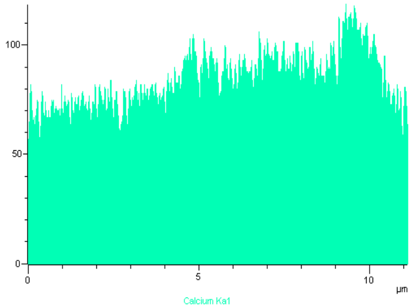


Figure 13g-Calcium HREDS of catalyst particle from plug region

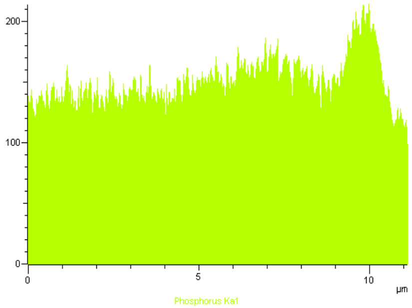


Figure 13h-Phosphorus HREDS of catalyst particle from plug region

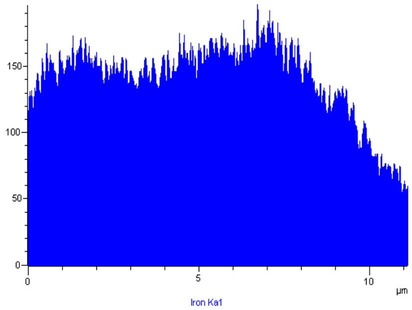


Figure 13i-Iron HREDS of catalyst particle from plug region

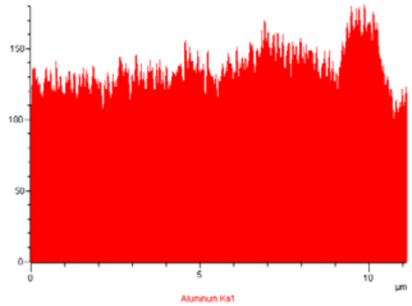


Figure 13j-Aluminum HREDS of catalyst particle from plug region

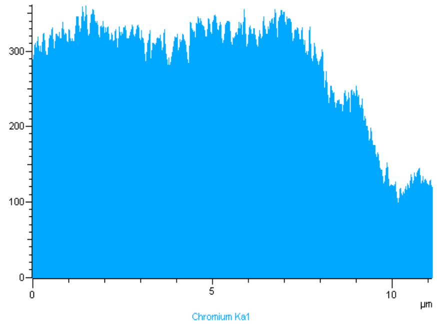


Figure 13k-Chromium HREDS of catalyst particle from plug region

Mixed Wood bio-oil with Pd-C Catalyst from Silcosteel CR lined 304SS reactor

The Silcosteel lining appeared to have little effect on the catalyst materials in the plug. As seen in this SEM image the catalyst particles had the bright edging seen before. Analysis of this material showed the same palladium on carbon dispersed catalytic formulation, but the edge material had significant clusters of nickel and sulfur and others of primarily palladium but also zinc, nickel and iron along with some sulfur. The spots within the catalyst pellet appeared to be the same silicon and oxygen material (silica deposits).

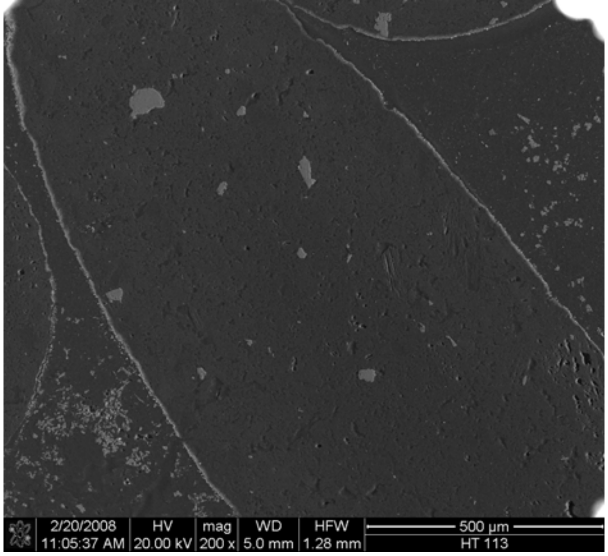


Figure 14: SEM of Pd-C Catalyst& Plug from mixed wood bio-oil in Silcosteel CR lined 304SS reactor

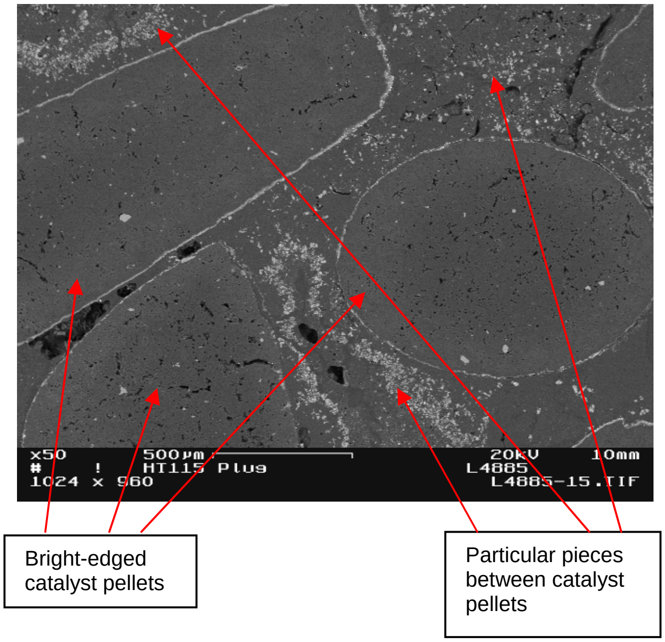


Figure 15: SEM of Several Pd-C Catalyst Particles and plug in lined reactor with Hastelloy insert

<u>Mixed wood bio-oil with Pd-C catalyst from SilcosteelCR lined 304SS reactor with a Hastelloy liner insert</u>

This plug also looked very much like others. In this SEM, several catalyst pellets can be seen as well as some particular material which has formed in the space between pellets within the coke matrix. The EDS analysis showed that the particular material was composed of iron and about half the amount of nickel, with lesser amounts of zinc and magnesium. As found with the other mixed wood bio-oil feedstock test discussed above, the bright edging contained zinc as well as nickel and iron. The palladium was also present in the bright edging along with sulfur. A portion of the bright edging is shown below in the SEM and the colorized form to show nickel/sulfur particles decorating the finely dispersed palladium.

Table 25 provides the bulk elemental analysis of 4 portions of the catalyst bed used to hydrotreated mixed wood bio-oil in the 304 SS reactor. The top portion of the bed is relatively coke free and contains primarily palladium catalyst although nickel has also been deposited. In the second portion, which contains the coked material, nickel and iron dominate with magnesium and chromium also elevated. The elements are largely diluted by carbon deposition. Below the coke plug the catalyst is mostly free of contaminant except for iron.

Analyte Name	**HT88 Top**	**HT88 Char**	**HT88 Mid**	**HT88 Bottom**
Pd	8920	46.2	15700	10900
S	1420	244	881	190
Ni	3650	6400	585	58.1
Fe	862	4930	1710	1450
Mg	130	399	157	210
Cr	45	448	175	297
Mo	184	261	156	123
Al	207	193	257	328
Zn	195	149	512	274
Si	141	124	389	129
K	115	208	273	429
Cu	67	110	42	64
Co	16	27	13	12
Mn	4	33	14	17
Ti	22	4	23	15
Ca	30	ND	8	ND

Table 25. Trace Element Analysis in Hydrotreating Mixed Wood Bio-oil, ppm

<u>Sulfided mixed wood bio-oil with Pd-C catalyst from the Hastelloy reactor (HT121)</u>

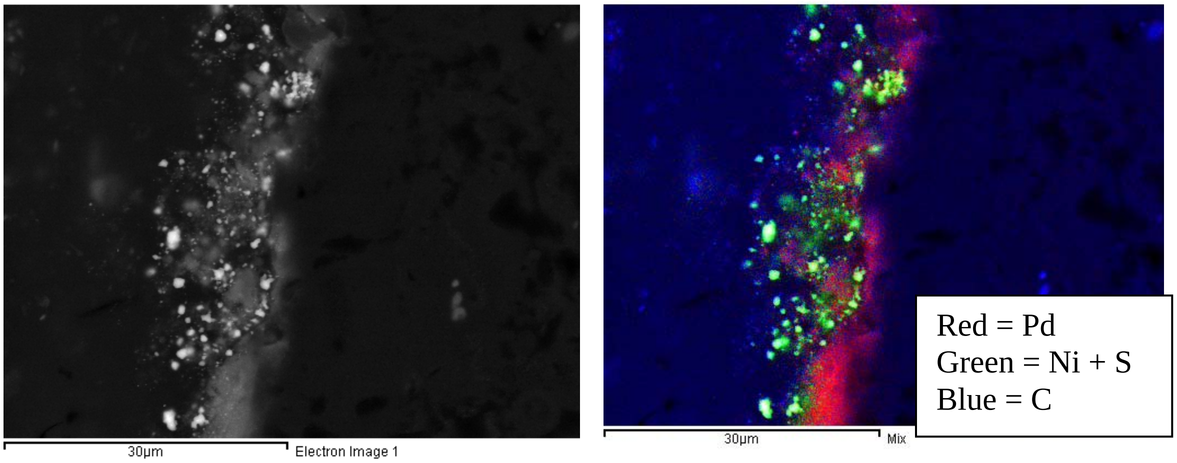


Figure 16: SEM of Sulfided mixed wood bio-oil with Pd-C catalyst from the Hastelloy reactor (HT121)

This sample is from a non-isothermal hydroprocessing test such that the Pd catalyst bed was operated at 250°C. Examination of this catalyst showed essentially the same things:

- carbon catalyst particles and carbon matrix between the particles;
- catalyst particles contain small silica particles;
- palladium is primarily edge-coated;
- sulfur is found throughout the catalyst;
- bright edging is composed of nickel/sulfur particles or palladium with iron, nickel and sulfur;
- in the mixed wood bio-oil tests, zinc is also found in the palladium bright edging and zinc/sulfur particles are also found in the bright edging.

Sulfided mixed wood bio-oil with UOP Hydrotreating catalyst from the Hastelloy reactor (HT122)

This sample is from a non-isothermal hydroprocessing test such that the Pd catalyst bed was operated at 250°C. The only difference in this test was the use of the UOP Hydrotreating catalyst in the hydrotreating zone. The analysis of the catalyst showed similar results. Although the bulk catalyst was an alumina support, sulfur was present throughout. Since molybdenum and sulfur can not be distinguished in this method, molybdenum might have been, and was expected to be, present throughout. There was a range of 25 to 28 wt% carbon found in the catalyst particles. Nickel was found at about 2 to 3.5%. The pieces of particulate visible in the coke matrix were the nickel/iron material (except this time it was nickel with half the amount of iron) with slightly more magnesium than zinc. There were also phosphorus particles near the edge of the catalyst pieces. There was a bright edge to the catalyst that seemed to be mostly nickel/sulfur, but the presence of molybdenum was also possible. The nickel was highly concentrated at the edge of the catalyst particles.

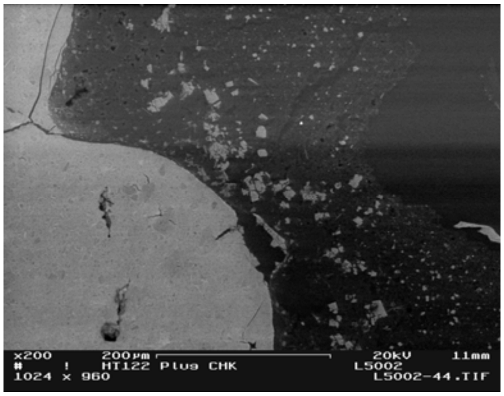


Figure 17: Sulfided mixed wood bio-oil with UOP Hydrotreating catalyst from the Hastelloy reactor (HT122)

Corn stover bio-oil with Ru on TiO_2 catalyst in 304 SS reactor

The coked catalyst sample was analyzed at two main sites, the edge of the coke from the sidewall of the reactor (as shown at right in B&W and colorized) and along the edge of a catalyst pellet, as shown below. The coke along the reactor wall contained significant metal both as a nickel/sulfur crust and as distinct nickel, iron, chromium pieces imbedded in the crust and coke, as indicated in the colorized version. Also identified in the coke were crystalline formations of iron and phosphorus, aluminum and phosphorus, barium and sulfur and calcium (possibly as carbonate).

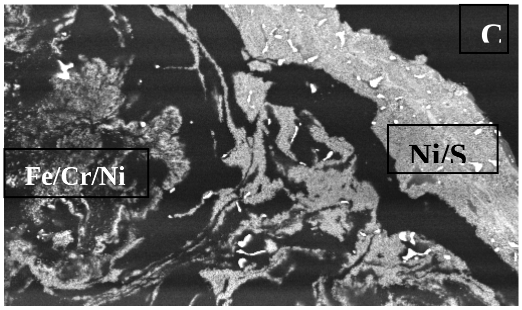


Figure 18 SEM of Catalyst and Plug with Ru/TiO2 catalyst in 304 SS reactor

The analysis of the catalyst pellet edge (shown in Figure 19) showed a similar deposit formation with this ruthenium on rutile titania as was seen earlier with the other catalysts. The nickel/sulfur crust highlighted the catalyst edge. The elemental mapping also showed that the ruthenium was concentrated near the edge of the titania extrudate.

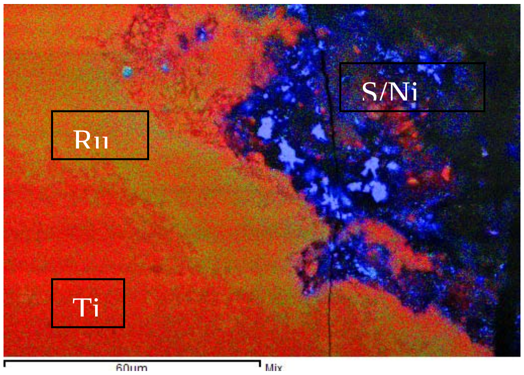


Figure19: HREDS Analysis of Catalyst and Plug with Ru/TiO2 catalyst in 304 SS reactor

Table 26 provides the bulk elemental analysis of three portions of the front end of the catalyst bed. The first 1 inch is free of coke; the section from 1-3 inches is the coke plug material; and the section from 3-5 inches is coke free again. The titania and ruthenium are the catalyst. The low recovery of titania is a function of the sample preparation. This analysis clearly shows the deposit of nickel, iron, calcium, chromium, copper and phosphorus along with an elevated level of sulfur. The elevated level of iron and chromium carry into the portion of the bed following the plug as well.

Analyte Name	**Top 1**	**Top 1-3**	**Top 3-5**	**inches from top**
Ti 334.903	366	638	644	
Ru 240.272	14700	11700	14400	
S 180.669	1320	3930	1250	
Ni 231.604	414	7620	395	
Fe 238.204	900	2280	2310	
Ca 317.933	492	2780	257	
Na 589.592	315	266	148	
K 766.490	194	186	197	
Al 396.153	144	106	74	
Si 251.611	257	95	126	
Cr 267.716	74	716	330	
Cu 327.393	47	263	43	
Zr 343.823	21	5	6	
P 178.221	4	92	-18	
Mg 285.213	36	38	78	
Zn 206.200	1	-2	-3	
	titania pellets	plug	titania pellets	

Table 26. Trace Element Analysis in Hydrotreating 2^{nd} Corn Stover Bio

Hot-filtered poplar bio-oil with Pd on carbon catalyst in 304 SS reactor

The SEM images (**Figure 20** in low and high resolution) showed the highly porous carbon structure which was decorated with heavy element (bright) particles. Analysis of these particles confirmed that they were primarily palladium, with lesser amounts (1/10th) of iron and less of zinc. Different from the other tests, edge analysis showed a lack of nickel or sulfur.

The relationship of the bio-oil sulfur content relative to the coke deposit composition seems to be important. Although the poplar bio-oil was found to have relatively high sulfur content compared to the other bio-oils by the thermal method, the ICP analysis showed that its sulfur content was much lower than for the other bio-oils. Similarly, the poplar bio-oil was low in nickel, yet had notable iron and zinc content. These differences were also reflected in the deposits on the catalyst in the coked region of the bed. The higher nickel content in the mixed wood and corn stover bio-oils may be a significant factor in the deposit formations in those tests, irrespective of the reactor metal of construction. Alternatively, although the Hastelloy metal components were visibly more resistant to pitting corrosion, the high nickel content may have actually contributed to the deposit formation. Hastelloy metal components are considered to be more resistant to corrosion by acids, but the high nickel content may have actually contributed to the deposit formation through a more uniform corrosion mechanism.

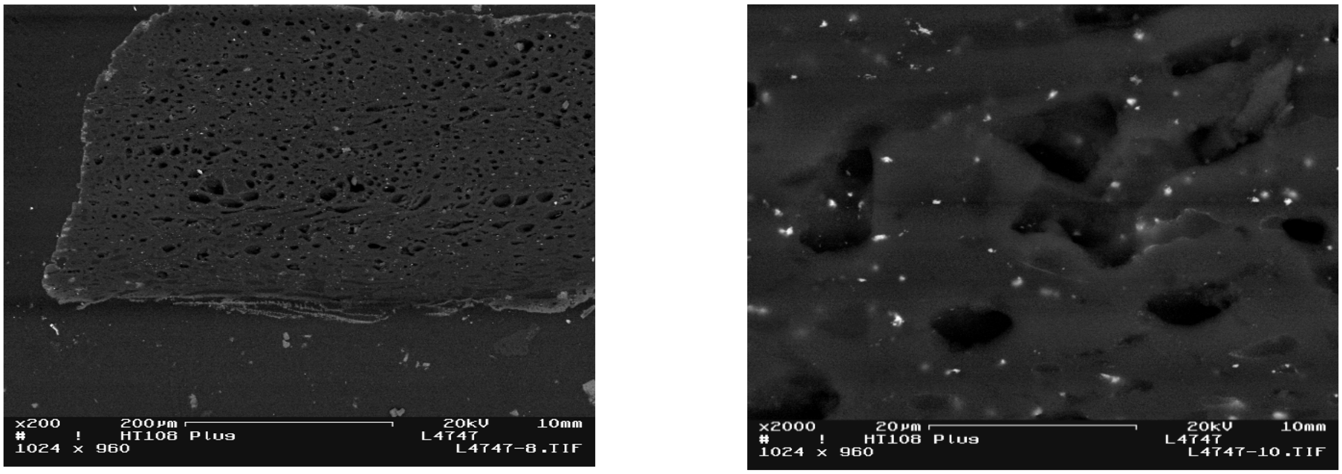


Figure 20: Low (L) and High (R) resolution SEM of catalyst and plug from Hot-filtered poplar bio-oil with Pd on carbon catalyst in 304 SS reactor

4.6 Hydrocracking Process Results

The hydrocracking tests were performed with the UOP Hydrotreating catalyst from UOP in its sulfided form as received from UOP. By using the hydrotreated bio-oil as the feedstock it was possible to perform the tests at lower pressure and higher temperature than the hydrotreating of the as-produced bio-oil. In these tests the yield structure was highly biased toward the oil layer as opposed to the high water yields in the hydrotreating tests. The splits ranged from 2-3 times as much oil with the wood bio-oil, which contained 8% moisture, to 4-6 times as much oil with the hot-filtered poplar bio-oil, which contained less than 3% moisture.

These results from **Table 27** showed a consistently higher oil product yield. Gas generation was substantially more in all cases and was primarily hydrocarbons rather than carbon dioxide. A significant bed heating suggested a strongly exothermic reaction. The hydrogen consumption was much higher in the hydrocracking step than in the hydrotreating step.

bio-oil	**oil yield, g/g dry feed**	**aqueous yield, g/g wet feed**	**gas yield, g/g carbon feed**	**Hydrogen consumption, liter/liter feed**	**Relative exotherm versus setpoint**
mixed wood	0.61	0.24	0.087	290	+16°C
corn stover light phase	0.74	0.13	0.100	550	+12°C
corn stover heavy phase	0.82	0.14	0.077	510	+17°C
2nd corn stover	0.81	0.14	0.090	490	+20°C
poplar	0.80	0.17	0.116	430	+17°C

405°C, 1500 psig, 0.2 LHSV

Table 27. Feedstock Effect on Hydrocracking Process Results

4.7 Effect of Feedstock in Hydrocracking

The initial conclusion drawn from the results of the hydrocracking tests, as shown in **Table 28**, was that the final products were even more similar than the bio-oil products regardless of the original biomass feedstock. In all five cases tested, high quality hydrocarbon products could be produced after appropriate processing conditions were identified.

bio-oil source	**C**	**H**	**O**	**N**	**S**	**moisture**	**density**	**TAN**
mixed wood	86.6	12.9	0.4	<0.06	0.01	0.01	0.85	2.5
corn stover light phase	86.6	12.5	0.8	<0.1	<0.01	0.01	0.81	0.5
corn stover heavy phase	87.6	12.1	0.4	0.6	<0.01	0.14	0.86	1.5
2nd corn stover	86.8	12.2	0.6	0.5	<0.01	0.15	0.87	2.7
hot-filtered poplar	87.4	12.0	0.3	0.2	0.01	0.06	0.87	2.0

405°C, 1500 psig, 0.2 LHSV

Table 28. Composition of Hydrocracked Products

Many of the products from hydrocracking were also analyzed by GC to better understand the specific component composition of the bio-oils and products. The same system of GC-MSD, to identify specific components, and GC-FID, to quantify the components, was used. The relative response for the hydrocarbon products was much more uniform; as a result, the table of quantities shown below should be more accurate. However, a single representative standard was used for all components. Again, the trends in the data were evident. The chromatographs were less complex and more easily resolved.

Table 29. provides data on product oils from hydrocracking the hydrotreated mixed wood bio-oil. The data listed under Feed 1 are comparable to the products of mixed wood bio-oil hydrotreating given in Table 11. O1, O2, O3, and O4 are data for four different hydrocracked products from a single test (HT107). The data demonstrate consistent catalyst activity throughout the test. The products are essentially all hydrocarbons, largely cyclic in nature (naphthenes and aromatics). The unknowns are higher molecular weight material, for the most part, and may represent oxygenated components.

Component Groups	**O1**	**O2**	**O3**	**O4**	**Feed 1**
component group	0.00%	0.00%	0.00%	0.00%	0.00%
unsaturated ketones/aldehydes	0.00%	0.00%	0.00%	0.00%	0.00%
carbonyls (hydroxyketones, aldehydes)	70.77%	67.88%	69.67%	71.63%	4.22%
Total alkanes	0.00%	0.00%	0.00%	0.00%	0.00%
saturated guaiacols(diol,ones)	0.00%	0.00%	0.00%	0.00%	15.68%
phenol and alkyl phenols	0.00%	0.00%	0.00%	0.00%	22.67%
alcohols & diols	12.02%	14.05%	11.53%	12.82%	10.51%
HDO aromatics	0.00%	0.00%	0.00%	0.00%	12.84%
Total saturated ketones	0.00%	0.00%	0.00%	0.00%	11.89%
Total acids & esters	0.00%	0.00%	0.00%	0.00%	0.00%
Total furans & furanones	0.00%	0.00%	0.00%	0.00%	3.28%
Total tetrahydrofurans	0.00%	0.00%	0.00%	0.00%	0.00%
Complex guaiacols	0.00%	0.00%	0.00%	0.00%	18.91%
guaiacol and alkyl guaiacols	11.72%	13.62%	13.18%	10.32%	0.00%
unknowns	5.49%	4.45%	5.62%	5.24%	0.00%
TOTAL	100.00%	100.00%	100.00%	100.00%	100.00%

Table 29. Hydrocracking Product Oil Chemical Components

4.8 Catalyst Coking in Hydrocracking

There was little evidence of catalyst coking in these tests. No pressure drop developed over the reactor and the tests were terminated voluntarily when the feedstock was exhausted. Other than a slight crust of coke at the very top (1/8”) of the reactor in the quiescent zone around the edge there were no coke deposits in the catalyst bed.

4.9 Non-Isothermal Process Results

The non-isothermal hydroprocessing tests were performed to test a low-temperature first step in combination with a high-temperature second step without product phase separation between steps. Bio-oil was used as the feedstock. In these tests the yield structure was highly biased toward the aqueous layer with the combination of the high water yields at low temperature and further hydrodeoxygenation and water formation at higher temperature without intermediate water separation. The splits ranged from 1.2 to 1.6 times as much aqueous phase as oil phase, except up to 3 with the corn stover bio-oil, which contained significantly more water.

These results from **Table 30** showed a consistently higher aqueous product yield but the carbon loss is low as the carbon content in the aqueous phase is less than 0.5% in all cases except the hot-filtered poplar. Gas generation was substantially more in all cases and was primarily hydrocarbons along with carbon dioxide. A very significant bed heating suggested a very strongly exothermic reaction in the lower, high-temperature bed. The hydrogen consumption was very high as a combination of utilization in both the hydrocracking step and the hydrotreating step.

bio-oil	**oil yield, g/g dry feed**	**aqueous yield, g/g wet feed**	**gas yield, g/g carbon feed**	**Hydrogen consumption, liter/liter feed**	**Relative exotherm versus setpoint**
mixed wood	0.50	0.48	0.192	710	+32°C
oak, 500°C	0.54	0.44	0.320	640	+45°C
oak, 550°C	0.53	0.52	0.290	655	+39°C
2nd corn stover	0.37	0.64	0.323	490	+26°C
hot-filtered poplar	0.48	0.46	0.259	630	+60°C

250-410°C, 2000 psig, 0.15 LHSV

Table 30. Feedstock Effect on Non-isothermal Processing Results

4.10 Effect of Feedstock in Non-isothermal Tests

A conclusion similar to that recognized in the hydrocracking tests was that the final products were uniform, as shown in **Table 31,** despite the variation in the source of the bio-oil or the original biomass feedstock. In all cases tested, except the hot-filtered poplar, high quality hydrocarbon products could be produced in this once-through process. The lower quality product with the hot-filtered bio-oil was attributed to a lower activity catalyst (even though it exhibited the largest exotherm).

bio-oil source	**C**	**H**	**O**	**N**	**S**	**moisture**	**densit**	**TAN**

							y	
mixed wood	87.7	11.6	0.6	<0.05	0.01	0.07	0.84	1.6
oak, 500°C	87.7	11.7	0.3	0.05	0.06	0.04	0.84	0.8
oak, 550°C	86.9	12.5	0.2	0.06	0.005	0.002	0.82	0.1
2nd corn stover	87.4	11.9	0.4	0.40	0.005	0.06	0.84	2.5
hot-filtered poplar	85.2	10.2	4.9	0.14	0.19	0.51	0.92	6.1

250-410°C, 2000 psig, 0.15 LHSV

Table 31. Composition of Non-isothermal Hydroprocessed Products

4.11 Effect of Catalyst in Non-isothermal Tests

With two exceptions, in the tests listed in **Table 29**, the catalysts used were a Pd/C granule in the low-temperature bed and the UOP Hydrotreating hydrocracking catalyst (pre-sulfided) in the high-temperature bed. The exceptions were the use of a CoMo/alumina catalyst for the entire bed with the hot-filtered poplar bio-oil and the use of the HC-43 (presulfided) in place of the UOP Hydrotreating in the 500°C oak test. How the CoMo catalyst could have had the largest exotherm, reacted a large amount of hydrogen, produced a large amount of hydrocarbon gases, yet produced such an inferior oil product in terms of deoxygenation was unexplained. The use of the UOP Hydrocracking instead of the UOP Hydrotreating was indistinguishable by these data.

4.12 Catalyst Coking in Non-isothermal Tests

Plugging was not an issue in these tests. The lower temperature in the front bed seemed to retard the coke formation. No pressure drop build up was noted in these tests even though the bio-oil throughput ranged up to 7.8 liters per square inch of cross section of the reactor in the case of the hot-filtered poplar bio-oil. The mixed wood bio-oil was processed up to 2.5 L/in^2 without plugging (compared to 0.8 to 2.1 with plugging at 340°C in a 304SS reactor) and the corn stover test reached 6.3 L/in^2 (compared to 3.7-4.2 with plugging at 340°C). These differences suggest the value of operation at lower temperature to avoid plugging. The two oak tests extended for 3.6 and 2.1 L/in^2 for the 500°C bio-oil and 550°C bio-oil, respectively. Although no pressure drop developed in processing the 500°C oak bio-oil, in fact, a plug was found in the catalyst bed following the test. Apparently the test was near to being ended with a plug formation.

However, in subsequent tests in the Hastelloy reactor the coke formation problem became evident again. Two tests of mixed wood bio-oil and a third with the heavy phase separated from the mixed wood bio-oil by water addition all ended when a significant pressure drop developed. These three tests all produced quality products early on, but, as seen in **Table 32,** showed signs of deactivation over time and eventually plugged. Note that in all three of these cases the wood derived bio-oil carried the added sulfiding agent ditertbutyldisulfide. These tests are also different from those in Table 16 in that they were performed in the reactor with the smaller cross-sectional area. These mixed wood bio-oil tests achieved from 3.59 to 5.23 L/in^2 before significant pressure drop was noted. These numbers are better than the Hastelloy result in Table 12 for operation at 340°C (1.5 L/in^2), underscoring the value of operation at lower temperature and the thermal instability of bio-oil.

bio-oil source	C	H	O	N	S	moisture	density	TAN
mixed wood, sulfided	87.4	12.1	0.3	<0.05	<0.005	0.011	0.85	0.07
mixed wood sulfided	87.6	11.8	0.3	<0.05	<0.005	0.023	0.87	0.09
mixed wood, heavy phase, sulfided	87.4	12.2	0.5	0.565	<0.005	0.105	0.88	<0.1

250-390°C, 2000 psig, 0.14 LHSV

Table 32. Composition of Non-isothermal Hydroprocessed Products from Hastelloy Reactor

Overall Assessment

Hydrotreating followed by hydrocracking can be applied to bio-oil to produce hydrocarbon products. Table 23 provides some relevant data for three feedstocks. The first step of hydrotreating bio-oil produces a viscous bio-oil product with a reduced amount of oxygen and dissolved water. A separate aqueous phase is also produced which carries a portion of the hydrotreated bio-oil as dissolved organic. Gas production, primarily as carbon dioxide, results in a noticeable byproduct stream with relatively low hydrogen consumption. The second step of hydrocracking the hydrotreated bio-oil produces a nearly oxygen-free hydrocarbon product. There is additional aqueous byproduct which carries very little organic material. Gas production is up to twice that resulting from hydrotreating and it contains significant hydrocarbon components. The hydrogen consumption is much higher in hydrocracking ranging from 40% higher to over 6 times higher in the three cases presented here.

The results of the consecutive step operation (HT/HC total in Table 23) can be compared to our non-isothermal operation in which the two steps are operated in a two-stage reactor without intermediate product recovery and separation. In non-isothermal operation the overall oil product yield is higher by 4% to 35%. The byproduct water product is reduced, as is the loss of dissolved organic, because the aqueous product is very low in organic contamination. The overall gas yield is higher by 2 to 3 times, but much of this gas is hydrocarbon material that can be reused in hydrogen production. The reduced loss of organic in the aqueous phase and the higher gas yield suggests that the low-molecular weight oxygenates in the water are being gasified by reaction with hydrogen in the hydrocracking step; at the same time some are converted to hydrocarbon liquids. In the non-isothermal case the hydrogen consumption is higher by 25 to 84%.

Table 23. Comparative Yields of Two-stage Processing versus Non-isothermal Processing

		Hydro-treating	Hydro-cracking	HT/HC total	Non-isothermal
Mixed Wood	dry oil yield, g/g	0.62	0.61	0.37	0.50
	aqueous yield, g/g	0.48	0.24	0.63	0.48
	C gas g/g	0.062	0.087	0.116	0.192

	H_2 consumption, L/L	205	290	385	710
2nd Corn Stover	dry oil yield, g/g	0.45	0.81	0.35	0.37
	aqueous yield, g/g	0.61	0.14	0.67	0.64
	C gas g/g	0.066	0.090	0.106	0.323
	H_2 consumption, L/L	76	490	296	490
Hot-filtered poplar	dry oil yield, g/g	0.59	0.80	0.46	0.48
	aqueous yield, g/g	0.46	0.17	0.56	0.46
	C gas g/g	0.060	0.116	0.128	0.259
	H_2 consumption, L/L	252	430	506	630

Database Development

As part of this CRADA project, PNNL developed an ACCESS Database to collect the process data for all portions of this project. It included biomass feed analyses (ultimate, proximate, ash composition, and heating value), pyrolysis oil analyses (ultimate analysis, water content, ash component analysis, density, pH, and compound classification), and pyrolysis oil production material balance data based on input from NREL as well as some product analyses performed by PNNL. The Database also included similar tables related to hydrotreating experiments as well as for the hydrocracking experiments. Tables included process parameters and product analyses, including oil and aqueous phases and gaseous products. The tables were also included for the non-isothermal processing experiments; however, for those experiments there was no recovery of hydrotreated products. As a result, there were no data entries in the tables for hydrotreated oil products, hydrotreated aqueous products or hydrotreated gas products for those tests which were non-isothermal in nature. The product analyses for the non-isothermal tests were recorded in hydrocracking products tables. In addition, the gas calculations and mass balances were recorded on the hydrocracking process table and not the hydrotreating process table.

Analyses and Characterization

Various analytical methods were employed at UOP to determine the properties of fuels derived from hydroconverted pyrolysis oils. Gas chromatography was a major technique used in the compositional characterization of bio-derived fuels. Other ancillary techniques that determined elemental compositions of the oils were also employed.

Gas chromatographic methods

Simulated Distillation, D2887

This method is used for petroleum fractions or products that have a final boiling point of 538°C. Boiling range distributions obtained by this test method are essentially equivalent to those obtained by true boiling point (TBP) distillation (i.e. Test Method D 2892). D2887 was used in determining the boiling range distribution of components in hydroconverted pyrolysis oil, as well as in the gasoline and diesel fractions from the spinning band distillation of the hydroconverted pyrolysis oil.

Detailed Hydrocarbon Analysis (DHA)

This method is useful in the determination of hydrocarbon groups and prediction of some physical properties of reformulated gasoline, e.g. Density, RON/MON, etc. The analysis uses a high resolution capillary GC column, which can provide a detailed analysis, specifying individual compounds. This method was used in characterizing the composition of hydroconverted pyrolysis oils, as well as gasoline and diesel fractions obtained from the spinning band distillation of the hydroconverted pyrolysis oils.

Paraffins, Isoparaffins, Olefins, Naphthenes, Aromatics (PIONA)

PIONA is another analysis that can provide information on the hydrocarbon composition of reformulated gasoline. Unlike the DHA, it does not provide identification of individual hydrocarbon compounds. It yields group type separation of n-paraffins, isoparaffins, naphthenes, olefins, and aromatics by carbon number distribution. While this method was originally designed for use on FCC gasoline, it was used in the compositional characterization of the gasoline fraction from the hydroconverted pyrolysis oil, derived from spinning band distillation.

GC x GC FID

This is a relatively newer technique that utilizes 2 gas chromatographic columns of differing selectivities, in the separation of components in complex mixtures, such as hydroconverted pyrolysis oils. The method is applicable to naphtha to VGO range fractions. The components are separated from one another on the basis of two properties: boiling point and polarity. Their respective locations on a contour plot gives information on which molecular types they belong to, i.e. paraffins, olefins, naphthenes, aromatics, as well their carbon numbers. This analysis is quantitative since a Flame Ionization Detector (FID) is used. A variant of this method is being developed at UOP, to specifically quantitate oxygenated components in partially deoxygenated pyrolysis oils.

Elemental analysis

Percent Total Oxygen

This technique uses high temperature pyrolysis which converts oxygen contained in the sample to carbon monoxide. The carbon monoxide produced is detected by a Thermal Conductivity Detector (TCD), and its concentration is related to the total oxygen in the sample. This method was used in the determination of oxygen content in hydroconverted pyrolysis oil, which is a measure of the degree of deoxygenation.

Total Sulfur, XRF

This technique uses high energy X-ray bombardment of the sample to produce fluorescence radiation. The resultant characteristic emission line from a specific element, e.g. sulfur, is isolated by means of a WDXRF spectrometer. The signal from the characteristic photon is detected and integrated and the measured intensity is related to elemental composition by the use of a calibration procedure. This technique was used in measuring sulfur, associated with the catalyst being used in the hydrotreatment of raw pyrolysis oils.

Total Chloride

The hydrocarbon sample to be analyzed is injected onto a quartz boat, which is sent into a furnace in a pyrohydrolytic environment. The products of combustion are HCl and Cl2. The resultant gases are absorbed in an aqueous solution which is injected into a Ion Chromatograph, where the chloride species are detected and measured. This method was used in the evaluation of raw and processed pyrolysis oil, to determine the levels of chloride, associated with corrosion in process equipment.

Carbon, Hydrogen, Nitrogen (CHN)

This technique employs combustion of a sample in the presence of oxygen. Catalysts aid in the formation of CO from carbon, H2O from hydrogen.

The oxides of nitrogen formed in the combustion are reduced to diatomic nitrogen via a different catalyst. All products formed are separated by gas chromatography and detected by a Thermal Conductivity Detector.

Carbonyl Number

Known as UOP 624, this method is a spectrophotometric determination of the carbonyl number, present as ketone or aldehyde carbonyl, and defined as "milligrams of carbonyl function per liter of sample using acetophenone as the standard.". The typical analysis range for carbonyl number is 0.1 to 100 mg/L carbonyl. The sample must be colorless. This method was used in determining degree of decarboxylation of hydroconverted pyrolysis oil, particularly in the evaluation of the gasoline fractions from spinning band distillation.

Physical methods

Specific Gravity, API Gravity

ASTM D4052 was used in determining the specific gravity and API gravity of raw and hydroconverted pyrolysis oils, as well as for gasoline and diesel fractions generated from spinning band distillation.

Cetane Number

Measurement of the cetane number of the diesel fraction obtained by spinning band distillation of hydroconverted pyrolysis oil was done by ASTM D6890, Derived Cetane Number. This automated test method measures the ignition delay and utilizes a constant volume combustion chamber with direct fuel injection into heated, compressed air. The minimum volume required for this test is 35 mL.

Spinning Band Distillation

A form of distillation which involves the use of a rotating helical spinning band to create a high number of theoretical plates. The spinning band forces rising vapors to be in close contact with the condensate. This intimate contact between the two phases enhances a good separation between components in a mixture. This was used in fractionating hydroconverted pyrolysis oils into gasoline, diesel, and bottoms fractions.

Database Development

As part of this CRADA project, PNNL developed an ACCESS Database to collect the process data for all portions of this project. It included biomass feed analyses (ultimate, proximate, ash composition, and heating value), pyrolysis oil analyses (ultimate analysis, water content, ash component analysis, density, pH, and compound classification), and pyrolysis oil production material balance data based on input from NREL as well as some product analyses performed by PNNL. The Database also included similar tables related to hydrotreating experiments and hydrocracking experiments. Tables included process parameters and product analyses, including oil and aqueous phases and gaseous products. . The tables were also included for the non-isothermal processing experiments; however, for those experiments there was no recovery of hydrotreated products. As a result, there were no data entries in the tables for hydrotreated oil products, hydrotreated aqueous products or hydrotreated gas products for those tests which were non-isothermal in nature. The product analyses for the non-isothermal tests were recorded in hydrocracking products tables. In addition, the gas calculations and mass balances were recorded on the hydrocracking process table and not the hydrotreating process table. The Database is included as Appendix B to this report.

These appendices will be provided in electronic form as files on a CD.

Process Data Sheets from Hydrotreating, Hydrocracking and Non-isothermal Hydroprocessing Confidential Submission to DOE

Database Tables for Pyrolysis, Hydrotreating and Hydrocracking Confidential Submission to DOE

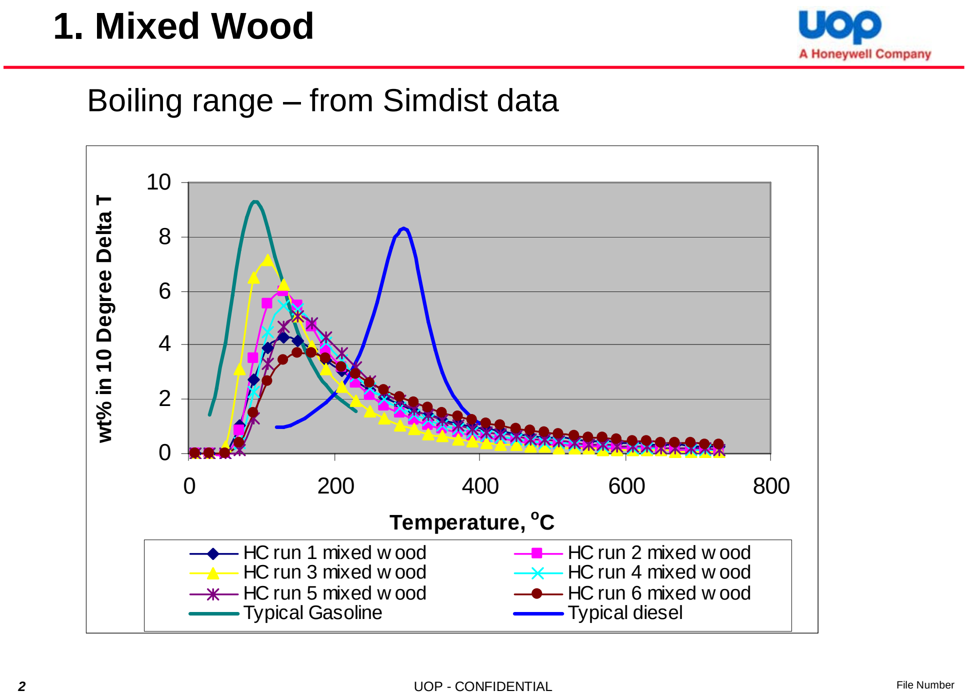
Summary Tables and Plots The limited amount of hydrotreated pyrolysis oil produced per run has made it difficult to follow a particular bio feedstock from pyrolysis all the way to the final hydrocracked product. Nevertheless, an attempt has been made below to do this for the 3 different feedstocks: Mixed Wood (**Table 33**), Corn Stover (**Table 34**), and Poplar (**Table 35**). Where more that one run was used, ranges are indicated for conditions and product properties.

1. Mixed Wood

	Pyrolysis, 1 run	Hydrotreating, 1 run	Hydrocracking, 6 runs	
	NREL:	PNNL:	PNNL:	
	(2006)	Catalyst: Pd/C	UOP HC/UOP HT	
Temp, °C	480	342	359-429	
Pressure, psig	res time =1.6sec	1900	1525-1570	
LHSV	N2 carrier	0.28	0.14-0.36	
	Yields:	Yields:	Yields:	
	Pyrolysis oil: 70wt%	HT oil: 66 vol%	HC oil: >95%	
	Aqueous phase: -	Aqueous phase: 48wt%		
	Char: 12wt%	(10%C)		
	Gas: 15wt%			
	Py oil analysis:	HT oil analysis:	HC oil analysis:	
N, wt %	0.18	0.37	0.03-0.71	
O, wt %	48.0	20.1	3.5-6.3 (0.2-1)	
S, wt %	-	-	19-64 ppm	
Density, g/ml	-	1.06	0.77-0.90	
TAN, mg KOH/g oil	-	85.0	-	
H/C (mol)	1.85	1.49	1.74-1.84	
ICP, wt%				
				PIONA-Oxy
alkanes			8-22	paraffines: 5-10%
cyclic alkanes			64-79	iso-paraffins: 15-25%
hydroaromatics			3.9-27.2	olefins: 0.5-1%
phenols			0.13-0.42	naphthenes: 40-55%
alcohols/diols			0	aromatics: 10-30%
ketones			0	oxygenates: 0.1-0.8%
acids/esters			0 (0.2)	
tetrahydrofurans			0	calc MON=75
guaiacols and syringols			0 (0.6)	calc RON=82

Table 33-Summary of Mixed Wood Bio-Oil Runs

A simulated boiling point analysis was done on the final hydrocracked product. The figure below includes a comparison with typical gasoline and diesel boiling ranges. It shows that the mixed wood product has a boiling range similar to gasoline, although some higher boiling components are present as well.



1. Mixed Wood

Boiling range – from Simdist data

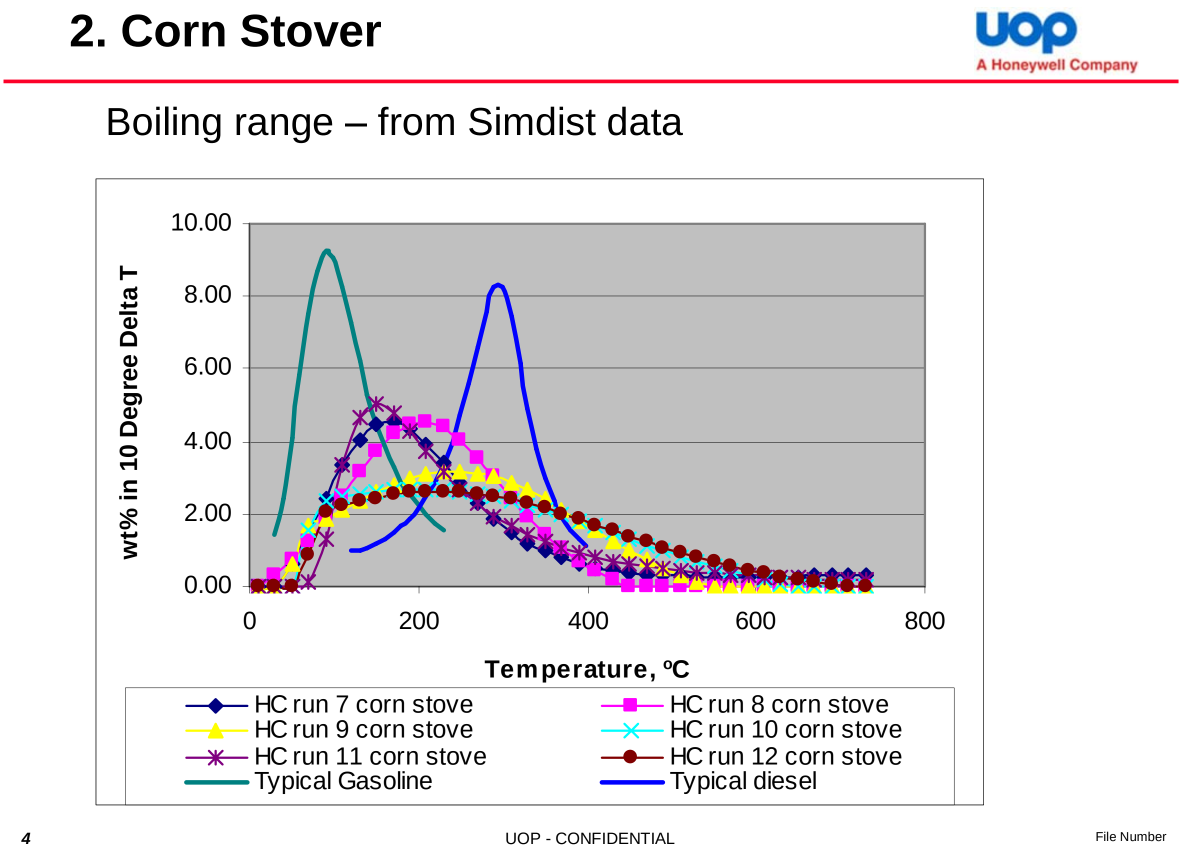
2 UOP - CONFIDENTIAL File Number

Figure 21: Simulated Distillation of Mixed Wood Products

2. Corn Stover

	Pyrolysis, 2 runs	Hydrotreating, 3 runs	Hydrocracking, 6 runs	
	NREL:	PNNL:	PNNL:	
	(2006)	Catalyst: Pd/C	UOP Hydroprocessing	
Temp, °C	480	339-343	399-410	
Pressure, psig	res time =1.6sec	1933-1944	1508-1542	
LHSV	N2 carrier	0.26-0.28	0.13-0.25	
	Yields:	Yields:	Yields:	
	Pyrolysis oil: 8/47 wt%	HT oil: 35-55 vol%	HC oil: >95%	
	Aqueous liq: 45/- wt%	Aqueous liq: 60-75 wt%		
	Char: 25 wt%	(9%C, 0.2%N)		
	Gas: 13 wt%			
	Py oil analysis:	HT oil analysis:	HC oil analysis:	
N, wt %	0.8/1.4	1.3-2.0	0.03-0.61	
O, wt %	36/40	9.5-11.4	0.42-0.95 (0-0.6)	
S, wt %	-/0.1	0.03-0.04	8-28 ppm	
Density, g/ml	-	1.02-1.04	0.78-0.87	
TAN, mg KOH/g oil	-	51-57	0.5-1.6	
H/C (mol)	1.55/1.78	1.51-1.61	1.66-1.96	
ICP, wt%				
				PIONA-Oxy
alkanes			8.7-12.4	paraffins: 8-11%
cyclic alkanes			57-67	iso-paraffins: 15-17%
hydroaromatics			18-28	olefins: 0.2-0.3%
phenols			0.14-0.71	naphthenes: 40-55%
alcohols/diols			0	aromatics: 16-35-30%
ketones			0	oxygenates: 0%
acids/esters			0	
tetrahydrofurans			-	Calc MON=75
guaiacols and syringols			0	Calc RON=84

Table 34 - Summary of Corn Stover Bio-Oil Runs



2. Corn Stover

Boiling range – from Simdist data

4 UOP - CONFIDENTIAL File Number

Figure 22: Simulated Distillation of Corn Stover Products

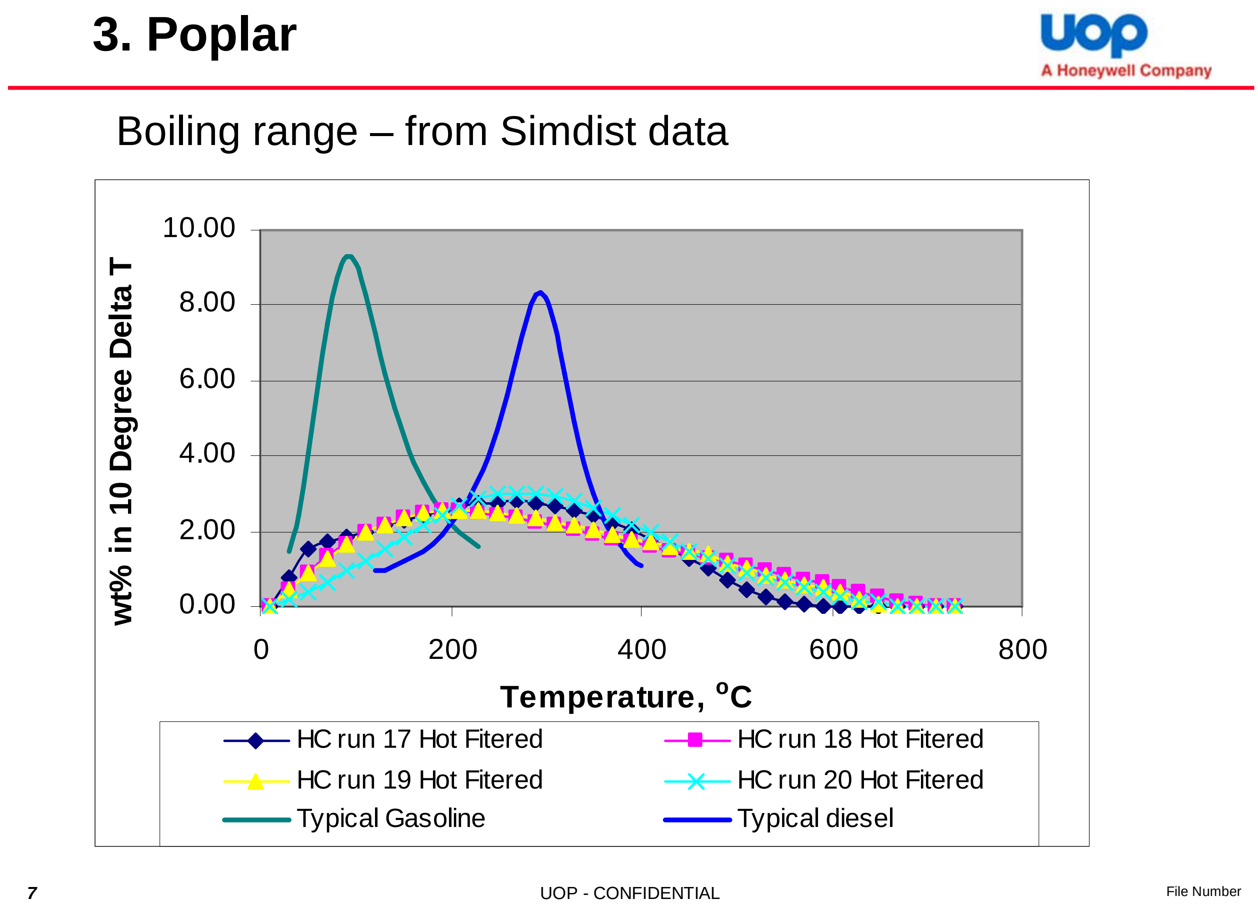
2. Poplar

	Pyrolysis, 1 run	Hydrotreating, 2 runs	Hydrocracking, 4 runs
	NREL:	PNNL:	PNNL:
	(1996)	Catalyst: Pd/C	UOP Hydroprocessing
	T=480C?	T=342/237*	T=394-408/445*
	t=1.6 sec	~1950 psig	1486-1505/1975*
	N2 carrier	LHSV=0.23 / 0.14*	LHSV=0.12-0.24
	Yields:	Yields:	Yields:
	Pyrolysis oil: NA	HT oil: 0.69 vol%	HC oil: NA
	Char: NA		
	Gas: NA		
	Aqueous phase: NA	Aqueous phase: NA	
	Py oil analysis:	HT oil analysis:	HC oil analysis:
N, wt %		0.23	0.07-0.29/0.12*
O, wt %		17.2	0.3/4.8*
S, wt %		0.17	1-20 ppm
Density, g/ml		1.05	0.85-0.87/0.92*
TAN, mg KOH/g oil		57.0	1.8-2.0/4.0*
H/C (mol)		1.40	1.65/1.41*

alkanes		-	8-10
cyclic alkanes		-	77-79/46*
hydroaromatics		0.0	11-14/4*
phenols		15.7	0.22/40.3*
alcohols/diols		22.7	0
saturated ketones		14.3	-
acids/esters		25.1	0
tetrahydrofurans		3.3	-
guaiacols and syringols		18.9	0

* = dual bed

Table 35-Summary of Poplar Bio-Oil Runs


3. Poplar

UOP A Honeywell Company

Boiling range – from Simdist data

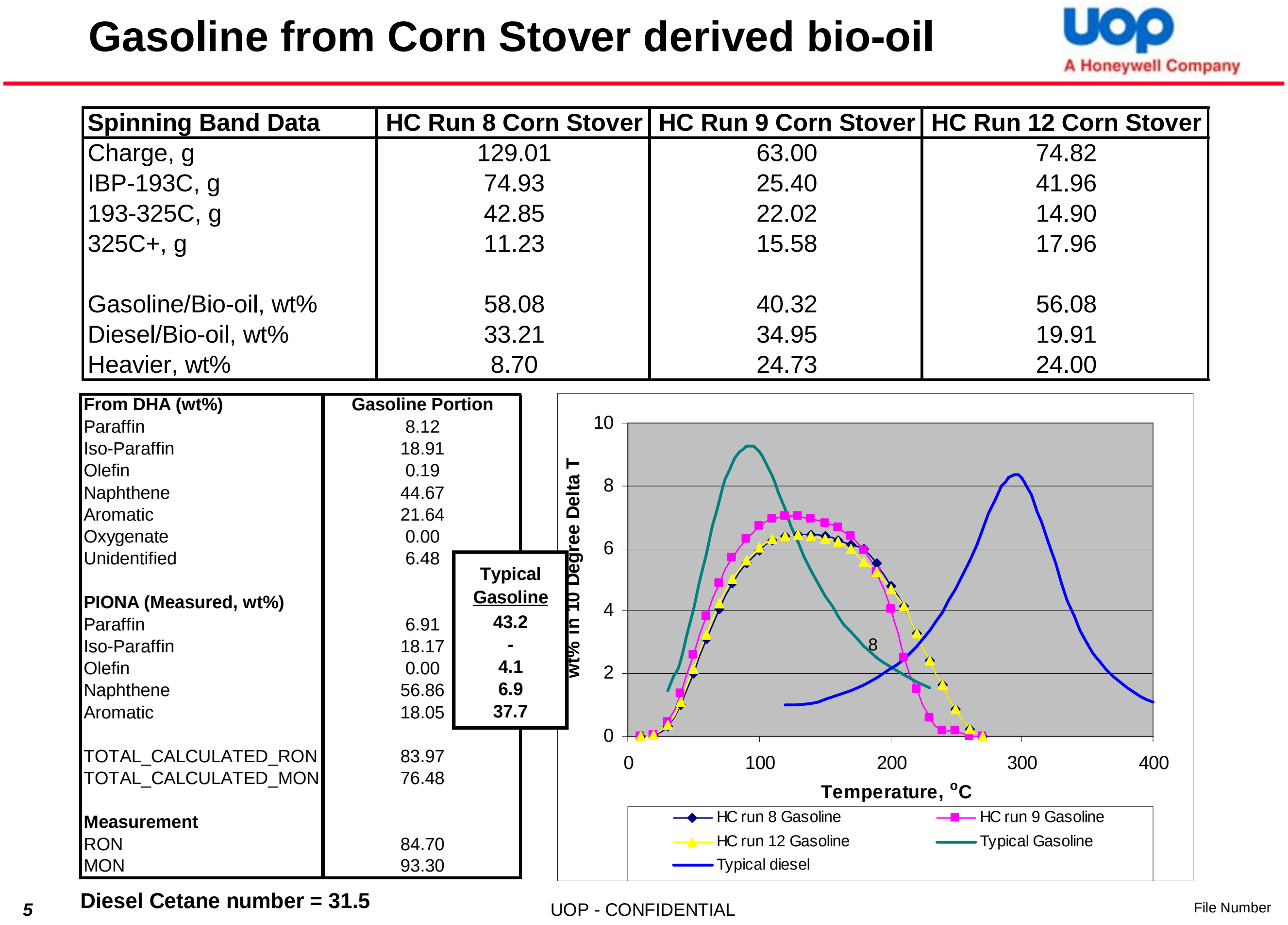
7 UOP - CONFIDENTIAL File Number

Figure 23: Simulated Distillation of Poplar Product

For all 3 feedstocks we see a significant reduction in oxygen level across each processing step. Only phenols are left in the final hydrocracked product. During the hydrocracking step the density goes down and the H/C ratio goes up, indicative of the reduction in size of the hydrocarbon components in this reaction.

As mentioned above for the case of the mixed wood, the final hydrocracked product boils mainly in the gasoline range. The corn stover and poplar products, however, show a wider boiling range distribution and a significant fraction boils in the diesel (and even heavier) range.

Comparison of Fuels from Mixed Wood, Corn Stover and Poplar In the case of the corn stover product, for 3 hydrocracking runs the final product was separated in a gasoline fraction and a diesel fraction by spinning band distillation. The details are shown below in **Figures 24.**. The gasoline fraction has lower total paraffin content, lower aromatics content and much higher naphthene content than typical gasoline. Calculated RON and MON for this case were 84 and 76.5 respectively. The diesel fraction had a cetane number of 31.5.



Gasoline from Corn Stover derived bio-oil

Spinning Band Data	HC Run 8 Corn Stover	HC Run 9 Corn Stover	HC Run 12 Corn Stover
Charge, g	129.01	63.00	74.82
IBP-193C, g	74.93	25.40	41.96
193-325C, g	42.85	22.02	14.90
325C+, g	11.23	15.58	17.96
Gasoline/Bio-oil, wt%	58.08	40.32	56.08
Diesel/Bio-oil, wt%	33.21	34.95	19.91
Heavier, wt%	8.70	24.73	24.00

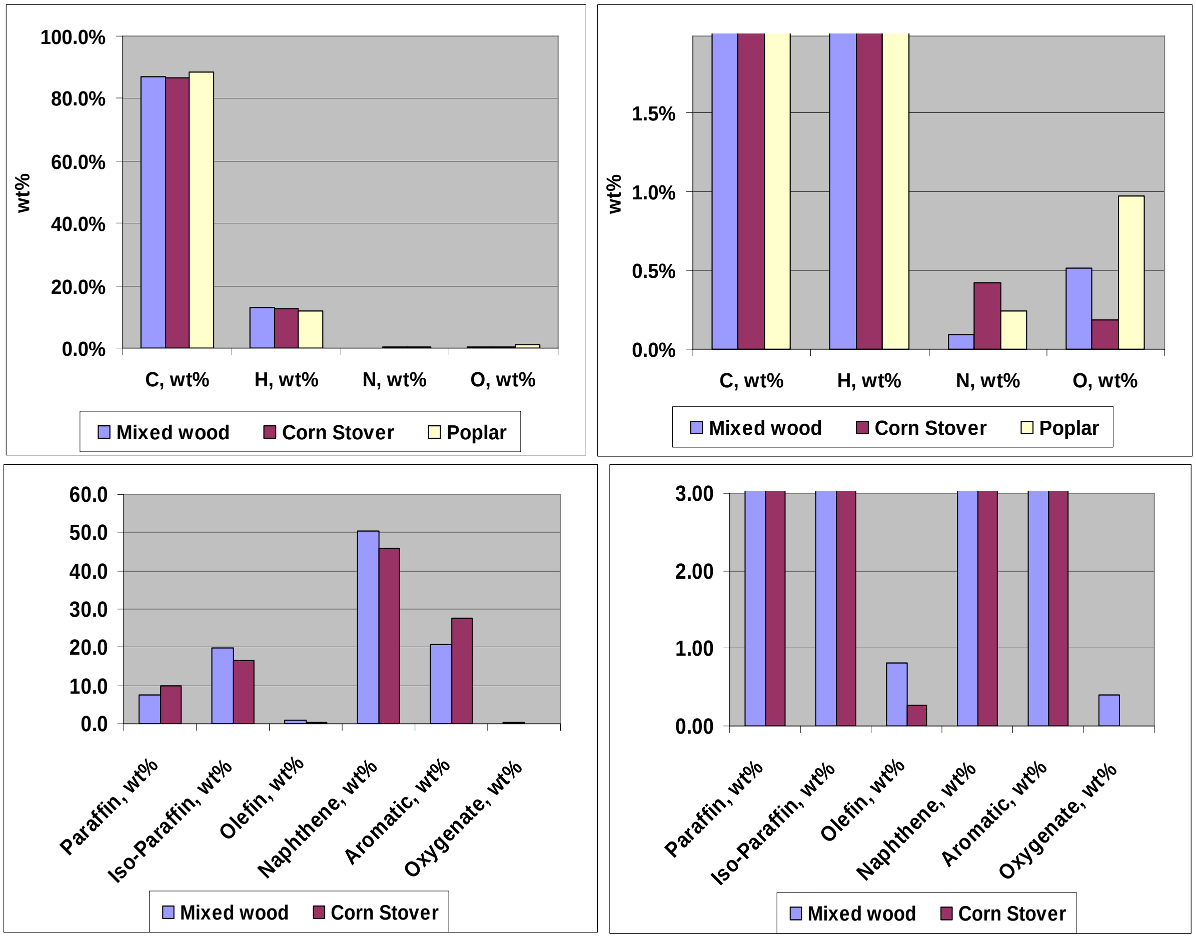
From DHA (wt%)	**Gasoline Portion**	**Typical <u>Gasoline</u>**
Paraffin	8.12	
Iso-Paraffin	18.91	
Olefin	0.19	
Naphthene	44.67	
Aromatic	21.64	
Oxygenate	0.00	
Unidentified	6.48	
PIONA (Measured, wt%)		
Paraffin	6.91	**43.2**
Iso-Paraffin	18.17	**-**
Olefin	0.00	**4.1**
Naphthene	56.86	**6.9**
Aromatic	18.05	**37.7**
TOTAL_CALCULATED_RON	83.97	
TOTAL_CALCULATED_MON	76.48	
Measurement		
RON	84.70	
MON	93.30	

Diesel Cetane number = 31.5

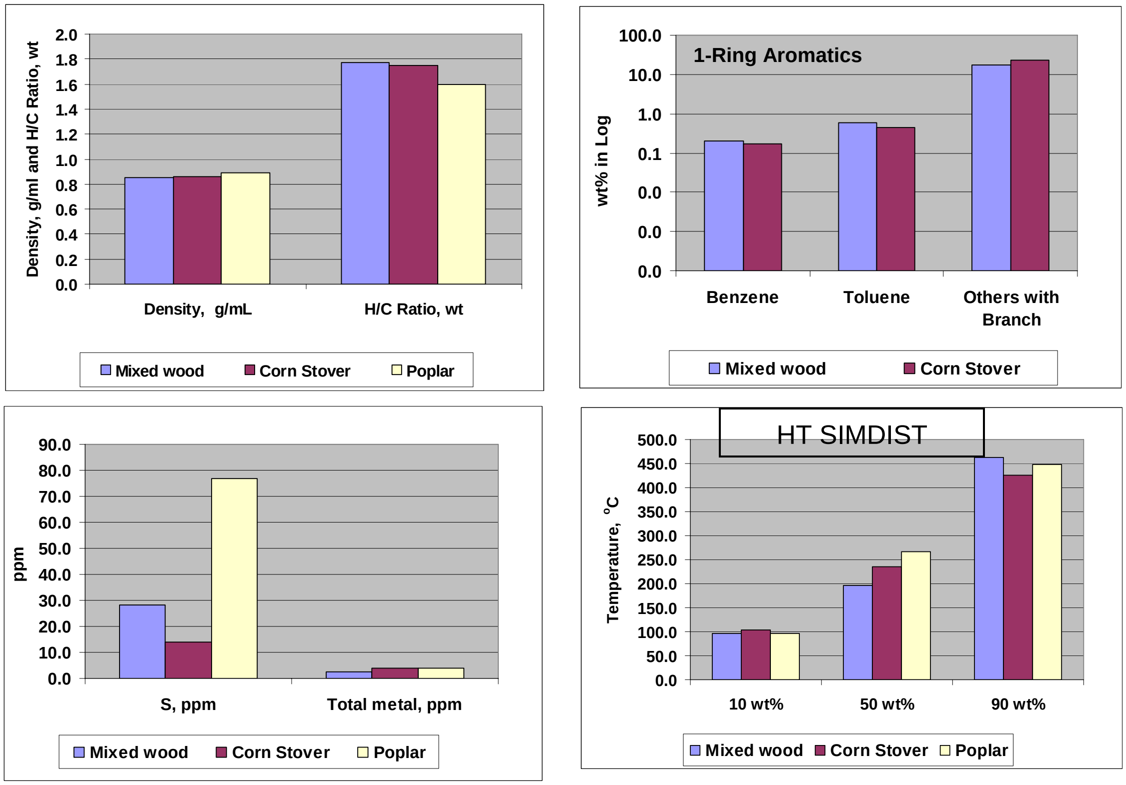
5 UOP - CONFIDENTIAL File Number

Figure 24: Summary of Corn Stover Runs

In the **Figures 25 a-h** below, the products of the 3 feedstocks are compared in a number of additional properties. Most properties – elemental composition, density, hydrocarbon types, boiling range (simdist) – turn out to be quite similar for the different feed sources.



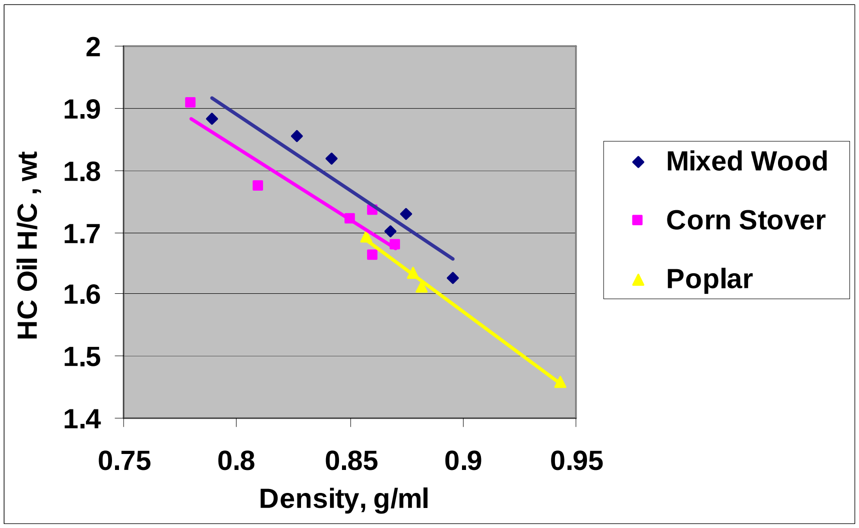
Figures 25 a-d Chemical Analysis of Product from Three Types of Biomass



Figures 25 e-h Physical & Chemical Analysis of Products from Three Types of Biomass

Inspection of a number of product properties suggests that density and H/C ratio are good indicators of hydrocracking severity/efficiency. The density was shown to increase consistently with time on stream**(Figure 26 a,b).** This suggests that the catalysts are deactivating during the hydrocracking phase. It also complicates the data analysis.

Density, H/C measure of hydrocracking efficiency?



Density increase during HC run → deactivation

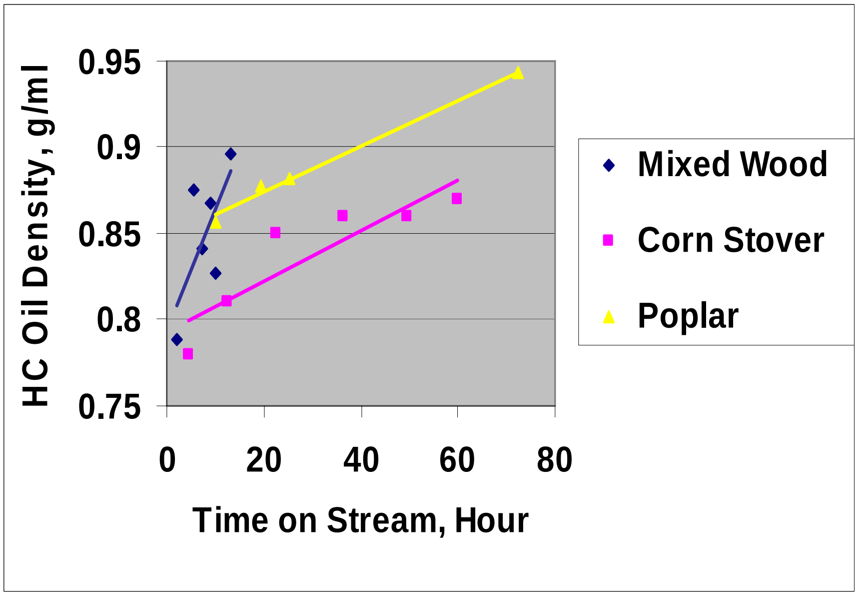


Figure 26 a. H/C ratio as a function of density b. Density as a function of time on stream.

Life Cycle Assessment

A life cycle assessment (LCA) totaling environmental flows was done on a corn stover pyrolysis process, from the production of the feedstock to end use in a vehicle. This LCA model is by no means an exact accounting of environmental and energy flows in a corn stover pyrolysis process. When using this LCA model, it is important to consider the assumptions, detailed in this report, used to arrive at these numbers. Life cycle inventory data for corn stover production and stover transportation come from a previous LCA performed on a corn stover E85 ethanol process (Sheehan, et al. 2000). The data for pyrolysis and refining processes in the LCA model are based on data from runs by UOP and analysis by UOP, Pacific Northwest National Laboratory (PNNL), or the National Renewable Energy Laboratory (NREL). The pyrolysis process flow is derived from NREL milestone report FY04-545 (Putsche 2004). Emissions from heaters and combustors are estimated from the Environmental Protection Agency's *AP-42 Air Pollutant Emissions Factors* (EPA 2007). Emissions from the use of fuel in vehicles are calculated from EPA emissions data from test cars (EPA 2000). Resource inputs and emissions outputs for some steps in the LCA are taken from standard modules in the TEAM LCA software package database (ECOBILAN 2003).

The bulk of carbon dioxide emissions from fossil fuel sources occurs during the production of the corn stover. When compared to a corn stover process producing E85 ethanol, the LCA model shows fossil fuel carbon dioxide emissions, electricity input, and raw corn stover input favor the pyrolysis process on a per vehicle mile traveled basis. When compared to an unleaded gasoline life cycle, the pyrolysis LCA is favorable from oil use and fossil fuel carbon dioxide emissions perspectives.

Scope

The objective of this LCA model is to track emissions through the life cycle of corn stover from corn production to end use. The processes included are stover production, stover transportation, stover pyrolysis, transportation to refinery, refining, fuel distribution, and fuel use **(Figure 27)** . Material flows from processes are tracked from "cradle to grave"—from the natural resource acquisition to eventual emission or disposal. While emissions from the processes are included, emissions from production of capital goods are not. For example, emissions from production and use of diesel fuel in tractors are included, but the emissions from the manufacture of the tractor are not.

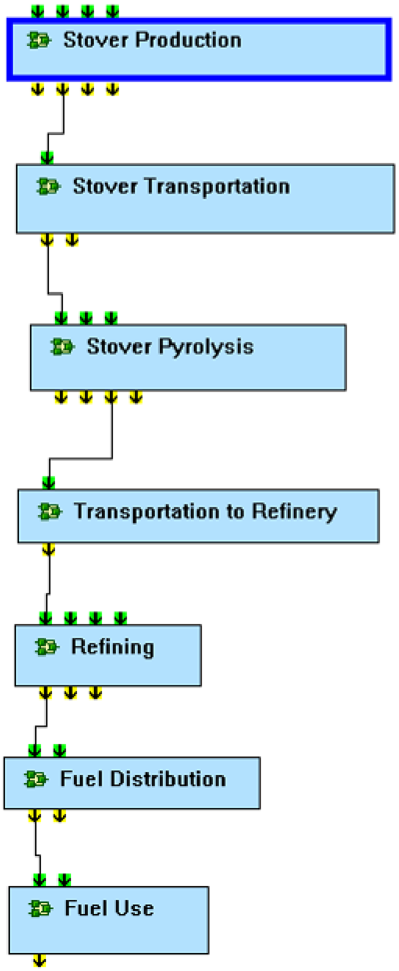


Figure 27. Processes in Corn Stover Pyrolysis Production of Gasoline and Diesel

Methods

The software for this LCA is ECOBILAN's TEAM 4.0 (ECOBILAN 2003). TEAM includes a stock database, called DEAM, of emissions from various processes. The production of electricity and manufacture of hydrogen gas are two of the DEAM modules used in this model.

Material and energy data come from or are derived from several sources. Pyrolysis and refining material balance data are from experiments run by UOP and analyzed by UOP, PNNL, or NREL (CRADA 2007). The pyrolysis process design is based on an NREL Aspen Plus$^{\text{TM}}$ model for wood pyrolysis (Putsche 2004). Several modules are taken from an NREL LCA on corn stover production of E85 ethanol (Sheehan, et al. 2000). Emissions data for heaters and combustors are based on the Environmental Protection Agency's AP-42 Air Pollutant Emissions Factors (EPA 2007).

Processes Modeled

Stover Production

The stover production LCA is unchanged from the previous NREL model for corn stover production of E85 ethanol (Sheehan, et al. 2000). The output of this process is raw corn stover, and the inputs include fertilizer, diesel oil, tractor lube oil, and crop information from Iowa counties.

Stover Transportation

The stover transportation LCA is also based on the 2000 NREL model. In that model, distances from each Iowa County to appropriately located ethanol plants are tabulated. This model assumes that a JCB tractor with wagon will transport the stover to the ethanol plant, which likely overestimates the fuel use and emissions. For the pyrolysis model, the stover transportation LCA was simplified to assume that stover travels an average of 33 miles, based on a 50 mile collection radius (Aden, et al. 2002). With this modification, sensitivity to varying distance from farms to pyrolysis plants could be analyzed.

Stover Pyrolysis

The stover pyrolysis process is based on the 2004 Aspen Plus model for wood pyrolysis (Putsche 2004). Figure 4 shows the steps in stover pyrolysis, with block names corresponding to the Aspen Plus model names. Because life cycle assessment is only concerned with mass and energy flowing into or out of the process, the LCA model is not concerned with recycle streams and does not include the level of unit operation detail found in an Aspen Plus model process design.

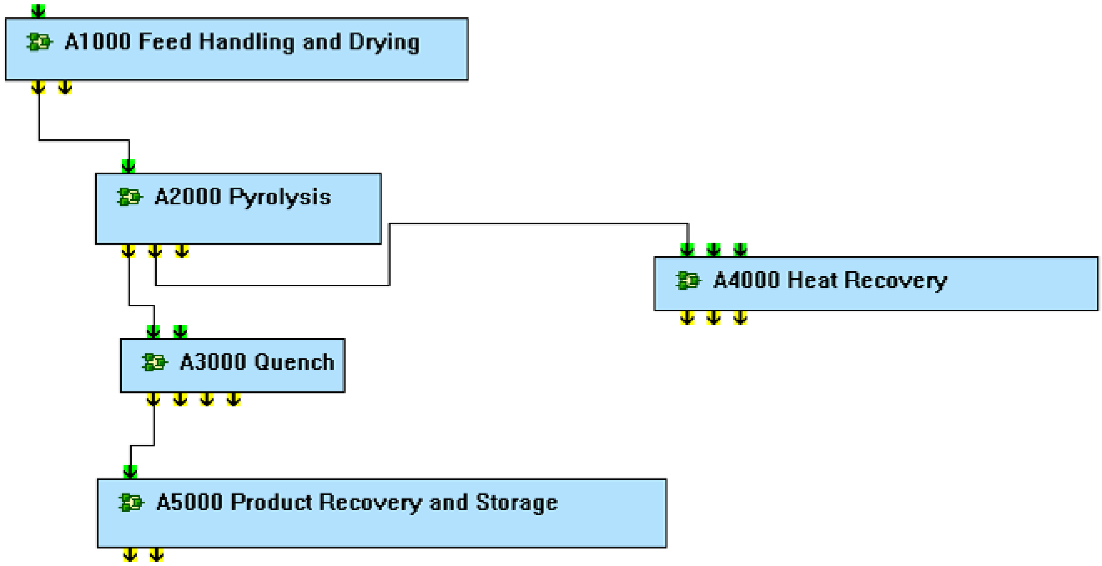


Figure 28. Stover Pyrolysis Process

Feed Handling and Drying

"A1000 Feed Handling and Drying" includes a dryer to remove moisture from the corn stover. Because the water content of the corn stover is included as part of the data from UOP's pyrolysis step, the water removed is not accounted for in this drying step, but instead, in the "A2000 Pyrolysis" step. The purpose of this drying step in the LCA is to tally the emissions from operating a dryer. The emissions from the dryer are taken from AP-42 emissions for a particleboard, softwood, direct wood-fired, rotary dryer with a multiclone particulate matter emission control device, based on mass of the softwood. In this case, the mass of the raw corn stover was used. The energy necessary for drying is not accounted for in this step, but included in a net electricity term in the "A3000 Quench" step. The largest emission from this step is particulates.

Pyrolysis

The actual pyrolysis step of converting corn stover into pyrolysis oil is represented by "A2000 Pyrolysis." The pyrolysis unit converts the raw corn stover to pyrolysis oil, char, and gas. Conversion data for the pyrolysis unit are taken from UOP pyrolysis run 2, which provided a better overall mass balance than run 3. In the Aspen Plus model, the char combustor in "A4000 Heat Recovery" combusts the carbon monoxide produced in the pyrolysis unit. As a result, CO is not listed as an emission in this step. In addition, although the char combustor in the Aspen Plus model has ash as an input and output, in the LCA, ash is separated out at the pyrolysis unit as "Waste: Slags and Ash." The energy needed for pyrolysis is also not considered in this step but included in a net electricity term in the "A3000 Quench" step. The largest emission in this step is CO_2 from biomass sources.

Heat Recovery

Heat recovery includes inputs and outputs from the char and gas combustor and a rotary filter. Incoming char and carbon monoxide is mixed with air to produce CO_2 and water. Carbon dioxide produced from combustion is calculated assuming that all the carbon in the char (55%) is combusted. The water produced from combustion is calculated by scaling the water output from the Aspen Plus wood pyrolysis model by the ratio of CO_2 output in the LCA corn stover pyrolysis to CO_2 in the Aspen Plus model. In addition to the products of combustion, there are emissions from the combustion process. These emissions are once again calculated from AP-42 emission factors for wood residue combustion in boilers with a fabric filter particulate matter control device. The energy recovered from combustion is included in the net electricity term in the "A3000 Quench" step.

The rotary filter requires a quench water stream. This amount of circulated water is calculated by scaling the water required from the Aspen Plus wood pyrolysis model by the ratio of the corn stover mass to the wood mass. The water needed as an input is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

Quench

The quench includes the net electricity generated from the char combustor minus the energy needed for pyrolysis and other unit operations. The inventory for this step includes the input water needed to replenish the 3% blowdown in the steam recycle loop (based on the Aspen Plus model) and the output water in the blowdown stream.

Product Recovery and Storage

The product recovery and storage step includes the cooling water to cool the product to 20°C. This water is taken and outputted without wastewater treatment. The water needed as an input is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

Transportation to Refinery

For the pyrolysis oil to be transported to the refinery, the oil is assumed to be transported by rail, 300 miles away to refineries in the Chicago area. The emissions and resources in the process are calculated using two DEAM modules for diesel oil production and rail transport (**Figure 29**).

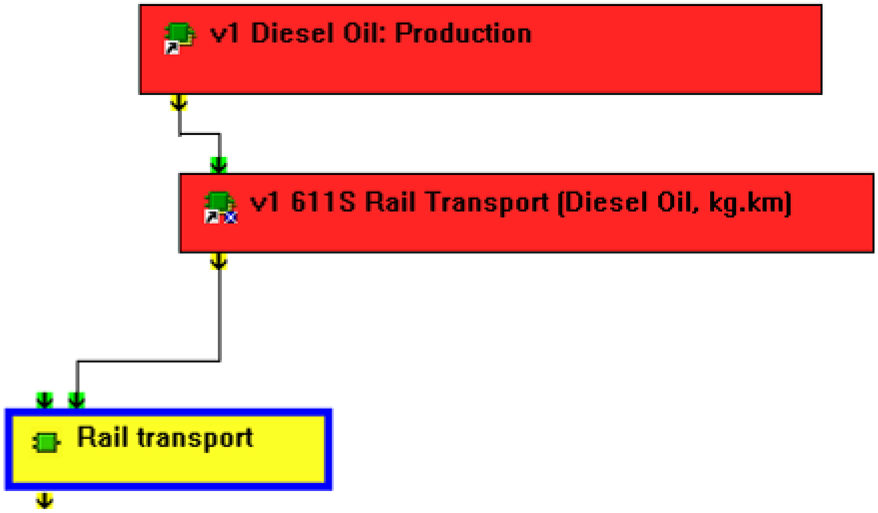


Figure 29. Transportation to Refinery Modules

Refining

The refining step includes upgrading of the pyrolysis oil and then separation of the refinery products (**Figure 30**).

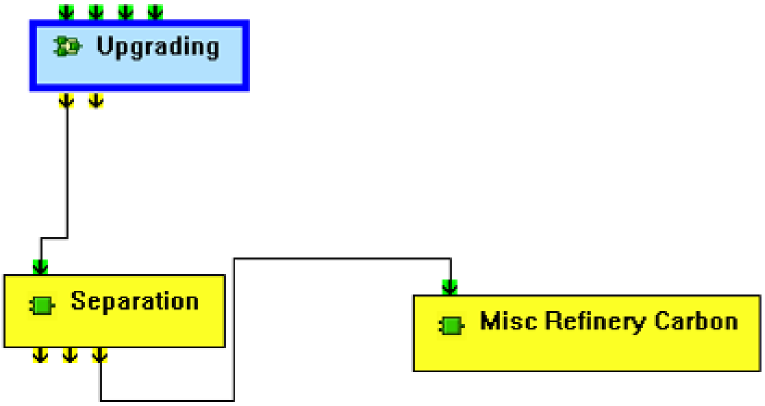


Figure 30. Refining Modules

Upgrading the pyrolysis oil into gasoline and diesel requires hydrotreating and hydrocracking. The modules needed for refining are shown in **Figure 31**.

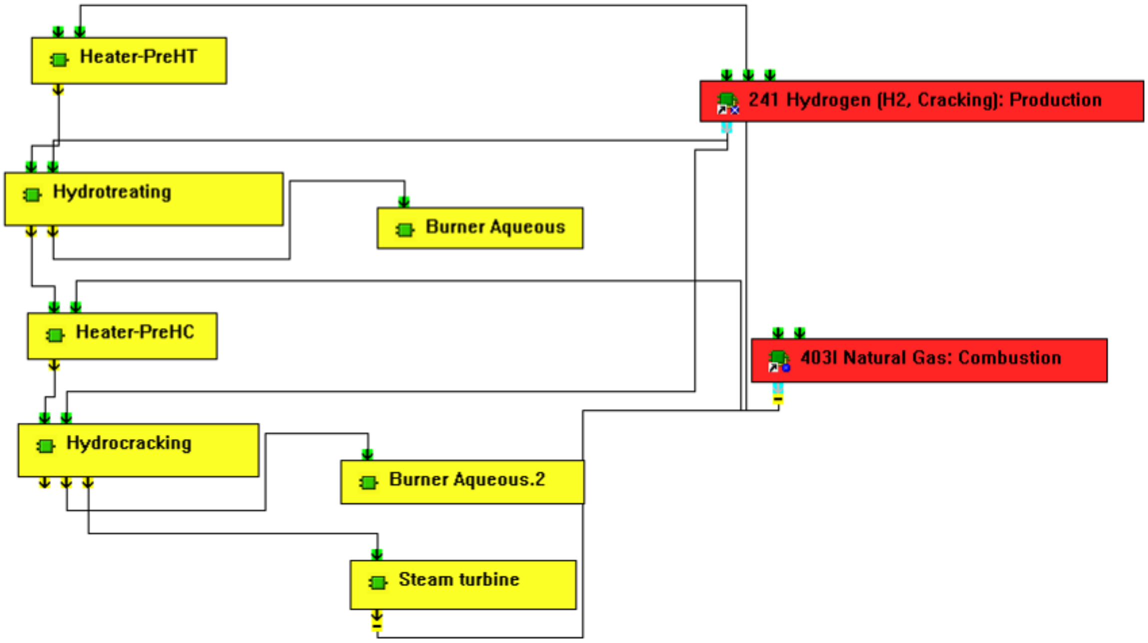


Figure 31. Upgrading Modules

Hydrotreating

For the hydrotreating process design, two generic process configurations published in Hydrocarbon Processing's Refining Processes 2004 Handbook are used. One is by CB&I Howe-Baker Process and Technology (**Figure 32**), and the other is by UOP LLC(**Figure 33**). Fuel energy, electricity, and cooling water data are averaged from these two processes for input into the LCA model. The water used is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

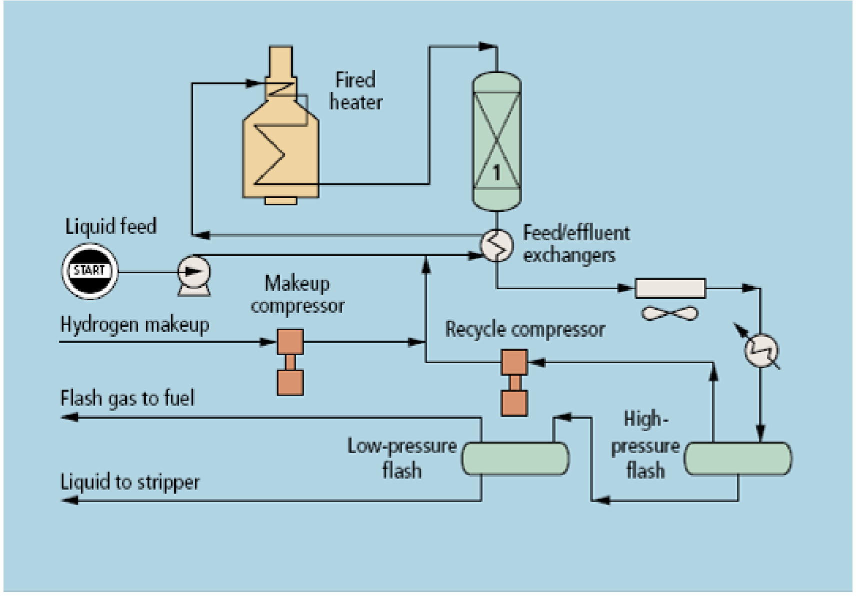


Figure 32: CB&I Howe-Baker Process and Technology Hydrotreating Process Design (Hydrocarbon Processing 2004)

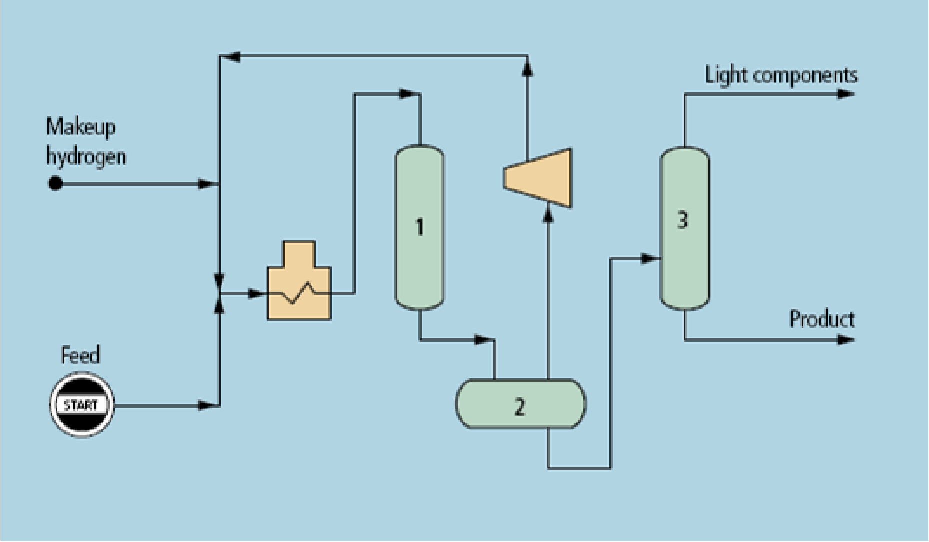


Figure 33. UOP LLC hydrotreating Process Design (Hydrocarbon Processing 2004)

The fuel energy needed for the heater in the hydrotreating process is determined from the fuel energy data from Hydrocarbon Processing's Refining Processes 2004 Handbook. This energy is supplied by natural gas combustion, which has its life cycle inventory represented by a DEAM module.

The products of hydrotreating are based on UOP hydrotreating run 32 (CRADA 2007). This run had an oil yield of 0.79 l/l and was selected in order to help the overall LCA carbon balance. The pyrolysis oil density in the calculations is 1.16 g/ml. The required input hydrogen is based on the hydrogen consumption data rather than the overall hydrogen feed, since it was assumed the hydrogen would be recycled in the final process. The difference in the sulfur content in the pyrolysis oil and the hydrotreated oil is assumed to leave as hydrogen sulfide. The aqueous material goes to an aqueous burner. Because energy data are not available from the burning of the aqueous material, the burner only generates CO_2 based on the carbon percentage of the aqueous material and polluted water.

Hydrocracking

The hydrocracking inputs and outputs are based on four process designs from Hydrocarbon Processing's Refining Processes 2004 Handbook. These are by Axens, ExxonMobil, Chevron Lummus Global(CLG) LLC, and UOP LLC. Fuel energy, steam, water, and electricity data are averaged among the processes for which data are available. The most used process designs are the ones by ExxonMobil and CLG. The water used is taken as 3.7% of the cooling water rate, based on the 2007 NREL thermochemical ethanol design report (Phillips, et al. 2007).

The energy for the heater ("Heater-PreHC")in the hydrocracking process is determined from the fuel energy data from Hydrocarbon Processing's Refining Processes 2004 Handbook. Natural gas combustion supplies the energy for this heater.

The hydrogen input is based on hydrogen consumption data, and the emissions from the production of hydrogen are tracked using a DEAM module. The output of the hydrocracking process is based on hydrocracking run 10 (CRADA 2007). This run, with an oil yield of 0.98 l/l was selected to help the overall LCA carbon balance.

The steam output from the hydrocracking process is used to generate electricity. The electricity is calculated from scaling the electricity from a steam turbine in the Aspen Plus wood pyrolysis model by the ratio of the mass of steam in each process. This electricity output is used to offset some of the natural gas combustion needed by the hydrocracking heater.

As with hydrotreating, hydrocracking produces an aqueous byproduct, which may be burnt. In the LCA model, this aqueous portion does not produce energy or electricity, only carbon dioxide and polluted water waste.

Separation

The resulting hydrocracked oil is separated into gasoline, diesel, and miscellaneous refinery product cuts. From the distillation curve for HT-101 (0935-1135), the gasoline cut is taken as the fraction (0.684) with a boiling point below 330°C, the diesel cut is the fraction (0.296) with a boiling point between 330°C and 600°C, and miscellaneous refinery products are the remaining fraction (0.020) (CRADA 2007).

From analysis of the hydrocracked oil, the carbon weight percent is 87%. The "Misc Refinery Carbon" module accounts for the carbon unaccounted for after considering the carbon emissions from the end use of diesel and gasoline. This carbon is emitted as carbon dioxide. The mass of carbon needed to make up the difference is currently greater than the mass of the miscellaneous refinery products. This suggests that the emissions from the gasoline and diesel cuts should have more CO_2 output.

Fuel Distribution

The gasoline and diesel oil is distributed from refineries to bulk storage terminals to retail outlets(**Figure 34**). The LCA modeling of this stage is taken from the previous E85 ethanol LCA TEAM model, with the assumption that diesel oil is transported the same way as gasoline . The model assumes that only rail and pipeline are used to transport the gas and diesel from refineries to bulk storage terminals and only trucks are used to transport the fuel to retail outlets. Barge and tanker are not used in this LCA model.

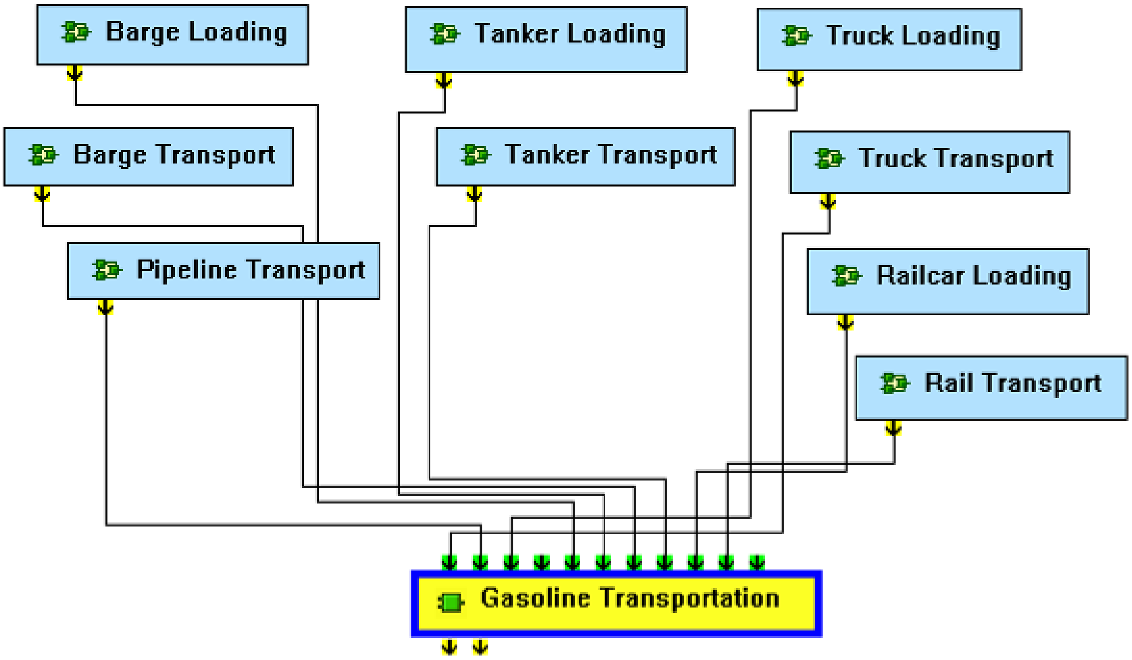


Figure 34. Fuel Distribution (not all modes of transportation are used)

Fuel Use

Emissions and fuel economy for gasoline use are based on the corn stover E85 ethanol LCA model. In that model, the vehicle basis is a 2000 Ford Taurus flexible fuel vehicle. Emissions from diesel are based mainly on tailpipe emission data for a 2000 Volkswagen Jetta diesel vehicle (EPA 2000). For sulfur dioxide and non-methane hydrocarbon emissions from the diesel vehicle, data were taken from a DEAM module for diesel fuel use in a truck, which overestimates these emissions. Diesel fuel economy is taken as 33% better than gasoline (U.S. DOE 2007).

Results

Inputs

The total fossil fuel and water used in this pyrolysis process is shown in Table 36. The breakdown of the fossil fuel inputs is shown in **Figure 35**. The largest fossil fuel use comes from the production of the stover. The second largest impact is in the refining (hydrotreating and hydrocracking), from both the steam reformation of methane and the natural gas needed for heaters.

	g/mile
(r) Coal (in ground)	4.6
(r) Natural Gas (in ground)	16.1
(r) Oil (in ground)	9.7
Water Used (total)	148.9

Table 36. Total Fossil Fuel and Water Input

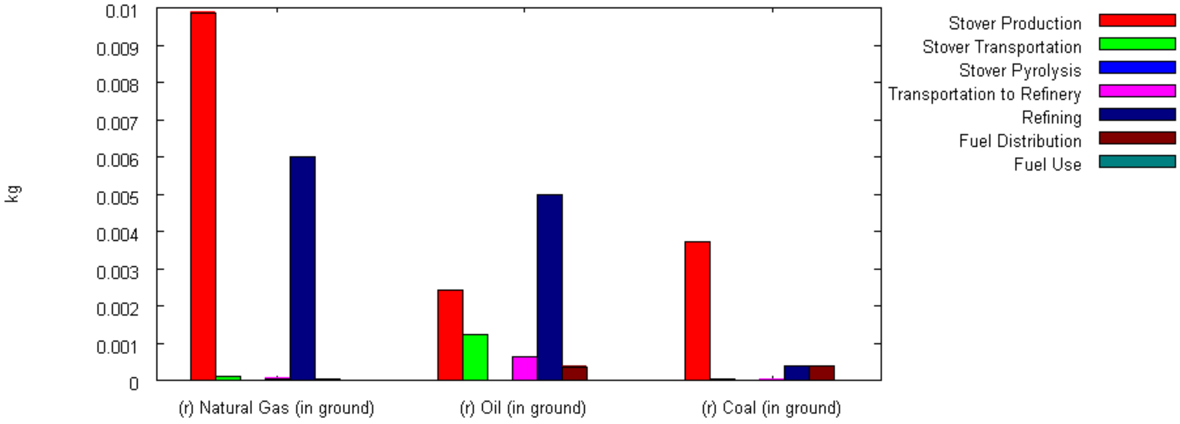


Figure 35. Fossil Fuel Inputs

Water use is dominated by stover production (**Figure 36**). Cooling water constitutes most of the water needed in the pyrolysis and refining steps. Stover production consumes the most electricity, followed by refining (**Figure 37)**. The pyrolysis step, through the char combustor, produces electricity.

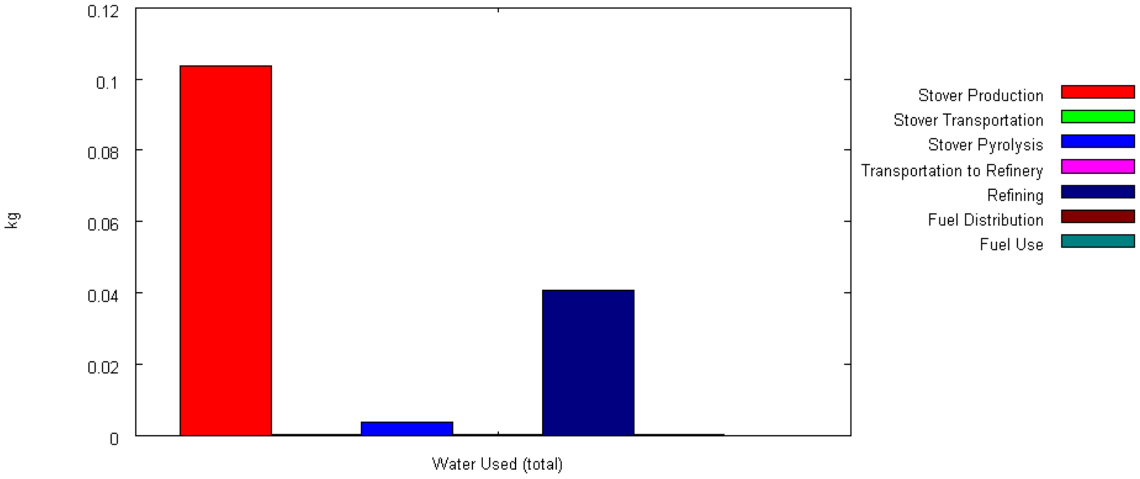


Figure 36. Water Use

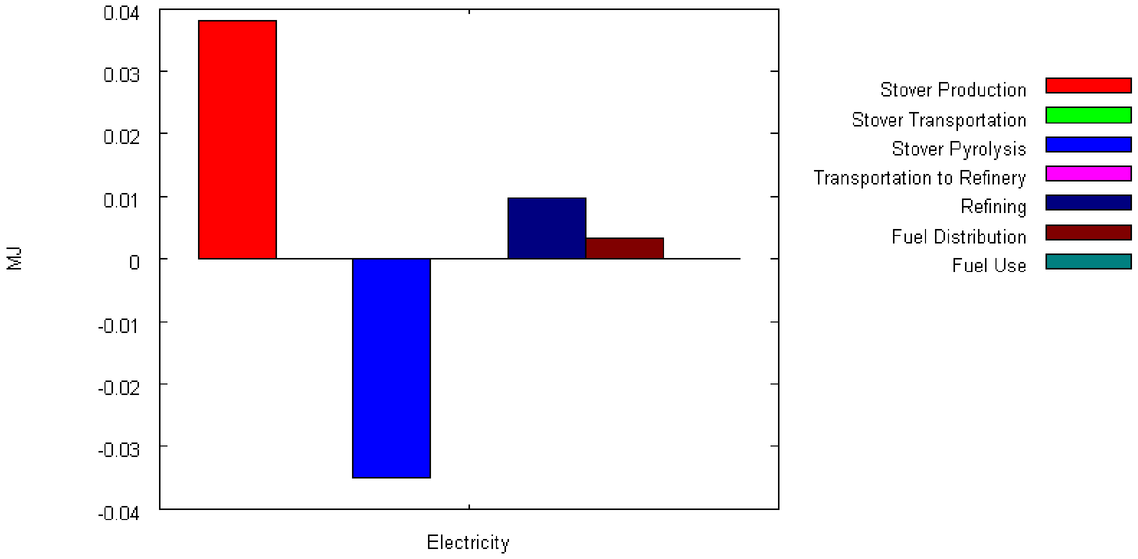


Figure 37. Electricity Use

Outputs

As a greenhouse gas, carbon dioxide emissions are of particular interest in this LCA. Carbon dioxide emissions should be split into emissions from fossil fuel sources and emissions from biomass sources. Because corn takes in carbon dioxide from the atmosphere in the corn plant's lifetime, the release of this biomass carbon dioxide back into the atmosphere is not as deleterious as releasing carbon dioxide sequestered in fossil sources for millions of years.

The total emissions of three main greenhouse gases—carbon dioxide, methane, and nitrous oxide—are shown in Table 11. One column shows the total mass in grams of the emission. The other column is adjusted by the 100-year global warming potential of each gas to report a CO_2 equivalent mass (methane has a GWP of 23, and nitrous oxide has a GWP of 296) (IPCC 2001).

	g/mile	**g/mile, CO_2 equivalent**
(a) Carbon Dioxide (CO_2, fossil)	47	47
(a) Methane (CH_4)	0.93	21
(a) Nitrous Oxide (N_2O)	0.26	77

Table 37. Total Emissions from Main Greenhouse Gases

As shown in **Figure 38**, the biomass carbon dioxide is negative during the stover production step, denoting an intake of carbon dioxide. This biomass carbon dioxide is released over the pyrolysis, refining, and fuel use steps. Some of the original biomass carbon dioxide intake is released as other hydrocarbon sources, such as carbon monoxide or methane. It is more appropriate to look at the biomass carbon, rather than just carbon dioxide. However, because carbon dioxide still constitutes the bulk of the biomass carbon emissions, the results do not change much when considering all carbon sources (**Figure 38**). In this LCA, the carbon balance is 93% satisfied.

Although the production of corn stover takes in carbon dioxide from the atmosphere, the corn stover also requires a large amount of fossil carbon to fertilize, grow, and harvest (**Figure 39**). The refining step also results in fossil carbon dioxide emissions. Since the electricity needed for the hydrotreating and hydrocracking heaters are calculated based off of traditional petrochemical processes, the actual natural gas combustion used for refining of corn stover pyrolysis oil may be significantly different. As calculated in this report, this impact of the refining heaters on carbon dioxide emissions is minimal. The hydrotreating heater's electricity demand results in 0.3 g of CO_2 emissions, constituting 0.5% of the total carbon dioxide emissions. The hydrocracking process net natural gas combustion demand (heater demand minus electricity from steam output) results in 0.6 g of CO_2 emissions, constituting 1% of the total carbon dioxide emissions. The transportation steps have a lesser fossil carbon dioxide output, with the stover transportation step the largest emitter because the mode of transportation (tractor) is the least efficient.

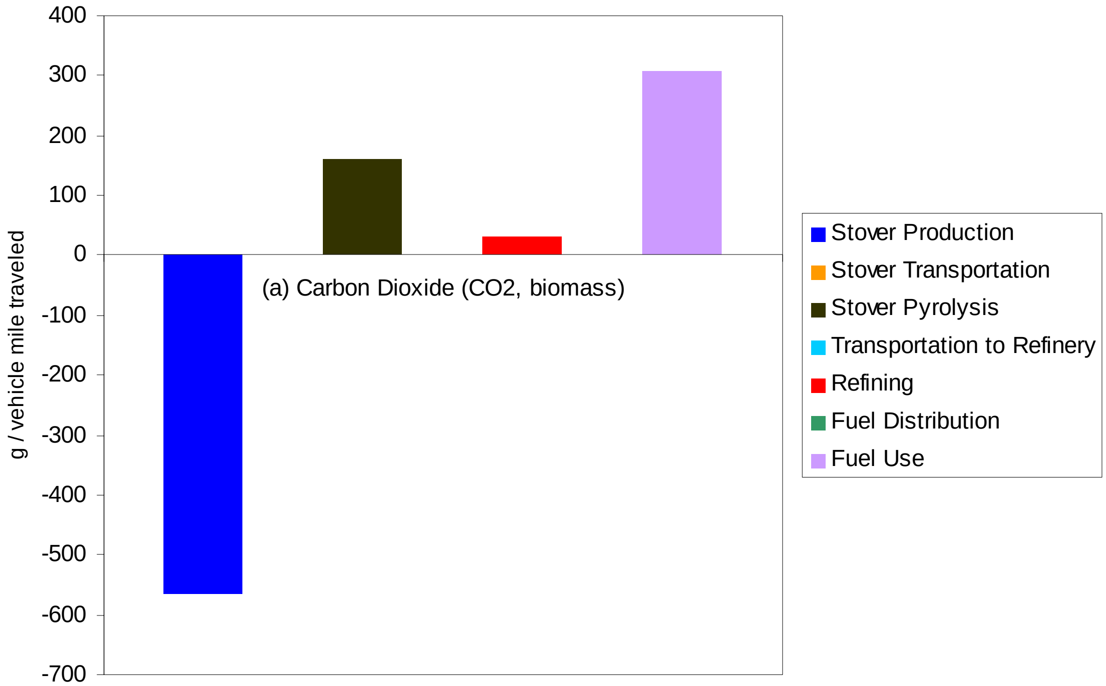


Figure 38. Carbon dioxide emissions from biomass sources

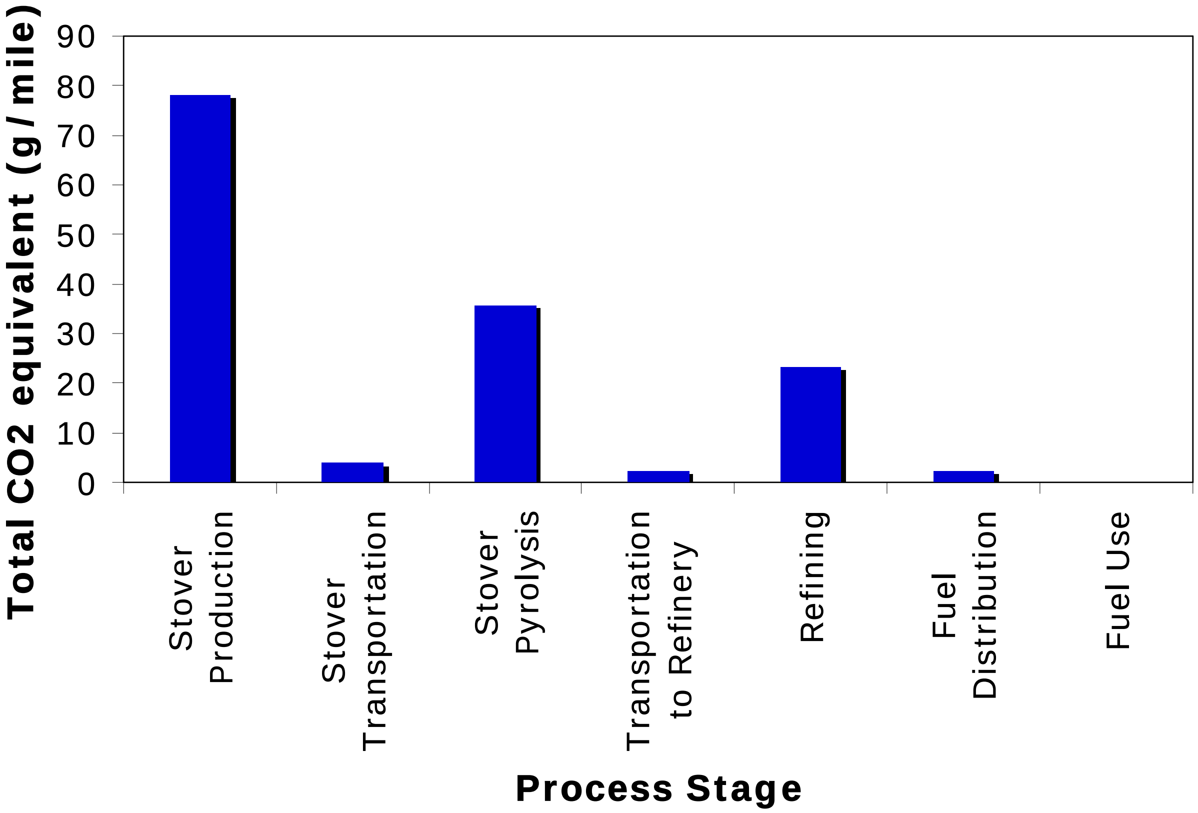


Figure 39. Carbon dioxide emissions from fossil fuel sources

Some of the carbon dioxide emitted to the atmosphere comes from sequestered carbon in the soil. This carbon dioxide is released only in the stover production stage (**Figure 10**). The total carbon dioxide emissions from all sources is shown in **Figure 41**.

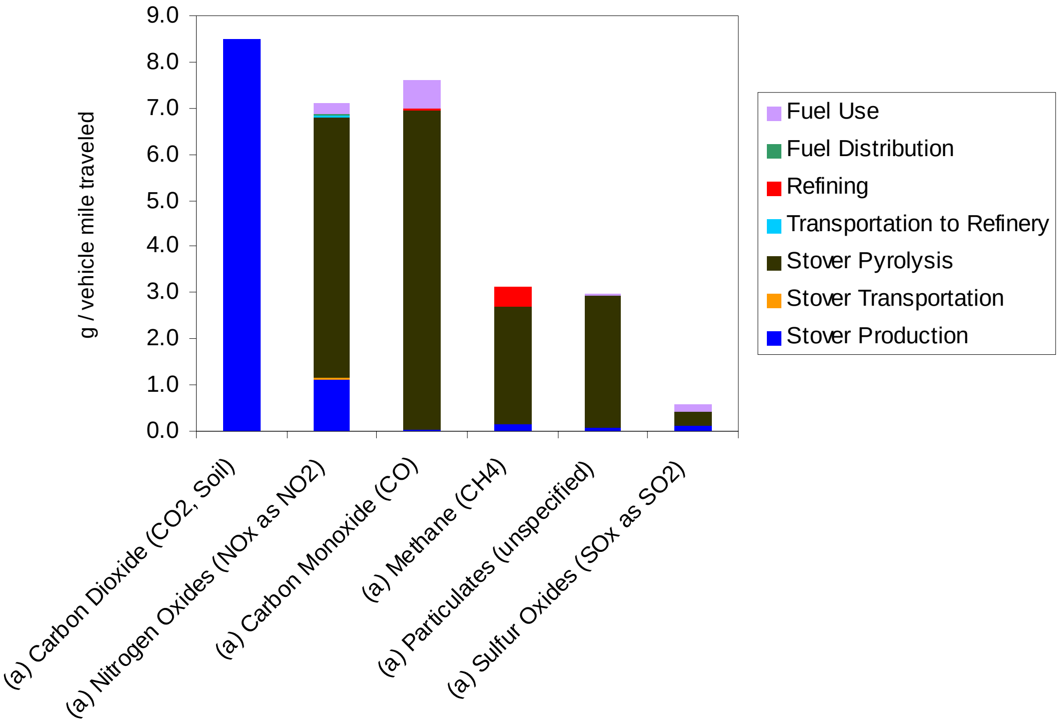


Figure 10. Carbon dioxide from soil and other gaseous emissions

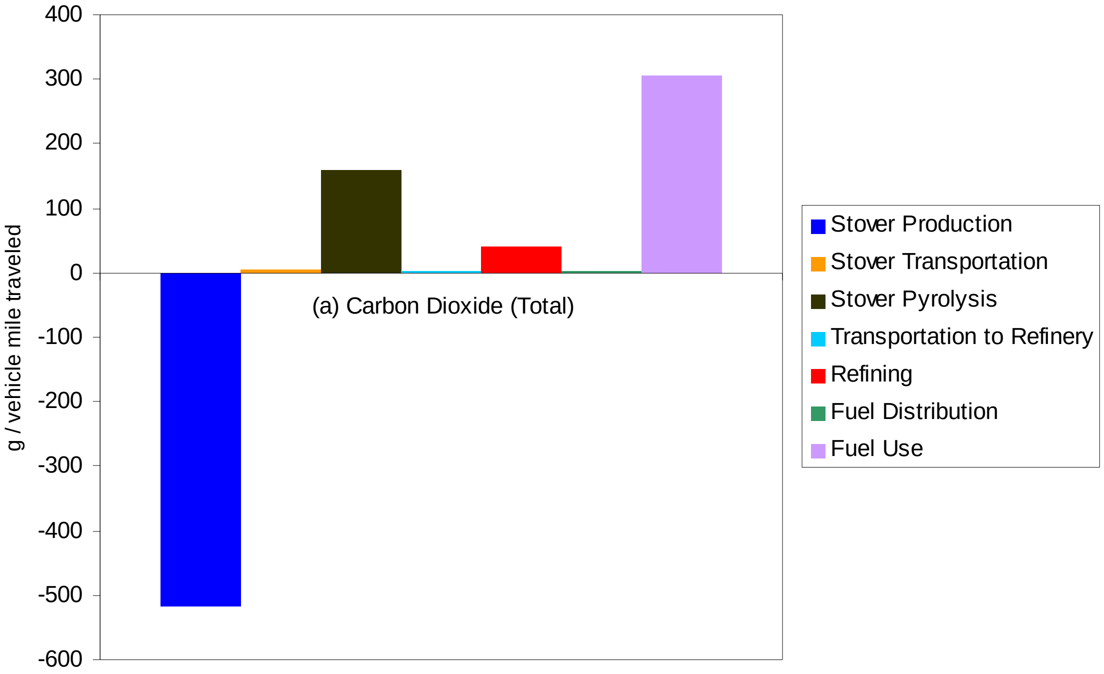


Figure 41. Total carbon dioxide emissions

As seen in **Figure 10**, the nitrogen oxide emissions are high, with most of the emissions coming from the pyrolysis step, specifically the char combustor. Nitrogen oxides are air pollutants, but have not been characterized with a global warming potential by the IPCC. These emissions can be reduced with different assumptions and NO_x emission control. NO_x emissions at the combustor can be reduced by 80% using selective catalytic reduction (Cooper 2004). This would require addition of ammonia gas to reduce NO_x to nitrogen and water (**Figure 42**). Additional sources of NO_x emission reduction include taking the best NO_x emission data from the AP-42 source for external combustion, taking the best Volkswagen Jetta NO_x tailpipe emission data, and taking the actual Volkswagen Jetta fuel economy improvement over the Ford Taurus FFV. The results of all these scenarios are shown in 38. If all the factors were taken as best case, the NO_x level would be 74% less than the base case, with 54% of the NO_x emissions coming from stover production. The NO_x emissions in the stover production process come from the assumption that 5% of the nitrogen in the fertilizer will be volatized as NO_x (Sheehan, et al. 2000). The disadvantage of the catalytic reduction is that the production of ammonia results in increased CO_2 emissions. Adding the catalytic reduction alone will increase the CO_2 emissions by 48 g or 82%. If all factors are added together, the CO_2 emissions increase is 12 g or 20%.

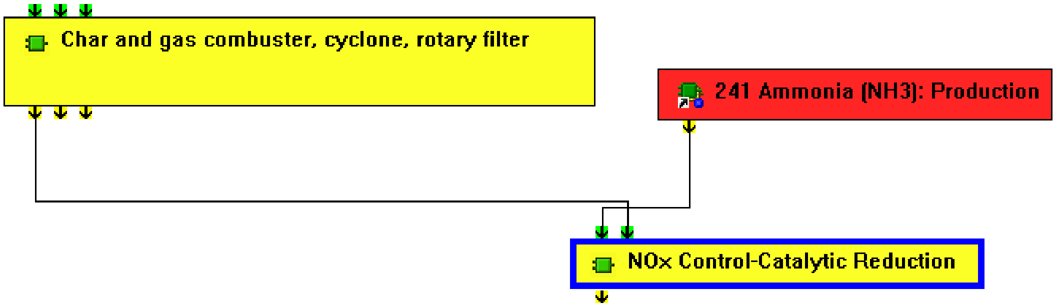


Figure 42. Catalytic reduction of NO_x emissions

Factor	Original value	Low NO_x value	% change in parameter	NO_x level [g]	% change in NO_x
Original	-	-	-	7.101	-
Best combustor emissions	0.49	0.187	-61.8%	3.675	-48.2%
Catalytic reduction (fraction NO_x remaining)	1	0.2	-80.0%	2.813	-60.4%

Best VW Jetta emission	0.625	0.53	-15.2%	7.066	-0.5%
VW Jetta diesel efficiency over gasoline	1.33	1.66	24.8%	6.563	-7.6%
Combine all				1.882	-73.5%

Table 38. NO_x reduction scenarios

The waste streams are shown in **Figure 43**. The waste total from the stover pyrolysis is due to the ash. The high metals emissions are mainly the result of emissions from diesel oil production (**Figure 44**).

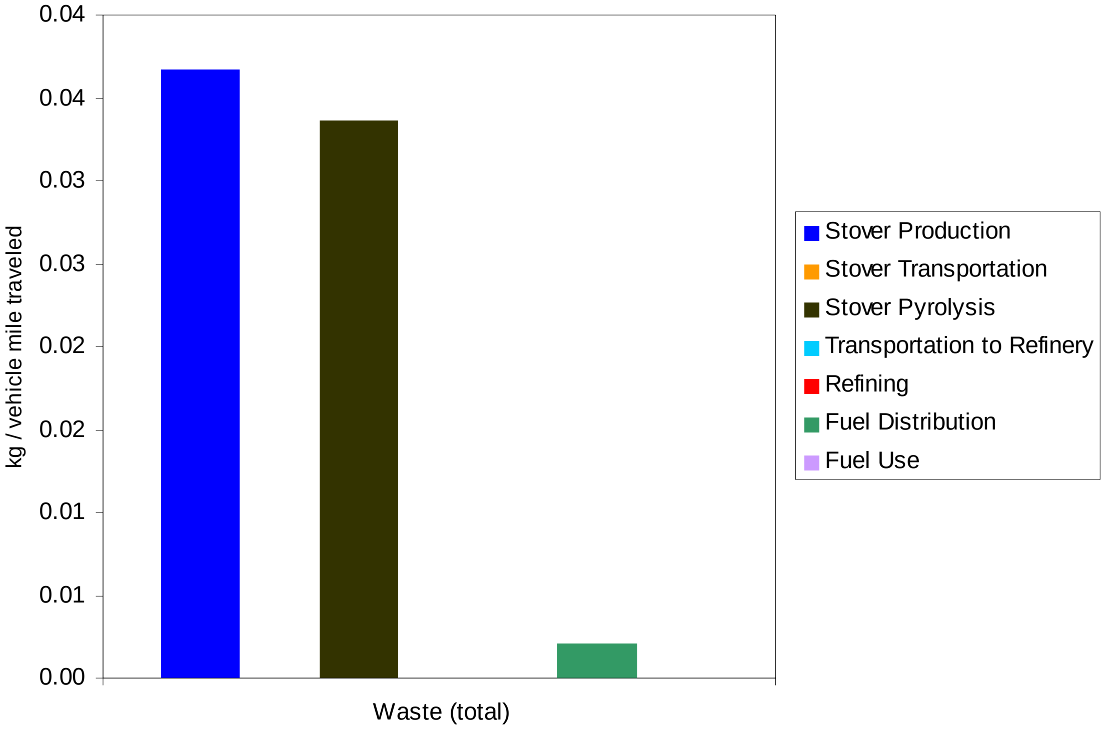


Figure 43. Waste

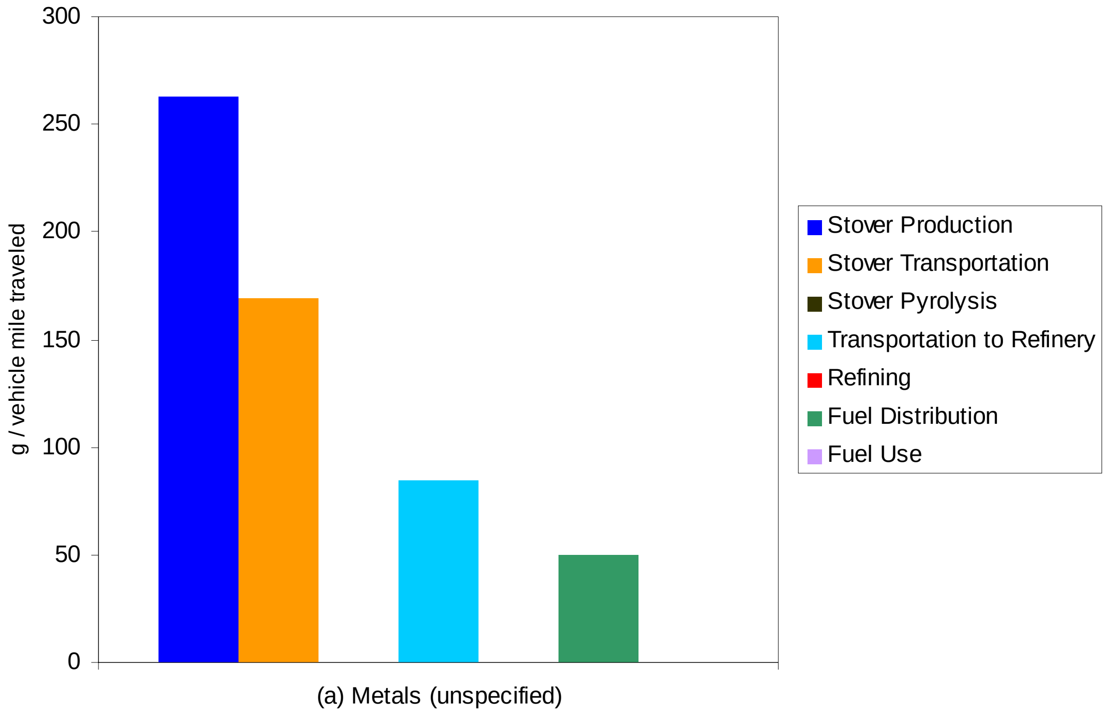


Figure 44. Metals

Comparison with Ethanol and Gasoline Life Cycles

Inputs and outputs were compared with two other transportation fuel life cycle assessments. One comparison was with the biochemical conversion of corn stover to create ethanol in an E85 process. The original LCA model is modified by removing an unleaded gasoline avoided impact module and the model is corrected to account for the 15% moisture in the corn stover. The other comparison is with the life cycle assessment of unleaded gasoline. The LCA of unleaded gasoline is taken from parts of the analysis for production of E85 ethanol from corn stover (Sheehan, et al. 2000).

The unleaded gasoline LCA consists of the production, transportation, and distribution of unleaded gasoline, denoted in **Figure 45** as “Unleaded Gasoline,” and the use of gasoline in the vehicle, denoted in **Figure 45** as “Gasoline Use.” The production, both domestic and foreign, transportation, and distribution of gasoline is shown in more detail in **Figure 46** and is explained in greater detail in Corn Stover Life Cycle Analysis (Sheehan, et al. 2000). The emissions from gasoline use are based on EPA tailpipe emissions for a 2000 Ford Taurus flexible fuel vehicle using only gasoline for 50,000 miles.

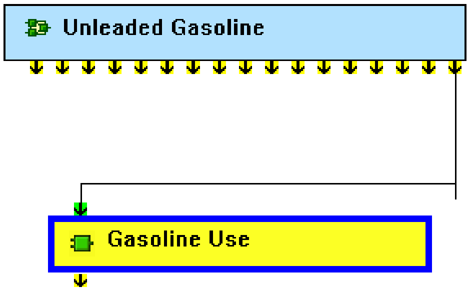


Figure 45. Unleaded gasoline LCA

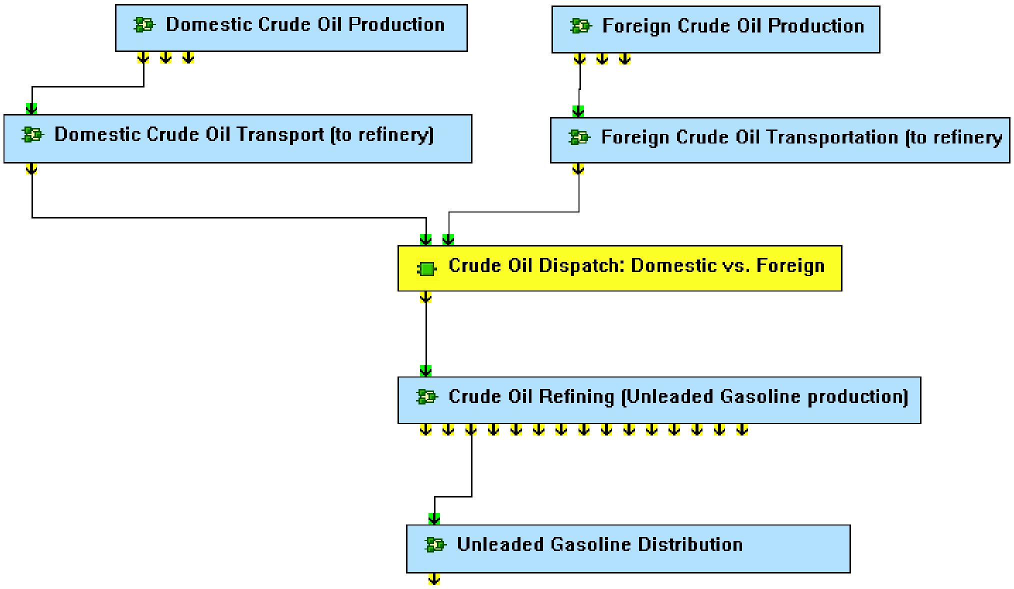


Figure 46. Production and distribution of unleaded gasoline

Figure 47 shows a comparison of various inputs for the three processes. The coal and natural gas usage for pyrolysis and ethanol are greater than or equal to usage for gasoline, but both pyrolysis and ethanol processes consume considerably less oil. As seen in **Figure 48**, the pyrolysis process uses more water than the gasoline process but less water than the ethanol process. In general, the pyrolysis process requires fewer resources than the ethanol process. This can be attributed directly to the smaller amount of corn stover and cropland needed in the pyrolysis case (**Figure 49** and **Figure 50**). The electricity used in the pyrolysis process is less than what is used in both the ethanol and gasoline processes (**Figure 51**). Although electricity and corn stover are used in these processes, they are technically not inputs because the life cycle assessment takes into account the natural resources needed to produce electricity and corn stover.

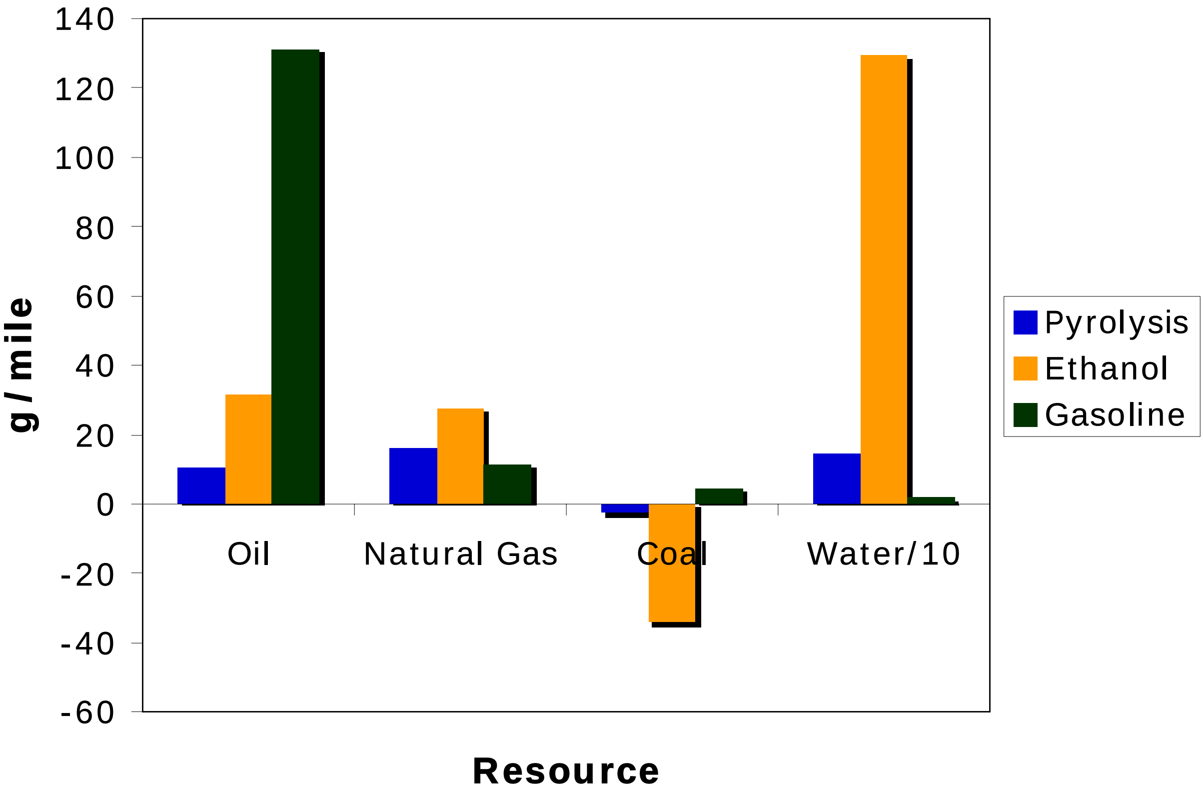


Figure 47. Comparison of various inputs

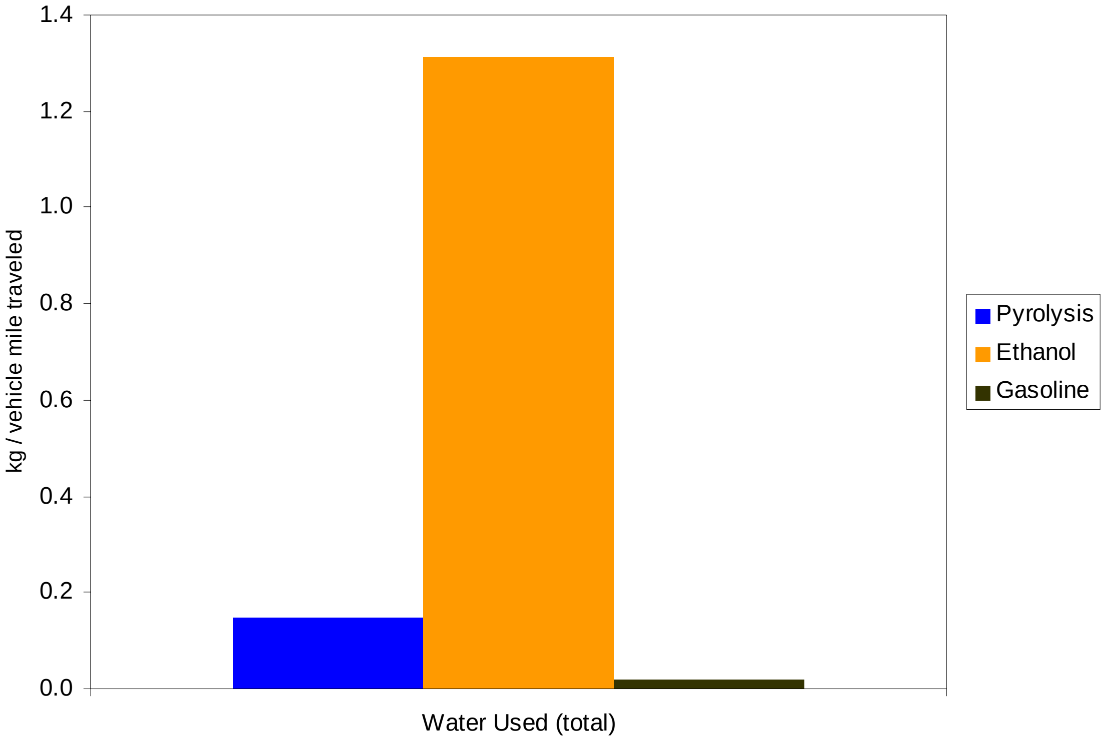


Figure 48. Water usage comparison

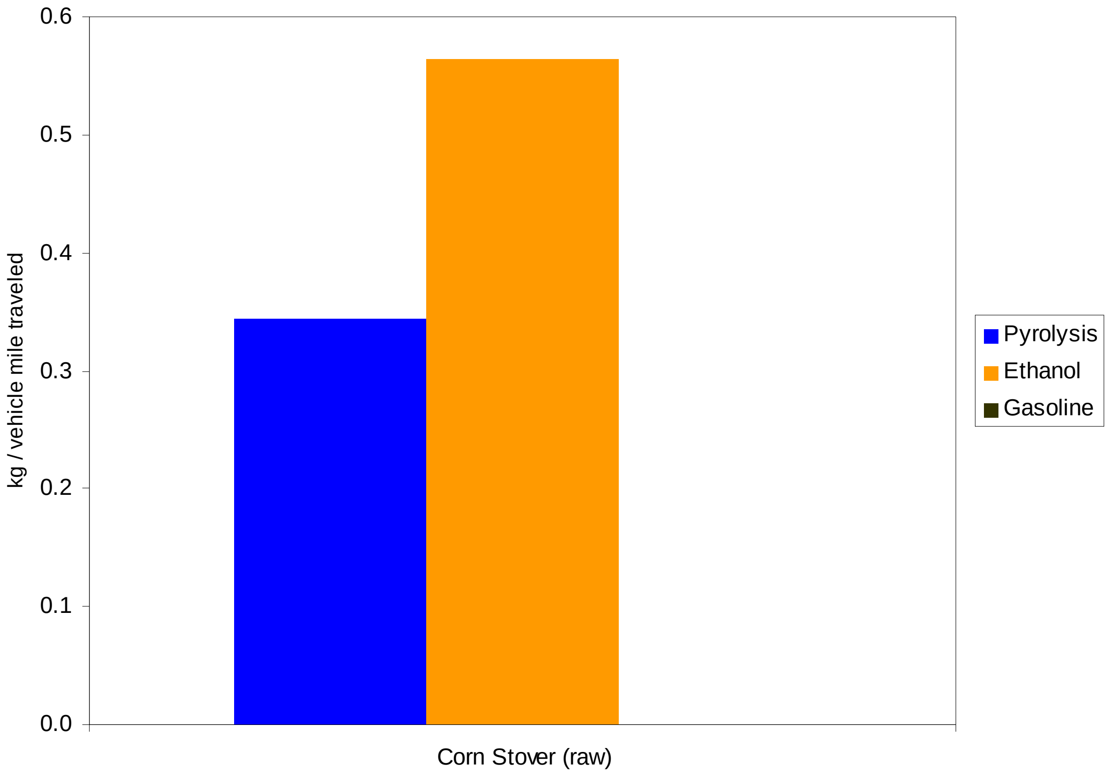


Figure 49. Corn stover input comparison

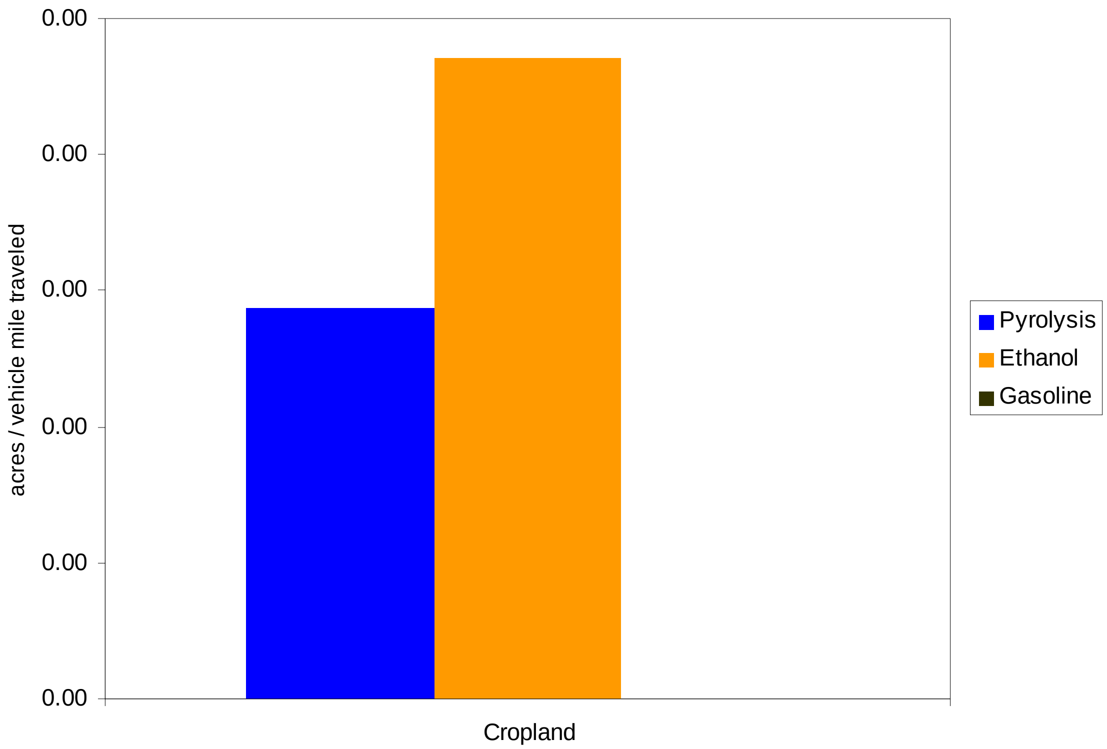


Figure 50. Cropland comparison

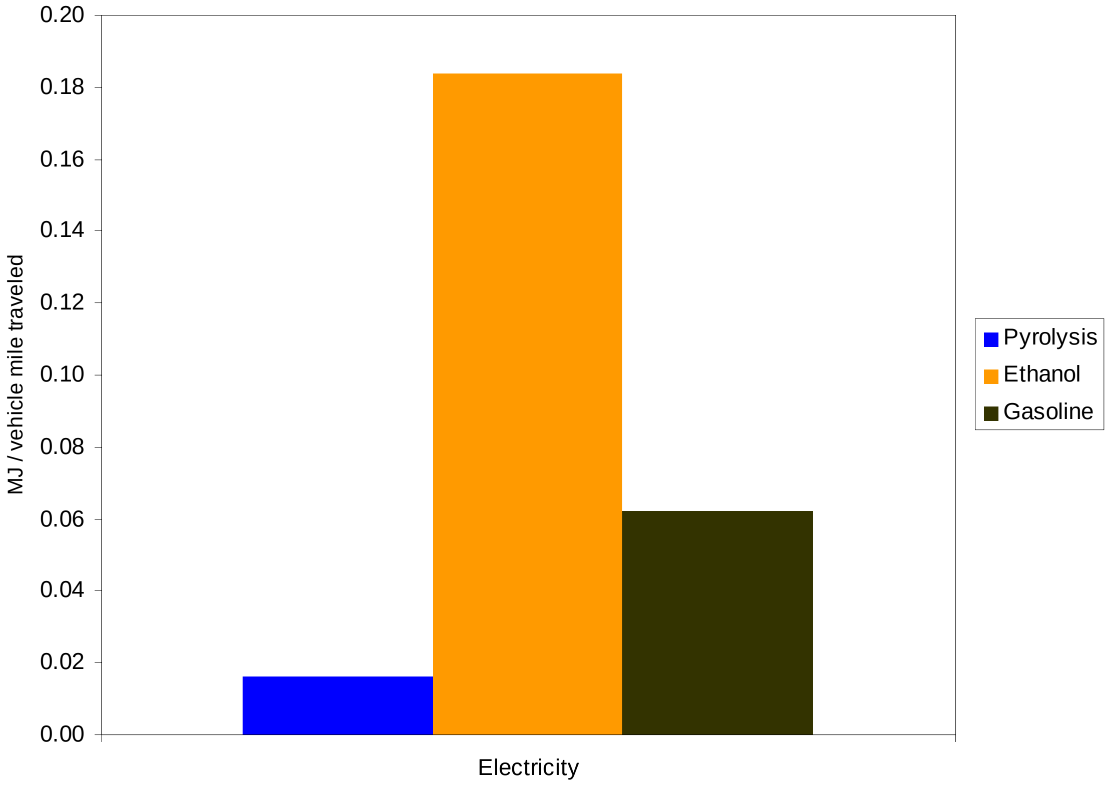


Figure 51. Electricity input comparison

Pyrolysis has more carbon dioxide emission from fossil fuel sources than ethanol, but less emission than gasoline. There is a net decrease in carbon dioxide emission from biomass sources for both pyrolysis and ethanol. The sum of the carbon dioxide released to the atmosphere from fossil, biomass, and soil sources is shown in **Figure 52**. Both the pyrolysis and ethanol processes emit less total carbon dioxide than the unleaded gasoline process.

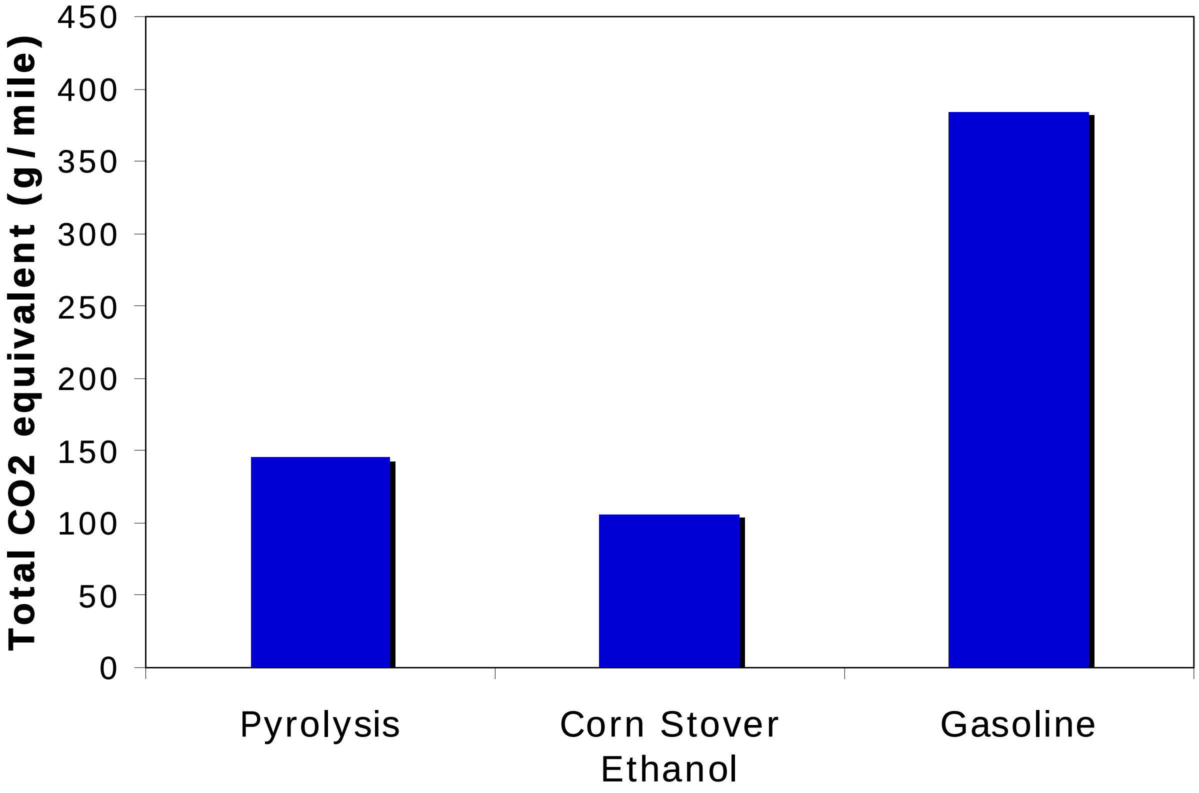


Figure 52. Total carbon dioxide equivalent output comparison

In **Figure 53**, various output flows with amounts in the gram range are shown. Pyrolysis has higher flows than E85 ethanol and gasoline in many flows, including carbon monoxide, nitrogen oxides, methane, and particulates.

Figure 54 shows water and waste output streams. The “Water (unspecified)” flow denotes water that does not need to be treated. The “Water: Chemically Polluted” flow is water that would need to be sent to a wastewater treatment center. Pyrolysis produces more wastewater than the E85 ethanol process in part because the water used for enzyme production eventually becomes solid waste. The gasoline process has the highest “Water: Chemically Polluted” output flow.

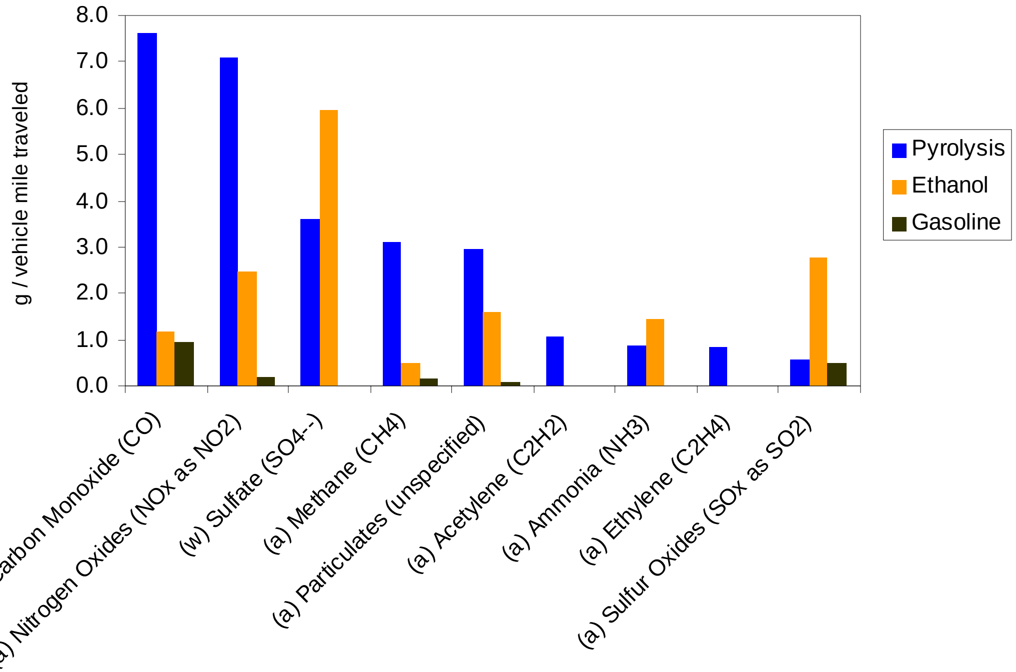


Figure 53. Various output flows comparison

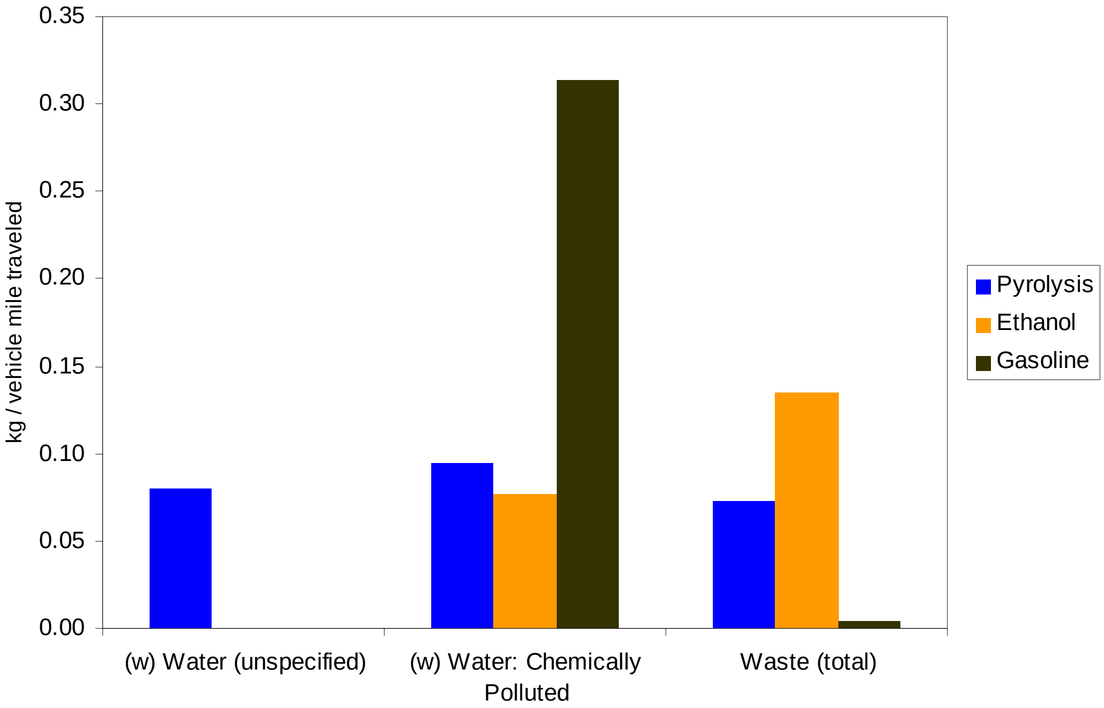


Figure 54. Waste comparison

A comparison of the three main greenhouse emissions and NO_x and SO_x air emissions is shown in **Table 39**. Fossil carbon dioxide emissions are noticeably lower in the pyrolysis and ethanol life cycles than in the unleaded gasoline life cycle. Methane, nitrous oxide, and nitrogen oxides, however, are higher in the pyrolysis life cycle. Methane and nitrous oxide have higher global warming potentials than carbon dioxide, but the increase in these emissions is more than offset by the reduction in CO_2. The production of nitrogen oxides, namely NO_2, is higher in pyrolysis than unleaded gasoline, even under the most aggressive NO_x emission control scenarios. Additional decreases in NO_x in pyrolysis could come from reductions in fertilizer use or reductions in emissions of NO_x below the 5% assumption used in the LCA.

Greenhouse Gas Emission	Units	Pyrolysis	Corn Stover Ethanol	Gasoline
Carbon dioxide (fossil)	g/mile	39	48	380
Carbon dioxide (soil)	g/mile	8.0	12	
Methane	g/mile	0.93	0.22	0.13
Nitrous oxide	g/mile	0.26	0.14	0.005
Total CO_2 equivalent	g/mile	145	106	384

Table 39. Comparison of air emissions from pyrolysis and gasoline LCAs.

Summary

A life cycle assessment of the corn stover pyrolysis process was done, using data from a previous LCA on corn stover E85 ethanol process (Sheehan, et al. 2000), a wood pyrolysis AspenPlus model (Putsche 2004), data from pyrolysis, hydrotreating, and hydrocracking runs by UOP, and EPA emissions factors (EPA 2007). Most carbon dioxide coming from fossil fuel sources are emitted during the production of corn stover. The corn stover pyrolysis produces fewer greenhouse gas emissions than a corn stover ethanol process and an unleaded gasoline process. While pyrolysis and ethanol processes consume less oil than the gasoline process, they both consume equal or more coal and natural gas. The pyrolysis process requires more water than the gasoline process, but less than the ethanol process. Much of the water required occurs during the production of corn stover. Although the pyrolysis process consumes fewer resources and emits less greenhouse gases than the ethanol process, this LCA also shows that the production of corn stover is a particularly resource intensive step, with most of the carbon dioxide from fossil fuel sources and the water required coming in this step.

References for LCA

Aden, A; Ruth, M.; Ibsen, K.; Jechura, J.; Neeves, K.; Sheehan, J.; Wallace, B;. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover.* NREL/TP-510-32438. Golden, CO: National Renewable Energy Laboratory, June 2002. http://www.nrel.gov/docs/fy02osti/32438.pdf.

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U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy. U.S. Environmental Protection Agency. 2007. *Fuel Economy Guide.* Gaithersburg, MD: Office of Energy Efficiency and Renewable Energy. http://www.fueleconomy.gov/feg/FEG2007.pdf.

Proposed Flowscheme

The UOP Hydrocracking flowscheme shown in **Figure 33** will be the basis for the economic analysis

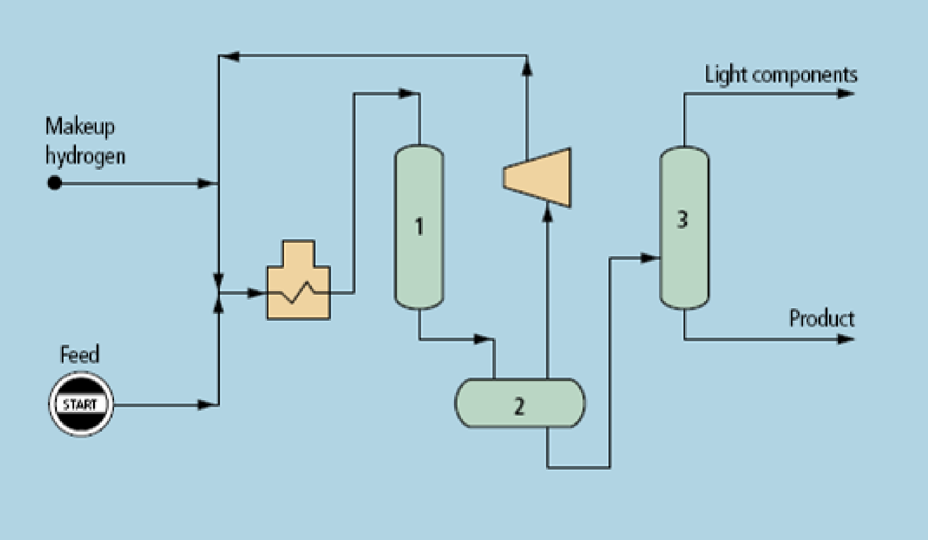


Figure 33. UOP LLC hydrotreating Process Design (Hydrocarbon Processing 2004)

Economic Analysis

Basis:

The prices used in the study were derived from the UOP standard price set for 2008 which were slightly adjusted, as requested by NREL and PNNL, to be consistent with a $100/bbl gasoline price which is needed for comparison with other DOE projects. NREL provided the biomass price of $46/ton and NREL also provided the pyrolysis oil price of $25/bbl which they calculated based on their economic analysis of the costs of production of pyrolysis oil including capital charges. NREL's standard pyrolysis oil price is based on a pyrolysis unit processing 2000t/d of biomass. Their standard pyrolysis unit design includes capital costs for the feed preparation, pyrolysis, fluid bed combustion of the char and generation of electricity from the char combustion.

Table 41- Pyrolysis Oil to Gasoline Price Basis

CRADA Price structure

Pyrolysis Oil	$25/bbl
Biomass Feedstock	$46/ton
Gasoline	$100/bbl
Diesel	$100/bbl
VGO(650-1000 F)	$76/bbl
H2	2100/MT
Fuel gas	$410/MT

Table 41 shows the price structure used in the CRADA economics.

Yields and material balances for the pyrolysis oil section were based on NREL results which show 70% yield of pyrolysis oil from wood biomass. These yields are typical for pyrolysis oil from wood reported in the literature. Yields and material balances for the pyrolysis oil upgrading section were based on PNNL results which were generated in the CRADA. Doug Elliot reviewed the data used in the study and picked the most representative results as the basis for the economic study.

The material balance used in the economics is shown in **Table 42.**

Table 42 – Pyrolysis Oil Upgrading Material Balances

Material Balance T/d

	Wood feed	Corn stover feed
Feedstock	2000	2000
Pyrolysis oil	1400(7160bpd)	946(5130bpd)
H2 required	39 (2.8%)	22.7(2.4%)
gasoline	280(2073bpd)	194(1400bpd)
diesel	168(1249bpd)	117(844bpd)
VGO	58(428bpd)	40(289bpd)
Total products	506(3748bpd)	350(2534bpd)

Table 42-Pyrolysis Oil Upgrading Material Balances

The landmass requirements for feeding a 2000T/d pyrolysis oil plant are large but not outrageous. A 2000t/d pyrolysis unit could be fed from a biomass circle of 12 miles diameter if wood or switch grass are used as the basis. Algae would require a much smaller landmass of only 5.3miles diameter. This comparison is shown in **Table 43**.

Landmass Requirements for a Pyrolysis Unit

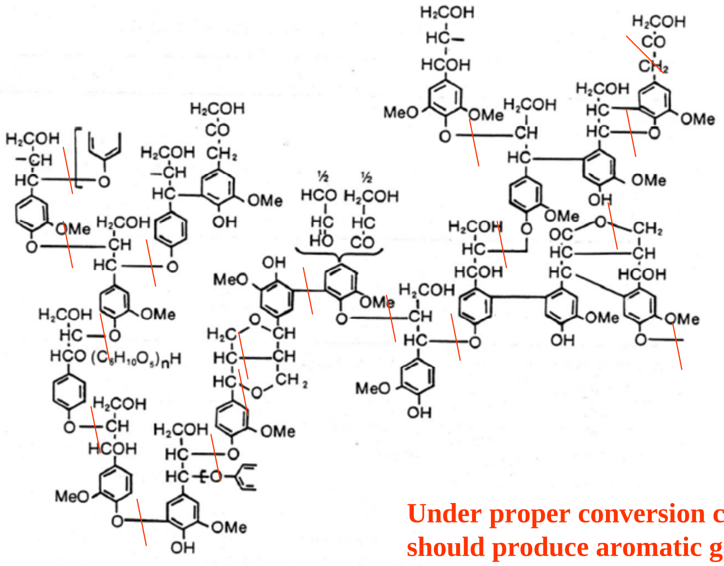
Size of Pyrolysis unit t/d	Biomass yield/acre/yr	Square miles of biomass(acres)	Biomass Circle diameter miles	Bpd of pyrolysis oil	Bpd of finished HC products
2000	10(wood, switch grass)	112(72,000)	12	7160	4000
2000	5 (wood, switchgrass)	224(144,000)	17	7160	4000
2000	50(algae)	22.4(14,400)	5.3	7160	4000
1000	10(wood, switch grass)	56(36,000)	8.5	3580	2000
1000	5 (wood, switchgrass)	112(72,000)	12	3580	2000
1000	50(algae)	11.2(7200)	3.8	3580	2000
500	10(wood, switch grass)	28(18,000)	6.0	1790	1000
500	5 (wood, switchgrass)	56(36,000)	8.5	1790	1000
500	50(algae)	5.6(3600)	2.7	1790	1000

Table 42- Landmass requirements to feed a Pyrolysis Unit

Pyrolysis oil conversion using hydroconversion, which has been done as part of the CRADA with PNNL and NREL, has primarily been done with a PNNL catalyst of Pd-C in the first stage and UOP Hydrotreating catalyst in the second stage. Although PNNL has referred to the first stage as hydrotreating and the second stage as hydrocracking, this terminology is misleading since in both stages the oxygen is being removed and the molecules are breaking where the oxygen linkages are removed not because C-C linkages are broken. In standard terminology, heteroatom removal is typically called hydrotreating whereas the breakage of C-C bonds is typically called hydrocracking.

When the oxygen is removed from pyrolysis oils the molecules naturally fall apart to make gasoline(55%), diesel(33%) and VGO(11%) since so many oxygen linkages are present. The effect of oxygen removal is depicted for a typical lignin molecule in **Figure 48**. Because there is so much oxygen in biomass when the oxygen is removed the pieces left will be small.

Typical Structure of Lignin-Hydrocarbon part



Under proper conversion conditions
should produce aromatic gasoline

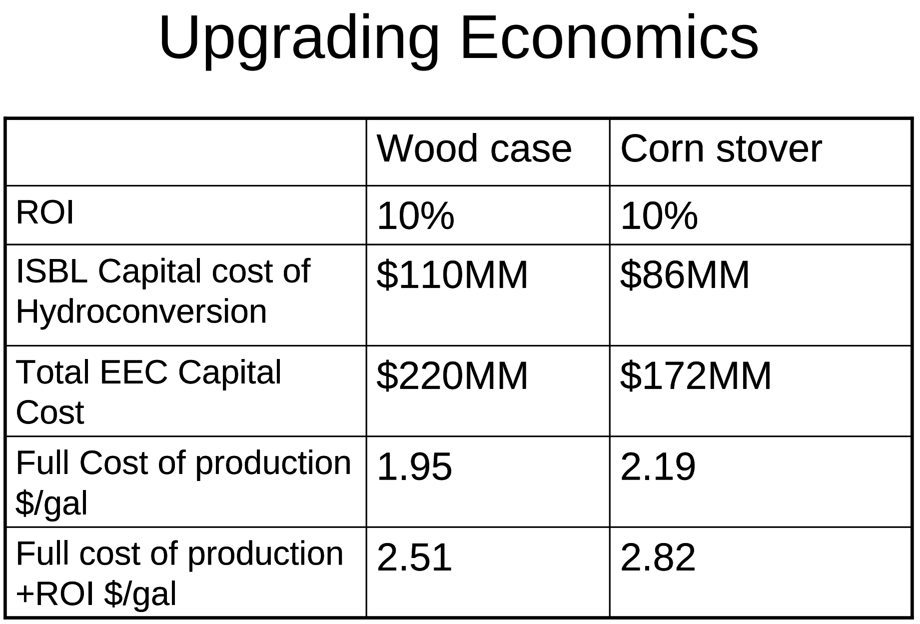
Figure 3-10: Representative Structure of Coniferous Lignin

Figure 48- Biomaterial Cracking when Oxygen is Removed

Economics for Gasoline and Diesel Production:

The economics for upgrading the pyrolysis oil to gasoline are shown in **Tables 44 and 45**. ISBL capital cost for the hydroconversion step were taken as \$110MM for upgrading 7160 bpd of pyrolysis oil. These capital costs assume that 1 step upgrading could be done with a NiMo catalyst in a fixed bed unit. If upgrading must be done in a slurry bed or ebullated bed design it will increases capital costs. The capital costs do not include a H2 plant and instead it is assumed that H2 is purchased and fuel gas is sold. An alternative case would use the fuel gas to produce H2 and build a H2 plant. If a H2 plant is built, capital charges would increase and H2 feed costs would decrease but the economics should be equivalent.

Table 34- Pyrolysis Oil Upgrading Economics

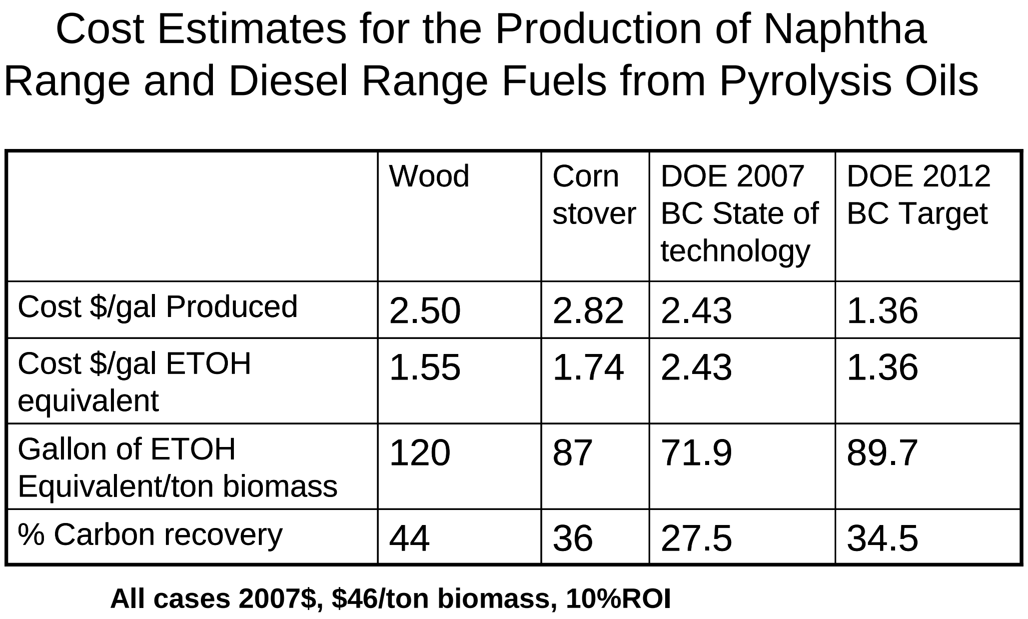


Upgrading Economics

	Wood case	Corn stover
ROI	10%	10%
ISBL Capital cost of Hydroconversion	$110MM	$86MM
Total EEC Capital Cost	$220MM	$172MM
Full Cost of production $/gal	1.95	2.19
Full cost of production +ROI $/gal	2.51	2.82

Table 44-Pyrolysis Oil Upgrading Economics

Table 44-$/gallon costs of Bio-Gasoline and Green Diesel produced from Pyrolysis Oil Upgrading



Cost Estimates for the Production of Naphtha Range and Diesel Range Fuels from Pyrolysis Oils

	Wood	Corn stover	DOE 2007 BC State of technology	DOE 2012 BC Target
Cost $/gal Produced	2.50	2.82	2.43	1.36
Cost $/gal ETOH equivalent	1.55	1.74	2.43	1.36
Gallon of ETOH Equivalent/ton biomass	120	87	71.9	89.7
% Carbon recovery	44	36	27.5	34.5

All cases 2007$, $46/ton biomass, 10%ROI

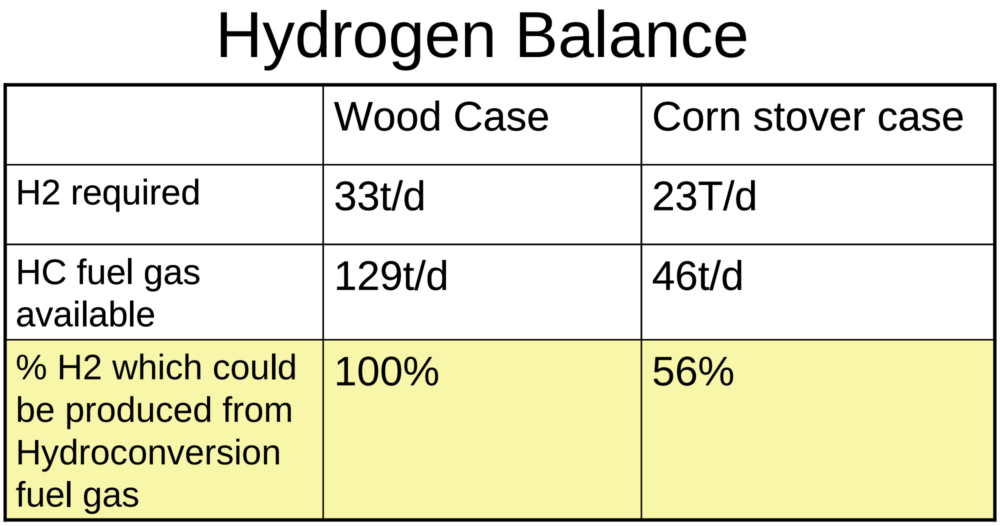
Table 45-$/gallon costs of Bio-Gasoline and Green Diesel produced from Pyrolysis Oil Upgrading

The H2 required for the upgrading is based on the H2 requirements measured at PNNL. Many paper studies have assumed that all the oxygen in the pyrolysis oil is removed as water which results in much higher H2 requirements. In reality (based on the PNNL data) much of oxygen is removed as CO2 and much of the

H2 needed for upgrading is produced in situ from the water gas shift reaction of CO with water to make CO2 and H2.

Analysis of the H2 required and the fuel gas produced shows that all of the H2 required for upgrading can be produced from the fuel gas byproduct made in the upgrading. For the case of wood, all of the H2 required could be produced from the fuel gas and for the case of corn stover, 56% of the H2 required could be produced from byproduct fuel gas. This is shown in **Table 46**.

Table 45- Hydrogen Balance for Pyrolysis Oil Upgrading



Hydrogen Balance

	Wood Case	Corn stover case
H2 required	33t/d	23T/d
HC fuel gas available	129t/d	46t/d
% H2 which could be produced from Hydroconversion fuel gas	100%	56%

Table 46- Hydrogen Balance for Pyrolysis Oil Upgrading

Economics of Fuel Oil Production:

Pyrolysis oil is a fuel oil with very low heating value, high acidity and poor stability. In order to better market this fuel oil, it is believed that stability should be improved. Stability typically means that the viscosity and phases do not change over time (solids don’t fall out and no separate phases are formed upon standing). Literature data has shown that pyrolysis oil stability is good once metals are removed through hot filtering. It is believed that alkali metals in pyrolysis oil catalyze polymerization reactions which lead to viscosity increases and solids formation. Therefore it is likely that metals removal can result in the production of stable pyrolysis oil. Removal of metals will also be needed for hydrotreating applications in fixed beds since it has been shown that high alkali metals will plug fixed beds and deactivate hydroconversion catalyst.

Metals removal of 100’s of ppm metals with hydroconversion catalyst would cause plugging in a fixed bed but could be done in an ebullated bed or slurry bed system but would add catalyst and equipment cost. **Table 47** shows the costs and size of the hydroconversion catalyst needed to remove large quantities of metals for a 2 year life.

Table 46- Metals Removal using Hydroconversion Catalyst

Removal of Metals from Pyrolysis oils using Hydroconversion Catalyst

	Typical Hydroconversion Guard Bed	Wood pyrolysis oil	Corn stover
Metals, ppm	10	100,250 Avg 175	640,987,522 Avg 524
Guard bed size,ft3 for 6500bpd feed	671	15266	45708
Guard bed section dimension	7.5ft length x 10.7 ft diameter	172 ft length x 10.7 ft diameter	511 ft length X 10.7 ft diameter
Catalyst cost, $MM	.2	4.6	11.4

Table 47-Metals Removal using Hydroconversion Catalyst

Reduction of TAN (total acid number) naturally occurs when hydroconversion is done since oxygen is removed, however experimental work at PNNL has shown that TAN number is not reduced to less than 5 (where standard metallurgy could be used) until almost all of the oxygen is removed from the pyrolysis oil. This data is shown in **Figure 49**.

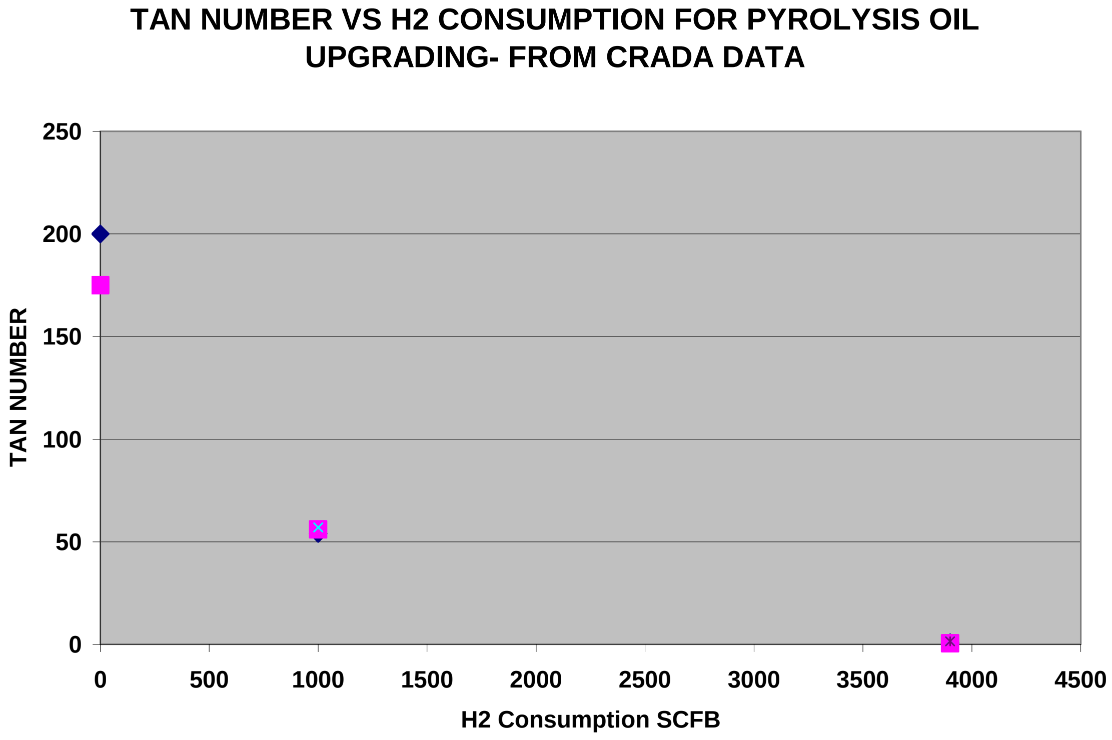
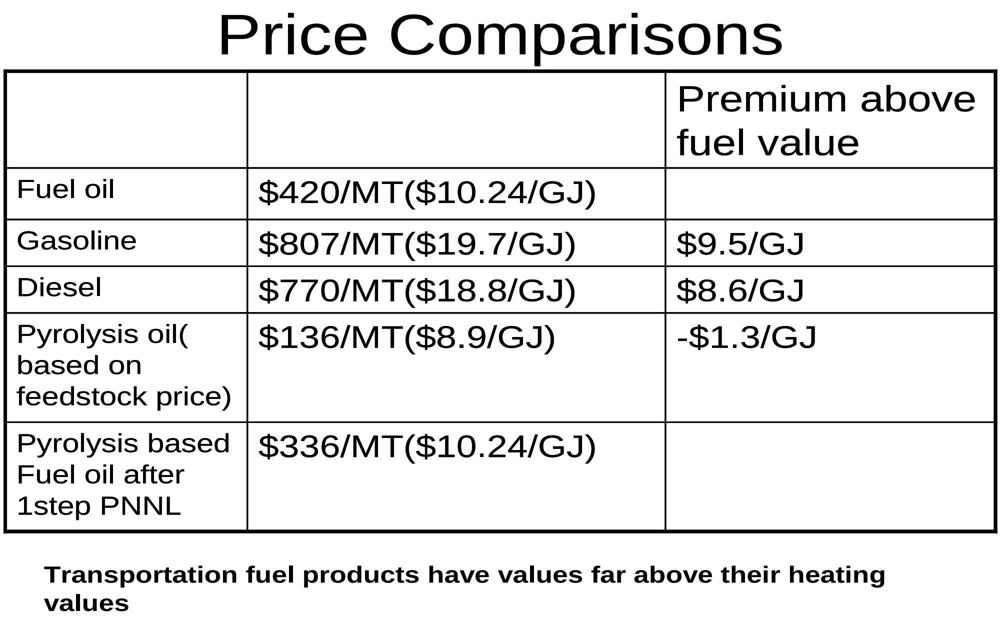


Figure 49- TAN Number vs H2 Consumption

The economics of upgrading pyrolysis oil to fuel oil are a function of the value of the fuel oil. At best pyrolysis based fuel oil would have a value equivalent to its heating value. Gasoline and diesel fuels have values significantly above their heating value as shown in **Table 48**.



Price Comparisons

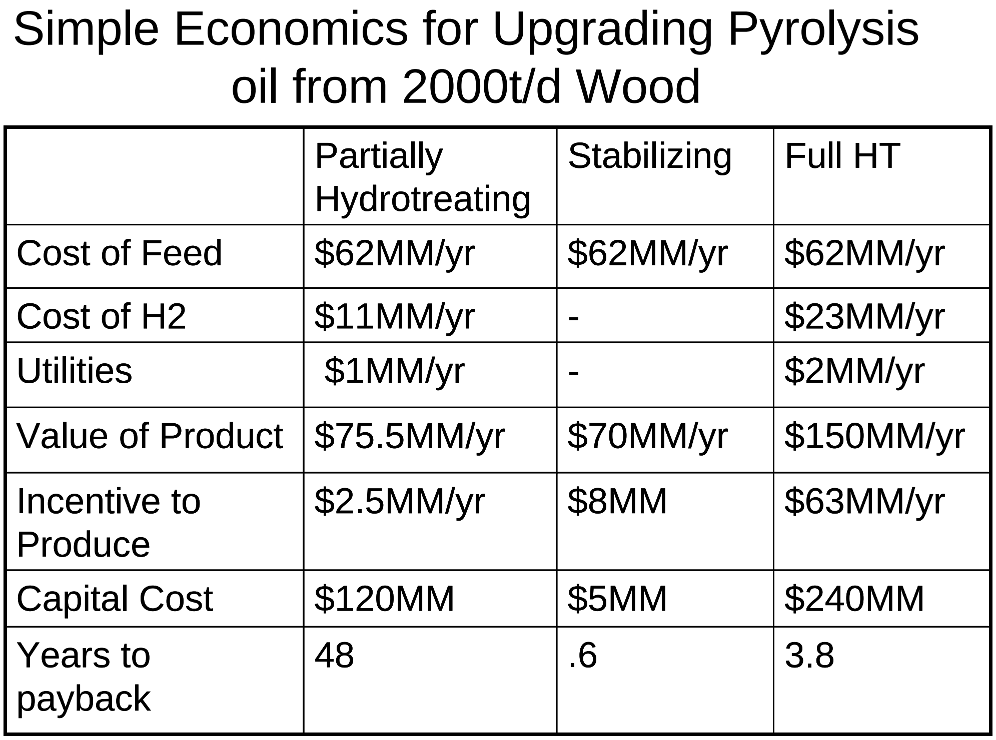
		Premium above fuel value
Fuel oil	$420/MT($10.24/GJ)	
Gasoline	$807/MT($19.7/GJ)	$9.5/GJ
Diesel	$770/MT($18.8/GJ)	$8.6/GJ
Pyrolysis oil(based on feedstock price)	$136/MT($8.9/GJ)	-$1.3/GJ
Pyrolysis based Fuel oil after 1step PNNL	$336/MT($10.24/GJ)	

Transportation fuel products have values far above their heating values

Table 47- Price comparisons of Fuel Oil with Gasoline and Diesel

The low value of pyrolysis fuel oil provides very little incentive for upgrading through hydroconversion to make a fuel oil product. **Table 49** compares the economics of stabilizing pyrolysis oil by metals removal to make fuel oil versus partial hydrotreating to make a stable fuel oil versus full hydroconversion to make gasoline and diesel. Stabilizing the pyrolysis oil by doing a simple metals removal step such as hot filtering, assuming that significant yield loss does not occur, would be quite valuable and have 0.6years to payback. Fully upgrading pyrolysis oil to make gasoline and diesel has 3.8 years to payback and is also attractive. However partially hydrotreating pyrolysis oil to make a stable fuel oil, using the first step of the PNNL process, would cost a lot and produce a low valued product.

Table 48- Economics for Upgrading Pyrolysis Oil



Simple Economics for Upgrading Pyrolysis oil from 2000t/d Wood

	Partially Hydrotreating	Stabilizing	Full HT
Cost of Feed	$62MM/yr	$62MM/yr	$62MM/yr
Cost of H2	$11MM/yr	-	$23MM/yr
Utilities	$1MM/yr	-	$2MM/yr
Value of Product	$75.5MM/yr	$70MM/yr	$150MM/yr
Incentive to Produce	$2.5MM/yr	$8MM	$63MM/yr
Capital Cost	$120MM	$5MM	$240MM
Years to payback	48	.6	3.8

Table 49- Economics for Upgrading Pyrolsis Oil

Economics Summary:

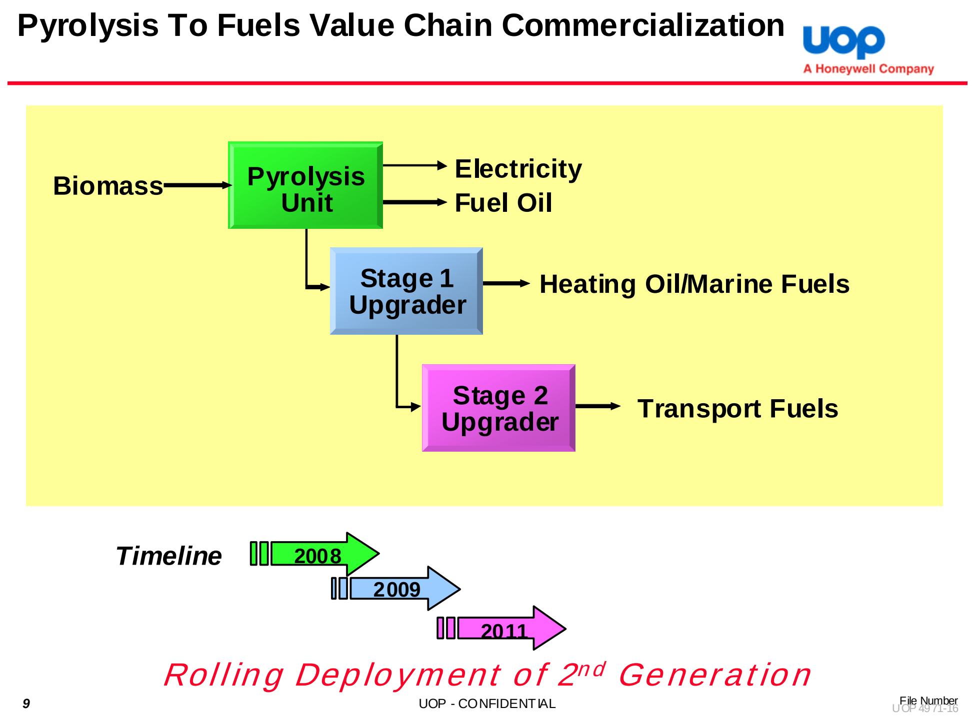
Upgrading pyrolysis oil to make a stabilized fuel oil through a simple metals removal step (or other low capital cost treatments) has excellent economics. Upgrading pyrolysis oil to gasoline and diesel has good economics. Upgrading pyrolysis oil by partial hydroconversion to fuel oil has extremely poor economics and is not recommended unless it could be done extremely cheaply, and the water-hydrocarbon separation problems could somehow be eliminated.

Path to Commercialization

Commercializing this technology value chain may actually be less of a challenge than some alternates. The critical differentiator is that the pyrolysis technology is commercially available already, meaning that reliable capex and opex data can be provided, and small commercial / demonstration units can be visited. These critical elements mitigate much of the risk associated with investment in new technology.

Downstream of the pyrolysis oil unit, whilst stabilization and upgrading is as yet commercially unproven, the concepts and equipment are well understood within the refining sector. Companies which can demonstrate significant experience in the adjacent hydroprocessing sector of the oil refining industry, should be able to successfully bridge the gap between research and commercial offering for pyrolysis upgrading based upon hydroprocessing.

The difference in technology maturity between the upstream [pyrolysis oil] and downstream [stabilizing/upgrading] units lends itself to a potential strategy of rolling investment and commercialization**(Figure 50)**.



Pyrolysis To Fuels Value Chain Commercialization

A Honeywell Company

Biomass → Pyrolysis Unit → Electricity, Fuel Oil

Pyrolysis Unit → Stage 1 Upgrader → Heating Oil/Marine Fuels

Stage 1 Upgrader → Stage 2 Upgrader → Transport Fuels

Timeline

2008

2009

2011

Rolling Deployment of 2nd Generation

9

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Figure 50 Rolling Deployment of 2nd Generation Technology

In this rolling commercialization strategy, potential clients will be able to build pyrolysis oil units early, enabling them to gain experience in operation and biomass logistics whilst the research on downstream unit technology is completed. The immediate use of pyrolysis oil for thermal or power applications means that the pyrolysis unit can provide significant value in its early years. Under a Cap and Trade structure or GHG limited world, using the pyrolysis oil to substitute for fossil-derived fuel oils will enable users to move into compliance early. As the downstream technologies become available, without a significant increase in GHG, the product slate is changed from thermal to transport, possibly also with the addition of further pyrolysis capacity.

Without a need to have the pyrolysis units in the same location as the Upgrading unit, we would also see early opportunity in deploying pyrolysis within industries that don't yet have a direct interest in transport fuels. Examples of these maybe the utilities, cement, or paper and pulp industries. As pyrolysis oil production capacity grows, and as the Upgrading technology is rolled out, these incumbent pyrolysis oil producers will then find alternate outlets for their oil, slowly creating a market for pyrolysis oil as a traded commodity. In turn, as supply increases, refiners who might not otherwise invest in the entire value chain, may consider Upgrader investments using oil produced by others.

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Appendix

Life Cycle Inventory Tables

Appendix: Inventory Tables

Table A1. Life Cycle Inventory (LCI) inputs, sorted by amount, restricted to mass greater than 1 mg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution
Nitrogen (N2)	kg	0.771419	0	0	0.771419	0	0	0
Oxygen (O2)	kg	0.192855	0	0	0.192855	0	0	0
(r) Phosphate Rock (in ground)	kg	1.71E-02	1.71E-02	0	0	0	1.65E-09	0
(r) Natural Gas (in ground)	kg	1.61E-02	9.88E-03	1.07E-04	0	5.33E-05	6.01E-03	3.46E-05
(r) Oil (in ground)	kg	9.66E-03	2.42E-03	1.24E-03	0	6.21E-04	5.00E-03	3.74E-04
(r) Potassium Chloride (KCl, as K2O, in ground)	kg	5.32E-03	5.32E-03	0	0	0	9.6E-09	0
(r) Coal (in ground)	kg	4.58E-03	3.73E-03	3.88E-05	0	1.94E-05	3.88E-04	3.98E-04
(r) Limestone (CaCO3, in ground)	kg	3.43E-04	2.96E-04	7.35E-06	0	3.67E-06	4.16E-06	3.27E-05
(r) Sodium Chloride (NaCl, in ground or in sea)	kg	3.15E-05	2.94E-05	1.36E-10	0	0	2.04E-06	1.88E-10
Raw Materials (unspecified)	kg	2.16E-05	2.16E-05	0	0	0	0	0
(r) Iron (Fe, ore)	kg	1.80E-05	1.28E-05	0	0	0	5.17E-06	0
(r) Lignite (in ground)	kg	1.30E-05	1.21E-05	0	0	0	9.14E-07	0
(r) Pyrite (FeS2, ore)	kg	7.87E-06	6.94E-06	0	0	0	9.24E-07	0
Biomass (unspecified)	kg	7.18E-06	0	0	0	0	7.18E-06	0
(r) Barium Sulfate (BaSO4, in ground)	kg	4.33E-06	4.33E-06	0	0	0	0	0

(r) Sulfur (S, in ground)	kg	3.25E-06	3.25E-06	0	0	0	0	0
Peat	kg	2.57E-06	0	0	0	0	2.57E-06	0
(r) Bentonite (Al2O3.4SiO2.H2O, in ground)	kg	1.52E-06	4.09E-07	0	0	0	1.11E-06	0
(r) Clay (in ground)	kg	1.21E-06	8.11E-07	0	0	0	3.99E-07	0
Cropland	acres	1.44E-04	1.44E-04	0	0	0	0	0
Land Use (II -> IV)	m2a	1.87E-10	1.87E-10	0	0	0	0	0
Land Use (II -> III)	m2a	1.54E-10	1.54E-10	0	0	0	0	0
Land Use (III -> IV)	m2a	2.12E-13	2.12E-13	0	0	0	0	0
Water Used (total)	liter	0.148896	0.103642	2.86E-04	3.87E-03	8.64E-05	0.0407917	2.16E-04
Water: Public Network	liter	0.116291	0.0862705	0	3.87E-03	0	0.0261464	0
Water: Unspecified Origin	liter	1.87E-02	1.50E-02	1.13E-04	0	0	3.46E-03	1.65E-04
Water: Sea	liter	6.65E-03	0	0	0	0	6.65E-03	0
Water: River	liter	4.54E-03	0	0	0	0	4.54E-03	0
Water: Well	liter	3.78E-09	0	0	0	0	3.78E-09	0

Table A2. LCI air emission outputs, sorted by amount, mass greater than 1 μg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
Nitrogen (N2)	g	7.71E+02	0	0	7.71E+02	0	0	0	0
(a) Metals (unspecified)	g	5.67E+02	2.63E+02	1.69E+02	0	8.48E+01	3.78E-06	5.00E+01	0
(a) Carbon Dioxide (CO2, fossil)	g	5.79E+01	3.92E+01	4.13E+00	0	2.09E+00	1.03E+01	2.21E+00	0
Oxygen (O2)	g	3.96E+01	0	0	3.96E+01	0	0	0	0
(a) Carbon Dioxide (CO2, Soil)	g	8.50E+00	8.50E+00	0	0	0	0	0	0
(a) Carbon Monoxide (CO)	g	7.62E+00	3.23E-02	1.40E-02	6.90E+00	6.97E-03	5.22E-02	4.55E-03	0.606798
(a) Nitrogen Oxides (NOx as NO2)	g	7.10E+00	1.12E+00	3.89E-02	5.64E+00	3.45E-02	1.44E-02	1.68E-02	0.241008
(a) Methane (CH4)	g	3.13E+00	1.61E-01	1.49E-03	2.52E+00	7.51E-04	4.39E-01	2.17E-03	0
(a) Particulates (unspecified)	g	2.97E+00	7.80E-02	8.83E-04	2.86181	4.41E-04	4.71E-03	2.62E-03	0.020092
(a) Acetylene (C2H2)	g	1.07E+00	9.42E-12	0	1.07E+00	0	0	0	0
(a) Ammonia (NH3)	g	8.79E-01	8.79E-01	2.89E-08	0	2.65E-09	3.79E-06	2.44E-07	0
(a) Ethylene (C2H4)	g	8.27E-01	1.30E-03	0	8.25E-01	0	1.73E-04	0	0
(a) Sulfur Oxides (SOx as SO2)	g	5.67E-01	1.24E-01	6.09E-03	2.83E-01	3.04E-03	0	5.33E-03	0.145635
(a) Propylene (CH2CHCH3)	g	4.13E-01	4.12E-07	0	4.13E-01	0	5.64E-09	0	0
(a) Butene (1-CH3CH2CHCH2)	g	3.27E-01	2.14E-07	0	3.27E-01	0	3.86E-09	0	0
(a) Ethane (C2H6)	g	3.10E-01	4.47E-04	8.42E-09	6.56E-02	0	2.44E-01	2.20E-08	0
(a) Propane (C3H8)	g	2.80E-01	1.27E-04	1.81E-11	1.55E-01	0	1.25E-01	3.43E-09	0
(a) Nitrous Oxide (N2O)	g	2.55E-01	1.07E-01	4.11E-04	1.47E-01	2.23E-05	5.54E-06	2.35E-04	0
(a) Hydrogen Sulfide (H2S)	g	2.31E-01	5.97E-05	9.11E-06	0	4.54E-06	2.31E-01	2.74E-06	0
(a) Hydrocarbons (except methane)	g	2.09E-01	9.56E-03	3.02E-03	0	1.04E-04	1.00E-02	7.70E-04	0.185893
(a) VOC (Volatile Organic Compounds)	g	1.92E-01	0	0	1.92E-01	0	9.83E-05	0	0
(a) Hydrocarbons (unspecified)	g	1.73E-01	7.78E-03	1.64E-03	0	2.42E-03	3.71E-02	7.95E-02	0.044214
(a) Butene (2-CH3CHCHCH3)	g	1.26E-01	0	0	1.26E-01	0	0	0	0
(a) C10 alkanes (unspecified)	g	1.15E-01	0	0	1.15E-01	0	0	0	0
(a) Butane (C4H10)	g	5.11E-02	1.52E-07	5.71E-09	0	0	5.11E-02	1.49E-08	0
(a) Formaldehyde (CH2O)	g	2.42E-02	1.75E-05	3.74E-06	2.41E-02	1.86E-06	1.43E-06	1.20E-06	0.000127
(a) Benzaldehyde (C6H5CHO)	g	2.06E-02	1.28E-12	0	2.06E-02	0	1.70E-13	0	0
(a) Aldehyde (unspecified)	g	1.91E-02	1.77E-04	1.44E-07	1.89E-02	6.41E-08	3.79E-06	1.98E-05	0
(a) Methanol (CH3OH)	g	1.89E-02	1.36E-08	0	1.89E-02	0	1.81E-09	0	0
(a) Pentane (C5H12)	g	1.79E-02	1.38E-04	7.06E-09	0	0	1.78E-02	1.85E-08	0
(a) Acetone (CH3COCH3)	g	1.44E-02	1.90E-08	0	1.44E-02	0	2.53E-09	0	0
(a) Sulphur Oxides (SOx as SO2)	g	1.38E-02	0	0	0	0	1.38E-02	0	0
(a) Particulates (PM 10)	g	9.88E-03	3.14E-03	4.68E-03	0	8.45E-04	0	1.21E-03	0
(a) Organic Matter (unspecified)	g	3.47E-03	4.43E-04	1.36E-06	0	2.93E-07	3.02E-03	3.75E-06	0
(a) Hydrogen Chloride (HCl)	g	2.65E-03	2.21E-03	2.08E-05	0	1.04E-05	1.67E-04	2.38E-04	0
(a) Acetaldehyde (CH3CHO)	g	2.24E-03	1.10E-06	4.14E-11	2.24E-03	0	1.50E-08	1.10E-07	0
(a) Crotonaldehyde (C4H6O)	g	1.72E-03	0	0	1.72E-03	0	0	0	0
(a) Alkane (unspecified)	g	3.51E-04	3.10E-04	0	0	0	4.05E-05	0	0
(a) Hydrogen Fluoride (HF)	g	3.38E-04	2.97E-04	2.61E-06	0	1.30E-06	7.61E-06	2.97E-05	0
(a) Butane (n-C4H10)	g	1.15E-04	1.03E-04	0	0	0	1.16E-05	0	0
(a) Benzene (C6H6)	g	6.04E-05	5.31E-05	4.34E-07	0	1.39E-07	5.70E-06	1.03E-06	0
(a) Aromatic Hydrocarbons (unspecified)	g	3.42E-05	3.92E-06	5.70E-13	0	0	3.02E-05	7.88E-13	0
(a) Hydrogen (H2)	g	3.02E-05	4.07E-17	0	0	0	3.02E-05	0	0

(a) Toluene (C6H5CH3)	g	2.59E-05	2.30E-05	4.04E-11	0	0	2.86E-06	4.78E-08	0
(a) Magnesium (Mg)	g	2.13E-05	1.91E-05	7.99E-10	0	0	1.76E-08	2.12E-06	0
(a) Acetic Acid (CH3COOH)	g	1.82E-05	1.60E-05	0	0	0	2.14E-06	0	0
(a) Lead (Pb)	g	1.12E-05	7.05E-06	1.34E-10	0	0	3.79E-06	3.36E-07	0
(a) Zinc (Zn)	g	1.02E-05	6.35E-06	1.09E-10	0	0	3.83E-06	5.11E-09	0
(a) Chromium (Cr III, Cr VI)	g	9.46E-06	5.11E-06	2.30E-10	0	0	3.78E-06	5.67E-07	0
(a) Hydrogen Sulphide (H2S)	g	9.24E-06	0	0	0	0	9.24E-06	0	0
(a) Chlorinated Matter (unspecified, as Cl)	g	7.70E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Chlorine (Cl2)	g	7.70E-06	3.93E-06	5.78E-14	0	0	3.78E-06	2.59E-13	0
(a) Mercaptans	g	7.70E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Arsenic (As)	g	7.19E-06	3.07E-06	1.51E-10	0	0	3.78E-06	3.39E-07	0
(a) Manganese (Mn)	g	6.97E-06	6.26E-06	2.42E-10	0	0	7.93E-08	6.32E-07	0
(a) Nickel (Ni)	g	6.52E-06	6.04E-06	1.32E-09	0	0	1.45E-08	4.65E-07	0
(a) Vanadium (V)	g	5.04E-06	5.01E-06	2.87E-09	0	0	1.25E-08	1.06E-08	0
(a) Polycyclic Aromatic Hydrocarbons (PAH, unspecified)	g	5.00E-06	1.07E-06	6.34E-16	0	0	3.92E-06	8.76E-16	0
(a) Cyanide (CN-)	g	4.81E-06	4.32E-06	1.82E-10	0	0	4.50E-10	4.82E-07	0
(a) Hexane (C6H14)	g	4.29E-06	4.22E-06	4.90E-09	0	0	3.75E-08	2.57E-08	0
(a) Fluorides (F-)	g	4.02E-06	4.01E-06	4.12E-11	0	1.35E-15	0	9.24E-09	0
(a) Cadmium (Cd)	g	4.01E-06	2.09E-07	8.79E-12	0	0	3.78E-06	2.20E-08	0
(a) Mercury (Hg)	g	4.01E-06	2.11E-07	9.43E-12	0	0	3.78E-06	2.11E-08	0
(a) Copper (Cu)	g	3.84E-06	5.58E-08	1.69E-11	0	0	3.78E-06	3.77E-10	0
(a) Antimony (Sb)	g	3.82E-06	3.90E-08	6.83E-12	0	0	3.78E-06	4.36E-09	0
(a) Asbestos	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Carbon Disulphide (CS2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Fluorine (F2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Halogenated Hydrocarbons (unspecified)	g	3.78E-06	4.93E-17	3.17E-18	0	0	3.78E-06	4.38E-18	0
(a) Hydrogen Cyanide (HCN)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Sulphuric Acid (H2SO4)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Selenium (Se)	g	2.55E-06	2.30E-06	1.01E-10	0	0	5.03E-09	2.51E-07	0
(a) Potassium (K)	g	2.51E-06	2.22E-06	0	0	0	2.95E-07	0	0
(a) Heptane (C7H16)	g	2.00E-06	1.98E-06	0	0	0	1.79E-08	0	0
(a) Sodium (Na)	g	1.90E-06	1.89E-06	1.09E-09	0	0	7.57E-09	2.00E-09	0
(a) Iron (Fe)	g	1.72E-06	1.60E-06	4.10E-10	0	0	1.23E-07	7.52E-10	0
(a) Benzyl Chloride (C7H7Cl)	g	1.34E-06	1.21E-06	5.09E-11	0	0	0	1.35E-07	0
(a) Silicon (Si)	g	1.21E-06	1.10E-06	1.84E-10	0	0	1.08E-07	3.37E-10	0
(a) Isophorone	g	1.11E-06	1.00E-06	4.21E-11	0	0	0	1.12E-07	0
(a) Calcium (Ca)	g	1.10E-06	1.01E-06	1.84E-10	0	0	9.31E-08	3.37E-10	0
(a) Methyl Chloride (CH3Cl)	g	1.02E-06	9.16E-07	3.85E-11	0	0	0	1.02E-07	0

Table A3. LCI of water outputs, sorted by amount, above 1 μg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(w) Water: Chemically Polluted	liter	9.44E-02	5.18E-03	3.08E-03	0	1.54E-03	8.37E-02	9.24E-04	0
(w) Water (unspecified)	liter	7.97E-02	9.90E-09	0	4.01E-02	0	3.97E-02	0	0
(w) Sulfate (SO4--)	g	3.62E+00	3.62E+00	9.68E-10	0	0	0	1.20E-07	0
(w) Dissolved Matter (unspecified)	g	1.88E-01	8.71E-02	5.60E-02	0	2.80E-02	9.20E-05	1.65E-02	0
(w) Acids (H+)	g	1.86E-01	1.86E-01	1.01E-12	0	0	1.51E-05	4.57E-12	0
(w) Sodium (Na+)	g	8.50E-02	4.08E-02	2.30E-02	0	1.15E-02	2.83E-03	6.89E-03	0
(w) Chlorides (Cl-)	g	6.91E-02	3.64E-02	1.78E-02	0	8.90E-03	6.41E-04	5.35E-03	0
(w) COD (Chemical Oxygen Demand)	g	2.51E-02	1.13E-02	7.05E-03	0	3.52E-03	1.21E-03	2.10E-03	0
(w) Suspended Matter (unspecified)	g	2.07E-02	1.28E-02	3.78E-03	0	1.89E-03	1.12E-03	1.13E-03	0
(w) BOD5 (Biochemical Oxygen Demand)	g	3.74E-03	1.94E-03	8.34E-04	0	4.16E-04	2.95E-04	2.48E-04	0
(w) Sulphate (SO4--)	g	3.17E-03	0	0	0	0	3.17E-03	0	0
(w) Oils (unspecified)	g	1.71E-03	7.83E-04	4.13E-04	0	2.06E-04	1.81E-04	1.23E-04	0
(w) TOC (Total Organic Carbon)	g	1.20E-03	7.01E-04	9.50E-12	0	0	5.00E-04	1.31E-11	0
(w) Barytes	g	8.88E-04	7.84E-04	0	0	0	1.04E-04	0	0
(w) Calcium (Ca++)	g	6.01E-04	5.65E-04	0	0	0	3.57E-05	0	0
(w) Ammonia (NH4+, NH3, as N)	g	4.31E-04	2.06E-04	1.22E-04	0	6.09E-05	5.97E-06	3.65E-05	0
(w) Carbonates (CO3--, HCO3-, CO2, as C)	g	2.87E-04	0	0	0	0	2.87E-04	0	0
(w) Metals (unspecified)	g	1.97E-04	5.94E-05	3.45E-05	0	1.72E-05	7.56E-05	1.03E-05	0
(w) Chlorinated Matter (unspecified, as Cl)	g	1.41E-04	1.25E-04	0	0	0	1.66E-05	0	0
(w) Hydrocarbons (unspecified)	g	1.36E-04	5.77E-06	1.15E-06	0	5.73E-07	1.29E-04	3.45E-07	0
(w) Strontium (Sr II)	g	6.78E-05	6.36E-05	0	0	0	4.13E-06	0	0
(w) Phenol (C6H5OH)	g	6.76E-05	3.12E-05	1.60E-05	0	8.00E-06	7.64E-06	4.77E-06	0
(w) Potassium (K+)	g	6.71E-05	6.12E-05	0	0	0	5.97E-06	0	0
(w) Organic Dissolved Matter (unspecified)	g	5.68E-05	3.92E-06	0	0	0	5.29E-05	0	0
(w) Nitrate (NO3-)	g	5.50E-05	9.51E-06	6.58E-10	0	0	4.54E-05	1.33E-07	0
(w) Dissolved Organic Carbon (DOC)	g	5.00E-05	4.41E-05	0	0	0	5.87E-06	0	0
(w) Triethylene Glycol (C6H14O4)	g	5.00E-05	4.41E-05	0	0	0	5.87E-06	0	0
(w) Saponifiable Oils and Fats	g	4.94E-05	4.94E-05	0	0	0	0	0	0
(w) Nitrogenous Matter (unspecified, as N)	g	4.67E-05	8.76E-06	1.71E-13	0	0	3.79E-05	2.36E-13	0
(w) Iron (Fe++, Fe3+)	g	3.84E-05	3.12E-05	2.73E-10	0	1.35E-10	7.24E-06	1.17E-09	0
(w) Magnesium (Mg++)	g	3.78E-05	3.10E-05	0	0	0	6.78E-06	0	0
(w) Barium (Ba++)	g	2.99E-05	2.94E-05	3.04E-12	0	0	5.38E-07	4.20E-12	0
(w) Aluminum (Al3+)	g	2.68E-05	2.68E-05	1.54E-09	0	0	0	2.13E-09	0
(w) Fluorides (F-)	g	2.18E-05	1.62E-05	1.39E-07	0	6.96E-08	4.71E-06	6.02E-07	0
(w) Salts (unspecified)	g	1.74E-05	1.54E-05	1.75E-08	0	0	2.01E-06	2.42E-08	0
(w) Aluminium (Al3+)	g	1.11E-05	0	0	0	0	1.11E-05	0	0
(w) Aromatic Hydrocarbons (unspecified)	g	1.02E-05	9.64E-06	9.50E-13	0	0	5.81E-07	1.31E-12	0
(w) Xylene (C6H4(CH3)2)	g	1.00E-05	9.97E-06	0	0	0	5.90E-08	0	0
(w) Lead (Pb++, Pb4+)	g	8.11E-06	4.28E-06	1.27E-14	0	0	3.83E-06	1.75E-14	0
(w) Cyanide (CN-)	g	7.78E-06	4.00E-06	4.43E-15	0	0	3.78E-06	6.13E-15	0
(w) Organic Dissolved Matter (chlorinated)	g	7.70E-06	3.92E-06	0	0	0	3.78E-06	0	0
(w) Manganese (Mn II, Mn IV, Mn VII)	g	4.99E-06	1.13E-06	0	0	0	3.86E-06	0	0

(w) Zinc (Zn++)	g	4.97E-06	1.05E-06	1.27E-13	0	0	3.91E-06	3.76E-13	0
(w) Nickel (Ni++, Ni3+)	g	3.96E-06	1.62E-07	6.34E-15	0	0	3.80E-06	8.76E-15	0
(w) Copper (Cu+, Cu++)	g	3.94E-06	1.42E-07	6.34E-14	0	0	3.80E-06	8.76E-14	0
(w) Arsenic (As3+, As5+)	g	3.84E-06	5.71E-08	0	0	0	3.79E-06	0	0
(w) AOX (Adsorbable Organic Halogens)	g	3.80E-06	2.22E-08	4.05E-15	0	0	3.78E-06	5.60E-15	0
(w) Cadmium (Cd++)	g	3.79E-06	8.62E-09	3.17E-15	0	0	3.78E-06	4.38E-15	0
(w) Bromates (BrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chlorates (ClO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chlorine (Cl2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chromites (CrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Mercury (Hg+, Hg++)	g	3.78E-06	4.21E-11	1.46E-17	0	0	3.78E-06	2.01E-17	0
(w) Organic Matter (unspecified)	g	3.78E-06	1.16E-10	2.68E-12	0	0	3.78E-06	1.20E-11	0
(w) Sulphide (S--)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) VOC (Volatile Organic Compounds)	g	3.54E-06	3.54E-06	0	0	0	0	0	0
(w) Alkane (unspecified)	g	2.01E-06	1.93E-06	0	0	0	8.14E-08	0	0
(w) Benzene (C6H6)	g	2.01E-06	1.93E-06	9.62E-17	0	4.82E-17	8.17E-08	2.84E-17	0
(w) Phosphates (PO4 3-, HPO4--, H2PO4-, H3PO4, as P)	g	2.01E-06	3.21E-07	6.31E-12	0	0	1.69E-06	8.75E-12	0
(w) Toluene (C6H5CH3)	g	1.72E-06	1.65E-06	1.39E-13	0	0	7.36E-08	1.93E-13	0
(w) Titanium (Ti3+, Ti4+)	g	1.63E-06	1.44E-06	0	0	0	1.92E-07	0	0
(w) Iode (I-)	g	1.02E-06	1.02E-06	0	0	0	5.07E-10	0	0

Table A4. LCI of solid, waste, recovered matter outputs, sorted by amount, above 1 μg

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(s) Calcium (Ca)	g	2.50E-04	2.21E-04	0	0	0	2.94E-05	0	0
(s) Carbon (C)	g	1.88E-04	1.66E-04	0	0	0	2.21E-05	0	0
(s) Iron (Fe)	g	1.25E-04	1.10E-04	0	0	0	1.47E-05	0	0
(s) Aluminum (Al)	g	5.53E-05	5.53E-05	0	0	0	0	0	0
(s) Sulfur (S)	g	3.31E-05	3.31E-05	0	0	0	0	0	0
(s) Phosphorus (P)	g	3.13E-06	2.77E-06	0	0	0	3.68E-07	0	0
(s) Manganese (Mn)	g	2.50E-06	2.21E-06	0	0	0	2.94E-07	0	0
Waste (total)	kg	7.24E-02	3.67E-02	2.20E-05	3.36E-02	1.06E-05	4.12E-05	2.04E-03	0
Waste: Slags and Ash (unspecified)	kg	5.26E-02	1.70E-02	7.14E-07	3.36E-02	0	2.19E-05	0.00189783	0
Waste: Mineral (inert)	kg	1.84E-02	1.84E-02	2.81E-11	0	0	4.76E-06	3.89E-11	0
Waste (unspecified)	kg	9.75E-04	8.76E-04	3.62E-08	0	0	3.02E-06	9.61E-05	0
Waste: FGD Sludge	kg	6.10E-05	5.49E-05	2.30E-09	0	0	0	6.12E-06	0
Waste (municipal and industrial)	kg	6.01E-05	2.91E-05	1.85E-05	0	9.27E-06	-2.24E-06	5.48E-06	0
Waste (hazardous)	kg	1.47E-05	4.41E-06	2.71E-06	0	1.35E-06	5.37E-06	8.07E-07	0
Waste: Non Toxic Chemicals (unspecified)	kg	7.50E-06	1.73E-07	6.59E-12	0	0	7.33E-06	9.11E-12	0
Waste (unspecified, to incineration)	kg	1.39E-06	3.36E-07	1.42E-10	0	0	1.06E-06	2.61E-10	0
Waste: Low Radioactive (class A)	kg	6.18E-08	6.18E-08	0	0	0	0	0	0
Waste: Non Mineral (inert)	kg	1.99E-08	1.99E-08	0	0	0	0	0	0
Waste: Radioactive (unspecified)	kg	9.86E-09	9.86E-09	0	0	0	0	0	0
Waste (tailings)	kg	3.78E-09	0	0	0	0	3.78E-09	0	0
Waste: Bauxite Residues (red mud)	kg	2.35E-09	2.04E-09	1.31E-10	0	0	0	1.81E-10	0
Recovered Matter (total)	kg	2.17E-04	1.96E-04	7.34E-09	0	0	1.44E-06	1.95E-05	0
Recovered Matter: Ash	kg	1.94E-04	1.75E-04	7.34E-09	0	0	0	1.95E-05	0
Recovered Matter (unspecified)	kg	2.28E-05	2.14E-05	0	0	0	1.44E-06	0	0

Table A5: All Life Cycle Inventory (LCI) Inputs

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution
(r) Barium Sulfate (BaSO4, in ground)	kg	4.33E-06	4.33E-06	0	0	0	0	0
(r) Barium Sulphate (BaSO4, in ground)	kg	5.80E-07	0	0	0	0	5.80E-07	0
(r) Bauxite (Al2O3, ore)	kg	1.28E-07	2.67E-08	4.83E-10	0	0	1.00E-07	6.67E-10
(r) Bentonite (Al2O3.4SiO2.H2O, in ground)	kg	1.52E-06	4.09E-07	0	0	0	1.11E-06	0
(r) Calcium Sulfate (CaSO4, ore)	kg	5.46E-10	5.46E-10	0	0	0	0	0
(r) Calcium Sulphate (CaSO4, ore)	kg	1.06E-07	0	0	0	0	1.06E-07	0
(r) Chromium (Cr, ore)	kg	4.72E-09	8.33E-10	0	0	0	3.89E-09	0
(r) Clay (in ground)	kg	1.21E-06	8.11E-07	0	0	0	3.99E-07	0
(r) Coal (in ground)	kg	4.58E-03	3.73E-03	3.88E-05	0	1.94E-05	3.88E-04	3.98E-04
(r) Copper (Cu, ore)	kg	4.80E-09	4.24E-09	0	0	0	5.64E-10	0
(r) Dolomite (CaCO3.MgCO3, in ground)	kg	4.54E-08	0	0	0	0	4.54E-08	0
(r) Feldspar (ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Fluorspar (CaF2, ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Granite (in ground)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Gravel (unspecified)	kg	8.97E-08	7.46E-08	0	0	0	1.51E-08	0
(r) Iron (Fe, ore)	kg	1.80E-05	1.28E-05	0	0	0	5.17E-06	0
(r) Iron Sulfate (FeSO4, ore)	kg	3.39E-14	3.39E-14	0	0	0	0	0
(r) Lead (Pb, ore)	kg	5.28E-09	1.32E-09	0	0	0	3.96E-09	0
(r) Lignite (in ground)	kg	1.30E-05	1.21E-05	0	0	0	9.14E-07	0
(r) Limestone (CaCO3, in ground)	kg	3.43E-04	2.96E-04	7.35E-06	0	3.67E-06	4.16E-06	3.27E-05
(r) Manganese (Mn, ore)	kg	5.5E-10	4.85E-10	0	0	0	6.46E-11	0
(r) Mercury (Hg, ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Natural Gas (in ground)	kg	1.61E-02	9.88E-03	1.07E-04	0	5.33E-05	6.01E-03	3.46E-05
(r) Nickel (Ni, ore)	kg	4.1E-09	2.82E-10	0	0	0	3.82E-09	0
(r) Oil (in ground)	kg	9.66E-03	2.42E-03	1.24E-03	0	6.21E-04	5.00E-03	3.74E-04
(r) Olivine ((Mg,Fe)2SiO4, ore)	kg	3.02E-08	0	0	0	0	3.02E-08	0
(r) Perlite (SiO2, ore)	kg	9.44E-07	4.38E-07	2.82E-07	0	1.41E-07	0	8.32E-08
(r) Phosphate Rock (in ground)	kg	1.71E-02	1.71E-02	0	0	0	1.65E-09	0
(r) Potassium Chloride (KCl, as K2O, in ground)	kg	5.32E-03	5.32E-03	0	0	0	9.6E-09	0
(r) Pyrite (FeS2, ore)	kg	7.87E-06	6.94E-06	0	0	0	9.24E-07	0
(r) Sand (in ground)	kg	7.72E-07	1.35E-07	2.96E-10	0	0	6.37E-07	4.09E-10
(r) Silver (Ag, ore)	kg	2.38E-11	2.1E-11	0	0	0	2.8E-12	0
(r) Sodium Chloride (NaCl, in ground or in sea)	kg	3.15E-05	2.94E-05	1.36E-10	0	0	2.04E-06	1.88E-10
(r) Sulfur (S, in ground)	kg	3.25E-06	3.25E-06	0	0	0	0	0
(r) Sulphur (S, in ground)	kg	7.50E-07	0	0	0	0	7.50E-07	0
(r) Talcum (4SiO2.3MgO.H2O, ore)	kg	3.78E-09	0	0	0	0	3.78E-09	0
(r) Titanium (Ti, ore)	kg	2.27E-09	0	0	0	0	2.27E-09	0
(r) Uranium (U, ore)	kg	1.29E-07	5.44E-08	9.24E-10	0	4.61E-10	6.93E-08	3.99E-09
(r) Zinc (Zn, ore)	kg	3.81E-09	3.08E-11	0	0	0	3.78E-09	0
Biomass (unspecified)	kg	7.18E-06	0	0	0	0	7.18E-06	0
Cropland	acres	1.44E-04	1.44E-04	0	0	0	0	0
Diesel Oil	kg	5.93E-02	0	0	0	0	0	2.97E-02
Explosive (unspecified)	kg	4E-13	4E-13	0	0	0	0	0
Ferromanganese (Fe, Mn, C)	kg	3.78E-09	0	0	0	0	3.78E-09	0
Iron Scrap	kg	4.14E-08	4.14E-08	0	0	0	0	0
Land Use (II -> III)	m2a	1.54E-10	1.54E-10	0	0	0	0	0
Land Use (II -> IV)	m2a	1.87E-10	1.87E-10	0	0	0	0	0
Land Use (III -> IV)	m2a	2.12E-13	2.12E-13	0	0	0	0	0
Nitrogen (N2)	kg	0.771419	0	0	0.771419	0	0	0
Oxygen (O2)	kg	0.192855	0	0	0.192855	0	0	0
Peat	kg	2.57E-06	0	0	0	0	2.57E-06	0
Raw Materials (unspecified)	kg	2.16E-05	2.16E-05	0	0	0	0	0
Steel	kg	3.96E-08	3.96E-08	0	0	0	0	0
Water Used (total)	liter	0.148896	0.103642	2.86E-04	3.87E-03	8.64E-05	0.0407917	2.16E-04
Water: Public Network	liter	0.116291	0.0862705	0	3.87E-03	0	0.0261464	0
Water: River	litre	4.54E-03	0	0	0	0	4.54E-03	0
Water: Sea	litre	6.65E-03	0	0	0	0	6.65E-03	0
Water: Unspecified Origin	liter	1.87E-02	1.50E-02	1.13E-04	0	0	3.46E-03	1.65E-04
Water: Well	litre	3.78E-09	0	0	0	0	3.78E-09	0

Wood	kg	1.76E-07	1.52E-07	0	0	0	2.40E-08	0

Table A6: LCI outputs above 1 μg, air emissions A-M

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(a) Acetaldehyde (CH3CHO)	g	0.002237	1.1E-06	4.14E-11	0.002235	0	1.5E-08	1.1E-07	0
(a) Acetic Acid (CH3COOH)	g	1.82E-05	0.000016	0	0	0	2.14E-06	0	0
(a) Acetone (CH3COCH3)	g	0.014445	1.9E-08	0	0.014445	0	2.53E-09	0	0
(a) Acetylene (C2H2)	g	1.06614	9.42E-12	0	1.06614	0	0	0	0
(a) Aldehyde (unspecified)	g	0.019116	0.000177	1.44E-07	0.018915	6.41E-08	3.79E-06	1.98E-05	0
(a) Alkane (unspecified)	g	0.000351	0.00031	0	0	0	4.05E-05	0	0
(a) Ammonia (NH3)	g	0.8793	0.879296	2.89E-08	0	2.65E-09	3.79E-06	2.44E-07	0
(a) Antimony (Sb)	g	3.82E-06	3.9E-08	6.83E-12	0	0	3.78E-06	4.36E-09	0
(a) Aromatic Hydrocarbons (unspecified)	g	3.42E-05	3.92E-06	5.7E-13	0	0	3.02E-05	7.88E-13	0
(a) Arsenic (As)	g	7.19E-06	3.07E-06	1.51E-10	0	0	3.78E-06	3.39E-07	0
(a) Asbestos	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Benzaldehyde (C6H5CHO)	g	0.020635	1.28E-12	0	0.020635	0	1.7E-13	0	0
(a) Benzene (C6H6)	g	6.04E-05	5.31E-05	4.34E-07	0	1.39E-07	5.7E-06	1.03E-06	0
(a) Benzyl Chloride (C7H7Cl)	g	1.34E-06	1.21E-06	5.09E-11	0	0	0	1.35E-07	0
(a) Butane (C4H10)	g	0.051061	1.52E-07	5.71E-09	0	0	0.051061	1.49E-08	0
(a) Butane (n-C4H10)	g	0.000115	0.000103	0	0	0	1.16E-05	0	0
(a) Butene (1-CH3CH2CHCH2)	g	0.32672	2.14E-07	0	0.32672	0	3.86E-09	0	0
(a) Butene (2-CH3CHCHCH3)	g	0.126102	0	0	0.126102	0	0	0	0
(a) C10 alkanes (unspecified)	g	0.114524	0	0	0.114524	0	0	0	0
(a) Cadmium (Cd)	g	4.01E-06	2.09E-07	8.79E-12	0	0	3.78E-06	2.2E-08	0
(a) Calcium (Ca)	g	1.1E-06	1.01E-06	1.84E-10	0	0	9.31E-08	3.37E-10	0
(a) Carbon Dioxide (CO2, fossil)	g	57.9034	39.1612	4.13153	0	2.08922	10.3152	2.20619	0
(a) Carbon Dioxide (CO2, Soil)	g	8.50212	8.50212	0	0	0	0	0	0
(a) Carbon Disulphide (CS2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Carbon Monoxide (CO)	g	7.61673	0.032253	0.014013	6.89991	0.006973	0.052225	0.004553	0.606798
(a) Chlorinated Matter (unspecified, as Cl)	g	7.7E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Chlorine (Cl2)	g	7.7E-06	3.93E-06	5.78E-14	0	0	3.78E-06	2.59E-13	0
(a) Chromium (Cr III, Cr VI)	g	9.46E-06	5.11E-06	2.3E-10	0	0	3.78E-06	5.67E-07	0
(a) Copper (Cu)	g	3.84E-06	5.58E-08	1.69E-11	0	0	3.78E-06	3.77E-10	0
(a) Crotonaldehyde (C4H6O)	g	0.00172	0	0	0.00172	0	0	0	0
(a) Cyanide (CN-)	g	4.81E-06	4.32E-06	1.82E-10	0	0	4.5E-10	4.82E-07	0
(a) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Ethane (C2H6)	g	0.309908	0.000447	8.42E-09	0.065631	0	0.24383	2.2E-08	0
(a) Ethylene (C2H4)	g	0.826871	0.0013	0	0.825398	0	0.000173	0	0
(a) Fluorides (F-)	g	4.02E-06	4.01E-06	4.12E-11	0	1.35E-15	0	9.24E-09	0
(a) Fluorine (F2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Formaldehyde (CH2O)	g	0.024227	1.75E-05	3.74E-06	0.024074	1.86E-06	1.43E-06	1.2E-06	0.000127
(a) Halogenated Hydrocarbons (unspecified)	g	3.78E-06	4.93E-17	3.17E-18	0	0	3.78E-06	4.38E-18	0
(a) Heptane (C7H16)	g	0.000002	1.98E-06	0	0	0	1.79E-08	0	0
(a) Hexane (C6H14)	g	4.29E-06	4.22E-06	4.9E-09	0	0	3.75E-08	2.57E-08	0
(a) Hydrocarbons (except methane)	g	0.209355	0.009555	0.003017	0	0.000104	0.010015	0.00077	0.185893
(a) Hydrocarbons (unspecified)	g	0.172597	0.007777	0.001635	0	0.002422	0.037072	0.079476	0.044214

(a) Hydrogen (H2)	g	3.02E-05	4.07E-17	0	0	0	3.02E-05	0	0
(a) Hydrogen Chloride (HCl)	g	0.002646	0.002211	2.08E-05	0	1.04E-05	0.000167	0.000238	0
(a) Hydrogen Cyanide (HCN)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Hydrogen Fluoride (HF)	g	0.000338	0.000297	2.61E-06	0	1.3E-06	7.61E-06	2.97E-05	0
(a) Hydrogen Sulfide (H2S)	g	0.23092	5.97E-05	9.11E-06	0	4.54E-06	0.230844	2.74E-06	0
(a) Hydrogen Sulphide (H2S)	g	9.24E-06	0	0	0	0	9.24E-06	0	0
(a) Iron (Fe)	g	1.72E-06	1.6E-06	4.1E-10	0	0	1.23E-07	7.52E-10	0
(a) Isophorone	g	1.11E-06	0.000001	4.21E-11	0	0	0	1.12E-07	0
(a) Lead (Pb)	g	1.12E-05	7.05E-06	1.34E-10	0	0	3.79E-06	3.36E-07	0
(a) Magnesium (Mg)	g	2.13E-05	1.91E-05	7.99E-10	0	0	1.76E-08	2.12E-06	0
(a) Manganese (Mn)	g	6.97E-06	6.26E-06	2.42E-10	0	0	7.93E-08	6.32E-07	0
(a) Mercaptans	g	7.7E-06	3.92E-06	0	0	0	3.78E-06	0	0
(a) Mercury (Hg)	g	4.01E-06	2.11E-07	9.43E-12	0	0	3.78E-06	2.11E-08	0
(a) Metals (unspecified)	g	567.098	263.037	169.339	0	84.7659	3.78E-06	49.9562	0
(a) Methane (CH4)	g	3.12652	0.161389	0.001489	2.52205	0.000751	0.43867	0.002169	0
(a) Methanol (CH3OH)	g	0.018915	1.36E-08	0	0.018915	0	1.81E-09	0	0
(a) Methyl Chloride (CH3Cl)	g	1.02E-06	9.16E-07	3.85E-11	0	0	0	1.02E-07	0

Table A7: LCI outputs above 1μg, air emissions N-Z, solid outputs, and water emissions A-L

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(a) Nickel (Ni)	g	6.52E-06	6.04E-06	1.32E-09	0	0	1.45E-08	4.65E-07	0
(a) Nitrogen Oxides (NOx as NO2)	g	7.10081	1.11613	0.038865	5.63917	0.034462	0.014385	0.016796	0.241008
(a) Nitrous Oxide (N2O)	g	0.254547	0.106909	0.000411	0.146965	2.23E-05	5.54E-06	0.000235	0
(a) Organic Matter (unspecified)	g	0.003472	0.000443	1.36E-06	0	2.93E-07	0.003024	3.75E-06	0
(a) Particulates (PM 10)	g	0.009879	0.003137	0.004683	0	0.000845	0	0.001215	0
(a) Particulates (unspecified)	g	2.96859	0.078034	0.000883	2.86181	0.000441	0.004708	0.002623	0.020092
(a) Pentane (C5H12)	g	0.017916	0.000138	7.06E-09	0	0	0.017778	1.85E-08	0
(a) Polycyclic Aromatic Hydrocarbons (PAH, unspecified)	g	0.000005	1.07E-06	6.34E-16	0	0	3.92E-06	8.76E-16	0
(a) Potassium (K)	g	2.51E-06	2.22E-06	0	0	0	2.95E-07	0	0
(a) Propane (C3H8)	g	0.279602	0.000127	1.81E-11	0.154762	0	0.124713	3.43E-09	0
(a) Propylene (CH2CHCH3)	g	0.412699	4.12E-07	0	0.412699	0	5.64E-09	0	0
(a) Selenium (Se)	g	2.55E-06	2.3E-06	1.01E-10	0	0	5.03E-09	2.51E-07	0
(a) Silicon (Si)	g	1.21E-06	1.1E-06	1.84E-10	0	0	1.08E-07	3.37E-10	0
(a) Sodium (Na)	g	1.9E-06	1.89E-06	1.09E-09	0	0	7.57E-09	2E-09	0
(a) Sulfur Oxides (SOx as SO2)	g	0.566833	0.12411	0.006092	0.282624	0.003041	0	0.005331	0.145635
(a) Sulphur Oxides (SOx as SO2)	g	0.013812	0	0	0	0	0.013812	0	0
(a) Sulphuric Acid (H2SO4)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) Toluene (C6H5CH3)	g	2.59E-05	0.000023	4.04E-11	0	0	2.86E-06	4.78E-08	0
(a) Vanadium (V)	g	5.04E-06	5.01E-06	2.87E-09	0	0	1.25E-08	1.06E-08	0
(a) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(a) VOC (Volatile Organic Compounds)	g	0.192283	0	0	0.192184	0	9.83E-05	0	0
(a) Zinc (Zn)	g	1.02E-05	6.35E-06	1.09E-10	0	0	3.83E-06	5.11E-09	0
(s) Aluminum (Al)	g	5.53E-05	5.53E-05	0	0	0	0	0	0
(s) Calcium (Ca)	g	0.00025	0.000221	0	0	0	2.94E-05	0	0
(s) Carbon (C)	g	0.000188	0.000166	0	0	0	2.21E-05	0	0
(s) Iron (Fe)	g	0.000125	0.00011	0	0	0	1.47E-05	0	0
(s) Manganese (Mn)	g	2.5E-06	2.21E-06	0	0	0	2.94E-07	0	0
(s) Phosphorus (P)	g	3.13E-06	2.77E-06	0	0	0	3.68E-07	0	0
(s) Sulfur (S)	g	3.31E-05	3.31E-05	0	0	0	0	0	0
(w) Acids (H+)	g	0.185864	0.185848	1.01E-12	0	0	1.51E-05	4.57E-12	0
(w) Alkane (unspecified)	g	2.01E-06	1.93E-06	0	0	0	8.14E-08	0	0
(w) Aluminium (Al3+)	g	1.11E-05	0	0	0	0	1.11E-05	0	0
(w) Aluminum (Al3+)	g	2.68E-05	2.68E-05	1.54E-09	0	0	0	2.13E-09	0
(w) Ammonia (NH4+, NH3, as N)	g	0.000431	0.000206	0.000122	0	6.09E-05	5.97E-06	3.65E-05	0
(w) AOX (Adsorbable Organic Halogens)	g	3.8E-06	2.22E-08	4.05E-15	0	0	3.78E-06	5.6E-15	0
(w) Aromatic Hydrocarbons (unspecified)	g	1.02E-05	9.64E-06	9.5E-13	0	0	5.81E-07	1.31E-12	0
(w) Arsenic (As3+, As5+)	g	3.84E-06	5.71E-08	0	0	0	3.79E-06	0	0
(w) Barium (Ba++)	g	2.99E-05	2.94E-05	3.04E-12	0	0	5.38E-07	4.2E-12	0
(w) Barytes	g	0.000888	0.000784	0	0	0	0.000104	0	0
(w) Benzene (C6H6)	g	2.01E-06	1.93E-06	9.62E-17	0	4.82E-17	8.17E-08	2.84E-17	0
(w) BOD5 (Biochemical Oxygen Demand)	g	0.003736	0.001943	0.000834	0	0.000416	0.000295	0.000248	0
(w) Bromates (BrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0

(w) Cadmium (Cd++)	g	3.79E-06	8.62E-09	3.17E-15	0	0	3.78E-06	4.38E-15	0
(w) Calcium (Ca++)	g	0.000601	0.000565	0	0	0	3.57E-05	0	0
(w) Carbonates (CO3--, HCO3-, CO2, as C)	g	0.000287	0	0	0	0	0.000287	0	0
(w) Chlorates (ClO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chlorides (Cl-)	g	0.06911	0.036387	0.017834	0	0.008898	0.000641	0.005351	0
(w) Chlorinated Matter (unspecified, as Cl)	g	0.000141	0.000125	0	0	0	1.66E-05	0	0
(w) Chlorine (Cl2)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Chromites (CrO3-)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) COD (Chemical Oxygen Demand)	g	0.025139	0.01125	0.007053	0	0.003522	0.001215	0.002099	0
(w) Copper (Cu+, Cu++)	g	3.94E-06	1.42E-07	6.34E-14	0	0	3.8E-06	8.76E-14	0
(w) Cyanide (CN-)	g	7.78E-06	0.000004	4.43E-15	0	0	3.78E-06	6.13E-15	0
(w) Dichloroethane (1,2-CH2ClCH2Cl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Dissolved Matter (unspecified)	g	0.187815	0.087147	0.056007	0	0.028035	0.000092	0.016534	0
(w) Dissolved Organic Carbon (DOC)	g	0.00005	4.41E-05	0	0	0	5.87E-06	0	0
(w) Fluorides (F-)	g	2.18E-05	1.62E-05	1.39E-07	0	6.96E-08	4.71E-06	6.02E-07	0
(w) Hydrocarbons (unspecified)	g	0.000136	5.77E-06	1.15E-06	0	5.73E-07	0.000129	3.45E-07	0
(w) Iode (I-)	g	1.02E-06	1.02E-06	0	0	0	5.07E-10	0	0
(w) Iron (Fe++, Fe3+)	g	3.84E-05	3.12E-05	2.73E-10	0	1.35E-10	7.24E-06	1.17E-09	0
(w) Lead (Pb++, Pb4+)	g	8.11E-06	4.28E-06	1.27E-14	0	0	3.83E-06	1.75E-14	0

Table A8: LCI outputs above 1μg, water emissions M-Z, waste, miscellaneous, carbon/electrocity/stover reminders

Flow	Units	Total	Stover Production	Stover Transportation	Stover Pyrolysis	Transportation to Refinery	Refining	Fuel Distribution	Fuel Use
(w) Magnesium (Mg++)	g	3.78E-05	0.000031	0	0	0	6.78E-06	0	0
(w) Manganese (Mn II, Mn IV, Mn VII)	g	4.99E-06	1.13E-06	0	0	0	3.86E-06	0	0
(w) Mercury (Hg+, Hg++)	g	3.78E-06	4.21E-11	1.46E-17	0	0	3.78E-06	2.01E-17	0
(w) Metals (unspecified)	g	0.000197	5.94E-05	3.45E-05	0	1.72E-05	7.56E-05	1.03E-05	0
(w) Nickel (Ni++, Ni3+)	g	3.96E-06	1.62E-07	6.34E-15	0	0	3.8E-06	8.76E-15	0
(w) Nitrate (NO3-)	g	0.000055	9.51E-06	6.58E-10	0	0	4.54E-05	1.33E-07	0
(w) Nitrogenous Matter (unspecified, as N)	g	4.67E-05	8.76E-06	1.71E-13	0	0	3.79E-05	2.36E-13	0
(w) Oils (unspecified)	g	0.001706	0.000783	0.000413	0	0.000206	0.000181	0.000123	0
(w) Organic Dissolved Matter (chlorinated)	g	7.7E-06	3.92E-06	0	0	0	3.78E-06	0	0
(w) Organic Dissolved Matter (unspecified)	g	5.68E-05	3.92E-06	0	0	0	5.29E-05	0	0
(w) Organic Matter (unspecified)	g	3.78E-06	1.16E-10	2.68E-12	0	0	3.78E-06	1.2E-11	0
(w) Phenol (C6H5OH)	g	6.76E-05	3.12E-05	0.000016	0	0.000008	7.64E-06	4.77E-06	0
(w) Phosphates (PO4 3-, HPO4--, H2PO4-, H3PO4, as P)	g	2.01E-06	3.21E-07	6.31E-12	0	0	1.69E-06	8.75E-12	0
(w) Potassium (K+)	g	6.71E-05	6.12E-05	0	0	0	5.97E-06	0	0
(w) Salts (unspecified)	g	1.74E-05	1.54E-05	1.75E-08	0	0	2.01E-06	2.42E-08	0
(w) Saponifiable Oils and Fats	g	4.94E-05	4.94E-05	0	0	0	0	0	0
(w) Sodium (Na+)	g	0.084965	0.040822	0.022964	0	0.011457	0.002831	0.006891	0
(w) Strontium (Sr II)	g	6.78E-05	6.36E-05	0	0	0	4.13E-06	0	0
(w) Sulfate (SO4--)	g	3.6179	3.6179	9.68E-10	0	0	0	1.2E-07	0
(w) Sulphate (SO4--)	g	0.003175	0	0	0	0	0.003175	0	0
(w) Sulphide (S--)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) Suspended Matter (unspecified)	g	0.02071	0.01279	0.003783	0	0.001889	0.001122	0.001126	0
(w) Titanium (Ti3+, Ti4+)	g	1.63E-06	1.44E-06	0	0	0	1.92E-07	0	0
(w) TOC (Total Organic Carbon)	g	0.0012	0.000701	9.5E-12	0	0	0.0005	1.31E-11	0
(w) Toluene (C6H5CH3)	g	1.72E-06	1.65E-06	1.39E-13	0	0	7.36E-08	1.93E-13	0
(w) Triethylene Glycol (C6H14O4)	g	0.00005	4.41E-05	0	0	0	5.87E-06	0	0
(w) Vinyl Chloride (CH2CHCl)	g	3.78E-06	0	0	0	0	3.78E-06	0	0
(w) VOC (Volatile Organic Compounds)	g	3.54E-06	3.54E-06	0	0	0	0	0	0
(w) Water (unspecified)	liter	0.079711	9.9E-09	0	0.040058	0	0.039654	0	0
(w) Water: Chemically Polluted	liter	0.094402	0.00518	0.003084	0	0.001539	0.083674	0.000924	0
(w) Xylene (C6H4(CH3)2)	g	0.00001	9.97E-06	0	0	0	5.9E-08	0	0
(w) Zinc (Zn++)	g	4.97E-06	1.05E-06	1.27E-13	0	0	3.91E-06	3.76E-13	0
(wr) Radium (Ra226)	kBq	1.01E-06	1.01E-06	0	0	0	0	0	0
(wr) Radium (Ra228)	kBq	1.01E-06	1.01E-06	0	0	0	0	0	0
(wr) Thorium (Th228)	kBq	2.03E-06	2.03E-06	0	0	0	0	0	0
Farmland	acres	0.000144	0.000144	0	0	0	0	0	0
Nitrogen (N2)	kg	0.771419	0	0	0.771419	0	0	0	0
Oxygen (O2)	kg	0.039588	0	0	0.039588	0	0	0	0
Recovered Matter (total)	kg	0.000217	0.000196	7.34E-09	0	0	1.44E-06	1.95E-05	0
Recovered Matter (unspecified)	kg	2.28E-05	2.14E-05	0	0	0	1.44E-06	0	0
Recovered Matter: Ash	kg	0.000194	0.000175	7.34E-09	0	0	0	1.95E-05	0
Waste (hazardous)	kg	1.47E-05	4.41E-06	2.71E-06	0	1.35E-06	5.37E-06	8.07E-07	0

Waste (municipal and industrial)	kg	6.01E-05	2.91E-05	1.85E-05	0	9.27E-06	-2.2E-06	5.48E-06	0
Waste (total)	kg	0.072405	0.036653	0.000022	0.033637	1.06E-05	4.12E-05	0.002041	0
Waste (unspecified)	kg	0.000975	0.000876	3.62E-08	0	0	3.02E-06	9.61E-05	0
Waste (unspecified, to incineration)	kg	1.39E-06	3.36E-07	1.42E-10	0	0	1.06E-06	2.61E-10	0
Waste: FGD Sludge	kg	0.000061	5.49E-05	2.3E-09	0	0	0	6.12E-06	0
Waste: Mineral (inert)	kg	0.018379	0.018374	2.81E-11	0	0	4.76E-06	3.89E-11	0
Waste: Non Toxic Chemicals (unspecified)	kg	7.5E-06	1.73E-07	6.59E-12	0	0	7.33E-06	9.11E-12	0
Waste: Slags and Ash (unspecified)	kg	0.052564	0.017006	7.14E-07	0.033637	0	2.19E-05	0.001898	0
Corn Stover (raw)	kg	0.343916	0	0	0.343916	0	0	0	0
Electricity	MJ elec	0.016042	0.038064	0	-0.03502	0	0.009756	0.003241	0

Database Contents-to be stored electronically. A confidential copy will be given to DOE.

Economic Calculations

ECONOMICS FOR PYROLYSIS OIL UPGRADING

Assumes $100/bbl gasoline

	T/day	density	bbl/d	l/l	$/ton	$/gal	$MM	$MM/yr	SCFB	SCFD	% C	Carbon recover
Type of feed	**Mixed Wood**											
Size of Pyrolysis unit	2000										49.58	
Cost of Pyrolysis Unit						**0.51**						
Yield of Pyrolysis oil	0.7											
Amount of Pyrlysis oil	1400	1.18	7463.299			**0.59**		67.5033			45.7	0.64521
Hydrogen for HT	16.0454			157	**2100**			12.2988	932.1204			
Yield from HT	0.485											
Amount of Feed to HC	679	1.06	4029.477								75.4	0.5163
Hydrogen for HC	16.83864684			292	**2100**			12.90682	1733.625			
Total H2	32.88404684							25.20562	2665.746	9.992938		
Total methane required for H2	118.2879383										**75**	
Total cost								92.70892				
Yield from HCK	0.746											
Yield Oil T/D Case 2	506.534	0.85	3748.647								86.8	0.4433
Overall yields	0.253267											
Final product sample #	HC16											
% diesel boiling range	0.333		1248.299			**2.38**		45.5447				
% Gasoline boiling range	0.553		2073.002			**2.38**		75.63429				
% VGO range	0.114		427.3457			1.8		11.79218				
Total prodcut value			3748.647					132.9712				
Total Incentive								40.26225				
Fuel gas from HT	51.17											
Fuel Gas from HCK	78.085											
Total HC available	129.255											
Hydrotreating conditions												
LHSV	0.22											
Pressure	2025											
Temp C	342											
Catalyst	Pd/C											
Cost of HT per annual gallon	0.169602087						19.40458					
Utilities for HT	1252.2048	0.07						0.701235				
Hydrocracking conditions												
LHSV	0.25											
Pressure	1515											
Temp C	405											
Catalyst	NiMo											
Cost of HCK	0.508806262						31.42992					
Utilities of HCK	1257.408651	0.07						0.704149				
Total capital							50.8345					
	T/day	density	bbl/d	l/l	$/ton	$/gal	$MM	$MM/yr	SCFB	SCFD		

Type of feed	**New Corn Stover**														
Size of Pyrolysis unit	2000										42.29		845.8		907.14713
Cost of Pyrolysis Unit						**0.51**									
Yield of Pyrolysis oil	0.473														
Amount of Pyrlysis oil	946	1.16	5130.007			**0.59**		46.39938			33.77	0.3777066	319.4642		
Hydrogen for HT	4.281596			62	**2100**			3.281843	368.0985						
Yield from HT	0.466														
Amount of Feed to HC	440.836	1.04	2666.42								76	0.3961165	335.0354		
Hydrogen for HC	18.45774047			493	**2100**			14.14786	2926.977						
Total H2	22.73933647							17.4297	3295.075	8.349781					
Total methane required for H2	81.79617436										**75**		61.34713		
Toatl Cost of feeds								63.82908							
Yield from HCK	0.795														
Yield Oil T/D Case 2	350.46462	0.87	2534.018								86.8	0.3596634	304.2033	0.359663	0.3353406
Overall yields	0.17523231														
Final product sample #	HC12 in database		5/11/07 02:50-10:20												
Gas from HT	43.516														
Gas from HCK	37.47106														
fr diesel boiling range	**0.333**		843.8281			**2.38**		30.78741							
fr Gasoline boiling range	**0.553**		1401.312			**2.38**		51.12743							
fr VGO range	**0.114**		288.8781			1.8		7.971302							
Total product			2534.018					81.91484							
total incentive								18.08576							
Fuel gas from HT	8.26804														
Fuel Gas from HCK	37.47106														
Total HC available	45.7391														
Hydrotreating conditions		kw													
LHSV	0.26														
Pressure	1944														
Temp C	343														
Catalyst	Pd/C														
Cost of HT per annual gallon	0.169602087						13.33802								
Utilities for HT-kw	339.9026262	**0.07**						0.190345							
Cost of Catalyst															
Hydrocracking conditions															
LHSV	0.25														
Pressure	1533														
Temp C	410														
Catalyst	NiMo-S														
Cost of HCK per annual gallon	0.508806262						20.79808								
Utilities of HCK-kw	1404.818819	**0.07**						0.786699							
Total Capital							34.13609								

MIXED WOOD CASE

HT fuel gas	vol%	MW	wt	wt%
Co2	55	44	2420	0.57062
CO	0.5	32	16	0.003773
c1	24	16	384	0.090545
c2	4	32	128	0.030182
c3	2.5	44	110	0.025937
c4	0.5	58	29	0.006838
c5	0.5	72	36	0.008489
c6+	13	86	1118	0.263617
			4241	1
sum Hydrocarbons				0.42938

Corn Stover case

HT fuel gas	vol%	MW	wt	wt%
Co2	75	44	3300	0.812408
CO	0	32	0	0
c1	14	16	224	0.055145
c2	6	32	192	0.047267
c3	2	44	88	0.021664
c4	0	58	0	0
c5	0	72	0	0
c6+	3	86	258	0.063516
			4062	1
sum Hydrocarbons				0.187592