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# STUDIES ON FUSHUN SHALE OIL FURFURAL REFINING

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*Solvent refining of Fushun shale oil with furfural as a solvent extraction agent was investigated. The results showed that raffinate yield decreased with either the increasing of agent/oil mass ratio or reaction temperature; the extract yield increased under the same conditions, while the quality of raffinate oil was better. At agent/oil mass ratio of 3/1, reaction temperature of 60 °C and residence time of 30 min, the raffinate yield was 55.37%, and the extract yield 43.60%. The heavy component from the extract oil was used for blending different grades of asphalt such as heavy-traffic paving asphalt and building asphalt, the light component from the extract oil was used for separation of non-hydrocarbon compounds; a range of light fuel oil was produced through catalytic cracking experiment with the denitrified raffinate oil, the removed nitrogen compounds were also used for separation of non-hydrocarbon compounds.*

## Introduction

Shale oil is a product of oil shale low-temperature carbonization. It is similar to petroleum, but rich in unsaturated hydrocarbons and nitrogen-, sulfur-, and oxygen-containing organic compounds. These unsaturated hydrocarbon and non-hydrocarbon compounds are the main reason for an increasing resin formation in the oil. The sediment formed largely accounts for low stability and black color. Shale oil is an important alternative resource of energy. Reserves of shale oil exceed normal petroleum reserves greatly, nowadays intense focus is on increasing energy sources, therefore the developing shale oil industry may help to resolve the problem of energy supply security. In China shale oil is usually used as a boiler fuel or bunker fuel oil at present. It is very irrational to restrict the use of shale oil to these low-value applications. Confronted with shortage of resources, reasonable processing steps should be carried out to gain a better economic benefit for the product.

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There are two kinds of processing methods for shale oil: hydrotreating and non-hydrotreating [1]. Liquid fuel products derived from hydrotreating of shale oil, such as diesel oil, naphtha and gasoline, were produced with good stability of diesel, high yield of products, no "three wastes" discharge through hydrotreatment. Such processes are most suited to large refinery applications due to high one-time investment and high equipment cost as well as high ongoing operating cost; while the latter method is suitable for the middle-sized refinery due to lower investment in equipment, simple operation and lower operating cost. The non-hydrotreating method generally includes procedures of acid-base refining, solvent refining, adsorption refining, adding stabilizer and so on.

For non-hydrotreating of shale oil, most methods used at present are directed toward the light fractionation of shale oil. For example, sulfuric acid-alkali washing method was used to produce the product qualified as light diesel from the diesel fractions of shale oil [2], but a large volume of acid-alkali sludge produced in the process is difficult to dispose of, so there was little to take up in current industrial applications. S. Zhang [3] explored a two-step complex method of separating nitrogen compounds from shale oil fractions (<350 °C distillate) using titanium tetrachloride and copper-chloride dihydrate. The method enables to reduce both the content of resin in oil and acidity to levels which meet the standard of qualified diesel. In State Key Laboratory of Heavy Oil Processing of Petroleum University [4] gas oil of shale oil was refined using a complex solvent method. Stability of the refined oil was improved to a large extent and refined oil yield was about 80%.

All methods concentrating on light fractionation of shale oil are not widely used in industrialized applications. In this paper a new refining method is proposed for Fushun shale oil. The method is easily applicable to batch method in industry, with the aim of processing the full cut of shale oils produced in FMG vertical retorts. The effects of agent/oil ratio, reaction temperature and residence time on the raffinate and extract yields were studied. The raffinate oil and extract oil were analysed, in addition high-value heavy-traffic paving asphalt and non-hydrocarbon compounds rich in nitrogen, sulfur and oxygen were gained through further processing of the extract oil containing much non-hydrocarbon compounds to produce compounds which are similar to petroleum asphalt. The quality of raffinate oil resembles that of 20# diesel, which can be used directly or as the raw material for catalytic cracking after denitrogenation to get more products. The non-hydrotreating processing method was fully realized for Fushun shale oil. It has a particular significance for processing of shale oil. The process is easy to operate, and the objective is to industrialise the technology after a future successful pilot plant test.

# Experimental

## Material

Fushun shale oil produced by Shale Oil Refinery of Fushun Mining Group Co., Ltd. in vertical Fushun retorts was used as the raw feed material. The analysis results are given in Table 1. Furfural was used as the solvent extraction agent in the experiments.

*Table 1.* **Properties of Fushun shale oil**

| Item | Value | Item | Value |
|---|---|---|---|
| | | Elemental composition, wt.% | |
| Density (20 °C), g/cm$^3$ | 0.9033 | C | 86.05 |
| Kinematic viscosity (50 °C), mm$^2$/s | 11.3 | H | 11.51 |
| Solidification point, °C | 33 | O | 0.69 |
| Open cup flash point, °C | 137 | S | 0.56 |
| Phenol, % | 3.1 | N | 1.19 |
| Asphaltene, % | 0.85 | C/H | 7.49 |
| Wax, % | 20.0 | Basic nitrogen, % | 0.6509 |
| Resin, % (sulphate process) | 42 | Boiling range: | |
| Carbon residue, % | 1.63 | <200 °C | 3% |
| | | 200–350 °C | 35% |
| | | >350 °C | 62% |

## Experimental procedure

The mixture of shale oil and solvent in the required proportions was put into a container, heated up to the required temperature and stirred to ensure good contact between shale oil and extracting agent.

After stirring the mixture was allowed to settle naturally, the extract phase was decanted to separate the extract phase and the raffinate phase.

Extract oil and raffinate oil were produced by separating the extracting agents through atmospheric distillation.

# Results and discussion

## Effect of temperature on raffinate yield and extract yield

Effect of temperature (50, 60, 70, 80 °C) on the yield of raffinate at a mass ratio of extracting agent to oil of 3:1 and residence time of 30 min using technical furfural as the extracting solvent was investigated and the results are shown in Fig. 1. Properties of raffinate oil are listed in Table 2 and some main quality indexes of 20# heavy diesel (Chinese standard) in Table 3.

As can be seen in Fig. 1, the ability of dissolving the target unwanted component in furfural at low temperatures is very low because some of the unwanted non-hydrocarbon compounds and heavy aromatics do not separate fully. With the increasing temperature, the solubility of the target unwanted components in furfural enhances, however, at the same time the solubility of the required product fractions increases. The optimum separation using furfural is possible as the selectivity of solvent decreases resulting in the decrease in the raffinate oil and in the increase in the extract oil at a temperature of 60 °C. As shown in Table 2, the quality of raffinate oil increases with increasing temperature. Comparing the results given in Tables 2 and 3, it can be seen that the raffinate oil extracted at 60 °C can be saled as 20# heavy diesel and, on the other hand, the raffinate oil can be saturated after treatment in conditions of catalytic cracking, because nitrogen content in the raffinate oil meets the standard of catalytic cracking after solvent refining. Considering the cost consumption, low temperature 60 °C was chosen as the best temperature for extraction.

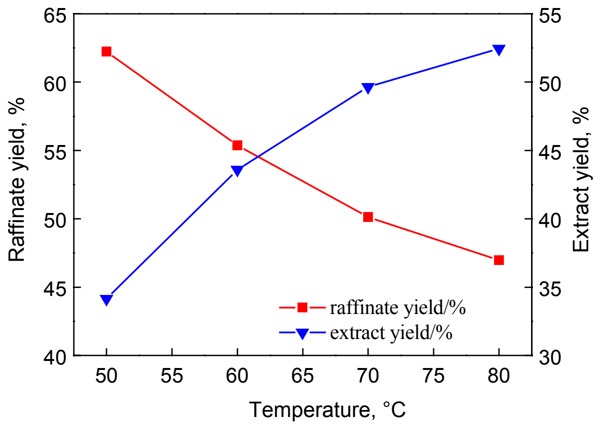


*Fig. 1*. The effects of temperature on raffinate and extract yields.

*Table 2*. **Properties of raffinate oil extracted at different temperatures**

| Items | Temperature, °C | | | |
|---|---|---|---|---|
| | 50 | 60 | 70 | 80 |
| Solidification point, °C | 30 | 34 | 29 | 32 |
| Kinematic viscosity (50 °C), $mm^2/s$ | 10.9 | 15.4 | 20.1 | 30.8 |
| Open cup flash point, °C | 100 | 168 | 175 | 184 |
| Carbon residue, % | 1.56 | 0.31 | 0.27 | 0.20 |
| Ash content, % | 0.08 | 0.0035 | 0.0030 | 0.0024 |
| Water soluble acid or alkali | None | None | None | None |
| Sulfur content, % | 0.43 | 0.37 | 0.29 | 0.21 |
| Basic nitrogen, ppm | 62.45 | 42.88 | 35.46 | 21.37 |
| Total nitrogen, ppm | 187.23 | 124.37 | 94.25 | 61.54 |

*Table 3*. **Main quality indexes of 20 # heavy diesel**

| Item | Quality index | Test method |
|---|---|---|
| Kinematic viscosity (50 °C), $mm^2/s$, not greater than | 20.5 | GB/T 265 |
| Carbon residue, %, not greater than | 0.5 | GB/T 268 |
| Ash content, %, not greater than | 0.06 | GB/T 508 |
| Sulfur content,%, not greater than | 0.5 | GB/T 387 |
| Mechanical impurity, %, not greater than | 0.1 | GB/T 511 |
| Water content, %, not greater than | 1.0 | GB/T 260 |
| Flash point (closed cup), °C, not lower than | 65 | GB/T 261 |
| Solidification point, °C, not higher than | 20 | GB/T 510 |
| Water soluble acid or alkali | None | GB/T 259 |

*Table 4.* **Properties of raffinate oil extracted at different agent to oil ratio**

| Items | Agent to oil ratio | | | |
|---|---|---|---|---|
| | 1:1 | 2:1 | 3:1 | 4:1 |
| Solidification point, °C | –45 | –30 | –34 | –25 |
| Kinematic viscosity (50ºC), $mm^2/s$ | 8.7 | 10.9 | 15.4 | 28.1 |
| Open cup flash point, °C | 100 | 128 | 168 | 184 |
| Carbon residue, % | 1.56 | 0.76 | 0.31 | 0.20 |
| Ash content, % | 0.08 | 0.04 | 0.0035 | 0.0024 |
| Water soluble acid or alkali | None | None | None | None |
| Sulfur content, % | 0.56 | 0.43 | 0.37 | 0.21 |
| Basic nitrogen, ppm | 62.45 | 56.22 | 42.88 | 21.37 |
| Total nitrogen, ppm | 187.23 | 158.56 | 124.37 | 61.54 |

### Effect of mass ratio of agent to oil on raffinate and extract yields

The mass ratio of refining solvent to oil is called agent/oil ratio. Effect of the agent/oil ratio on raffinate and extract yields at 60 °C and residence time 30 min is shown in Fig. 2. The properties of raffinate oil are shown in Table 4. The results show that adding more solvent altered the proposed original balance state and that resulted in decreasing concentration of unwanted component in furfural, and it will favor the transfer of the unwanted component into furfural to reach a new equilibrium. Thus, the larger the agent/oil ratio, the better the quality of oil. In summary, increasing agent/oil ratio results in lower processing capacity of the material requiring a larger equipment, moreover, increasing solvent amount results in higher operating costs, so an agent/oil ratio of 3:1 is preferred.

### Effect of residence time on raffinate and extract yields

Effect of residence time on removal rate of basic nitrogen at agent to oil ratio 3:1, reaction temperature 60 °C with furfural as extracting agent was also investigated and the results are shown in Fig. 3. As can be seen in Fig. 3, the raffinate yield and extract yield both increase with the extension of residence time, for times exceeding 30 min both raffinate yield and extract yield vary little because the dissolution of the unwanted component in furfural has reached saturation and the two phases are fully separated. So the optimal time is 30 min.

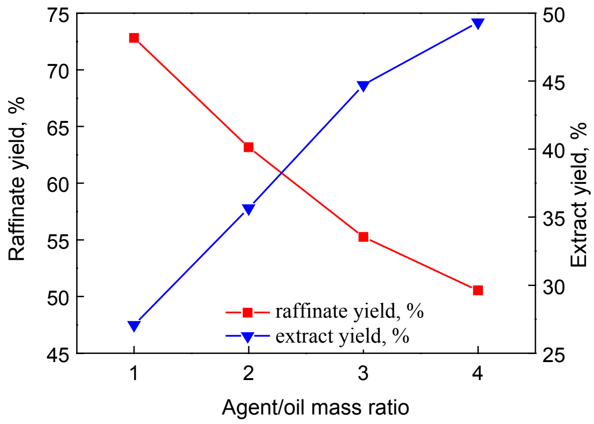


*Fig. 2.* The effect of agent/oil ratio on raffinate and extract yield.

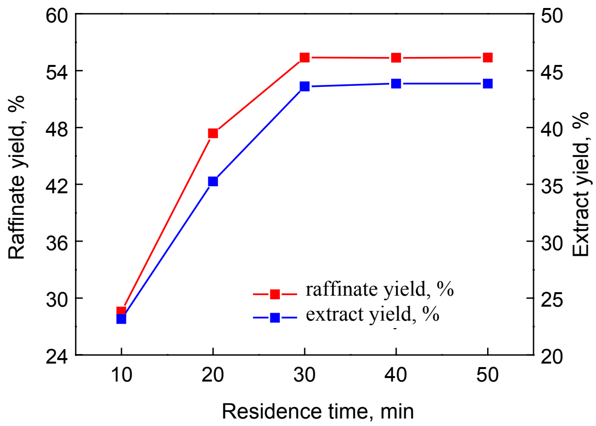


*Fig. 3.* The effect of residence time on raffinate and extract yields.

## Analysis of the quality of raffinate oil

Raffinate oil is a brown pasty solid at room temperature, conventional analysis data are given in Table 5. We can see that the solidification point of the raffinate oil is much higher than that of normal crude oils, sulfur and nitrogen content are higher as well. Sulfur and nitrogen content resembles that of the petroleum residual oil; wax content is up to 34.5%, which is higher than that of Chinese crude oil; the index of carbon residue is 0.31%, kinematic viscosity (50 °C, $mm^2/s$) 8.6 $mm^2/s$ resembles the quality of 20#

heavy gas oil. Comparing the two analyses, all indexes for the raffinate meet the requirements for 20# heavy gas oil except the solidification point is higher.

This raffinate product is not suitable to be used as feed for catalytic cracking due to its high nitrogen content, but it can be used to produce light fuel oil after denitrogenation. The removal of nitrogen compounds was also used to separate non-hydrocarbon compounds; the denitrogenated oil can be processed according to the technology for wax oil.

*Table 5.* **Properties of raffinate oil**

| Item | Analytic value | |
|---|---|---|
| Carbon residue, wt.% | 0.31 | |
| Density (20 °C), g/cm$^3$ | 0.8568 | |
| Kinematic viscosity (50 °C), mm$^2$/s | 8.6 | |
| Solidification point, °C | 34 | |
| Open cup flash point, °C | 168 | |
| Fire point, °C | 174 | |
| Asphaltene, % | 0.350 | |
| Ash, % | 0.0035 | |
| Sulfur, % | 0.3744 | |
| Nitrogen, % | 0.5089 | |
| Basic nitrogen, % | 0.1743 | |
| Wax, % | 34.5 | |
| Resin, % | 6.15 | |
| Boiling range, °C | IBP | 210 |
| | 10% | 313 |
| | 14% | 350 |

## Analysis of the quality of extract oil

Extract oil is a thick black substance at room temperature, conventional analysis data are given in Table 6. We can see that the extract oil cannot be directly used for making asphalt because its softening point is low and needle penetration deep. Light components were distilled from the extract oil through true boiling point distillation. The distillate can be used as a solvent

*Table 6.* **Properties of extract oil**

| Item | Value | Item | Value |
|---|---|---|---|
| Density (20 °C), g/cm$^3$ | 1.0231 | Elemental composition, wt.% | |
| Kinematic viscosity (50 °C), mm$^2$/s | 15.3 | C | 86.44 |
| Solidification point, °C | 31 | H | 10.09 |
| Open cup flash point, °C | 143 | O | 0.91 |
| Phenol, % | 3.7 | S | 0.75 |
| Asphaltene, % | 1.58 | N | 1.81 |
| Wax, % | 7.2 | C/H | 8.65 |
| Resin, % (sulphate process) | 53 | Softening point, °C | <25 |
| Carbon residue, % | 4.06 | Needle penetration/0.1mm | >300 |

to enhance the separation of non-hydrocarbon compounds. In addition, important chemical materials such as phenols, pyridines and quinoline, etc. can be derived from the distillate; the resultant residue (heavy component) from extract oil can be used for blending different grades of asphalt such as heavy-traffic paving asphalt and building asphalt.

## Conclusions

1. At agent/oil mass ratio of 3/1, reaction temperature of 60 °C residence time of 30 min, and technical furfural as extracting agent, the raffinate oil yield was 55.37%, and the extract yield 43.60%.
2. The raffinate oil after solvent refining with furfural can be sold as 20# heavy diesel; the removed nitrogen compounds and the extract oil can be used for separation of non-hydrocarbon compounds.

## Acknowledgements

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