

[Research Note]

Deep Hydrotreatment of Middle Distillates Obtained by Pyrolysis of Oil Shale and Oil Sands Bitumen

Yoshikazu SUGIMOTO*, Janchig NARANGEREL^{†1)}, and Hiroshi OZAWA

National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, JAPAN

(Received July 8, 2009)

Middle distillates obtained by pyrolysis of oil shale and oil sands bitumen were denitrogenated by complex formation with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which reduced the nitrogen contents from 9900 to 2700 wtppm and from 1300 to 700 wtppm, respectively, without any change in the sulfur contents. The original and denitrogenated oils were hydrotreated over a conventional NiMo catalyst in a fixed-bed continuous flow reactor. The pre-removal of nitrogen compounds greatly enhanced hydrodenitrogenation (HDN) and hydrodesulfurization (HDS), and the rate constants were increased by 4.9–27 for HDN and 2.8–5.4 for HDS. As a result, the nitrogen and sulfur contents of the denitrogenated oils were reduced to < 1 and < 10 wtppm, respectively, under the conditions of H_2 8 MPa, LHSV 1 h^{-1} and 350°C .

Keywords

Shale oil, Oil sands bitumen, Middle distillate, Deep hydrotreatment, Nitrogen pre-removal

1. Introduction

Demand for oil is increasing and conventional crude oil resources are declining, so the interest in unconventional oil resources such as oil shale and oil sands is increasing, especially because of the huge reserves. Meanwhile, stringent environmental specifications for liquid fuels have been introduced worldwide, and allowable sulfur levels for diesel fuel will be lowered to 10 or 15 wtppm in many developed countries. This change is important because middle distillates of pyrolysis products of oil shale and oil sands bitumen contain much larger amounts of sulfur and nitrogen than those of conventional oils, so the deep hydrotreatment to levels of S, N < 10 wtppm requires much more severe reaction conditions^{1)–3)}.

Nitrogen compounds are the least reactive and inhibit removal of other heteroatoms during hydrotreatment. Therefore, nitrogen removal before hydrotreatment is a promising way to produce ultra-clean fuels from nitrogen-rich feedstocks. Pre-removal of nitrogen by complex formation with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is efficient for synthetic crude oils such as shale oil⁴⁾, and HDN and HDS of the denitrogenated oils in a batch-type autoclave are greatly accelerated⁵⁾.

In this study, a fixed-bed continuous flow reactor was used to investigate the effect of nitrogen pre-removal on the hydrotreatment reactivities of middle distillates derived from oil shale and oil sands bitumen.

2. Experimental**2.1. Feedstocks and Catalyst**

The feedstocks used were middle distillates of pyrolysis products of oil shale (SO) and oil sands bitumen (OS), and mixed Middle East crudes (ME). The catalyst was a commercial NiMo/Al₂O₃ catalyst (Ni; 3 wt%, Mo; 13 wt%, surface area; 155 m²/g).

2.2. Separation of Nitrogen Compounds from Middle Distillate

300 g of SO or OS was mixed with 30 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and magnetically stirred for 2 h at 65°C . The liquid layer was recovered by simple decantation, and the precipitate was washed with hexane. The recovered oil was diluted with three volumes of hexane and the further precipitate was separated. The denitrogenated oil (DNSO or DNOS) was recovered by the evaporation of hexane followed by vacuum distillation. The recovery yields of DNSO and DNOS were 74 wt% and 90 wt%, respectively. The low recovery yield of DNSO was due to the adsorption of polyaromatic and polar components on the hydrophobic complex.

2.3. Hydrotreatment Tests

Hydrotreatment tests were carried out using a continuous down-flow tubular reactor (9.4 mm i.d. and

* To whom correspondence should be addressed.

* E-mail: y-sugimoto@aist.go.jp

^{†1)} (Present) Central Laboratory for Coal Research, P.O.Box 297, Ulaanbaatar 210628, MONGOLIA

Table 1 Properties of Feedstocks

Properties		SO	DNSO	OS	DNOS	ME
Sulfur	[wtppm]	71000	71000	45000	44000	8800
Nitrogen	[wtppm]	9900	2700	1300	700	40
GC distillation (ASTM D 2887)						
10 vol%	[°C]	211	217	259	259	234
30 vol%	[°C]	255	256	285	286	274
50 vol%	[°C]	291	291	305	305	296
70 vol%	[°C]	325	323	324	325	315
90 vol%	[°C]	363	360	350	352	340
Types by HPLC						
saturates	[wt%]	24	30	43	44	74
monoaromatics	[wt%]	27	31	18	18	14
polyaromatics	[wt%]	27	28	34	34	12
polar	[wt%]	22	11	5	4	<1

500 mm overall length) containing a packed mixture of the catalyst (4 ml, 3.48 g) and SiC (4 ml, 6.88 g). The catalyst was presulfided using ME containing 2 wt% dimethyldisulfide at increasing temperature up to 330°C. The standard reaction conditions were as follows; Temperature 330°C and 350°C, LHSV 1 and 2 h⁻¹, H₂ pressure 8 MPa (constant), H₂/oil ratio 500 N//l (constant). Product samples were collected at 2-3 h intervals after a stabilization period of more than 5 h under each set of conditions. Any H₂S and NH₃ trapped in the product sample were removed by bubbling nitrogen gas.

The HDS and HDN data were analyzed based on the following power law kinetic equation:

$$k = (1/(C_p)^{(n-1)} - 1/(C_f)^{(n-1)}) \times (\text{LHSV})/(n-1)$$

where k = rate constant (h⁻¹), C = sulfur or nitrogen content (wtppm), subscripts f and p = feed and product, and n = apparent reaction order, respectively. In the ultra-deep HDS region, the reaction order is 1.2-1.5^(6,7). In this study, both the HDN and HDS data were analyzed assuming the reaction order of 1.3 which gave the best-fit correlations.

2.4. Analysis

The sulfur and nitrogen contents were measured by an APS-35 analyzer. The boiling-point distribution was determined by GC-simulated distillation (ASTM D 2887). The compound types were identified by high performance liquid chromatography (HPLC).

3. Results and Discussion

3.1. Properties of Feedstocks

Table 1 shows the properties of the original middle distillates (SO, OS, ME) and the denitrogenated oils (DNSO, DNOS). The sulfur and nitrogen contents were 71000 and 9900 wtppm for SO, 45000 and 1300 wtppm for OS, and 8800 and 40 wtppm for ME. The differences in the nitrogen contents of the three feedstocks were extremely large, whereas the differences in the sulfur contents were relatively small. The nitro-

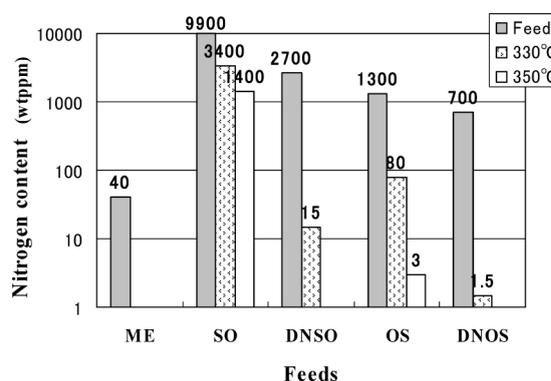


Fig. 1 Nitrogen Contents of Feeds and Product Oils at 330°C and 350°C (H₂ 8 MPa, LHSV 1 h⁻¹, H₂/oil 500 N//l)

gen contents of DNSO and DNOS were reduced to 2700 and 700 wtppm, respectively, whereas the sulfur contents were not affected by the denitrogenation pretreatment with CuCl₂·2H₂O. SO and OS contain large amounts of polyaromatic and polar components, and ME contains abundant saturates. The polar components of SO were decreased remarkably by the denitrogenation pretreatment, and the contents of saturates and monoaromatics were increased. There was no significant difference in the compound-type distribution between OS and DNOS because only a small amount of nitrogen compounds was removed selectively.

3.2. Hydrodenitrogenation

Figure 1 shows the nitrogen contents of the feeds and the products obtained at LHSV 1 h⁻¹, although the data points below 1 wtppm are not shown because of limited analysis accuracy. HDN of ME was very fast and the residual nitrogen content was less than 1 wtppm even at 330°C and LHSV 2 h⁻¹. Therefore, the supplementary hydrotreatment tests of ME were carried out at 330°C and LHSV 3, 4.5, 6 h⁻¹ to determine the rate constant. SO was least reactive and the residual nitrogen contents were 3400 wtppm at 330°C and 1400 wtppm at 350°C. HDN of OS was faster than that of SO, and the nitrogen content was reduced from 1300 to

Table 2 Effect of Denitrogenation Pretreatment on HDN and HDS Rate Constants

	Rate constant k [h^{-1}]					Enhancement factor	
	ME	SO	OS	DNSO	DNOS	$k_{\text{DNSO}}/k_{\text{SO}}$	$k_{\text{DNOS}}/k_{\text{OS}}$
HDN (330°C)	5.4	0.08	0.55	1.3	2.7	16	4.9
HDN (350°C)	n.d.	0.16	2.0	4.3	n.d.	27	n.d.
HDS (330°C)	2.1	0.16	0.24	0.45	0.78	2.8	3.3
HDS (350°C)	n.d.	0.35	0.89	1.9	3.6	5.4	4.0

n.d.; not determined because of the inaccuracy of the analysis.

80 wtppm at 330°C and to 3 wtppm at 350°C. The pre-removal of nitrogen compounds could change the situation drastically. For example, the residual nitrogen content at 330°C was 15 wtppm for DNSO and 1.5 wtppm for DNOS. The nitrogen contents of both DNSO and DNOS were reduced to < 1 wtppm at 350°C.

Table 2 shows the reaction rate constants and relative rate constants which illustrate the enhancement factor of the reaction rate by nitrogen pre-removal. The HDN rate constants at 330°C were 5.4 for ME, 0.08 for SO and 0.55 h^{-1} for OS, and those at 350°C were 0.16 for SO and 2.0 h^{-1} for OS. The HDN rate constant of DNSO was 1.3 h^{-1} at 330°C and 4.3 h^{-1} at 350°C, or 16 and 27 times larger than those of SO, respectively. The HDN rate constant of DNOS at 330°C was 2.7 h^{-1} which was 4.9 times larger than that of OS. The rate constant of DNOS at 350°C could not be measured accurately because the residual nitrogen content was below 1 wtppm even at LHSV 2 h^{-1} . The batch-type experiments in the previous work showed that the HDN rate of denitrogenated SO at 350°C was 2.0-4.4 times larger than that of SO depending on the degree of nitrogen pre-removal⁵⁾. The effect of nitrogen pre-removal on the HDN rate of the continuous flow reaction was much larger than that of the batch-type reaction. The reason for the big difference between batch and flow reaction systems is not clear, but might be due to the different oil/catalyst ratio and/or the effective desorption of H_2S and NH_3 in the H_2 gas stream of the flow reaction system.

The major nitrogen compounds in synthetic crude oils are alkyl-substituted pyridinic and pyrrolic compounds, which were removed completely or partly by complex formation with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Shale oils also contain *n*-alkyl nitriles, amides, and diazaaromatics⁸⁾ which could not be extracted by complex formation with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ⁵⁾. *n*-Alkyl nitriles are abundant in DNSO⁵⁾ and reactive in catalytic hydrotreatment¹⁾, which would lead to the great increase in HDN rate of DNSO.

3.3. Hydrodesulfurization

Figure 2 shows the sulfur contents of the feeds and products obtained at LHSV 1 h^{-1} . HDS of ME was much faster than the other feeds as well as HDN. The HDS rate constants of ME, SO and OS at 330°C were 2.1, 0.16 and 0.24 h^{-1} , and those of SO and OS at 350°C

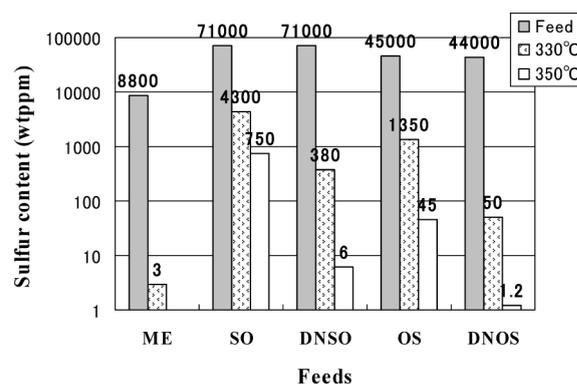


Fig. 2 Sulfur Contents of Feeds and Product Oils at 330°C and 350°C (H_2 8 MPa, LHSV 1 h^{-1} , H_2/oil 500 N/l)

were 0.35 and 0.89 h^{-1} , respectively (**Table 2**). The pre-removal of nitrogen compounds had no influence on the sulfur contents, but promoted HDS significantly. The HDS rate constants of DNSO and DNOS were 0.45 and 0.78 h^{-1} at 330°C, and 1.9 and 3.6 h^{-1} at 350°C, which means that the HDS rates were enhanced by factors of 2.8-5.4 by nitrogen pre-removal. Nitrogen compounds are well known to adsorb on a catalyst more strongly and inhibit the removal of nitrogen itself and other heteroatoms such as sulfur. The enhancement of HDS rates was caused by the reduced amount of nitrogen and the rapid conversion to ammonia which causes less inhibition. The previous study showed that HDS rates obtained by batch-type experiments at 350°C were increased by factors of 1.0-1.8 for SO and 1.8 for OS⁵⁾. The enhanced effect of nitrogen pre-removal on HDS rates in the continuous flow reaction system was attributed to the great increase in the HDN rates.

3.4. Hydrodearomatization

Reducing aromatic content along with heteroatom content is generally desirable with respect to both environmental preservation and diesel fuel quality. **Figure 3** shows the distribution of compound-type fractions of the feeds and product oils obtained at LHSV 1 h^{-1} . ME contains 26% aromatics which were reduced readily to 7.0% at 330°C and 3.6% at 350°C. Therefore, monoaromatics are not so difficult to hydrogenate if the nitrogen content of the feed is low. SO contains large amounts of polyaromatics and polar compounds which decreased gradually with increasing

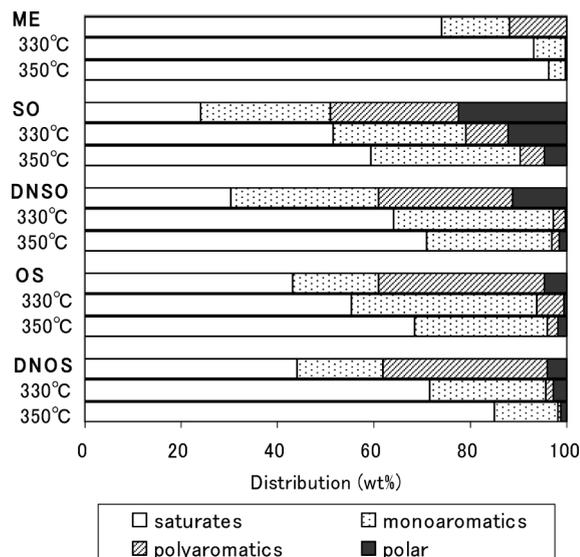


Fig. 3 Distribution of Compound-type Fractions of Feeds and Product Oils at 330°C and 350°C (H_2 8 MPa, LHSV 1 h^{-1} , H_2 /oil 500 N/l)

reaction temperatures. Reduction of these compounds was much promoted by the pre-removal of nitrogen compounds, but not of monoaromatics. Ammonia and water produced would inhibit the hydrogenation of monoaromatics. Polyaromatics in OS were decreased rapidly but monoaromatics still remained in significant amounts after the hydrotreatment. Monoaromatics in DNOS were hydrogenated more easily due to the lower amount and higher reactivity of the nitrogen compounds.

4. Conclusions

Middle distillates of shale oil (SO) and pyrolyzed

products of oil sands bitumen (OS) were denitrogenated by complex formation with $CuCl_2 \cdot 2H_2O$, and the original and denitrogenated oils were hydrotreated using a continuous fixed-bed reactor. The hydrotreatment of Middle East middle distillate (ME) was also examined for comparison. SO and OS contained large amounts of sulfur and nitrogen and deep hydrotreatment to levels of S, N < 10 wtppm could not be achieved under the conditions used, whereas almost all sulfur and nitrogen compounds in ME were removed at 330°C and LHSV 2 h^{-1} . The denitrogenation pretreatment of SO and OS greatly enhanced HDN and HDS, and the rate constants were increased by 4.9-27 for HDN and 2.8-5.4 for HDS. As a result, the residual nitrogen and sulfur contents of the denitrogenated oils could be reduced to < 1 and < 10 wtppm, respectively, under the conditions of H_2 8 MPa, LHSV 1 h^{-1} and 350°C.

References

- 1) Holmes, S. A., Thompson, L. F., *Fuel*, **62**, 709 (1983).
- 2) Thompson, L. F., Holmes, S. A., *Fuel*, **64**, 9 (1985).
- 3) Landau, M. V., *Catal. Today*, **36**, 393 (1997).
- 4) Choi, H. W., Dines, M. B., *Fuel*, **64**, 4 (1985).
- 5) Narangerel, J., Sugimoto, Y., *J. Jpn. Petrol. Inst.*, **51**, (3), 165 (2008).
- 6) Inoue, S., Takatsuka, T., Wada, Y., Hirohama, S., Ushida, T., *Fuel*, **79**, 843 (2000).
- 7) Fujikawa, T., Kato, M., Kimura, H., Kiriya, K., Hashimoto, M., Nakajima, N., *J. Jpn. Petrol. Inst.*, **48**, (2), 106 (2005).
- 8) Harvey, T. G., Matheon, T. W., Pratt, K. C., Stanborough, M. S., *Ind. Eng. Chem., Proc. Des. Dev.*, **25**, 52 (1986).

要 旨

オイルシェールおよびオイルサンドピッチューメンの熱分解中質油留分の深度水素化処理

杉本 義一, Janchig NARANGEREL^{†1)}, 小澤 浩

(独)産業技術総合研究所, 305-8565 茨城県つくば市東1-1-1 産総研つくば中央第5事業所

^{†1)} (現在) Central Laboratory for Coal Research, P.O.Box 297, Ulaanbaatar 210628, MONGOLIA

シェールオイルおよびオイルサンドピッチューメンの熱分解油中の中間留分(それぞれSO, OSと記す)をクリーンな輸送用燃料に転換するため, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ による脱窒素処理と市販 $\text{NiMo}/\text{Al}_2\text{O}_3$ による水素化処理について検討した。SOおよびOSの窒素含量はそれぞれ9900, 1300 wtppmであったが, 脱窒素処理により, それぞれ2700, 700 wtppmに減少した。SOおよびOSの水素化脱窒素・脱硫反応は中東系直留軽油に比べて

著しく遅く, 350°C , $\text{LHSV } 1 \text{ h}^{-1}$ の条件下においても10 wtppmレベルへの低減は困難であった。脱窒素処理により反応性は大きく向上し, 脱窒素処理油のHDN反応速度は4.9~27倍, 脱硫速度は2.8~5.4倍と著しく増加した。その結果, H_2 8 MPa, $\text{LHSV } 1 \text{ h}^{-1}$, 350°C の条件下において, 脱窒素処理油の窒素含量は<1 wtppmに, また硫黄含量は<10 wtppmに低減した。

.....