

Solution behavior of asphaltic residues and deasphalted oil prepared by extraction of heavy oil



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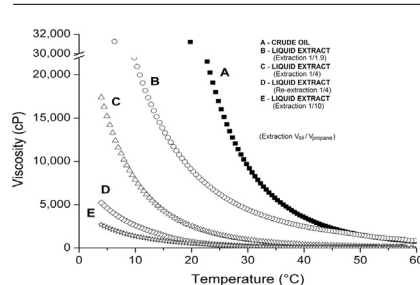
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HIGHLIGHTS

- Heavy petroleum was fractionated into solid and liquid with propane at HT-Hp.
- Components with functional groups predominate in solid residue.
- The solid residue contains heptane, hexane and pentane-soluble components.
- The deasphalted liquid extract from crude still presents a relatively high viscosity.
- Petroleum viscosity depends on other polar compounds not included in asphaltenes.

GRAPHICAL ABSTRACT



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ABSTRACT

An experimental setup to mix crude oil with propane or other gases at high pressure and high temperature is described. The system permitted the injection of predefined volumes of oil and pressurized gas above its saturation pressure to get a homogeneous mixture and subsequent fractionation of the sample into a solid residue and a liquid extract. For propane, the solubility parameter prevailing in the mixing cell was estimated in the range of 13.0 and 12.6 MPa^{0.5} which is lower than the values usually used for asphaltenes separation with n-heptane (15.3 MPa^{0.5}) or n-pentane (14.5 MPa^{0.5}). As expected, this experimental procedure reduces to a largely the asphaltic materials from the crude oil and incorporates to the solid residue part of the component usually separated in the resins fraction. These components in spite of their lower solubility parameter seem to enhance in some way the stability of the residue solution in toluene. Elemental analysis indicates that the heteroatoms accumulate in the solid residue but some polar compounds still remain in the liquid extract which presents a relatively high solubility parameter (20.3 MPa^{0.5}), comparable to the value obtained for the crude oil (21.2 MPa^{0.5}). The deasphaltation process reduces the crude oil viscosity from 30,320 cP in the crude oil to 2510 cP in the extract and a re-extraction of the liquid extract with n-propane further reduces the viscosity to 720 cP. These results are interpreted as an indication that components not necessarily included in the asphaltenes fraction may significantly contribute to crude viscosity.

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1. Introduction

Since the earlier studies on the properties of heavy oils and natural bitumen [1–4], the polar fractions, and more specifically to the asphaltenes fraction, have been identified as the cause of the

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rheological properties of these fossil fluids. Many experimental studies and theoretical models have been developed to correlate heavy oil viscosity with asphaltenes concentration, structure and aggregation [5–8]. In most of these studies, the strategy has been to isolate the asphaltenes from crude oil using n-pentane or n-heptane as the precipitating agent and characterize these fractions and their solutions in hydrocarbon solvents in order to correlate the rheological behavior of the original oil to the physical and chemical properties of these model systems. For this purpose, asphaltenes have been assumed to correspond to a crude oil fraction consisting of polar molecules presenting a rather high molecular weight, capable of self-associate at a critical concentration following the pattern described for surfactants in aqueous solutions [9,10]. The effect of the rest of the oil however has not been examined in detail and asphaltenes and resins have been considered different fractions that in addition to the saturates and aromatics comprehend the whole crude oil. In some cases, it has assumed that asphaltenes particles would be dispersed by the peptizing effect of the resins, which would reduce the oil viscosity [11], whereas in other studies it has been suggested that resins adsorption on asphaltenes particles would increase the asphaltenes particles hydrodynamic radius, which would result in an increase in viscosity. Some of these concepts have been re-examined along recent years [12–18] generating new conceptual basis to outline heavy oil and bitumen physical and chemical properties. In this contribution an experimental setup assembled to mix crude oil with propane or other gases at high temperatures and pressures is described. Using this experimental device heavy oil samples were separated into a solid residue and a liquid extract. The solution behavior of these fractions, prepared under different pressure and temperature conditions, was examined and compared with the properties of the original crude oil. These experimental developments and the preliminary information gathered in the work were used to improve our understanding of heavy oil rheological properties.

2. Experimental

2.1. Materials

Toluene, ethanol, n-pentane (C5), n-hexane (C6), n-heptane (C7), xylene, decalin and cyclohexane were purchased from Vetec Química Fina Ltda, Rio de Janeiro, Brazil, and methanol was purchased from Petroquímicos Ltda. Decane (>99%), *trans*-decalin (99%), *cis*-decalin (99%) and tetralin (1,2,3,4-tetrahydronaphthalene) (99%) were supplied by Sigma–Aldrich, São Paulo, Brazil. Methyl cyclohexane, methyl naphthalene and n-octane were obtained from Merck. Isooctane (2,2,4-trimethyl pentane) was obtained from Tedia Brazil and 1-pentanol was obtained from Riedel-de Hæn. All chemicals were reagent grade products (99% or better), except xylene and methyl naphthalene (98% and 95%, respectively), and were used without further purification. Nonyl phenol (technical grade) was supplied by Oxiten do Nordeste S.A., São Paulo, Brazil. Propane (99.5% purity), C3, was obtained from White Martins and it was maintained at room temperature in 45 kg cylinders.

The crude used was a sample produced in an offshore platform from Campos Basin, Brazil. The asphaltic residue (ASPR) was obtained from a local refinery that operates an industrial propane de-asphaltation unit (Duque de Caxias Refinery, Rio de Janeiro State, Brazil). The dead oil sample from Marlim field, Campos Basin, Brazil, was used as reference oil for the precipitation onset test.

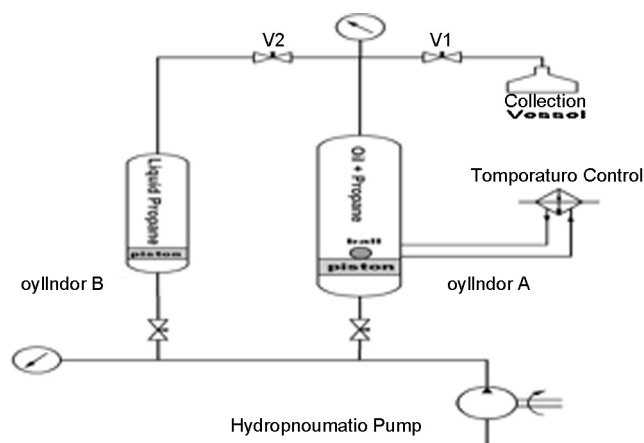


Fig. 1. Schematic diagram of the experimental setup used to crude oil fractionation under controlled pressure and temperature conditions.

2.2. Methods

2.2.1. Asphaltenes extraction

The asphaltenes extraction was carried out using two alternative procedures. For the asphaltic residue, approximately 15 g of solids were mixed with 5 mL of toluene and left to dissolve under mild agitation overnight. One liter of n-heptane was then added to this solution and left to precipitate under moderate agitation for 24 h. The precipitated solids were separated by filtration under vacuum using 45 μm filter membranes and Soxhlet extracted with n-heptane up to complete removal of the n-heptane-soluble material present in the sample. In the case of crude oil, the asphaltenes were separated by a laboratory procedure similar to the IP-143 standard method [19].

The resins used in this study were separated by the following procedure: the n-heptane filtrate recovered from the asphaltenes precipitation step and the n-heptane used to extract the soluble components that co-precipitate with the asphaltenes were mixed at the end of the process. The mixture was evaporated to complete dryness in a vacuum rotary evaporator. For ASPR, this fraction corresponds to C7–C3 resins. In the case of crude oil however some C3-soluble non-volatile components may be also present.

2.2.2. High pressure fractionation unit

Fig. 1 shows a schematic diagram of the experimental setup used to induce the precipitation of the asphaltic fractions. The equipment consisted of a high pressure high temperature mixing cell (cylinder A) provided with a motorized rocking system to gently shake and agitate the cell with the assistance of a steel ball, a gas injection modulo (cylinder B) and a hydro-pneumatic pump. The system permitted the injection of predefined volumes of oil and gas pressurized above its saturation pressure to get a homogeneous mixture with the reservoir fluid. This setup allows operating at temperatures up to 110 °C and pressures up to 6000 psi.

In a typical test, a defined mass of crude oil was conditioned at a temperature of 68 °C in the cylinder A and subsequently vacuum deaerated and pressurized to 40 bar by water injection at the bottom of the cylinder using the hydro-pneumatic pump. Following this, the volume of liquid propane necessary to get the required propane/oil ratio was transferred from the cylinder B to the cylinder A by carefully drainage of the water contained under the piston of the mixing cell (cylinder A). Then the pressure and temperature of the oil-liquid mixture were then readjusted at 40 bar and 68 °C and the cylinder A was isolated closing valves V2 and V1. The motorized rocking system was switched on and the liquid mixture was maintained under agitation for 6 h, and then undisturbed

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