

CATALYTIC HYDROTREATING OF BIOMASS-DERIVED OILS

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INTRODUCTION

Pacific Northwest Laboratory (PNL) is investigating the catalytic upgrading of biomass-derived oils to liquid hydrocarbon fuels. Tests have been conducted in a 1-liter, continuous feed, fixed-bed catalytic reactor at 250-450°C and 2,000 psig. This is envisioned as the second stage in a two-stage process to produce hydrocarbon fuels from biomass. Given that biomass can be converted to a liquid product, widely reported as phenolic (1-4), then oxygen removal and molecular weight reduction are necessary to produce usable hydrocarbon fuels. Upgrading biomass derived oils differs from processing petroleum fractions or coal liquids because of the importance of deoxygenation. This topic has received only limited attention in the literature (5-9).

HYDROTREATING BIOMASS-DERIVED OILS

Two types of biomass-derived oils have been studied at PNL. The first type of oil is produced by high pressure liquefaction at relatively long residence times. Oils identified as TR7 and TR12 in Table 1 were produced by this type of process at the Albany, Oregon Biomass Liquefaction Experimental Facility. These highly viscous oils consist primarily of substituted phenols and naphthols. The other type of oil is produced by low pressure flash pyrolysis at somewhat higher temperature and very short residence times. These oils are highly oxygenated and contain a large fraction of dissolved water. Because of the soluble water these have a much lower viscosity. The flash pyrolysis oil produced at Georgia Tech is typical of this type of oil. The fourth oil shown in Table 1 was made at PNL by pretreating the Georgia Tech pyrolysis oil to produce an oil more similar to the high pressure oils. Details of the pretreating step are given by Elliott and Baker (10).

Figure 1 shows some model reactions that are typical of what is required to produce liquid hydrocarbon fuels from biomass-derived oils. The three compounds, 2-methyl-2-cyclopentene-one, 4-methyl guaiacol, and naphthol are typical components of biomass-derived oils. The single ring compounds are upgraded primarily by deoxygenation. Hydrogenation of the aromatic structure is not desirable if high octane gasoline is the intended product, but it may be necessary as part of the pathway to cracking multiple ring compounds. Previous studies showed CoMo, NiMo and in particular sulfided CoMo to be the most effective catalysts for this combination of reactions (6). The heavy fraction of biomass-derived oils is not as well characterized and the reaction mechanism for upgrading is unknown. Use of an acidic support (such as a zeolite) compared to alumina may be beneficial for upgrading the high molecular weight fraction.

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RL0 1830.

TABLE 1. Feedstock Oils for Hydrotreating Tests

	TR7		TR12		Georgia Tech Pyrolysis Oil		Treated Georgia Tech Pyrolysis Oil	
	As Fed	Dry	As Fed	Dry	As Fed	Dry	As Fed	Dry
	Elemental Analysis, wt %							
Carbon	74.8	77.5	72.6	76.5	39.5	55.8	61.6	71.6
Hydrogen	8.0	7.9	8.0	7.8	7.5	6.1	7.6	7.1
Oxygen	16.6	14.1	16.3	12.5	52.6	37.9	30.8	21.1
Nitrogen	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ash	0.5	0.5	3.0	3.0	0.2	0.3	0.0	0.0
Moisture	3.5	0.0	5.1	0.0	29.0	0.0	14.1	0.0
Density, g/ml @ 55°C	1.10	--	1.09	--	1.23	--	1.14 ^(a)	
Viscosity, cps, @ 60°C	3,000	--	17,000	--	10 ^(c)	--	14,200	
Carbon Residue, wt% ^(b)	13.5	13.9	26.9	28.3	--	27-31 ^(c)	--	

a) at 20°C

b) TGA simulated Conradson carbon, see reference 12

c) Viscosity and carbon residue were measured for other similar pyrolysis oils

EXPERIMENTAL

The reactor system used for this study is a nominal 1-liter, continuous feed, fixed-bed reactor operated in an upflow mode. It has been described in detail previously (10,11). Operation in the downflow mode (trickle-bed) plugged the outlet line of the reactor with coke-like material and tests in this mode were discontinued. The oil feedstock, preheated to 40-80°C, is pumped by a high-pressure metering pump. Hydrogen from a high-pressure cylinder is metered through a high-pressure rotameter into the oil feed line prior to entering the reactor vessel. The reactor is 7.5 cm I.D. by 25 cm and holds approximately 900 ml of catalyst.

A two phase flow pattern exists in the reactor. Gas and volatile products move through the reactor quite rapidly. Unconverted, non-volatile material does not leave the reactor until it reaches the top of the liquid level and overflows into the product line. Pressure in the system is maintained by a Grove back-pressure regulator. Liquid product is recovered in a condenser/separator and the offgas is metered and analyzed before it is vented.

Catalysts used in the most recent hydrotreating tests are shown in Table 2. The Harshaw catalysts are conventional extruded CoMo and NiMo hydrotreating catalysts. The Haldor Topsoe catalysts are a composite system using low activity rings in the bottom of the bed to prevent plugging from carbon and metals, and high activity extrudates in the top of the bed. The last two catalysts are specialty catalysts incorporating a zeolite in the base to provide more acidity and promote cracking reactions.

TABLE 2. Catalysts Used for Hydrotreating Tests

Supplier Catalyst ID	Harshaw		Haldor Topsoe ^(b)			PNL/ Union Carbide	Amoco
	HT-400	HT-500	TK-710	TK-750	TK-770	CoMo/Y	NiMo/Y
Active metals, wt%	3% CoO 15% MoO ₃	3.5% NiO 15.5% MoO ₃	2% CoO 6% MoO ₃	2.3% CoO 10% MoO ₃	3.4% CoO 14% MoO ₃	3.5% CoO 13.9% MoO ₃	3.5% NiO 18% MoO ₃ 2.5% P ₂ O ₅
Support	Al ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃	Y-zeolite/ Al ₂ O ₃	Y-zeolite/ Al ₂ O ₃
Form ^(a)	1/8-in E	1/8-in E	3/16-in R	3/16-in R	1/16-in E	1/16-in E	1/16-in E

a) E - Extrudate, R- Rings, size given is O.D.

b) All three catalysts used in a layered bed

RESULTS AND DISCUSSION

The following discussion deals primarily with recent tests with TR12 oil and CoMo catalysts. Results of previous tests with other oils and catalysts will be summarized as they relate to the most recent efforts.

Tests with Cobalt-Moly Catalysts

Most of the test work has been done with the TR12 and TR7 oils and various sulfided CoMo catalysts. Table 3 shows results obtained with the TR12 oil and the Haldor Topsoe composite catalyst system at about 400°C, 2,000 psig and three different space velocities. Typically, the liquid product yield from the TR12 oil is about 0.9 l/l of oil fed. At the low space velocity (0.11) the oil is 96% deoxygenated and is about one-third high quality aromatic gasoline (C₅ - 225°C). At even lower space velocities (~0.05) a liquid product containing about 60% gasoline and almost no oxygen can be produced. At higher space velocities (up to 0.44) deoxygenation is still good, nearly

TABLE 3. Results of Hydrotreating TR12 Oil with Haldor Topsoe Composite Catalyst

Run No.	HT-34	HT-34	HT-34
Temperature, °C	397	395	403
Pressure, psig	2,020	2,015	2,030
Space Velocity, LHSV, hr ⁻¹	.11	.30	.44
Hydrogen Consumption, l/l oil fed	548	296	212
Product Yield, l/l oil fed	.92	.88	.94
Deoxygenation, wt%	96	87	79
Product Inspections			
Oxygen, wt%	0.8	2.5	3.8
H/C ratio, mole/mole	1.5	1.3	1.3
Density, kg/l	0.91	1.0	1.03
Yield C ₅ - 225°C, LV%	37	24	11

80%, but hydrogen consumption decreases 50% or more resulting in a lower H/C ratio, higher density, and lower gasoline yield. The theoretical hydrogen requirement to deoxygenate TR12 is about 200 l/l of oil. This indicates that at the low space velocity 350 l H₂/l oil is being used for hydrogenation, hydrocracking and other reactions. At the highest space velocity only about 50 l H₂/l oil is being used by these other reactions.

Table 4 shows results from hydrotreating TR7 with Harshaw CoMo/Al₂O₃ catalyst. Tests with the Harshaw catalyst and TR12 oil were similar to those with the Haldor Topsoe composite catalyst indicating the differences between Tables 3 and 4 are due primarily to the oil. At similar processing conditions, the products from TR7 are higher quality than those obtained from TR12. Analysis of TR7 and TR12 oils indicates TR7 is primarily single ring phenolics which when deoxygenated become gasoline boiling range aromatics. The TR12 oil is primarily double ring phenolics which require additional cracking and hydrogenation to produce light distillates.

When the Georgia Tech pyrolysis oil was hydrotreated with a sulfided CoMo catalyst at conditions similar to those used with TR7 and TR12 the runs had to be terminated due to severe coking in the bed. The temperature had to be reduced to 250^o-270^oC to prevent coking. The properties of the oil produced at these low temperatures are shown in Table 1 under the heading of treated Georgia Tech pyrolysis oil. This oil was further hydrotreated at 350^oC and 2,000 psig with a sulfided CoMo catalyst and the results were similar to those obtained with TR7 and TR12. This is the basis for a proposed two stage upgrading process for biomass pyrolysis oils (10).

Results to date indicate 400^oC is about the optimum temperature for hydrotreating biomass-derived oils. At 350^oC a much poorer quality oil is produced. At 450^oC the product quality improves somewhat compared to 400^oC but the yield is reduced due to increased gas production.

TABLE 4. Results of Hydrotreating TR7 Oil with Harshaw CoMo/Al₂O₃*

Run. No.	HT-15	HT-14	HT-14
Temperature, °C	398	394	389
Pressure, psig	2,003	2,021	2,026
Space Velocity, LHSV, hr ⁻¹	0.10	0.30	0.55
Hydrogen Consumption, l/l oil fed	616	435	202
Product Yield, l/l oil fed	0.99	1.0	0.88
Deoxygenation, wt%	~100	94	88
Product Inspections			
Oxygen	0.0	1.1	2.6
H/C ratio, mole/mole	1.65	1.41	1.32
Density, kg/l	0.84	0.91	0.96
Yield C ₅ -225 ^o C, LV%	>87	60	28

* adapted from reference 11

Other Catalysts

In early tests with the TR7 oil where gasoline boiling range material was the primary product, the CoMo catalysts were preferred over NiMo because they retained the aromatic character and antiknock properties of the product. The NiMo catalysts were more active for hydrogenation and produced primarily saturated cyclic compounds (naphthenics) with a lower octane rating. With the TR12 oil a more active hydrogenation catalyst such as NiMo may be beneficial. Adding a cracking component such as γ -zeolite to the catalyst may also be advantageous with the TR12 oil. Preliminary tests with a NiMoP/ γ -zeolite/ Al_2O_3 catalyst obtained from Amoco are promising in this regard.

Catalyst Deactivation

A 48-hour test run was recently completed with TR12 oil and the Haldor Topsoe catalyst to evaluate catalyst deactivation. Figure 2 shows the trend of deoxygenation and hydrogen consumption at an LHSV of 0.1. Hydrogen consumption and the H/C mole ratio (not shown) fell rapidly in the early stages of the test and then leveled off. Deoxygenation fell throughout the test.

Two causes of deactivation have been postulated. The initial deactivation is likely due to coking of the catalyst which we have shown in earlier tests occurs primarily in the first ten hours (11). The longer term deactivation is probably due to buildup of metals, primarily sodium, from the oil. The TR12 oil contains about 3% ash, mostly residual sodium catalyst from the liquefaction process.

CONCLUSIONS

A variety of biomass-derived oils have been upgraded by catalytic hydrotreating in a 1-liter reactor system. Specific conclusions from our studies are as follows:

- High yields of high quality gasoline (C_5 - 225°C boiling range) can be produced from biomass-derived oils, however, low space velocities (long residence times) are required. At high space velocities a low oxygen, highly aromatic crude oil is produced.
- Cracking and hydrogenation of the higher molecular weight components are the rate limiting steps in upgrading biomass-derived oils. Catalyst development should be directed at these reactions.
- The TR7 oil is superior to TR12 and both are much superior to pyrolysis oils as feedstocks for catalytic hydrotreating to produce hydrocarbon fuels.
- Pyrolysis oils can be upgraded by catalytic hydrotreating, however, a catalytic pretreatment step is required.
- Residual sodium catalyst needs to be removed from liquefaction products to prevent rapid catalyst fouling.

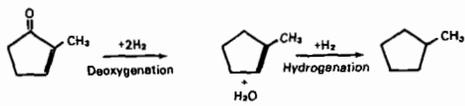
ACKNOWLEDGEMENT

The authors acknowledge the dedicated efforts of W. F. Riemath and G. G. Neuschwander of PNL who assisted in reactor operation and product analysis. The work was funded by the Biomass Thermochemical Conversion Program office at PNL under the direction of G. F. Schiefelbein, D. J. Stevens, and M. A. Gerber. We would also like to acknowledge the support of S. Friedrich of the Biofuels and Municipal Waste Technology Division of the U. S. Department of Energy.

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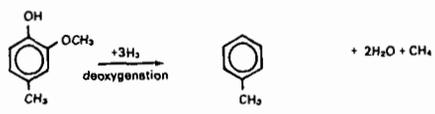
2 - Methyl - 2 - Cyclopentene - One Methyl Cyclopentene Methyl Cyclopentane



4 - Methyl Guaiacol

Toluene

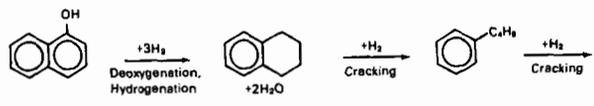
Methane



Naphthol

Tetralin

Butyl Benzene



Benzene

Butene



C₄H₁₀

FIGURE 1. Some Reactions in Catalytic Hydrotreating Biomass-Derived Oils

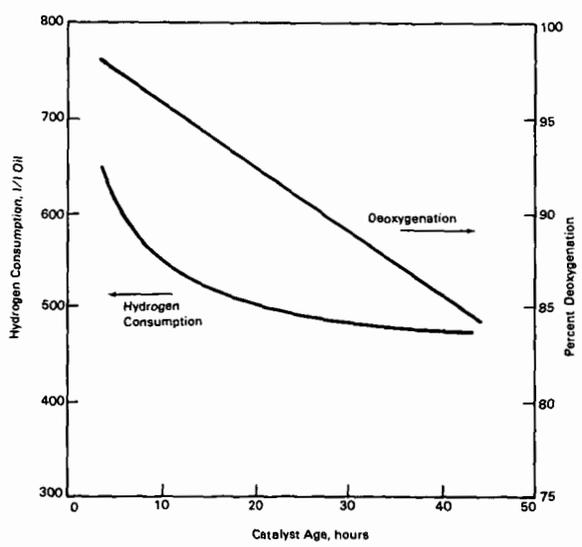


FIGURE 2. Effect of Catalyst Age on Deoxygenation and Hydrogenation, 400°C, 2,000 psig, LHSV = 0.1