CHARACTERIZATION AND HYDROTREATMENT OF SHALE OILS OF MONGOLIAN OIL SHALES

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Abstract. The shale oils of oil shales from Mongolian Khoot, Tesegtiin honhor, Uvurjargalant and Zuun bulag deposits, as well as their distillates were studied by the hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) processes for the possibility of improving the quality of liquid products. Elemental and chemical compositions of the shale oils, distillates and hydrotreated oils were examined qualitatively and quantitatively, using a Thermo Scientific FLASH2000 CHNS analyzer and an Agilent 6890A gas chromatograph (GC). Hydrotreatment of Khoot shale oil (KH) under different reaction conditions showed that with increasing reaction temperature from 330 to 370 °C, HDN, HDS and HDO increased from 13 to 37%, from 65 to 92% and from 59 to 81%, respectively. Among the shale oils hydrotreated at a temperature of 350 °C for 2h, the Uvurjargalant shale oil (UJ) had the highest conversion by HDN (39%), HDS (89%) and HDO (71%).

Keywords: shale oils of Mongolian oil shales, distillate fractions, hydrotreatment, hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, gas chromatography.

1. Introduction

Hydrotreatment as a means of reducing sulfur, nitrogen and oxygen contents in fuels continues to be one of the main catalytic processes in petroleum refining. It is currently the key technology in production of clean fuels from

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heteroatom-containing synthetic oils, such as shale oils, coal liquids and tar sands [1, 2].

In Mongolia, 13 oil shale fields have been identified over a 312 000 km² area, which contain approximately 40 deposits. The total geological resource of oil shale in these deposits is 788.0 billion tons. Several studies on characterization and conversion of Mongolian oil shales were performed to obtain value added products [3, 4]. However, studies on deep hydrotreatment and detailed characterization of shale oil distillates obtained from Mongolian oil shales are very few. In this research work, we aim to compare the characteristics and hydrotreating reactivities of shale oils obtained from oil shale samples from Mongolian Khoot, Tesegtiin honhor, Uvurjargalant and Zuun bulag deposits.

2. Experimental

2.1. Samples

Oil shales were sampled from the surface (Khoot, Tesegtiin honhor, Uvurjargalant, Zuun bulag) and the underground (Khoot) of the deposits. Pyrolysis of the samples using a Fisher assay retort was carried out at the National University of Mongolia. The samples with a particle size of 3–5 mm were heated under a nitrogen flow of 20 ml/min from 20 to 520 °C at a heating rate of 10 °C/min and kept at this temperature for 20 min. The yields of shale oils were the following: 15.9% (Khoot surface, KH), 7.14% (Khoot underground, KG), 4.36% (Tesegtiin honhor, TH), 4.67% (Uvurjargalant, UJ) and 3.47% (Zuun bulag, ZB). The shale oil samples were subsequently taken to the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, and used for the current research.

2.2.Vacuum distillation

The shale oil samples, each about 12 g, were distilled using a GTR-350 vacuum distillation unit (Sibata Scientific Technology Ltd., Japan). Four fractions were obtained: light distillate (LD; < 220 °C), middle distillate (MD; 220–350 °C), heavy distillate (HD; 350–500 °C) and vacuum residue (VR; > 500 °C). The yield of fraction was determined based on the weight of the residual oil.

2.3. Reaction apparatus

The batch type autoclaves (50 ml and 80 ml) and a shaking type furnace were used for hydrotreatment tests and catalyst pre-sulfidation. The inner diameter of the 50 ml autoclave was 12 mm and length 300 mm, the respective dimensions of the 80 ml autoclave were 15 mm and 300 mm. The furnace was equipped with electric heaters and was shaken at a speed of

30 times per minute after the autoclaves were inserted into the holes of the furnace block.

2.4. Catalyst and its pre-sulfidation

The commercial catalyst (3% Ni-15% Mo/Al₂O₃) was pulverized to < 60 mesh and pre-sulfided as shown below. The catalyst (2 g), light gas oil (LGO, 10 g) and dimethyldisulfide (DMDS, 0.5 g) were added in a glass tube which was later packed in the 80 ml autoclave. The autoclave was filled with hydrogen of 5 MPa and inserted into the furnace. The temperature was increased gradually to 350 °C for 1.5 h and held constant for 3 h. After cooling down and purging the gas, the pre-sulfided catalyst was washed with toluene and filtered *in vacuo* under a nitrogen stream. The catalyst was stored in hexane and filtered and dried *in vacuo* just before the hydro-treatment tests.

2.5. Hydrotreatment test procedure

A batch type autoclave with an inner volume of 50 ml was used for hydrotreatment tests. The autoclave was charged with 4 g of the shale oil, 0.2 g of the pre-sulfided catalyst and 0.02 g of elemental sulfur, and pressurized under a hydrogen pressure of 6 MPa. The autoclave was inserted into the preheated electric furnace. The following four sets of the reaction conditions were investigated using KH as a feed: 1) 330 °C, 2 h; 2) 350 °C, 2 h; 3) 370 °C, 2 h; 4) 330 °C, 4 h. The other shale oils and distillates of KH were hydrotreated under the conditions of 350 °C, 2 h and 6 MPa H₂ (initial). The gaseous product was collected into a gas pack and analyzed by gas chromatography-thermal conductivity detector (GC-TCD). Hydrogen consumption was determined by the gas volumes before and after the hydrotreatment test and the hydrogen concentration of the product gas. The hydrotreated oil was recovered from the autoclave by decantation. The catalyst was recovered by washing the autoclave with toluene and filtering.

2.6. Analysis

The elemental composition of shale oils and hydrotreated oils was determined using a Thermo Scientific FLASH2000 CHNS analyzer and the oxygen content was obtained by difference. The shale oils, distillates and hydrotreated oils were examined qualitatively and quantitatively, employing an Agilent 6890A gas chromatography system coupled with a flame ionization detector (FID), a sulfur chemiluminescence detector (SCD) and a mass selective detector (MSD).

3. Results and discussion

3.1. Characterization of shale oils

3.1.1. Distillation of shale oils

Distillation results are shown in Figure 1. The yields of LD, MD, HD and VR were 8–11%, 30–37%, 43–49% and 9–16%, respectively. The distribution of distillates was relatively similar. HD was the most abundant in shale oils, followed by MD.

Table 1 presents the elemental composition of shale oils and distillates. The carbon and hydrogen contents of shale oils are 82.6-84.0 and 10.3-11.0%, respectively, and the atomic ratio of hydrogen to carbon (H/C) is between 1.49 and 1.60. The hydrogen content of TH is lower compared to other shale oils, which means that TH is more abundant in aromatic compounds.



Fig. 1. Yields of distillation fractions of shale oils.

Table 1. Elemental composition of shale oils and distillates, wt%

Shale oil/		H/C				
distillate	С	Н	Ν	S	O (diff)	
КН	83.18	11.04	0.91	0.36	4.51	1.59
KG	83.87	10.98	1.52	0.45	3.18	1.57
TH	83.29	10.32	2.13	0.35	3.91	1.49
UJ	82.64	11.01	1.32	0.43	4.60	1.60
ZB	84.01	10.92	1.59	0.21	3.27	1.56
KH-LD	79.00	11.71	0.60	0.23	8.46	1.78
KH-MD	83.74	11.93	0.75	0.34	3.24	1.71
KH-HD	84.88	11.33	0.97	0.38	2.44	1.60

Note: diff-difference.

The nitrogen, sulfur and oxygen contents are 0.91-2.13%, 0.21-0.45% and 3.2-4.6%, respectively. The average organic nitrogen contents of most shale oils are 0.5-2.5 wt%, compared to around 0.1 wt% in conventional oil, therefore in the case of shale oils, the major target is the removal of nitrogen. The relatively high content of oxygen (8.46%) in KH-LD may be caused by evaporation of low-boiling components prior to the CHNS analysis. In such case, the contents of C, H, N and S of KH-LD should be somewhat higher than the values shown.

3.1.2. GC-FID, GC-SCD and GC-MS analyses of distillates

The GC-FID and GC-SCD chromatograms of distillates of KH are shown in Figures 2–7 together with chromatograms of the corresponding hydrotreated oils. The pairs of peaks of *n*-alkanes and *n*-1-olefins appeared regularly in the GC-FID chromatograms of LD. Some aromatic compounds such as toluene (To) and xylenes (Xy) were identified by GC-MS but many peaks could not be assigned because cyclic alkanes and olefinic compounds have the same molecular weights. The GC-SCD chromatogram shows that thiophene (T) and its alkylated homologues are major sulfur compounds in LD. Benzothiophene (BT) also exists but in lower amount.

There are pairs of distinguishing peaks of n-alkanes and n-1-olefins in the GC-FID chromatograms of MD. Thiophenes, benzothiophene and their alkyl derivatives are present in the GC-SCD chromatogram. More peaks than expected are present probably due to the existence of olefinic substituents.

Only *n*-alkanes and *n*-1-olefins could be assigned in the GC-FID chromatogram of HD. The great hump of the chromatogram shows the existence of a large number of small overlapping peaks.

3.2. Hydroteating of shale oil

3.2.1. Hydrotreating of Khoot shale oil under different reaction conditions

Hydrotreating of Khoot shale oil was carried out under four sets of the reaction conditions (Table 2). The gas yields and hydrogen consumption were determined by GC-TCD analysis and the initial and recovered gas volumes were measured. The yields of hydrocarbon gases C_1 – C_3 were very low, 0.09–0.25%, which showed that the cracking of C–C bonds scarcely occurred in the temperature range of 330–370 °C. The hydrogen consumption was 1.3–1.9%. The relatively high hydrogen consumption of run KH-4 was probably caused by the longer time of hydrogenation of olefinic compounds.

The elemental composition of hydrotreated oils of Khoot shale oil is given in Table 3. Compared to the shale oil, the hydrogen content increased from about 11.0% (Table 1) to 12.3-12.7% and the contents of heteroatoms decreased. Hydrogen was also spent for the removal of heteroatoms. The sulfur content could be reduced to < 0.1%, but the nitrogen contents were

Run	Hydrotreat	ment	Gas recovered,	Yield of	C ₁ C _{3,}	H_2 consumed,			
	Temperature, °C	Time, h	ml	Methane	Ethane	Propane	Sum	wt%	
KH-1	330	2	2070	0.017	0.030	0.044	0.09	1.33	
KH-2	350	2	1940	0.028	0.043	0.056	0.13	1.56	
KH-3	370	2	1900	0.085	0.076	0.090	0.25	1.69	
KH-4	350	4	1780	0.036	0.054	0.062	0.15	1.90	

Table 2. Yields of hydrocarbon gases $C_1\!-\!C_3$ and hydrogen consumption of Khoot shale oil

Table 3. Elemental composition of hydrotreated oils of Koot shale oil, wt%

Hydrotreated		H/C				
oil	С	Н	Ν	S	O (diff)	
KH-1H	84.88	12.31	0.81	0.13	1.87	1.74
KH-2H	85.17	12.49	0.71	0.08	1.55	1.76
KH-3H	85.87	12.62	0.59	0.03	0.89	1.76
KH-4H	86.06	12.66	0.67	0.04	0.57	1.77

Note: diff-difference.

still higher than 0.6%. The order of difficulty in removing the heteroatoms by hydrotreatment was $S < O \ll N$ [5, 6], so, nitrogen was the most difficult-to-remove heteroatom. Organic nitrogen compounds strongly adsorbed on catalyst active sites and inhibited the removal of both nitrogen-and other heteroatom-containing compounds during hydrotreatment. Basic nitrogen compounds, even at levels of tens of ppm, are believed to severely inhibit HDS [7]. Therefore the removal of nitrogen by HDN was highly important.

During the hydrotreatment, the shale oil was reacted with hydrogen and converted into hydrocarbon gases (C_{1-3}), H_2O , H_2S , NH_3 , coke and hydrotreated oil. The coke was deposited on the catalyst and its yield could be determined by the weight and carbon content of the recovered catalyst. However, the coke yield could not be determined due to the low recovery of the catalyst from the autoclave in these experiments. Generally, the coke yield was below 1% when hydrotreating this kind of shale oil under the above reaction conditions. Therefore, the coke formation was neglected in this work as it only had a weak influence on the shale oils conversion by HDN, HDS and HDO. In this case, the yields of NH_3 , H_2S , H_2O and hydrotreated oil could be calculated by solving the following equations:

$$Y_{NH3} = 17/14 \times (N_f - (N_p \times Y_{oil})/100),$$
(1)

$$Y_{H2S} = 34/32 \times (S_f - (S_p \times Y_{oil})/100),$$
(2)

$$Y_{H2O} = 18/16 \times (O_f - (O_p \times Y_{oil})/100),$$
(3)

$$Y_{oil} = 100 + Y_{H2} - Y_{Cl-C3} - Y_{NH3} - Y_{H2S} - Y_{H2O},$$
(4)

where Y denotes yield, N, S, O mean the contents of nitrogen, sulfur and oxygen, respectively, and the scripts f and p mean the shale oil and product, respectively. For example, N_f and N_p mean the nitrogen contents of the shale oil and hydrotreated oils, respectively. The conversions by HDN, HDS and HDO were calculated as follows;

$$HDN\% = 14/17 \times Y_{NH3}/N_f \times 100,$$
 (5)

HDS% =
$$32/34 \times Y_{H2S}/S_f \times 100$$
, (6)

$$HDO\% = 16/18 \times Y_{H2O}/O_f \times 100.$$
(7)

Table 4 presents the yields of NH₃, H₂S, H₂O and hydrotreated oil of KH, and the conversions by HDN, HDS and HDO. With increasing reaction temperature from 330 to 370 °C, HDN, HDS and HDO increased from 13 to 37%, from 65 to 92% and from 59 to 81%, respectively. The increased reaction time also led to the increase of HDN, HDS and HDO. The nitrogen content of the hydrotreated oils was still too high compared with that of transportation fuels. Longer reaction time was preferable for increased hydrogen consumption, but HDN might proceed deeper at higher temperature than for longer time.

Table 4. Yields of NH_3 , H_2S , H_2O and hydrotreated oil and conversions of Khoot shale oil

Run	Hydrotrea	atment		Y	Conversion, %				
	Tempera- ture, °C	Time, h	NH ₃	H_2S	H ₂ O	Hydrotreated oil	HDN	HDS	HDO
KH-1	330	2	0.14	0.25	3.02	97.8	13	65	59
KH-2	350	2	0.26	0.30	3.38	97.5	24	77	67
KH-3	370	2	0.41	0.35	4.11	96.6	37	92	81
KH-4	350	4	0.32	0.34	4.46	96.6	29	88	88

3.2.2. Hydrotreating of shale oils

The shale oils samples were hydrotreated at 350 °C for 2 h in order to compare the reactivities of HDN, HDS and HDO. Table 5 presents the yields of hydrocarbon gases C_1-C_3 and hydrogen consumption. TH provided the highest yields of C_1-C_3 and its hydrogen consumption was the highest.

The elemental composition of hydrotreated oils of shale oils is given in Table 6. Their sulfur content was reduced to < 0.1%, but the nitrogen contents were still very high, 0.7-1.7%. The nitrogen content of hydrotreated TH (TH-H) was much higher and its hydrogen content was lower than those

Shale	Gas	Yield of	H ₂			
oil	recovered, ml	Methane	Ethane	Propane	Sum	consumed, wt%
KH	1940	0.028	0.043	0.056	0.13	1.56
KG	2040	0.037	0.053	0.085	0.18	1.38
TH	1750	0.063	0.091	0.113	0.27	2.02
UJ	1930	0.032	0.059	0.066	0.16	1.65
ZB	1940	0.054	0.070	0.079	0.20	1.61

Table 5. Yields of hydrocarbon gases C_1 – C_3 and hydrogen consumption of shale oils

 Table 6. Elemental composition of hydrotreated oils of shale oils, wt%

Hydrotreated		H/C				
oıl	С	Н	Ν	S	O (diff)	
КН-Н	85.17	12.49	0.71	0.08	1.55	1.76
KG-H	85.29	12.12	1.13	0.10	1.36	1.71
TH-H	84.91	11.63	1.67	0.09	1.70	1.64
UJ-H	85.27	12.46	0.83	0.05	1.39	1.75
ZB-H	85.38	12.12	1.07	0.07	1.36	1.70

Note: diff – difference.

of the other shale oils. This result is consistent with the results of elemental composition of the shale oil. Nitrogen-containing heterocyclic aromatic compounds such as quinoline and pyridine, which were very resistant to HDN, might be present in TH in abundance, compared with the other shale oils.

Table 7 presents the yields of NH_3 , H_2S , H_2O and hydrotreated oils as well as conversions of shale oils by HDN, HDS and HDO. Among the shale oils examined, UJ exhibited the highest conversions by HDN, HDS and HDO, while ZB had the lowest conversions by HDS and HDO. The conversion of KH and TH in HDN was lower than in HDS and HDO. As Table 7 reveals, all the studied shale oils were much more difficult to convert by HDN than by HDS and HDO.

Table 7. Yields of NH₃, H₂S, H₂O and hydrotreated oils and conversions of shale oils

Shale		Y	/ield, wt%		Conversion, %			
oil	NH ₃	H_2S	H ₂ O Hydrotreated oil		HDN	HDS	HDO	
KH	0.26	0.30	3.38	97.5	24	77	67	
KG	0.50	0.37	2.07	98.3	27	78	58	
TH	0.59	0.28	2.52	98.4	23	75	57	
UJ	0.63	0.41	3.66	96.8	39	89	71	
ZB	0.65	0.15	2.17	98.4	34	67	59	

3.2.3. Hydrotreating of distillate fractions of Khoot shale oil

Shale oil contains asphaltene and minerals which are known to be poisoning and deactivating materials for the hydrotreating catalyst. Therefore, the distillation bottom, atmospheric or vacuum residue, had better be removed for the deeper hydrotreating and longer catalyst life. The gas yield and hydrogen consumption in the hydrotreating of KH distillates at 350 °C for 2 h are presented in Table 8. The hydrogen consumption of KH-LD was relatively low.

The elemental composition of hydrotreated distillates of Khoot shale oil is given in Table 9. Being around or below the detection limit of the CHNS analyzer, the sulfur content of the distillates could not be determined. Therefore, it was found by GC-SCD analysis of the shale oil and hydrotreated oils via the following equation:

$$\mathbf{S} = \mathbf{S}_f \times \mathbf{A}_p / \mathbf{A}_f,\tag{8}$$

where S_f is the sulfur content of the shale oil, and A_p and A_f are the total peak areas of the GC-SCD chromatograms of the product and shale oil, respectively.

Table 10 gives the yields of NH_3 , H_2S , H_2O and hydrotreated oil and conversions of Khoot shale oil distillates by HDN, HDS and HDO. The conversions of KH-LD by HDN and HDS were both over 90%, while that by HDO could not be established due to the very low accuracy of the oxygen content. The order of HDN conversion was KH-LD > KH-MD > KH-HD, which is common for the hydrotreating of distillate fractions. The HDS of LD usually proceeds much faster than that of MD. The reversed result might

Table 8. Yields of hydrocarbon gases C_1 - C_3 and hydrogen consumption of Khoot shale oil distillates

Shale oil	Gas	Yield of	Yield of hydrocarbon gases C1-C3, wt%				
distillate	recovered, ml	Methane	Ethane	Propane	Sum	wt%	
KH-LD	2540	0.013	0.033	0.062	0.11	0.85	
KH-MD	1920	0.030	0.040	0.057	0.13	1.80	
KH-HD	2090	0.033	0.045	0.066	0.14	1.37	

Table 9. Elemental composition of hydrotreated distillates of Khoot shale oil

Hydrotreated		U/C				
distillate	С	Н	Ν	S*	O (diff)	n/C
KH-LDH KH-MDH KH-HDH	79.21 84.65 86.22	12.95 13.15 12.40	0.06 0.37 0.75	0.019 0.022 0.059	7.76 1.81 0.57	1.96 1.86 1.73

Note: * - content determined by GC-SCD analysis; diff - difference.

Shale oil		•	Yield, wt%	Conversion, %			
distillate	NH ₃	H_2S	H ₂ O	Hydrotreated oil	HDN	HDS	HDO
KH-LD	0.66	0.22	0.88	99.0	90	92	_
KH-MD	0.46	0.34	1.63	99.2	51	94	45
KH-HD	0.28	0.34	2.11	98.5	24	85	77

Table 10. Yields of NH_3 , H_2S , H_2O and hydrotreated oil and conversions of Khoot shale oil distillates

Note: "–" not established.

be caused by the complete vaporization of LD in the autoclave and its relatively low accessibility for the catalyst.

To understand the reactions of each component, GC-FID, GC-SCD and GC-MS analyses were performed. Figures 2 and 3 show the gas chromatograms of KH-LD before and after hydrotreating. In the FID chromatogram the peaks of alkenes and unknown compounds disappeared during the hydrotreating. The peak area of toluene (To) was 401 for KH-LD and 375 for hydrotreated KH-LDH, which indicated that the hydrogenation of a monoaromatic compound was not significant.



Fig. 2. GC-FID chromatograms of Khoot shale oil light distillate before and after hydrotreating.



Fig. 3. GC-SCD chromatograms of Khoot shale oil light distillate before and after hydrotreating.

Figures 4 and 5 show the GC-FID and GC-SCD chromatograms of KH-MD before and after hydrotreating. By hydrogenating olefinic compounds, in the FID chromatogram the peaks of alkenes and unknown compounds disappeared and that of *n*-alkane became more pronounced. The content of *n*-alkanes reached 50.5 mass% of KH-MD after hydrotreating. The SCD chromatogram of KH-MD contains a large number of thiophenes and benzothiophenes, and the peaks of refractory sulfur compounds such as methyl-dibenzothiophene (DBT) remained after the hydrotreating.

Figures 6 and 7 show the GC-FID and GC-SCD chromatograms of KH-HD before and after hydrotreating. In the FID chromatogram the peaks of alkenes and unknown compounds disappeared by the hydrotreating, similarly to those of KH-LD and KH-MD. The SCD chromatogram of KH-HD contains a large number of benzothiophenes and other unknown compounds, and the hump of the chromatogram is very large. After the hydrotreating, the hump decreased remarkably and the peaks of refractory sulfur compounds such as 4-methyl-DBT and C₂-DBT appeared.



Fig. 4. GC-FID chromatograms of Khoot shale oil middle distillate before and after hydrotreating.



Fig. 5. GC-SCD chromatograms of Khoot shale oil middle distillate before and after hydrotreating.



Fig. 6. GC-FID chromatograms of Khoot shale oil heavy distillate before and after hydrotreating.



Fig. 7. GC-SCD chromatograms of Khoot shale oil heavy distillate before and after hydrotreating.

4. Conclusions

The properties and hydrotreating reactivity of the shale oils of Mongolian Khoot, Tesegtiin honhor, Uvurjargalant and Zuun bulag oil shales were examined for suitability to produce clean transportation fuels. The distillate yields of the shale oil samples were relatively similar. The yields of low, middle and heavy distillates and vacuum residue were 8-11%, 30-37%, 43-49% and 9-16%, respectively. Since the total yields of heavy distillate and vacuum residue were relatively high, 52-61%, they must be cracked to lighter distillates.

The contents of nitrogen, sulfur and oxygen in the shale oils studied were 0.9–2.1%, 0.2–0.5, 3.2–4.6%, respectively. Among the shale oils, the Tesegtiin honhor shale oil contained the highest amount of nitrogen and the lowest amount of hydrogen, indicating its richness in aromatic compounds.

The hydrotreating of Khoot shale oil under different reaction conditions showed that with increasing reaction temperature from 330 to 370 °C, hydrodenitrogenation, hydrodesulfurization and hydrodeoxygenation increased from 13 to 37%, from 65 to 92% and from 59 to 81%, respectively. Longer reaction time was preferable for increased hydrogen consumption, but HDN might proceed deeper at higher temperature than for longer time.

The Uvurjargalant shale oil had the highest conversion by all hydrotreatment processes: HDN (39%), HDS (89%) and HDO (71%). At the same time, the conversions of Khoot and Tesegtiin honhor shale oils by HDN were the lowest, 23% and 24%, respectively. The conversion of Khoot shale oil light distillate by HDN and HDS was relatively high (respectively 90% and 92%), compared to its middle and heavy distillates. The content of *n*-alkanes reached 50.5 mass% of Khoot shale oil middle distillate after hydrotreating.

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