[Regular Paper]

Studies on Catalytic Hydrotreating of Recycled Solvents from Coal Liquefaction Process (Part 1) Characteristic Changes of Recycled Solvents during Hydrotreating

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A bituminous coal liquefaction process, called the NEDOL process, is under development by the New Energy and Industrial Technology Development Organization (NEDO). Important features of this process include the capacity to produce hydrogen-donatable solvents, obtained by hydrogenation of middle distillates of coal derived oils, and to recycle these solvents to a liquefaction stage as hydrogen donor solvents. These recycled solvents, obtained by liquefaction of Wandoan coal, and their catalytic hydrotreated oils, have been extensively characterized, using a variety of analytical methods. The following items have been examined and are discussed in this study: (1) Influence of chemical hydrogen consumption on the reactivities of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrogenation of aromatic-rings, during hydrotreating; (2) Changes in composition of hydrocarbon types, nitrogen- and oxygen-containing compounds, as a function of chemical hydrogen consumption; (3) Changes of average molecular weights; (4) Characteristics changes of oxygen- and nitrogen-containing compounds, and reactivities of HDO and HDN; (5) Characteristics changes of donatable hydrogens as a function of a degree of hydrogenation (Δfa).

1. Introduction

Since liquefied coal can be utilized as a source of clean energy to replace petroleum, coal liquefaction is under intensive development, worldwide. In Japan, New Energy and Industrial Technology Development Organization (NEDO) is the center for the development of coal liquefaction processes. Several coal liquefaction technologies with hydrogenation process of solvents have been studied and developed¹⁾, such as EDS process²⁾. The new process (NEDOL process) under development by NEDO can also produce solvents containing high donatable hydrogen, which were obtained by hydrogenation of the middle distillates of coal-derived oils and recycled back to a liquefaction stage as hydrogen donor solvents. Here, the authors report on the extensive results of characterization of the recycled solvents, obtained by the 1 t/day liquefaction of Wandoan coal, and their catalytic hydrotreated oils.

The following items have been examined and discussed in this study:

- (1) Influence of chemical hydrogen consumption on the reactivities of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrogenation of aromatic-rings, during hydrotreating.
- (2) Changes in composition of hydrocarbon types, nitrogen- and oxygen-containing compounds, as a function of chemical hydrogen consumption.
- (3) Changes of average molecular weights.
- (4) Characteristics changes of oxygen- and nitrogen-containing compounds, and reactivities of HDO and HDN.
- (5) Changes of donatable hydrogens as a function of a degree of hydrogenation (Δfa).

2. Experimental

2.1. Feed Solvents

Table 1 shows properties of the feed solvents, coal derived middle distillates (recycled solvents) which were obtained by the 1 t/day liquefaction

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Table 1 Properties of Feed Solvents

Feed solvents	A	B
Specific gravity, d25/4°C	1.0104	1.0434
Ultimate analysis [wt%]		
Carbon	89.23	88.58
Hydrogen	8.26	8.12
Oxygen	2.2	2.7
Nitrogen	0.41	0.70
Sulfur	0.07	0.03
Average molecular weights ^{a)}	181	211
<i>n</i> -Paraffins [wt%]	9.0	13.7
Aromaticity (<i>fa</i>) ^{b)}	0.68	0.67
350°C+ fraction [wt%]	17	40

a) Obtained from FI-Mass spectrum.

b) Obtained from ¹³C-NMR spectrum.

unit of Wandoan coal. The difference of characteristics is the degree of "heaviness"; that is, solvents A and B include 17 and 40 wt% of 350°C+ fraction, respectively.

2.2. Catalysts and Reactions

The hydrotreating tests were performed, utilizing fixed-bed reactors holding 200 ml of catalyst⁹⁾. The catalyst was a commercial by available Ni-Mo/alumina, cylindrical extrudate type of 1/16 inch diameter. The reaction conditions were: temperature, 320-400°C; hydrogen pressure, 50-100 kg/cm²-G; LHSV, 1-3 h⁻¹; hydrogen to liquid ratio in volume, 1,000 NL/l.

2.3. Analysis

Analysis of physico-chemical properties and chemical composition were performed according to the standards summarized in **Table 2**.

n-Paraffin contents were obtained by GC and/or GC-MS analysis. GC analysis were performed by a Hewlett Packard (HP) 5880 chromatograph with a computer data system. The column was a 60 m×0.25 μm i.d. fused silica capillary (SPB-11). Using the same GC conditions, GC-MS analysis were performed on a 5880 chromatograph, directly interfaced to a JEOL JMS-DX300 mass selective detector. Mass spectra were analyzed using a computer data system, JMA-3100.

Type analysis of hydrocarbons and hetero-atom compounds were performed by GC-MS (JEOL JMS-DX300) and FT-IR^{4)~6)} (JEOL JIR-100),

Fig. 1 Reactivities during Hydrotreating

respectively.

The ¹H- and ¹³C-NMR spectra for chemical structural analysis were recorded on a JEOL JNM GX-270 spectrometer. For ¹H and ¹³C measurements, CDCl₃ was added as a solvent and as a signal lock. The chemical shifts were expressed in ppm relative to tetramethylsilane (TMS) internal standards.

The average molecular weights were determined by field ionization (FI)-MS recorded on a JEOL JMS-DX300⁷⁾.

3. Results and Discussion

3.1. Features of Reactions in Hydrotreating

Chemical hydrogen consumption is an indicator of reaction severity in hydrotreating of recycled solvents. The influence on both the conversion rate for the removal of hetero-atom compounds and on hydrogenation are shown in **Fig. 1**. The order of the reactivity was:

The rates of conversion for hetero-atoms re-

Table 2 Analytical Methods

Physico-chemical properties	
Specific gravity	ASTM D 4052
Distillation	ASTM D 1160, D 2887
Chemical composition	
Carbon/Hydrogen	ASTM D 3178 (HALLIKAINEN M-1325)
Sulfur	ASTM D 2622 (XRF, PHILIPS PW-1400)
Oxygen	Coulometric titration (Oxygen Analyzer, Mitamura Riken Co., Ltd.)
Total nitrogen	Chemiluminescence (DOHRMANN DN-10)
Basic nitrogen	UOP 269

Fig. 2 Dependencies of Reactions on Chemical Hydrogen Consumption during Hydrotreating

Fig. 3 Degree of Hydrogenation (Δfa) versus Chemical Hydrogen Consumption of C_5^+ Oils

removal is higher than that for hydrogenation. The hydrogenation of aromatic-rings, however, is a more dominant process in hydrotreating of the feed solvents, as described below.

The influence of total chemical hydrogen consumption on hydrogen consumption needed for the removal of hetero-atom and the hydrogenation of aromatic-rings are shown in **Fig. 2**, which indicates that most of the hydrogen is consumed during hydrogenation. Hydrogen input plays a very important role in hydrotreating of recycled solvents in a coal liquefaction process. Shown in **Fig. 3** is the change in the degree of hydrogenation with consumption of chemical hydrogen of C_5^+

Fig. 4 Changes in Composition of Hydrocarbon Type Compounds as a Function of Chemical Hydrogen Consumption

fraction of feed solvents. Attributed to the conversion of hydroaromatics from aromatics, the degree of hydrogenation (Δfa) is proportional to the chemical hydrogen consumption in the hydrogenation of C_5^+ oils; the degree of hydrogenation is not dependent on the feed solvent; the difference in aromaticity, between the feed solvent and the product (Δfa), was obtained from ^{13}C -NMR spectrum.

$$\Delta fa = fa(\text{feed}) - fa(\text{product})$$

$$\text{where } fa = \frac{\text{aromatic carbons}}{\text{total carbons}}$$

(The standard operating condition in the NEDOL process is to limit $\Delta fa=0.1$.)

3.2. Changes in Composition during Hydrotreating

Changes in chemical composition of recycled solvents are important considerations for design and operation of the solvent hydrotreating process during coal liquefaction. From this viewpoint, changes in composition of hydrocarbon types and major compounds were investigated.

The quantitative changes in composition of hydrocarbon types (aromatics, hydroaromatics, naphthenes and *n*-paraffins) during hydrotreating of feed solvents, as a function of chemical hydrogen consumption, are shown in **Fig. 4**. It indicates that the major change in composition is attributed to the conversions of hydroaromatics from aromatics by hydrogenation. *n*-Paraffins were not decomposed during hydrotreating. The changes in composition of hydroaromatics show gradual

Fig. 5 Changes in Composition of Naphthalene Derivatives during Hydrotreating

increases over 150 N/l of chemical hydrogen consumption, indicating the conversion of hydroaromatics to naphthenes. These results demonstrate the fact that the concentration of donatable hydrogens increase gradually over 150 N/l of chemical hydrogen consumption. Indicated in **Fig. 4**, the following reactions occur consecutively during hydrotreating of the feed solvents.

The changes in major compounds occurring in the feed solvents during hydrotreating are described hereinafter.

3. 2. 1. Naphthalenes

As shown in **Fig. 5**, the contents of naphthalene and methylnaphthalenes decrease, being due to hydrogenation during hydrotreating, producing in a large amount of tetralin and only a small amount of hydrogenated decalins. It was concluded, therefore, that step “a” in the following consecutive reaction schemes^{8)~10)} is dominant and governs the hydrogenation over the Ni-Mo/alumina catalyzed reaction.

3. 2. 2. Phenanthrenes

The reaction scheme for the hydrogenation of phenanthrene, shown below, was proposed by Veluswamy⁹⁾. From the test results shown in **Fig. 6**, the amount of 9,10-dihydrophenanthrene formed as an intermediate, at 140 N/l of chemical hydrogen consumption, was greater than the amount of 1,2,3,4-tetrahydrophenanthrene formed. In both reaction pathways, octahydrophenan-

Fig. 6 Changes in Composition of Phenanthrene Derivatives during Hydrotreating

threnes are produced, but these results suggest that step “b”, where 9,10-dihydrophenanthrene is the intermediate, is rather dominant over Ni-Mo/alumina catalyzed reaction.

3. 2. 3. Pyrenes

As shown in **Fig. 7**, at 140 N/l of chemical hydrogen consumption, the content of pyrene decreases appreciably during hydrotreating of the feed solvent, while the contents of dihydropyrene and tetrahydropyrene as intermediates increase.

Additionally, the pyrene content decreases with the increase in the content of hexahydropyrene. Tetrahydropyrene will convert into hexahydropyrene. In the following reaction scheme, it was

Fig. 7 Changes in Composition of Pyrene Derivatives during Hydrotreating

concluded from the result shown in **Fig. 7** that the route through steps "a" and "c" is the dominant pathway. Hydropyrenes with three or four saturated rings were not detected by GC/MS, in this work.

3. 2. 4. Nitrogen-containing Compounds

The distinct changes in the content of carbazole, a major neutral nitrogen compound in the feed solvents, are shown in **Fig. 8**. It was observed that an increase of tetrahydrocarbazole content corresponded to a decrease in carbazole content. These results indicate that the reaction proceeds through route II and that step "b" is dominant in the following reaction scheme¹¹⁾.

3. 2. 5. Oxygen-containing Compounds

The change in product composition as to dibenzofurans and phenols, major oxygen-containing compounds in the feed solvents, during hydrotreating are shown in **Fig. 9**. The contents of dibenzofurans decreases gradually with the consumption of hydrogen, while those of phenols

Fig. 8 Changes in Composition of Carbazole Derivatives during Hydrotreating

Fig. 9 Changes in Composition of Dibenzofurans and Phenols during Hydrotreating

decreases abruptly. Land¹²⁾ has reported the hydrogenation mechanism of dibenzofurans by the following reaction scheme.

3. 3. Characteristics Changes of Oxygen- and Nitrogen-containing Compounds

The characteristics changes of oxygen- and nitrogen-containing compounds, analyzed quantitatively by FT-IR^{4)~6)}, and the reactivities on HDO and HDN, were investigated. Distinct and quite unique results were obtained on the above two points, indicating that the behavior of heteroatoms, consisting of phenolic and non-phenolic oxygen compounds and neutral and basic nitrogen compounds during hydrotreating, could be searched. As shown in **Fig. 10**, phenolic oxygen is much more easily reduced than non-phenolic oxygen (*e.g.*, dibenzofurans). Further, basic nitrogen (*e.g.*, quinolines) is more easily reduced than neutral nitrogen (*e.g.*, carbazoles).

The kinetic investigation of the removal of these characteristic compounds indicates that each reaction is of first-order, as shown in **Fig. 11**, while the reaction rate constants were calculated as follows:

Oxygen-containing compounds		
• Phenolic oxygen	1.40	[h ⁻¹]
• Non-phenolic oxygen	0.2	
Nitrogen-containing compounds		
• Neutral nitrogen	0.46	
• Basic nitrogen	0.86	

Fig. 10 Changes in Contents of Oxygen and Nitrogen as a Function of Chemical Hydrogen Consumption

Reaction conditions:

Temperature 340°C, Hydrogen pressure 100 kg/cm²-G.

C_F: Concentration of feed.

C_P: Concentration of product.

Fig. 11 First-order Plots for Hydrodeoxygenation and Hydrodenitrogenation

3. 4. Average Molecular Weights

The changes in average molecular weights during hydrotreating were investigated. The average molecular weights were obtained by FI-MS in accordance with the following equation:

$$Mn = \sum M_i \cdot I_i / \sum I_i$$

where, M_i : mass number of i -peak,

I_i : intensity of i -peak

Fig. 12 Changes in Average Molecular Weights during Hydrotreating

Indicated in Fig. 12, during hydrotreating, hydrocracking reaction with changing of skeletons hardly occurs, under this condition.

3. 5. Change of Donatable Hydrogens

A relationship of major significance exists between the degree of hydrogenation and the content of donatable hydrogens, for recycled solvents in hydrotreating of the coal liquefaction process. The content of the donatable hydrogens, in feed solvents and their hydrotreated oils, were obtained by using both ¹H-NMR and GC/MS^{13,14}.

- Donatable hydrogen content by ¹H-NMR (wt%):

$$D_H(\text{NMR}) = H_D \cdot H_T$$

where, $H_D = (h_\alpha/x) + (h_n/y)$

h_α : the ratio of protons of α -methylenes to total protons from ¹H-NMR spectrum (δ 2.3-3.0 ppm of ¹H chemical shift)

h_n : the ratio of protons of β -methylenes to total protons (1.6-2.0 ppm of ¹H chemical shift)

H_T : total hydrogen content (wt%)

$x = y = 2$

- Donatable hydrogen content by GC/MS (wt%):

$$D_H(\text{GC/MS}) = \sum \{ (1.008 H_{N_i} \cdot W_i) / M_i \}$$

where, W_i : content of each hydroaromatic compound (wt%)

M_i : molecular weight of each hydroaromatic compound

H_{N_i} : maximum donatable hydrogen numbers per hydroaromatic molecule

(Representative H_{N_i} are given in Table 3.)

Shown in Fig. 13 is the change of donatable hydrogen content as a function of the degree of hydrogenation (Δfa). The difference of $D_H(\text{NMR}) < D_H(\text{GC/MS})$ is due to the fact that methylenes of indans, acenaphthenes and some n -paraffins do not always have donatable-hydrogen, but accord-

Table 3 Donatable Hydrogens of Various Hydroaromatic Compounds

Partially hydrogenated aromatic compounds	Molecular weight (M_i)	Maximum donatable hydrogen number (H_{Ni})
Tetralin	132	4
2-Methyltetralin	146	4
1-Methyltetralin	146	4
6-Methyltetralin	146	4
Dimethyltetralin	160	4
Ethyltetralin	160	4
Tetrahydroacenaphthene	158	4
G3-Alkyl tetralin	174	4
Tetrahydromethylacenaphthene	172	4
C4-Alkyl tetralin	188	4
Tetrahydrodimethylacenaphthene	186	4
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene	186	4
9,10-Dihydrophenanthrene	180	2
1,2,3,4,5,6,7,8-Octahydrophenanthrene	186	8
Tetrahydrophenanthrene	182	4
9,10-Dihydromethylphenanthrene	194	2
Phenyltetralin	208	4
9,10-Dihydrodimethylphenanthrene	208	2
Tetrahydropyrene	206	4
Tetrahydromethylphenanthrene	196	4
Hexahydropyrene	208	6
Dihydropyrene	204	2
Tetrahydromethylpyrene	220	4
Hexahydrobenzofluorene	222	6
Dihydromethylpyrene	220	4
Hexahydrochrysene	218	2
Tetrahydrochrysene	234	6
Tetrahydrochrysene	232	4
Tetrahydrobenzopyrene	256	4
Hexahydrobenzopyrene	258	6

Fig. 13 Changes of Donatable Hydrogen in Product Composition

ing to ^1H -NMR methodology they are considered to have theoretical donatable hydrogens. The content of donatable hydrogen from both methods shows a similar gradual increase of about 0.15 of Δfa . These results indicate that hydroaromatics tend to reach saturation at a certain level of chemical hydrogen consumption. Good linear correlation between D_H (NMR) and D_H (GC/MS) was obtained (Fig. 14), suggesting that the skeletons of indans and acenaphthenes did not decompose.

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Fig. 14 Correlation between Donatable Hydrogens Obtained by ^1H -NMR and GC/MS, Respectively

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要 旨

石炭液化プロセスからの循環溶剤の接触水素化处理に関する研究 (第 1 報) 水素化处理に伴う循環溶剤の特性変化

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新エネルギー・産業技術総合開発機構 (NEDO) で開発中である, 新しいれき青炭液化プロセス (NEDOL プロセス) の特徴の一つは, 石炭液化油からの中間留分を水素化することによって得られる水素供与能の大きな溶剤を製造するところにある。そしてその溶剤は水素供与の付加を目的として液化工程に循環される。

著者らはその溶剤の接触水素化处理に関する一連の研究を行ってきた。ここでは, ワンドアン炭の液化油から得られた循環溶剤およびその水素化处理油を対象として, 詳細な性状分

析, 化学構造解析を行いこれらの特性を把握した。すなわち, 次の項目について検討した。(1) 接触水素化处理に伴う脱硫, 脱窒素, 脱酸素および芳香族化合物の水素化の反応性, (2) 炭化水素タイプ, 含窒素および含酸素化合物の化学組成変化, (3) 平均分子量の変化, (4) 水素化脱酸素および水素化脱窒素の反応性, (5) 接触水素化处理の運転試験でのモニターである原料油と生成油の芳香族分率の差 (Δf_a) と供与性水素の量的および質的变化の関係。

Keywords

Coal liquid, Hydrogenation, Hydrotreating, Characterization, NMR, GCMS