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Experimental and modeling studies of phase behavior for propane/Athabasca bitumen mixtures

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ABSTRACT

Recent developments in heavy oil recovery methods indicate that the co-injection of solvent and steam can result in higher oil production rates. To investigate the performance and gain a better understanding of this newly developed process, it is essential to study the phase behavior of solvent/heavy crude oil mixtures and measure the saturated phase properties. This study attempts to provide insight into the phase behavior of propane/bitumen mixtures over wide ranges of temperatures and pressures, where the conditions would be applicable for both Vapex and ES-SAGD processes. Thus, phase behavior experiments for propane/Athabasca bitumen mixtures were conducted over temperature range of 323–473 K and at pressures up to 10 MPa. The results indicate that the mixture of propane and bitumen forms vapor–liquid and liquid–liquid phase separations over the studied temperature and pressure ranges. The variation of solubility with equilibrium pressure was found to be more significant at low temperatures. There were crossovers for gas-saturated bitumen density and viscosity which highlights the effect of solubility at low temperatures that is more significant than the effect of temperature on the bitumen density and viscosity. Thus, lower saturated properties were obtained at low temperatures and high pressures. The solubility and saturated liquid density were well predicted by Peng–Robinson equation of state and the saturated bitumen viscosities were reasonably correlated with Pedersen's correlation.

1. Introduction

Vapour extraction (Vapex) process was described and patented by Butler and Mokrys in 1991 [1]. It is an oil recovery process with the same analogy as the SAGD process using solvent instead of steam. It has application in thin reservoirs, where SAGD cannot be applied due to high heat loss. A series of experimental studies by Butler and Mokrys [2,3] show that this technique can be economically applied for heavy oil recovery. Propane is one of the best solvents which can be considered for Vapex process in Alberta reservoirs. Low dew point pressure makes propane a favorable solvent for Vapex process. Its mixtures with non-condensable gases such as methane and nitrogen enable to adjust the dew point pressure of the mixture. Propane has high solubility in heavy oil and bitumen compared to methane, ethane, and nitrogen and leads to significant viscosity reduction. The diluted oil is mobile at reservoir condition with an economical production rate. In addition, propane can also contribute to an *in-situ* upgrading process which leads to the production of higher oil quality by deasphalting [4]. *In-situ* upgrading improves the oil quality and reduces the processing cost of the produced oil. In addition to solvent-based recovery processes such as Vapex, propane can be considered as an additive to steam-based processes. As previously mentioned, in steam-based processes such as cyclic steam injection and SAGD, a small amount of additive solvent can be co-injected with steam to improve the process performance.

The application of propane for the *in-situ* heavy oil recovery has widely been evaluated. Mokrys and Butler [5] investigated the de-asphaltening phenomena and oil upgrading during propane injection into a physical model. They considered two different cases, the injection of pure propane and the co-injection of propane with steam. The results indicated that the recovery for both cases are comparable while the steam-propane co-injection is more energy efficient compared to pure steam injection. In another study, Jiang [6] came up with a similar finding as Mokrys and

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Butler [5] and found out that, propane concentration in the oil must exceed a certain value (critical concentration) to have oil upgrading (asphaltene precipitation) in the reservoir.

Goite et al. [7] conducted a series of lab experiments for heavy oil recovery (API gravity of 13.5) from the Morichal field, Venezuela. They determined the influence of the use of propane and its optimum concentration as an additive during steam injection. In subsequent study, Ferguson et al. [8] used the same oil and apparatus as Goite et al. and found out that oil production rate is accelerated when propane was used as an additive to steam compared to pure steam. They obtained almost the same optimum propane concentration as Goite et al. [7].

Venturini and Mamora [9] performed a simulation study to evaluate the steam-propane co-injection, for the production of Hamaca heavy crude oil. Both experimental and simulation studies showed that oil production is accelerated by 20% when steam-propane was co-injected compared to pure steam injection. Deng [10] did a numerical study of hybrid process with propane and steam co-injection and simulated the process under different operating strategies and investigated the effect of the use of propane as additive in the hybrid process. Deng [10] concluded that there is an optimum value for propane to steam ratio in the injection gas, and the co-injection of propane in large amount has a negative effect on the process.

Apart from the application of propane for *in-situ* oil recovery, supercritical propane has been tested for its capability to extract bitumen from oil sands. Jacoby [11] performed experimental studies on the extraction of Athabasca oil sands using solvents such as ethane, propane, butane, and pentane in the supercritical and liquid states. Subramanian [12] conducted supercritical fluid extraction of Whiterock and PR Spring bitumens using propane as the solvent.

Based on the above-mentioned applications and research studies, the bitumen/propane interaction and its phase behavior and thermodynamic properties are extremely important to design and optimize the recovery and extraction processes. There are limited data (Deo et al. [13]; Han et al. [14]; Frauenfeld et al. [15]; Luo et al. [16]; Badamchi-Zadeh et al. [17]) in the literature for the phase behavior study of bitumen/propane systems, and the data have been limited to the low temperatures ($<$373 K) and to pressures less than the vapor pressure of propane.

In the present study, the experimental phase behavior experimental data for Athabasca bitumen/propane systems are presented over wide ranges of temperatures and pressures. The reported data are the solubility of propane in bitumen, the density and viscosity of the saturated bitumen at temperatures, 50 to 200 °C. Then, the measured data for solubility and densities is correlated with Peng–Robinson equation of state. The saturated densities are also estimated with available correlations. The viscosity of propane-satuarted bitumen is correlated with Pedersen's correlation which is based on corresponding state theory.

2. Experimental

2.1. Materials

The propane was purchased from Praxair with a minimum purity of 99.5 mol%. The bitumen sample was provided by an oil company operated a SAGD project (Table 1). The bitumen sample was taken from the production unit, and sand and water were removed. The water and sand have been removed from the bitumen using centrifuge (water and solid contents were less than 0.1 wt%). The density of sample was 1009 kg/m^3 at 296 K and 1 atm [18]. The molecular weight measurement was done using freezing point depression (cryoscopy method) and an average molecular weight of 539.2 ± 7.9 g/mol was measured [18]. The SARA analysis was done on the bitumen sample to separate different fractions (saturates, aromatics, resins, and asphaltenes). The asphaltene fraction was separated and precipitated using *n*-heptane solvent. The SARA compositional analysis of bitumen is presented in Table 2.

The compositional analysis was done the bitumen sample using ASTM D7169 to obtain the boiling points up to a maximum temperature of 993 K. The elution of *n*-C100 occurs at this temperature. Table 3 summarizes the boiling points for the sample.

Table 1
Chemical sample specifications.

Chemical name	Source	Initial purity	Purification method
Propane	Praxair	0.995 mole fraction	None
Bitumen	Field	–	None

Table 2
Properties of bitumen sample.

Fractions	Weight percent
Saturates	12.26
Aromatics	40.08
Resins	36.53
Asphaltenes	11.13

2.2. Apparatus

The detail of experimental apparatus was presented elsewhere [19]. It has equilibration cells, a density measuring cell, a viscometer, four sampling cells, feeding cells, and two Quizix automated pressure activated pumps. The cells (equilibrium and sampling), viscometer, and density measuring cell are inside a temperature-controlled Blue M oven. Quizix pumps measure and control the system pressure. Phase detection and accurate volume measurements are done with viscometer and density measuring cell. The fluid density is measured with the Anton Paar custom densitometer that has been calibrated using wide range method. Nitrogen and water density data were used to calibrate densitometer. The Cambridge viscometer, equipped with SPL-440 sensor, measures the fluid viscosity in the viscosity range of 0.2–10,000 mPa s. The viscometer is factory calibrated. Different pressure transducers measure the pressure inside the apparatus. An inline Rosemount transducer (3051CG5A) measures the pressure in the range 0–13.9 MPa with 0.04% accuracy. The pumps also have pressure transducers. A Blue M oven is used to keep a constant temperature during the experiments. The temperature is controlled with the oven within ±0.1 K.

2.3. Procedure

Before a phase behavior measurement, the whole setup was cleaned to remove any potential contaminants. To be sure that no contaminants left in the lines and cells, they were evacuated successively. Bitumen was charged into the equilibrium cell and the mass of the bitumen was calculated by the density and volume at a constant pressure and temperature. Next, the propane was injected into the equilibrium cell using the same procedure. The equilibrium cell was rocked to enhance and increase mixing for the mixture at fixed temperature and pressure. For the duration of the mixing, the injected volume of water to have a constant pressure in the cell was measured. No variation in the cumulative volume of the water shows the equilibrium state.

To displace and transfer the equilibrium fluids from the equilibration cell, the cell was maintained in the vertical direction for few hours. This ensured, we have fluids vertically segregated in