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Physical and rheological properties of deasphalted oil produced from solvent deasphalting

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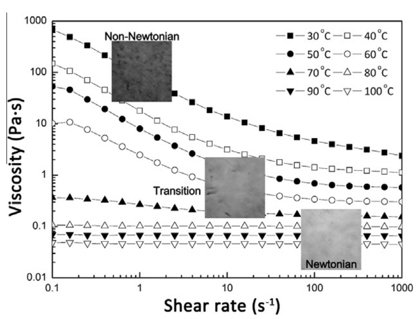
HIGHLIGHTS

- The physical and rheological properties of deasphalted oil (DAO) were investigated.
- The portion of asphaltenes in DAO is reduced, resulting in low contaminant contents.
- DAO has upgraded properties than vacuum residues.
- There is a transition temperature where rheological properties of DAO significantly change.

GRAPHICAL ABSTRACT



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ABSTRACT

Because of the depletion of conventional oil and its increasing price, technologies that use unconventional oil and low-value crude residues are attracting great attention. Unconventional oil and low-value crude residues contain large amounts of asphaltene, which leads to high viscosity and includes a considerable amount of nitrogen, sulfur, and various metals. Therefore, to utilize such energy resources, asphaltene-removal processes (e.g., solvent deasphalting) are required to obtain deasphalted oil (DAO). DAO is generally used for lube base oils and is converted into transportation fuel and petrochemical raw materials by additional refinement. Herein, the physical and rheological properties of DAO were investigated to develop a better understanding of the DAO characteristics and its efficient utilization. The physical properties of DAO were analyzed by measuring elemental compositions; American Petroleum Institute gravity; saturates, aromatics, resins, and asphaltenes fractions; and boiling-point distributions, and the properties were compared with those of vacuum residues. The DAO viscosity was characterized using a rotational rheometer at various temperatures to analyze the effect of temperature on the DAO fluidity. The DAO viscosity greatly decreased with increasing temperatures and a distinctive transition was observed at ~70 °C. In the shear viscosity and modulus analyses, DAO exhibited non-Newtonian behavior below 70 °C and Newtonian behavior above 70 °C.

1. Introduction

Since the 20th century, crude oil has been the most important global energy resource [1]. However, the price of conventional oil has risen gradually because of the increasing worldwide energy demand and depletion of conventional oil reserves. Recently, the International Energy Agency reported that because of the growing economies of China and India (the 2nd and 4th largest

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oil consumers in the world, respectively), the growth of the oil demand in Asia is dominating the global oil-demand growth [2]; in contrast, the demand in the Organisation for Economic Co-operation and Development (OECD) countries decreased between 2009 and 2012 [3].

A potential solution for tackling the shortage of conventional oil and its increasing price is to utilize unconventional oil and low-value crude residues, because there are large amounts of untapped unconventional oil and inefficiently used crude residues. The worldwide reserves of unconventional oils such as extra heavy oil, oil sand bitumen, and kerogen oil are ~6 trillion barrels. Currently, Canada and Venezuela have already started exploiting their unconventional oil resources [4–6]. Moreover, because ~40% of unconventional oil feedstock is remained as vacuum residue (VR) after vacuum distillation whereas VR generated from conventional oils comprises only 10–25% of the feedstock, the production of low value crude residues is also increasing according to the increasing production of unconventional oils [7,8]. However, the production of unconventional oil and crude residues still remains relatively low because of their low economic value, high density (less than 20 American Petroleum Institute (API) gravity), and high viscosity (100–10,000 cP) [6]. In addition, unconventional oil and crude residues generally contain a large amount of asphaltene, nitrogen, sulfur, and heavy metals, which restrict their utilization [9–12].

Asphaltenes are the heaviest components in crude oils and have a dominant effect on the viscosity of unconventional oils and crude residues [13–16]. A high viscosity causes poor mobility, leading to problems in the refinement, transportation, and reforming processes [17–19]. Therefore, to efficiently utilize unconventional oils and crude residues, efficient and economical technologies are required to remove asphaltene.

Among many heavy-oil-upgrading processes, solvent deasphalting (SDA) has been used to separate asphaltenes from VR. SDA is a unique physical separation technique based on differences in density, while other heavy-oil-upgrading processes are based on thermal treatment or hydrogen addition. In SDA, VR is separated into light fractions, deasphalted oil (DAO), and a pitch composed of heavy fractions such as asphaltenes. Different light hydrocarbon solvents such as propane, butane, or a mixture of propane and butane can be used for SDA, depending on the required quality and yield of products. Because nitrogen, sulfur, and heavy metals are generally condensed in the heavy fractions and because light hydrocarbon solvents dissolve aliphatic compounds but not asphaltenes, DAO is rich in paraffinic compounds and has low contaminant (i.e., metals and carbon residues) contents. DAO is generally used for lube base oils, and is converted into transportation fuels, petrochemical raw materials, and the feedstock for fluid catalytic cracking (FCC) or hydrocracking [6,11,20–23].

In this study, the physical and rheological properties of DAO were investigated to understand the characteristics of DAO, which are essential for efficient transportation and utilization. Physical properties such as elemental compositions; API gravity; saturates, aromatics, resins, and asphaltenes (SARA) fractions; and boiling-point distributions were analyzed and compared with those of VR. In addition, the rheological behavior, including viscosity and modulus, of DAO was characterized using a rotational rheometer at various temperatures to elucidate the effect of temperature on the fluidity of DAO.

2. Materials and methods

2.1. Measurement of physical properties

DAO was obtained from a commercial SDA process in S-Oil (Ulsan, Korea) and VR from SK Innovation (Ulsan, Korea). The elemental composition (C, H, O, N, and S) of the samples was analyzed using an elemental analyzer (Flash EA 1112 series/CE Instruments). The analyzer was initially calibrated with sulfanilamide (41.8% C, 4.68% N, 16.27% H, 18.58% S, and 18.62% O). For analysis, 2 mg of the sample was used at the combustion temperature 1100 °C.

The API gravity scale, implemented by the American Petroleum Institute, is a measure of how heavy or light a petroleum liquid is compared to water, and is used to compare the relative densities of petroleum liquids [24]. The API gravity of the samples was calculated using the following Eq. (1):

$$\text{API gravity} = \frac{141.5}{\text{specific gravity (at } 60^{\circ}\text{F)}} - 131.5 \quad (1)$$

Because API gravity is related to the inverse of relative density, API gravity increases with decreasing specific gravity and has been widely used in the petroleum industry to establish the quality and properties of oils [25,26]. In general, crude oil with an API gravity of less than 20–22° is defined as heavy oil, while that with an API gravity of less than 10° is classified as extra heavy oil [27,28].

Crude oils can generally be separated into four fractions of SARA based on their different solubility [29]. The SARA fraction of the samples was examined using a thin layer chromatography-flame ionization detector (TLC-FID, IATROSCAN MK-6s). TLC-FID is easier and faster than clay-gel adsorption chromatography and the SARA analysis is inexpensive with TLC-FID [30–32].

The boiling-point distributions of the samples were measured by a simulated distillation (SIMDIS) technique (ASTM 2887 method) using a gas chromatography analysis system (HP/AC SIMDIS Alliance Product G1540A) [33].

2.2. Viscosity measurements

The rheological properties of a substance provide useful information regarding flow and deformation characteristics, and are conventionally measured using a rotational rheometer or a capillary rheometer. In this study, a rotational rheometer (AR2000, TA instruments, DE, USA) was used to analyze the rheological characteristics of DAO. The AR2000 allows the application of shear force to a sample and has a peltier plate for temperature control. In the experiments, a parallel-plate fixture with a 40-mm diameter and a 1-mm gap thickness was used instead of the conventional cone-and-plate fixture to prevent potential friction forces by the solid content of DAO near the center regime between the cone and plate, which had a very narrow gap. Viscosity was measured at shear rates varying from 0.1 to 1000 s^{-1} and there was no problem of sample leakage in this range. The peltier plate could be controlled at the maximum temperature of 150 °C by the peltier effect (gen-

Table 1
Specific gravity and API gravity of deasphalted oil and vacuum residue.

	DAO	VR
Specific gravity at 60 °F	0.934	1.035
API gravity	20.3	5.12

Table 2
Elemental analysis of deasphalted oil and vacuum residue.

Elemental composition (%)	DAO	VR
C	81.45	79.75
H	10.30	9.37
O	1.20	1.48
N	0.13	0.47
S	1.63	4.20