Hydrotreating of heavy distillate derived from Wandoan coal liquefaction

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Abstract

Hydrotreatment of coal-derived heavy distillate, obtained from the liquefaction of Wandoan coal using a 1 t/day bench unit, was performed to clarify the effects of catalyst species, reaction temperature and hydrogen pressure on the chemical composition of the product. Experimental runs were carried out over alumina-supported Co–Mo and Ni–Mo catalysts in a fixed bed reactor of 20 ml in volume at 350–390°C under hydrogen pressure of 50–150 kg/cm^2 G with liquid hourly space velocity (LHSV) of 0.5–2 h^{-1}. The product, as analyzed by gas chromatography, indicated that larger amounts of alkylbenzenes such as toluene or xylenes were produced at the elevated temperature of 390°C, but the concentrations of condensed aromatics such as naphthalene, biphenyl, fluorene and phenanthrene decreased with the severity of reaction conditions. Pyrene and methylpyrene decreased in amount with a shorter LHSV and higher hydrogen pressure, but increased at higher temperature of 390°C. Shorter LHSV and higher hydrogen pressure are much more effective in hydrogenation, hydrodenitrogenation and hydrodeoxygenation than the higher reaction temperature up to 390°C. Total amounts of n-paraffins in the feed oil and in the product oils do not show a big change. Therefore, hydrocracking of the n-paraffin does not occur under these reaction conditions. Denitrogenation of the heavy distillate did not proceed so much compared with the middle distillate. Heavy neutral nitrogen compounds, such as carbazole and its alkyl homologues, are only detected with traces of quinoline. © 1997 Elsevier Science B.V.

Keywords: Ni–Mo/Al$_2$O$_3$ catalyst; Hydrotreatment; Hydrodenitrogenation

1. Introduction

It has been reasonably well understood in the solvent recycle mode operation of coal liquefaction process that a variety of distillates ranging from light oil to SRC are obtained from coal. It has also been understood that a portion of light oil is actually produced directly from the liquefaction of coal as well as indirectly from the hydrocracking of a heavy solvent fraction, derived from coal during the course of several recycle runs of operation. Therefore, in a desirable process, heavy distillate derived from the first-stage coal liquefaction should be hydrocracked successively to the lighter fraction with high quality for fuel oil and, in others, hydrogenated to produce a hydrogen donating solvent for the next steps of the recycle. Thus it is important for the plant design to have an essentially high level of coal conversion as well as to keep a steady balance of high quality solvent. In two-step liquefaction of coal, the secondary solvent hydrogenation process or hydrotreating of

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the liquefied product is the important reaction process to promote upgrading of the heavy product from coal and to improve the quality of solvent and light fuel oil.

We have studied the hydrotreating of coal-derived middle distillate produced from the liquefaction of Australian sub-bituminous coal using a 1 t/day plant. Changes in the composition of the middle distillate with varying reaction conditions using Co–Mo/Al$_2$O$_3$ and Ni–Mo/Al$_2$O$_3$ commercial catalyst have already been reported [1]. Higher activities in hydrogenation of the aromatic nucleus and in hydrodenitrogenation have been observed with Ni–Mo/Al$_2$O$_3$ catalyst than with Co–Mo/Al$_2$O$_3$ catalyst. Moreover, the higher hydrogen pressure is recognized to be more effective than the elevation of reaction temperature for the hydrogenation activity of the catalyst.

Several investigations have already been reported on the evaluation of coal liquid for gasoline or diesel fuel [2,3] and on the denitrogenation behavior of heavy fraction from coal using different catalysts [4]. But the change of components by the hydrotreating of recycle solvent has not been reported. As mentioned above, light fraction and partially hydrogenated aromatic compounds are produced from the hydrotreating of heavy solvent fraction. Therefore, it is very important to optimize the combination of the first liquefaction, secondary upgrading of coal liquid and hydrotreating of recycle solvent based on the compositional analysis.

In this study, hydrotreating of coal-derived heavy distillate, whose boiling point ranges up to 538°C, has been performed to examine the hydrogenation reactivity of three and four rings condensed aromatic compounds. This experiment was also used to study the degree of denitrogenation on the basis of detailed compositional analysis of product oil. It has been necessary to prepare hydrogen donating recycle solvent as well as to produce clean fuel.

2. Experimental

Reactant oil, used here, was the coal-derived heavy distillate (b.p. 350–538°C) prepared from the liquefaction of Wandoan coal (Australian sub-bituminous coal) in a 1 t/day bench plant. Elemental analyses of heavy and middle distillate are listed in Table 1. Experimental runs were carried out over an alumina supported Ni–Mo catalyst (KF-840, Nippon Ketjen) using a high pressure continuous apparatus equipped with a fixed bed reactor of 20 ml in volume at 350–390°C under hydrogen pressure of 50–150 kg/cm^2 G with liquid hourly space velocity (LHSV) of 0.5–2 h^{-1} and hydrogen to reactant oil volume ratio of 1000. From our previous results [1] on the Co–Mo/Al$_2$O$_3$ and Ni–Mo/Al$_2$O$_3$ catalyst, we chose Ni–Mo/Al$_2$O$_3$ catalyst, in this study, by its higher activities in hydrogenation, and in hydrodenitrogenation, to prepare hydrogen donating solvent, and light product oil with low nitrogen content. Presulfiding of the catalyst was performed by feeding commercial gas oil containing 1% CS$_2$, using the above mentioned continuous apparatus at 300°C under hydrogen pressure of 40 kg/cm^2 G with LHSV of 1 h^{-1} and sulfiding time of 15 h.

Table 1
Elemental analyses of feed oil and hydrotreated products

Reaction conditions			C (wt%)	H (wt%)	N (wt%)	O (wt%)	H/C atomic ratio
Temperature (°C)	LHSV (h^{-1})	H$_2$ pressure (kg/cm^2 G)					
350	1.0	100	88.4	10.5	0.12	0.60	1.4
370	2.0	100	88.1	10.4	0.11	0.82	1.4
370	1.0	100	88.3	10.6	0.05	0.50	1.4
370	0.5	100	88.3	11.0	0.02	0.33	1.5
370	1.0	50	88.7	10.5	0.09	0.73	1.4
370	1.0	150	88.4	11.0	0.03	0.44	1.5
390	1.0	100	88.5	10.8	0.03	0.46	1.5
Heavy distillate (b.p. 350–538°C)			87.8	9.7	0.25	1.58	1.3
Middle distillate (b.p. 180–450°C)			88.8	8.8	0.33	1.83	1.2

Conditions of presulfiding for this catalyst were discussed in detail and the optimum ones were selected in our previous paper [5].

Hydrotreating of the heavy distillate started continuously after presulfiding of the catalyst, and the activity of the catalyst was stabilized by feeding reactant heavy distillate for about 50 h at the reaction condition. Sampling of the product heavy distillate was taken at a time period of 6–10 h or more after changing the reaction condition to confirm the constant catalytic activity.

Activity change of the catalyst during the total reaction time on stream of about 120 h was checked by the comparison of the product oil obtained at the beginning with the last one sampled under the same conditions. Elemental and compositional analyses showed no significant differences between these samples within the error limit.

Elemental analysis of the product oil was performed by a CH analyzer for C, H; chemiluminescence method for N; and coulometric titration method for O. Generally oxygen content is estimated by the subtraction from the other atoms; however, we analyze oxygen directly in this study. Liquid products were also subjected to conventional gas chromatographic analysis using OV-101 glass capillary column (i.d.: 0.2 mm, length: 50 m) and by GC–MS for identification purposes. For the detailed analysis of polar compounds, extraction with 10 wt% NaOH and 15 wt% H_2SO_4 solutions was conducted and the extracts were subjected to GC and total nitrogen analyses. In addition, nitrogen compounds in the product oil were analyzed by gas chromatography specially equipped with a nitrogen detector. Details of experimental procedure, analytical method and presulfiding condition are described in our previous reports [1].

3. Results and discussion

3.1. Effect of reaction condition on the composition of product oil

From the elemental analysis of the heavy distillate shown in Table 1 together with the data of the middle distillate, contents of nitrogen and oxygen in the heavy distillate were somewhat lower and, conversely, H/C atomic ratio showed a higher value of 1.3 than that of

1.2 in the middle distillate. According to the compositional analyses of coal-derived distillates shown in Table 2, the principal framework in the chemical structure of constituents in both feed oil was almost the same. Heavy and middle distillates consisted mainly of tetralin, naphthalene, biphenyl, acenaphthene, fluorene, dibenzofuran, phenanthrene, pyrene and their hydrogenated and/or alkyl derivatives with n-paraffins and small portion of phenols. Unknowns in each fraction and others in Table 2 are total of the compounds of very small amounts, and each of them are expected to alkyl derivatives of the identified compounds. But the distribution of the lighter aromatics such as tetralin, naphthalene, dibenzofurane, fluorene and phenanthrene was relatively smaller and, contrary to these, the concentration of heavy aromatics such as pyrene, fluoranthene, etc., was shown to be larger in the heavy distillate. Moreover, the concentration of n-paraffins in the heavy distillate increased to approximately 3-fold of that in the other. Therefore, a lower value of nitrogen and oxygen as well as higher H/C in the heavy distillate, as shown in Table 1, was reasonably accounted for as due to the dilution of aromatic and hetero compounds with a larger amount of n-paraffins.

According to the elemental analyses of reactant heavy distillate and product oil as shown in Table 1 with reaction conditions, H/C atomic ratio increased and the concentration of nitrogen and oxygen decreased with the reaction temperature, hydrogen pressure and LHSV. Within these data, shorter LHSV and higher hydrogen pressure are much effective in hydrogenation, hydrodenitrogenation and hydrodeoxygenation than the higher reaction temperature up to 390°C. From the analyses of each component in Table 2, larger amounts of alkylbenzenes such as toluene or xylenes were produced at the elevated temperature of 390°C, but the concentrations of condensed aromatics such as naphthalene, biphenyl, fluorene, phenanthrene, etc., decreased with the severity of reaction conditions. Pyrene and methylpyrene decreased in amount with a shorter LHSV and higher hydrogen pressure, but increased at the higher temperature of 390°C. In the case of fluoranthene, an opposite reaction behavior from the case of pyrene was observed. The amounts of tetralin, methyltetralin, tetrahydroacenaphthene, hydrophenanthrene, hydrofluoranthene

Table 2
Products distribution of the hydrotreated oil from coal-derived distillate

Reaction temperature (°C)			350	370	370	370	370	370	390
Hydrogen pressure (kg/cm^2 G)			100	100	100	100	50	150	100
LHSV (h^{-1})			1	2	1	0.5	1	1	1
H$_2$/feed ratio (vol/vol)			1000	1000	1000	1000	1000	1000	1000
Component	Middle distillate	Heavy distillate	Composition of products from heavy distillate (wt%)						
Cyclohexane	0.01	0.02	0.09	0.18	0.20	0.13	0.11	0.22	0.29
Methylcyclohexane	0.01	0.05	0.29	0.46	0.50	0.33	0.32	0.55	0.59
Toluene	0.04	0.03	0.08	0.13	0.15	0.13	0.16	0.13	0.22
Dimethylcyclohexane									
Ethylcyclohexane									
o-Xylene	0.01		0.06	0.08	0.09	0.09	0.11	0.08	0.13
m-, p-Xylene	0.03	0.05	0.09	0.13	0.18	0.19	0.18	0.19	0.25
Ethylbenzene									
Ethylmethylcyclohexane									
Isopropylcyclohexane									
n-Propylcyclohexane									
Phenol	0.07	0.06	0.03	0.04	0.04	0.05	0.06	0.04	0.06
n-Propylbenzene									
Ethyltoluene		0.01	0.06	0.08	0.11	0.13	0.12	0.11	0.15
>Trimethylbenzenes		0.11	0.12	0.13	0.17	0.19	0.16	0.20	0.20
o-Cresol	0.22	0.18	0.03	0.04	0.04	0.04	0.03	0.05	0.04
m-, p-Cresol	0.61	0.59	0.05	0.06	0.06	0.08	0.07	0.07	0.08
Unknown[a]	0.14	0.01	0.48	0.52	0.57	0.60	0.52	0.67	0.65
n-Butylbenzene		0.18	0.21	0.23	0.26	0.28	0.26	0.31	0.31
trans-Decalin	0.04	0.15	0.20	0.22	0.20	0.30	0.21	0.45	0.28
1-Methylindane	0.38	0.31	0.30	0.31	0.28	0.27	0.34	0.27	0.29
Methylindanes	0.33								
cis-Decalin	0.12	0.17	0.09	0.10	0.09	0.15	0.10	0.20	0.15
Tetralin	5.09	2.95	2.93	2.95	3.09	3.10	3.41	3.85	3.09
Naphthalene	11.08	1.48	0.65	0.59	0.43	0.34	0.98	0.33	0.44
Dimethylindanes	1.06	1.85	1.77	1.78	1.68	1.71	1.68	1.70	1.63
c>2-Methyltetralin	0.90	1.84	1.96	1.90	1.98	1.98	1.81	2.19	1.88
1-Methyltetralin	0.47	0.46	0.51	0.52	0.51	0.54	0.54	0.58	0.54
6-Methyltetralin	1.82	3.01	3.29	3.27	3.64	3.77	3.46	3.82	3.65
5-Methyltetralin	0.71	1.08	1.01	1.07	1.00	1.05	1.01	1.08	0.95
2-Methylnaphthalen	8.45	2.73	1.30	1.08	0.94	0.66	1.72	0.60	0.96
1-Methylnaphthalen	2.69	0.66	0.34	0.30	0.21	0.14	0.48	0.09	0.22
Bicyclohexyl	1.01	2.55	2.61	2.54	2.71	3.01	2.53	2.98	2.82
Phenylcyclohexane									
Dimethylnaphthalenes		1.53	0.87	1.14	0.79	0.75	0.98	0.64	0.81
Dimethyltetralins	5.25	1.60	2.22	2.16	2.15	2.11	2.14	1.87	2.06
Methylbiphenyls		0.49	0.39	0.37	0.38	0.38	0.39	0.35	0.36
Ethylbiphenyls		2.00	1.68	1.55	1.38	1.35	1.56	1.26	1.51
Ethyltetralins	0.40	0.74	0.94	0.93	0.99	1.04	0.91	0.97	1.00
Biphenyl	2.78	1.51	1.27	1.22	1.24	1.21	1.32	1.22	1.19
Tetrahydroacenaphthene	0.68	0.70	1.14	1.10	1.15	1.14	1.11	1.12	1.10
Acenaphthene	2.55	1.01	0.43	0.40	0.38	0.35	0.57	0.32	0.36
Dibenzofuran	3.26	1.22	0.74	0.69	0.65	0.45	0.79	0.63	0.51
Unknown[b]	8.21	9.71	8.59	7.83	8.96	9.75	7.95	9.42	8.94
C$_4$-Naphthalenes		1.01	0.70	0.68	1.08	0.66	0.71	0.61	0.64
Fluorene	2.28	1.03	0.80	0.91	0.72	0.57	0.82	0.67	0.60
Dimethylbiphenyls	1.87	2.04	1.62	1.83	1.47	1.24	1.56	1.28	1.21

Table 2
(Continued)

Component	Middle distillate	Heavy distillate	Composition of products from heavy distillate (wt%)						
Ethylbiphenyls									
9,10-Dihydrophenanthrene	0.96	0.31	0.45	0.35	0.28	0.09	0.28	0.21	0.14
Methylfluorene	0.47	0.47	0.37	0.36	0.35	0.24	0.35	0.27	0.30
1,2,3,4,5,6,7,8-Octahydrophenanthrene	0.76	0.58	0.92	0.94	1.20	1.55	0.94	1.67	1.26
1,2,3,4-Tetrahydrophenanthrene	0.55	0.75	0.58	0.61	0.54	0.40	0.74	0.33	0.57
Phenanthrene	5.08	1.17	0.64	0.64	0.48	0.13	0.81	0.21	0.34
Anthracene									
Dimethylfluorene		0.44	0.99	0.97	0.97	0.93	0.91	0.98	0.88
Methylphenanthrene		0.81	0.76	0.77	0.68	0.39	0.81	0.48	0.63
Hydrofluoranthene		0.08	0.17	0.13	0.10	0.06	0.10	0.08	0.06
Phenylnaphthalene		0.11	0.06	0.05	0.05	0.03	0.06	0.03	0.03
Dihydropyrene		0.51	0.69	0.58	0.52	0.42	0.41	0.34	0.49
Fluoranthene		0.18	0.07	0.08	0.10	0.14	0.09	0.17	0.07
Pyrene	0.83	1.47	0.77	0.92	0.77	0.55	1.08	0.32	0.90
Methylpyrene		0.61	0.42	0.51	0.46	0.38	0.53	0.26	0.52
Tolylnaphthalene		0.28	0.27	0.26	0.19	0.11	0.22	0.10	0.17
Unknown[c]	7.30	7.01	10.52	11.23	11.05	10.36	10.06	10.72	10.40
n-C$_{15}$–C$_{26}$-Paraffin	5.86	14.77	13.41	13.64	13.94	14.21	12.91	13.73	13.67
Other paraffins	3.55	6.14	5.55	5.58	5.54	2.52	5.41	5.36	5.35
Others	12.07	19.17	23.45	22.86	22.31	24.23	23.11	23.62	24.06

[a]Mainly mono-aromatic compounds.
[b]Mainly biphenyl derivatives.
[c]Mainly condensed aromatic compounds.

and dihydropyrene in the oil product from the reaction at 390°C were the same or lower than that obtained at 370°C. Higher contributions of these compounds were generally observed in the products within the condition of a shorter LHSV and higher hydrogen pressure at 370°C.

The effect of reaction temperature and LHSV on the distribution of naphthalene and its hydrogenated products are illustrated in Figs. 1 and 2, respectively. It is known that n-butylbenzene and 1-methylindane are produced from the thermal reaction of tetralin [6]. The amount of 1-methylindane did not change with the reaction temperature and LHSV. Decalins, tetralin and n-butylbenzene increased with a higher temperature and shorter LHSV. In contrast, naphthalene decreased under the same reaction condition and especially showed the lowest value at 370°C with LHSV of 0.5 h^{-1} under hydrogen pressure of 100 kg/cm^2 G and also with LHSV of 1 h^{-1} under 150 kg/cm^2 G of hydrogen. In these reaction conditions, hydrogenation of naphthalene proceeds effectively. But the

amount of naphthalene increased at 390°C in spite of the elevation of reaction temperature. This indicates that the hydrocracking of alkylnaphthalene to produce naphthalene occurred, together with the hydrogenation of naphthalene and tetralin at 390°C. The total amount of naphthalene homologues also increased at 390°C.

A different reaction behavior has been observed in the case of phenanthrene and its hydrogenated derivatives, as shown in Figs. 3 and 4. 1,2,3,4,5,6,7,8-Octahydrophenanthrene increased with hydrogen pressure of 150 kg/cm^2 G (Fig. 4). Phenanthrene and 9,10-dihydrophenanthrene as well as the total amounts of these derivatives decreased with the severity of reaction conditions. This suggests that the amounts of alkylphenanthrenes which would be hydrocracked to produce phenanthrene, are not so high in the reactant heavy distillate. Total amount of phenanthrene derivatives might be, of course, decreased by the consecutive hydrogenation to perhydrophenanthrenes. Typically hydrocracking of
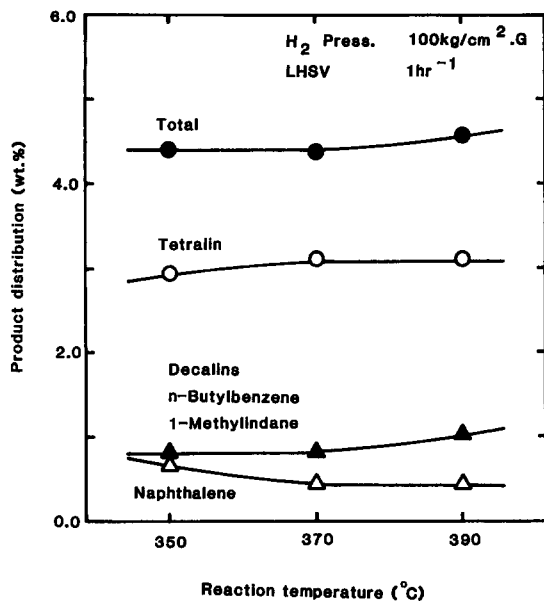
Fig. 1. Effect of reaction temperature on the distribution of naphthalene derivatives.
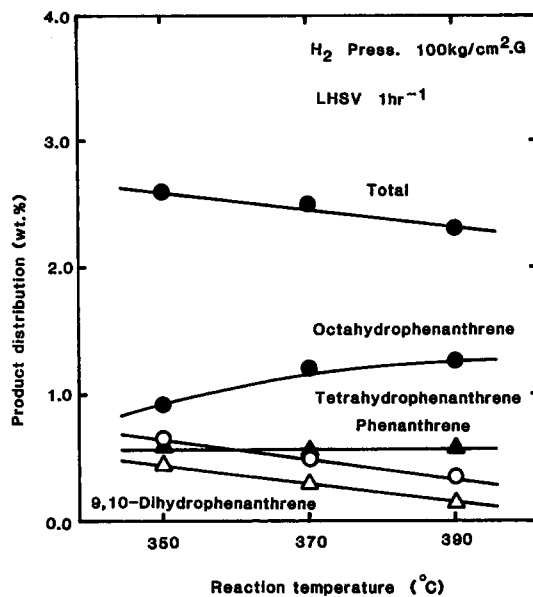

Fig. 3. Effect of reaction temperature on the distribution of phenanthrene derivatives.
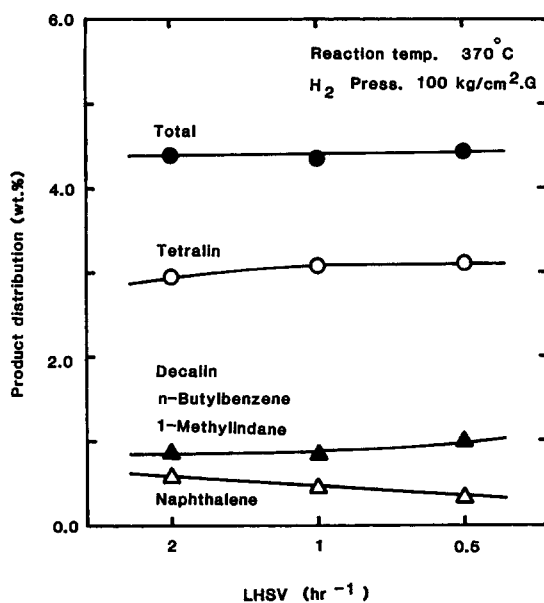

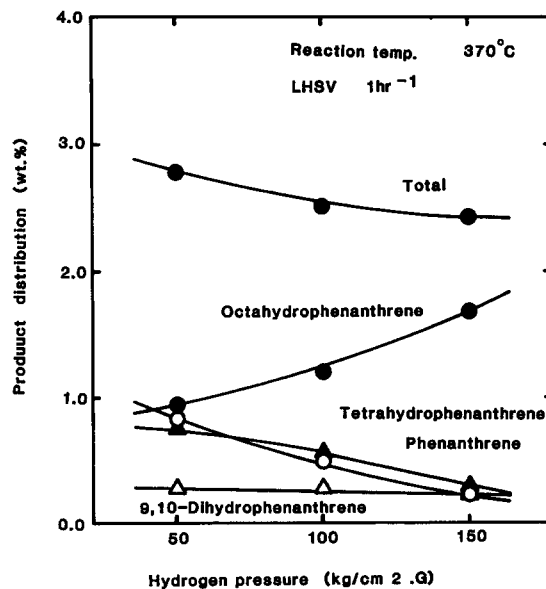Fig. 2. Effect of LHSV on the distribution of naphthalene derivatives.

Fig. 4. Effect of hydrogen pressure on the distribution of phenanthrene derivatives.

phenanthrene and its hydrogenated derivative occurred at 390°C, and hydrogenation occurs predominantly with shorter LHSV of $0.5\,h^{-1}$ and higher hydrogen pressure of $150\,kg/cm^2\,G$ at 370°C.

The effect of hydrogen pressure on the distribution of n-paraffins with a carbon number in the product oils is illustrated in Fig. 5. No significant differences can be observed with hydrogen pressure from 50 to
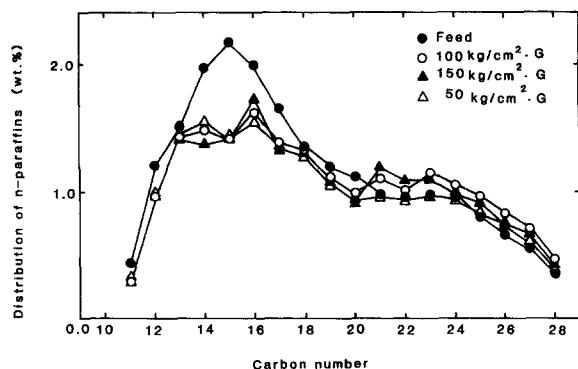
Fig. 5. The effect of hydrogen pressure on the distribution of *n*-paraffins in the oil products.

150 kg/cm² G. The minor change in the concentration of *n*-paraffin in the product oil at a carbon number ranging from 14 to 17 with that from feed oil was considered due to the difficulties of separation from the nonparaffinic compounds by GC analysis. Total amounts of *n*-paraffins in the feed oil and in the product oils do not show a big change as listed in Table 2. Therefore, hydrocracking of the *zn*-paraffin does not occur under these reaction conditions.

3.2. Denitrogenation

The effect of the reaction condition on the denitrogenation of coal-derived heavy distillate is illustrated in Fig. 6. Percent denitrogenation of the heavy distillate increased up to approximately 90 wt% with the elevation of reaction temperature and hydrogen pressure as well as with shorter LHSV. Nitrogen content in the product oil decreased down to 200–300 ppm under severe reaction conditions, as shown in Table 1. As compared with the data from the hydrotreatment of the middle distillate described also in Fig. 6, however, percent denitrogenation reached nearly 100 wt% at a higher temperature of 390°C and shorter LHSV of 0.5 h^{-1} at 370°C. Nitrogen content in the product oil from the hydrotreatment of the middle distillate under the same conditions revealed less than 100 ppm.

Distributions of nitrogen compounds in both feed oils and in the product oils measured by gas chromatography equipped with a special detector for nitrogen compound (NPD detector) are illustrated in Fig. 7 and Table 3. Identifications of nitrogen compounds were performed by the extraction of hetero compounds using an Alumina N cartridge column with THF–
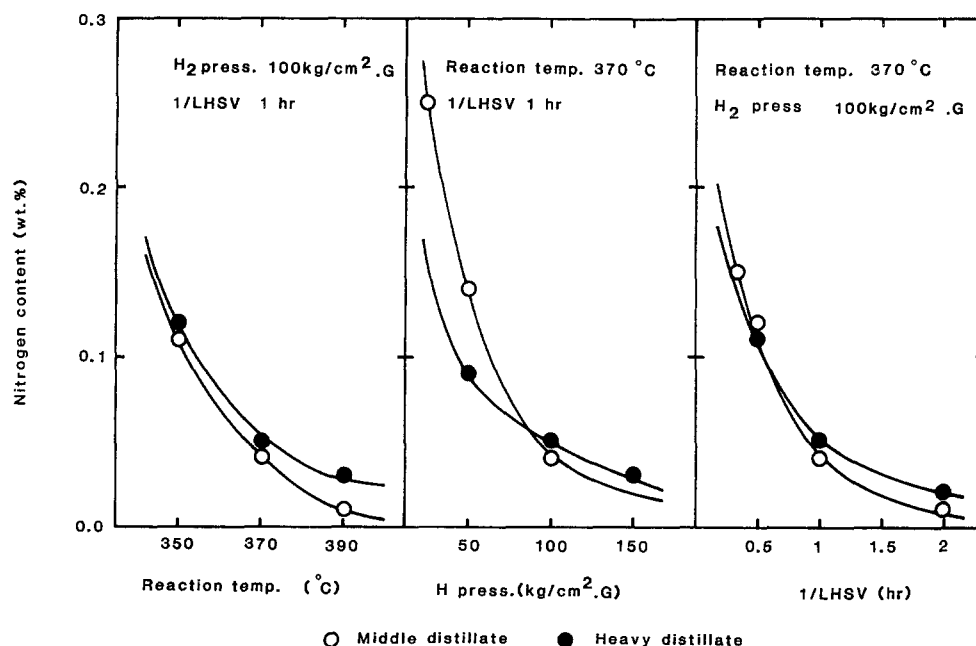

Fig. 6. Effect of reaction conditions on nitrogen content in the product oil.
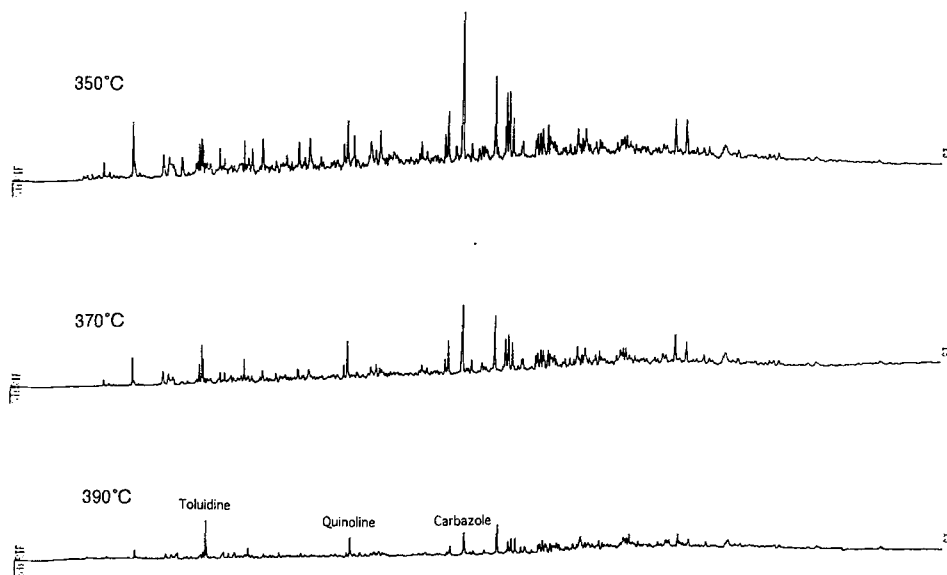
Fig. 7. Gas chromatogram of nitrogen compounds in the products (hydrogen pressure: 100 kg/cm^2 G , LHSV: 1 h^{-1}).

ethanol solvent and an acid–base separation followed by GC and GC–MS analyses. In comparing feed oil from the heavy distillate with that from the middle distillate, the distribution patterns of the nitrogen compound are quite different.

Typically, the area ratio of carbazole to quinoline of 1.2 in the middle distillate rises to 7.3 in the heavy distillate. Alkylcarbazoles and other heavy nitrogen compounds also appear more in the heavy distillate. On the other hand, larger amounts of light nitrogen compounds such as pyridines, anilines and quinolines are found in the middle distillate. From the distribution of nitrogen compounds in the product oils obtained from the hydrotreatment at 370°C under hydrogen pressure of 100 kg/cm^2 G with LHSV of 1 h^{-1}, only traces of light nitrogen compounds can be detected in the case of the middle distillate. Contrary to this, carbazole and its alkyl homologues, together with quinoline and toluidine can still be found in the product oil from the heavy distillate.

Semiquantitative analyses of some of the main nitrogen compounds in the product oil from various reaction conditions have also been tried on the basis of NPD–gas chromatography using acridine as an internal standard. From the estimated results listed in Table 3, basic nitrogen compounds such as aniline, quinolin and neutral nitrogen compounds such as

indole, carbazole and their alkyl homologues were found in the product oil treated under a mild condition, i.e. 350°C, 100 kg/cm^2 G of hydrogen, LHSV 1 h^{-1}; 370°C, 100 kg/cm^2 G of hydrogen, LHSV 2 h^{-1}; and 50 kg/cm^2 G of hydrogen, LHSV 1 h^{-1}. Then denitrogenation of the basic nitrogen compounds with alkyl substituents first takes place with the increasing severity of reaction conditions. However, several basic nitrogen compounds, e.g. toluidine, quinoline, and neutral species, e.g. cabazole or alkylcarbazole, still remain in the product oil under the medium condition of 370°C with a hydrogen pressure of 100 kg/cm^2 G and LHSV of 1 h^{-1}. At the severe reaction condition under higher reaction temperature or hydrogen pressure of 390°C or 150 kg/cm^2 G of hydrogen as well as shorter LHSV of 0.5 h^{-1} at 370°C, only heavy neutral nitrogen compounds, e.g. carbazole and its alkyl homologues, are detected with traces of quinoline.

4. Conclusions

Hydrotreating of the heavy distillate derived from Wandoan coal liquefaction was studied using alumina-supported Co–Mo and Ni–Mo catalysts in a fixed bed reactor to examine the hydrogenation reactivity of

Table 3
Nitrogen compound distribution of the hydrotreated oil from coal-derived heavy distillate

| Reaction temperature (°C) | | | 350 | 370 | 370 | 370 | 370 | 370 | 390 |
| Hydrogen pressure (kg/cm² G) | | | 100 | 100 | 100 | 100 | 50 | 150 | 100 |
LHSV (h⁻¹)			1	1	2	0.5	1	1	1
Component	Middle distillate	Heavy distillate	Composition of products (wt%)×10^4						
Aniline	5.85	8.74	1.43	1.00	2.77		2.34		
Toluidine	24.57	23.22	8.51	7.25	14.13	0.42	12.20	1.13	1.67
o-Ethylaniline	17.88	5.41	4.21	4.18	7.22	0.47	7.50	1.04	1.79
Indoline		2.77	3.40	1.10	3.23		1.83		
Quinoline	110.76	19.04	3.05	5.80	5.16	2.49	6.38	3.44	4.56
Isoquinoline	3.56	2.30	3.08	2.78	4.05		3.35		
Indole	33.78	15.94	1.67	2.73	3.90	0.98	2.93	1.03	
1-Methylisoquinoline	13.37		3.33	1.76	3.13			0.45	
6-Methylisoquinoline	6.57	5.67	3.34	2.41	4.01		3.57		
5-Methylindole	42.32	11.71	4.95	4.43	7.14		6.83		
o-Aminobiphenyl	7.57		3.66	1.60			2.42		
1,2,3,4,5,6,7,8-Octahydroacridine			1.75	1.47	1.57		0.25		
Phenazine		6.06	2.77	2.84	6.22		3.32		
1,2,3,4-Tetrahydrocarbazole	4.37	5.45	2.63	3.28	5.56		4.99	0.23	0.78
α-Naphthoquinoline	4.76	4.86	3.51	6.30	10.68		8.40	1.22	1.67
Carbazole	246.18	31.70	17.20	17.91	27.83	1.45	27.53	4.04	4.00
Methylcarbazole	34.00	12.94	9.80	10.23	14.57	1.22	11.63	2.53	4.34
Methylcarbazole	28.79	18.83	7.98	7.75	11.96		8.40	1.71	2.25
Methylcarbazole	25.61	13.48	7.00	8.37	10.13	0.59	7.99	1.80	2.47
Methylcarbazole	25.27	17.20	3.23	5.59	7.79	0.48	5.54	0.76	2.40
Tetrahydrobenzocarbazole			4.92	7.19	8.10	0.65	4.78	1.20	1.77
Tetrahydrobenzocarbazole			6.01	6.26	8.07		5.16	0.59	1.35

condensed aromatic compounds and the denitrogenation on the basis of compositional analysis of product oil. The heavy distillate mainly consisted of three and four rings condensed aromatic compounds such as phenanthrene, pyrene and their alkyl derivatives with two-ring aromatics such as tetralin and naphthalene. Hydrogen pressure was most effective to hydrogenate aromatic rings; the total amounts of phenanthrene and its hydrogenated compounds decreased with the reaction temperature and hydrogen pressure. Denitrogenation of the heavy distillate did not proceed so much compared with that of the middle distillate. According to the analysis using gas chromatography with a nitrogen detector, aromatic nitrogen compounds such as carbazole, methylcarbazole with quinolin were still detected in the hydrotreated oil at severe reaction conditions.

References

[1] Y. Sato, K. Ukegawa, T. Kondo, A. Matsumura, K. Koguchi, E. Nakamura, Sekiyu Gakkaishi 27(5) (1984) 433.
[2] P.-Z. Zhou, J.J. Marano, R.A. Winschel, Am. Chem. Soc. Div. Fuel Chem. Prep. 37(4) (1992) 1847.

[3] P.S. Herrera, M.C. Oballa, A.F. Somogyvari, J. Monnier, Am. Chem. Soc. Div. Fuel Chem., Prep. 37(4) (1992) 1855.

[4] M.F. Wilson, Am. Chem. Soc. Div. Fuel Chem., Prep. 38(3) (1993) 1058.

[5] Y. Sato, K. Miki, M. Shiraishi, Sekiyu Gakkaishi 30(6) (1987) 424.

[6] Y. Sato, T. Yamakawa, I&EC (Fundamentals) 24(1) (1985) 12.