# Article

On the Combination of Solvent Deasphalting and Partial Catalytic Hydrotreating to Produce Transportable Heavy Oil

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#### Abstract

Solvent deasphalting was combined with partial catalytic hydrotreating for the upgrading of heavy oil to obtain upgraded oil for transportation by pipeline. The deasphalted oil was obtained using n-heptane. Hydrotreating was conducted with commercial NiMo catalyst in a batch reactor at 100 kg/cm<sup>2</sup>, 400°C, 4 h, and a stirring rate of 750 rpm. The heavy oil, the deasphalted oil, and the hydrotreated product were characterized by sulfur, metals (Ni, V), asphaltene content, kinematic viscosity, and API gravity. It was shown that both solvent deasphalting and hydrotreating operating at low reaction severity conditions (low pressure) is sufficient to achieve transportation properties of heavy oil.

Keywords: Hydrotreating; Heavy oil; Asphaltene; Deasphalting.

### 1. Introduction

The pipeline transportation of heavy petroleum is a great task due to limitations for flowing in an easy manner. The transportation of heavy petroleum is problematic when it does not have the required values of viscosity and API gravity, which is owed to the elevated energy demand that is needed for handling the high-pressure drop in pipelines <sup>[1]</sup>.

It is well recognized that the challenge for pipeline transportation is the high viscosity and low API gravity of the heavy petroleum that require suitable methods (efficient and economical) to be transferred. In addition, the high concentration of asphaltenes is another issue that may cause problems of incompatibility during the storage, blending, and processing of crude oils.

The fluid properties (viscosity and API gravity) of heavy crude oils depend mainly on the molecular attraction of the oil components (asphaltenes and resins), which are influenced by their molecular weight and polarity. It has been demonstrated that asphaltene concentrations higher than 4 wt% tend to form a colloidal system, which will finally contribute to the high viscosity. In addition, asphaltenes are associated with resins by intermolecular hydrogen bonds, which are the main source of the high viscosities in heavy oil <sup>[2]</sup>.

It is widely accepted that the viscosity value for the transportation varies depending on the crude oil. However, for practical purposes, viscosity higher than 250 cSt at 100°F will difficult the transportation of the crude oil. In general terms, the value of API gravity for such a viscosity specification is around 16°.

There are various commercial methods in the literature to upgrade heavy oils. Most of them operate at high pressure and high temperature (severe reaction conditions or total conversion), by means of which high conversion of heavy oil is obtained. Due to these operating conditions, these processes require high investment and operating costs <sup>[3]</sup>. As was stated before, the issue of high viscosity of heavy oils is mainly attributed to the asphaltenes content. Hence, removing this heavy fraction will contribute significantly to the reduction of viscosity. Solvent deasphalting (SDA) is a mature process technology that is used to produce a reduced-impurity content deasphalted oil (DAO). DAO is a suitable feed that can be further hydrotreated to produce a low-viscosity oil <sup>[4]</sup>. This concept is not new. However, the economics

of the combined process is mainly dictated by the operating conditions of the hydrotreating process, which, if operated at total conversion, will need high investment costs. Therefore, an economical combined process scheme (DAO and HDT) must operate at low severity conditions in the HDT unit, in other words, at the so-called partial upgrading.

The objective of this study is to evaluate the viscosity reduction of heavy oil by means of a combination of solvent deasphalting and partial catalytic hydrotreating in experiments carried out in a batch reactor.

## 2. Experimental

A vacuum residue ( $538^{\circ}C+ VR$ ) from Maya crude oil was used for all experiments. The properties of the vacuum residue are given in Table 1. For the deasphalting step, this heavy feed was put in a pressurized reactor (Parr model 4522), which is equipped with controls for stirring, temperature, and pressure, and vent. From the deasphalting, a feed to hydrotreating was obtained at the following operating conditions: 5 mL/g of solvent-to-oil ratio, 1000 rpm of stirring rate, 30 min of stirring time, 25 kg/cm<sup>2</sup> of nitrogen pressure, and 100°C of temperature. Nitrogen was used to pressurize the reactor. Stirring was initiated when the temperature reached the specified value. Stirring was kept for the desired time, stopped, and then the reactor content was settled for 60 min, and withdrawn by means of a valve located at the bottom of the reactor. The remaining sample adhered to reactor walls was removed with nheptane washing and collected in a beaker. The reactor content was filtered by using a vacuum system and a Whatman 3 filter paper with 6 µm pore size to retain asphaltenes. The deasphaltenes.

Table 1. Properties of VR, DAO, and hydrotreated products

	VR	DAO	HDT VR	HDT DAO
API gravity	1.13	4.31	10.44	16.02
Total S, wt%	5.32	4.89	3.06	2.75
Viscosity at 100°F, cSt	>>>> 250	>> 250	> 250	< 250
nC7 insol., wt%	28	15	16	10
Ni, wppm	140	87	124	64
V, wppm	698	450	534	278
Total Ni+V, wppm	838	537	658	342

For the partial catalytic hydrotreating (HDT) experiment, a catalyst with the following main properties was used: 0.58% Ni, 2.2% Mo, 197 m<sup>2</sup>/g specific surface area, 0.85 cc/g pore volume, and 173 Å mean pore diameter. Hydrotreating test was carried out in a batch reactor (1 L, Parr model 4573). The following constant hydrotreating conditions were utilized: 100 kg/cm<sup>2</sup> hydrogen pressure, 400°C reaction temperature, 750 rpm stirring rate, and 4 h reaction time. Temperature and pressure (corresponding to partial upgrading conditions) and stirring are controlled automatically using a digital controller. In the experiment, 5 g of catalyst and 200 g of sample were loaded to the reactor. Prior to the activity tests, the catalyst was sulfided *ex-situ* in a fixed-bed glass reactor at the following conditions: atmospheric pressure, 400°C temperature, 40 mL/min  $H_2$ , and 3 h. Hydrogen is passed through a container having carbon disulfide, and then the  $H_2/CS_2$  mixture is passed through the glass reactor. The sulfided catalyst was transferred into the batch reactor in a nitrogen atmosphere so that contact with air was avoided. After closing the reactor, it was purged several times with hydrogen to assure there was no air left inside the reactor. Heating was then started from room temperature to 400°C. The reaction began until all conditions were established and the stirring rate was initiated. After the reaction, the reactor was depressurized, and the hydrotreated product was filtered to separate the catalyst from liquids.

Oil samples were characterized by sulfur content, Ni and V contents, API specific gravity, and kinematic viscosity. Asphaltene is defined as that material insoluble in n-heptane. More details of experiment conditions, setup, and procedure are given elsewhere <sup>[5]</sup>.

## 3. Results and discussion

The experimental method used for preparing DAO has been previously validated to reproduce the content and quality of the product in comparison with the ASTM method <sup>[6]</sup>. However, it was not possible to use it for obtaining a small reduction in the asphaltene content because of the high pressure and temperature used. Due to this, it was decided to blend a low asphaltene content sample (0.45 wt%) with the VR sample (28 wt% asphaltene) in such amounts that a 15 wt% asphaltene content sample was prepared. Around 50% of asphaltene reduction was decided for blend preparation so that SDA can be operated at low severity conditions, thus having a low investment and operating costs process.

Apart from the reduction of asphaltenes content from 28 to 15 wt%, other reductions in impurities due to blending were observed, which were not so high: 8% in sulfur and 36% in metals. API gravity increases slightly (from 1.13 to 4.31°API), and viscosity reduction was minimum still being very high than 250 cSt, which indicates that SDA alone is not sufficient to achieve the required value for oil transportation.

From the partial catalytic hydrotreating experiment, it is observed that with the direct processing of VR, the API is enhanced to 10.44°API (HDT VR), which is lower than the desired value (16°API). Viscosity, although reduced substantially, is also still higher than 250 cSt. However, when hydrotreating the DAO (HDT DAO), these specifications of API gravity and viscosity are indeed obtained. The other impurities (sulfur and metals) exhibited minor reductions. This is because during deasphalting, not only asphaltenes precipitate but also sulfur and metals attached to them do. The remaining impurities are present in DAO. All this behavior is expected since both SDA and HDT are operated on low reaction severity conditions. The effects of combining SDA and partial HDT are summarized in Figure 1.

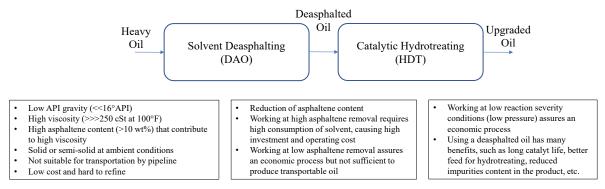


Figure 1. Combination of SDA and partial HDT to produce a transportable oil

The increase of API gravity indicates that hydrotreating was more selective when using DAO as a feed. This is due to the less aromatic nature of DAO <sup>[7]</sup>.

The results presented in this study indicate that upgrading of heavy oil by the combination of solvent deasphalting and partial catalytic hydrotreating processes, both operating at low reaction severity conditions, is a promissory approach to obtain upgraded oil with suitable properties for transportation. Low investment and operating costs are expected due to the low pressure and temperature used in both processes as compared with typical commercial technologies.

## 4. Conclusion

Deasphalted oil with 15 wt% of asphaltene content obtained from vacuum residue of Maya crude was hydrotreated in a batch reactor at low reaction severity (partial upgrading), whereby a partially upgraded oil was obtained, which exhibits the required values of API gravity and viscosity for its transportation in pipelines.

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