Studies on Hydrodesulfurization of Heavy Distillates (Part 3)

Physical and Chemical Properties of Product Oils

Toshiaki HISAMITSU* and Hiromi OZAKI

Central Research Laboratories, Nippon Mining Co., Ltd.,
3-17-35, Niizo-Minami, Toda, Saitama 335

(Received September 12, 1985)

Vacuum gas oil was hydroprocessed over a Co-Mo-Al₂O₃ catalyst at temperatures of 380, 400, and 420°C and at pressures of 4.0 and 7.9 MPa. The physical and chemical properties of the product oils, viz., middle distillate and vacuum gas oil fractions were correlated. Also the properties of these oils were correlated with reaction conditions and with the results of cracking, desulfurization, and denitrogenation conversions. It was expected that the middle distillate produced by mild hydrocracking of vacuum gas oil would be less suitable as fuel oil and that the vacuum gas oil fraction in the product is a suitable feedstock for such upgrading process as fluidized catalytic cracking.

1. Introduction

In our preceding paper¹⁾ we reported the results of the kinetics of hydrocracking(HC), hydrodesulfurization(HDS), and hydrodenitrogenation(HDN) reactions involved in the hydroprocessing of vacuum gas oil under rather severe reaction conditions as compared to those in the conventional indirect HDS reaction. To evaluate mild hydrocracking (MHC) process as a means of increasing conversion of vacuum gas oil into middle distillate by utilizing the existing indirect HDS facilities, detailed data on the properties of not only middle distillate but also of vacuum gas oil, and also data on reaction kinetics will be necessary.

Concerning the properties of the product oil produced by MHC process, attention is focused mostly on the smoke point, cetane number, aniline point of the middle distillate fraction. The smoke point of kerosene and cetane number of the middle distillate are reported to be about 12 mm and 40—55, respectively.^{2),3)} Cetane number increases with increasing boiling point, and cetane number 43 for the fraction boiling between 243 and 321°C increases to 53 for the fraction boiling between 321 and 360°C.³⁾ Also the cetane number of the fraction boiling between 166 and 343°C increases from 37 to 41 by removing the lighter fractions boiling below 249°C.²⁾ As regards to MHC process, available information on the correlation between

reaction conditions and properties especially of the vacuum gas oil fraction remaining unconverted is limited.

This paper deals with the physical and chemical properties of the middle distillate and vacuum gas oil fractions obtained from the hydroprocess studies reported in the preceding paper.

2. Experimentals

Hydroprocessing of vacuum gas oil was carried out over a Co-Mo-Al₂O₃ catalyst at temperatures of 380, 400, and 420°C and at pressures of 4.0 and 7.9 MPa. Experimental details have been described in the preceding paper.¹⁾

2.1 Elemental Analysis

Hydrogen and carbon contents were determined with a CHN-analyzer using a Perkin-Elmer model 240-C.

2.2 Physical Properties

Specific gravity, viscosity, refractive index were determined according to the procedures of JIS-K2249, JIS-K2283, and JIS-C2101, respectively. Specific gravity and refractive index were determined at 20°C for Middle Distillate and at 50°C for Vacuum Gas Oil.

2.3 Aromatic Carbon Content

The ratio of the aromatic carbon content to the total carbon content, C_a, in Middle Distillate and Vacuum Gas Oil was determined according to the n-d-M method.^{4),5)}

* To whom correspondence should be addressed

3. Results and Discussion

The properties of the feedstock and the whole range of product oil (Whole Product Oil) obtained by hydroprocessing, and the properties of the two fractions, Middle Distillate (b.p. 182 to 360°C) and Vacuum Gas Oil (b.p. >360°C), separated from the feedstock and Whole Product Oil, except for the data already reported in the preceding paper,

are summarized in **Table 1**.

3.1 Whole Product Oil

Specific gravity and viscosity of Whole Product Oil were plotted as a function of the reciprocal of LHSV in **Figs. 1** and **2**, respectively. With increasing 1/LHSV, both the specific gravity and viscosity decrease, however, with different rates depending on the reaction temperature and pressure. As shown in **Fig. 1**, the curves of 400°C at 4.0

Table 1 Experimental Results

React. Condition			Whole Product Oil		Middle Distillate (b.p.=182–360°C)							
Temp. (°C)	Press. (MPa)	LHSV (hr ⁻¹)	SP. GR. (15/4°C)	VIS (cSt/50°C)	Yield (wt%)	SP. GR. 20°C	VIS. (cSt) 37.8°C	98.9°C	N _D ²⁰	H (%)	C (%)	C _A (%)
420	7.9	0.69	0.8579	5.130	42.2	0.8574	2.933	1.166	1.4821	12.7	87.8	25.8
		2.01	0.8770	12.30	21.3	0.8683	4.038	1.427	1.4880	12.6	87.7	24.6
		1.02	0.8659	7.227	31.8	0.8636	3.434	1.300	1.4858	12.7	88.3	25.6
400	7.9	1.01	0.8776	13.54	17.3	0.8682	4.314	1.489	1.4861	12.8	88.5	22.1
		0.66	0.8696	10.77	20.6	0.8646	3.808	1.374	1.4832	12.9	87.8	21.7
		1.98	0.8842	17.87	13.9	0.8737	5.098	1.649	1.4890	12.6	87.8	21.7
380	7.9	1.01	0.8854	19.55	11.1	0.8738	5.063	1.634	1.4873	12.7	87.5	20.0
		0.51	0.8795	16.33	15.4	0.8696	4.786	1.586	1.4850	—	—	19.6
		0.42	0.8754	14.30	17.1	0.8677	4.714	1.571	1.4839	—	—	17.7
420	4.0	1.00	0.8796	8.234	29.5	0.8655	3.314	1.259	1.4903	12.5	88.6	30.0
		0.50	0.8630	4.166	40.8	0.8592	3.023	1.190	1.4881	12.4	87.8	31.2
		2.04	0.8855	13.69	18.4	0.8718	4.171	1.453	1.4930	—	—	28.3
400	4.0	1.03	0.8855	16.26	14.1	0.8751	4.490	1.521	1.4940	12.4	87.8	27.4
		0.68	—	12.77	17.7	0.8709	3.903	1.396	1.4917	12.4	88.2	27.8
		2.01	0.8913	19.84	13.4	0.8741	5.346	1.695	1.4941	—	—	26.7
380	4.0	1.01	0.8904	21.24	10.2	0.8753	4.886	1.620	1.4928	12.4	87.8	25.4
		0.51	0.8889	18.41	12.6	0.8723	4.379	1.497	1.4912	—	—	25.8
		0.40	0.8842	16.43	13.6	0.8692	4.397	1.505	1.4916	—	—	26.1
Feed Oil			0.9121	30.67	8.3	0.8685	5.527	1.757	1.4871	—	—	21.2

React. Condition			Vacuum Gas Oil (b.p.>360°C)									
Temp. (°C)	Press. (MPa)	LHSV (hr ⁻¹)	Yield (wt%)	SP. GR. 50°C	VIS. (cSt) 37.8°C	98.9°C	N _D ²⁰	S (%)	N (ppm)	H (%)	C (%)	C _A (%)
420	7.9	0.69	53.7	0.8496	19.52	4.043	1.4710	0.004	20	13.2	87.2	9.7
		2.01	77.0	0.8710	39.89	5.664	1.4812	0.040	140	12.9	87.0	10.8
		1.02	63.3	0.8618	28.18	4.777	1.4760	0.010	52	13.2	87.3	9.6
400	7.9	1.01	80.1	0.8680	39.31	5.886	1.4775	0.032	110	13.3	87.4	7.1
		0.66	75.3	0.8630	34.73	5.541	1.4751	0.012	66	13.4	88.1	7.1
		1.98	84.8	0.8752	46.21	6.330	1.4815	0.096	200	13.1	87.3	8.9
380	7.9	1.01	87.2	0.8739	46.82	6.487	1.4814	0.087	180	13.0	86.9	9.1
		0.51	83.4	0.8640	41.90	6.104	1.4766	0.028	96	13.3	87.4	8.2
		0.42	80.5	0.8633	40.39	5.997	1.4751	0.017	70	13.4	87.2	6.2
420	4.0	1.00	68.4	0.8709	30.91	4.881	1.4884	0.037	—	—	—	18.7
		0.50	50.1	0.8695	18.74	3.833	1.4860	0.009	150	12.8	87.8	17.3
		2.04	79.5	0.8721	39.89	5.864	1.4921	0.145	380	12.7	87.6	21.2
400	4.0	1.03	83.9	0.8756	42.92	6.185	1.4879	0.127	360	12.8	87.6	15.2
		0.68	79.8	0.8726	37.82	5.760	1.4860	0.066	300	12.9	88.0	14.7
		2.01	85.5	0.8783	50.62	6.664	1.4917	0.264	420	12.7	87.3	17.9
380	4.0	1.01	88.9	0.8740	49.77	6.624	1.4890	0.233	410	12.6	87.8	16.9
		0.51	86.5	0.8723	44.47	6.367	1.4850	0.103	340	12.9	87.9	13.4
		0.40	84.5	0.8714	42.56	6.221	1.4840	0.076	300	13.1	87.7	12.8
Feed Oil			91.7	0.8920	65.17	7.612	1.4995	1.98	600	12.1	86.1	20.0

Fig. 1 Specific Gravity of Whole Product Oil vs. 1/LHSV

Fig. 2 Viscosity of Whole Product Oil vs. 1/LHSV

MPa and 380°C at 7.9 MPa and the curves of 420°C at 4.0 MPa and 400°C at 7.9 MPa overlap with each other. Accordingly, the effect of increasing the pressure from 4.0 to 7.9 MPa on specific gravity is nearly equal to the effect of increasing the temperature by 20°C. As reported in the preceding paper,¹⁾ the effect of pressure on specific gravity is similar to that observed on the sulfur content of Whole Product Oil. This is confirmed by the fact that sulfur removal correlates closely with the decrease in specific gravity independently of pressure and temperature, as shown in **Fig. 3**. If changes in specific gravity and sulfur removal are differently affected by pressure, the curve shown in **Fig. 3** would separate into two

Fig. 3 Decrease in Specific Gravity vs. Sulfur Removal in Whole Product Oil

Fig. 4 Decrease in Viscosity in Whole Product Oil vs. Hydrocracking Conversion

curves for 4.0 and 7.9 MPa as observed in the relationship between sulfur and nitrogen removals.

While the effect of pressure on decreasing the viscosity seems to be relatively small, the effect of pressure on hydrocracking conversion was likewise small as reported in the preceding paper.¹⁾ This is supported by the fact that, as shown in **Fig. 4**, the decrease in viscosity and that in hydrocracking conversion are also correlated by a single curve independent of pressure and temperature.

On the other hand, the nitrogen and sulfur removals are correlated with two curves distinguished by pressure difference as shown in **Fig. 5**. This is consistent with the concept that HDS and HDN reactions are affected differently by pressure. As

reported in the preceding paper, the effect on the sulfur and nitrogen contents of Whole Product Oil of increasing the pressure from 4.0 to 7.9 MPa corresponded to increasing the temperature by 20 and 40°C, respectively.

Furthermore, **Figure 6** shows that the relationship between sulfur removal and hydrocracking conversion is affected differently by temperature and pressure. In other words, HDS and HC reactions are affected differently by pressure and temperature. The same relationship observed above is also expected to exist between nitrogen removal and hydrocracking conversion, because the nitrogen removal is correlated with that of sulfur

(symbols the same as for Fig. 1)

Fig. 5 Nitrogen Removal vs. Sulfur Removal in Whole Product Oil

(symbols the same as for Fig. 1)

Fig. 6 Sulfur Removal in Whole Product Oil vs. Hydrocracking Conversion

independent of temperature as shown in **Fig. 5**. This is consistent with the concept described in the preceding paper,¹⁾ that HC reaction proceeds through two mechanisms which are different from each other: one, like HDS and HDN both of which take place only on the catalyst surface, and the other that takes place by thermal cracking in absence of a catalyst. The results shown in **Fig. 6** also indicate that hydrocracking conversion increases with increasing temperature even when the sulfur content is kept constant by increasing LHSV or decreasing pressure to cancel the effect of increasing temperature.

3.2 Middle Distillate

The ratio of the aromatic carbon content to the total carbon content (C_a) in Middle Distillate is plotted as a function of the reciprocal of LHSV in **Fig. 7**. C_a varies with change in $1/LHSV$, and it is higher at higher temperature and at lower pressures; C_a for 380°C at 4.0 MPa is almost equal to that for 420°C at 7.9 MPa. It is known that the equilibrium state between hydrogenation of aromatic rings and dehydrogenation of naphthenic rings shifts toward dehydrogenation as temperature increases and also as hydrogen pressure decreases. Therefore, the effect of increasing the temperature from 380 to 420°C on the equilibrium state is just about canceled by the reverse effect of increasing the pressure from 4.0 to 7.9 MPa.

The C_a of hydroprocessed Middle Distillate varies in the range from 17.7 to 25.8% at 7.9 MPa and from 25.4 to 31.2% at 4.0 MPa. Most of these values are higher than 21.2% for Middle Distillate separated from the feedstock. Accordingly, it is

(symbols the same as for Fig. 1)

Fig. 7 C_a of Middle Distillate vs. $1/LHSV$

anticipated that the smoke point and cetane number of Middle Distillate produced by MHC process are low in comparison to those of corresponding straight-run fractions obtained from the Middle Eastern crude oil.

Although not all of the Middle Distillate samples were subjected to hydrogen analysis, the hydrogen content does not seem to be sensitive to changes in reaction conditions compared to C_a . The hydrogen content is between 12.6 and 12.9 wt% for Middle Distillate obtained at 7.9 MPa and between 12.4 and 12.5 wt% for that at 4.0 MPa, as shown in **Table 1**.

In the present study, Middle Distillate boiling between 182 and 360°C was collected as a single fraction without separating it into kerosene and diesel fuel oil because of the low yields of Middle Distillate for some product oils obtained under milder reaction conditions. Therefore, the properties of the Middle Distillates separated from the feedstock and that separated from Whole Product Oil were not strictly comparable, because the former consisted of only a diesel fuel oil fraction, while the latter contained both kerosene and diesel fuel oil fractions.

3.3 Vacuum Gas Oil

Figure 8 shows the relationship between C_a in Vacuum Gas Oil and $1/LHSV$. Comparing the effect of pressure on its C_a with that on C_a in Middle Distillate, pressure seems to have a greater effect on C_a in Vacuum Gas Oil. However, the effect of temperature is rather unclear. C_a s for 420°C and 400°C almost level off at $1/LHSV$ higher than 1.0, while, C_a for 380°C continues to decrease and

(symbols the same as for Fig. 1)
Fig. 8 C_a of Vacuum Gas Oil vs. $1/LHSV$

Fig. 9 Hydrogen Content of Vacuum Gas Oil vs. $1/LHSV$

acrosses the line for 400°C with further increase in $1/LHSV$. This may imply that the reaction rates of hydrogenation and dehydrogenation attain an equilibrium state at 400 and 420°C at $1/LHSV$ about 1.0, but the reaction rate at 380°C is too slow to attain an equilibrium state even at $1/LHSV$ of 2.5.

Figure 9 shows the plots of hydrogen content of Vacuum Gas Oil vs. $1/LHSV$. With increase in $1/LHSV$, the hydrogen content increases with different rates in the range from 12.9 to 13.4 wt% at 7.9 MPa and from 12.6 to 13.1 wt% at 4.0 MPa depending on temperature. Although the hydrogen content varies within a rather narrow range, the change in hydrogen content coincides with the change in C_a shown in **Fig. 8**. And the atomic ratio of hydrogen to carbon, H/C , correlates satisfactorily with C_a except for the feedstock, as shown in **Fig. 10**. This disparity of the feedstock indicates that part of the hydrogen consumed by hydroprocessing is taken into the product oil without decreasing C_a . This observation may be attributable to the hydrogenolysis of aliphatic carbon-sulfur bond and aliphatic carbon-nitrogen bond. Such hydrogenolysis is known to take place relatively easily and proceeds in the early stages of reaction. In addition, the decrease in C_a and the increase in hydrogen content imply that hydroprocessed Vacuum Gas Oil consists of more paraffinic and naphthenic molecules than the feedstock and that hydroprocessed Vacuum Gas Oil may be suitable as a feedstock for fluidized catalytic cracking.

Many studies on HDN reaction mechanism of polynuclear heterocyclic nitrogen compounds such as quinoline,^{6),7)} indole,⁸⁾ carbazole,⁹⁾ and acridine

(symbols the same as for Fig. 1)

Fig. 10 Hydrogen/Carbon Atomic Ratio vs. Aromatic Carbon Content in Vacuum Gas Oil

(symbols the same as for Fig. 1)

Fig. 11 Nitrogen Removal vs. Aromatic Carbon Content in Vacuum Gas Oil

ine¹⁰) have been reported. It is generally accepted that HDN of those compounds apparently consumes a much larger amount of hydrogen than does HDS of the homologous heterocyclic sulfur compounds, because not only the heterocyclic rings but also the adjacent aromatic rings have to be hydrogenated prior to the hydrogenolysis of the nitrogen-carbon bonds. Accordingly, it might be expected that there is some relationship between nitrogen content and C_a or H/C of the product oil. **Figures 11 and 12** show the plots of nitrogen removal as a function of C_a and H/C, respectively. As shown in these figures, nitrogen removal seems to be well correlated with C_a and H/C at 380 and 400°C regardless of pressure. However, the plot for 420°C deviates significantly from these correlations toward higher C_a and lower H/C. This may indicate that dehydrogenation reaction of the naphthenic rings becomes significant at 420°C due to the shift of the equilibrium state toward higher aromaticity and that the contribution of dealkylation reaction to increasing aromaticity is also considered significant.

4. Conclusions

The results of the present study on the properties of the product oil obtained from mild hydrocracking of vacuum gas oil are summarized as follows;

(1) Concerning the properties of the whole range of product oil there exist a good correlation between decrease in viscosity and hydrocracking conversion and also a good correlation between de-

(symbols the same as for Fig. 1)

Fig. 12 Nitrogen Removal vs. Hydrogen/Carbon Atomic Ratio in Vacuum Gas Oil

crease in specific gravity and sulfur removal; both correlation are independent of temperature and pressure.

(2) Compared to the corresponding straight-run fractions produced from Middle Eastern crude oils, the middle distillate fraction produced contains an appreciably higher amount of aromatic carbon, and the fraction is expected to have a lower smoke point and cetane number.

(3) The unconverted vacuum gas oil, which contains less aromatic carbon and more hydrogen than the feedstock, seems to be a suitable feedstock for fluidized catalytic cracking.

References

- 1) Hisamitsu, T., Ozaki, H., *Sekiyu Gakkaishi*, **29**, 295 (1986).
- 2) Gembicki, V. A., Andermann, R. E., Tajbl, D. G., *Oil Gas J.*, 116, Feb. 21 (1983).
- 3) Billon, A., Bigeard, P. H., Morel, F., Peries, J. P., Paper presented to Petrol. Refin. Cong. of Japan Petrol. Inst., Nov. 15—16 (1982).
- 4) Fujita, M., Ed. by Funasaka, W., “Nenryo Bunseki Shikhenho”, 457 (1968), Nankodo, Tokyo.
- 5) Van Nes, K., “Aspects of the Constitution of Mineral Oils”, 334 (1951), Elsevier, New York.
- 6) Aboul-Gheit, A. K., *Can. J. Chem.*, **53**, 2575 (1975).
- 7) Satterfield, C. N., Cocchetto, J. F., *Ind. Eng. Chem. Process Des. Dev.*, **20**, 53 (1981).
- 8) Stern, E. W., *J. Catal.*, **57**, 390 (1979).
- 9) Nagai, M., Sawahiraki, K., Kabe, T., *Nippon Kagaku Kaishi*, **1979**, 69.
- 10) Nagai, M., Sawahiraki, K., Kabe, T., *Nippon Kagaku Kaishi*, **1979**, 1350.

要 旨

重質留出油の水素化脱硫の研究 (第3報) 生成油の物理的および化学的性状

久光 俊昭, 尾崎 博己

日本鉱業(株)総合研究所, 335 埼玉県戸田市新首南 3-17-35

前報にて報告した中東系減圧軽油の水素化精製油を分留して得た中間留分と減圧軽油留分の物理的, 化学的性状相互間の関連性, およびこれらの性状と反応条件, さらに分解, 脱硫, 脱窒素の転化率との関連性について検討した。

反応温度と圧力が比重および粘度の変化に及ぼす影響の大きさは, おおの脱硫率と分解率への影響の大きさとほぼ等しい (Figs. 1, 2)。従って, 生成油の比重と硫黄含量の減少率 (Fig. 3), および粘度減少率と分解率 (Fig. 4) との間には, 反応温度や反応圧力の影響を受けない良い相関がある。脱硫率と脱窒素率との相関は (Fig. 5), 反応温度では変化しないが, 反応圧力の影響は受ける。一方, 脱硫率と分解率の関係は (Fig. 6), 反応温度および反応圧力のいずれが変化しても変わる。脱窒素率と分解率の関係についても, 同じことがいえる。

生成油に含まれる中間留分, 減圧軽油留分中の芳香族炭素含

量 (C_a) の変化も, 反応温度と反応圧力の両者の影響を受ける (Figs. 7, 8)。原料油に含まれる中間留分, および減圧軽油留分と比較すると, 生成油中の C_a は, ほとんどの中間留分において増加しているのに対し, 減圧軽油留分では減少している。また, 減圧軽油留分の水素含量は C_a の変化と良く相関しており, いずれの条件においても原料油よりも高くなっている (Figs. 9, 10)。従って, 減圧軽油のマイルド・ハイドロクラッキングで生成する中間留分の燃料油としての性状は, 直留油より劣るが, 減圧軽油留分は, 接触分解等の二次処理の原料油として適していると考えられる。

脱窒素率は反応温度が 420°C と高い場合を除き, C_a および H/C のいずれとも良い相関を示す (Figs. 11, 12)。 420°C では, 芳香性の高い方向へ平衡が移動することの影響が大きいため, 前記の相関からはずれると考えられる。

Keywords

Aromaticity, Cobalt molybdenum catalyst, Heavy distillate, Mild hydrocracking, Product oil property