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LIQUID FUELS BY LOW-SEVERITY HYDROTREATING OF BIOCRUDE

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Abstract
Biocrude (fast pyrolysis oil from wood) was hydrotreated to minimize the negative aspects of this fuel. The instability of the oil was reduced by reaction of the most unstable functional groups. Concurrently, the oxygenated component of the oil was also reduced, resulting in an improved energy density. Changes in the physical handling properties were also modified. All of this change was accomplished at less severe processing conditions (lower temperature, shorter residence time) than that required for the earlier processing for gasoline production. Improved conversion was achieved by the use of a downflow reactor system. The experiments reported include those performed with clean (filtered hot vapor) biocrude just recently available from processing systems in the U.S.
Key words: biocrude, catalysis, fast pyrolysis, fuel oil, hydrotreating, upgrading

1 Introduction

Low-severity hydrotreating is one means to improve the fuel properties of biocrude (fast pyrolysis oils from wood). As produced, biocrude has some undesirable properties as fuel, such as: some thermally unstable components which can lead to gum formation, low energy density because of dissolved water and highly oxygenated compounds, a corrosive organic acid component, and phase instability with a tendency toward phase separation. High-severity hydrotreating, involving complete hydrodeoxygenation, some hydrocracking and minimal hydrogenation to produce an aromatic hydrocarbon fuel, is an expensive way to remedy these problems. As an alternative, we are developing low-severity hydrotreatment methods to improve the fuel oil properties. Low-severity hydrotreating involves partial hydrodeoxygenation, minimal hydrocracking, and effective hydrogenation to stabilize the biocrude and improve its energy density and handling properties.

Hydrotreating of biocrude has been under development for a decade. Initial efforts were stymied by the instability of the biocrude which required development of process modifications to specifically address the instability. A low-temperature catalytic hydroprocessing has been identified as an important first step in the overall process [1]. But low-temperature catalytic hydroprocessing alone does not yield a useful fuel oil product from the biocrude [2] [3] [4] [5]. The product is a viscous black tar which is more thermally stable and can even be distilled; but it still contains high levels of chemically combined oxygen and dissolved water.

Hydrodeoxygenation by catalytic processing has been developed for biocrude based on the initial stabilization by low-temperature hydroprocessing. Hydrocarbon products with gasoline and light fuel oil distillation ranges were produced from the biocrude. The hydrogen consumption for this processing was high with overall product yields in the range of 30% by weight of the biocrude [4] [6]. Initial estimates of the processing costs were high [7] [8]. Catalyst stability and gum formation in the biocrude feed lines were identified as process uncertainties.

As a result of the high costs calculated for gasoline production from biocrude, emphasis has shifted to lower cost processing to produce heavier products such as turbine fuel for electricity generation or as a first step toward cofeeding to a conventional petroleum refinery. Low-severity hydrotreating is an attempt to upgrade biocrude to a useful fuel oil product with a minimum of cost through catalytic hydroprocessing. Low-severity hydrotreating for upgrading biocrude has been under investigation for the past several years. Laurent et al. [9] pointed out the better economic possibilities in low severity processing to heavy fuel oils. A resulting design for a pilot plant considered turbine fuel production by low-severity hydrotreating [10]. Initial attempts show that the low-severity product can be produced at a lower cost [11], but the level of upgrading required versus the product properties needs to be further investigated.

Experimental attempts to produce low-severity hydrotreating products at Pacific Northwest National Laboratory (PNNL) have been reported with limited success [12]. Non-steady-state operations have plagued the experiments. Product quality has been lower than expected with higher viscosities (far outside the turbine fuel specification range) and oxygen contents of 20% and higher. The results led the researchers to redesign the continuous-feed reactor system to the down-flow configuration reported here. This research is also making use of the recent developments in biocrude cleanup via hot vapor filtration as well as catalyst improvements for hydrodeoxygenation of biocrude.

2 Bench-scale systems for hydroprocessing biocrude

The biocrude feedstocks used in these experiments was provided to us by Union Electrica Fenosa SA (UF) and the National Renewable Energy Laboratory (NREL). The UF oil was produced from eucalyptus in a fluidized bed flash pyrolysis system. The sample was over a year old at the time of our experiments. It was not filtered in the production process. The NREL oil was produced from hybrid poplar in an ablative fast pyrolysis system (M2-Run 6 at Hazen). The hot pyrolysis vapors were cleaned in a filter bag house prior to condensation and collection. The biocrude was only two months old at the time of the hydrotreating experiments. A sample from Ensyn Technologies, Inc. (RTP3) was also tested for comparison. The sample was at least 4 years old at the time of our testing. Analyses of these oils in given in Table 1.

2.1 Continuous-feed fixed-bed reactor system

The reactor system included two vessels containing fixed catalyst beds. The system was run in a down-flow (trickle bed) configuration in which the top bed (100 mL) served as the low-temperature stabilization reaction vessel and the bottom bed (425 mL) served as the main hydrotreater at higher temperature.

As shown in Figure 1, the oil was fed by a reciprocating high-pressure pump and the hydrogen entered the oil feed line from a gas manifold prior to the two reactor vessels. Pressure was controlled in the system by a dome-loaded back-pressure regulator (Teflon diaphragm) in the

product line. Liquid and gaseous products were separated in a two- stage system of coolers and gas/liquid separators before they were recovered and analyzed.

Table 1. Biocrude Feedstocks for Low-Severity Hydrotreating

property	NREL	UF	RTP3
carbon, %	46.7	44.8	39.4
hydrogen, %	7.6	7.2	7.9
oxygen, %	45.7	48.1	52.7
nitrogen, %	0.2	0.2	0.2
sulfur, %	0.032*	NA	NA
ash, %	0.016*		0.1*
HHV, MJ/Kg	NA	NA	16.7*
density, g/mL	1.19		1.19
viscosity, cps	127	1510	43
suspended solids, %			
moisture, %	18.9*	NA	~24
K, ppm	5*	NA	30*
Ca, ppm	6*	NA	260*
Na, ppm	4*	NA	43*
Cl, ppm	8*	NA	NA

* analysis provided by NREL

The system was constructed of stainless steel (300 series) throughout all wetted parts. It is rated to 21 MPa. Feed lines were 6 mm (¼"), and the reactor effluent lines were 13 mm (½"). The feed lines were insulated and heat traced. Line heating up to 50°C was used with the Union Fenosa oil, while the other oils required no line heating for smooth pumping. Temperatures in the two reactor beds were controlled independently. The first bed temperature was controlled in two levels. Strong exothermic reactions occurred at times in the reactor beds. These were believed to result if pyrolysis condensation reactions overwhelmed the hydrogenating function of the catalyst. Coke formation in the catalyst bed resulted. The exotherms were controlled by sufficient low temperature hydrotreating to stabilize the biocrude before allowing the oil to be heated above 300°C.

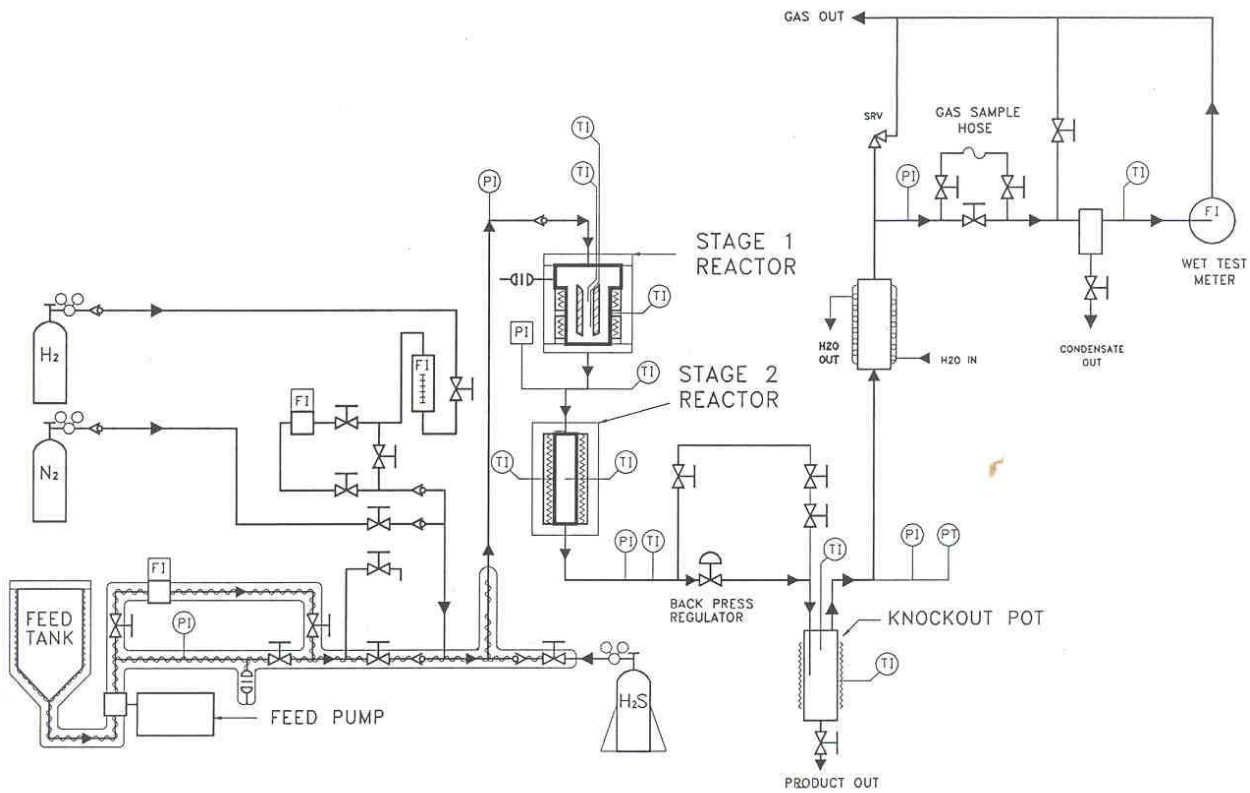

Fig. 1. A schematic of the bench-scale, continuous-feed, fixed-bed reactor system.

3 Experimental Results

The goal of this research was to determine the types and amounts of product oils which could be produced from biocrude at low-severity conditions. The work included both preliminary tests with highly active hydrogenation catalysts at low temperatures to evaluate the types of products which might be produced and developmental tests in the continuous-feed reactor to verify production rates and yields at a range of low severity conditions with conventional hydrotreating catalysts. The batch reactor results are presented in a separate report.

The results presented in this chapter were produced in recent experiments in the continuous feed catalytic hydrotreater at PNNL operated in a downflow configuration. The tests were made with three different biocrudes as described in Table 1. The bulk of the tests were made with a single batch of NiMo on alumina catalyst (Haldor Topsoe TK-751, 1 mm extrudates). The catalyst was placed in both reactors and presulfided with hydrogen sulfide 10% in hydrogen with a temperature ramp up to 400°C. A single charge of the NiMo catalyst was replaced in the first stage reactor after the initial test in which temperatures went outside the acceptable operating range and plugging occurred. The same catalyst charge was used in the balance of the NiMo tests. A second catalyst was also tested (BASF K8-11). This CoMo catalyst is unlike the NiMo in that the support is a spinel

not the conventional high surface area γ-alumina. Better chemical stability of the support was envisioned, but the catalyst exhibited much lower activity overall.

The results of these tests are summarized in Table 2 below. Higher levels of conversion were seen in the downflow configuration compared to earlier upflow tests. High levels of hydrogen consumption and high product quality were seen even at much higher space velocity. Product oils were analyzed to quantify the effect of space velocity on the product properties. The two catalysts had significantly different activities. The different feed oils also had different levels of reactivity. The results are compared with literature values below.

Table 2. Biocrude hydrotreating results

	NREL -- downflow -- NiMo/alumina catalyst							CoMo/spinel	
1st temperature, °C	150	148	148	150	150	148	148	148	157
2nd temperature, °C	380	375	354	349	349	362	355	400±15	435±45
LHSV, L/L/hr	0.28	0.30	0.29	0.29	0.29	0.43	0.38	0.38	0.31
WHSV, g/g/hr	0.52	0.54	0.53	0.53	0.54	0.78	0.70	0.64	0.51
Yield, g/g biocrude	0.42	0.39	0.38	0.44	0.49	0.47	0.53	0.21	0.21
Deoxygenat'n, %	98.6	97.9	96.3	95.1	95.0	94.5	95.8	97.6	97.1
Density, g/mL	0.82	0.84	0.84	0.86	0.86	0.86	NA	NA	NA
Gasificat'n, %Carbon	27	20	22	25	33	29	29	23	22
H_2 Consumpt'n, L/L	881	746	727	808	813	791	779	494	313
Carbon balance, %	92	79	79	91	107	101	109	54	53

4 Discussion and Conclusions

4.1 Space velocity effects

The experimental reactor results are evaluated in terms of deoxygenation, which incorporates the effects of temperature, pressure and catalyst. The deoxygenation is defined as the percent of chemically combined oxygen in the biocrude removed when compared to the oil product. Deoxygenation as a function of space velocity shows a dramatic effect. In Figure 2 space velocity is presented in terms of volume (liquid hourly space velocity, LHSV). By this measure the new downflow results in this paper stand out clearly compared to all of the earlier published results. Earlier, we agreed with VEBA that the difference between downflow and upflow operation was small considering the overall reaction and the little difference between our earlier upflow results and those of VEBA (on a LHSV basis). However, Figure 3 provides a data comparison on a weight basis (weight hourly space velocity, WHSV) wherein the effect of the diluted CoMo catalyst bed used by VEBA is dramatic. By using the diluted CoMo catalyst bed, VEBA achieved much higher processing rates based on the weight of catalyst. The one unexplained result is the poor showing of the NiMo catalyst in the downflow experiments at VEBA. Again, our downflow results are much improved compared to our earlier upflow results. In all of these tests the catalysts are supported on an alumina base. The differences in the results comparing the use of CoMo with NiMo in our earlier tests are relatively small in light of the differences in results achieved with downflow operation compared to upflow.

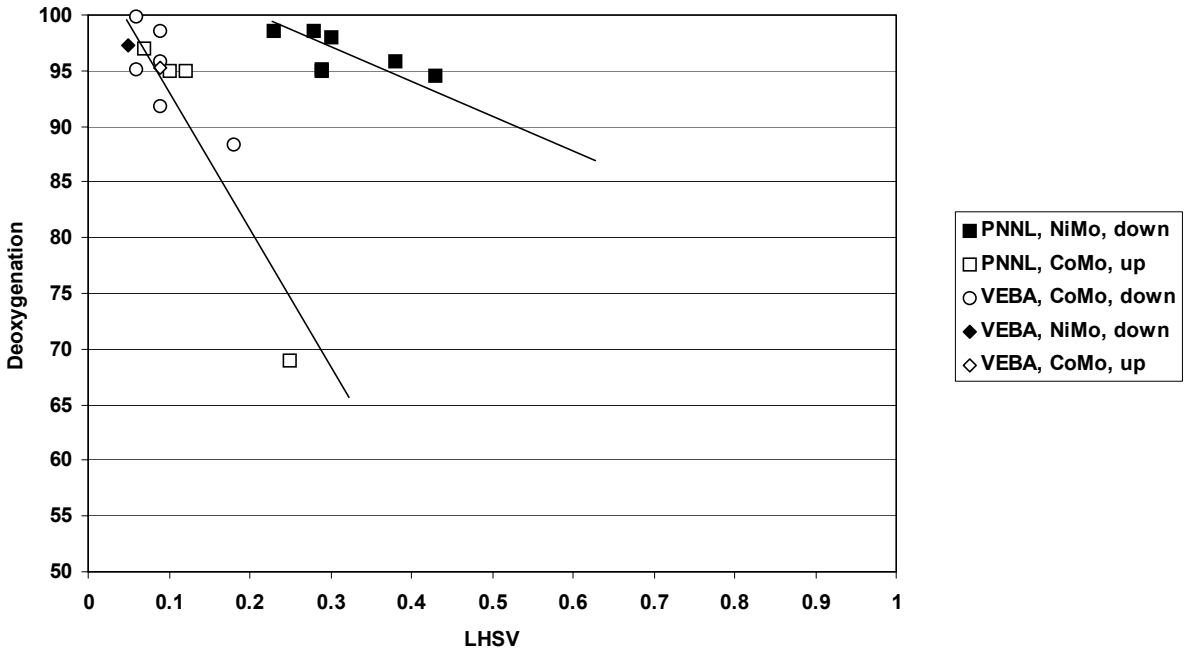

Fig. 2. Deoxygenation on a liquid hourly space velocity basis

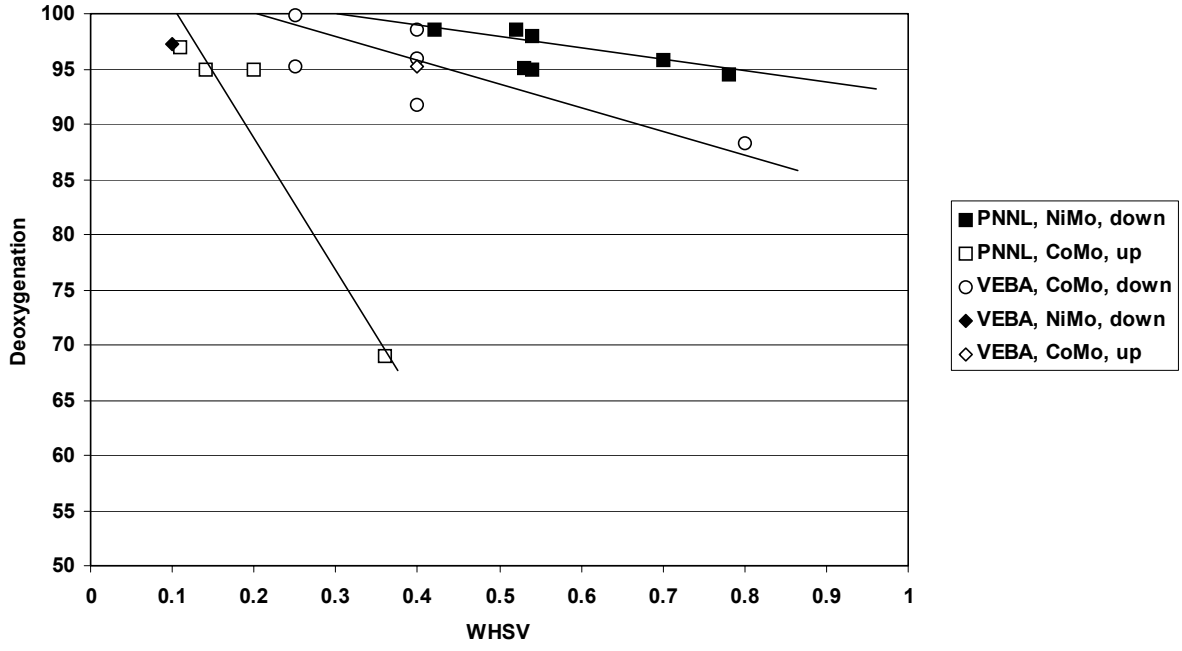

Fig. 3. Deoxygenation on a weight hourly space velocity basis

4.2 Product oil properties

The product oil density is clearly a function of product oil oxygen content as seen in Figure 4. The molecular weight may also be correlated with the oxygen content as they may both be changing coincidentally as a function of processing severity. Figure 4 shows that the function of oxygen content and density seems to apply to the full range of products reported in the literature as well as those from these tests. An important conclusion to draw from these data is that the product oil density approaches 1 at a relatively low oxygen content, about 10%. Products with oxygen contents around 10-15% and densities around 1 tend to form mixtures (emulsions?) with the water byproduct and can not be easily separated from the water. This lack of separation defeats one important purpose of the hydrotreating which is to remove the water and, thereby, dramatically improve the energy content of the oil.

Viscosity of the product oil is also a function of the oxygen content, as seen in Figure 5. The range shown goes all the way from the low viscosity required for turbine fuels of less than 5 cps to the heavy tar products with high oxygen contents and viscosities >100,000 cps whose pour points would be around room temperature. These results suggest that only the highly upgraded oils with oxygen contents of 5% or less have potential for direct use as turbine fuels because of viscosity limitations. Figure 4 also includes the data for the 3 biocrudes. The raw biocrudes show decreasing viscosity with increasing oxygen content because of increasing water content in the raw biocrude. These biocrude numbers suggest the use of oxygenated solvents to decrease the biocrude viscosity to the useful range for turbines thus allowing its direct use without chemical processing. However, use of water as the solvent for viscosity reduction of the biocrude does not appear feasible because phase separation would occur before the viscosity would be reduced to a level useful in turbines.

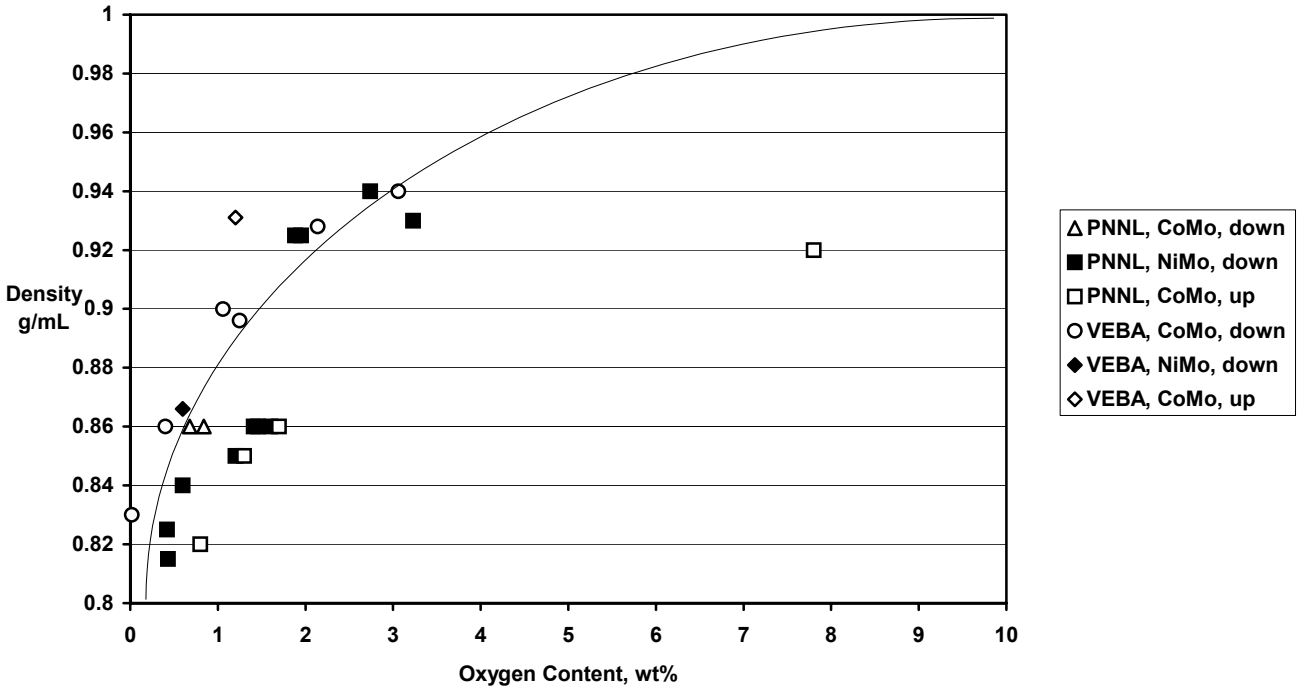

Fig. 4. Relation of product oil density to oxygen content

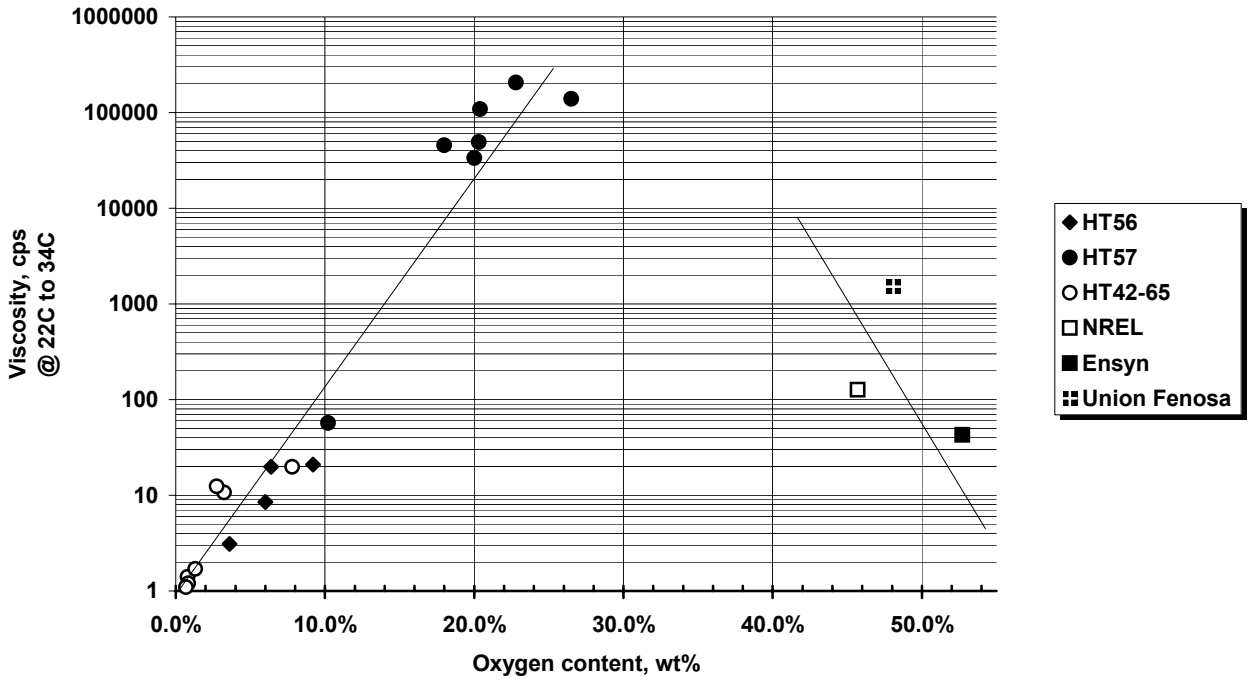

Fig. 5. Relation of oil viscosity to oxygen content

Figure 6 shows the effect of temperature on viscosity of several of the heavy oil products. These results suggest that the highly oxygenated products could not be used as turbine fuels because of high viscosity even with preheating. The 10% oxygen oil might be used as turbine fuel with preheating to 50°C or higher.

4.3 Byproduct water contamination

Organic contamination of the water byproduct from hydrotreating is a concern relative to the overall wastewater treatment requirements for the plant. Figure 7 clearly shows that the contamination of the byproduct water as represented by the carbon content increases with the oxygen content of the product oil up to a range of 5 to 10 wt% when the product oil oxygen content is >10%. At that level the oil water separation is difficult and oil phase contamination of the water samples leads to great variation in the results. Samples representing part and all of the oil product for 2-stage upflow tests are given.

4.4 Biocrude feed effects

The effect of biocrude feed properties on the reactivity can be significant. Whereas the work in our lab in earlier years used a number of biocrude oils including several hardwood oils from different fluid-bed pyrolysis reactors, pine oil from ablative pyrolysis, hardwood oil from vacuum pyrolysis, and poorly-humified-peat oil from fluid-bed pyrolysis without identifying any major differences in reactivity; the current work shows large differences between poplar oil from ablative pyrolysis and eucalyptus oil from fluid-bed pyrolysis. Table 3 provides some of the results. Although the

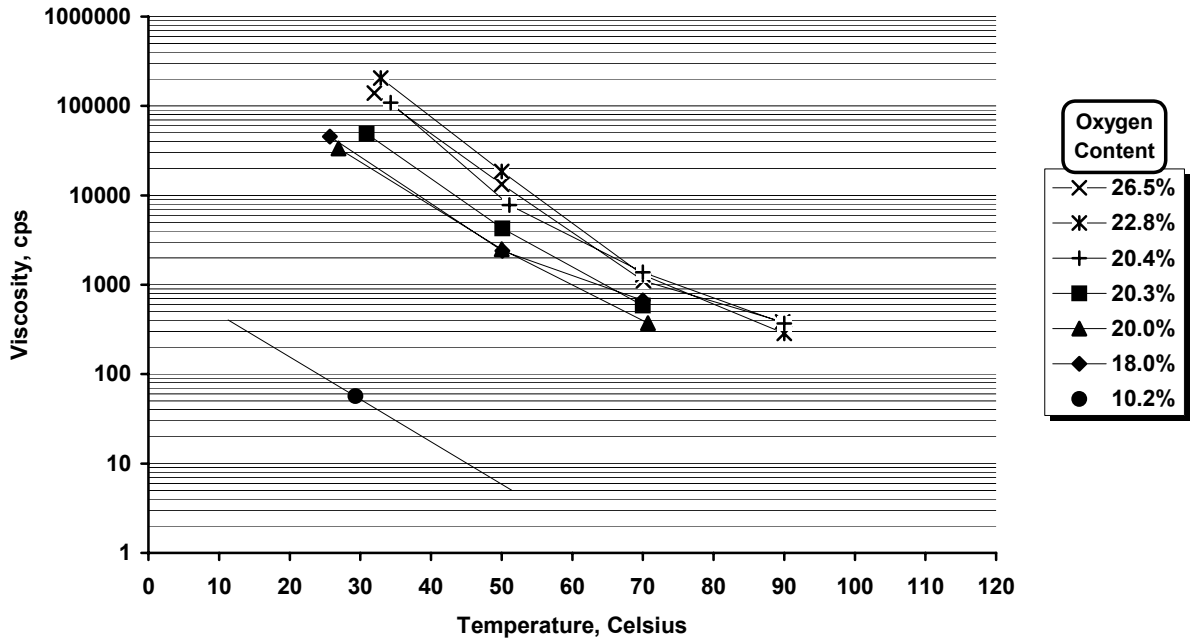

Fig. 6. Effect of temperature on oil viscosity

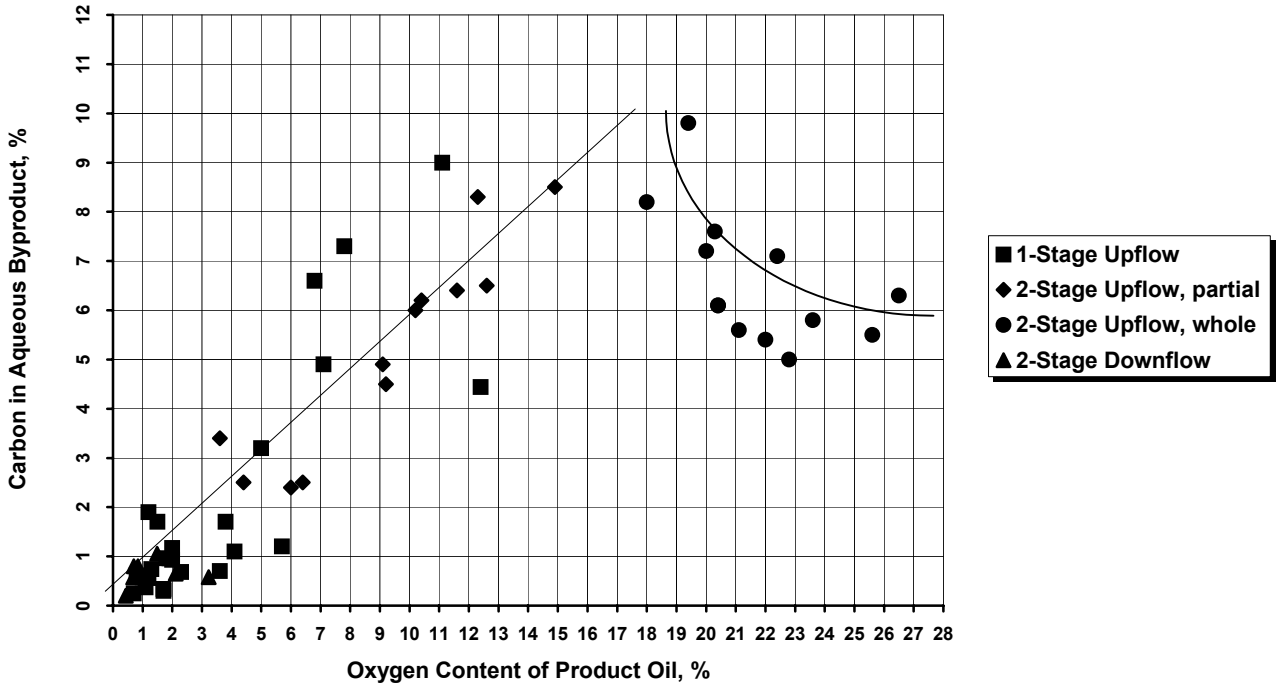

Fig. 7. Relation of carbon in the aqueous phase to the oxygen content of the oil

eucalyptus oil test was performed at higher temperature and lower space velocity, the product oil quality was significantly lower, i.e., higher oxygen content and density. Further substantiating the conclusion of lower reactivity is the lower gas yield and also the lower hydrogen consumption. The combination of high viscosity and poor pumping performance with the lower reactivity make the eucalyptus oil more difficult to hydrotreat.

Table 3. Hydrotreating results with different biocrudes

	NREL	Union Fenosa
Temperature, °C	355	365
WHSV, g oil/g catalyst/hr	0.70	0.54
Yield, g/g biocrude	0.53	0.41
Deoxygenation, %	96	92
Product density, g/mL	0.86	0.94
Gasification, % carbon	29	17
Hydrogen consumption, L/L oil	779	554
Carbon balance, %	109	85

4.5 Effect of catalyst support

The tests with the spinel supported CoMo catalyst (see Table 2) show the dramatic effect of lower catalyst activity. Without a strong hydrotreating catalyst effect in the reactor, exothermic pyrolysis condensation reactions caused major temperature excursions and lead to coke buildup on the catalyst. Buildup of heavy tar products in the reactor and effluent lines caused plugging and premature experiment terminations. Product fractionation occurred, similarly to the upflow experiments, in which the excess hydrogen gas exiting the reactor carried a substantial portion of the light products out while leaving most of the biocrude still as a heavy tar product. Total carbon balances were difficult to measure, but very low space velocities would be required to effectively hydrotreat the biocrude over this catalyst..

4.6 Hydrotreating economics

The four major cost factors in hydrotreating biocrude are 1) Biocrude cost, 2) Capital cost, 3) Hydrogen cost, and 4) Relative product value. The cost of the biocrude is the largest component in the hydrotreated product costs, therefore the product yield is a primary consideration for process optimization. The cost of capital is significant for this high-pressure process, therefore volume space velocity is a critical factor to maximize in order to reduce the capital cost per unit processed. Hydrogen consumed in the process is a significant cost. It typically can be generated by steam reforming of the byproduct gases. To minimize the cost of the reforming systems or the cost of procured hydrogen, the hydrogen consumption should be efficiently focused on the reactions which provide the product properties of importance, i.e., removing the unstable functional types, like olefinic and carbonyl groups; and removing oxygen. In the end, the process needs to be optimized based on the product oil value relative to the expenditures for the other three factors.

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