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Effects of Small Amounts of Nitrogen Compounds in Feedstock on Performance of Hydrocracking Catalyst

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Poisoning by very small amounts of nitrogen compounds was investigated for the catalysts for two types of hydrocracking processes. Nitrogen-free vacuum gas oil was used as feedstock with carbazole and tributyl amine as the model nitrogen compounds. Carbazole is abundant in hydrotreated oil as carbazole is difficult to remove. Tributyl amine is easily converted to ammonia in the reactor.

Vacuum gas oils containing various amounts of carbazole were passed over the main hydrocracking catalyst of the two-stage hydrocracking process. Strong effects on both hydrocracking activity and middle distillate selectivity were observed, especially if nitrogen content was less than 2 wtppm. The nitrogen poisoning effect was stronger on the catalyst with higher activity than on the catalyst with lower activity.

Poisoning of the main hydrocracking catalyst of the single-stage hydrocracking process, which is affected by both organic nitrogen compounds and ammonia, was evaluated with several ratios of combinations of carbazole and tributyl amine, maintaining total nitrogen concentration at 300 wtppm. Increased carbazole ratio lowered the hydrocracking activity and increased the middle distillate selectivity especially if the concentration of nitrogen as carbazole was less than 20 wtppm. These experimental results indicate that there is an optimum range of nitrogen concentration in the effluent to the main hydrocracking reactor to maximize middle distillate selectivity without severely affecting the hydrocracking activity.

Keywords

Vacuum gas oil, Hydrocracking, Poisoning, Ammonia, Carbazole

1. Introduction

The hydrocracking (HC) process for heavy oils has become more important recently because of the increased demand for cleaner middle distillates. The most common catalysts for the HC process are bifunctional with acidic and hydrogenation functions¹⁾. The acidic function usually depends on crystalline or uncrystalline aluminosilicates, but these materials have strong affinity with nitrogen compounds in the feedstock. Therefore, the nitrogen compounds have a large effect on the performance of the hydrocracking catalysts²⁾, and the processing of nitrogen compounds is a key technology for the HC process^{3)~5)}. However, nitrogen compounds also have a positive effect that increases the selectivity for middle distillate. Both positive and negative effects are caused by adsorption of the nitrogen compounds on the strong acid sites of HC catalysts, which have hydrocracking activity even for less reactive middle distillate.

The process flow of hydrocracking processes can be

classified into two main types^{6),7)} (**Fig. 1**). The “two-stage hydrocracking process” consists of two reactors with the gas/liquid separator between the reactors. The first reactor operates as a hydrotreater for hydrogenation of unsaturated molecules, hydrodesulfurization, and hydrodenitrogenation, as well as partial hydrocracking, and the second reactor completes the hydrocracking process. Most organic nitrogen compounds are converted to ammonia in the first reactor, and generated ammonia is removed at the gas/liquid separator. Therefore, the main HC catalyst in the second reactor is exposed only to the remaining organic nitrogen compounds⁷⁾, typically at levels of less than 100 wtppm.

The “single-stage hydrocracking process” converts most of the organic nitrogen compounds in the feedstock to ammonia in the first reactor, but the generated ammonia is not removed and remains in the effluent to the second reactor, as no gas separator is present between the first and the second reactors. The total nitrogen content in the effluent from the first reactor is determined by the fresh/recycle feed ratio regardless of the denitrogenation level in the first reactor.

Many studies to improve the efficiency of HC pro-

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handle than ammonia, was added to the feedstock with carbazole to evaluate the effect of hydrodenitrogenation level in the first hydrotreatment reactor on HC in the second reactor.

2. Experimental

2.1. Feedstock and Model Nitrogen Compounds

Two series of experiments were performed to quantitatively evaluate the nitrogen poisoning phenomena on the main HC catalysts in both the two-stage and the single-stage HC processes.

For the two-stage HC, poisoning behaviors on three amorphous silica-alumina catalysts (Cat-A, Cat-B, and Cat-C) with different HC activities were evaluated with vacuum gas oils containing various amounts of carbazole (N-VGO-1 to 4) and a nitrogen-free vacuum gas oil (NF-VGO), which was a recycle oil from an actual hydrocracking unit. The properties of the NF-VGO are shown in **Table 1**.

For the single-stage HC, the poisoning effect on a catalyst (Cat-D) consisting of silica-alumina and a small amount of USY zeolite was evaluated with vacuum gas oils containing carbazole and TBA at several ratios (N-VGO-5 to 9), but maintaining the total nitrogen content at 300 wtppm, which approximately corresponds to the expected nitrogen content in the effluent to the second reactor, which can be calculated from the fresh and recycle feedstock flow rate. N-VGO-5 to 9 were prepared by the addition of carbazole and TBA to NF-VGO. The nitrogen contents in the N-VGOs and

NF-VGO are shown in **Table 2**.

Metal loadings and other catalyst properties that affect the HC performance are shown in **Table 3**.

2.2. Hydrocracking Reaction

The catalyst (100 ml) was filled in a fixed bed flow reactor with α -alumina (100 ml) as diluent, and used for the hydrocracking reaction. The hydrocracking conditions were as follows.

Evaluation test for two-stage HC: Catalyst; Cat-A, B, C, H₂ pressure; 14.7 MPa, H₂/oil ratio; 800 n/l, operation temperature; 360, 370, 380, 390°C (NF-VGO), 370, 380, 390°C (N-VGOs), liquid hourly space velocity (LHSV); 1.36 h⁻¹.

Evaluation test for single-stage HC: Catalyst; Cat-D, H₂ pressure; 14.7 MPa, H₂/oil ratio; 800 n/l, operation temperature; 330, 340, 350, 360°C (NF-VGO), 390, 400, 410°C (N-VGO-5), 380, 390, 400°C (N-VGO-6 to 8), 390, 400°C (N-VGO-9), LHSV; 1.60 h⁻¹.

Before providing the feedstocks, catalysts were sulfided with nitrogen-free gas oil containing 1 vol% carbon disulfide. Liquid samples were obtained after oil/gas separation. Concentrations of gas products were analyzed by GC (gas chromatography).

2.3. Analysis of Product Oils

The evaluation tests for the two-stage HC measured HC activity and the yield of each fraction at 60 wt% conversion of the 293°C⁺ fraction. The evaluation test for the single-stage HC measured HC activity and the yield of each fraction at 70 wt% conversion of the 360°C⁺ fraction. These performance parameters were based on the actual operation conditions of the specific HC units. The targeted fraction of the two-stage HC

Table 1 Properties of Nitrogen-free Vacuum Gas Oil (NF-VGO)

		NF-VGO
Density (15°C)	[g/ml]	0.8249
Sulfur	[wt%]	< 0.001
Nitrogen	[wtppm]	< 1
Distillation	(ASTM D 2887)	
IBP	[°C]	263
T10	[°C]	335
T30	[°C]	375
T50	[°C]	398
T70	[°C]	424
T90	[°C]	470
T95	[°C]	501
FBP	[°C]	554

Table 2 Nitrogen Contents in Feedstocks

	Nitrogen as carbazole [wtppm]	Nitrogen as TBA [wtppm]
NF-VGO	0	0
N-VGO-1	0.5	0
N-VGO-2	2	0
N-VGO-3	8	0
N-VGO-4	16	0
N-VGO-5	0	300
N-VGO-6	10	290
N-VGO-7	20	280
N-VGO-8	50	250
N-VGO-9	75	225

Table 3 Properties of Hydrocracking Catalysts

	W [wt%]	Ni [wt%]	Silica-alumina weight per volume [g/cm ³]	USY weight per volume [g/cm ³]	Metal (W + Ni) / Silica-alumina ratio [wt%/wt%]
Cat-A	11	1	0.485	—	0.177
Cat-B	22	2	0.480	—	0.430
Cat-C	10	1	0.607	—	0.128
Cat-D	22	2	0.468	0.02	0.450

Table 4 293°C⁺ Conversion of NF-VGO and N-VGOs

Sample number [—]	Time [h]	Feed [—]	Nitrogen in feedstock [wtppm]	Operation temperature [°C]	293°C ⁺ conversion		
					Cat-A [wt%]	Cat-B [wt%]	Cat-C [wt%]
1	54	NF-VGO	0	390	82.4	71.8	93.8
2	67	NF-VGO	0	380	66.8	49.8	82.8
3	78	NF-VGO	0	370	46.0	25.4	61.7
4	91	NF-VGO	0	360	27.1	14.6	38.5
5	102	NF-VGO	0	390	79.0	62.3	94.7
6	115	NF-VGO	0	380	62.7	38.2	78.3
7	138	N-VGO-1	0.5	390	76.4	55.2	91.8
8	151	N-VGO-1	0.5	380	54.2	34.4	73.5
9	164	N-VGO-1	0.5	370	34.9	20.4	46.9
10	188	N-VGO-2	2.0	390	70.8	49.8	86.3
11	201	N-VGO-2	2.0	380	46.8	—	62.5
12	214	N-VGO-2	2.0	370	28.0	16.6	36.8
13	237	N-VGO-3	8.0	390	56.4	39.8	72.1
14	250	N-VGO-3	8.0	380	30.8	22.8	40.8
15	263	N-VGO-3	8.0	370	15.8	11.4	21.4
16	287	N-VGO-4	16.0	390	30.9	23.9	43.1
17	300	N-VGO-4	16.0	380	13.7	12.0	20.2
18	313	N-VGO-4	16.0	370	6.7	6.0	10.2
19	337	NF-VGO	0	390	50.2	27.4	72.5
20	349	NF-VGO	0	390	57.8	33.4	—
21	361	NF-VGO	0	390	60.9	34.4	—
22	373	NF-VGO	0	390	—	38.7	—

H₂ pressure; 14.7 MPa, H₂/oil ratio; 800 nll, liquid hourly space velocity (LHSV); 1.36 h⁻¹.

unit discussed in the present paper is jet fuel (= kerosene) fraction and the cut point was set at 293°C whereas the single-stage HC is targeted at middle distillates (kerosene and gas oil) and the cut point was set at 360°C.

Distillation properties of liquid samples obtained from hydrocracking reaction were evaluated with the ASTM D 2887 method to determine the 293°C⁺ conversion defined as Eq. (1).

$$293^{\circ}\text{C}^{+} \text{ conversion (wt\%)} = (C_0 - C_1) / C_0 \times 100 \quad (1)$$

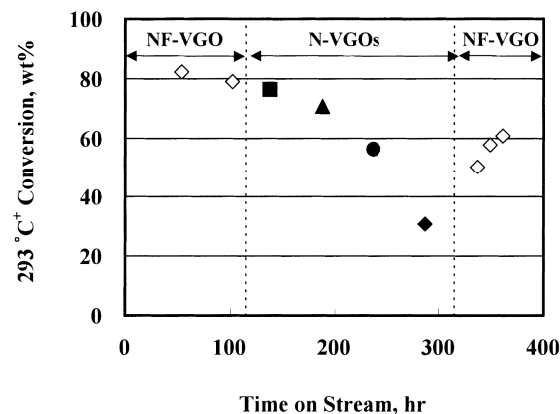
$$\text{where } C_0 \text{ (wt\%)} = 293^{\circ}\text{C}^{+} \text{ fraction of feedstock} \quad (2)$$

$$C_1 \text{ (wt\%)} = 293^{\circ}\text{C}^{+} \text{ fraction of product oil} \quad (3)$$

The 360°C⁺ conversion was calculated with a similar equation.

Yields of each fraction were also derived from the result of ASTM D 2887 analysis. Boiling ranges were as follows: naphtha (boiling point: C5-127°C), kerosene (127-293°C), gas oil (293-360°C), bottom oil (360°C⁺). The gas fraction consisted of methane, ethane, propane, butane, and isobutane.

Required operation temperatures for 60 wt% and 70 wt% conversion (ROT60 and ROT70) were calculated from Arrhenius plots assuming that the HC reaction is second order. Approximate yields of each fraction at 60 wt% or 70 wt% conversion were calculated from the correlation curve of conversion and yield of each fraction.



◇ NF-VGO, ■ N-VGO-1 (0.5 wtppm), ▲ N-VGO-2 (2 wtppm), ● N-VGO-3 (8 wtppm), ◆ N-VGO-4 (16 wtppm).

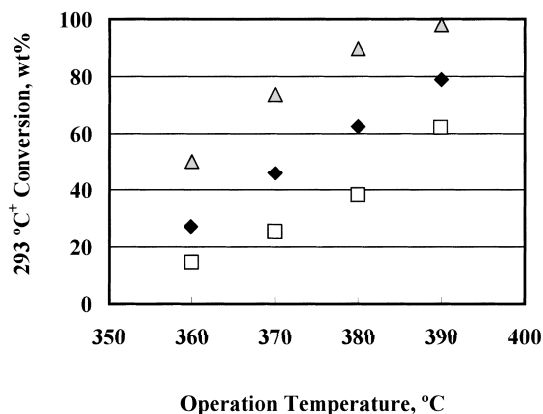
Note: In Fig. 2, 293°C⁺ conversions at 390°C operation with Cat-A were extracted from Table 4.

Fig. 2 Change in Hydrocracking Activity for Vacuum Gas Oils with and without Nitrogen Compounds

3. Results and Discussion

3.1. Effects of Nitrogen Compounds on Two-stage Hydrocracking Catalysts

The results of the evaluation tests for poisoning of two-stage hydrocracking catalysts and 293°C⁺ conversion are summarized in Table 4. Figure 2 compares the 293°C⁺ conversion at 390°C operation on Cat-A, and shows that HC activity was almost stable with NF-



◆ Cat-A, □ Cat-B, △ Cat-C.

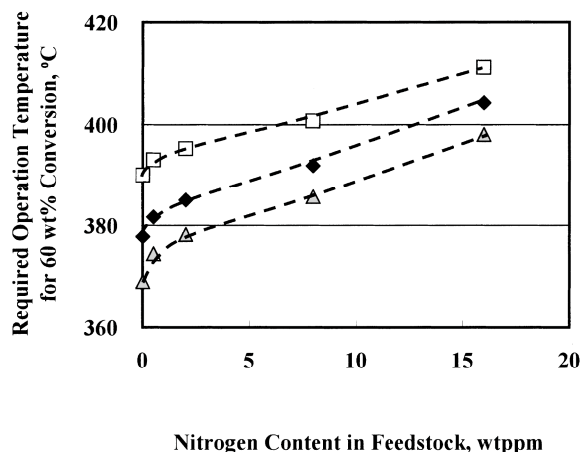
Fig. 3 Hydrocracking Activity of the Present Catalysts for Nitrogen-free Vacuum Gas Oil (NF-VGO)

VGO feed, declined according to the increase of nitrogen content, and after 315 h recovery of HC activity with NF-VGO was observed. NF-VGO was supplied for almost 50 h and HC activity recovered gradually, but 50 h was apparently still on the path of recovery. This result demonstrated the reversibility of nitrogen poisoning of HC activity and that the changes in HC activity observed during the present study were caused by nitrogen poisoning.

The HC activities of Cat-A, Cat-B and Cat-C for nitrogen free vacuum gas oil (NF-VGO) are compared in Fig. 3. The highest HC activity was observed for Cat-C and the lowest for Cat-B. The highest HC activity of Cat-C can be interpreted as the highest concentration of silica-alumina and the lowest metal/silica-alumina ratio. The lowest HC activity of Cat-B can be explained by the very high metal/silica-alumina ratio.

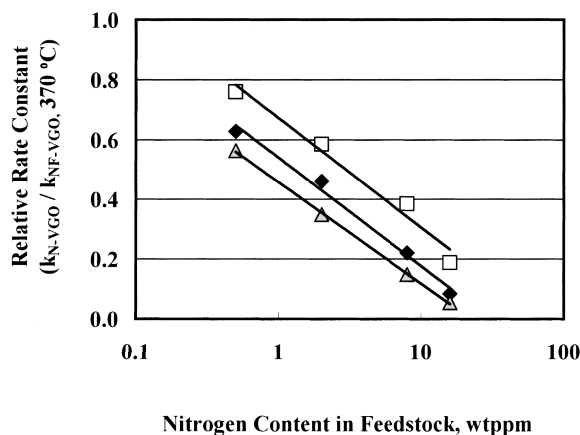
Figure 4 shows the effect of nitrogen in the feedstock (N-VGO-1 to 4) on the activity of catalysts (Cat-A, Cat-B and Cat-C). Even very small amounts of nitrogen compounds at less than 10 wtppm greatly lowered the HC activity of the catalysts. The decrease of HC activity of all catalysts was rapid at nitrogen content between 0 and 2 wtppm, and ROT60 increased gradually with nitrogen content of more than 2 wtppm.

Figure 5 shows the relative rate constant at 370°C as expressed by the division of the rate constants for N-VGOs (k_{N-VGO}) by that of NF-VGO (k_{NF-VGO}). The effect of nitrogen poisoning is stronger for the hydrocracking catalyst with higher activity. Figure 5 also indicates the logarithmic relationship between the rate constant of the HC reaction and nitrogen content. Figures 6 to 10 show the effect of nitrogen on the yields of gas, naphtha, kerosene, gas oil, and vacuum gas oil (VGO) at 60 wt% conversion, respectively. The gas yields were almost constant regardless of the



◆ Cat-A, □ Cat-B, △ Cat-C.

Fig. 4 Required Operation Temperature for 60 wt% Conversion as a Function of Nitrogen Content in VGO Feedstock

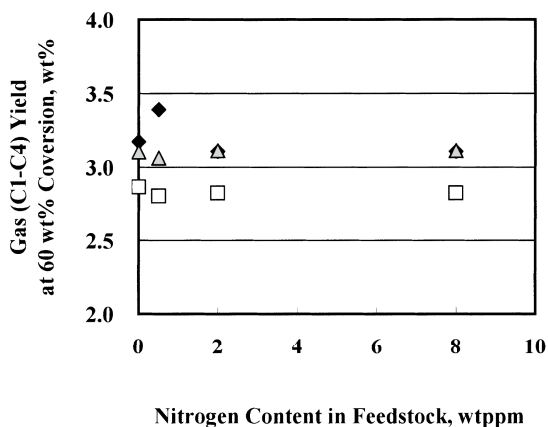


◆ Cat-A, □ Cat-B, △ Cat-C.

Fig. 5 Effects of Nitrogen Content in VGO Feedstock on Relative Rate Constant of the Hydrocracking Reaction at 370°C (second order)

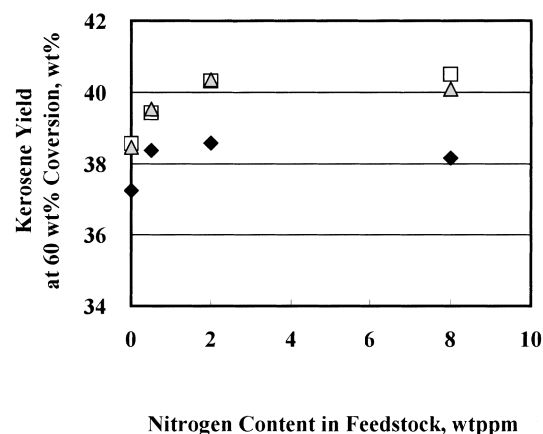
employed catalyst or the nitrogen content, but the yields of liquid fractions were affected by nitrogen content of less than 2 wtppm.

The strong acid sites that crack small or medium size molecules decrease the middle distillate yield by secondary cracking. Therefore, the increases in kerosene and gas oil yields with nitrogen contents of less than 2 wtppm can be attributed to poisoning of the strong acid sites. On the other hand, increase of nitrogen content to more than 2 wtppm did not improve the yield balance, whereas the HC activity was strongly affected by nitrogen content. This result indicates that most of the strong acid sites are deactivated by nitrogen of 2 wtppm. The acid sites that are deactivated by nitrogen of more than 2 wtppm can be regarded as weak acid sites that hardly convert the middle distillates (ker-



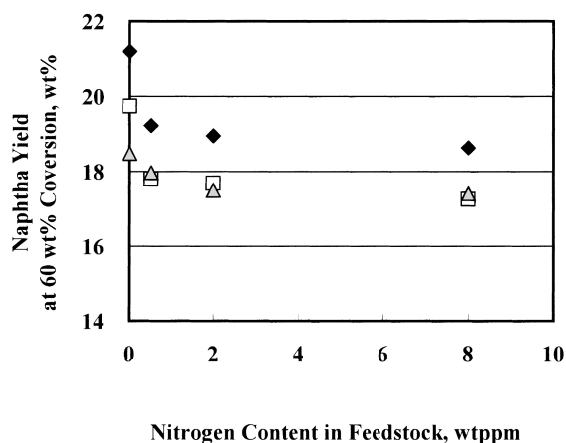
◆ Cat-A, □ Cat-B, △ Cat-C.

Fig. 6 Relationship between Nitrogen Content in VGO Feedstock and Yield of Gas Fraction (C1-C4) at 60 wt% Conversion



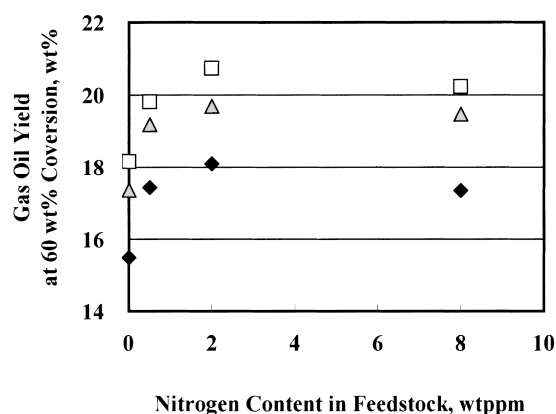
◆ Cat-A, □ Cat-B, △ Cat-C.

Fig. 8 Relationship between Nitrogen Content in VGO Feedstock and Yield of Kerosene Fraction at 60 wt% Conversion



◆ Cat-A, □ Cat-B, △ Cat-C.

Fig. 7 Relationship between Nitrogen Content in VGO Feedstock and Yield of Naphtha Fraction at 60 wt% Conversion



◆ Cat-A, □ Cat-B, △ Cat-C.

Fig. 9 Relationship between Nitrogen Content in VGO Feedstock and Yield of Gas Oil Fraction at 60 wt% Conversion

osene and gas oil) to the lighter fraction.

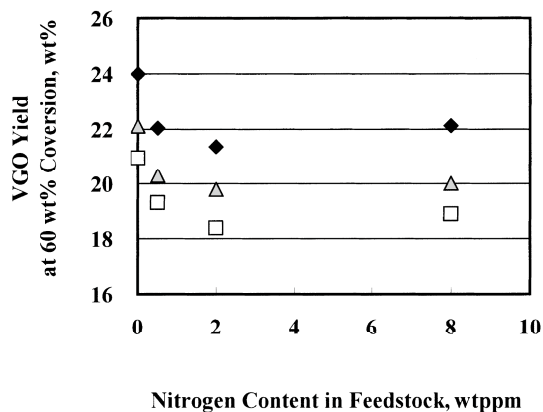
3. 2. Effects of Nitrogen Compounds on Single-stage Hydrocracking Catalysts

The correlation between the nitrogen content of carbazole in the feedstock and ROT70 is shown in **Fig. 11**. ROT70 increased with increased carbazole ratio in the feedstock, indicating decreased HC activity. With the nitrogen content of carbazole at less than 20 wtppm, the carbazole ratio affects HC activity more than with the nitrogen content of carbazole at more than 20 wtppm. ROT70 increased by 0.27°C/wtppm and 0.04°C/wtppm with nitrogen contents of carbazole of less than 20 wtppm and more than 20 wtppm, respectively.

The contents of organic nitrogen compounds in product oils, carbazole or TBA in the present study, were less than the detectable limit of 1 wtppm with all samples, which indicates that the stronger poisoning effect

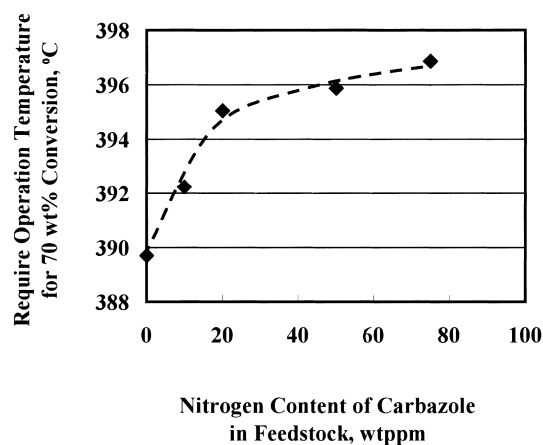
of carbazole than that of TBA on HC activity only persists until the carbazole is converted to ammonia. The difference in the strength of poisoning between carbazole and TBA suggests that the denitrogenation reaction of carbazole does not proceed immediately as for TBA, so carbazole has a significantly stronger poisoning effect than TBA.

The activation energies of the HC reaction, assuming that the HC reaction is apparent second order, are also strongly affected by the carbazole/TBA ratio (**Fig. 12**). These trends suggest that the affinity of carbazole with the active sites on the catalyst is stronger than that of ammonia. Various nitrogen compounds were tested in the poisoning of thiophene hydrodesulfurization on NiMo/Al₂O₃ catalyst¹⁰. The calculated adsorption equilibrium constants of ammonia and carbazole were 0.048 kPa⁻¹ and 0.51 kPa⁻¹, respectively. The size/



◆ Cat-A, □ Cat-B, △ Cat-C.

Fig. 10 Relationship between Nitrogen Content in VGO Feedstock and Yield of VGO Fraction at 60 wt% Conversion



Note: In Figs. 11-17, nitrogen contents originated from carbazole were varied maintaining total nitrogen contents constant at 300 wtppm balanced by tributyl amine.

Fig. 11 Required Operation Temperature for 70 wt% Conversion as a Function of Content of Nitrogen as Carbazole in the VGO Feedstock

mass of the poison molecule affects the strength of poisoning as well as basicity⁸⁾. These previous findings also support the stronger effects of carbazole than ammonia on the HC reaction.

The correlation between the carbazole ratio and the yields of each fraction at 70 wt% conversion are shown in Figs. 13-16. If the nitrogen content of carbazole was less than 20 wtppm, with increased carbazole ratio, gas yield increased, naphtha yield decreased, gas oil yield increased, and kerosene yield was almost constant. The increase of gas oil yield continued up to approximately 3 wt%, which corresponds to the decrease of naphtha yield. On the other hand, if the nitrogen content as carbazole was more than 20 wtppm, the yield balance of each fraction was almost constant regardless

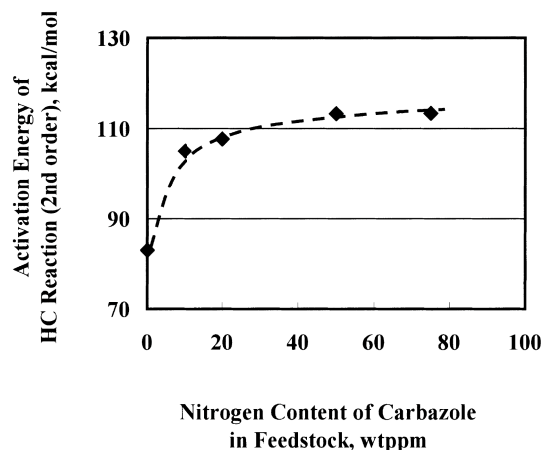


Fig. 12 Relationship between Content of Nitrogen as Carbazole in VGO Feedstock and Activation Energy (second order)

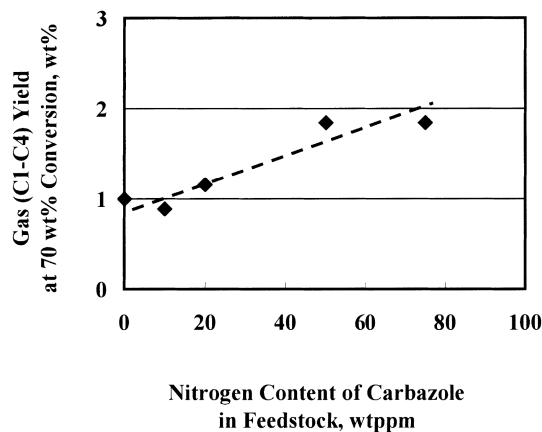


Fig. 13 Relationship between Content of Nitrogen as Carbazole in VGO Feedstock and Gas Yield (C1-C4) at 70 wt% Conversion

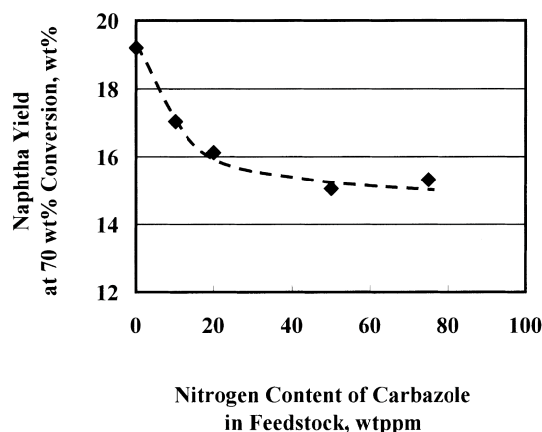


Fig. 14 Relationship between Content of Nitrogen as Carbazole in VGO Feedstock and Naphtha Yield at 70 wt% Conversion

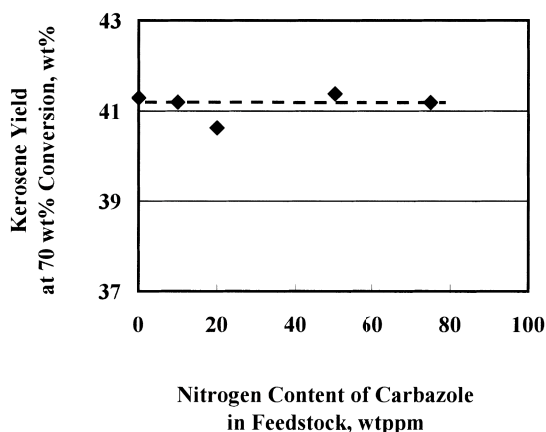


Fig. 15 Relationship between Content of Nitrogen as Carbazole in VGO Feedstock and Kerosene Yield at 70 wt% Conversion

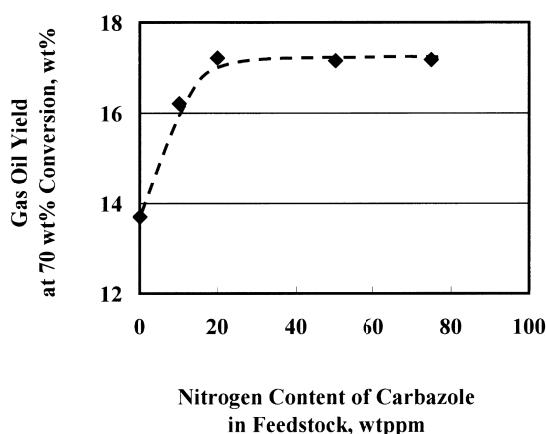
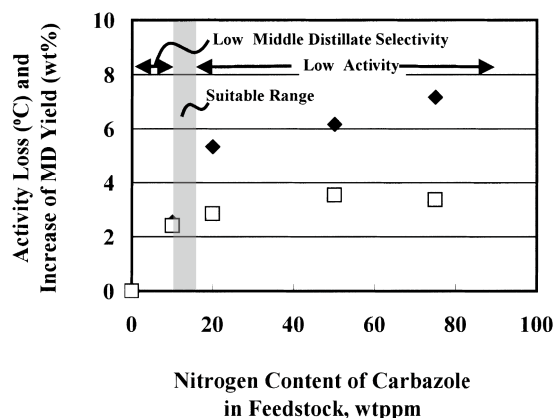


Fig. 16 Relationship between Content of Nitrogen as Carbazole in VGO Feedstock and Gas Oil Yield at 70 wt% Conversion

of the carbazole ratio. The constant yield of kerosene is attributed to the low reactivity of the molecules in the kerosene fraction, and the increase of gas fraction with increased carbazole ratio is due to the increased ROT70.

These results suggest that there is a suitable range of the denitrogenation target for the hydrotreatment step in the first reactor. **Figure 17** indicates that 10 wtppm of nitrogen as carbazole significantly increases the yield of middle distillate, whereas more than 10 wtppm nitrogen as carbazole results in almost constant middle distillate yield regardless of the nitrogen content of carbazole. On the other hand, HC activity declines according to the increase of the nitrogen content as carbazole until 80 wtppm. From these results, we conclude that 10 to 15 wtppm of nitrogen could significantly increase the middle distillate selectivity without severely affecting the HC activity. On the other hand, in the two-stage HC, 2 wtppm of nitrogen is adequate for improvement of the middle distillate yield, as shown in



◆ ROT70, °C, □ Middle distillate (MD) yield, wt%.

Fig. 17 Optimum Nitrogen Content for High Middle Distillate Yield

Figs. 8 and 9. The difference can be attributed to the number of strong acid sites on the catalysts, as the catalyst employed for the evaluation of single-stage HC catalyst in the present study contains zeolite whereas those for two-stage HC are amorphous catalysts.

4. Conclusion

Poisoning by very low concentrations of nitrogen compounds was investigated for the catalysts used for the two types of hydrocracking processes. Nitrogen-free vacuum gas oil was used as the feedstock with model nitrogen compounds, carbazole and tributyl amine.

Strong effects both on hydrocracking activity and middle distillate selectivity were observed for two-stage hydrocracking, especially if the nitrogen content was less than 2 wtppm. Increased carbazole ratio lowered the hydrocracking activity and increased the middle distillate yield for single-stage hydrocracking. Those effects were especially strong if the nitrogen concentration derived from carbazole was less than 20 wtppm.

These experimental results indicate the suitable range of nitrogen content in the effluent to the main hydrocracking reactor to maximize the middle distillate selectivity without unacceptable decrease of HC activity. The present study suggests that around 2 wtppm and 10-15 wtppm are suitable for two-stage and single-stage hydrocracking, respectively.

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要 旨

原料油中の微量窒素化合物が水素化分解触媒性能に及ぼす影響

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原料油中の微量窒素化合物の水素化分解触媒に対する影響を2種類の水素化分解プロセスについて評価した。原料油には窒素化合物を含まない減圧軽油をカルバゾール, トリブチルアミンといったモデル窒素化合物とともに用いた。カルバゾールは難脱窒素化合物であるため水素化処理された油中に多く残存することが知られ, またトリブチルアミンは反応器中で容易にアンモニアに転換される。

二段式水素化分解プロセスの水素化分解触媒に対しては, カルバゾールを数種の濃度で含む減圧軽油を適用し, カルバゾール由来の窒素濃度が水素化分解活性および中間留分収率の双方に対して強い影響を与えることが分かった。特に, 窒素濃度が2 wtppm以下の時に大きな影響が見られ, 水素化分解活性に関しては高い活性を有する触媒ほど強く被毒効果を受けることが

分かった。

一段式水素化分解プロセスの水素化分解触媒は有機窒素化合物およびアンモニア双方の影響を受けるため, その触媒に対する被毒効果をカルバゾールおよびトリブチルアミン由来の窒素総量を300 wtppmに保ちながら数種の比率で組み合わせることにより検討した。カルバゾール比率を増加させた場合, 水素化分解活性は低下し, 中間留分収率は増加した。その影響は特にカルバゾール由来の窒素量が20 wtppm以下の時に顕著であった。

これらの実験結果から, 後段水素化分解反応塔への原料油に関し, 分解反応性を大きく損なわずに中間留分選択性を向上させることができる最適な窒素濃度範囲があることが分かった。