[Technical Report]

Separation of Asphaltene by Dimethyl Ether

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Solvent deasphalting (SDA) of heavy oil generally uses alkanes, from propane to heptane. The solvent power of propane is the weakest, and that of heptane is the strongest. Ethyl ether has slightly stronger solvent power than heptane. Dimethyl ether (DME), an alternative to diesel fuels, is thus expected to have good solvent power for SDA. DME was used for asphaltene separation from vacuum residue of Arabian Light crude oil (AL-VR) at DME/AL-VR weight ratio of 10-60, and compared with separation using pentane by the conventional method. The recoveries of maltene and asphaltene were comparable with pentane more at DME/AL-VR ratio by weight of over 40. Both maltene and asphaltene recovered by DME and pentane had almost the same H/C atomic ratio, hydrogen distribution and carbon aromaticity, respectively. The deasphalting performance of DME was equivalent to that of pentane.

Keywords

Dimethyl ether, Asphaltene, Separation, Heavy oil

1. Introduction

Solvent deasphalting (SDA) is an important technology to prevent coking problems during upgrading. Many solvents have been proposed^{1)~7)} including liquefied gases such as propane and butane^{2),3)}, alkanes such as pentane⁴⁾, hexane⁵⁾ and heptane¹⁾, and ethers such as ethyl ether⁶⁾. Solvent power of alkanes for heavy oil increases with higher number of carbon atoms, and ethyl ether had slightly stronger solvent power than heptane.

Dimethyl ether (DME) is a unique material because it is both an ether and a type of liquefied gas with a similar vapor pressure and a boiling point to butane. It has been expected for an alternative fuel to diesel fuel in the last decade. In addition, several studies and patents have proposed the use of DME for the dehydration of solid materials or the extraction of natural products^{7)~10)}. However, the solvent power of DME for SDA remains unclear. DME is expected to have higher solvent power than propane, but weaker than ethyl ether for heavy oil.

We previously reported the extraction of phenols from water and the reactivation of silica gel using DME^{11),12)}. In this paper, we studied the performance of DME on SDA, and compared the performance with conventional solvents.

2. Experiment**2.1. Materials**

Vacuum residue from Arabian Light (AL-VR) was used as a feedstock. DME was purchased in a 12-l cylinder from Tomoe Shokai. Pentane (extra-pure) was purchased from Wako Pure Chemical Industries, Ltd. Flusin T (150-180 μ m), a column packing for gas chromatography made from polychloro-trifluoroethylene (PCTFE), was purchased from GL Science Inc.

2.2. Apparatus

A schematic diagram of the separation unit is shown in **Fig. 1**. The main parts of the unit are DME server, asphaltene separator, strainer, and receiver. The asphaltene separator is made of stainless steel with a volume of about 60 ml. The separator has two ports, the nitrogen inlet port for pressurizing the vessel, and the DME inlet/outlet port at which a pipe is extending down to the bottom. The end of the pipe is open upwards to prevent aspiration of precipitates.

Two hyper-glass cylinders (type HPG-96-1 and HPG 96-5, Taiatsu Techno Corp.) were used for the receiver and DME server, respectively. A strainer made of teflon tube column packed with Flusin-T (inner diameter: 6 mm, column length: 100 mm) is mounted at the outlet line of the asphaltene separator to strain precipitates carried by the DME flow.

2.3. Extraction Procedure

Prior to the experiment, the asphaltene separator and the receiver were weighed. Approximately 0.7-4 g of

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Fig. 1 Schematic Diagram of a Separation Unit

feedstock was charged into the asphaltene separator. Then the asphaltene separator was attached to the unit, and filled with liquid DME (about 40 g) from the DME server. The ratios of DME/feedstock (D/F) ranged between 10 and 60 (wt/wt). The asphaltene separator was detached from the unit, and heated at 70°C with magnetic stirring for 1 h before standing overnight.

After the asphaltene separator was attached to the unit again, DME was drained by pressurizing the vessel with nitrogen at room temperature. The outlet velocity of liquid DME was controlled using the needle valve at the inlet of the receiver, and the pressure of the receiver was controlled to receive DME solution as liquid using the valve at the outlet line of the receiver, and to allow quite slow evaporation of the DME in the receiver.

The asphaltene separator was filled with fresh liquid DME from the DME server under nitrogen pressure. The mixture was stirred for 1 h and allowed to settle for 30 min, and then DME was drained as described above. This operation was repeated three times in most cases. When DME was drawn out, about 5 ml of DME remained inside the vessel, which was about 6 vol% of charged DME. Therefore, less than 0.1 wt% of maltene was expected to remain in the asphaltene separator after this operation. The asphaltene separator and the receiver were left overnight to release DME slowly by releasing the valves. Both the asphaltene separator and the receiver were detached from the unit, and then they were dried under vacuum at 80°C.

Besides the experiment described above, maltene and asphaltene were separated using pentane by a conventional method as follows. About 5 g of feedstock were charged into a 300 ml flask, and dissolved in 200 ml of pentane, with pentane/feedstock ratio (P/F) of 40 (vol/wt), which was 25 times by weight. The solution was refluxed for 1 h under a nitrogen atmosphere, and then stood at room temperature overnight. The precipitate (asphaltene) was separated using a high-speed centrifuge (15,000 rpm, 15 min), and then collected and washed with 200 ml of pentane. Maltene was recovered by

Table 1 Properties of Dimethyl Ether

Density (20°C)	[g/cm ³]	0.667
Boiling point	[°C]	-24
Critical temperature	[°C]	126.94
Critical pressure	[MPa]	5.33
Vapor pressure (70°C)	[MPa]	1.9

evaporating pentane. Both maltene and asphaltene were dried under vacuum at 80°C.

The recoveries of maltene and asphaltene were obtained from the percentages of the residues in the receiver and the asphaltene separator based on the charged feedstock.

2. 4. Analysis

The recovery rates and the properties of samples recovered using DME were compared with those recovered using pentane. H/C atomic ratio was determined by elemental analysis, hydrogen distribution was determined by nuclear magnetic resonance spectrometry (¹H-NMR) using a JEOL model Lambda 500 spectrometer¹³, and classified into aromatic hydrogen (Ha), benzylic hydrogen (Hα), hydrogens attached to methyl groups in long side chains (Hγ), and other aliphatic and naphthenic hydrogens (Hβ). Carbon aromaticity was determined by ¹³C-NMR using an inverse gated decoupling system (NNE, pulse width of 4.85 μs, acquisition time of 0.967 s, pulse delay of 7 s). The resulting spectrum was the product of 7000 scans.

3. Results and Discussion

3. 1. Properties of DME

DME has a boiling point of about -24°C¹⁴ and condenses under 0.6 MPa at room temperature (Table 1)¹⁵, so is similar to butane. DME is an ether, and have a solubility parameter of 17.3 MPa^{1/2} which is higher than that of butane (14.1 MPa^{1/2})¹⁶. Thus, DME is expected to dissolve more maltene in heavy oil than butane.

3. 2. Dissolution of Feedstock

The feedstock was solid at room temperature, and insoluble in liquid DME. The asphaltene separator was filled with the feedstock and DME was heated up to 70°C to dissolve the feedstock in DME. The pressure of DME reached about 2 MPa at that temperature according to a pressure-temperature diagram (Fig. 2)¹⁵.

During draining of DME from the asphaltene separator, no asphaltene was trapped on the strainer. Asphaltene may have settled rapidly because the density of DME is as low as 0.667 g/cm³ at 20°C.

3. 3. Recoveries of Maltene and Asphaltene

Figure 3 shows the effect of D/F on the recovery of maltene. The recoveries of maltene and asphaltene were 44 and 56 wt% at $D/F = 10$, respectively. The recovery of maltene increased with higher D/F , and reached 80-82 wt% at $D/F = 39$, with no significant

Fig. 2 Pressure-temperature Correlation of Dimethyl Ether

Fig. 3 Recoveries of Maltene and Asphaltene at Various Dimethyl Ether/Feedstock Ratios

increase above this ratio. The recovery of asphaltene was almost in mass balance, because the sum of both recoveries was more than 97 wt%.

The recovery of maltene at $D/F=60$ was 79 wt%, which was slightly smaller than that at $D/F=39$. However, the weighing error for those experiments were estimated at 1.5 and 1 wt%, respectively, because the feedstock was charged 0.7 and 1 g, and the accuracy of the balance used was 0.01 g. Therefore, both recoveries were considered to agree within the experimental error.

Figure 3 also shows the recoveries of maltene (82.1 wt%) and asphaltene (17.9 wt%) using pentane by the conventional method. The recovery of maltene using DME seemed to be slightly smaller than that using pentane at the same weight ratio, but the ultimate recovery at $D/F \geq 39$ was almost the same as that obtained by the conventional method.

3. 4. Properties of Maltene and Asphaltene

Figure 4 shows the H/C atomic ratios of the maltene and asphaltene fractions. Using DME, both H/C

Fig. 4 Dependences of H/C Atomic Ratio on Dimethyl Ether/Feedstock Ratios

atomic ratios decreased with higher D/F ratios, and reached certain values at $D/F \geq 39$.

Table 2 shows that the properties of feedstock, maltene and asphaltene fractions recovered using DME at $D/F=39$ and pentane by the conventional method, respectively. The H/C atomic ratios, hydrogen distribution and carbon aromaticity of both maltene and asphaltene were practically the same. These results indicate that both maltene and asphaltene fractions recovered using DME at $D/F \geq 39$ had the same quality as those recovered using pentane.

SDA using DME was employed on only AL-VR. Further experiments are required to confirm the performance of DME using other heavy oils.

4. Conclusion

Asphaltene separation from AL-VR was performed using DME at D/F of 10-60 by weight at room temperature. The recovery of maltene increased with higher D/F , and reached the same level at $D/F \geq 39$ as that using pentane by the conventional method. The H/C atomic ratios of maltene and asphaltene were almost the same as those recovered using pentane. DME has similar solvent power to pentane under such conditions.

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Table 2 Properties of Feedstock and Recovered Fractions Using Pentane and Dimethyl Ether

Solvent		AL-VR				
		Feedstock	Pentane ^{a)}		DME ^{b)}	
			Maltene	Asphaltene	Maltene	Asphaltene
Recovery	[wt%]		82	18	82	18
Elemental analysis	[wt%]					
C		84.2	84.0	83.0	83.0	82.9
H		10.4	11.0	7.6	11.1	7.6
N		0.38	0.27	0.90	0.27	0.80
S		4.78	4.17	7.35	4.16	7.17
O (by diff.)		0.29	0.50	1.20	1.42	1.52
H/C atomic ratio		1.47	1.56	1.09	1.60	1.09
¹ H-NMR	[%]					
Ha		6.1	5.5	10.7	5.7	10.4
H α		12.5	9.2	19.8	11.8	16.9
H β		64.0	63.7	52.4	64.2	53.7
H γ		17.4	21.5	17.1	18.2	19.0
fa%		33.8	28.6	52.7	27.7	52.8

a) Pentane/AL-VR = 25/1 by weight (40/1 by volume/weight).

b) DME/AL-VR = 39/1 by weight.

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要 旨

ジメチルエーテルによるアスファルテンの溶剤分離

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重質油の溶剤脱れきでは、プロパンからヘプタンまでのアルカンが溶剤としての実績があり、これらの中ではマルテンの溶解力はプロパンが最も小さく、ヘプタンが最も大きい。アルカン以外ではエチルエーテルも有効な溶剤としての報告があり、溶解力はヘプタンよりやや大きい。近年、代替燃料として注目されているジメチルエーテル（DME）はエーテル類の1種であることから、ある程度の溶解力があると予想される。本報告で

はDMEの脱れき効果を確認するため、アラビアンライト減圧残油成分（AL-VR）のDMEによる脱れきをDME/AL-VR=10～60の範囲で行い、ペンタンを用いた従来法による脱れきと比較した。その結果、DME/AL-VR重量比39以上ではマルテンとアスファルテンの回収率、および回収されたマルテン、アスファルテンのH/C原子比、水素分布、炭素芳香族性ともにほぼ等しくなった。