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Experimental and modeling studies of MacKay River bitumen and water

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ABSTRACT

Understanding of thermodynamic and thermo-physical properties of water-bitumen system is the necessary requirement towards better design and successful operation of thermal recovery processes of bitumen and heavy oils. This work reports the new experimental data of water solubility in MacKay River bitumen. Water solubility in bitumen is measured at temperatures up to 493 K. Density and viscosity of bitumen rich phase are measured to investigate effect of water dissolution on thermo-physical properties of bitumen phase. We apply the Peng-Robinson equation of state (PR-EoS) coupled with Henry's law to model the measured data and to predict the water solubility in bitumen. Density and viscosity of water-bitumen mixture are correlated to represent the experimental data of the water saturated bitumen. The results presented in this work can be applied in simulation and studies of thermal bitumen recovery processes.

1. Introduction

Water as the energy carrier is the main constituent in the thermal bitumen and heavy oil recovery processes such as steam assisted gravity drainage (SAGD) and cyclic steam stimulation (CSS). Water solubility in bitumen and heavy oils becomes significant at high temperature conditions (Glandt and Chapman, 1995). The dissolved water in oleic phase plays an important rule on properties of the oleic phase such as density and viscosity, the dominant properties in steam assisted gravity drainage (SAGD) and expanding solvent- steam assisted gravity drainage (ES-SAGD). Water dissolution in bitumen decreases the viscosity and density of the oleic phase. Dissolved water in oleic phase comes out of solution in low temperature regions and forms a water-in-oil emulsion resulting in higher viscosity (Glandt and Chapman, 1995; Kokal, 2005). Therefore, measurement of water solubility in bitumen and heavy oils and its effect on viscosity and density of bitumen are important in heavy oil and bitumen production studies.

Experimental data for water dissolution in hydrocarbon fluids at high temperatures (T > 380 K) was reported by Griswold and Kasch (1942) and Glandt and Chapman (1995). Griswold and Kasch (1942) measured the solubility of water in kerosene (M=182 g/mol) and lubricating oil (M=425 g/mol) using the cloud point technique. Their data covers a wide range of temperatures. They concluded that water solubility is independent of the molecular weight of the petroleum fractions. Their finding does not agree with the results of Glandt and Chapman (1995). Results of Glandt and Chapman (1995) indicate that water dissolution in bitumen is dependent on molecular weight and polarity of the bitumen. Glandt and Chapman (1995) used the Karl-Fischer technique to measure water dissolution in several bitumens and heavy crudes. Their data is at high temperatures, which is of interest in thermal oil recovery processes. They found that water dissolution in bitumen increases with increasing crude polarity. A comparison between molecular weight and the polarity of crudes shows that polarity increases as the molecular weight of the bitumen increases. Glandt and Chapman (1995) reported the viscosity of bitumen in the absence and presence of water to study the effect of water dissolution on bitumen viscosity.

Amani et al. (2013) determined the water solubility of Athabasca bitumen over a temperature range of 520–640 K. They also obtained the density of the bitumen-rich phase. Their results show an exponential increase in water dissolution in bitumen when the temperature increases above ~373 K. This data is more applicable for bitumen refining because it is not within the temperature range of the thermal recovery processes.

In this work, new measurements were conducted to measure water solubility in MacKay River bitumen. Fig. 1 shows the temperaturemolecular weight condition of water solubility data in hydrocarbon crudes available in the literature. The new measured data for MacKay River bitumen is also shown. This figure shows the temperature condition of the experimental data for different hydrocarbon fluids versus their molecular weight. The experimental conditions completely cover the temperature range required for thermal heavy oil and bitumen recovery processes. The wide range of molecular weights of

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Fig. 1. T-MW condition of the experimental data of water dissolution in hydrocarbon crudes. Experimental data obtained from Griswold and Kasch (1942) ($\mathbf{\nabla}, \mathbf{X}$), Glandt and Chapman (1995) ($\mathbf{\Phi}, \mathbf{A}, \mathbf{\Xi}, \mathbf{\Phi}$) and measured data in this work ($\mathbf{\Phi}$).

the crudes shows the variation in experimental data from light petroleum fractions (kerosene) to very heavy bitumen (Cat Canyon) with a molecular weight of 678.

In addition to the experimental measurements, water dissolution in bitumen is modeled using Peng-Robinson equation of state (PR-EoS) (Peng and Robinson, 1976) coupled with Henry's law to treat the oleic and aqueous phases, respectively. Also, density and viscosity of watersaturated bitumen phase were measured to investigate the effect of water dissolution on density and viscosity of oleic phase. Several models and correlations on calculation of water solubility in bitumen and hydrocarbons can be found in literature (Amani et al., 2014; Oliveira et al., 2007; Zirrahi et al., 2015). A comprehensive literature review can be found from Amani et al. (2014) and Oliveira et al. (2007).

The rest of this paper is organized as follows: first, experimental apparatus and procedure is presented. Then, thermodynamic modeling is described followed by results and discussion section. The final part is summary and conclusion.

2. Experimental apparatus

To measure solubility of water in bitumen an experimental set-up was designed and fabricated as shown in Fig. 2. This figure shows schematic diagram of the experimental set-up. The main part of the apparatus is the equilibrium cell (5) made of stainless steel. This cell is placed in a Blue M oven to maintain a constant temperature. An injection cell (4) was used to inject water into the equilibrium cell. Using a Quizix pump, water was injected into the equilibrium cell to keep the pressure constant. Also, the pump was used to discharge the bitumen from the equilibrium cell and sampling from bitumen phase.

To evenly mix water and bitumen and saturate the bitumen phase, a mixing mechanism was applied where a stainless steel ball was placed inside the equilibrium cell to accelerate the equilibrium time. The equilibrium cell was designed to be able to rotate 180 °C. At low temperatures, density of water can be higher or lower than bitumen (Prakoso et al., 2016). Our bitumen sample showed lower density than water at low temperature conditions. Thus, bitumen is more buoyant and is the upper phase in equilibrium cell. When temperature increases to higher than 127 °C (400 K), there is an inversion between light and dense phases such that water phase becomes less dense than bitumen and floats on top of bitumen.

Viscosity and density of bitumen phase were measured using an inline viscometer (8) and a densitometer (7). A factory calibrated Cambridge viscometer was used to measure the viscosity. This viscometer was calibrated for temperatures up to 200 °C (473 K) and pressures up to 10.2 MPa. Evaluation of this viscometer to measure the

viscosity of hydrocarbons reveals an inaccuracy of less than 5%. Density measurement was carried out using an Anton Paar densitometer (Model DMA HPM) with accuracy of 0.001-0.0001 g/cm³ applicable for the density range of $0-3 \text{ g/cm}^3$. The working temperatures and pressures for the density meter are up to 473 K and 70 MPa, respectively. To evaluate the fabricated PVT system, vapor-liquid equilibrium properties of CO₂-1-propanol system was measured and compared with the experimental data of Secuianu et al. (2008). Experimental CO₂ solubility in 1-propanol was re-measured with deviation less than 4%. Capability of PVT system to measure the solubility and thermo-physical properties of bitumen containing systems was examined using bitumen-ethane system. Solubility of ethane in MacKav River bitumen as well as density and viscosity of bitumenrich phase were measured and compared with experimental data reported by Nourozieh. (2013) Deviations less than 5% for solubility data, 1% for density data and 5% for viscosity data were observed. More details on PVT apparatus validation can be found from Zirrahi (2016).

To displace the bitumen rich phase from the equilibrium cell (5) to cell (6), water was injected from the transfer cell (4) into the equilibrium cell while cell (6) was the receiving cell at constant pressure. Sampling cell (9) was used to take the sample from bitumen phase for solubility measurements. Solubility of water was measured using Karl-Fischer titration (Fischer, 1935). Tetrahydrofuran (THF) was used as the solvent for solubility measurements. THF can dissolve both water and bitumen and make a homogenous mixture. A Karl Fischer coulometric titrator model C20 made by Mettler Toledo Co. was used. The Karl-Fischer does not require calibration and can use samples that are less than 1 ml.

To carry out each experiment first the lines and cells were washed with toluene followed by acetone. Then, they were dried using air. At 90 °C (363.15 K), 200 ml of bitumen and 200 ml of water were charged into the equilibrium cell. Then, the equilibrium cell was vacuumed to remove the air. At 90 °C (363.15 K) and vacuumed condition, water boiled and water vapor filled the empty space of the equilibrium cell. Then, vacuum was turned off and water was injected into equilibrium cell to fill the cell and reaching to the desired pressure. After reaching to the desired temperature, equilibrium cell was rocked for 4-5 h. After rocking, the phases in the cell were allowed to separate overnight. To discharge the bitumen from the equilibrium cell and measure its properties, first the line from equilibrium cell to receiving cell (6) was filled with water. Then the valve between receiving and equilibrium cell was opened. Bitumen was discharged by injection of water from cell (4) and receiving with cell (6). While bitumen was discharging from the equilibrium cell, its viscosity and density were measured. About 5-7 ml of bitumen was taken using sampling cell (9) for solubility measurements.

To measure water solubility in bitumen the bitumen sample was dissolved in 150 ml of THF. Then, water content of the solution was determined using Karl-Fischer titration method. For each experiment, water content of THF was measured. Water content of bitumen is calculated using material balance as:

$$(W_{THF} + W_{Bitumen})wt_m = W_{THF}wt_{THF} + W_{Bitumen}wt_{Bitumen}$$
(1)

where W is the mass, wt is the water content. Weight percent of the dissolved water in bitumen ($wt_{Bitumen}$) is calculated as:

$$wt_{Bitumen} = \frac{(W_{THF} + W_{Bitumen})wt_m - W_{THF}wt_{THF}}{W_{Bitumen}}$$
(2)

where wt_m is the water content of mixture of bitumen and THF measured using Karl-Fischer. $W_{Bitumen}$ is the weight of bitumen sample. wt_{THF} is the water content of THF used as the blank in the mixture. Water content of THF has been measured each time before mixing it with bitumen. All the experiments were repeated two times and average values for viscosity and density were reported. In each test, two samples were taken for solubility measurements. Karl-Fischer

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