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Application of GC–MS chromatography for the analysis of the oil fractions extracted by supercritical CO_2 at high pressure

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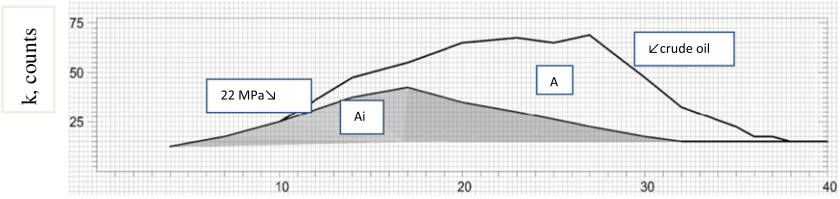
HIGHLIGHTS

- The extraction of crude oil by supercritical carbon dioxide was investigated at 22–56 MPa and 60 °C.
- The fingerprints of extracted oil fractions illustrate the stages of the extraction progression.
- The oil recovery obtained experimentally can be calculated from chromatograms.

GRAPHICAL ABSTRACT



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ABSTRACT

GC–MS chromatographic analysis has been applied for the investigation of the fractions of oil extracted by supercritical carbon dioxide at a temperature of 60 °C and at pressure values ranging from 22 to 56 MPa. The observations revealed, that the whole extraction process is clearly reflected in the chromatograms, demonstrating how the heavier hydrocarbon fractions were gradually involved in the extraction process. The shape of the chromatograms alters with increasing pressure from triangle to trapezoid, approaching the shape of the chromatogram of the crude oil. The observation of the fingerprints of chromatograms allows them to be used for the qualitative evaluation of extraction progression. It can also be noticed, that the area under the spectrum of the chromatograms of oil samples extracted at various pressures is increasing with an increase in pressure. The oil recoveries, evaluated as the ratio of the area under the spectrum or the baseline of the chromatogram of the sample extracted at the specific pressure value to the area under the spectrum or the baseline of the chromatogram of the crude oil, showed a close correlation with the oil recoveries obtained from the experiment. This allows the use of the chromatographic method for the quantitative evaluation of oil recovery.

1. Introduction

Solvent injection is greatly used in many enhanced oil recovery (EOR) processes [1–5]. The injections of hydrocarbon gases, nitrogen, carbon dioxide and their combinations are implemented to improve the sweep efficiency. When solvents are injected in the reservoir, they finger into the oil and spread in the reservoir by diffusion or dispersion [6]. The viscosity of oil decreases, diluted by the solvent miscible with oil. Achievement of miscibility between carbon dioxide and oil is determined from laboratory tests. CO_2 is injected into the reactor, under pressure, to displace oil. The results of the ratio of the extracted amount to the initial amount of oil in percents or parts of units (oil recovery) are plotted versus the values of the corresponding extraction pressure. The breakover point, as shown in Fig. 1, is defined as a Minimum Miscibility Pressure (MMP) [3]. Below the MMP, the extraction process is considered to be immiscible; whereas it is miscible above the MMP. The breakover point does not necessarily mean that full miscibility is achieved. According to Holm and Josendal, the MMP value should have a minimum recovery rate of 80% [4] to make the process economical. Very low values of recovery indicate that the gas injection will leave a lot of oil behind. The light oils have lower MMP values than heavy oils [2]. The presence of even an insignificant amount of

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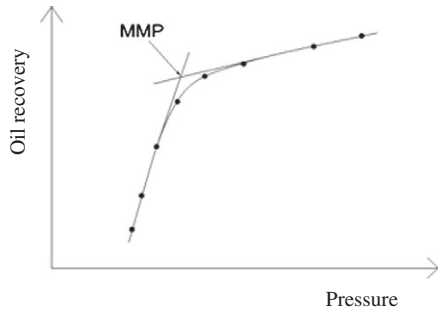

Fig. 1. Schematic graph of Minimum Miscibility Pressure (MMP) determination in slim tube experiment.

heavy components can increase the MMP notably. Ungerer et al., found that 1 mol% of heavy hydrocarbon may increase the dew point pressure by 20 MPa, in some cases [7].

The oil interaction with carbon dioxide, depending on oil composition, temperature, pressure and presence of other substances, can exhibit diverse and more complicated types of relation than that shown in Fig. 1. The composition of hydrocarbon fractions, extracted at different pressure values, varies. At lower pressures, solvents may dilute more light ends that are of greater value than heavy ends. The produced, diluted oil is upgraded in situ and has a lower density, as well as a higher market value, than the initial crude oil [6]. However, such selective extraction can cause the undesired problem of asphaltene precipitation in the reservoir. Dehghan et al., found that asphaltenes tend to precipitate more while mixing with a low molecular weight solvent, because they are less stable in low molecular weight environment. This problem may arise when MMP is not attained at the reservoir conditions. In addition, the oil is displaced immiscibly instead of expected miscible, the sweep efficiency worsens and oil production rates decrease. Therefore, there is a need in a mean to evaluate the degree of miscibility of oil and dense carbon dioxide that occurs in the oil formation. The chromatographic analysis of the oil samples produced seems to be an available way to observe the transformations that oil undergoes by solvent injection in CO_2 EOR. Whether such possibility exists should be investigated first in a laboratory experiment (see Table 1).

The change in oil compositions are studied by true boiling point (TBP) distillation and by measuring the properties of the collected fractions for hydrocarbon groups or individual components [8]. Because conventional distillation is time consuming and requires a large oil sample, simulated distillation by gas chromatography (GC) has been studied by several investigators [8–12] as a method for obtaining equivalent data. GC analysis can yield nearly identical results to true boiling point distillation in a short time, using only small samples of oil [12].

Chromatography is also routinely applied for oil characterization [13]. The uniqueness of oil from different oilfields is clearly reflected at the chromatographic fingerprints that have distinctive characteristics. The patterns are developed for the recognition of the oil from various originations and the phases of oil degradation [14,15]. The fingerprints and the composition of the weathered oils are often changed to such a great extent that they unrecognizably differ from the chromatograms of unweathered oil of the same type [16,17]. Presumably, in the same manner, the alterations in composition of crude oil undergoing enhanced oil recovery can be recognized from fingerprints of the extracted fractions of oil to obtain a quick means of the control for the fractions actually extracted by CO_2.

The purposes of this study included:

- Experimentation on oil extraction by supercritical carbon dioxide, to measure the amounts of extracted oil at different pressure values and to determine the breakover point.
- Analysis of extracted oil samples by GC–MS (gas chromatography–mass spectrometry), to obtain the fingerprints of oil fractions extracted at specific pressure values by supercritical CO_2 for qualitative evaluation of the fractions to trace the phases of displacement.
- Numerical comparison of the results of experiment and chromatographic analysis to find out whether chromatographic results can be used as a quantitative method for evaluation of the extraction rates.

Table 1
The results of the extraction rates from experiment and chromatography.

Pressure (MPa)	Extraction rates (p.u.)			
	Experiment		Chromatographic analysis	
	Collected	Calculated	Spectrum-based	Baseline based
22	0.05	0.15	0.18	0.5
27	0.13	0.22	0.48	0.57
35	0.13	0.22	0.49	0.7
40	0.13	0.25	0.54	0.7
45	0.09	0.22	0.51	0.69
50	0.16	0.27	0.64	0.82
56	0.48	0.75	0.89	0.85

2. Materials and experimental procedure

2.1. Materials and sample preparation

The 99.9% pure carbon dioxide was supplied by Strandmollen A/S, Denmark. The oil for experiment was supplied by Maersk Oil company from the North Sea oilfield. Analysis of crude oil were made by Saybolt, Division of Core Laboratories Sales N.V. According to ASTM D 4052, the oil density at 15 °C (dry) is 0.8573 kg/L and API gravity at 60 °F is 33.55 kg/L. According to ASTM D 445, viscosity at 20 °C $Q = 9163$ mm^2/s, viscosity at 40 °C $Q = 5138$ mm^2/s, viscosity at 50 °C $Q = 4177$ mm^2/s. Initial boiling point was <36 °C and final boiling point was >750 °C (ASTM D 5307) [18].

The towels of 9.5 cm × 9.5 cm consisting of 80% viscose, 20% polypropylene manufactured by Multi Line were used as carriers for crude oil to prevent oil leaking from vertically set reactor and to assure that the oil was extracted instead of displaced.

Towels of equal size, with weight 5 ± 0.5 g, were soaked in the oil for 2 days. The oil-saturated towels were weighed, and the excess oil removed, to ensure that the weight of the oil adsorbed was 40 g. Each towel was placed in the reactor for 30 min of interaction between CO_2 and oil, followed by 10 min of oil collection.

2.2. Apparatus description

The supercritical extractor Spe-ed SFE was used for the experiment. The scheme of the equipment and operational details are given in Fig. 2. The reactor (7), which is a thick steel tube, containing the sample (9) was placed into the extractor (8) of SFE vertically, and closed tightly on both ends by cap-ends. Inlet (2) and outlet (10) valves were closed. As soon 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) until the required pressure was achieved. The system was left for 30 min to equilibrate. Carbon dioxide was continuously delivered through the system by the pump (4) to attain the required pressure.

Afterwards, outlet (10) as well as vent valve (11) was opened to collect the extracted oil during approximately 15 min until it was visually observed that no further extracted crude oil was being