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Improvement of Hydrodenitrogenation (HDN) in Co-refining of Coal-derived Liquid and Petroleum Fraction

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The improvement in hydrodenitrogenation (HDN) of coal-derived liquids by co-refining with a petroleum fraction results principally from lowering the nitrogen content of the feedstock (coal-derived liquid) by blending with a nitrogen-free petroleum fraction. Effects of different fractions of coal-derived liquids on HDN and hydrodeoxygenation (HDO) were also examined. The HDN improvement by co-refining could be interpreted in terms of Langmuir-Hinshelwood mechanism.

1. Introduction

The high contents of nitrogen, oxygen and aromatic compounds in coal-derived liquids are in contrast to the low contents of nitrogen compounds to the high content of sulfur compounds in petroleum fractions^{1)~5)}. The nitrogen content in coal-derived liquids must be reduced to produce fuels alternative to petroleum transportation fuels. Severer hydrotreating conditions are required in the reduction of nitrogen content in coal-derived liquids than that in the corresponding petroleum fractions. Severer conditions of hydrodenitrogenation (HDN) lead to high investment and operational costs for the upgrading coal-derived liquids. However, one of the feasible options for reducing the severity of the HDN, thus reducing costs, is to perform co-refining of coal-derived liquids with a nitrogen-free petroleum fraction^{6)~8)} utilizing the moderate hydrotreating facilities of the refinery. In the present study, the mechanism of HDN improvement observed by co-refining was examined to assess such feasibility.

2. Experimental

2.1. Preparation of Feedstocks

Coal-derived liquids were obtained from 1 t/day Process Support Unit (PSU) of NEDOL process with liquefied Illinois #6 coal. Two fractions were prepared for the experiments: one was IBP-

180°C fraction, and the other was IBP-200°C fraction. The properties of these fractions and the petroleum straight-run naphtha for co-refining are tabulated in Table 1. Five model feedstocks of toluene solutions were prepared by blending with commercial reagents of aniline and pyridine without further purification (more than 99% pure) and whose contents are given in Table 2. Pyridine was chosen as a representative nitrogen compound having relatively strong adsorption strength and low HDN reactivity, while aniline was chosen as a representative nitrogen compound having weak adsorption strength and high HDN reactivity. The nitrogen compounds were added to a toluene solvent containing 0.2 S-% of carbon disulfide to maintain sulfided state of the Ni-Mo-P/alumina catalyst. Five solutions containing different contents of nitrogen were prepared for examining the improvement in HDN by co-refining of coal-derived liquid and petroleum fraction. Aniline and pyridine were added in the same amount to each solution.

2.2. Reaction Apparatus and Procedures

All hydrodenitrogenation (HDN) reactions were carried out over a commercially available Ni-Mo-P/alumina catalyst packed in a conventional down-flow stainless steel tubular reactor as mentioned in a previous paper⁹⁾. The catalyst was presulfided at 300°C for 60 h with a flowing straight-run light gas oil containing 1.6 wt% of sulfur at hydrogen pressure of 3.0 MPa. At the completion of sulfiding, the light gas oil was switched to the feedstock. The HDN reactions

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Table 1 Properties of Coal-derived and Petroleum-derived Naphtha

Fraction		Illinois #6 IBP-180°C	Illinois #6 IBP-200°C	Petroleum IBP-150°C
Specific gravity		0.7898	0.8256	0.7044
Elemental analysis				
Nitrogen	[wt-ppm]	1290	2900	<1
Oxygen	[wt%]	1.2	2.1	<0.1
Sulfur	[wt-ppm]	1810	1950	220
GC analysis (NPD)	[wt-ppm]			
Pyridine		11	11	0
Pyrrole		52	41	0
Aniline		53	308	0
GC analysis (AED)	[wt%]			
Phenol		1.14	1.64	0.00
<i>o</i> -Cresol		0.02	0.36	0.00
<i>m</i> -Cresol		0.0	0.3	0.0
<i>p</i> -Cresol		0.0	0.2	0.0
FIA	[vol%]			
Paraffin & Naphthene		78.4	73.7	94.1
Olefin		9.7	5.2	0.0
Aromatics		11.9	21.1	5.9
Distillation	[°C]			
IBP		15	15	23
5%		41	63	31
10%		68	83	35
20%		84	99	60
30%		92	117	69
40%		102	134	76
50%		117	151	93
60%		132	164	99
70%		144	171	114
80%		160	180	126
90%		170	189	137
95%		173	195	146
EP		219	211	162

Table 2 Properties of Model Oil for Co-refining

Sample No.		1	2	3	4	5
Aniline	[wt-ppm]	1490	1211	910	608	324
Pyridine	[wt-ppm]	1460	1175	910	613	312
Total nitrogen	[wt-ppm]	2950	2386	1820	1221	636

Toluene solution containing 0.2 wt% S (CS₂).

both for coal-derived liquids and model feedstocks were performed at 300°C and total pressure of 3.0 MPa, except for hydrogen to oil ratio; it was 80 Nm³/kl for the former and 700 Nm³/kl for the latter. All liquid reactants were vaporized under the above conditions at the reactor inlet. The products from the reactor outlet were led to a high pressure separator and then to a low pressure separator. The gaseous products were analyzed by on-line gas chromatography. After performing on-line analysis, nitrogen gas was injected into the liquid to remove any HDN product of ammonia remaining therein and move it into the off-gas line. Liquid products free of ammonia were obtained from the outlet of the low pressure separator and quantified by a load cell. The overall mass balance was calculated from such elements as hydrogen and feed flow at the reactor inlet, off-gas flow and its composition, and liquid products. The HDN products were collected after

the catalyst activity had reached its steady state. The standard conditions were set for the first and last samples of each run to check the catalyst activity.

2. 3. Analysis of Liquid Products

The total nitrogen content of the HDN products was determined with a chemiluminescence nitrogen analyzer (Mitsubishi Chemicals, TN-05). Components of HDN products were quantified by gas chromatograph (HP5890 II) equipped with a nitrogen-phosphorous selective detector (NPD)^{10,11}, an atomic emission detector (AED), and a mass selective detector (MSD). Most of the components could be completely separated with a capillary tubular column, which was derived for separation of nitrogen compounds^{11,12}, and could be identified by combining the MSD and co-elution of standard reagents. The content of each component of the products was determined by use of external standard method^{13,14}.

Fig. 1 Changes in Partial Pressure of Nitrogen and Oxygen Compounds in HDN (A) and HDO (B) Conversion *vs.* Space Time under the Conditions of 300°C, 3.0 MPa, Treat Gas Ratio of 80 Nm³/kl

3. Results

3. 1. Properties of Coal-derived Liquid

As shown in Table 1, high contents of aromatics and nitrogen- and oxygen-containing compounds are found in the coal-derived naphtha fraction as compared with the petroleum naphtha. Though petroleum fractions generally contain higher sulfur contents than the corresponding coal liquid fractions, the petroleum fraction employed in this experiment contained a smaller amount of sulfur than that of coal-derived liquid. Oxygen and nitrogen contents of the coal-derived naphtha in the IBP-200°C fraction were about twice as high as those in the IBP-180°C fraction. There were three types of nitrogen compounds of pyridine, pyrrole, aniline and one type of oxygen compound of phenol contained in the Illinois #6 coal-derived naphtha, and their alkyl derivatives. Pyridine, pyrrole and their alkyl derivatives were contained in about same amount in both IBP-180°C and IBP-200°C fractions. Aniline, phenol, and their alkyl derivatives were contained more in the IBP-200°C fraction than in the IBP-180°C fraction, because their boiling points were higher than those of pyridines and pyrroles.

Although all nitrogen compounds of coal-derived naphtha fraction were composed of alkyl derivatives of pyridine, pyrrole, and aniline, the content of each of the three nitrogen compounds had not been quantitatively determined. Alkyl derivatives of pyridine were considered to have reactivities and adsorption

strengths onto the catalyst surface similar to those of pyridine, and also similar to those of pyrrole and aniline. Therefore, the nitrogen compounds of pyridine, pyrrole, and aniline were employed for analysis of hydrodenitrogenation (HDN) reactions as mentioned in the previous section.

3. 2. Co-refining Coal-derived Liquid and Petroleum

Hydrodenitrogenation (HDN) reactions by co-refining were examined by changing the blending ratio of coal-derived liquid to petroleum fraction under the conditions used in hydrotreating petroleum naphtha fractions: temperature of 300°C, pressure of 3.0 MPa, liquid hourly space velocity of 3.0 h⁻¹, and hydrogen to oil ratio of 80 Nm³/kl. With increasing petroleum fraction, both HDN and HDO conversions increased as shown in Fig. 1. The HDN and HDO conversions were higher in the IBP-180°C fraction than those in the IBP-200°C fraction at any blending ratio. This is caused by the high contents of aniline and phenol types of compounds in IBP-200°C fraction which are weakly adsorbed on the catalyst surface. By increasing the petroleum fraction from 50 to 90%, the improvement in HDO from 0 to 100% was more pronounced than that in HDN from 75-95% to 100%.

3. 3. HDN of Model Compounds

It was assumed from the results of co-refining coal-derived liquids that the improvement in HDN and HDO by co-refining resulted from lowering the nitrogen content in the feedstock by increasing the amount of petroleum fraction blended. Lowering especially of nitrogen compounds,

-----; predicted, ●, ▲, ▼, ■, ◆; experimental in case of LHSV=2.0, 3.0, 5.0, 8.0, 10.0 h⁻¹, respectively.

Fig. 2 Effect of Dilution by Nitrogen Free Solvent on HDN Conversion under the Conditions of 300°C, 3.0 MPa, Treat Gas Ratio of 700 Nm³/kl

which are strongly adsorbed onto the catalyst surface, is effective for improving HDN reaction. Model HDN reactions were carried out to examine whether or not there was any HDN improvement by co-refining. **Figure 2** shows HDN conversion *versus* nitrogen free solvent under the following conditions: 300°C, 3.0 MPa, LHSV of 3.0 h⁻¹, and hydrogen to oil ratio of 700 Nm³/kl. The hydrogen to oil ratio was higher by about one order of magnitude than that used in the coal-derived liquid to prevent drops in the hydrogen partial pressure in the HDN and HDO reactions¹⁵.

Similar HDN performance in the coal-derived liquid was obtained for model HDN reactions; the greater the amount of nitrogen-free solvent, the higher was HDN conversion. **Figure 3** shows the change in aniline and pyridine+piperidine partial pressure as a function of space time. Pyridine HDN proceeds *via* hydrogenation of pyridine to give piperidine in which the ratio of pyridine to piperidine remains constant throughout the reaction, because hydrogenation of pyridine to piperidine attains equilibrium immediately¹⁵. It was assumed in this study that pyridine and piperidine had the same strength to adsorb onto the catalyst surface to simplify kinetic analysis¹⁶. Aniline HDN was severely inhibited by strongly adsorbed pyridine+piperidine. While pyridine HDN was not largely dependent on the initial partial pressure of pyridine+piperidine, the aniline HDN was significantly inhibited by the content of pyridine+piperidine. Moreover, the rate of aniline HDN depended largely on the content of co-existing pyridine. The HDN was improved overall by lowering the content of aniline, and by enhancing aniline HDN by lowering the content of co-existing pyridine+piperidine.

3. 4. Prediction of HDN Improvement

Inhibition of aniline HDN by pyridine+piperidine could be expressed in terms of Langmuir-Hinshelwood competitive equations mentioned in one of our previous paper¹⁶. Not only the rate constants of pyridine and aniline but also their adsorption equilibrium constants and HDN product of ammonia were taken into account in the

(A), (B); model reactions using sample No. 1 and No. 3 in Table 2, respectively, -----; predicted by Langmuir-Hinshelwood equations.

Fig. 3 Changes in Partial Pressure of Pyridine+Piperidine (●) and Aniline (▲) in the Simultaneous Reactions under the Conditions of 300°C, 3.0 MPa, Treat Gas Ratio of 700 Nm³/kl

Table 3 Calculated k and K in Kinetic Analysis

	Adsorption constant K/kPa^{-1}	Rate constant of HDN $k/(\text{kPa})(\text{g mol oil})(\text{g-cat h})^{-1}$
Pyridine/Piperidine	3.0	0.5
Aniline	0.04	4.0
Ammonia	0.04	—

equations as follows: the rate determining steps were C–N bond scission of piperidine in pyridine HDN and hydrogenation of benzene ring in aniline HDN¹⁵. It was assumed in the Langmuir–Hinshelwood equations that pyridine and piperidine adsorbed on the hydrogenation and hydrogenolysis sites with equal strength as did aniline¹⁶.

$$r_{\text{ANI}} = \frac{K_{\text{ANI}}P_{\text{ANI}}}{1 + K_{\text{PYD}}P_{\text{PYD}} + K_{\text{ANI}}P_{\text{ANI}} + K_{\text{AM}}P_{\text{AM}}} k_{\text{ANI}} \quad (1)$$

$$r_{\text{PYD}} = \frac{K_{\text{PYD}}P_{\text{PYD}}}{1 + K_{\text{PYD}}P_{\text{PYD}} + K_{\text{ANI}}P_{\text{ANI}} + K_{\text{AM}}P_{\text{AM}}} k_{\text{PYD}} \quad (2)$$

where

r_{ANI} , r_{PYD} are the rate of aniline and pyridine+piperidine,

k_{ANI} , k_{PYD} are the rate constants of aniline and pyridine+piperidine,

P_{ANI} , P_{PYD} , P_{AM} are the partial pressures of aniline, pyridine+piperidine and ammonia,

K_{ANI} , K_{PYD} , K_{AM} are the adsorption equilibrium constants of aniline, pyridine+piperidine, and ammonia.

The rate constants and adsorption constants have already been determined in a previous study¹⁶ as shown in Table 3. The rate constant of aniline was greater than that of pyridine+piperidine, while the adsorption constant of pyridine+piperidine was greater than that of aniline and that of ammonia. Equations (1) and (2) were integrated by using the fourth-order Runge–Kutta routine to predict the experimental results of improving the HDN reaction. The improvement in HDN observed in the model reactions was quantitatively predicted by the Langmuir–Hinshelwood equations as shown in Fig. 2.

4. Discussion

4.1. HDN Improvement in Co-refining

The HDN is improved by blending a petroleum fractions in hydrotreating coal-derived liquids.

The HDN reaction is known to be influenced by such as content of hydrogen sulfide^{17–24}, type of co-existing reactant^{25–32}, and partial pressure of hydrogen¹⁵. Hydrogen sulfide affects HDN reactions in two ways: one is by changing the properties of active sites of HDN, and the other is by inhibiting the adsorption of nitrogen compounds. Hydrogen sulfide slightly inhibits the hydrogenation step, but strongly enhances the C–N bond cleavage after the hydrogenation step in pyridine HDN and in quinoline HDN under similar conditions used in the study^{17–23}. Hanlon²³ studied the influence of hydrogen sulfide on pyridine HDN over a sulfided Ni–Mo–P/alumina catalyst. He reported that overall HDN conversion was promoted slightly by increasing the $\text{H}_2\text{S}/\text{H}_2$ ratio because of the enhancement of C–N bond cleavage by changing the properties of the catalytic site. In the present study, however, the improvement in HDN observed in co-refining of coal-derived naphtha with petroleum naphtha was not caused by increasing hydrogen sulfide, because the sulfur content in the petroleum naphtha was lower than that in the coal-derived naphtha. The effect of inhibition of hydrogen sulfide on HDN could also be excluded, because the adsorption strength of hydrogen sulfide is much smaller than the adsorption strengths of nitrogen compounds. Gultekin *et al.*²⁴ observed that although ammonia inhibited hydrogenation of propylbenzene strongly, hydrogen sulfide inhibited it weakly, but hydrogen sulfide exerted no influence on the hydrogenation when it was in co-existence with ammonia. The hydrogen sulfide adsorbs much more weakly onto the catalyst surface compared with ammonia. The adsorption constants of ammonia and aniline were smaller by about two order of magnitude than those of pyridine+piperidine as tabulated in Table 3. The adsorption constant of hydrogen sulfide would then be smaller at least by more than two order of magnitude than that of pyridine and that of piperidine. Therefore hydrogen sulfide could not affect any improvement in HDN by co-refining.

The effect of solvent was examined in our previous study. In general, aromatics were adsorbed onto the catalyst surface more strongly than

paraffins^{25)~29)}. However, the HDN of aniline was not influenced by changing the solvent from toluene to heptane in our previous examination. In addition to the solvent effect, toluene was scarcely hydrogenated in our HDN study¹⁵⁾. These results indicated that the nitrogen compounds had adsorbed onto the catalyst surface so strongly compared with hydrocarbons that the difference in the improvement brought about by aromatic and paraffinic solvents could not be observed in HDN reactions. Therefore, HDN reaction by co-refining was not improved by blending with a petroleum fraction to increase paraffinic solvency.

The influence of hydrogen partial pressure was observed slightly in co-refining. Increasing the partial pressure by about one order with respect to hydrogen improved aniline HDN, but did not improve pyridine HDN¹⁵⁾. While the maximum difference in hydrogen consumption between neat treating of coal-derived naphtha and the co-refining was about 20 Nm³/kl, the pressure drop was only one fourth of the initial hydrogen partial pressure. Therefore, increasing the pressure resulting from decreasing hydrogen consumption by blending a petroleum fraction could be neglected in co-refining.

The HDN improvement in co-refining is principally caused by the dilution of coal-derived naphtha with a nitrogen free solvent. While pyridine HDN was not influenced by aniline, the aniline HDN was strongly inhibited by co-existing pyridine+piperidine¹⁶⁾. The more the nitrogen content is decreased, the more is the increase in aniline HDN. Lowering the initial pyridine and piperidine contents by dilution with a nitrogen-free petroleum fraction enhanced aniline HDN, that resulted in the improvement of overall HDN by co-refining.

4. 2. HDO Reaction and the Effect of Petroleum Fraction Range

Both the improvement in hydrodeoxygenation (HDO) and the effect of the range of petroleum fraction could also be interpreted in terms of the competitive reactions mentioned above. Phenolic compounds, which are the major oxygen compounds in the coal-derived naphtha, were more strongly inhibited to be adsorbed onto the catalyst surface than the aniline type by such basic nitrogen compounds as pyridine and piperidine⁹⁾. Therefore, the improvement in HDO of phenolic compounds was more pronounced than that content of aniline types by increasing the petroleum contents as shown in Fig. 1. The HDO of phenols was improved more than the HDN of anilines by increasing the unoccupied active sites.

The HDO conversion of IBP-200°C fraction was lower than that of IBP-180°C fraction by co-refining. This is caused by the higher contents of aniline and phenolic compounds in the IBP-200°C fraction than in the IBP-180°C fraction as shown in Table 1.

4. 3. Model Reaction of Co-refining

The improvement in HDN reaction was observed when a mixture containing aniline and pyridine was diluted with a nitrogen-free solvent. The improvement in HDN observed in the model reaction was similar to that observed in the co-refining of coal-derived naphtha with petroleum naphtha. The difference in the HDN performance in model oil and in coal-derived naphtha was caused by the difference in the distribution of nitrogen compounds. The HDN improvement in the model reaction was also predicted by Langmuir-Hinshelwood equations, in which the order of the rate and equilibrium adsorption constants were consistent with the order found in the literature^{33)~37)}. Neither the hydrogen sulfide nor the type of solvent used affected the improvement of HDN reactions. Therefore, it is concluded that the principal cause of improving HDN by co-refining is lowering of the total nitrogen content by diluting with a nitrogen-free solvent petroleum naphtha.

The improvement in HDN would be observed when both strongly adsorbed nitrogen compounds like pyridines and their hydrogenated intermediates of piperidines and weakly adsorbed nitrogen compounds like anilines are contained in the coal-derived liquid. The improvement in HDN was also observed by co-refining heavier fractions of coal-derived liquid such as middle distillates which contained no anilines. Ukegawa *et al.* observed the improvement in HDN by co-refining coal-derived middle distillates and corresponding petroleum fractions⁸⁾. The middle distillates usually contain quinolines, indoles, and carbazoles as typical nitrogen compounds. These nitrogen compounds and their hydrogenated intermediates are strongly adsorbed like such nitrogen compounds as pyridines. Weakly adsorbed aniline-type compounds are also produced as hydrogenated intermediates in HDN of quinolines, indoles, and carbazoles³⁸⁾. The improvement in HDN could be observed in the same manner as in co-refining heavier fractions of coal-derived liquids and petroleum fractions. It is assumed from the results that a recycle process could be another option for upgrading coal-derived liquids, because the improvement in HDN by blending a nitrogen-free recycle solvent was observed.

5. Conclusions

The reaction of HDN was improved when a mixture or solution containing aniline and pyridine as a coal-derived liquid was co-refined with a petroleum fraction. The improvement in HDN by co-refining was effected principally by dilution of the nitrogen-containing compounds with a nitrogen-free solvent. The improvement in HDN could be quantitatively interpreted by Langmuir–Hinshelwood mechanism.

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要 旨

石炭液化油の石油留分との混合処理における
水素化脱窒素反応の促進効果町田 基^{†1)}, 小野 重好^{†2)}, 服部 英^{†3)}^{†1)} 出光興産(株)石油技術センター, 299-02 千葉県袖ヶ浦市上泉 1280^{†2)} 出光興産(株)新燃料部, 107 東京都港区北青山 1-3-6^{†3)} 北海道大学 エネルギー先端工学研究センター, 060 札幌市北区北 13 条西 8 丁目

石炭液化油は窒素含量が高いために石油留分と比べて過酷な水素化精製条件が必要であるが、石炭液化油を一部石油に混合して水素化処理すると HDN 反応が促進され、石油精製条件に近い条件で水素化処理が可能となる。これまで石炭液化油と石油との混合による HDN 反応の促進効果は報告されてきたが、そのメカニズムについては明確に分かっていなかった。本論文では HDN のモデル反応により、石炭液化油の HDN

反応の促進は石油混合希釈による出発原料の窒素濃度の低減が要因となっていることを実験的に検証した。また、水素化脱酸素 (HDO) も促進されるが、HDN と同様に窒素濃度の低減が反応促進の要因であると推定した。窒素濃度低減による HDN 反応の促進効果は、ラングミュアー型の競争吸着機構で説明できることを示した。

Keywords

Coal liquid, Co-refining, Hydrodenitrogenation, Hydrodeoxygenation, Langmuir-Hinshelwood equations, Adsorption equilibrium constant