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LIQUID HYDROCARBON FUELS FROM BIOMASS

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INTRODUCTION

Renewable resources can provide a substantial energy resource for the United States. The direct production of liquid fuels from renewable resources, however, is limited to the use of biofuels. Liquids are preferred for use as transportation fuels because of their high energy density and handling ease and safety. Both biomass and municipal waste are being studied as the feedstock for production of liquid fuels [1]. Liquid fuel production from these feedstocks can be accomplished by several processes including hydrolysis and fermentation of the carbohydrates to alcohol fuels, thermal gasification and synthesis of alcohol or hydrocarbon fuels, direct extraction of biologically produced hydrocarbons such as seed oils or algae lipids, or direct thermochemical conversion of the biomass or municipal waste to liquids and catalytic upgrading to hydrocarbon fuels. This paper discusses direct thermochemical conversion to achieve biomass liquefaction.

BIOMASS LIQUEFACTION

Direct liquefaction of biomass by thermochemical means has been studied as a process for fuel production for the last twenty years. Modern development of the process can be traced to the early work at the Bureau of Mines as an extension of coal liquefaction research [2,3] and to the work on municipal waste at the Worcester Polytechnical Institute [4]. Ongoing work at universities and national laboratories in the U.S., Canada, and Scandinavia has resulted in much progress since the mid-1970's [5 and references therein]. Currently the research has focused on two general processing configurations, high-pressure liquefaction and atmospheric flash pyrolysis.

High-pressure liquefaction of biomass, shown conceptually in Figure 1, has been studied at a number of sites around the world and includes a number of process variations. The processing temperature is generally in the range of 350°C with operating pressures in excess of 1000 psig. The feedstock is generally fed as a slurry, with the nature of the slurry vehicle being a major variable in the studies. Engineering of the high-pressure feeding system is a major difficulty in the development of this type of process. The presence of added reducing gas or catalyst is another important variable. Most studies show that the operation in the presence of alkali facilitates the formation of liquids with lower oxygen contents. Product recovery is also a major issue and is highly dependent on the slurry vehicle. Various systems of centrifugation, distillation, and solvent fractionation have been tested.

The atmospheric flash pyrolysis concept, shown in Figure 2, can be traced to the ancient process of charcoal manufacture. Modern engineering methods have optimized the yield of liquid product through control of feedstock particle

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size, residence time, and processing temperature. Current process development utilizes short residence time, <1 second, in isothermal, fluidized- or entrained-bed reactors. The feedstock is carried by an inert gas carrier into the reactor where it thermally decomposes to tar vapors, water vapor, gases, and char solids. Recovery of the vapors as liquid product is a major difficulty for this process. Various systems for vapor quench and recovery have used complicated condensing and coalescing systems including electrostatic precipitators, cyclones, filters, and/or spray towers.

The products from the high-pressure liquefaction and atmospheric flash pyrolysis processes are vastly different from each other. The properties of the two products are summarized in Table 1. The high-pressure product is a viscous, phenolic oil. Its physical properties of high viscosity, high boiling point, and limited water solubility are readily understood as resulting from the oxygenated and aromatic character of the product components. The flash pyrolyzate is much more oxygenated and is more water soluble. As a result of the high level of dissolved water in the product, the flash pyrolyzate is much less viscous. The more oxygenated components in the product, acids and aldehydes/ethers, cause it to be more corrosive and more thermally unstable, respectively.

UPGRADING BIOMASS-DERIVED LIQUIDS

Because of the chemical differences in the two products described above, different upgrading schemes have been derived for converting the products into usable hydrocarbon fuels. Catalytic hydroprocessing is an obvious choice based on the existing knowledge of sulfur removal from petroleum products. Catalytic hydrodeoxygenation of the products has been studied in several laboratories [6,7,8]. Developments in further product refinement by catalytic cracking and hydrocracking have also been presented [9,10]. This type of processing is most directly applicable to the high-pressure liquefaction products; however, a process has been identified which allows the use of catalytic hydroprocessing of the thermally unstable pyrolyzate product [11]. Another alternative, which has been used successfully with the pyrolyzate products, is the catalytic cracking of the vapors over a zeolite catalyst without the intermediate quenching and recovery of the tars [12]. Further discussion of the products from this type of processing is not included in this paper.

Catalytic hydroprocessing of biomass-derived liquid products has been investigated at Pacific Northwest Laboratory (PNL) in a fixed-bed, continuous-feed, catalytic reactor system (shown schematically in Reference 6). Products from both high-pressure processes and flash pyrolysis processes have been upgraded [13,14]. The reactor system includes gas feed from a high-pressure (6000 psig) bottle, oil feed by positive displacement pump, a 1-liter reactor vessel containing 850 mL of alumina-supported metal sulfide catalyst (sulfided in place), pressure control by a back-pressure regulator, and product recovery in a cooled, atmospheric-pressure gas-liquid separator. Feed gas is measured by a mass flow meter; feed oil is measured in a volume flow meter; and off-gas is measured in a wet test meter. The off-gas is analyzed by gas chromatography using both a thermal conductivity detector for fixed gases and a flame ionization detector for hydrocarbon vapors up to C7.

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ANALYSIS OF PRODUCTS FROM HYDROPROCESSING BIOMASS-DERIVED OILS

A range of products has been produced in the PNL hydrotreater depending on the processing conditions and the feedstock. Several representative samples are presented in Table 2. In comparison with the biomass-derived oils shown in Table 1, the hydrotreated products are significantly upgraded. The oxygen content is greatly reduced and, coincidentally, so is the density of the products. The density difference has a significant impact because, although the mass yield of the hydrotreated products is in the range of 80%, the volume yield in many cases exceeds 100%. A primary concern throughout the research has been the maintenance of the aromatic character of the biomass oil in order to minimize hydrogen consumption and to produce a higher octane gasoline blending stock. As seen in Table 2, the hydrogen-to-carbon ratio in the products is highly variable depending on the processing conditions. The extent of saturation as shown by the H/C ratio is a useful indicator of the aromatic character of the product. Saturation of the aromatic components has a strongly deleterious effect on the octane of the product. A review of the literature shows that cyclic hydrocarbons have poor octanes similar to straight-chained hydrocarbons. Our analyses also show that although the crude hydrotreated products do contain minor amounts of oxygen, water solubility in the products remains low. In addition, although sulfided catalysts are used in the hydrotreating, little incorporation of sulfur into the nearly sulfur-free biomass oils is occurring.

COMPONENT ANALYSIS IN GASOLINE-RANGE DISTILLATES

More detailed analysis of several gasoline-range distillates from the hydro-treated biomass-derived oils has been undertaken. These analyses provide additional detail on the makeup of the products and also further substantiate the relationships of the product composition to product properties. As seen in Table 3, elemental compositions can be compared with component fractionations and component analysis by instrumental methods. To fractionate the components of the distillates, we used the ASTM D 1319 method for determining hydrocarbon types by fluorescent indicator adsorption. By nuclear magnetic resonance (NMR) of carbon-13, similar component groups can be identified and quantified.

For most of the samples listed in Table 3, the D 1319 data compare quite favorably with the C-13 NMR results. The aromatic and aliphatic portions are nearly identical. The D 1319 consistently shows a small olefin fraction in the oil, while the NMR analysis detects essentially no olefinic carbon atoms. Further analysis of the fractions from the D 1319 separation was performed by gas chromatography with a mass selective detector (HP 5970). Individual components in each fraction were identified and semi-quantitatively determined by the intensity of the total ion current for each peak. Components in each of the fractions are listed in Table 4. With this analysis, the NMR results were confirmed, as the primary components of the olefin fraction were found to be bicyclic components. Some difficulty was encountered with this analysis because of the small fraction size and the contamination by the aliphatic fraction. However, no mass spectra of olefin components were confirmed, and the primary components in the fraction could be determined by comparison with the aliphatic fraction analysis.

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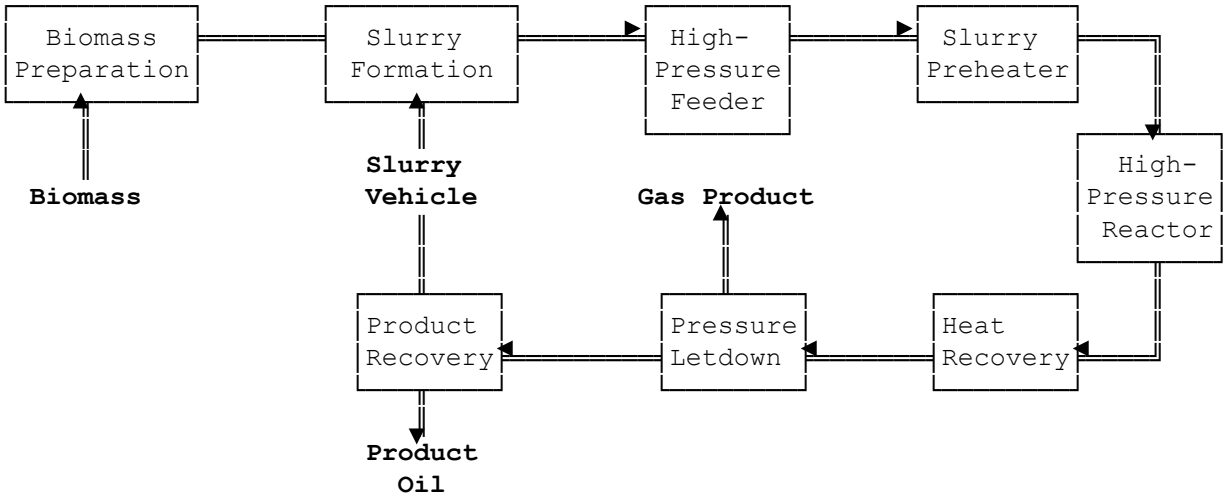

FIGURE 1. Conceptual High-Pressure Liquefaction Process

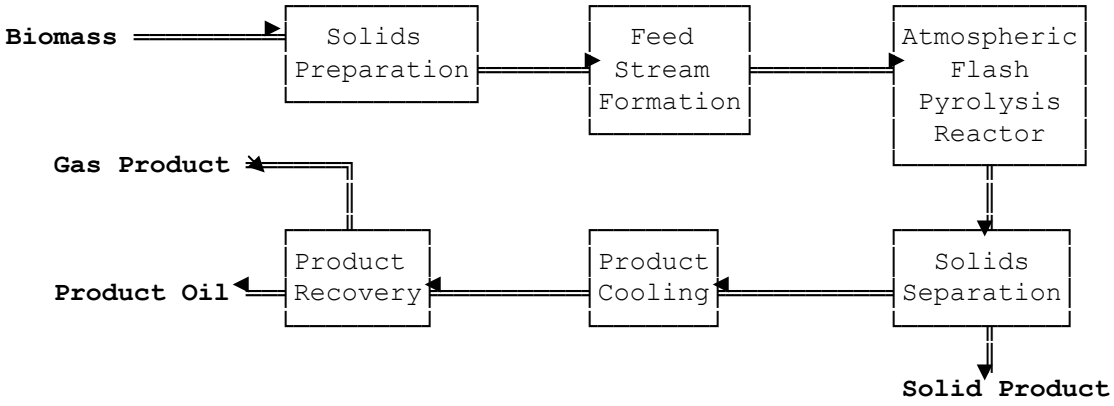

FIGURE 2. Conceptual Atmospheric-Pressure Flash Pyrolysis Process

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TABLE 1. Properties of Direct Liquefaction Products from Biomass

	High-Pressure Liquefaction	Flash Pyrolysis
Elemental Analysis		
Carbon, wt%	72.6	43.5
Hydrogen, wt%	8.0	7.3
Oxygen, wt%	16.3	49.2
Sulfur, ppm	<45	29
H/C atom ratio (dry)	1.21	1.23
Density, g/mL	1.15	1.23
Moisture, wt%	5.1	24.8
HHV, Btu/lb	15,340	9,710
Viscosity, cps	15,000 @ 61°C	59 @ 40°C
Distillation Range		
IBP-225°C	8%	44%
225°C-350°C	32%	coked
350°C-EP(°C)	7%	

TABLE 2. Range of Properties of Hydrotreated Biomass Liquefaction Products

Elemental Analyses	
Carbon, wt%	85.3 - 89.2
Hydrogen, wt%	10.5 - 14.1
Oxygen, wt%	0.0 - 0.7
Sulfur, ppm	50
H/C atom ratio	1.40 - 1.97
Density, g/mL	0.796 - 0.926
Moisture, ppm	10 - 80
HHV, Btu/lb	18200 - 19500
Viscosity, cps	1.0 - 4.6 @ 23°C
Aromatic/ Aliphatic Carbon	38/62 - 22/78
Distillation Range	
IBP-225°C	>97% - 36%
225°C-350°C	0% - 41%
EP(°C)	188°C - 348°C

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TABLE 3. Distillate Products from Hydrotreatment

								C-13 NMR					
ELEMENTAL ANALYSIS, %				Density	HHV	gasoline	BP range	aromatic/	actual*	aromatic / aliphatic / olefin	Octane Numbers		
carbon	hydrogen	H/C ratio	oxygen	g/mL	Btu/lb	IBP-225ºC		aliphatic	aromatic	D1319	MON	RON	R+M/2
86.6	12.1	1.66	1.3	0.844		100%	23-225	28/72	43%	44.1 / 55.1 / 0.8	72.0	77.0	74.5
85.4	12.5	1.74	2.2	0.791		100%	68-176	29/71	25.4%	39.5 / 53.6 / 6.9			
87.1	12.0	1.64	0.9	0.859		100%	23-225	30/70	29.0%	47.4 / 48.3 / 4.3			
86.2	13.1	1.81	0.6	0.823	18990	100%	23-225	24/76	32%	33.9 / 63.3 / 2.8	72.8	78.1	75.5
				0.810		100%	23-165	20/80	28%	28.3 / 69.9 / 1.8			
86.0	12.7	1.75	1.3	0.803		100%	72-157	22/78	29%	33.7 / 59.1 / 7.2			
84.3	13.7	1.93	1.5	0.782		100%	57-183	12.4/87.6	18%	18.1 / 77.1 / 4.8			
85.6	13.3	1.84	1.2	0.802		100%	63-149	16/84	20%	28.3 / 68.6 / 3.1			

* "actual aromatic" is the sum of the aromatic carbon and the non-aromatic substituents on the aromatic rings.

TABLE 4. Components of D 1319 Chromatography Fractions
(within each fraction, from highest total ion current)

Saturated Hydrocarbons	Olefinic Hydrocarbons
ethylcyclohexane	octahydroindene
propylcyclohexane	octahydropentalene
methylethylcyclohexane	methyloctahydropentalene
methylcyclohexane	
methylpropylcyclohexane	
methylethylcyclohexane	
methylpropylcyclopentane	
ethylpropylcyclohexane	
dimethylcyclohexane	
methylcyclopentane	

Aromatic Hydrocarbons	Alcohol Soluble Components
ethylmethylbenzene	dimethylphenol
methylpropylbenzene	naphthalene
propylbenzene	ethylphenol
C4-alkyl-benzene	cresol
C2-alkyl-tetralin	ethylmethylphenol
methyltetralin	cresol
tetralin	methylnaphthalene
methylindan	ethylmethylphenol
C5-alkyl-benzene	dimethylphenol
methylpropylbenzene	ethyl phenol