

HYDROTREATING AND PRODUCTION OF TRANSPORTATION FUEL FROM COPROCESSED DISTILLATES

T. Ohuchi, M. Carmichael, A. Chambers and K. Muehlenbachs*

Coal and Hydrocarbon Processing Department
Alberta Research Council
1 Oilpatch Drive, Bag # 1310
Devon, Alberta, Canada, T0C 1E0

*Geology Department, University of Alberta
Edmonton, Alberta, Canada, T6G 2E3

Keywords: Coprocessing, hydrotreating, isotope

INTRODUCTION

Production of refinery feedstocks and transportation fuels from coprocessing liquids were the objectives of this study. Coal-heavy oil coprocessed products are significantly different from conventional petroleum. In most coprocessing schemes, the first stage coprocessed products contain high concentrations of nitrogen and sulfur, directly inherited from the feed coal and the feed heavy oil. Nitrogen and sulfur must be removed from these first stage products by further catalytic hydrotreating to produce a synthetic crude to be marketed directly to existing refineries for further upgrading. The investigation of nitrogen and sulfur removal focused on producing refinery acceptable products with reference to existing refinery specifications.

An initial study of transportation fuels from coprocessing liquids resulted in production of one gasoline and two diesel products from distillate and gas oil fractions. They were engine tested to evaluate octane and cetane number and other properties which were then compared to the Canadian Standard Specifications.

The isotopic analysis of $^{13}\text{C}/^{12}\text{C}$ ratio provides information for quantifying amounts of coal derived matter incorporated into product slates. In the coprocessing of coal and heavy oil, both components of feed are upgraded simultaneously. Quantitative assessment of coal transformation into product fractions would give kinetic and engineering data for efficient development of coprocessing schemes. Using isotopic mass balance techniques, coal incorporation into the first stage coprocessed products (experimental feeds) and secondary upgraded products were calculated.

Consequently, this study consisted of (a) investigation of nitrogen and sulfur removal from coprocessed liquids, (b) preliminary production of transportation fuels, and (c) quantitative assessment of coal derived material incorporated into both first stage and secondary upgraded products.

EXPERIMENTAL

Feedstock. Coprocessed slurry was obtained from a process development unit operated by Canadian Energy Developments Inc. (CED). Feed to the unit consisted of an Alberta subbituminous coal (Vesta) and an iron based catalyst

slurried with Cold Lake vacuum bottoms. This slurry was then processed at temperature above 400°C and pressure above 17 MPa. The coprocessed slurry was separated by distillation into naphtha (below 177°C), distillate (178 to 343°C) and gas oil (344 to 508°C) fractions. Table 1 gives the analyses of starting feeds and nitrogen and sulfur concentration of distillables compared to refinery specifications. These fractions were secondary upgraded separately; the ratio of hydrogen flow to feed (vol./vol. ratio) was 1000 unless otherwise provided.

Catalysts. Three commercial catalysts were used: a Ni/Mo for hydrotreating, a different Ni/Mo for hydrocracking and platinum catalyst for reforming. Following presulfidation of the catalyst, and prior to hydrotreating/hydrocracking experiments, the catalysts were conditioned for a minimum 30 hours using a bitumen derived distillate feed. The platinum catalyst was used as received.

Hydrotreating. A continuous flow trickle bed reactor system was used, having a volume of 100 ml. For hydrotreating experiments of the naphtha fraction, a two level factorial experimental design was used. The two levels of three variables were selected as follows: 390 and 420°C, 8.3 and 12.4 MPa, 1.0 and 3.0 h⁻¹. For the distillate and gas oil fractions, a Box-Behnken statistical experimental design approach was used to study the simultaneous effect of varying reaction temperature (400 to 440°C), pressure (6.9 to 11.0 MPa) and WHSV (1.0 to 4.0 h⁻¹)²

Preliminary Production of Transportation Fuels. For gasoline production, the feed naphtha was hydrotreated at 420°, 12.4 MPa, WHSV of 3.0 h⁻¹ followed by reforming at 500°C, 3.5 MPa, 1.0 h⁻¹ and H₂/feed (vol./vol.) of 300. Two diesel products were obtained. One diesel product was produced by hydrotreating of the first stage distillate fraction at 440°C, 6.9 MPa and 2.5 h⁻¹. The other was obtained from the gas oil fraction by hydrotreating at the same conditions used for the distillate followed by further hydrocracking of the hydrotreated gas oil (which was separated by distillation) at 420°, 6.9 MPa and 1.0 h⁻¹

Distribution Of Coal In Product Slates. In order to quantify the amounts of coal derived matter incorporated into product fractions, an isotopic analysis of 13C/12C ratio was carried out. The procedure is described elsewhere³.

RESULTS AND DISCUSSION

(a) Nitrogen and Sulfur Removal From First Stage Coprocessed Products.

Naphtha. Table 2 summarizes the results of hydrotreating of the naphtha fractions and whether the resulting products met refinery specifications (Table 1). Even though the experimental conditions were varied for a two level statistical analysis, the small differences between concentrations of heteroatoms in the products of different experiments did not allow a meaningful analysis of the effect of hydrotreating conditions on nitrogen and sulfur removal. Product specifications for nitrogen were met under all operating conditions; however, those for sulfur were not.

Distillate. The experimental results of the three level test matrix for hydrotreating of the distillate fraction were fit using a quadratic fraction.

Figure 1 illustrates calculated response surfaces of change in concentration of nitrogen in the total liquid product against both reactor temperature and WHSV for hydrotreating of the distillate fraction. These figures show the relative order of effects on nitrogen removal for this range of conditions to be: WHSV > temperature > pressure. Also, some interaction of the three parameters was noted; decreasing WHSV at 400°C dramatically decreased nitrogen content of products but had a lesser effect at 440°C. For all of the conditions studied, the nitrogen concentration of products was below 200 ppm, meeting the specifications of nitrogen content. In terms of sulfur removal, the pressure required to produce acceptable refinery feeds was 6.9 MPa, the lowest in the entire experiments studied. Figure 2 shows the relationship between sulfur concentration in the products and hydrotreatment temperature with varying WHSV at a pressure of 6.9 MPa. This figure illustrates the sensitivity of sulfur content to reaction temperature, especially above 410°C. Decreasing WHSV from 4.0 to 3.0 h⁻¹ also reduced sulfur content but further reduction had little effect.

Gas Oil. Figure 3 gives the response surfaces of nitrogen content in products of hydrotreating of the gas oil. Increasing temperature, decreasing WHSV and increasing pressure maximized nitrogen removal. Little interaction of three parameters was observed. The effect of pressure on sulfur removal from the gas oil was negligible. Figure 4 gives contours of sulfur concentration in products with varying WHSV at 6.9 MPa. It provides a range of operating temperature and WHSV that would be available to produce refinery acceptable feeds at 6.9 MPa. Also, using the estimated values from these curves, the activation energy with respect to sulfur removal was calculated using a first order model giving an activation energy of 56.3 kJ/mole.

(b) Preliminary Study of Transportation Fuel Production From Coprocessed Liquids.

In order to maximize the yield of value-added product such as diesel, the conversion of gas oil to distillate should be high. The response surface in Figure 5 shows the yield of distillate from gas oil hydrotreating. The relative order of parameter effects on the yield was temperature > WHSV with pressure having negligible effect. Generally, increasing temperature improved distillate yield. At high temperatures, decreasing WHSV increased distillate yield, while at low temperature, the change in yield from a change in WHSV was negligible.

Selected fractions from the products of secondary upgrading were further processed and tested for their properties as transportation fuels. Table 3 shows the results of an overall mass balance in the secondary upgrading experiments of first stage coprocessed liquids. The difference of 2.0% between amounts of feed and those of upgraded products represents amounts of gaseous products and some experimental errors involved.

Gasoline Product. The hydrotreated naphtha and the naphtha obtained from the product of hydrotreated distillate were combined and then reformed for engine testing as a gasoline product. This product had an octane number of 76.6, slightly less than the Canadian Specification minimum of 83.6 (January, Alberta). Either blending or different reforming conditions would be required to produce an unleaded gasoline product to meet the specifications.

Diesel Product. Table 4 gives the properties of diesel fractions obtained from two different sources compared to the Canadian specifications. One diesel was from hydrotreating of distillate fraction of first stage, and the other from hydrocracking of hydrotreated gas oil fraction. Key measures of diesel quality are cetane number and sulfur concentration. The results of engine testing of the first diesel product (produced from the distillate fraction) gave a cetane number of 40.9, slightly exceeding the minimum specification of 40. Sulfur concentration of this diesel was 349 ppm, much less than the 0.5% maximum specification, indicating that this diesel can be sold to market directly. The second diesel product (produced from the gas oil fraction) had a low cetane number of 28.6; however, the sulfur concentration was again well below the specification. In order to increase the cetane number of the second diesel product, more hydrogen must be added into this fraction, suggesting that further process options must be investigated. Most of the other diesel specification parameters can be adjusted by addition of fuel improvers.

(c) Distribution of Coal Incorporated Into Product Slates

Using a combination of isotopic analysis, elemental analysis of carbon and yield data of the feeds and the hydrotreated products, the concentration of coal derived carbon in each product fraction can be calculated. Figure 6 gives the distribution of coal derived carbon incorporated into the first stage coprocessed products. Figures 7 and 8 illustrate those of the hydrotreated products, indicating that the majority of coal derived carbon existed in the heavier fractions. However, significant amounts of coal derived carbon existed in the distillable products. After hydrotreating, the combined results gave the following concentrations of coal derived carbon in the product fractions: 20.3% in naphtha, 9.2% in distillate and 15.8 % in gas oil.

CONCLUSIONS

The following was concluded from this study:

1. Synthetic crude refinery feedstock specifications for nitrogen and sulfur content could be met for the distillate and gas oil fractions of coal-bitumen coprocessing.
2. The relative effectiveness on nitrogen removal during hydrotreating was $WHSV - \text{temperature} > \text{pressure}$.
3. On sulfur removal during hydrotreating, temperature had the greatest impact and pressure had a negligible effect.
4. Hydrotreating of distillate fraction directly produced a diesel which met several of the Canadian specifications.
5. Hydrotreatment followed by hydrocracking of gas oil produced a diesel fraction which did not meet the cetane number specification.
6. Coal derived carbon concentrations in the naphtha, distillate and gas oil product fractions after secondary upgrading were 20.3, 9.2 and 15.8 % respectively.

ACKNOWLEDGEMENT

This study was funded from the Alberta/Canada Energy Resources Research Fund, a fund jointly established by the Government of Canada and Alberta. The

project was administered by the Alberta Office of Coal Research and Technology. The project staff are indebted to Canadian Energy Developments, Inc. for supplying first stage coprocessing products.

REFERENCES

1. T. Dhuchi, K. Muehlenbachs, M. Bombin, J. Steer, J. Wilson and A. Chambers, "The Use of Stable Isotopic Ratios For Tracer Study: Applications of $^{13}\text{C}/^{12}\text{C}$ and D/H ratios in Hydrocarbon Processing." 1989 International Conference on Coal Science, Tokyo, October, 1989, Proceedings, P. 771.
2. G.E.P. Box and D. W. Behuken, "Some New Three Level Designs for the Study of Quantitative Variables", Technometrics, Vol. 2, p. 455-475, 1960.
3. J. Steer, T. Dhuchi and K. Muehlenbachs, "Efficacy of Coal-Bitumen Coprocessing As Determined by Isotopic Mass Balance Calculations", Fuel Processing Technology, 15 (1987), P. 429.

Table 1 ELEMENTAL ANALYSES OF FEEOSTOCKS AND REFINERY SPECIFICATIONS

Starting material as received(%)				
	C	H	N	S
Vesta Coal	49.7	3.2	0.94	0.36
Cold Lake V.B.	83.1	9.9	0.75	5.77

Heteroatom concentrations of feeds and refinery specifications(ppm)				
	Feeds		Specifications	
	N	S	N	S
Naphtha(<177 C)	770	5200	10	15
Distillate(178-343 C)	3120	17500	200	1000
Gas Oil(>3444 C)	5200	24500	<2100	-
Total Blend				<3100

Table 2 HDN AND HDS: Hydrotreating of Naphtha from CED #1

Process Temperature °C		390	420
Pressure (MPa)	WHSV (hr ⁻¹)	0	0
		0	0
8.3	1.0 N	0	0
	S	0	0
3.0	N	0	0
	S	0	0
12.4	1.0 N	0	0
	S	0	0
3.0	N	0	0
	S	0	0

0: meets refinery specifications
*: does not meet

Table 3

MASS BALANCE
(Based on slurry without water and gas)

% Feed	% Product		
	Naphtha (gasoline)	Distillate (diesel)	GO
Naphtha 4.9	4.9 **		
Distillate 14.7			
	Hydrotreating 1.7	12.3 **	
Gas Oil 24.4			
	Hydrotreating 1.2	1.8	(20.7*)
	*Hydrocracking (0.4)	(1.3)	(15.4)
(Subtotal)	8.2	10.4**	15.4
Total 44.0		42.0	

** Engine Tested

Table 4

PROPERTIES OF DISTILLATES COMPARED TO DIESEL SPECIFICATIONS

Property	Type of Diesel A	From Distillate	From Gas Oil
Ignition Quality	40	40.9	28.6
Cetane Number			
Sulfur, % Mass Max.	0.5	0.035	0.019
Flash Point °C, Min.	40	46.0	77.5
Cloud Point °C, Max.	-34	-27	-22
Pour Point °C, Max.	-39	-30	-15
Kinematic Viscosity at 40°C, cSt, Min.	1.3	2.01	3.05
	Max.	4.1	
Distillation:			
90% Recovered °C, Max.	315	314.5	323
Total Acid Number Max.	0.10	0.009	0.01

Figure 1 HYDROTREATING OF DISTILLATE FROM COPROCESSING PRODUCTS:
NITROGEN CONCENTRATION IN PRODUCTS

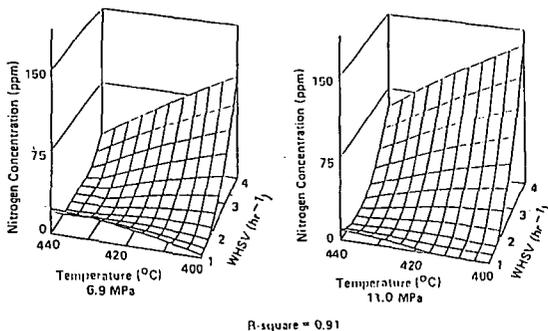


Figure 3 HYDROTREATING OF GAS OIL FROM COPROCESSING PRODUCTS:
NITROGEN CONCENTRATION IN PRODUCTS

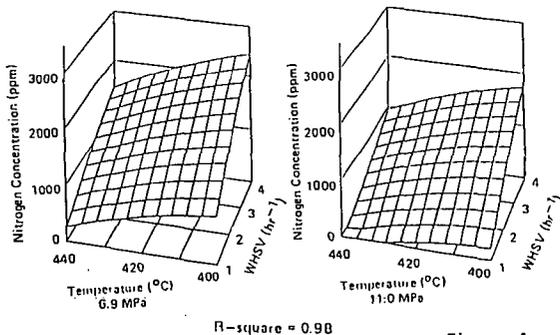


Figure 2 HYDROTREATING OF DISTILLATE FROM COPROCESSING PRODUCTS:
EFFECTS OF WHSV AND TEMPERATURE AT 6.9 MPa ON SULFUR REMOVAL

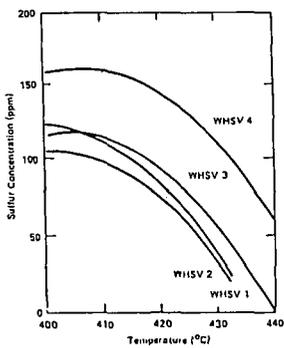


Figure 4 HYDROTREATING OF GAS OIL FROM COPROCESSING PRODUCTS:
EFFECTS OF WHSV AND PROCESS TEMPERATURE AT 6.9 MPa
ON SULFUR REMOVAL

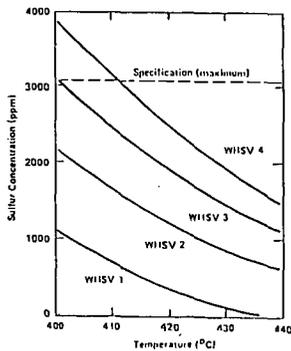


Figure 5
DISTILLATE YIELD PRODUCED FROM GAS OIL OF COPROCESSING
PRODUCTS BY HYDROTREATING

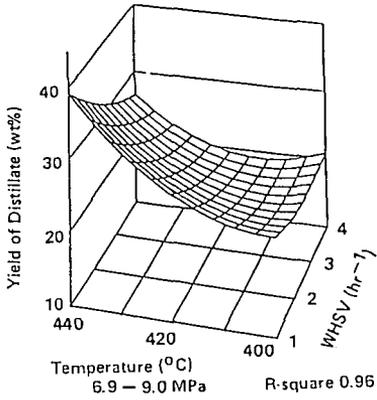


Figure 6
First Stage Coprocessing
Distribution of Coal Derived Carbon by Isotopic Analysis

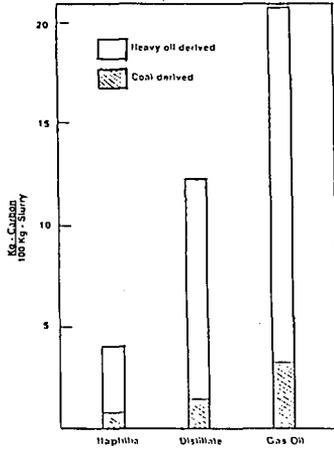


Figure 7
Secondary Upgrading of Distillate from Coprocessing;
Distribution of Coal Derived Carbon by Isotopic Analysis

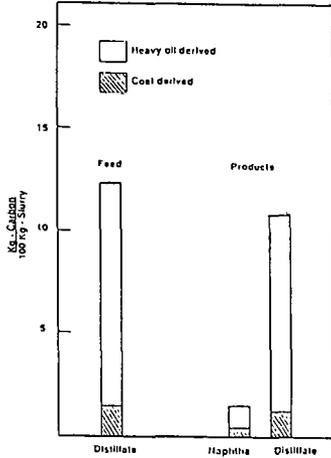


Figure 8
Secondary Upgrading of Gas Oil from Coprocessing;
Distribution of Coal Derived Carbon by Isotopic Analysis

