

HYDRODESULFURIZATION AND HYDRODENITROGENATION OF DIESEL DISTILLATE FROM FUSHUN SHALE OIL

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Relatively high content of nitrogen and sulfur in shale oil can have an adverse influence on its potential utilization as a substitute fuel. In this paper, the results of preliminary investigation into catalytic hydrotreating of diesel fraction (200–360 °C) of Fushun shale oil are presented. Hydrogenation was carried out in a fixed-bed reactor using sulfided catalysts Ni-W/Al₂O₃ and Co-Mo/Al₂O₃. The influence of temperature, pressure, liquid hourly space velocity (LHSV) and hydrogen/feedstock ratio on hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) was investigated. Catalytic activities of two catalysts were compared. The results showed that increasing temperature, high pressure and long residence time (reciprocal of LHSV) promoted the removal of sulfur and nitrogen, while the impact of hydrogen/feedstock ratio was smaller. The degree of nitrogen removal was substantially higher than that of sulfur. HDS efficiencies of two catalysts were comparable in severe conditions. The catalyst Ni-W/Al₂O₃ was much more active at HDN than Co-Mo/Al₂O₃ catalyst in all conditions selected. The oil cleaned in optimum conditions is characterized by low content of sulfur, nitrogen and alkenes. It can be used as a more valuable fuel.

Introduction

Dependence on non-conventional resources for energy and petrochemical industry feedstock will likely increase in the coming future because of the shortage of petroleum resource. Shale oil, coal-derived liquids and oil sand are promising resources for long-range alternatives to petroleum. Shale oils derived *via* pyrolysis of oil shales whose deposits are widely distributed throughout the world contain considerable amounts of heteroatomic compounds and unsaturated hydrocarbons. High concentrations of heteroatomics and alkenes in shale oils prevent their direct utilization as transport fuels.

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The heteroatomic compounds in shale oil may cause serious problems producing pollutants and lowering stability in storage. Moreover, nitrogen compounds act certainly as inhibitors at hydrotreating and cracking process [1–2].

Catalytic hydrotreating as the most efficient approach to remove heteroatomic compounds *prior* to further upgrading has also been applied to shale oils [3–10]. However, many papers show that HDN of shale oil is more difficult than HDS. The concentrations of heteroatomic compounds in shale oils can be reduced to a level which is still too high to use oils transportation fuels. Many factors, such as catalysts, operation parameters, and feedstock quality can have a significant influence on the removal of heteroatomic compounds [11–12]. In order to deepen the degree of heteroatoms' removal and to get a high-quality product, the diesel distillate (200–360 °C) of Fushun shale oil was chosen for catalytic hydrotreating in this work. Two types of catalysts were used to compare their activities at heteroatom removal.

Experimental

Feedstock preparation

The shale oil used in the present study was obtained from Fushun, China. The diesel distillate was prepared by fractionation of the crude shale oil using a true-boiling-point distillation apparatus.

Hydrotreating experiments

The experiments on catalytic hydrotreating were carried out in a fixed-bed microreactor unit. The schematic diagram of the unit is shown in Fig. 1. Liquid feed was pumped to the upside of the reactor, mixed with H₂, and fed into the reactor. The requested pressure in reactor was controlled by pressure-reducing and back-reducing regulators. The desired gas flow was limited by a mass flow meter. The unit had a cylindrical reactor with the inside diameter of 10 mm and a volume of 35 cm³. Produced oil and gas passed through condensator, after which the liquid product was collected in a container and the gas product was let out through a regulator.

The catalysts Ni-W/Al₂O₃ and Co-Mo/Al₂O₃ were used in the present study. The composition and physical properties of the catalysts are given in Table 1. For each test, 6 ml of crushed catalyst (20–40 mesh) was loaded into the isothermal zone of the reactor. The catalysts were presulfided with a solution of 5 wt% CS₂ in cyclohexane. The Ni-W catalyst was presulfided at 360 °C under pressure of 4 MPa with LHSV of 3 h⁻¹ and feedstock ratio (vol/vol) of 500, sulfiding time of 4 h. The Co-Mo catalyst was presulfided for 3 h while the other conditions were the same. Hydrotreating of this diesel distillate started after presulfiding of the catalyst, and the activity of the catalyst was stabilized by feeding the reactant diesel distillate for about 5 h

in the reaction conditions. Samples of the hydrotreated oils were taken more than 2 h after changing the reaction conditions to confirm the constant catalytic activity.

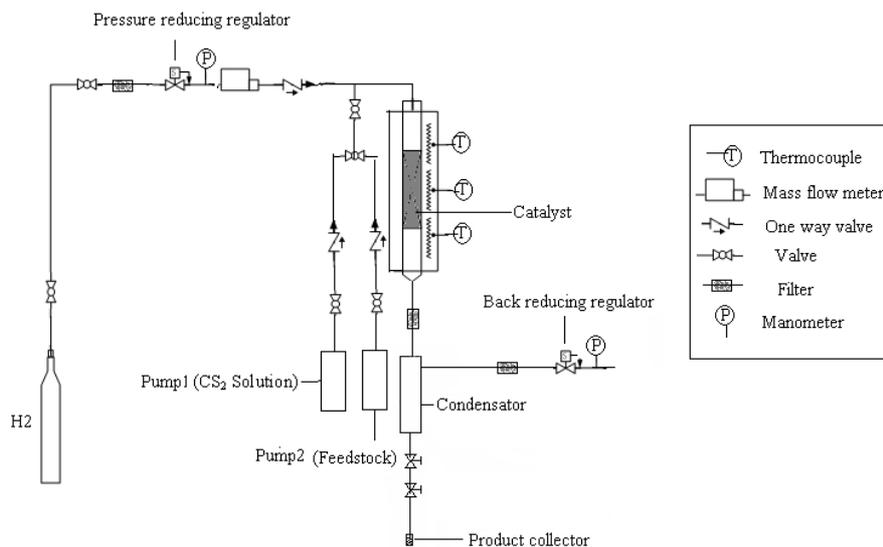


Fig. 1. Schematic diagram of the fixed-bed reactor.

Table 1. Properties of Ni-W/Al₂O₃ and Co-Mo/Al₂O₃ catalysts

	Ni-W/Al ₂ O ₃	Co-Mo/Al ₂ O ₃
NiO, wt%	2.9	–
WO ₃ , wt%	28.0	–
CoO, wt%	–	3.7
MoO ₃ , wt%	–	14.5
Surface area, m ² /g	150	180
Pore volume, ml/g	0.29	0.31

Shale oil analysis

The shale oil and the hydrotreated products were analyzed for the total amounts of nitrogen, sulfur and alkenes. The total sulfur content of oils was determined using a UV-fluorescence sulfur analyzer. The total nitrogen content was determined with a Chemical-Radiation nitrogen analyzer. Alkene content in oils can be judged by their bromine values measured by a bromine value analyzer. All these analyzing instruments were supplied by Taizhou Instrument Company, Jiangsu, China.

Results and discussion

Properties of Fushun shale oil and its diesel distillate

Table 2 gives some properties of the shale oil and its distillate. It is found that the share of diesel distillate in Fushun shale oil is large – about 41%. The shale oil is much heavier than the diesel distillate in terms of density. The concentrations of sulfur and nitrogen in crude are also substantially higher than in the distillate. HDS and HDN of the diesel distillate may be easier than that of crude shale oil.

Table 2. Properties of Fushun shale oil and its diesel distillate

	Crude shale oil	Diesel distillate
Percent in crude shale oil, wt%	100	41
Density (20 °C), g/ml	0.9033	0.8697
Sulfur content, wt%	0.83	0.51
Nitrogen content, wt%	1.27	1.03

Desulfurization of diesel distillate from Fushun shale oil

Experiments were conducted to compare HDS degrees of shale oil distillate over Ni-W and Co-Mo catalysts at different temperatures, pressures, LHSVs and hydrogen/feedstock ratios. When one of the four conditions was changed, the other conditions remained constant. The results are shown in Figures 2–5.

These figures demonstrate that sulfur removal in the presence of both catalysts was high even when temperature, pressure, and hydrogen/feedstock ratio were low and contact time (reciprocal of LHSV) short. This indicates that most of the sulfur-containing compounds in this distillate are reactive

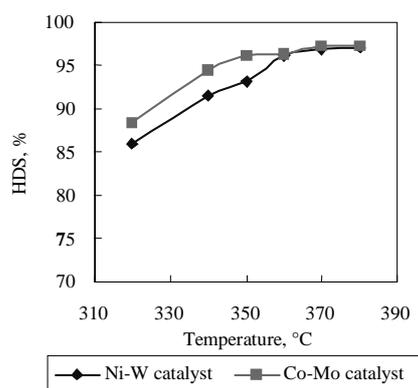


Fig. 2. HDS conversion on two catalysts vs. temperature. Reaction conditions: $P = 4$ MPa, $LHSV = 1 \text{ h}^{-1}$, hydrogen/feed = 1000 (v/v).

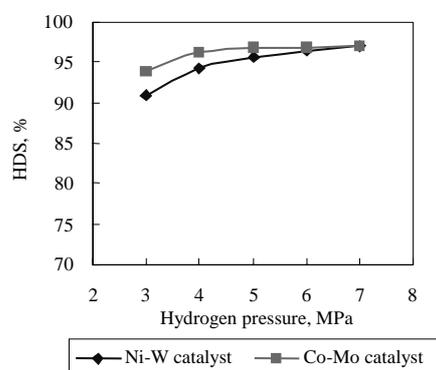


Fig. 3. HDS conversion on two catalysts vs. hydrogen pressure. Reaction conditions: $T = 360\text{ }^{\circ}\text{C}$, $\text{LHSV} = 1\text{ h}^{-1}$, hydrogen/feed = 1000 (v/v).

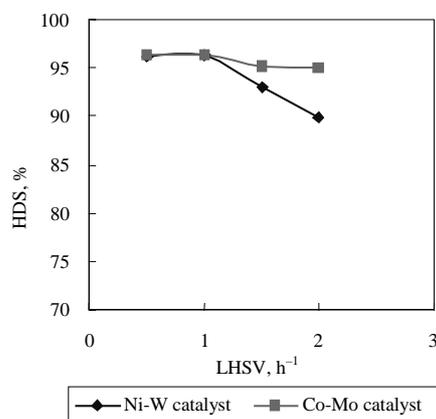


Fig. 4. HDS conversion on two catalysts vs. LHSV. Reaction conditions: $T=360\text{ }^{\circ}\text{C}$, $P = 4\text{ MPa}$, hydrogen/feed = 1000 (v/v).

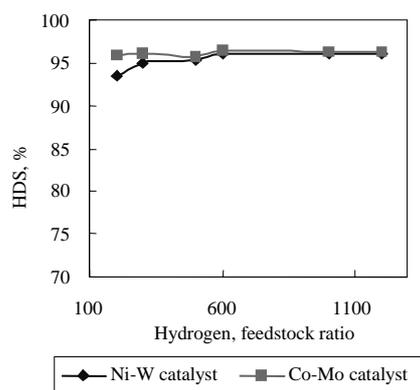


Fig. 5. HDS conversion on two catalysts vs. hydrogen/feedstock ratio. Reaction conditions: $T = 360\text{ }^{\circ}\text{C}$, $P = 4\text{ MPa}$, $\text{LHSV} = 1\text{ h}^{-1}$.

and can be easily converted during the catalytic hydroprocessing. HDS degrees over both catalysts were enhanced, as expected, when temperature, pressure and contact time were increased. However, when the hydrogen/feedstock ratio exceeded 300, the further increase in the ratio had small influence on HDS degrees. The effect of these factors on sulfur removal for both catalysts in severe conditions was small. This can be attributed to a small amount of refractory sulfur species present in this distillate. HDS activity over Co-Mo catalyst was higher than over Ni-W catalyst in moderate conditions. The difference became comparable when temperature, pressure and contact time were increased. These results indicate that at HDS of this oil feed Co-Mo catalyst was more active than Ni-W catalyst. However, the difference became negligible in severe conditions because there were different types of sulfur compounds present in shale oil.

Denitrogenation of diesel distillate from Fushun shale oil

Data on the HDN changes of shale oil diesel distillate for the two catalysts under different conditions are shown in Figures 6 to 9.

In contrast to HDS, the nitrogen removal was much less. Other research workers have also shown that sulfur is much more easily removable from shale oil during catalytic hydroprocessing than nitrogen. This may be ascribed to different mechanisms of sulfur and nitrogen removal as proposed by some authors [3–4]. It has been suggested that nitrogen removal during catalytic hydrotreating is a two-step process while sulfur removal is an one-step process. Both nitrogen and sulfur are found to occur mostly in composition of aromatic compounds. Hydrodenitrogenation is believed to require complete hydrogenation of aromatic rings because C–N bonds in an aromatic ring are much stronger than in the naphthenic structure. In contrast, the removal of sulfur does not require complete saturation of the aromatic ring containing sulfur but involves direct scission of the C–S bond. Besides,

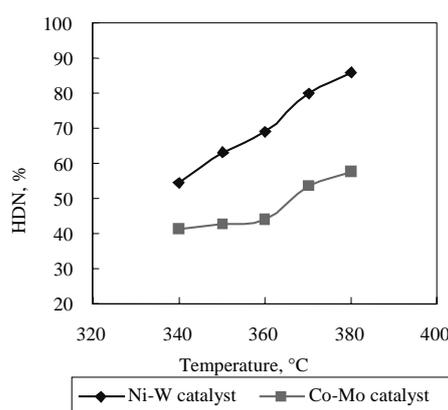


Fig. 6. HDN conversion on two catalysts vs. temperature. Reaction conditions: $P = 4 \text{ MPa}$, $\text{LHSV} = 1 \text{ h}^{-1}$, $\text{hydrogen/feed} = 1000 \text{ (v/v)}$.

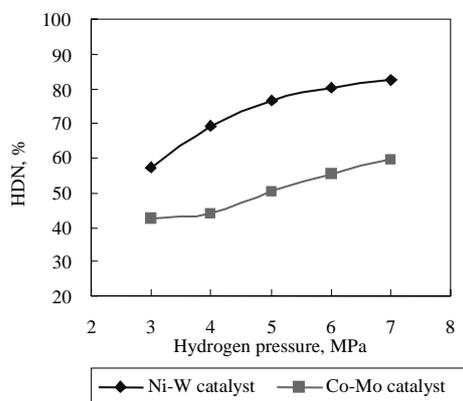


Fig. 7. HDN conversion on two catalysts vs. hydrogen pressure. Reaction conditions: $T = 360^\circ$, $LHSV = 1 \text{ h}^{-1}$, hydrogen/feed = 1000 (v/v).

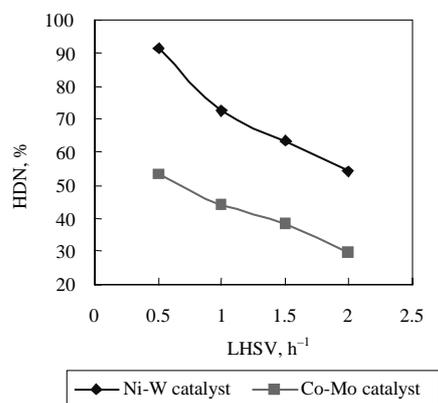


Fig. 8. HDN conversion on two catalysts vs. LHSV. Reaction conditions: $T = 360^\circ\text{C}$, $P = 4 \text{ MPa}$, hydrogen/feed = 1000 (v/v).

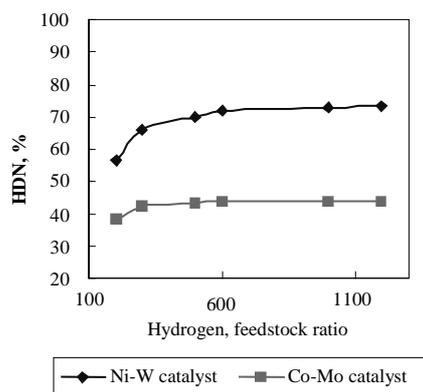


Fig. 9. HDN conversion on two catalysts vs. hydrogen/feedstock ratio. Reaction conditions: $T = 360^\circ\text{C}$, $P = 4 \text{ MPa}$, $LHSV = 1 \text{ h}^{-1}$.

removal of nitrogen increased significantly with an increase in temperature, pressure or contact time when catalyzed by two catalysts. The degrees of HDN on Ni-W catalyst were much higher than on Co-Mo catalyst in all conditions investigated. These results clearly showed that Ni-W catalyst was preferred for HDN in catalytic hydrotreating of this Fushun shale oil distillate.

Properties of produced oils

Optimum conditions (380 °C, 6 MPa, 1 h⁻¹ LHSV and hydrogen/feedstock of 600 (v/v)) for catalytic hydrotreating over two catalysts were chosen basing on the results above. Some properties of diesel product obtained using different catalysts are shown in Table 3. Sulfur content of products obtained is similar. Nitrogen content of produced oil catalyzed by Co-Mo catalyst is much higher than that of oil catalyzed by Ni-W. Density, cetane number and alkene content of two produced oils are comparable. The results presented in Table 3 clearly demonstrate that the Ni-W catalyst is more suitable for hydrotreating of the shale oil distillate.

Table 3. Properties of hydrotreated oils

Properties	Feedstock	Ni-W catalyst	Co-Mo catalyst
Density (20 °C), g/ml	0.8697	0.8129	0.8176
Sulfur, $\mu\text{g}\cdot\text{g}^{-1}$	5481	108	92
Nitrogen, $\mu\text{g}\cdot\text{g}^{-1}$	10280	140	2856
Br value, gBr/100g	55.2	1.3	2.4
Cetane number	40.2	61.2	60.5

Conclusions

Catalytic hydrotreating of diesel distillate from Fushun shale oil was investigated using two types of catalysts in different conditions. The results showed that the degrees of sulfur removal were high for both catalysts even in moderate conditions. It indicated that most of sulfur species in this distillate were reactive and easily convertible during the catalytic hydro-processing. However, denitrogenation was much more difficult than desulfurization even under severe conditions. The Ni-W/Al₂O₃ catalyst was more active at catalytic hydrotreating of this shale oil distillate. Under relatively mild conditions, it was possible to produce stable oil from Fushun shale oil distillate. The hydrogenated oil is characterized by low amounts of sulfur, nitrogen and alkenes, reduced density and increased cetane number. Hydrotreated product may be used as a domestic transportation fuel.

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