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Effect of heavy asphaltene on stability of residual oil

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Abstract

An asphaltene fractionation method was developed in order to investigate the effect of heptane (*n*-C7) insoluble asphaltene (C7-asphaltene) on residual oil stability. C7-asphaltene was separated into heavy and light fractions by a new method using a binary solvent system of toluene and heptane (*n*-C7). It was found that the heavy fraction of C7-asphaltene in residual oil, extracted by this method, consisted of highly condensed polynuclear aromatics. Our new fractionation method and the Heithaus stability evaluation method were applied to hydroprocessed residual oils. The peptizability of heavy fraction of C7-asphaltene defined by the Heithaus method decreased in accordance with structural condensation of that fraction. On the other hand, light fraction of C7-asphaltene was considered to influence the peptizing power. We proposed a new conceptual model: light asphaltenes would perform as peptizing material as well as resin, and heavy asphaltene would be peptized in oil. This model introduced from our new asphaltene fractionation method could be more effective for understanding the destabilization phenomenon of residual oil. Published by Elsevier Science B.V. All rights reserved.

Keywords: Asphaltene; Polynuclear aromatics; Peptizability; Heithaus stability evaluation method

1. Introduction

The stability of residual oils is one of the important factors in handling and various treatments [1]. The properties of asphaltenes have been considered to influence residual oil stability [2]. However, asphaltenes are different in quantity and quality depending on precipitants for separation [3,4]. Generally, asphaltene has been defined as heptane (*n*-C7) insoluble (C7-asphaltene), because the separation procedure of C7-asphaltene is easy and the repeatability of the operation is precise [4]. The substances that influence the oil stability would be included in the heavier portion of C7-asphaltene, because such heavier asphaltene should form sludge during blending, storage and various treatments. A new asphaltene fractionation method using a binary solvent system of toluene and heptane (*n*-C7) was developed and the lowest soluble fraction in C7-asphaltene was defined as 'heavy asphaltene', and the other fraction was defined as 'light asphaltene'. The fractionation method was applied to the asphaltenes from vacuum residue and its hydroprocessed oils, and the relationship between the properties of fractionated asphaltene and oil stability was investigated.

2. Experimental

2.1. Fractionation of asphaltenes

The major properties of Middle East vacuum residue (VR-1) which was used for a separation experi-

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Table 1
Properties of Middle East vacuum residue (VR-1).

Density at 15°C	1.036 (g/cm^3)
Sulfur	5.57 (wt%)
MCR	23.2 (wt%)
C7-asphaltene	14.3 (wt%)

MCR: Micro carbon residue

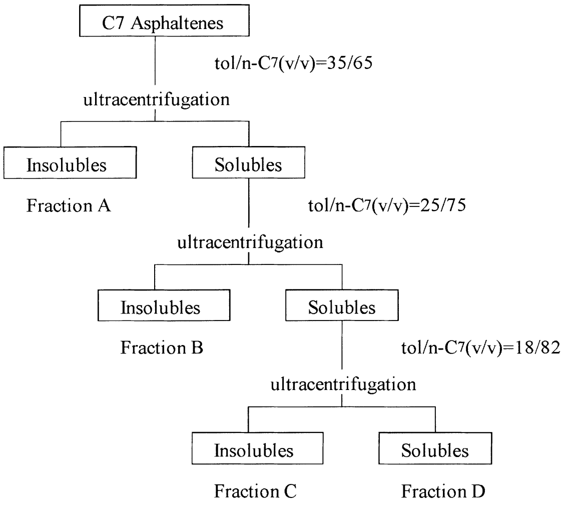

Fig. 1. Fractionation scheme of asphaltene.

ment are shown in Table 1. 100 g of the residue sample was dissolved in 1500 ml of heptane (*n*-C7) under reflux conditions. After cooling to room temperature, C7-asphaltene was separated as heptane (*n*-C7) insoluble, by a suction filtration method. The schematic procedure of our asphaltene fractionation method is shown in Fig. 1. 5 g of C7-asphaltene was dissolved in 140 ml of toluene completely under reflux conditions, and 260 ml of heptane (*n*-C7) was added to the solution. After cooling to room temperature, the fraction including the lowest soluble asphaltene, precipitated out from the solution, was recovered by ultracentrifugation (35 000×*g*). The remaining soluble portion of asphaltene in the toluene/heptane (*n*-C7) (35/65:volume ratio) solvent was recovered from the solution by evaporation. For the subsequent separation, the ratio of binary solvent was changed and the same procedure was repeated. The volume ratios of toluene/heptane (*n*-C7) at each separation step were 35/65 (140 ml/260 ml), 25/75 (100 ml/300 ml) and 18/82 (70 ml/320 ml), respectively. Consequently, the C7-asphaltene was separated roughly into the same amount of four fractions named as A, B, C and D. Fraction A was the lowest soluble portion in C7-asphaltene and D was the most soluble one. Each fraction was evaporated to dryness, then dissolved in benzene and refined by the freeze-drying method.

Table 2
Properties of Middle East vacuum residue (VR-2)

Density at 15°C	1.018 (g/cm^3)
Sulfur	3.83 (wt%)
MCR	21.2 (wt%)
C7-asphaltene	9.3 (wt%)

2.2. *Hydroprocessing of vacuum residue*

Hydroprocessing of Middle East vacuum residue (VR-2; as shown in Table 2) was carried out in a fixed bed reactor loading commercial hydrodesulfurization catalyst CDS-R25H (Catalysts and Chemical Ind.). The operational conditions were as follows: temperature 380–410°C, pressure 14.7 MPa, LHSV 0.33 h^{-1}, H_2/oil ratio 1000 nl/l.

2.3. *Analysis*

Compositions of Middle East vacuum residues and hydroprocessed oils were analyzed by a thin-layer chromatograph with FID detector (TLC-FID) to determine the amount of saturates, aromatics, resins and asphaltenes. C7-asphaltene defined as heptane (*n*-C7) insoluble, heavy and light fractions consisting of C7-asphaltene were characterized by H/C atomic ratio, carbon aromaticity (fa) and average molecular weight (MW). The H/C atomic ratio was determined by means of CHN CORDER with the model MT-5 (YANAKO, Japan). The carbon aromaticity was measured by ^{1}H-NMR spectroscopy using the model JNM-GS-X270 (JEOL, Japan).

The average MW was determined by vapor pressure osmometry using benzene as a solvent with the MW apparatus (CORONA, Japan). The stability of untreated vacuum residue and hydroprocessed oils was evaluated by the Heithaus method [5]. This method has been used generally to predict compatibility of heavy oils and is carried out basically by titration of a solution of a sample oil in an aromatic solvent with a paraffinic solvent to determine the flocculation rate. Flocculation rate of the solution was detected by the Model DIAPHOT TMD300 microscope (Nikon, Japan). In this study, the solvents used for measurements were α-methylnaphthalene as an aromatic solvent and *n*-hexadecane as a paraffinic solvent. The solvent ratios of α-methylnaphthalene to *n*-hexadecane were used in the range of 0.14–0.43. From these measurements, the three calculated parameters pa, po and P were obtained as a result of evaluation of the stability of a sample oil. The parameter pa is a measure of peptizability of asphaltene, and the parameter po indicates the peptizing power of maltene in the heavy oil. The parameter P is a measure of the overall state of peptization of the system. When the parameter P-value is smaller than 1, the oil is evaluated as unstable oil and sludge formation would be observed in the oil. The relationship among the three parameters has been represented in the following equation:

$$P = \mathrm{po}/(1 - \mathrm{pa})$$

where P is the the overall peptization of system, po, the peptizing power of maltene and pa is the peptizability of asphaltene.

3. Results and discussion

3.1. Asphaltene fractionation

Heptane insoluble (C7-asphaltene) content in VR-1 was 14.3 wt%. The C7-asphaltene was separated into roughly the same amount of four fractions by our new method as shown in Fig. 2. In this fractionation procedure, total recovery of each asphaltene to C7-asphaltene reached 98 wt%. The properties of each fraction are shown in Fig. 3. MW of the least soluble fraction A was 17 800, and that of the other fractions B, C, D were 11 100, 10 300 and 2530 respectively. Also there was a significant difference in fa and H/C between fraction A and fraction B, C, D. As shown in the above data, C7-asphaltene is a mixture of compounds with a wide range of properties, and the least soluble fraction A, especially, has larger MW, higher fa and lower H/C ratio than that of the other fractions B, C, D. Hence, we defined 'heavy asphaltene' as the least soluble fraction A and 'light asphaltene' as the other three fractions B, C, D based on solubility and properties of each fraction. Fraction A was the heaviest and the most aromatic portion of the separated four fractions in C7-asphaltene, and some heavier substances in fraction A would be precipitated first, when the system changes to an unstable state.

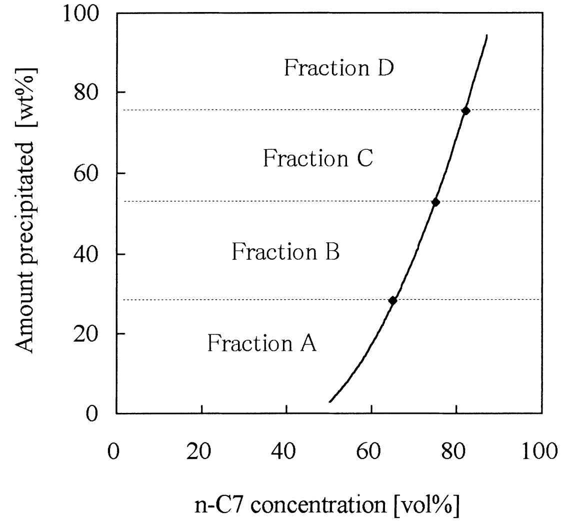

Fig. 2. Amount precipitated vs. *n*-heptane concentration in binary solvent system of toluene and *n*-heptane.

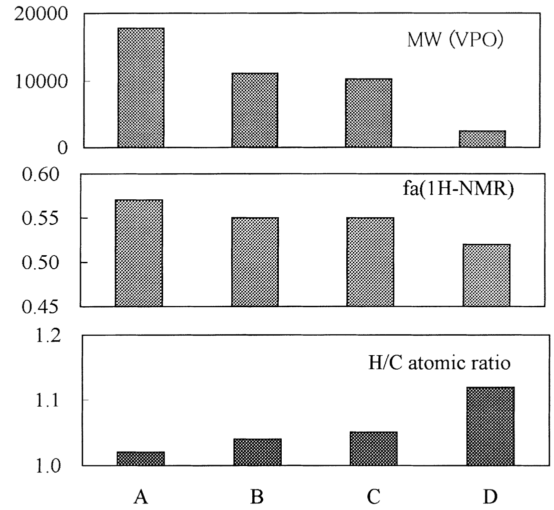

Fig. 3. Properties of asphaltene fractions. (A) toluene/*n*-C7 (35/65) insolubles (B) toluene/*n*-C7 (25/75) insolubles (35/65) solubles (C) toluene/*n*-C7 (18/82) insolubles (25/75) solubles (D) toluene/*n*-C7 (18/82) solubles.

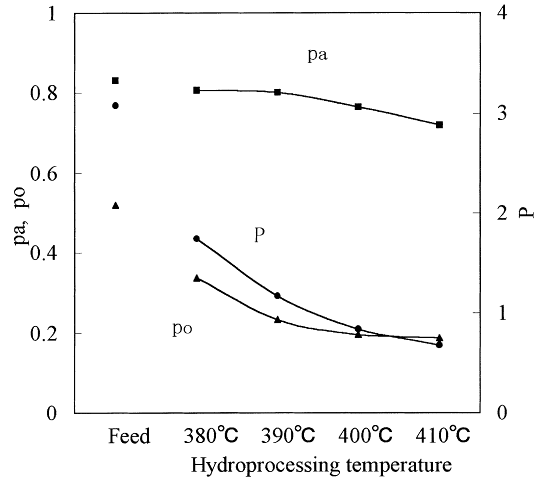

Fig. 4. Effect of hydroprocessing temperature in oil stability.

3.2. *Application of asphaltene fractionation for stability evaluation*

The stability of hydroprocessed oils was evaluated using the Heithas method, and the effect of hydroprocessing temperature in oil stability was shown in Fig. 4. The decrease of *P*-value accompanied by a rise in processing temperature corresponds to the deterioration of hydroprocessed oil. The po value, peptizing power, decreased significantly in the range of 380–390°C, while the pa value was constant in that range of hydroprocessing temperature. However, above 390°C, the pa value decreased, and the decrease of po value was less significant than that in the range of 380–390°C.

The asphaltene content in hydroprocessed oil was determined as shown in Fig. 5. The amount of C7-asphaltene decreased with increasing processing temperature, however, that of heavy asphaltene increased. Thus, there was a definite difference in the yield between heavy asphaltene and C7-asphaltene. Properties of heavy asphaltene were shown in Fig. 6. When the pa value decreased above 390°C processing temperature, the properties of heavy asphaltene changed remarkably as follows: MW and fa increased, and H/C atomic ratio decreased. Accordingly it is supported that heavy asphaltene would be easily condensed by high temperature hydroprocessing above 390°C. On the other hand, the properties of heavy asphaltene hardly changed below 390°C when pa was constant.

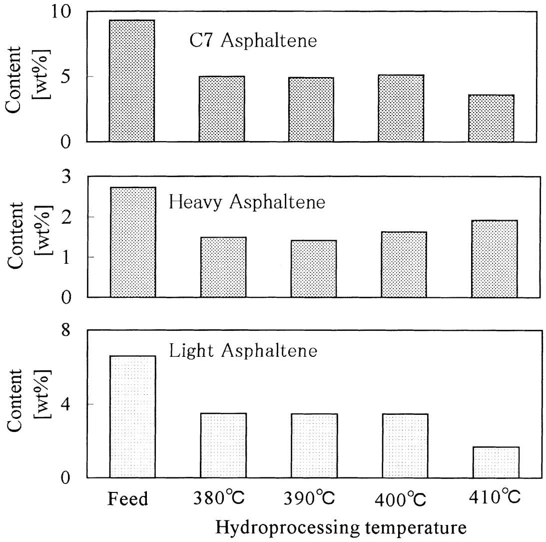

Fig. 5. Comparison of asphaltene content in hydroprocessed oils (1) Heavy Asphaltene: fraction A (2) Light Asphaltene: Fraction B+Fraction C+Fraction D.

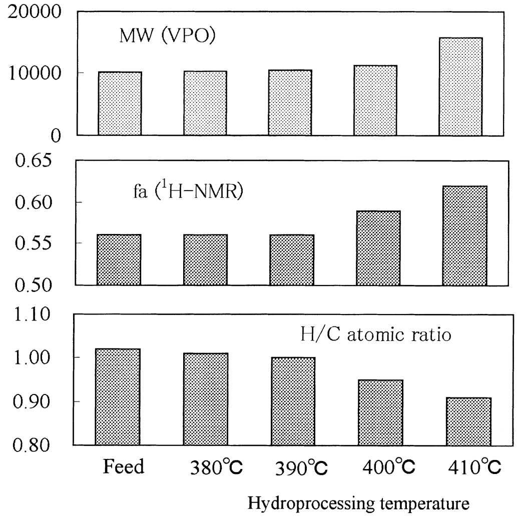

Fig. 6. Properties of heavy asphaltenes in hydroprocessed oils.

These results show that the peptizability of asphaltene would be controlled by properties of heavy asphaltene.

Residual oil consists of asphaltene and maltene. Generally asphaltene is reported to be peptized in oil by peptizing power of resin [6], and thus reduction in amount of resin is considered to reduce peptizing power of maltene. As shown in the compositional

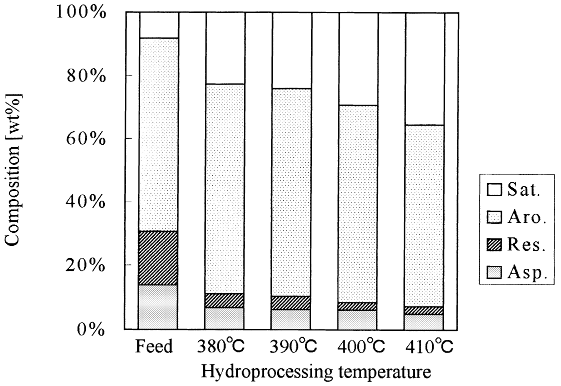

Fig. 7. Composition of hydroprocessed oils measured by TLC-FID.

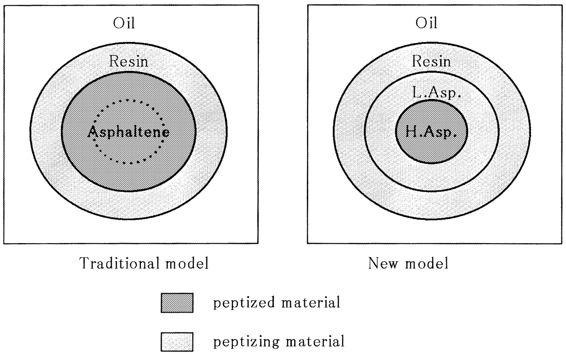

Fig. 8. Peptization model of asphaltene in residual oil.

analysis of hydroprocessed oil in Fig. 7, the amount of resin decreased corresponding to the decreasing po value of that oil. However, it should also be noted that the amount of light asphaltene decreased simultaneously, as well as resin, whereas heavy asphaltene increased as shown in Fig. 5. Accordingly, it is suggested that there was a significant difference in characteristics of hydroprocessing reaction between light asphaltene and heavy asphaltene. On the other hand, it is suggested that there were similar characteristics of hydroprocessing reaction between light asphaltene and resin, because both of them decreased corresponding to deterioration of hydroprocessed oil. These results show that light asphaltene could have similar properties to resin, so that light asphaltene could be considered to play a role like resin. Hence, the light asphaltene would make heavy asphaltene peptize in oil like a dispersant, and we proposed a new peptization model of asphaltene in residual oil as shown in Fig. 8. In our new model, the border between peptized material and peptizing material in oil is shifted to a heavier side than in the traditional model because a decrease in peptizing power of oil would be caused by decreased amount of light asphaltene as well as resin. Our peptization model of asphaltene, especially peptization of heavy asphaltene caused by peptizing power of light asphaltene, is a new concept. It would be more appropriate to understand the deterioration of hydroprocessed residual oil.

4. Conclusion

We developed a new asphaltene fractionation method using toluene–heptane binary solvent system to separate C7-asphaltene into heavy and light fractions. The heavy asphaltene consisted of the most highly condensed polynuclear aromatics in C7-asphaltene, and its characteristics would influence the peptizability of heavy asphaltene. In hydroprocessing reaction of residual oil, the amount of light asphaltene decreased and that of heavy asphaltene increased. We proposed that the heavy asphaltene should be regarded as peptized material, and light asphaltene and resin should be regarded as peptizing material. Our new peptization model of asphaltene would be more appropriate to understand the deterioration of hydroprocessed residual oil.

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