Oil Shale, 2005, Vol. 22, No. 3
pp. 359-366
ISSN 0208-189X

https://doi.org/10.3176/oil.2005.3.09

STUDY ON SHALE OIL DIESEL REFINING

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A new method of non-hydrofining is proposed to improve the stability of diesel fraction of Fushun shale oil. The experimental results show that solvent extraction is efficiently selective to remove nitrogen-, oxygen-, and sulfur-containing compounds. At the temperature of 10–30 °C, diesel fraction is continuously extracted by using the 7–10% additive-containing solvent three times at the ratio of solvent to oil of 0.2. Thereafter, the oil layer is washed by aqueous alkali and water. The recovery of refined oil is more than 75%, and the gum content is less than 70 mg/100 mL. All other parameters meet the requirements of quality specification of diesel product.

Introduction

Large quantities of diesel fuel are imported every year to fill the vacancy in China. Therefore, much work has been done on the research of diesel, such as FCC diesel, the production of diesel from waste plastics and tar, even the bio-diesel, etc. [1–6]. These methods have not been widely used in industry. Oil shale resources in China are estimated to be 400 billion tonnes, equivalent to 16 billion tonnes of shale oil [7]. China is one of several countries in the world which own shale oil industry. The annual shale oil production in Fushun reached 100,000 tonnes and the scale will be further enlarged. Diesel fraction of shale oil contains too much unsaturated hydrocarbons as well as oxygen-, nitrogen-, and sulfur-containing compounds. Its gum content is high, sediments may form and stability is low. Therefore, the diesel must be refined to obtain a stable and qualified diesel product.

Up to now, there are two methods to refine diesel – hydrofining and non-hydrofining. The quality of oil refined through hydrofining is high. This

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method cannot be used in a small refinery because of high investments and prime costs. The operation of a non-hydrofining process is simple and investmens low. The research of non-hydrofining has been focused on FCC diesel [8–9]. Little work has been performed on the non-hydrofining of diesel from shale oil. This paper presents the results of extractive refining of shale oil diesel fraction using a multicomponent solvent.

Experimental

Sample

Fushun shale oil fraction 180–360 °C was used in this study. The properties of the diesel fraction listed in Table 1 are compared with those of diesel No. 0. One can see that the content of carbon residue and gum in the diesel fraction of Fushun shale oil does not meet the standard. Especially the content of gum is 12 times more than that of the standard.

Table 1. **Properties of Diesel Fraction from Fushun Shale Oil**

Items	Specification	Diesel
Sulfur, %	<1.0	0.87
Water, %	Trace	Trace
Ash, %	<0.02	0.013
Cetane number	>45	51
Distillation 50%	<300 °C	298
Distillation 90%	<355 °C	335
Distillation 95%	<365 °C	358
Water-soluble acids and alkalis	no	no
Mechanical impurities, %	no	no
Solidification point, °C	<0	–2
Carbon residue, %	<0.4	2.12
Gum, mg 100 mL^{-1}	<70	804
Flash point, °C	>65	81

Method

Diesel fraction of Fushun shale oil was continuously extracted three times by using a solvent, containing 7–10% additive, at the ratio of solvent to oil of 0.1 to 0.6, at temperature 10–30 °C. Diesel fraction was treated with a multicomponent solvent in a separating funnel. Two layers were formed, the upper layer was the oil. After separating, the diesel yield was calculated and the gum content determined. The extracted diesel was treated with aqueous alkaline solution, the effect of alkali on stability of the treated diesel fraction was investigated.

Results and Discussion

The Choice of Solvent

Oxygen-, nitrogen- and sulfur-containing compounds are all polar compounds. According to the principle that similar compounds are soluble in each other, solvent A was chosen for extraction. It was found that the effect of solvent A was not satisfactory because the removal of gum was only 63% even at the ratio of 1.2 (of solvent to oil). The content of gum was still higher than established by specification. Consequently, it was necessary to add an additive in order to lower the content of gum. The effect of additive concentration on gum removal is seen in Fig. 1 (the ratio of solvent to oil 0.5).

As shown in Fig. 1, the content of gum decreases with an increase in additive concentration while there was only little effect on oil recovery. This can be explained by the fact that the additive can remove gum but it is also efficiently selective. That is to say that the additive reacts with unstable components of diesel. The decrease in gum content was not remarkable when additive concentration exceeded 10%. So, the additive concentration was chosen between 7% and 10%.

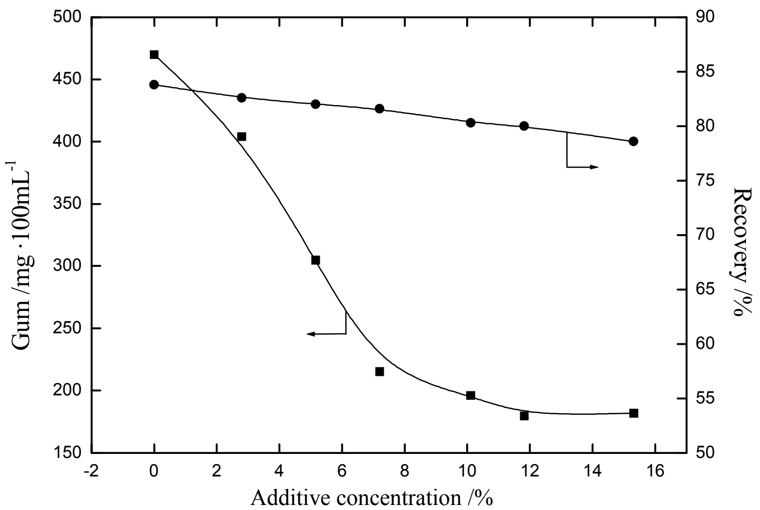

Fig.1 Effect of additive concentration on gum

The Influence of the Solvent to Oil Ratio

Tables 2 and 3 show the results of extraction using the solvent containing 9% additive at different ratios of solvent to oil.

Table 2. **Effect of Solvent to Oil Ratio on Gum Removal at Single-Stage Extraction**

Item	Solvent/oil ratio					
	0.1	0.2	0.3	0.4	0.5	0.6
Recovery, %	91.6	86.1	83.2	81.0	79.5	79.0
Gum, mg ·100 mL^{-1}	612	497	376	297	205	192
Gum removal, %	23.89	38.18	53.23	63.06	74.50	76.12

Table 3. **Effect of Solvent to Oil Ratio on Gum Removal at Multi-Stage Extraction**

Item	Solvent/oil, total process									
	0.3		0.4		0.5			0.6		
	Solvent/oil, each stage									
	0.2	0.1	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2
Recovery, %, each stage	86.1	92.5	86.1	90.9	86.1	90.9	98.8	86.1	90.9	98.6
Recovery, %, total	78.5		78.3		77.4			77.2		
Gum, mg ·100 mL^{-1}	341.1		259.3		182.8			146.4		
Gum removal, %	57.59		67.75		77.26			81.80		

The results in Table 2 and Table 3 show that the rate of gum removal increased. The color of refined diesel became lighter with increasing ratio of solvent to oil. The more times extracted, the higher the extraction efficiency at the same ratio of solvent to oil. There was a little effect on the rate of gum removal when the ratio of solvent to oil exceeded 0.6. Therefore, the suitable ratio of solvent to oil was found to be 0.5–0.6.

The Effect of Alkali Concentration

The stability of diesel fraction was greatly improved through treating with a multicomponent solvent, but the content of gum remained above the specification limit. The effects of alkali on diesel stability are shown in Table 4.

Table 4. **Effect of Alkali on Diesel Stability**

Alkali concentration	Alkali/oil ratio				
	1 : 5–1 : 50	1 : 75	1 : 100	1 : 150	1 : 200
	Gum, mg ·100mL^{-1}				
5%	Areas with serious emulsification	Decreasing emulsification gradually (→)			
10%					
15%		↓	88	110	132
20%			73	86	89
25%			47	65	72
30%			35	52	66

Emulsification can be observed during shale oil refining with aqueous alkali. The lower the alkali concentration and the larger the ratio of alkali to oil, the more intensive the emulsification. The full effect cannot be obtained even using electrical demulsification. The concentration of alkali should be increased and the dosage of the alkali reduced to liquidate the unstable composition testified in Table 4. For example, when the alkali concentration is 25% and the ratio of alkali to oil 1 : 150, the gum content of diesel is 65 mg/100 mL which is within the limitation, 70 mg/100 mL. The yield of refined oil is as high as 98.86%.

The Optimal Temperature and Shaking Time

The effect of temperature on oil recovery and gum removal is shown in Table 5. The additive concentration is 9%.

Table 5. **Effect of Temperature on Oil Recovery and Gum Removal**

	T, °C				
	15	25	32	40	48
	Recovery, %				
Solvent/oil ratio:					
0.2	88.3	87.5	86.6	86.1	85.3
0.2	93.6	90.5	91.4	90.9	89.8
0.1	98.9	98.9	98.7	98.8	97.1
Total recovery, %	81.7	78.3	78.1	77.4	74.4
Gum, mg ·100 mL^{-1}	35	46	68	77	96

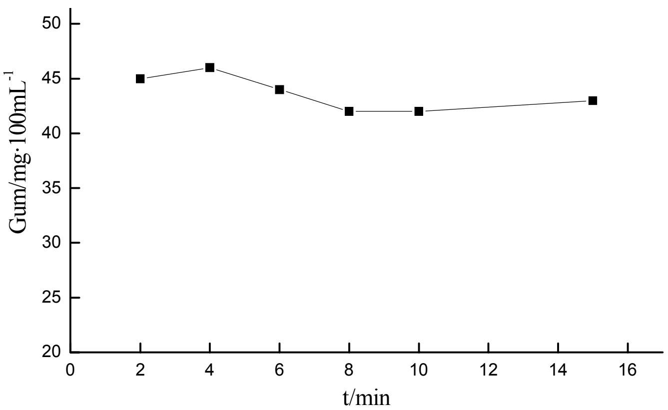

Fig. 2. Effect of extraction time on gum content

It was observed that the recovery decreased gradually with an increase in temperature. This can be explained by higher solubility of oil in the solvent at higher temperatures. A part of diesel was removed with the solvent. On the contrary, higher temperature is unfavorable for removing gum. However, lower temperature is not advisable as the fluidity of diesel is low and viscosity high, both disadvantageous to operation. So, the optimal temperature is 10–30 °C.

The transfer of oil and solvent is very fast so the balance can be reached in a short time (Fig. 2). 5–10 minutes are enough to shake the mixture.

The Recovery of Solvent

The boiling point of solvent A is low, so the mixture can be distilled at atmospheric pressure. The recovery of solvent is above 97%. In addition, the extraction effect of recovered solvent, which is reused and added to fresh solvent and additive, is investigated. The result is illustrated in Fig. 3.

It can be seen from Fig. 3 that there is no notable change in the gum content and the recovery of refined oil with increasing proportion of recovered solvent, and the gum content meets the requirements of the national diesel specification. Therefore, it is practical to add fresh solvent and additive to the recovered solvent when refining the diesel.

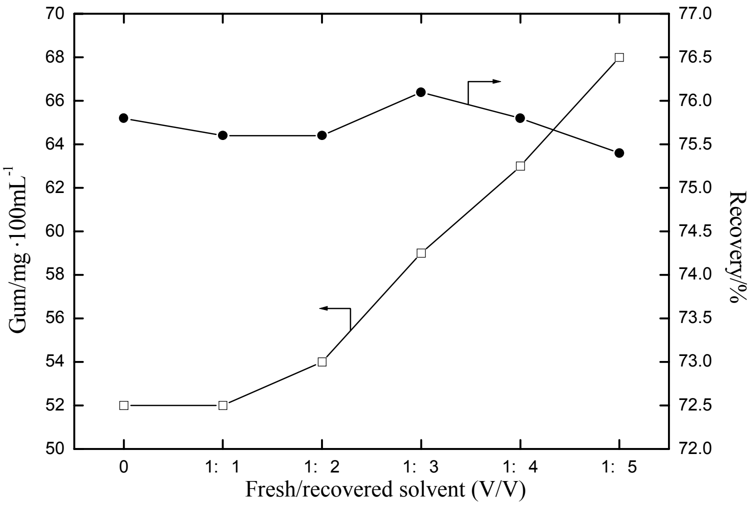

Fig. 3. Effect of recovered solvent on gum

The residual liquid after solvent recovering is extremely viscous at the room temperature (20 °C) and can be burned easily. It can be added to the heavier fraction of shale oil used as fuel oil.

The Elemental Composition of the Residue and Refined Oil

The stability of refined oil is improved greatly. To get the knowledge of which compounds are removed during solvent refining, the ultimate analysis is prerequisite. Table 6 presents the elemental composition of several samples.

Table 6. **Elemental Composition of Several Samples**

Samples	C, %	H, %	N, %	O, %	S, %	H/C
Shale oil	84.58	11.50	1.27	2.49	0.583	1.63
Diesel fraction	82.59	12.03	0.98	3.53	0.87	1.75
Refined diesel	85.60	12.49	0.37	0.45	0.36	1.75
Residue	83.25	9.88	2.56	4.50	0.98	1.42

It can be seen from Table 6 that nitrogen content of the diesel fraction is reduced by 62.2% in the refined diesel compared with the diesel fraction. At the same time, nitrogen content of the residue is 3 times higher than that of the diesel fraction. The removal of oxygen-containing compounds is efficient using solvent refining. Oxygen content decreases from 3.53 to 0.45%, and the removal rate is as high as 87.3%. About 58.6% of sulfur can be removed. Sulfur content can meet the national specification ($\leq 0.5\%$). Therefore, nitrogen-, oxygen- and sulfur-containing compounds can be removed by the method of solvent refining, and thus the stability of diesel is improved.

Conclusions

The multicomponent solvent is of efficient selectivity but also of good ability to remove gum. The optimum operating conditions are: temperature 10–30 °C, additive concentration 7–10%, the total ratio of solvent to oil 0.5–0.6, and three extraction stages. 62.2% of nitrogen, 87.3% of oxygen and 58.6% of sulfur present in the diesel fraction can be removed. The stability of diesel can be improved greatly.

A small quantity of heteroatomic compounds in the diesel after refining with multicomponent solvent can be removed by alkali washing. All the items can meet the requirements of the specification.

A lot of advantages have been shown such as cheapness, abundance, low toxicity and easy recyclability of the solvent. The additive is cheap and abundant, and its dosage is small.

Acknowledgements

The present study was financially supported by Beijing Municipal Education Committee (Project No. XK 114140479).

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Presented by Qian Jialin
Received November 9, 2004