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Two-stage hydroprocessing of synthetic crude gas oil

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Abstract

The hydrocracking of synthetic crude gas oils (SGO), which are commercially produced from Canadian oil sands, is strongly inhibited by nitrogen-containing species. To alleviate the pronounced effect of these nitrogenous compounds, SGO was hydrotreated at severe conditions prior to hydrocracking to reduce its N content from 1665 to about 390 ppm (by weight). Hydrocracking was then performed using a commercial nickel-tungsten catalyst supported on silica-alumina. Two-stage hydroprocessing of SGO was assessed in terms of product yields and quality. As expected, higher gas oil conversions were achieved mostly from an increase in naphtha yield. The middle distillate product quality was also clearly improved as the diesel fuel cetane number increased by 13%. Diesel engine tests indicated that particulate emissions in exhaust gases were lowered by 20%. Finally, pseudo first-order kinetic equations were derived for the overall conversion of the major gas oil components.

INTRODUCTION

Synthetic crudes are produced commercially from Alberta oils sands bitumen and account for about 15% of total Canadian oil production. Because of their origin and methods of production, synthetic crudes differ from conventional crudes particularly in composition, i.e., high aromaticity and high nitrogen content [1,2]. The presence of nitrogen-containing compounds degrades the quality of synthetic crude gas oil (SGO) as a feedstock for transportation fuels due to their strong adsorption on active sites of hydrocracking catalysts [1]. Thus, conversion of SGO to middle distillates and naphtha requires very severe operating conditions [3,4]. However, Chmielowiec [1] has demonstrated that yields can be remarkably enhanced in a two-stage approach where SGO is denitrogenated then hydrocracked. Also, Maxwell has indicated that severe hydrotreatment of petroleum feedstocks is required when zeolite-alu-

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mina supports are used in hydrocracking catalysts [5]. The two-stage hydroprocessing configuration has also found application in the upgrading of coalderived liquids where oxygenated compounds are showing on hydrocracking catalysts an inhibiting effect similar to that of nitrogen compounds [6,7].

The present paper evaluates a commercial nickel-tungsten catalyst in connection with the (second) hydrocracking stage in terms of increased production and improved quality of fuels by the two-stage hydroprocessing of SGO. A kinetic study is used to provide additional information about SGO and DSGO hydrocracking.

EXPERIMENTAL

Raw synthetic crude gas oil (SGO) containing 1665 ppm N was hydrotreated at 375°C and 10.2 MPa using a nickel-molybdenum hydrotreating catalyst (Shell 424) in a 1-L tubular reactor (3.8 cm ID) to prepare a denitrogenated feedstock (DSGO) with about 390 ppm N. The catalyst bed volume was about 800 mL. The reactor preheating and postheating zones were filled with ceramic beads. The reactor was operated in a downflow mode. Due to the severity of the hydrotreating conditions, SGO was mildly hydrocracked and about 15.2 wt% (15.8 vol%) of the first-stage products were removed by distillation as they were boiling below 315°C in the middle distillate temperature range. Table 1 presents the properties of both feedstocks after distillation adjustment (>315°C).

A commercial hydrocracking catalyst, which consisted of nickel-tungsten supported on silica-alumina, was used to hydrocrack SGO and DSGO in a

TABLE 1

Synthetic crude gas oil feed properties

Analysis	Feed	ć	• ,
	SGO	DSGO	
Density @15°C, g/mL	0.9440	0.9263	······
N, ppm	1665	394	
S, ppm	4100	375	, ,
Mass spectrometry, Mass%			
Paraffins	6.8	7.2	
Cycloparaffins	35.3	50.1	
Monoaromatics	23.8	24.9	
Polyaromatics	27.8	15.8	
Sulfuraromatics	3.6	1,5	

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microreactor system to determine the effect of hydrotreated SGO on product yields and quality. The 1.12 cm ID 316 SS tubular reactor was operated in the downflow mode over a range of temperatures (400 to 415 °C) and liquid space velocities (0.25 to $1.0 h^{-1}$). Reactor pressure was set at 18.7 MPa and H₂ to gas oil feed ratio was adjusted to 1000 L/L. Catalyst bed size was 15 mL. Once the steady state activity was reached at a given operating condition, which corresponded to a constant specific gravity of the liquid products, samples were collected for further characterization. Sulphur and nitrogen contents were determined. The total liquid products were fractionated into naphtha (initial boiling point to 195°C), middle distillates (195–315°C) and unconverted gas oil (>315°C). The hydrocarbon composition of each fraction was established by low resolution mass spectrometry.

Large-scale hydrocracking tests were also carried out in the same 1-liter isothermal reactor used for the hydrotreating tests, to produce large volumes of middle distillates and naphtha which were required for the determination of cetane and octane numbers and other transportation fuel characteristics. These tests were performed at 408°C, 18.7 MPa and 0.5 h⁻¹ with three different feedstocks: DSGO, a mixture of 30 vol% SGO in DSGO and SGO.

The catalysts were used as extrudates (1.59 mm OD) in the pilot plant reactor tests while they were crushed to a 0.6 to 1.0 mm size range for the microreactor tests. In all cases, the catalysts were presulphided *in situ*. Additional details on reactor systems and presulphiding procedures can be found in Silva [8].

RESULTS AND DISCUSSION

Figure 1 presents the yields of middle distillates and naphtha from hydrocracking SGO and DSGO at 18.7 MPa and in the 400 to 415°C temperature



Fig. 1. Effect of first-stage hydrotreatment on the yields of naphtha and middle distillate in hydrocracking synthetic crude gas oil. (\bigcirc) Naphtha/SGO, (\square) naphtha/DSGO, (\triangle) middle distillates/SGO, and (\bigtriangledown) middle distillates/DSGO.

range. The operating conditions corresponding to each data point of Fig. 1 are given in Tables 2 and 3 together with compositions of the liquid product fractions. As shown in Fig. 1, higher gas oil conversions were achieved when the feed had been pretreated prior to hydrocracking. With DSGO, the production of middle distillates reached a maximum value of about 45 vol% at about 85% gas oil conversion (408°C, $0.5 h^{-1}$). Below this point, the naphtha/middle distillate selectivity ratio remained constant and beyond 85% gas oil conversion, the naphtha selectivity rose sharply to 80–85% while that of middle dis-

TABLE 2

Temperature (°C)	400	400	400	408	408	408	415	415	415
LHSV (h^{-1})	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0
Product yield (wt%)								·····	
Gas	2.5	0.9	0.8	3.8	2.0	1.4	4.7	3.1	1.9
IBP-195°C	20.2	8.8	3.6	28.3	14.8	7.7	36.2	22.8	13.9
195–315°C	30.2	17.0	11.0	38.3	25.4	21.9	41.3	40.4	30.3
>315°C	47.1	73.2	84.7	29.7	57.7	69.0	17.8	33.7	53.9
Gas oil conv. (%)	52.9	26.8	15.3	70.3	42.3	31.0	82.2	66.3	46.1
Liquid product yield	(vol/vol d	of feed in	: %)						
IBP-195°C	24.6	10.7	4.3	34.7	18.1	9.3	44.6	27.6	17.0
195–315°C	32.3	18.0	11.5	41.0	27.0	23.0	44.5	43.2	32.1
>315°C	48.2	73.5	84.4	30.4	58.2	69.2	18.3	34.5	54.4
Total liquid yield	105.0	102.2	100.2	106.1	103.3	101.5	107.3	105.3	103.5
Naphtha, IBP-195°	C (vol%)		•			۰.		,	
Isoparaffins	24.2	26.9	29.9	25.6	25.7	26.9	25.4	24.3	28.2
n-Paraffins	15.9	16.5	14.7	15.1	17.4	16.3	17.4	13.9	15.4
Naphthenes	51.3	46.4	45.5	49.5	46.7	45.6	50.0	52.4	45.8
Aromatics	8.6	10.2	9.8	7.8	10.2	11.2	7.3	9.4	10.6
Middle distillate, 19	5–315°C	(vol%)							
Paraffins	13.3	13.3	12.8	13.7	13.8	11.7	14.2	13.0	13.1
Cycloparaffins	58.0	45.9	44.8	55.7	48.5	45.9	56.7	55.8	48.3
Monoaromatics	26.7	38.1	39.5	28.8	35.3	39.3	27.3	29.1	34.7
Polyaromatics	1.4	2.0	2.3	1.2	1.8	2.3	1.2	1.4	3.2
Gas oil, $> 315^{\circ}C$ (vol	1%)							: :	
Paraffins	10.2	8.1	4.4	12.0	9.0	5.0	13.6	7.9	5.5
Monocycloparaffins	15.1	12.7	7.7	15.4	14.0	8.1	17.1	11.2	9.2
Polycycloparaffins	43.7	36.8	40.3	41.7	37.7	41.9	38.1	50.9	43.5
Monoaromatics	19.1	23.8	22.4	18.7	22.5	20.9	18.1	15.4	20.6
Polyaromatics	10.0	15.9	21.6	10.4	14.7	21.4	11.1	12.4	19.0

Product characteristics from hydrocracking synthetic crude gas oil (SGO)

Product characteristics from hydrocracking denitrogenated synthetic crude gas oil (DSGO)

Temperature (°C)	400	400	400	408	408	408	415	415	415
LHSV (h ⁻¹)	0.25	0.5	1.0	0.25	0.5	1.0	0.25	0.5	1.0
Product yield (wt%)									
Gas	2.1	2.3	1.4	4.0	2.2	2.1	5.9	3.0	8.0
IBP-195°C	45.1	25.0	27.2	58.9	44.1	40.4	67.0	61.0	48.5
195–315°C	33.4	33.6	31.0	31.8	41.9	36.5	24.7	30.9	34.8
>315°C	15.5	39.1	40.4	5.3	11.9	21.0	2.5	5.0	8.7
Gas oil conv. (%)	84.5	60.9	59.6	94.7	88.1	79.0	97.5	95.0	91.3
Product yield (vol/ve	ol of feed	in %)							
IBP-195°C	55.5	30.4	33.1	73.2	53.5	49.5	83.2	75.6	59.8
195–315°C	37.2	36.6	33.8	35.9	46.3	40.4	27.8	34.7	38.8
>315°C	16.8	41.3	42.9	5.7	12.7	22.6	2.7	5.4	9.5
Total liquid yield	109.6	108.2	109.8	114.8	112.5	112.5	113.7	115.8	108.1
Naphtha, IBP-195°	C (vol%)								
Isoparaffins	25.3	25.9	27.3	28.6	26.6	26.7	32.0	32.3	31.3
n-Paraffins	14.0	10.1	8.9	14.9	11.6	12.6	12.0	11.9	12.2
Naphthenes	59.2	59.0	59.0	55.0	55.2	56.1	53.8	52.9	52.1
Aromatics	1.6	5.1	4.8	1.5	6.7	4.6	2.2	2.9	4.4
Middle distillate, 19	5-315°C	(vol%)							
Paraffins	19.4	13.0	13.5	26.5	24.7	19.6	26.8	28.0	30.7
Cycloparaffins	75.0	68.0	71.1	67.9	56.7	66.5	64.4	60.6	54.2
Monoaromatics	5.0	18.1	14.3	5.1	17.9	13.2	8.0	10.7	14.1
Polyaromatics	0.2	0.4	0.4	0.1	0.5	0.4	0.3	0.5	0.9
Gas oil, $> 315^{\circ}C$ (vo	l%)								
Paraffins	32.7	16.5	17.9	45.2	29.1	29.6	42.6	39.7	38.9
Monocycloparaffins	33.4	24.1	26.6	26.9	26.1	31.0	20.7	24.3	28.8
Polycycloparaffins	28.1	44.5	43.8	18.1	31.2	30.8	17.0	20.7	21.8
Monoaromatics	3.0	9.9	8.3	4.0	8.0	4.3	7.5	8.4	6.5
Polyaromatics	1.8	3.8	2.6	4.1	4.2	3.2	9.4	5.8	2.6

tillates declined. With SGO as feed, the data suggest that a similar optimum can be observed for the middle distillate yield. However, to confirm this would require to conduct catalytic tests under more severe conditions than those selected.

Following a different approach, the effect of feed pretreatment was evaluated at two conversion levels: 60 and 85%. To achieve the same conversions, SGO hydrocracking required higher temperatures than DSGO by about 15°C as indicated in Table 4. Product selectivity was also affected by feed hydro-

Effect of first-stage gas oil hydrotreatment on hydrocracking at fixed conversion levels

Property	60 wt% Co (LHSV ^a =	nv. 0.5 h ⁻¹)	85 wt% Conv. (LHSV=0.25 h ⁻¹)		
	SGO	DSGO	SGO	DSGO	
Conversion, wt%	60	60	82.2	84.5	
Temperature, °C	413	400	415	400	
Sulfur in TLP, ppm	50	11	n.d.	0	
Nitrogen in TLP, ppm	~ 5	0.5	1	0	
Yields, vol/vol of feed					
Naphtha (IBP ^b -195°C)	25	33	45	55.5	
Distillate (195-315°C)	39	35	45	37	
Distillate/naphtha ratio	1.5	1.0	1.0	0.7	
Naphtha N+2A°, vol%	75	75	72	69	
Distillate composition, vol%					
Paraffin	13	13	14	19	
Cycloparaffin	54	68	57	75	
Aromatic	33	19	28	5	

^aLHSV=liquid hourly space velocity (reciprocal residence time).

^bIBP=initial boiling point.

 $^{\circ}N+2A = [naphthenes]+2[aromatics].$

treatment as if shifted towards lighter hydrocarbons when DSGO was hydrocracked.

The quality of the middle distillate product was clearly improved by twostage hydroprocessing due to an appreciable drop in aromatics components as shown in Table 4. In fact, diesel fuels produced from DSGO hydrocracking contain less than 20 vol% aromatics, which is one of the requirements for meeting the new fuel specifications proposed by the Canadian government in order to reduce the particulate emission from diesel engines in trucks and buses [9]. Furthermore, diesel fuel from DSGO processed at 85% conversion would easily pass the sulphur and aromatics requirements set by the State of California, which are the strictest in North America [10].

With regard to naphtha, its quality as reformer feedstock, usually defined by the standard parameter ([naphthenes]+2[aromatics]), was not affected by the level of conversion and the feed nitrogen content. Although this parameter dropped slightly to 69 at 85% conversion using DSGO, it was still an excellent feedstock for a reformer unit.

Information concerning the kinetics of SGO and DSGO hydrocracking was obtained by fitting values of Y_{GO} , the percentage of unconverted gas oil, to

pseudo first- and second-order rate equations. Based on the sum of the squares of the residuals, shown in Table 5, the second-order kinetics equation gives a much better prediction of the gas oil hydrocracking rate than first-order equations regardless of the feed nitrogen content.

The total liquid products were also characterized by low resolution mass spectrometry to measure the concentration of the following hydrocarbon components: paraffins (PAR), monocycloparaffins (MCP), polycycloparaffins (PCP), monoaromatics (MAH) and polyaromatics (PAH). Their weight fraction is plotted in Fig. 2 on a logarithmic scale (ln) as functions of the residence time (inverse of space velocity) of DSGO and SGO in the catalytic bed. Based on the pseudo first-order kinetic constants listed in Table 6, one can rank all five hydrocarbon components in terms of reactivity: PAH>MAH>PCP>MCP>PAR.

The wide range of reactivity observed here explains why gas oil conversion cannot be adequately predicted by first-order kinetics modelling (Table 5), which implies the lumping of gas oil in a single entity. A comparison of the reactivities of the gas oil components in SGO and DSGO feeds at 400°C reveals

TABLE 5

Temp. (°C)	1/LHSV (h)	1st-Order rate – SGO Y _{GO} , wt%			2nd-Order rate – SGO Y _{GO} , wt%			2nd-Order rate – DSGO			
								Y _{GO} , v	Y _{GO} , wt%		
·		obs.	calc.	delta	obs.	calc.	delta	obs.	calc.	delta	
400	1.0	84.7	85.1	+0.4	84.7	82.8	-1.9	40.7	40.8	+0.1	
	2.0	73.2	73.2	0.0	73.2	71.3	-2.0	39.1	27.3	-11.8	
	4.0	47.1	51.0	+3.9	47.1	53.5	+6.4	15.5	15.1	0.4	
408	1.0	69.0	74.4	+5.4	69.0	69.1	+0.1	21.0	20.1	-0.9	
	2.0	57.7	55.3	-2.4	57.7	52.7	-5.0	11.9	11.7	-0.2	
	4.0	39.7	29.9	-9.8	39.7	35.4	-4.4	5.3	5.9	+0.6	
415	1.0	53.9	60.3	+6.4	53.9	53.3	-0.6	8.7	9.4	+0.7	
	2.0	33.7	36.7	+3.0	33.7	36.6	+2.9	5.0	5.3	+0.3	
	4.0	17.8	12.5	-5.3	17.8	21.7	+3.9	2.5	2.6	+0.1	
Sum of	squares										
of residu	uals			225			115			141	
Kinetic	sa										
SGO - 1	lst-order Ya	n = 100	exp[-8	$45 10^{21} \epsilon$	xn (-3	5.200/T	t1				
SGO - 2	2nd-order Y	$c_0 = 1/1$	0.01 + 8	.24 10 ²⁵ e	$x_{D}(-4)$	4.310/T	t]				
DSGO -	- 2nd-order	$Y_{GO} = 1$	/[0.01+	1.16 1036	³ exp (–	58,750/2	T				

Kinetics of gas oil hydrocracking - first order vs. second order reaction kinetics

 $^{a}T =$ temperature (K), and t =time (h).



Fig. 2. First-order kinetics plots from hydrocracking SGO (a) and DSGO (b) at 400°C and SGO (c) at 408°C for the following gas oil components: paraffins (\Diamond), monocycloparaffins (∇), polycycloparaffins (\Box), monoaromatics (Δ) and polyaromatics (\bigcirc).

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TABLE 6

First-order kinetic parameters (h^{-1}) for selected gas oil components in hydrocracking SGO and DSGO

Component	Feed/temperature							
	SGO/400°C	SGO/408°C	SGO/415°C	DSGO/400°C				
Polyaromatic hydrocarbons (PAH)	0.45	0.56	0.94	1.10				
Monoaromatic hydrocarbons (MAH)	0.08	0.37	0.76	1.0				
Polycycloparaffins (PCP)	0.06	0.19	0.33	0.52				
Monocycloparaffins (MCP)	0.05	0.14	0.41	0.24				
Paraffins (PAR)	0.09	0.16	0.07	0.09				

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that, while some inhibition of the hydrogenation reactions occurs, cracking reactions are affected most by the nitrogen components. In all cases, the reactivity patterns is similar to what has been reported for fluid catalytic cracking [11], with paraffins being the most refractory materials (besides polyaromatic hydrocarbons which are not hydrogenated in catalytic cracking).

A triangular kinetic model, shown below, has been applied to predict the gas oil conversion and the yields of middle distillate and naphtha observed for both feeds under the different reaction conditions tested.



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This model is similar to the one widely used in fluid catalytic cracking (FCC) [11-14] but where the gasoline and [gas+coke] fractions have been replaced by the middle distillate and naphtha fractions respectively. In this model, gas oil cracking to middle distillate and naphtha are second-order reactions, while middle distillate cracking to naphtha is a first-order reaction. The resulting equations and their integrations into expressions of gas oil and middle distillate yields are well described in the literature [12-15] and are not given here.

The triangular model allows for direct conversion of the gas oil feed into naphtha, which is the main distinction from a linear reaction scheme:

gas oil $[GO] \rightarrow middle distillates [MD] \rightarrow naphtha [N] + gas [G]$

Table 7 (where $K_0 = k_1 + k_3$) presents the best estimates of the kinetic parameters, calculated using a Marquardt non-linear regression algorithm [16], as well as the experimental and calculated yields. The ratio $K_1 = k_1/k_0$ reveals that 30 to 40% of the hydrocracked SGO was converted directly to naphtha. At low nitrogen level in the feed, direct hydrocracking to naphtha amounted between 45 and 55%. However, while (over)cracking of distillate (k_2) occurred at high severity and was more important on an absolute basis when the feed was pretreated, kinetics suggests that the distillate/naphtha selectivity is mostly determined by the gas oil cracking step. Indeed, at 415°C, direct gas oil cracking to naphtha is more pronounced when the feed is pretreated as indicated by $(1-K_1)$ which is equal to 0.57 and 0.30 for DSGO and SGO, respectively.

Results of the large-scale tests are shown in Table 8. As observed previously, gas oil conversion increased as the nitrogen level decreased, but mostly from an increase in naphtha yield. Naphtha quality was low in terms of octane number and was barely affected by the feed quality. Iso/normal paraffin ratio was high and the light fraction of this naphtha would make an excellent straightrun light gasoline. The rest of the naphtha cut would be a high-quality reformer

Triangular model parameters and middle distillate yield values in hydrocracking SGO and DSGO

Temp. (°C)	Synth	Synthetic crude gas oil (SGO)										
	k_0	$K_1 = k_1/k_0$	$K_2 = k_2/k_0$	k_1	k_2	1/LHSV (h)	Yield (wt%)					
							Obs.	Calc.	Delta			
400	0.21	0.635	0.000	0.13	0.000	1.0	10.96	10.96	0.00			
						2.0	17.04	18.23	+1.2			
						4.0	30.19	29.5	-0.7			
408	0.46	0.620	0.054	0.28	0.025	1.0	21.91	18.91	-3.0			
						2.0	25.42	28.42	+3.0			
						4.0	38.25	37.57	-0.7			
415	0.88	0.703	0.106	0.62	0.093	1.0	. 30,33	31.01	+0.7			
						2.0	40.38	39.48	-0.9			
						4.0	41.33	40.96	+0.4			
Temp.	Denitrogenated synthetic crude gas oil (DSGO)											
(0)	k_0	$k_0 \qquad K_1 = k_1/k_0$	$K_2 = k_2/k_0$	k_1	k_2	1/LHSV (h)	Yield (wt%)					
							Obs.	Calc.	Delta			
400	1.4	0.55	0.080	0.78	0.11	1.0	31.0	30.3	-0.7			
						2.0	33.6	34.5	+0.9			
						4.0	33.5	33.3	-0.2			
408	4.0	0.53	0.031	2.12	0.12	1.0	36.5	38.7	+2.2			
						2.0	41.9	38.9	- 3.0			
						4.0	31.8	32.8	+1.0			
415	9.5	0.43	0.015	4.10	0.15	1.0	34.8	34.2	-0.6			
						2.0	30.9	31.8	+0.9			
						4.0	24.7	24.3	-0.4			

feed, requiring only mild reforming to yield a high octane gasoline blending stock.

The middle distillate cetane number was well above the Canadian General Standards Board minimum specification of 40 irrespective of the nitrogen content in the feed [17]. It was nevertheless improved by nitrogen removal after the first-stage hydrotreating. The product sulphur content was less than 74 ppm (by weight). Among the other properties inspected, only the viscosity (ASTM D-445) did not meet Jet A specifications and was above the maximum specified, 8 cSt (mm²/s) [17]. However, this could be offset by blending or changing selected cut points.

Particulate exhaust emission measurements were done on the total middle distillates (195–315°C) using a one-cylinder diesel engine equipped with a dilution tunnel, operated under fixed conditions. The results shown in Table

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Effect of feed quality on product yield and quality from hydrocracking at 408°C, 0.5 $h^{-1},\,18.9$ MPa and 1000 L $\rm H_2/L$ feed

	Run		
	A	В	С
SGO/DSGO feed ratio (vol%/vol%)	0/100	30/70	100/0
Nitrogen in feed, ppm	391	780	1665
Gas oil conversion, wt%	78.5	60.0	46.2
Liquid volume yields, 100 (vol/vol) of feed			
Naphtha (IBP-195°C)	48.4	31.9	22.8
Light distillate (195-290°C)	33.1	29.1	20.5
Heavy distillate (290-315°C)	8.1	7.7	8.0
Gas oil (>315°C)	23.2	43.1	57.6
Distillate/naphtha ratio	0.85	1.15	1.25
Naphtha quality			
API gravity	56.7	54.9	52.5
RON ^a , clear	59.0	60.6	60.6
MON ^b , clear	59.0	59.5	59.6
Paraffins, vol%	31.1	27.0	22.6
iso/normal	3,0	2.6	2.4
Naphthenes, vol%	65.2	70.2	71.2
Aromatics, vol%	3.7	2.8	6.2
N+2A°	72.6	75.8	83.6
Middle distillate quality			
API gravity	38.3	36.0	33.1
Smoke point, mm	25.6	21.7	18.6
Pour point, °C	<-66	<-66	<-66
Cloud point, °C	-71	-71	-71
Viscosity -20° C, cSt ^d	10.7	11.7	18.6
Cetane number	47.2	44.5	41.8
Paraffins, wt%	15.0	9.3	8.9
Cycloparaffins, wt%	77.1	81.3	76.4
Aromatics, wt%	7.9	9.4	14.7
Total middle distillate – particulates in ex	haust emissions		
Total aromatics, wt%	9.9	11.1	16.8
Particulates, g/bHP · h	0.82	0.92	1.00
g/kg fuel	3.1	3.6	3.9

^aRON=research octane number.

^bMON=motor octane number.

 $^{c}N+2A = [naphthenes] + 2[aromatics].$ $^{d}1 cST \cong 1mm^{2}/s.$

6 indicate that particulate emission can be lowered by 20% when DSGO is used as feedstock. This reduction is the result of the lower aromatic content in the middle distillate products.

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CONCLUSIONS

In summary, the yields of naphtha and middle distillates were enhanced by hydrotreating synthetic crude gas oil prior to hydrocracking. The production of middle distillate fuels was maximized to 45% at a gas oil conversion of 85%. This level could be achieved only with a two-stage configuration. At the same time, the quality of the middle distillates was noticeably improved due to a decline in the volume of aromatic components to a level well below the coming Canadian government regulations on diesel and jet fuels. Finally, the triangular model used in the kinetics study of the hydrocracking stage indicated that an appreciable fraction of gas oil is directly converted to naphtha at the operating conditions investigated.

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REFERENCES

- 1 Chmielowiec, J., 1987. Impact of nitrogen compounds on the processing of synthetic gas oil. Final report to CANMET, Supply and Services Canada, Contract Serial No. 0SQ84-00095, Ottawa, Ont., Canada.
- 2 Wilson, M.F. and Kriz, J.F., 1984. Fuel, 63: 190-196.
- 3 Brunn, L.W., Kaparakos, N.E., Plesko, R.W. and Schoenroth, B.E., 1984. Oil Gas J., 82 (13): 90, 92, 94, 96.
- 4 Wilson, M.F., Simmons, R.A. and Notzl, H., 1987. Am. Chem. Soc. Div. Pet. Chem., Prepr., 32(2): 383-390.
- 5 Maxwell, I.E., 1987. Catalysis Today, 1: 385-417.
- 6 Nishijima, A., Yoshitomi, S., Shimada, H., Yoshimura, Y., Sato, T. and Matsubayashi, N., 1988. Catalyst design for two-stage upgrading of coal-derived liquids. In: M.J. Phillips and M. Ternan (Eds.), Proc. 9th Int. Congr. on Catalysis. Chemical Institute of Canada, Ottawa, Ont., Vol. 1, pp. 174–181.
- 7 Shimada, H., Sato, T., Yoshimura, Y., Hinata, A., Yoshitomi, S., Castillo Mares, A. and Nishijima, A., 1990. Fuel Processing Technol., 25: 153-165.
- 8 Silva, A.E., 1989. Evaluation of two-stage catalytic hydroprocessing of syncrude gas oil. Final report to CANMET, Supply and Services Canada, Contract Serial No. 23440-7-9218/01-SQ, Ottawa, Ont., Canada.
- 9 Hrobelsky, L.E., 1989. A plan to identify and assess emission reduction opportunities from transportation, industrial engines and motor fuels. Transport Canada/Environment Canada Report TP9773E, Ottawa, Ont., Canada.

- 10 Courtis, J., 1988. Proposed adoption of regulations limiting the sulphur content and aromatic hydrocarbon content of motor vehicle diesel fuel. State of California Air Resources Board, Sacramento, CA.
- 11 Gates, B.C., Katzer, J.R. and Schuit, G.C.A., 1979. Chemistry of Catalytic Processes. Mc-Graw-Hill, New York, NY, p. 29.
- 12 Weekman, V.W. Jr., 1968. Ind. Eng. Chem. Process Des. Dev., 7: 90-95.

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- 13 Voltz, S.E., Nace, D.M. and Weekman, V.W. Jr., 1971. Ind. Eng. Chem. Process Des. Dev., 10: 530-537.
- 14 Voltz, S.E., Nace, D.M. and Weekman, V.W. Jr., 1971. Ind. Eng. Chem. Process Des. Dev., 10: 538-451.
- 15 Froment, G.F. and Bischoff, K.B., 1979. Chemical reactor analysis and design. Wiley, New York, NY, p. 24.
- 16 Draper, N.R. and Smith, H., 1966. Applied Regression Analysis. Wiley, New York, NY, pp. 272–274.
- 17 National Standards of Canada, 1986. Turbine fuel, aviation, kerosine type. CAN/CGSB-3.23M88. Canadian General Standards Board, Ottawa, Ont., Canada.