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Removal of Nitrogen Compounds before Deep Hydrotreatment of Synthetic Crude Oils

Janchig NARANGEREL and Yoshikazu SUGIMOTO*

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

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Synthetic crude oils (SCOs) derived from oil shale, coal, and oil sands contain relatively large amounts of heteroatoms such as nitrogen and sulfur, and severe hydrotreating conditions are necessary to convert SCOs into substitute transport fuels. In this study, extraction of nitrogen compounds from SCOs by complex formation with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was carried out and the denitrogenated oils were hydrotreated to explore the effect of nitrogen pre-removal on hydrodenitrogenation (HDN) and hydrodesulfurization (HDS). Light gas oil fractions derived from shale oil, coal-derived liquid, and pyrolysis product of Athabasca bitumen were used as feedstocks. Hydrotreatment tests were carried out using a batch-type autoclave and commercial $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst at 350°C for 2–4 h under H_2 initial pressure of 5 MPa. The results showed that basic and heterocyclic nitrogen compounds could be separated efficiently from SCO by complex formation. The pre-removal of nitrogen compounds greatly enhanced the HDN reaction rates and greatly reduced the residual nitrogen content. The recovery of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was also possible by simply washing CH_2Cl_2 solution containing the complex with water. The proposed method is another option for the conversion of SCO to a high quality feedstock suitable for production of clean diesel fuels.

Keywords

Synthetic crude oil, Nitrogen removal, Hydrotreatment, Shale oil, Oil sands bitumen, Coal-derived liquid

1. Introduction

Increased energy requirements together with greater environmental constraints require more efficient and clean use of liquid fuels. Tighter sulfur specifications for diesel fuel have been introduced in many countries in recent years, and allowable sulfur levels will be reduced to below 10 wtppm in some developed countries in the near future^{1),2)}. Nitrogen compounds present in crude sources also constitute serious problems both for producers and consumers, in particular the poisoning of catalysts during the refining processes, and the degradation observed in fuels during storage and handling, and NO_x emissions from fuel combustion.

The recent high price of crude oil will probably stimulate the production of unconventional oils based on oil sands³⁾, oil shales, and coal⁴⁾. At a price of about 25 USD/barrel, synthetic oil is profitable to produce based on oil sands and extra heavy oil. At prices above 30 USD/barrel, oil production based on coal may also be competitive⁵⁾. However, the relatively high nitrogen and sulfur contents of synthetic crude oils (SCOs) create great problems with potential exploita-

tion as substitute transport fuels. The order of difficulty of removing the heteroatoms by hydrotreatment is $\text{S} < \text{O} < \text{N}^{6)-8)}$, so that nitrogen is the most difficult heteroatom to remove. Organic nitrogen compounds strongly adsorbed on catalyst active sites and inhibit the removal of both nitrogen- and other heteroatom-containing compounds during hydrotreatment. Basic nitrogen compounds, even at levels of a few tens of wtppm, are believed to severely inhibit hydrodesulfurization (HDS)⁹⁾. Average organic nitrogen contents of most shale oils are 0.5 to 2.5 wt%, compared to around 0.1 wt% in conventional oil. Therefore, deep hydrotreatment of SCO over commercial $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts will require much more severe conditions than those for hydrotreatment of conventional crude oils^{7),10),11)}.

Various approaches are based on combinations of conventional hydrotreatment with pre- or postprocess removal of nitrogen compounds. Silica, silica-alumina, zeolite-based materials and activated carbons with high surface area¹²⁾ show good adsorption characteristics of nitrogen species in conventional gas oil, but rather limited capacity for SCOs, which have considerably higher nitrogen content. Removal of nitrogen compounds from SCOs by extraction with solvent¹³⁾, mineral acids, treated minerals¹⁴⁾, acid-treated shale ash¹⁵⁾, and various transition metal salts¹⁶⁾ have been investigated.

* To whom correspondence should be addressed.

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

Table 1 Properties of Light Gas Oil Feedstocks from Different Fossil Fuels

Properties		SO	CL	OS	ME
Sulfur	[wtppm]	62800	800	44000	8800
Nitrogen	[wtppm]	9900	4500	1260	40
GC distillation (ASTM D 2887)					
10 vol%	[°C]	264	205	269	234
30 vol%	[°C]	290	232	300	274
50 vol%	[°C]	308	259	325	296
70 vol%	[°C]	326	289	349	315
90 vol%	[°C]	352	337	380	340
Acidic fraction	[wt%]	1.6	8.2	0.31	n.d. ^{a)}
Basic fraction	[wt%]	11.4	3.5	0.76	n.d.
Types by HPLC					
saturates	[wt%]	24	23	40	74
monoaromatics	[wt%]	23	27	19	14
polyaromatics	[wt%]	27	29	35	12
polars ^{b)}	[wt%]	26	21	6	< 1

a) n.d.; not determined.

b) Polars include basic, acidic and neutral polar compounds.

Ion-exchange resins¹⁷⁾ and zeolite¹⁸⁾ were also proposed as adsorbents for the separation of nitrogen compounds from hydrotreated shale oil. Studies on selective extraction of nitrogen compounds from shale oil with various transition metal salts have demonstrated that crystalline $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ can reduce the nitrogen content of shale oil very effectively, by more than 85% to levels below 0.2 wt%¹⁶⁾. The method is based on the formation of the insoluble complex of basic nitrogen compounds with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which acts as a Lewis acid. Basic nitrogen compounds are electron pair donors, which strongly bond with electron pair acceptors, such as metal ions. Basic nitrogen compounds are strong inhibitors of hydrotreatment reactions, so selective removal should highly promote the hydrodenitrogenation (HDN) of SCO.

Our preliminary study on different extraction methods¹⁹⁾ for the removal of nitrogen compounds, including methanol-water extraction, sulfuric acid extraction, and extraction using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, confirmed that the last method is much more effective than the two former methods. However, little is known about the effect of nitrogen pre-removal on hydrotreatment of SCOs.

In this study, basic and heterocyclic nitrogen compounds were removed from SCO by complex formation with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and the effect of nitrogen pre-removal on HDN and HDS was investigated using hydrotreatment.

2. Experimental

2.1. Materials

Shale oil and coal-derived liquid were obtained from pilot plants in Japan, and the pyrolysis product of Athabasca bitumen and Middle East light gas oil were supplied by Syncrude Canada and a Japanese refinery, respectively. These liquids were distilled and the light

gas oil fractions were used in this work. All other materials and reference nitrogen compounds were commercial products. Compared to light gas oil from Middle East crude (ME), the SCOs contained much larger amounts of nitrogen as shown in **Table 1**. Both sulfur and nitrogen contents of shale oil (SO) were very high. Coal-derived liquid (CL) was unique with high nitrogen content and the lowest sulfur content. SO and CL included large amounts of basic and acidic compounds. The boiling-point distributions of the feeds were quite similar except that of bitumen-derived light gas oil (OS), which included a relatively high amount of high boiling-point components.

2.2. Separation of Nitrogen Compounds

2.2.1. Extraction of SCO

25 g of SCO was mixed with the designated amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a flask and magnetically stirred for 2 h at 65°C. After the reaction, the products were cooled to room temperature. The complexes of SO and OS were separated from the denitrogenated oils (DNO) by simple decantation. The oils recovered by decantation from CL were diluted with three volumes of hexane for additional precipitation, which reduced the nitrogen contents of the DNOs by 5-10%, indicating that some complexes are soluble or finely dispersed in aromatic rich oils such as CL. The DNOs were finally recovered by distillation, and used for analysis and hydrotreatment tests.

2.2.2. Extraction of Model Compounds

Various nitrogen compounds including amines, pyridinic and pyrrolic compounds, carboxamide, nitriles, azabenzene, and some heterocyclic nitrogen compounds with 2 heteroatoms were used as model compounds. They divided into 4 groups and dissolved in *n*-decane or 1-methylnaphthalene. Concentrations of individual nitrogen compounds in the solutions varied from 0.3 to 0.7 wt%. Extraction experiments were conducted for

Table 2 Nitrogen Removal by Extraction of SCO with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

DNO	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{SCO}$		Denitrogenated oil (DNO)							Nitrogen removal [%]
	wt/wt	Cu/N [mol]	Yield [wt%]	N [wtppm]	S [wtppm]	SA [wt%]	MA [wt%]	PA [wt%]	PO [wt%]	
SO1	0.067	0.55	81	3750	63200	28	27	29	16	69.3
SO2	0.100	0.83	77	2500	61800	29	27	28	16	80.6
SO3	0.167	1.38	74	2370	65600	30	27	28	15	82.3
SO4	0.667	5.49	67	1780	62000	31	27	27	15	88.0
CL1	0.015	0.27	92	2450	n.d.	26	29	31	14	49.9
CL2	0.030	0.55	87	1650	n.d.	25	28	31	16	68.1
CL3	0.050	0.91	84	920	n.d.	26	30	31	13	82.8
CL4	0.100	1.83	77	740	n.d.	26	29	31	14	87.3
CL5	0.050	0.91	81	700	n.d.	29	32	34	5	87.4
OS1	0.015	0.97	98	770	40600	41	19	34	6	40.1
OS2	0.030	1.98	97	650	42500	41	20	35	4	50.0
OS3	0.050	3.26	97	520	44000	40	18	35	7	60.0
OS4	0.100	6.54	96	480	42300	40	18	35	7	63.4

SO1-SO4, CL1-CL4, OS1-OS4 are oils denitrogenated from SO, CL and OS, respectively, and CL5 is an oil denitrogenated from acid-removed CL. SA; saturates, MA; monoaromatics, PA; polyaromatics, PO; polars. n.d.; not determined.

2 h at 65°C by magnetically stirring the slurry consisting of solution and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (weight ratio 10 : 1). After extraction, the solution was separated from the complexes by filtration and analyzed by GC.

2. 3. Hydrotreatment Tests

Hydrotreatment tests were carried out using commercial NiMo/Al₂O₃ catalyst (NiO; 3 wt%, MoO₂; 16 wt%) and a batch-type micro-autoclave with an inner volume of 50 ml. Before the test, the catalyst was sulfided for 2.5 h at 400°C under a gas flow of H₂S (10 vol%)/H₂ mixture. Both SCOs and DNOs were used as the feed for hydrotreatment experiments. The autoclave was charged with 5 ml of the feed and 500 mg of the catalyst. The autoclave was pressurized under a hydrogen pressure of 5 MPa at room temperature and inserted into a preheated vertically shaking electric furnace. The hydrotreatment tests were performed at 350°C for 2 h and 4 h. After the tests, hydrotreated oils were cooled to room temperature and separated from catalyst fines by filtration under reduced pressure. H₂S and NH₃ gases trapped in the products were removed by passing nitrogen gas through the liquid before analyses of residual sulfur and nitrogen. The HDN and HDS rate constants were obtained by assuming first order reaction.

2. 4. Recovery of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ from Complex

100 g of OS or CL was mixed with 3.0 g or 5.0 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, respectively, and magnetically stirred for 2 h at 65°C. The precipitates were recovered and the DNO was added to three volumes of hexane. All precipitates were washed with a small amount of hexane and weighed. Some complexes were soluble or dispersed in the DNO. Therefore, additional precipitation by hexane dilution is an important step for increased nitrogen removal. Centrifugation and filtration of DNOs were ineffective compared to hexane dilution due to their high viscosity and solubility of some complexes.

The nitrogen complexes were well soluble in CH₂Cl₂

and acetone, poorly soluble in toluene and methanol, and not soluble in hexane. The complexes were dissolved in 100 ml of CH₂Cl₂, and washed with 200 ml of distilled water several times. Hexane solution of DNO from OS was also washed with 200 ml of distilled water. Water extracts were evaporated under vacuum at 60°C and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was recovered.

2. 5. Fractionation and Analysis

Acidic and basic fractions were separated from SCOs and some DNOs with 10% sodium hydroxide and 15% sulfuric acid solutions, respectively. The sulfur and nitrogen contents were measured with an APS-35 elemental analyzer. The boiling point distribution was determined by GC-simulated distillation (ASTM D 2887). The hydrocarbon types were identified by high performance liquid chromatography (HPLC). GC/FID, GC/NPD and GC/MS were used for identification of nitrogen compounds.

3. Results and Discussion

3. 1. Separation of Nitrogen Compounds from SCO

Table 2 and Fig. 1 show the results of the extraction of SCOs through complex formation with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Nitrogen removal was calculated with the following equation, which shows the percentage of the nitrogen removed by the extraction.

Nitrogen removal (%) = $(100 N_F - Y \times N_{\text{DNO}}) / N_F$
 where N_F , N_{DNO} = nitrogen contents of feed and DNO, respectively, and Y = yield of DNO (wt%). Nitrogen removal from SO and CL increased rapidly to around 80% as the molar ratio of Cu/feed-N increases to 0.83 or 0.91, but further increase of the Cu salt caused only a slight increase in nitrogen removal. Complete extraction of nitrogen compounds was not possible, as some nitrogen compounds did not form complexes. The nitrogen contents of the DNOs could be lowered to

Fig. 1 Effect of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ Amount on Nitrogen Removal from SCOs

1780 wtppm from 9900 wtppm for SO and to 740 wtppm from 4500 wtppm for CL. The nitrogen compounds of OS were more difficult to remove, probably due to their structural features, so nitrogen removal was around 60% at most.

The ratios of Cu/feed-N (mol/mol) of 0.55 for SO, and 0.27 and 0.55 for CL resulted in nitrogen removal of 69%, 50% and 68%, respectively. Therefore, the Cu salt can remove more than the molar equivalent of nitrogen compounds at lower ratios of Cu/feed-N. The optimum ratio of Cu/feed-N seems to be in the range between 0.5 and 0.8 for SO and CL, showing that removal is very effective regarding the usage of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The amount of Cu salt needed for nitrogen removal from SCO was quite different because of the very different initial nitrogen contents. Consequently, 5–10 wt%, 3–5 wt% and 1–2 wt% of the Cu salt is needed for efficient nitrogen removal from SO, CL, and OS, respectively.

High amounts of acidic compounds in CL, which consists mainly of alkyl phenols, might hinder the removal of basic nitrogen compounds due to the acid-base interaction. Supplementary experiments were conducted on the effect of these phenolic compounds on the complex formation. Two step extraction of CL, including removal of acidic compounds by extraction with 10% sodium hydroxide solution, and removal of nitrogen compounds by extraction ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{CL} = 0.05$ (wt/wt), 65°C , 2 h) resulted in a product (CL5) with the lowest nitrogen content (700 wtppm) among the DNOs of CL as shown in Table 2.

Assuming that the average molecular weight of nitrogen compounds in SCO is 168, the amount of nitrogen compounds will be 11.9 wt% for SO, 5.4 wt% for CL, and 1.5 wt% for OS. The relatively high viscosity of some oils could limit the mass transport process during the process and hinder complete precipitation of the

complexes. Also, some non-nitrogenous compounds may be entrained on the precipitated complexes, since the outer layer of the complex phase is largely organic in character and highly viscous. These factors may explain the low recovery yield of DNOs.

Table 2 also shows the sulfur contents and compound-type distributions of DNOs. The sulfur contents were almost unchanged after the extraction, and GC-SCD (sulfur chemiluminescent detector) analyses of the SCOs and DNOs showed no substantial differences in the content and type of the sulfur compounds. The extraction had little effect on the compound type distribution of OS. The polar fractions of SO and CL decreased after the extraction, and the other fractions consequently increased. The lower increase of polyaromatics might indicate that some polyaromatics were selectively adsorbed on $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. However, the compound type distribution of DNO was quite similar to that of the original SCO except for the polar fraction.

3.2. Separation of Nitrogen Compounds from Model Mixtures

The results of extraction of some selected model nitrogen compounds are summarized in Table 3. Relatively strong basic nitrogen compounds such as amines and pyridinic compounds could be completely removed. Hydrogenated derivatives of pyridinic compounds, which have higher basic strength than the base pyridinic compounds, were also easily removed. Relatively low extraction (about 50%) of 2,6-di-*t*-butylpyridine was probably due to the large substituent groups at the 2 and 6 positions in the pyridinic ring, which would directly hinder interaction of nitrogen with metals. In contrast, methyl substituents at the same positions did not hinder complex formation with metal ions. These results are in agreement with previous results¹⁵⁾, suggesting that molecular size and steric restrictions around the nitrogen atom are also important in the interaction.

Partial removal of carbazoles and complete removal of alkyl indoles confirmed that the relative basic strength of the compounds is not the only factor determining the degree of interaction. Some neutral heterocyclic nitrogen compounds can also form complexes with transition metal ions such as Cu. Compared to other pyrrolic compounds, N-alkyl carbazole was highly resistant to extraction, which occurred only after N-substitution. Typically SCO contains significantly fewer N-alkyl carbazoles compared to other alkyl substituted carbazoles, and the relative concentrations of these compounds could only be increased during hydro-treatment, as a result of resistance to reaction⁷⁾.

Extraction of amides, nitriles, and azacompounds from solution was not possible because of their chemical properties. Extraction of heterocyclic compounds containing two heteroatoms showed that oxygen and sulfur atoms in the N-containing heterocycles did not

Table 3 Extraction of Model Nitrogen Compounds with CuCl₂·2H₂O

Group no.	Model compounds	Feed		Product [wt%]	Extractability [%]
		[wt%]	N [wtppm]		
1	quinoline	0.56	607	0	100
1	acridine	0.46	360	0	100
1	2,4,6-trimethylpyridine	0.56	648	0	100
2	<i>N,N</i> -dimethylaniline	0.35	332	0	100
2	perhydroisoquinoline	0.35	353	0	100
2	2,6-di- <i>t</i> -butylpyridine	0.30	220	0.15	48
2	<i>n</i> -octanenitrile	0.35	400	0.33	7
2	phenothiazine	0.40	280	0	100
3	2,4,6-trimethylaniline	0.39	400	0	100
3	carbazole	0.38	320	0.22	40
3	phenoxazine	0.47	360	0	100
3	phenazine	0.47	730	0	100
4	<i>N</i> -ethylcarbazole	0.49	350	0.47	3
4	<i>N,N</i> -diethyldodecanamide	0.63	350	0.63	0
4	1,2-dimethylindole	0.45	430	0	100
4	4-biphenylcarbonitrile	0.49	380	0.49	0
4	azobenzene	0.30	230	0.30	0

Solvent was 1-methylnaphthalene for groups 1 and 2, and *n*-decane for groups 3 and 4.

hinder the complex formation of nitrogen atoms.

These studies with reference nitrogen compounds confirmed that extraction by CuCl₂·2H₂O could remove most pyridinic and pyrrolic compounds, including some alkylpyridinic and alkylindolic compounds which are the most refractory to hydrotreatment.

3.3. Nitrogen Compounds in SCOs and Their DNOs

Generally, heterocyclic nitrogen compounds such as alkyl substituted pyridinic and pyrrolic compounds are the major nitrogen components of SCO fractions^{(6),(7),(11),(20)~(25)}. The nitrogen in shale oils is also present as *n*-alkyl nitriles, amides, and diazaaromatics⁽¹¹⁾, and *n*-alkyl nitriles are the most abundant in some shale oils⁽²²⁾. Alkylated anilines are one of the major nitrogen compounds found in coal liquids⁽²⁴⁾. Some transition metal salts can form insoluble complexes with nitrogen bases, nitrogen heterocycles, and aromatic nitriles, and remove these compounds from oil fractions^{(26)~(28)}.

SCOs as well as their DNOs were separated into acidic, basic and neutral fractions, and analyzed by GC/NPD (nitrogen-phosphorus detection) and GC/MS. Relative contents of basic and neutral nitrogen compounds were quite different for each SCO as shown in **Table 4**. CL was rich in basic nitrogen compounds whereas OS contained more neutral nitrogen compounds. Extraction removed 81-91% of basic nitrogen compounds and 30-68% of non-basic compounds. Clearly the low nitrogen removal for OS was caused by the high content of neutral nitrogen with low extractability.

GC/NPD chromatograms are shown in **Figs. 2-4**. SO and CL contained relatively more low boiling point nitrogen compounds, whereas OS contained more high molecular weight nitrogen compounds. Quinolines,

Table 4 Removal of Nitrogen Compounds by Extraction with CuCl₂·2H₂O

Sample	Nitrogen content [wtppm]		
	Total	Basic	Neutral
SO	9900	6150	3750
SO2	2500	700	1800
CL	4500	3200	1300
CL3	920	430	490
OS	1260	500	760
OS2	650	100	550

Sample	Nitrogen removal [%]		
	Total	Basic	Neutral
SO2	80.6	91.2	63.0
CL3	82.8	88.7	68.3
OS2	50.0	80.6	29.8

isoquinolines, and their partially hydrogenated derivatives were major components in the basic fractions of SO and indoles, and *n*-alkylnitriles were predominant in the neutral fraction. Larger cyclic nitrogen compounds such as benzoquinolines and carbazoles were present in smaller amounts. The chromatogram of SO2 clearly shows that basic nitrogen compounds and indoles were extracted but *n*-alkylnitriles were not by complex formation. The other compound types in SO2 were unclear because of the low contents and very large numbers.

Clear peaks in **Fig. 3** indicate that the nitrogen compounds of CL contained no or only a few simple alkyl substituents such as methyl and ethyl. Alkylanilines were the most abundant nitrogen compounds in the CL basic fraction whereas carbazoles were rich in the neutral fraction. Quinolines/isoquinolines, benzoquinolines, indoles, and their partially hydrogenated

Fig. 2 GC-NPD Chromatograms of SO, Its Fractions and DNO

Fig. 3 GC-NPD Chromatograms of CL, Its Fractions and DNO

analogues were present in smaller amounts. The chromatogram of CL3 showed that most anilines, quinolines, benzoquinolines, and indoles were extracted, but carbazoles and sterically hindered alkyanilines persisted.

Figure 4 shows the chromatograms of OS, its basic and neutral fractions, and DNO (OS2). The basic

Fig. 4 GC-NPD Chromatograms of OS, Its Fractions and DNO

fraction of OS contained quinolines, isoquinolines, and their partially hydrogenated derivatives. A large number of unknown nitrogen species were present in the neutral fraction. The chromatogram of OS2 showed that most basic nitrogen compounds were extracted, which was consistent with the results of SO and CL, whereas the unknown neutral nitrogen species could not be removed and remained in the DNO (OS2).

3. 4. Hydrotreatment of SCOs and Their DNOs

Various studies of self-inhibition of the HDN rate by nitrogen compounds have suggested that basic nitrogen compounds are more strongly adsorbed on catalyst active sites and blocks HDN of these and other nitrogen compounds^{29),30)}. The inhibition effect of quinoline on HDN of indole was much higher than the inhibition effect of indole on HDN of quinoline³¹⁾. Acridine strongly inhibits the conversion of 1,4-dimethylcarbazole, a low reactivity alkylcarbazole which is highly converted otherwise³²⁾.

Table 5 shows the results of hydrotreatment of SCOs and their DNOs. The nitrogen contents of the hydrotreatment products obtained from the DNOs are much lower than those from the SCOs. The effective removal of basic and heterocyclic nitrogen compounds from the SCO feed by extraction significantly affected the HDN rates except for those of CL2 and CL3. According to the GC/NPD chromatograms (Figs. 2-4), the nitrogen compounds in SCOs and their DNOs are quite different. DNO from CL contains high amounts of low molecular weight carbazoles and sterically hindered anilines, which are well known to be refractory nitrogen compounds. DNO from CL also contains high amounts of phenolic compounds which can depress

Table 5 Nitrogen and Sulfur Contents of Hydrotreatment Feeds and Products, and HDN and HDS Reaction Rates

		SO	SO1	SO2	SO3	SO4	CL	CL2	CL3	CL4	CL5	OS	OS2
Nitrogen													
Feed	[wtppm]	9900	3750	2500	2370	1780	4500	2450	1650	920	740	1260	650
Product at 2 h	[wtppm]	5400	1300	540	290	100	1550	650	180	70	20	210	14
Product at 4 h	[wtppm]	4100	620	160	80	40	810	280	80	30	15	60	2
HDN reaction rate	[h ⁻¹]	0.24	0.47	0.70	0.89	1.05	0.45	0.38	0.45	0.65	0.88	0.79	1.54
Sulfur													
Feed	[wtppm]	62800	63200	61800	65600	62000	800	—	—	—	—	44000	42500
Product at 2 h	[wtppm]	9010	11940	7150	5250	2910	<10	—	—	—	—	4000	1110
Product at 4 h	[wtppm]	4510	4490	2180	2140	470	<10	—	—	—	—	1740	120
HDS reaction rate	[h ⁻¹]	0.72	0.70	0.88	0.94	1.28	—	—	—	—	—	0.89	1.54

Fig. 5 Effect of Nitrogen Removal on HDN Rate of SCOs

Fig. 6 Effect of Nitrogen Removal on HDS Rate of SCOs

HDN. DNO from SO contains large amounts of *n*-alkylnitriles which are considered to be reactive in catalytic hydroprocessing⁷⁾. The unknown nitrogen compounds of DNO from OS are supposed to undergo HDN easily.

The HDN and HDS rates were plotted against the nitrogen content of hydrotreatment feeds as shown in Figs. 5 and 6. In general, lower initial concentration of total nitrogen compounds resulted in higher HDN rate. The HDN rate of SO was increased by up to 4 times, whereas HDN of CL and OS were increased by about 2 times. Increased HDN rate of SO was probably promoted by the higher contents of reactive *n*-alkylnitriles. Removal of nitrogen compounds prior to hydrotreatment also promoted the HDS of sulfur compounds. HDS rates of SO and OS were increased up to about 1.8 times by the removal of nitrogen compounds. Sulfur contents of DNOs from SO and OS were reduced from 61900 to 470 wtppm and from 42400 to 120 wtppm, respectively. In comparison, hydrotreatment products from SO and OS feeds contained 4500 and 1700 wtppm sulfur. HDS of CL and its DNOs was very fast and the residual sulfur content was less than 10 wtppm for all product oils.

3. 5. Recovery of CuCl₂·2H₂O from Complex

Experiments on the recovery of CuCl₂·2H₂O are summarized in Table 6. The precipitates were dissolved in CH₂Cl₂ and washed with water several times. Direct treatment of the precipitates with water was not effective due to highly hydrophobic character. The recovery yields after extraction 3 times with water were 96.0% for CL and 83.3% for OS. Further water extraction of OS-CH₂Cl₂ solution led to an increase of recovery by 4.3%. Some of the OS complex was apparently not precipitated and remained in the DNO. The hexane solution of DNO was also washed with water, which led to an increase of recovery by 9.7%. These results showed that extraction using water at room temperature allows effective recovery of CuCl₂·2H₂O, consistent with previous findings¹⁶⁾. Re-use of the recovered CuCl₂·2H₂O for both CL and OS extraction showed no decrease in the complex forming capability.

4. Conclusions

Nitrogen compounds in synthetic crude oil (SCO) were removed by complex formation with crystalline

Table 6 Recovery of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ from Precipitate- CH_2Cl_2 and DNO-hexane Solutions

		CL	OS
Feed oil	[g]	100.0	100.0
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	[g]	5.0	3.0
Precipitate-1 ^{a)}	[g]	11.6	5.7
Precipitate-2 ^{a)}	[g]	2.4	2.1
Recovery from precipitate- CH_2Cl_2 solution			
3 times extraction	[g]	4.8	2.50
further 3 times extraction	[g]	—	0.13
Recovery from DNO-hexane solution			
3 times extraction	[g]	—	0.24
further 3 times extraction	[g]	—	0.05
Total recovery yield of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	[wt%]	96.0	97.3

a) Precipitate-1 was recovered by simple decantation, and Precipitate-2 was further recovered after dilution with hexane.

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The nitrogen contents of SO, CL and OS could be lowered from 9900 to 1780 wtppm, from 4500 to 740 wtppm and from 1260 to 480 wtppm, respectively. Basic nitrogen compounds were preferentially removed, and the relative content of neutral nitrogen compounds increased in the DNOs. *n*-Alkyl-nitriles, carbazoles, and sterically hindered anilines and pyridines remained in the DNOs.

Effective removal of basic and heterocyclic nitrogen compounds from the feeds significantly affected the hydrotreatment reaction rates. The HDN rates of SCO were highly enhanced by factors of 4.4, 1.9 and 1.5 for SO, OS and CL, respectively. The sulfur contents were also affected by nitrogen pre-removal, and the HDS rates were increased by a factor of 1.8 for both SO and OS due to the decreasing inhibition effect of nitrogen.

The process requires simple extraction and separation equipments, and can be conducted at 65°C and atmospheric pressure. The amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ required for the complex formation is relatively small (app. 10-1 wt% of oil feed) and more than 95% of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ can be recovered by washing the complex with water. The present method is another option for the conversion of light gas oils from SCOs to high quality feedstock suitable for the production of clean diesel fuels.

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要 旨

合成原油の深度水素化処理のための窒素化合物の分離

Janchig NARANGEREL, 杉本 義一

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

オイルシェール、石炭、オイルサンドから得られる合成原油は、窒素、硫黄などのヘテロ元素を多く含み、クリーンな輸送用燃料に転換するには厳しい水素化処理条件が必要となる。本研究では、比較的温和な反応条件下での深度水素化を達成するため、 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ との錯体形成による窒素化合物の分離処理と得られた脱窒素油の水素化処理を検討した。原料油としてシェールオイル、石炭液化油およびピチューメンの熱分解油の軽油留分を用いた。水素化処理実験は、小型オートクレーブを用い、水素初圧 5 MPa、反応温度 350℃、反応時間 2～4 h で行っ

た。

合成原油中の塩基性および複素環式窒素化合物の多くは、 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ との錯体形成により沈殿し、効率よく除去された。この窒素低減処理により、合成原油の水素化脱窒素速度が増大し、生成油中の窒素含量が大きく減少した。使用した $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ のほとんどは錯体の CH_2Cl_2 溶液を水で洗浄することにより回収できることから、本分離処理は窒素を多く含む原料油の深度水素化処理の前処理法として有用であると考えられる。

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