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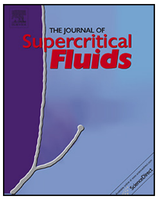

Supercritical extraction of crude oil by methanol- and ethanol-modified carbon dioxide

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ABSTRACT

The effect of ethanol and methanol cosolvents on the extraction yield and kinetics of crude oil originating from the Halfdan field of the North Sea by supercritical carbon dioxide was investigated across a pressure range of 20–60 MPa under a fixed temperature of 60 °C. Results inform that the pure carbon dioxide recovery varied between 43 and 77% while the recovery of the liquid phase of oil ranged between 22 and 56% across the entire pressure range. Using ethanol- and methanol-modified CO_2, the total recovery yield increased significantly averaging an additional 18.2% and 19.4% respectively when compared to pure carbon dioxide. The ethanol addition improved the recovery of the liquid phase of oil averaging 9.6% while the methanol addition improved it to 7.3% across the entire pressure range.

Study of the kinetics of extraction process indicated that heavier fractions were extracted faster with the ethanol- compared to the methanol-modified CO_2. GC–MS TIC chromatographic analysis of the extracted oil fractions showed that the extraction of C_{19}-C_{30} single carbon number groups with the addition of methanol is more dependent on pressure. Predominantly, ethanol addition was more efficient in extraction of C_{17}-C_{38} single carbon number groups while methanol contributed more in extraction of C_7-C_9 SCN groups.

1. Introduction

Carbon dioxide in a supercritical state (SC-CO_2) is implemented as a solvent for extraction in various chemical engineering processes and for enhanced oil recovery. The crude oil interaction with dense carbon dioxide depends predominantly on oil composition, temperature and pressure. The oil recovery improves as pressure rises at increasing density of carbon dioxide achieving maximum at miscibility conditions which occur in liquid–liquid or vapor–liquid–liquid regions [1]. The composition of oil fractions extracted by SC-CO_2 varies with pressure. At lower pressures, solvent dilutes more light ends that are in situ upgraded and have a lower density than the initial crude oil and more market value than heavy ends [2]. However, due to such selective extraction, the problem of asphaltene precipitation can arise in the reservoir. In this case, the deposited asphaltenes cause severe reservoir and wellbore plugging, downstream surface separation and treatment problems, wettability alteration, and significant reduction of the oil recovery [3].

Dehghan et al. [2] has shown that the amount of asphaltene deposition decreases as the molecular weight of the solvent increases because asphaltenes are less stable in low molecular weight solvent. The molecular weight of the solvent and the sweep efficiency of the method can be increased by adding small amounts of chemicals, generally called co-solvents, to modify the carbon dioxide. The most obvious solution is to identify additives that could improve the density and viscosity of the CO_2 or the extraction process via other mechanisms. This has been recognized as a Game-Changing technology for over 25 years, but has yet to be fully developed [4]. The recent rekindling of interest in the technique questions the selection and/or design of additives that are soluble in both SC-CO_2 and oil [5–7].

Various types of co-solvents to CO_2 were tested for chemical engineering processes based on their capabilities to specific interaction or density effect. It is generally accepted that chemicals having similar solubility parameters are optimal to consider as additive modifiers [8].

For volatile components, solubility parameters can usually be calculated with relative ease and accuracy [9]. Methane and nitrogen are known solvents in the petroleum industry; hexane, propane and butane are also used for the extraction of heavy oils. Their addition to CO_2 entails an increase of the solvent density [10] and, therefore, its capacity to solubilize substances. However, this solution is potentially more challenging due to the inherent complications of using the gases, e.g. in process handling as well as supplying.

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Traditionally, the choices of co-solvents are liquids that can vaporize in CO_2. Solvent testing strategies, such as the Kauri–Butanol test and predictions based on solubility parameters from regular solution (or Scatchard–Hildebrand) theory and its extensions, can result in poor solvent selection Lucia et al. [11]. Other procedures suggest that solubility parameters of non-volatile solutes are determined by measuring intrinsic viscosity or are based on the choice of solvent resulting in the lowest solvent/substance, e.g. Gibbs free energy of mixing for a given composition [12]. However, of the methods available, none is considered simple. This results in the application of a generic solution theory difficult and potentially inaccurate.

Presumably, those liquids which are soluble with oil could be also effective when introduced by SC-CO_2. Different author [12–22] have studied multi-component systems for chemical engineering processes positing how solute–solute or solute–solvent interactions in the supercritical fluid extraction process can lead to higher solubility of the components relative to their binary system, especially for solutes having a good hydrogen-bonding potential. Among the most studied additives are methanol and ethanol, which are selected because of their capacity to form hydrogen bonds either as a donor or acceptor [23–26].

In this study, the effect of methanol and ethanol modification to supercritical carbon dioxide on the oil extraction yield and kinetics in the broad range of pressure is investigated. The extracted oil fractions are analyzed by chromatographic analysis.

2. Materials and experimental procedure

2.1. Materials

The oil for the experiment was supplied by Maersk Oil from the Halfdan oilfield of the North Sea. According to ASTM D 4052 [27] the oil density at 15 °C (dry) is 0.8573 kg/L. The 99.9% pure carbon dioxide was supplied by Strandmollen A/S, Denmark. Ethanol and methanol, having 99.9% purity, were purchased from VWR Prolab. Multi Line 80/20% viscose/polypropylene towels of 9.5 cm × 9.5 cm size and weighing 5 g were used as carriers for the crude oil to avoid leaking and to assure that the oil was extracted instead of displaced.

2.2. Preparation of the sample

To prepare the sample, the towels were soaked in crude oil for 48 h in order to achieve the required saturation. To ensure a satisfactory saturation level had been achieved, excess oil was stripped from the towels after the 48 h and the towels reweighed to assure that 40 g of crude oil had been absorbed. Afterwards, the sample was put into the extractor vessel to commence the experiment.

2.3. Apparatus description

The extraction experiments were conducted using commercial high pressure extractor Spe-ed SFE, shown in Fig. 1 with more operational details described in [28]. The extractor vessel (7) containing the sample (9) was placed into the oven (8) of SFE vertically, and closed tightly on both ends by cap-ends. Inlet (2) and outlet (10) valves were closed. As soon as the system achieved the required temperature of 60 °C by heating, inlet valve (2) of the system was opened, and CO_2 was fed into the system from storage tank (1) continuously by pump (4) to attain the required pressure. Meanwhile, empty test tubes were weighed before the collection of the extracted liquid phase of oil. After 30 min, outlet (10) and vent valve (11) were opened to collect the extracted oil into the test tubes. The extraction of crude oil was terminated when it was visually observed that no further extracted crude oil was being collected.

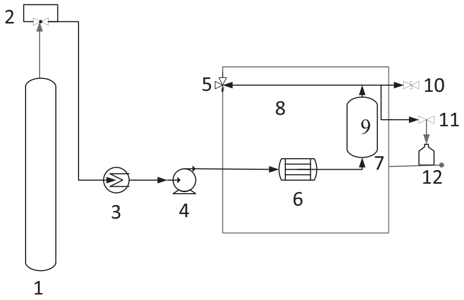

Fig. 1. Flow sheet diagram for supercritical fluid extractor: (1) CO_2 Storage tank, (2) CO_2 outlet valve, (3) cooler, (4) pump, (5) vent valve, (6) pre-heat coil, (7) extractor vessel, (8) oven, (9) sample (towel saturated with oil), (10) outlet valve, (11) exit valve, (12) sample collector.

Afterwards, the inlet valve (2) was closed and outlet valves (10, 11) were opened till CO_2 from the system vanished completely. The towel with the remaining oil was taken out from the extractor vessel (7) and weighed for calculations. The extractor vessel was cleaned properly in order to make it ready for the next experiment. The kinetics experiments were performed by collecting the extract every 4 min for 16 min. The extracted oil samples were collected in the several test tubes and weighed by using a balance. In further analysis of the oil extracts, the samples from first and second test tubes would be compared.

2.4. Application of co-solvent

The extraction of oil by CO_2 was tested at 9 pressure values in the range of pressure from 20 to 60 MPa at a fixed value of temperature of 60 °C. The tests were run in a random order to eliminate various types of biases. The first experiment was conducted with pure carbon dioxide to be used as a blank experiment for the comparison. The other tests in the same pressure range were performed by modified CO_2 with the addition of ethanol and methanol as co-solvents.

To bring the co-solvent into the system of oil and carbon dioxide, 3 g of methanol or ethanol was put on a cotton ball and set at the bottom of the reactor in the entry of CO_2 flow after oil-saturated towel was placed in it. When CO_2 was injected into the reactor, the co-solvent vaporized and interacted with the crude oil.

2.5. Chromatographic analysis

The chromatographic analysis of the crude oil sample and of all the samples collected in the test tubes in the process of extraction with and without addition of co-solvents was performed on a GC–MS system consisting of gas chromatograph GC-CP-3800 and a mass spectrometer MS-ION TRAP 2000. Separations were performed on a Factor Four VF-5ms capillary column (20 × 0.15 × 0.39) from Varian (Middelburg, The Netherlands). The initial temperature in the GC oven was 50 °C for 2 min, followed by an increase of the temperature up to 300 °C. The total time was 45 min. Helium was used as the carrier gas at a pressure of 20 psi. The split ratio was 100. The MS was operated in electron ionization mode. For the analysis, 0.5 ml of oil from each of the test tube with the extracted samples was diluted with approximately 1.5 ml of n-pentane.

2.6. Coloration analysis

In order to standardize coloration, the samples collected in the test tubes were photographed, and the obtained photos were analyzed using the RGB color mode of ImageJ software. The coloration was determined as a linear combination of red, green and blue represented with numbers/coordinates. The RGB descriptions of the samples are given in Table 1.