

HYDROTREATING OF COPROCESSING DERIVED LIQUIDS

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ABSTRACT

One task of a program, jointly sponsored by Electric Power Research Institute; Hydrocarbon Research, Inc.; Alberta Research Council and Ontario-Ohio Synthetic Fuels Corporation, was to determine the response of various coprocessing derived liquids to hydrotreating. The liquids were collected from an ebullated bed bench unit test performed by HRI. The feedstock was a 1:1 mixture of Ohio No. 5/6 coal and Cold Lake atmospheric resid. The product liquids were separated by distillation into naphtha (IBP to 185°C), distillate (185-343°C) and gas oil (343-470°C).

Scoping tests were performed in a fixed bed hydrotreater to determine suitable conditions for the production of reformer feedstock naphtha and diesel quality distillate. Variables investigated included temperature, pressure and space velocity. A Berty CSTR was employed to measure the kinetics of heteroatom removal from the distillate and gas oil. The resulting products met the specifications for synthetic crude oil feedstocks.

INTRODUCTION

The Alberta Research Council (ARC) has been investigating various coprocessing options to develop a new market for the subbituminous coal reserves and heavy oil/bitumen deposits which are located within the Province of Alberta (1). One promising process option for this purpose is the Hydrocarbon Research Inc., (HRI) coal/oil coprocessing technology which uses hydrocracking over an ebullated bed of supported catalyst to convert coal and heavy oil resids to distillable liquid products (2). In 1985, ARC joined a consortium of Electric Power Research Institute (EPRI), Ontario-Ohio Synthetic Fuels Corporation (OOSFC) and HRI, to develop this technology (Ontario-Ohio Synthetic Fuels Corporation received financial assistance from the State of Ohio, Coal Development Office). Phase I of the program confirmed that both bituminous and subbituminous coals could be converted to high quality liquid synthetic crude oils when coprocessed with heavy oil resids such as Cold Lake atmospheric tower bottoms. Coal conversions exceeded 94% under preferred conditions while distillable oil yields approached 75 wt%.

In 1986, a second phase of the program was initiated with the same contributors. The key objectives of the program were to test alternate feedstocks, to determine catalyst replacement rates and to answer specific questions regarding aspects of the chemistry of the upgrading pathways. One subtask was to investigate processing conditions for the secondary upgrading of distillable oil product fractions. The following paper reports on the activities completed by ARC on the hydrotreating of these coprocessing derived liquids.

EXPERIMENTAL

The distillable liquid product from a bench unit run completed by HRI in their New Jersey facility was separated by distillation into naphtha (IBP-185°C), middle distillate (185-343°C) and a gas oil (343-470°C). The bench unit run was performed on a 1:1 blend of Ohio No. 5/6 coal (dry basis) and Cold Lake atmospheric resid. Properties of these distilled liquids are shown in Table 1. These liquids approached

but did not meet specifications set by synthetic crude refiners or ASTM product requirements (diesel, No. 2 fuel oil).

All three fractions were initially hydrotreated in a Berty continuous flow stirred tank reactor (300 ml). Conditions were preselected based on historical data and literature reports. The required specifications for gas oil were met using a presulfided Amocat 1C catalyst. However, all the target specification for naphtha and middle distillations could not be achieved with this catalyst. It was therefore replaced with the more active Shell 324 or Shell 424 catalysts. Even then some target specifications were still unobtainable so the program was completed using a fixed bed reactor.

For the Berty reactor, five hours were allowed for the system to reach steady state. Product was then collected over a 2-3 hour period. Fresh presulfided catalyst (40 g) was charged into the reactor prior to each test. In the fixed bed reactor a two-hour period was adequate to reach steady state. This was followed by a 1 hour yield period. Conditions were then adjusted and the procedure repeated. In this manner, three runs could be completed within a single working day. A single charge of presulfided Shell 424 (50 g) was used throughout the fixed bed tests. Void space was packed with a silicon carbide filler. The operating parameters investigated were temperature, liquid hourly space velocity (LHSV), reported as g feedstock per g catalyst per hour, and hydrogen partial pressure.

Once conditions to produce a naphtha reformer feedstock had been established (Table 2), a production run was performed in the fixed bed hydrotreater. Over a 7 hour yield period, sufficient naphtha (about 0.5 litre) was produced to test the response of this material to reforming. The test unit for the reformer runs was the same fixed bed hydrotreater as had been used in the hydrotreating studies. Three flow rates were subsequently investigated, again in a single day of operation. The catalyst was Cyanamid PR-7, which was predried but otherwise untreated.

RESULTS AND DISCUSSION

The key objectives of the study were to determine suitable conditions for the production of feedstocks which would be acceptable to synthetic crude refineries or conditions to meet ASTM product specifications (No. 2 fuel oil and diesel fuel). The liquid products derived from the HRI coal/oil coprocessing technology are generally superior to those derived from many other upgrading processes. The catalytic conditions in the ebullated bed ensure that a high proportion of the heteroatoms are removed and that substantial hydrogen addition occurs. The conditions required for secondary hydrotreating therefore are less severe than those for most synthetic crude oils. Commercial coking-derived, synthetic crude oils are presently hydrotreated on site to meet pipeline specifications and again at the refinery to meet process specifications. The quality of the ebullated bed products ensures that on site hydrotreating can be eliminated.

The middle distillate and gas oil used in this study already met the sulfur specifications for synthetic feedstocks and fuels without additional hydrotreating. Nitrogen levels were excessive, however, and the cetane number was low (Table 2). Hydrotreating conditions were therefore selected to bring these properties to acceptable levels.

A secondary objective of the programme was to determine kinetic data for the desulfurization and denitrification reactions. However, the conditions were not initially selected for this purpose, so much of the data was within too narrow a range. Also sulfur analyses were highly scattered especially for the Berty reactor. Product samples were routinely flushed with helium gas to remove dissolved hydrogen sulfide but results were often still high. This effect disappeared after two runs with the fixed bed unit, suggesting that the catalyst may have been the source of the interference. These problems were not resolved within the constraints of the program

and the data was insufficient to complete a kinetic study.

NAPHTHA

In the fixed bed unit, nitrogen specifications (1 ppm) for production of a reformer feedstock were met whenever the hydrogen pressure exceeded 10.3 MPa (1500 psi) and temperature was greater than 315°C. To reduce the sulfur to the desired level required a minimum of 13.8 MPa and 330°C. The hydrogen consumption was calculated from the hydrogen content of the feed and product; values ranged from 0.4 to 1.0 g/100 g feed (300 - 700 SCF/bbl). The conditions selected for the production run were 13.8 MPa, 345°C and a liquid hourly space velocity of 1.40 hr⁻¹. Conditions were more severe for the Berty reactor but a reformer feedstock could be prepared from this unit.

The naphtha from the production run had over 50% naphthenes which indicated that it should be an excellent reformer feedstock. The conditions in the reformer (Table 2) were adequate to almost completely convert the naphthenes with a moderate gas yield (about 11%). Only two thirds of the naphthenes were converted to the desired aromatics, however, so that these components (43%) were slightly below specifications. Theoretically this would give a low octane number, but the gravity (42°API) was encouragement for a more acceptable research octane number (~99).

MIDDLE DISTILLATE

The end use of this fraction was assumed to be either diesel or No. 2 fuel oil. Nitrogen specifications for synthetic crude were readily obtained in both the fixed bed hydrotreater and Berty reactor. Over 95% of the nitrogen was removed even at 6.9 MPa (Fig. 1). This condition was insufficient to improve the cetane index or reduce the aromatic content to the level ascribed by Sullivan (3) or Kriz (4).

The cetane index reported here is an adapted version of ASTM procedure D-976. This method is based on the true 50% boiling point of the liquid and the gravity. The hydrotreating experiments did not produce sufficient liquid for a true boiling point distillation determination. It was therefore replaced by a simulated distillation. The calculated cetane index of the feedstock by this method was 37.5, similar to that previously published (2) by HRI for this fraction. An engine test gave a cetane number of 32.1 which showed the limitations of the cetane index method. To account for these limitations, a cetane index of 42 was set as the target specification.

The hydrogen pressure had to exceed 10.3 MPa before a significant change in cetane index and aromatic content was achieved. The temperature required was 330°C or higher. A space velocity of 2.0 would meet nitrogen specifications (Fig. 2) but not cetane index. Conditions vary greatly, therefore, dependant upon the end use of the product. The aromatic content of the product as close to 10% at the acceptable cetane index and this satisfied the predicted value of Sullivan. No runs came close to the 4% imposed by Kriz. Hydrogen consumption to make diesel grade product was approximately 1-1.2 g/100 g (700-850 SCF/Bbl) at preferred operating conditions.

GAS OIL

No tests were run on the fixed bed unit with this feedstock. The targetted specifications could be obtained with the Berty reactor. Based on the earlier experience with the naphtha and middle distillate, mild conditions of less than 370°C, 10.4 MPa and LHSV of greater than 2.0 hr⁻¹ should provide an acceptable product with either Shell 324 or Amocat 1C in a fixed bed. The requirements for the hydrotreating of gas oil are not highly stringent since it must subsequently be subjected to a cracking process. Up to 70% nitrogen removal was possible at the above conditions. Hydrogen consumption was about 0.7 g/100 g (500 SCF/Bbl).

CONCLUSIONS

Operating ranges for hydrotreating and reforming of coprocessing derived liquid were established. All product fractions met target specifications for a synthetic crude oil feedstock or commercial product.

REFERENCES

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2. Coal/Oil Coprocessing: Phase I, Electric Power Research Institute Report No. AP-5101, March 1987.
3. Richard F. Sullivan and Harry A. Frumkin, "Refining Coal Liquids: Where We Stand", Proceedings American Chemical Society, Division of Fuel Chemistry, April 13-18, 1986.
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Table 1
Properties of Coprocessing Derived Liquids

		Naphtha (L0-4749)	Middle Distillate (L0-4750)	Gas Oil (L0-4751)
Carbon	%	83.8	87.1	87.4
Hydrogen	%	13.7	12.1	11.1
Nitrogen	ppm	165	1022	4000
Sulfur	ppm	120	334	1630
API gravity	°	49.7	28.3	17.0
13C aromaticity	%	5	23	30
Distillation	°C			
IBP		57	151	323
50%		131	268	368
90%		177	338	402
FBP		253	387	(470)

Table 2

Product Quality and Reactor Conditions

	Product Quality		Operating Conditions				Hydrogen Consumption (SCF/Bbl)
	Nitrogen (ppm)	Sulfur (ppm)	Temperature (°C)	Pressure (MPa)	LHSV (hr ⁻¹)		
Naphtia							
Target	1	10	380	10.4	1.0		
Berty	1	12	330+	13.8	1.4		
Fixed Bed	1	10					~500
Reformer							
	Nitrogen (ppm)	Aromatics (%)	Yield (%)				
Target	1	45(PONA)	--				
Fixed Bed	1	43(PNA)	88	500	1.7	2.0	
Distillate							
	Nitrogen (ppm)	Aromatics ^a (%)	Cetane Index				
Target	200	10(4)	40 ^b				
Fixed Bed	10	10	42	330+	13.8	1.0	700-850
Berty	93	19	38				
Gas Oil							
	Nitrogen (ppm)	Gravity API					
Target	1200	18					
Berty	1130	18.4		370	10.4	2.0	~500

^aCarbon 13 NMR^bCetane number

FIGURE 1
Hydrogen Pressure vs Conversion Parameters (345°C)

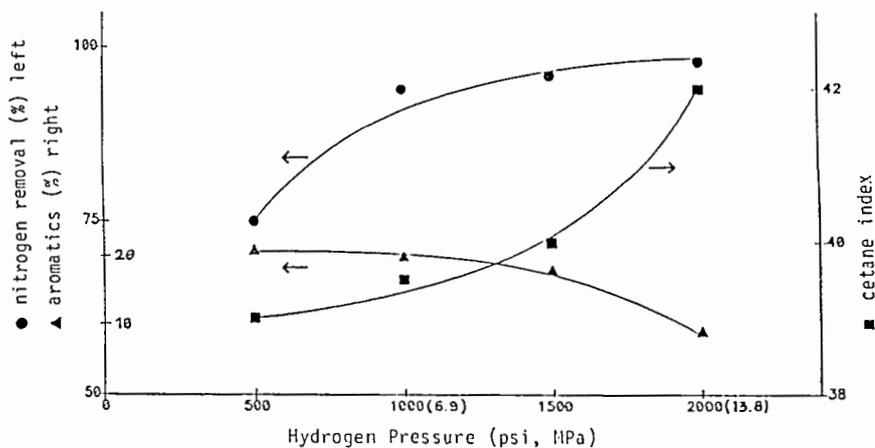


FIGURE 2
Space Velocity vs Conversion Parameters (345°C)

