

PRELIMINARY STUDY ON HYDROTREATING OF A HIGH SULFUR
CONTENT SHALE OIL

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ABSTRACT

Hydrotreating of whole fraction of a high sulfur content shale oil (S 8.52%, N 0.87%) was carried on a RN-1 catalyst in a fixed-bed reactor (100 ml) to clarify the relationship between operating conditions and the properties of product oils. The reaction conditions used are: hydrogen pressure 64 atm; reaction temperature range 300-400°C; LHSV 0.5 and 1.0 hr⁻¹; hydrogen and feedstock ratio 800 vol/vol. Most of the physical and chemical properties of the hydrotreated oils are improved. GC-MS analysis confirms that the sulfur-containing compounds in the shale oil are mainly in aromatic structures, such as thiophenic, benzothiophenic and dibenzothiophenic derivatives. The sulfur removal of the hydrotreating is more easier than that of nitrogen. As the reaction temperature raised from 300°C to 400°C, percentage of sulfur removal increased from 57.75 to 98.12, while nitrogen removal from 25.29 to 82.76. At the optimum condition of the study (H₂ pressure 64 atm, temperature 380°C, LHSV 0.5 hr⁻¹ and H₂/feedstock 800 vol/vol), sulfur and nitrogen contents of the product oil was reduced to 670 and 1100 ppm respectively, it may be suitable as a syncrude for the petroleum refinery.

INTRODUCTION

Shale oil is believed to be one of the important alternatives of petro-

leum. The chemical components of shale oil are quite similar with those of petroleum, but shale oil contains a number of unsaturated hydrocarbons and much more heteroatomic compounds. The characteristics of a shale oil vary to a large extent with different oil shale deposits and the retorting processes used. In order to remove the unsaturates and the heteroatoms, hydrotreating is generally employed as an effective shale oil refining process.

In early 50's, Chinese shale oil industry had successfully produced gasoline, air-craft fuel, kerosene and diesel from Fushun shale oil by means of hydrotreating.^[1] Frost et al.^[2,3] hydrotreated shale oils to produce naphtha and studied the effects of reaction conditions on the properties of the product oil. Barker et al.^[4] upgraded the shale oil naphtha by hydrotreatment. Hydrotreating was also investigated for the purpose of producing jet fuels from shale oil.^[5,6,7] Australia scientists^[8] made wide research works on a high sulfur-containing shale oil (S 5.7%) from Julia Creek oil shale to produce commercial transport fuels by hydrotreating. In this paper, a preliminary study on the whole fraction hydrotreating of a very high sulfur-content up to 8.52% shale oil is reported. It aims to explore the hydrotreating reaction conditions and to clarify the change of the component distribution of sulfur-containing compounds in the shale oil during the hydrotreating process.

EXPERIMENTAL

Feedstock The whole fraction crude shale oil was used as sample, which was produced from a high S-content oil shale in a 100 ton/day Fushun type retort. The primary properties of the feedstock are shown in Table 1.

Hydrotreating catalyst The catalyst used in the hydrotreating tests was a commercial catalyst RN-1 developed by RIPP of SINOPEC. The particle size of the catalyst is 2-3 mm.

Hydrotreating scheme The schematic diagram of hydrotreating is shown as Figure. 1.

The whole fraction crude shale oil in the feedstock container 1 flows down to feeding container 2, it is pumped to the upside of the reactor 6, after mixing with H_2 , the mixture enters into the reactor. 4 is a H_2 pressure regulator, 5 is a H_2 flow controller. The fixed-bed re-

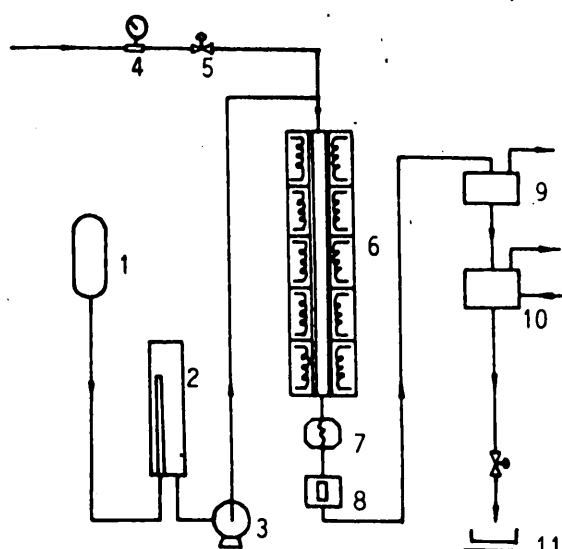


Fig. 1. Schematic Diagram of the Hydrotreating Apparatus
 1.Feedstock container 2.Feeding container 3.Feed Pump. 4.Pressure Regulator 5.Flow Controller 6.Reactor 7.Cooler 8.High Pressure Separator 9.Low Pressure Separator 10.Hydrogen Purifier 11.Electronic Balance

actor is divided into five temperature controlling sections. Catalyst is loaded beforehand in the third and fourth sections, and the first, second and fifth sections are packed with alumina particles of the same size as the catalyst. The mixture of feedstock and hydrogen is preheated to the designated temperature in the first and second sections, and then enters the catalyst sections in which the hydrotreating reactions are taking place. Product oil and gas pass through cooler 7, high pressure separator 8, low pressure separator 9 and hydrogen purifier 10, after which the product oil is accepted in a container for weighing and sampling.

The catalyst was packed as follows: divide 100 ml catalyst into four parts, 10 ml, 20ml, 30ml and 40ml and mix with 40ml, 30ml, 20ml and 10ml alumina respectively; pack the mixtures in the order of increasing concentration of the catalyst from the top to the bottom along the height of the catalyst bed. The reactor is made of stainless steel with 39x11mm in diameter and 1650 mm in height.

The catalyst is pre-sulfided in the presence of a flowing commercial aviation kerosene mixed with 2% CS₂ at 300°C and 64 atm of H₂. Then the catalyst is activated for 48 hours by a flowing of straight run diesel. After the activation follows the beginning of the shale oil hydrotreating. The reaction temperature is ranged from 300 to 400°C with 20°C as an interval. The hydrogen pressure is kept at 64 atm, with H₂ and feedstock ratio of 800 vol/vol and LHSV 1.0 to 0.5 hr⁻¹.

Analysis of sulfur-containing compounds A FINNIGAN-4021 gas chromatograph-mass spectrometer was employed for the analysis of the shale oil

constituents. Most of the regenerated ion chromatographic peaks were library-searched by a computer. A fused silica capillary column of 27mx0.25mm i.d. coating with SE-54 was used. The operating conditions of GC-MS were: column temperature, 60-280°C; program heating rate, 4°C/min; injection temperature, 290°C; scan scope m/e 35-400; scan speed 0.95 sec; ionization voltage, 70 eV and emitter current 0.25 mA.

GC-FID and GC-FPD analyses were performed by using a SP3700 gas chromatograph, coupled with FID, FPD, and a silica capillary column 0.25mm i.d.x 23m coated with SE-52. Qualitative analyses of sulfur-containing compounds in shale oils were accomplished by comparing GC-FID and GC-FPD spectra with the results of GC-MS, with the retention values of the standard compounds (thiophene, benzo[b]thiophene, dibenzothiophene) and with the literature data of retention index.^[10,11,12] The relative concentration of sulfur-containing compounds was quantified by normalizing the square root area of the FPD output and taking the sum of all the peak area detected as 100%.

RESULTS AND DISCUSSION

The operation conditions and the properties of the product oils are summarized in Table 1.

Removal of sulfur and nitrogen compounds in hydrotreating The correlation of sulfur and nitrogen removal percentages with the reaction temperature are shown in Fig. 2. It indicates that the percentages of the sulfur and nitrogen removal are directly increased with the raise of the reaction temperature, but the sulfur removal is easier than that of nitrogen. The data listed in Table 1 show that as the reaction temperature and other conditions are kept constant, the LHSV decreases from 1.0 to 0.5 hr⁻¹, the percentages of desulfurization and denitrogenation of the product oil increase from 97.89 to 99.21 and 70.11 to 87.36 respectively. The sulfur and nitrogen contents of product oil of the run JDHS0-06 are reduced to 670ppm for sulfur and 1100ppm for nitrogen.

Behavior of sulfur-compounds in hydrotreating GC-MS analysis shows that sulfur-containing compounds in the crude shale oil are mainly existed in forms of mono- and poly- alkyl substituted thiophenes, benzothiophenes and dibenzothiophenes with their derivatives. In general, these compounds are rather thermally and chemically stable in nature, however, their reaction

constant of hydrogenation are different^[9]:

sulfur-containing compound	relative value of reaction constant
thiophene	2.9
benzothiophene	2.8
octahydrodibenzothiophene	1.3
dibenzothiophene	1.0(taken arbitrarily)

Because of the different behaviors of sulfur containing compounds, the distribution patterns of these compounds in the hydrotreated product oils change with reaction conditions of hydrotreating. In the crude shale oil, the most abundant sulfur-containing compounds are detected to be alkyl substituted thiophenes with alkyl group carbon number of 1-26. The GC-FPD spectra of hydrotreated product oils indicates that for the increasing of reaction temperature and/or the decreasing of LHSV, the relative amount of more stable compounds increases, while less stable ones decreases. Fig. 3. to Fig.8 illustrate the different behaviors of different sulfur-containing compounds in the hydrotreating process. As shown in Fig. 3, the sum of C₁- to C₅- thiophene decreases rapidly when the temperature is raised from 300°C to 320°C, becomes slow down at 340°C and disappears as the temperature exceeds 360°C. Fig. 4 shows the difference of desulfurization between four isomers of C₄-thiophene. It can be ascribed perhaps to the steric effect of the substituting group locations on the sulfur removal. For example, the removal of sulfur in 2-methyl-5-propylthiophene is more difficult than the other three. Desulfurization of benzo[b]thiophene and 5-methyl-benzo-[b]thiophene, shown in Fig. 5, behaves similarly to certain extent with the thiophene homologs. The sulfur-containing compounds presented in Fig. 6, 7 and 8 may be considered as examples of the category in which it is rather difficult to remove S by hydrotreating. For the cases employed in the experiments, the relative amount of these compounds is increased under more severe operating conditions, i.e. at higher temperatures, elevated pressure and lowered LHSV.

In summary, for the sulfur-containing compounds of aromatic structure, the hydrodesulfurization of thiophenes is the easiest, benzothiophenes the next and dibenzothiophenes the last. Under the moderate operating conditions of hydrotreating, it is not so difficult to remove about 90% of sulfur containing compounds of the crude shale oil, however, it seems imprac-

Table 1 Properties of Feedstock and Product Oils

Run No.	Feedstock	JDHSO-01	JDHSO-02	JDHSO-03	HDHSO-04	JDHSO-05	JDHSO-06	JDHSO-07
Reaction conditions								
Temperature, °C		300	320	340	360	380	380	400
H ₂ pressure, atm		64	64	64	64	64	64	64
LHSV, hr ⁻¹		1.0	1.0	1.0	1.0	1.0	0.5	1.0
H ₂ /Feed, vol/vol		800	800	800	800	800	800	800
Properties ²⁰								
Gravity, d ₄		0.9690	0.9139	0.8856	0.8763	0.8697	0.8625	0.8606
Viscosity, cSt at 50°C.		13.42	8.54	8.23	7.00	5.77	4.65	3.84
Elemental analysis								
C %		78.73	83.09	84.77	84.69	86.04	86.70	86.48
H %		9.51	11.54	11.91	11.98	12.23	12.53	12.39
N %		0.87	0.61	0.54	0.40	0.26	0.11	0.15
S %		8.52	2.0	1.0	0.51	0.18	670(ppm)	0.16
H/C atomic ratio		1.456	1.667	1.686	1.697	1.706	1.734	1.719
GC distillation by ASTM-D2887								
IBP		159	176	178	177	177	177	179
10 %		269	265	267	257	248	234	223
30 %		335	320	320	311	300	297	271
50 %		389	368	368	358	347	333	317
70 %		444	424	424	416	406	394	375
95 %		545	523	524	521	512	504	481

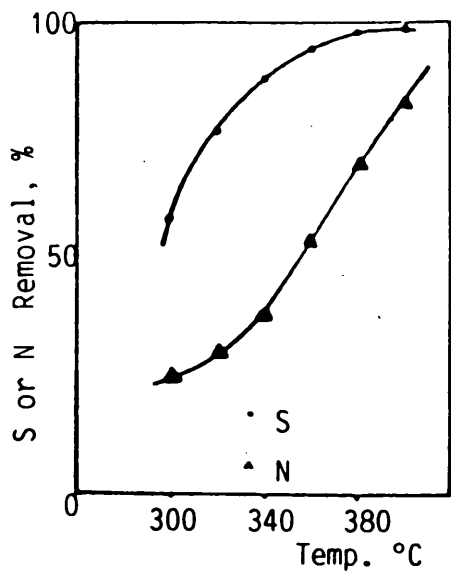


Fig. 2. Effect of Temp. on S and N Removal of Shale oil

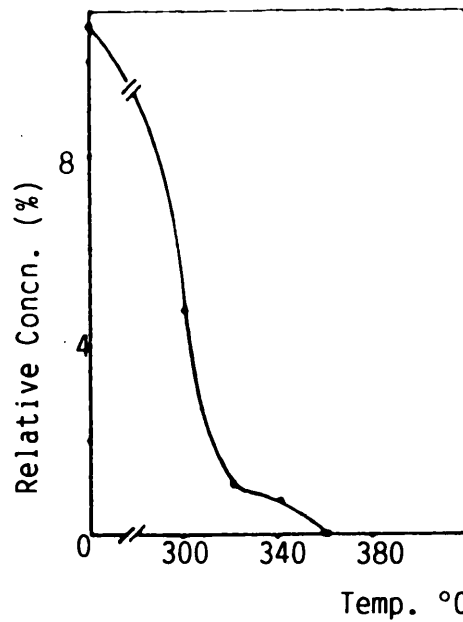


Fig. 3. Hydrodesulfurization of C₁-to C₅-Thiophenes vs. Temperature

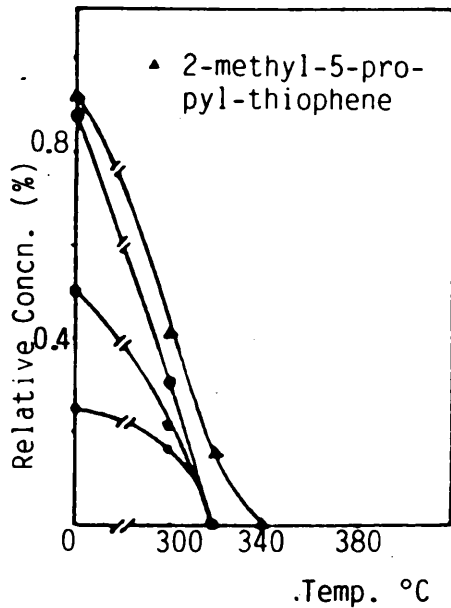


Fig. 4. Hydrodesulfurization of isomers of C₄-Thiophene vs. Temperature

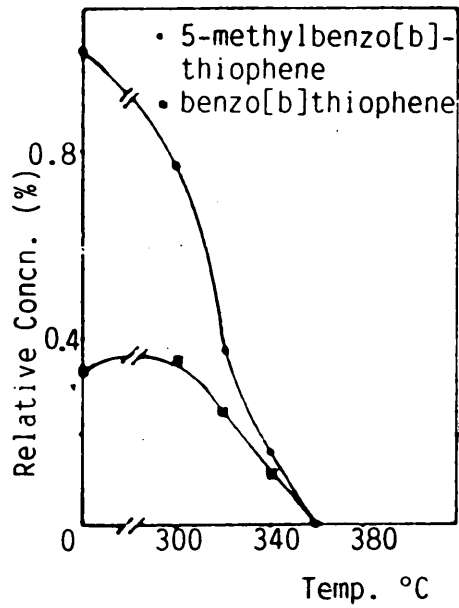


Fig. 5. Hydrodesulfurization of benzo-[b] thiophenes vs. Reaction Temperature

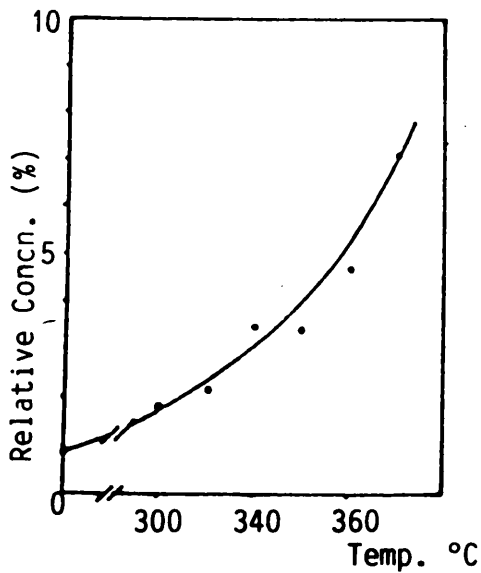


Fig. 6. Hydrodesulfurization of one of isomers of C₃-Benzo[b] thiophene vs. Temperature

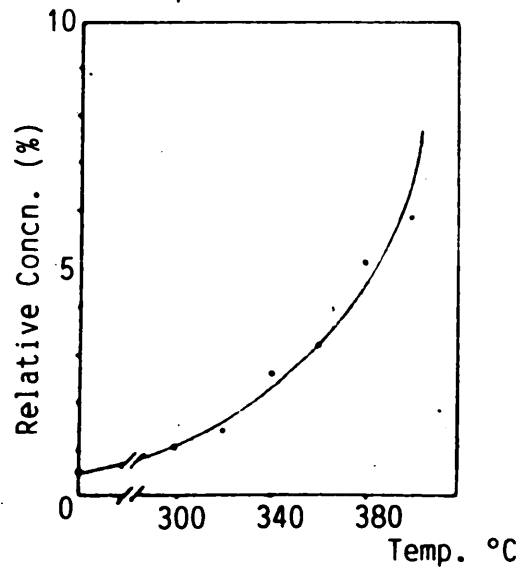


Fig. 7. Hydrodesulfurization of dibenzo-thiophene vs. Temperature

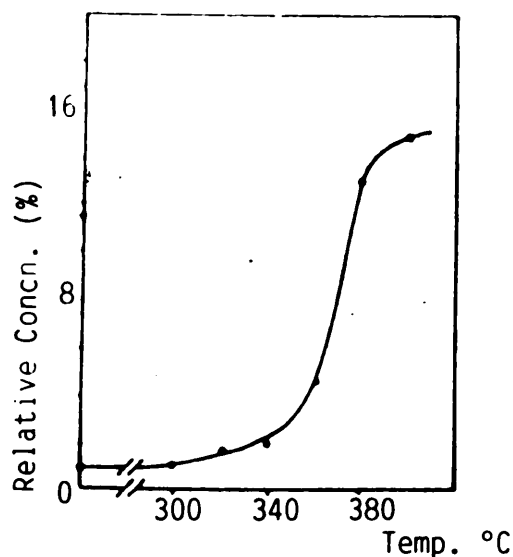


Fig. 8. Hydrodesulfurization of one of isomers of C_1 -dibenzothiophene vs. temperature

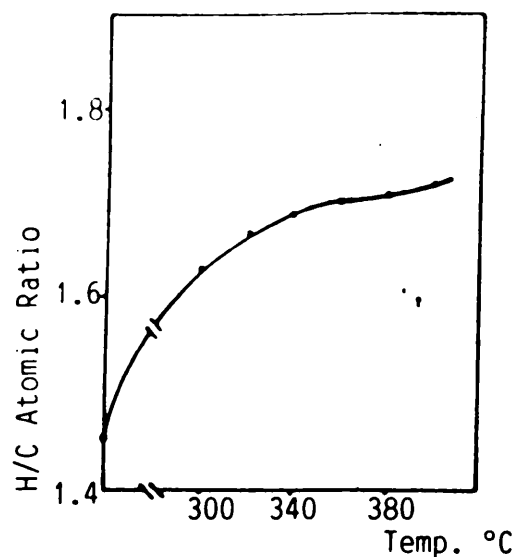


Fig. 9. Effect of Temperature on H/C Atomic Ratio of Hydrotreated Shale Oil

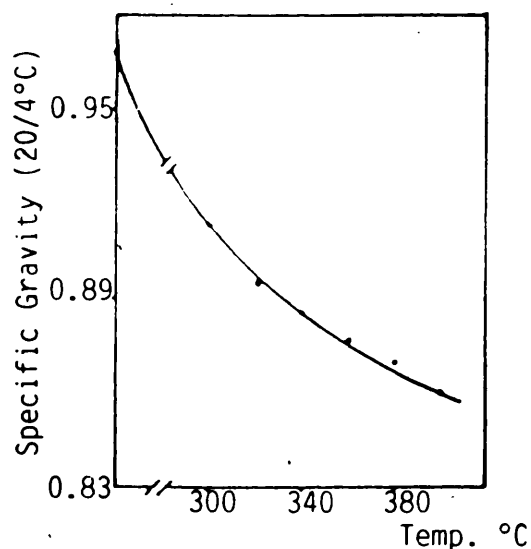


Fig. 10. Effect of Temperature on Specific Gravity of hydrotreated Shale oil

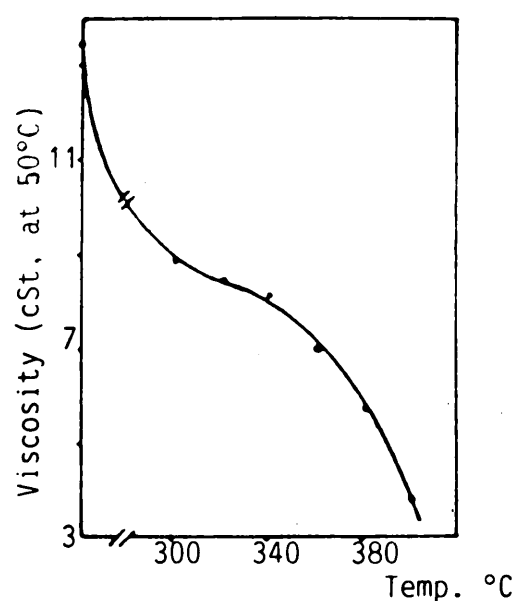


Fig. 11. Effect of Temperature on Viscosity of hydrotreated Shale Oil

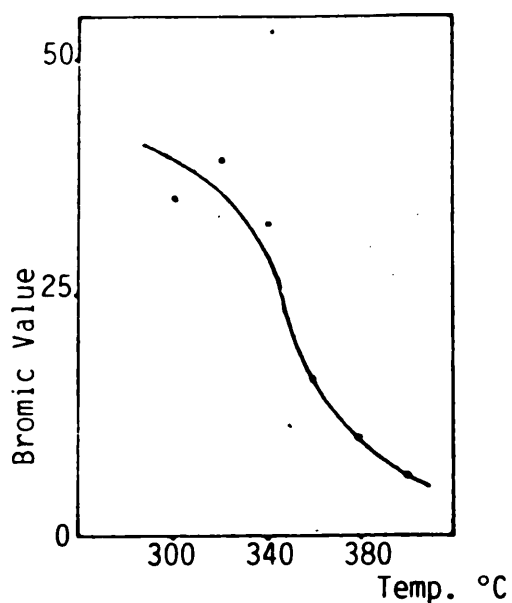


Fig. 12. Effect of Temperature on Bromine Number of Hydrotreated Shale Oil

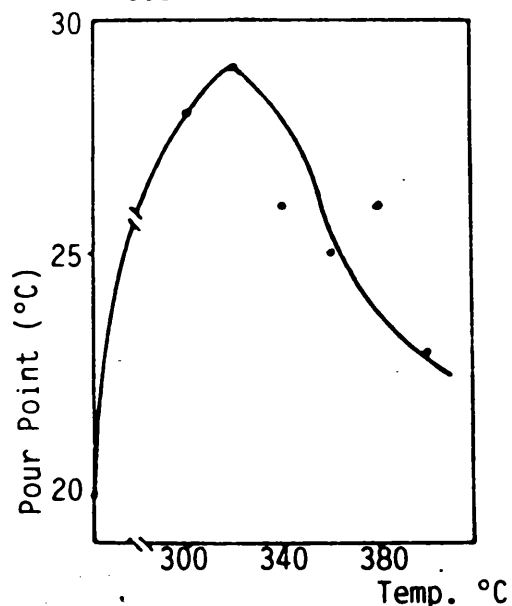


Fig. 13. Effect Temperature on Pour Point of Hydrotreated Shale Oil

tical to expect the complete removal of dibenzothiophenes and their derivatives.

Influences on general properties of product oils Fig. 9 to 12 show the relationships between hydrotreating temperature and H/C atomic ratio, specific gravity, viscosity and bromine number of the product oils respectively. From these figures, it is obvious that the increasing of reaction temperature would cause the decreasing of specific gravity and viscosity; and the increasing of H/C atomic ratio. Decreasing of LHSV also has the same effect on these properties of the product oils as increasing reaction temperature..

Fig. 13 gives the relationship between pour points of product oils with reaction temperature. The pour point of the product oil hydrotreated at 300°C sharply increased from 20°C of the crude shale oil to 28°C, it reached to a maximum of 29°C at 320°C, then turned to decreasing as the temperature further increased. The pour points of product oils are all higher than that of the crude oil, and it implies that under a mild condition of hydrotreating, the pour point of the product oil cannot be improved distinctly. The pour point is closely related to the paraffin content of the oil. The saturation of long chain olefins leads to the decreasing of bromine number (Fig. 12) and increasing of paraffin content. GC-FID analytical data show that the peaks of olefins nearly diminished for the product oil hydrotreated at 300°C. Another path of producing paraffins might be due to the hydrodesulfurization of long chain alkyl substituted thiophenes which had been confirmed to be present in abundance in the crude oil, so its contribution to the enhancement of pour point could not be underestimated.

CONCLUSIONS

1. A high sulfur content of 8.52% shale oil was hydrotreated at 64 atm hydrogen pressure using the RN-1 catalyst. The sulfur content can be reduced to 1% at mild conditions of temperature 340°C and LHSV 1.0 hr⁻¹; at the temperature 380°C and LHSV 0.5 hr⁻¹, the product oil sulfur content may be further reduced to 670 ppm and nitrogen from 8700 to 1100 ppm. The product oil is expected to be a syncrude for the refinery.

2. GC-MS and GC-FPD analyses had shown that alkyl substituted thio-

phenes are the main components of the sulfur-containing compounds, which can be removed readily by hydrotreating. The remaining sulfur in the hydrotreated oils are mostly presented in the structure of benzo- or dibenzothiophenes and their derivatives. The study on the distribution of sulfur-containing compounds in shale oils is beneficial both to the understanding of hydrodesulfurization process and to the investigating of kerogen structure and its mechanism of pyrolysis.

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