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Effect of temperature on crude oil extraction by SC-CO_2 at 40–70 °C and 40–60 MPa

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ABSTRACT

The extraction process of crude oil by supercritical CO_2 was simulated in a high pressure extractor at 40, 50, 60 and 70 °C, and at 20, 40 and 60 MPa in order to investigate the effect of temperature on oil recovery. The total recovery of oil increased by 30–40% at the pressure increase from 20 MPa to 60 MPa. The temperature effect on the total recovery at 40, 50 and 60 °C was insignificant while the total recovery increased by 10% as the temperature rose from 40 °C to 70 °C. The vapor recovery did not change substantially with the temperature and pressure increase at temperatures higher than 40 °C. The isotherms of liquid recovery formed a concave surface because of higher extraction results at 40 °C and 70 °C indicating a crossover pressure phenomenon. The fingerprints of the extracted oil fractions obtained by GC–MS chromatography at various pressures and temperatures exhibited a variety of shapes. A correlation was obtained between liquid oil recovery and sums of selective specific single carbon number groups. Lighter hydrocarbons of C_7-C_{10} group were representative at 20 MPa, intermediate hydrocarbons of C_{15}-C_{19} group at 40 MPa, and heavier hydrocarbons of C_{23}-C_{31} group at 60 MPa.

1. Introduction

1.1. CO_2 projects for the North Sea oil fields

Eighty-one active oilfields from the UK, the Norwegian and the Danish sectors of the North Sea have reserves higher than 73 Mbbl each. However, the European energy market faces the end of life of many of these oilfields which produce 73% of the crude oil in the European Economic Area (approximately 4 million barrels of oil daily) [1]. Decisions need to be taken for a number of oil fields to be either completely abandoned and the infrastructure dismantled, or to be kept operating through investments on improved oil recovery methods.

The combination of CO_2 injection (CO_2-EOR) and CO_2 storage (CCS) in the depleted oil fields can extend their lives significantly and remove large quantities of the greenhouse gas [2,3]. Because the majority of oil fields are offshore, major barriers to implementation of CO_2-EOR include the lack of availability of low cost CO_2 and the high cost of development of a CO_2 transport system [1].

Installation of the largest in the world CO_2 capture of the flue gases of a coal fired power station in Esbjerg, Denmark was initiated in 2006 but it has not been fulfilled. Meanwhile, more than 5000 km of pipeline already installed in the British part of the North Sea on the sea bed to bring gas from the gas fields can now be used to transport CO_2 for the injection into the depleted fields. Moreover, about 70% of Scotland's CO_2 emitters lie within 10–20 km of this pipeline, and can be linked in at low cost [4]. The CO_2 can also be delivered by vessels transporting the gas from Norway, Germany and Finland.

The technically achievable maximum potential for the 81 fields considered without taking into account the economic viability of the CO_2 projects was estimated as follows: 2.7 billion barrels (B bbl) (58% of the proven reserves) for the UK; 4.0 B bbl (38% of proven reserves) for Norway; 0.4 B bbl (28% of reserves) for Denmark [1].

1.2. Interaction of CO_2 and crude oil

CO_2 condenses into the oil and makes it lighter (condensing gas-drive); oil vaporizes into the CO_2 and makes it richer (vaporizing gas-drive) [5]. This continues until the gas is rich enough to be miscible with the oil. The miscibility of CO_2 and crude oil increases with rising pressure and depends on reservoir temperature and oil composition. The miscibility is considered independent of both the nature of the porous media and the velocity of displacement [6].

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Minimum miscibility pressure (MMP) which signifies the achievement of miscibility is typically determined as a breakover point on the curve of oil recovery obtained from experiments using slim tube filled with porous matter. Several other methods are also used for MMP determination. For example, equilibrium interfacial tension method [7] or acoustic method [8,9].

Various equations of state are used for the prediction of saturation pressure and MMP using single carbon number groups (SCN) [10–15]. Alston et al. [12] reported that the miscibility between crude oil and CO_2 is strongly related to reservoir temperature and oil composition, particularly C5 + molecular weight. Holm and Josendal [13] found that MMP was only affected by the type of hydrocarbons present in the range C5 to C30 fractions of the crude oil while the temperature only determines the pressure needed to achieve the required CO_2 densities. Yellig and Metcalfe [14] discovered a correlation as a straight line function of temperature but they found little significance of C7 + fractions on the MMP. The phase behaviour is more predictable at higher temperatures according to critical loci of various CO_2 + alkane groups, as noted by Enick et al. [10].

In general, the MMP increases steadily with increasing temperature and increasing oil molecular weight. Slim tube tests simulated by Bayat et al. [15], however, have shown that there might be no clear breakover points for heavier oil. Some of the curves gradually increased from 12 to 62 MPa without changing curvature, in the presence of co-solvents.

Experimental studies of CO_2 solubility in alkanes were undertaken by various authors for the purpose of numerical modelling of CO_2/crude oil systems [16]. Cismondi et al. [17], however, noted that modelling of the phase behaviour of such highly nonideal systems like crude oil have generally achieved only partially accurate results in the correlation of such data when considering wide ranges of temperature, pressure, and n-alkane molecular weight, despite the computational resources available nowadays. In addition, it is often quite difficult to identify trends regarding the effect of temperature, pressure, or n-alkane carbon number on mutual solubilities. Barros et al. [18] came to the conclusion that normal-alkanes can only approximately represent hydrocarbon fractions obtained by distillation.

Although extensive laboratory studies and field applications of supercritical CO_2 (SC-CO_2) flooding have been undertaken there are still questions which have to be addressed in understanding of crude oil/CO_2 behaviour. Because of the competing effect of pressure and temperature the dependency of phase behaviour from these two parameters is not straightforward. Several publications investigate crude oil/CO_2 systems at various temperatures and low pressures [7,13,17–21], but the data on the influence of temperature on SC-CO_2 extraction of crude oil at high pressures is scarce in the literature. The influence of the oil vapor phase on overall extraction results is also rarely investigated.

The investigation of a temperature effect on crude oil recovery in the present study was carried out using SC-CO_2 extractor over a large range of pressures (20, 40 and 60) MPa and at the temperatures of 40, 50, 60 and 70 °C. The extracted samples were analyzed by GC–MS chromatography in order to find relationships between the compositions of extracted oil fractions and extraction results.

2. Materials and methods

2.1. Materials

The 99.9% pure CO_2 was obtained from Strandmollen A/S, Denmark. Maersk Oil Company supplied the crude oil from the Halfdan oilfield (North Sea). The analyses of crude oil were made by Saybolt, a Division of Core Laboratories Sales N.V. The oil density is 0.8573 kg/L at 15 °C (ASTM D 4052), viscosity is 9163 mm^2/s at 20 °C (ASTM D 445). Initial boiling point was < 36 °C, and final boiling point was > 750 °C. The sulfur content is 0.261 mass% (ASTM D 2622) and nitrogen content is 1368 mg/kg (ASTM D 5762). Total acid number is 0.37 mg KOH/g (ASTM D 664). Towels of 9.5 cm × 9.5 cm consisting of 80% viscose and 20% polypropylene manufactured by Multi Line were used as carriers for crude oil.

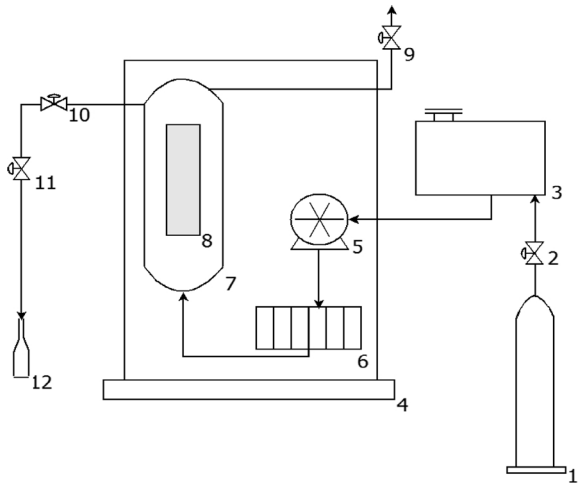

Fig. 1. Layout of the SC-CO_2 extraction system. 1- CO_2 gas cylinder, 2- gas cylinder control valve, 3- water cooler, 4- Experimental set up oven, 5-CO_2 compressor, 6- heater, 7- extraction cell, 8- sample, 9,10 – outlet valves, 11- flow control valve, 12 – test tube for oil collection.

2.2. Performance of experiment

All specific experimental details and explanations including use of towel as a carrying media, use of extractor, achievement of equilibrium and selection of operating modes can be found in our previous publications [22–24]. The experimental procedure is only briefly described in this study.

The samples are prepared from the towels of equal weight of 5 g saturated with 40 g of crude oil. The experiments are carried out using the high pressure extractor SFT-150 manufactured by Supercritical Fluid Technologies Inc., Newark, USA (Fig. 1). The CO_2 delivered from a CO_2 storage tank (1) passes through the water cooler (3) to the preheated extraction cell of 100 mL volume (7). The prepared sample is placed in the extraction cell and heated. Temperature and pressure are regulated using a gas compressor (5) and heating unit (6). As soon as the temperature increases, the CO_2 storage tank valve and CO_2 inlet valve are opened in order to pressurize the system at the gas flow rate of 150 mL/min.

As soon the desired pressure is reached, the valves are closed for the interaction between crude oil and CO_2 for 20 min that comprises the static mode. All valves (9, 10, 11) are closed while in a static mode. Afterwards, the outlet (10, 11) and vent (9) valves are opened to transport the extracted oil along the steel pipe into the collecting test tubes at flow rate 200 mL/min (12). The collection of extracted oil into test tubes occurs in dynamic mode during up to 20 min until the oil flow ceased. The experiments have been duplicated at all temperatures and the average difference between the two independent measurements is maximum 2%.

2.3. Numerical calculations of experimental results

The results of crude oil extraction by pure SC-CO_2 are represented by the total recovery, liquid recovery and vapor recovery or mass fractions of liquid and vapor phases. The total recovery *TR* is calculated as a ratio of the difference of weights of the towels before and after extraction to the initial oil amount contained in the towel of 40 g:

$$TR = \frac{W_{before} - W_{after}}{W_i} \cdot 100\% \quad (1)$$

The liquid recovery *LR* represents the collected liquid phase of oil