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Asphaltene precipitation, flocculation and deposition during solvent injection at elevated temperatures for heavy oil recovery

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HIGHLIGHTS

- Asphaltene flocculation and cluster formation with two different oil compositions were determined.
- The influence of temperature and pressure was investigated for both heavy oil samples (A and B).
- The effect of different types of light hydrocarbons as a solvent on asphaltene agglomeration was also studied.
- The thickness of the deposited asphaltene was measured.
- The thickness systematically increased with deceasing carbon number of the solvent.

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ABSTRACT

Asphaltene destabilization during solvent-based heavy oil and bitumen recovery applications is a common problem due to continuous changes of temperature, pressure, and oil composition. The effects of these characteristics on the recovery performance should be investigated for a wide range of solvent and oil types. In this paper, two heavy oil samples from fields in Alberta, Canada were destabilized using three different types of paraffin: propane, *n*-hexane, and *n*-decane. The solvent-based process was conducted at different reservoir conditions with alterations made to the temperature, pressure, and oil composition to determine the effect on asphaltene flocculation in the produced fluid and its deposition on the rock surface. Initially, experiments were carried out using a pressure, volume, and temperature (PVT) cell at different reservoir pressures and under different temperature conditions. Next, a Focused Ion Beam (FIB) and Scanning Electron Microscope (SEM) were used to characterize the morphology of the organic deposition on the glass beads surface through core flooding experiments. The results obtained through these two sets of experiments showed that temperature, pressure and oil compositions have a critical influence on asphaltene solubility. The PVT cell experiments and organic deposition surface roughness calculations were fundamentally important to explain the plugging formation in the reservoir under different operational conditions and with different oil types.

1. Introduction

The solvent-based injection processes improve heavy-oil production through the reduction of viscosity and capillarity forces, and the segregation of gravity drainage [7,9]. Molecular diffusion and oil dilution are two physicochemical mechanisms that take place during this process [7,25,26,9]. Viscosity reduction (and thereby oil mobility increase), via in situ upgrading, mainly occurs due to a decrease in the asphaltene solubility of oil.

Asphaltene has the highest molecular weight and is the most polar constituent from crude oil [25]. Asphaltene precipitation takes place due to the injection of light hydrocarbon solvent (e.g., propane, *n*-heptane, *n*-pentane, etc.), which usually has a surface tension lower than 25 dyne/cm at 25 °C; above this number the asphaltene becomes soluble in fluid (e.g., pyridine, toluene, benzene, etc.) [25]. Asphaltene solubility may decrease if resins are preferentially dissolved in the oil or solvent is added [3]. Hence, solvent selection based on application temperature and pressure values is one of the challenges in designing solvent-based processes.

Several studies related to pressure depletion processes showed that asphaltene solubility depends on oil composition, temperature, pressure, and solvent power. At high pressure conditions, the effects of pressure and oil composition are greater than the effect of temperature [14,21]. The effect of pressure on asphaltene flocculation is mostly placed at a pressure greater than the fluid

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saturation pressure and that maximum flocculation takes place at the saturation point [17,10,14,21]. Almehaideb [2] found that the increment of pressure from 101.31 kPa to 19,305 kPa decreases the asphaltene precipitation, however, from 24,131.6 kPa to 37,921.2 kPa the asphaltene precipitation increases because the values are closer to the saturation point of the fluid. On the other hand, Hilderbrand and Scott [15], Hirschberg et al. [16], and Andersen and Speight [3] showed that asphaltene precipitation depends on the temperature and pressure ranges of operation, not only in the pressure. They concluded that asphaltene solubility parameter decrease when the temperature and pressure start to decline.

Carbon number for the solvent is also an important parameter in this process. The refinery and pipe-line industries investigated on the best carbon number for deasphalting the crude oil for effective heavy oil/bitumen upgrading and transportation, respectively. Ferworn et al. [12], Hammami et al. [14] and Speight [25] observed that when the carbon number of the solvent decreases, the asphaltene flocculation and particle size increases. For example, asphaltenes and resins are insoluble in propane and butane and as a consequence of this, those solvents precipitate the two most polar compounds from crude oil (asphaltene and resin) [5,6,3]. On the contrary, *n*-heptane has a lower capability in the precipitation of the heavy ends, which results in less viscosity reduction compared to propane and butane [6,3].

Porous medium studies found that organic deposition (asphaltene and resins) takes place in the reservoir. Subsequently, cluster formations from this organic deposition can change the rock surface and permeability of the reservoir. However, it has not been clear until now how organic deposition plugs the porous median and how the organic deposition may be avoided or minimized using optimal operational conditions and different types of solvent. Redford and McKay [22] concluded that the use of solvents (propane and *n*-pentane) and steam injection in highly asphaltic crude, such as Albertan bitumen, does not lead to an appreciable loss in permeability. Butler and Jiang [8] studied the oil production effect after injecting solvents at 21–27 °C and 206–2068 kPa (butane or propane mixtures with a non-condensible gas, methane) and concluded that a high-temperature, high-pressure, and high-solvent/oil ratio increases oil production. They also reported a higher recovery factor using propane than butane or a mixture of both. Haghighat and Maini [13] carried out experiments using propane and butane as solvents at room temperature and at a pressure range of 750–850 kPa. They concluded that oil production with both solvents was reduced due to asphaltene deposition on the rock surface. Moreno and Babadagli [18,19] observed an increase in heavy-oil production when the carbon number of the solvent increased from C_3 to C_{15} due to the asphaltene solubility effect.

The solvent injection process can be an efficient process if the optimal type of solvent is utilized and ideal operational conditions are created. The solubility of fluid is the key parameter to developing this technology. As seen above, most of the studies on solvent dissolution capability of asphaltenes focused on different pressure conditions. Temperature is also a critical factor, especially in Canadian heavy-oil systems as the pressures in these reservoirs are rather low due to shallowness and solvents had to be used with steam for a more effective and efficient process. Therefore, it is critical to determine the role of pressure and temperatures that are compatible with this kind of heavy-oil reservoirs for different solvent types to determine the ideal solvent for heavy-oil recovery at elevated temperatures.

In order to understand the behavior of the asphaltene precipitation and flocculation (agglomeration) in the fluid when the operational conditions, solvent type, and oil type are changed, experiments were carried out using an optical pressure, volume, and temperature (PVT) cell at diverse pressures (1378–2068 kPa), and temperatures (40–120 °C) for two types of heavy-oil (8.6 °API and 10.28 °API). The asphaltene flocculation was calculated for the different operational conditions and the agglomeration and cluster formation were evaluated under the optical microscope. In order to establish the optimal injection conditions, the thickness measurements of deposited asphaltene from solvent displacement experiments for the same temperature and pressure ranges and solvent types were carried out under the focused ion bean-scanning electron microscope (FIB/SEM). The PVT cell and porous medium experiments were compared and the optimal operational conditions were established. The PVT cell experiment results were observed to be fundamentally important to explain the plugging formation in the reservoir at different operational conditions.

2. Experimental

2.1. Materials

The asphaltene precipitation from two heavy-oil samples, taken from two different fields located in Alberta, Canada was conducted using three *n*-alkane type solvent (C_3H_8, C_6H_{12} and $C_{10}H_{22}$). The purities of *n*-alkanes used as precipitants were 99.5 wt%, 99.9 wt% and 99.6 wt%. Correspondingly, the standard test method for the determination of asphaltenes (*n*-heptane insoluble) in crude petroleum and petroleum products (IP-143) was followed to determine the original asphaltene content of the two oil samples (Table 1). In addition, the carbon number distribution from both heavy oil samples was determined using the boiling point distribution of crude oil and vacuum residues (ASTM D7169) (Fig. 1). The envelopes from the dead oil are also presented in Fig. 2. Other important properties of the heavy oil samples, including elementary analysis (CHNS), asphaltene precipitation (*n*-heptane 99.4 wt% pure), API gravity, and SARA analysis, are presented in Table 1.

2.2. Experimental apparatus

The asphaltene precipitation at different operational conditions was carried out using a high-pressure and high temperature

Table 1
Heavy oil properties from two different oil samples (A and B).

	Oil sample A	Oil sample B
Heavy oil properties-ASTM D2007, IP 143 and ASTM D2549		
Saturates (wt%)	17.24	19.45
Aromatics(wt%)	38.60	45.60
Resin (wt%)	32.66	25.34
Asphaltene (wt%)	11.50	9.60
Heavy oil elementary analysis-ASTM D7578		
Carbon (wt%)	84.45	81.92
Hydrogen (wt%)	9.731	10.31
Sulfur (wt%)	3.715	3.536
Nitrogen (wt%)	0.553	0.6
Asphaltene elementary analysis-ASTM D7578		
Carbon (wt%)	82.06	79.6
Hydrogen (wt%)	7.957	7.095
Sulfur (wt%)	7.431	8.22
Nitrogen (wt%)	0.946	1.47
API gravity at 15.5 °C		
°API	8.67	10.28
Density (g/cm^3)		
25 °C	1.003	0.9919
40 °C	0.9959	0.9767
70 °C	0.9774	0.9503
Viscosity (cP)		
25 °C	87,651	20,918
40 °C	13,298	3571
70 °C	1450	421.3