3D Model of Extraction of Oil from North Sea Fields by Supercritical Carbon Dioxide

Svetlana Rudyk*, Pavel Spirov, Erik Sogaard

Section of Chemical Engineering, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Campus Esbjerg, Denmark, 6700 Esbjerg, Niels Bohr vej 8, sr@bio.aau.dk

The extraction of North Sea oil from the oil saturated chalk samples by supercritical carbon dioxide was investigated to determine the pressure value, at which the highest amount of oil can be extracted. The pressure of extraction was gradually increased at every next test to check out how the extraction of lighter hydrocarbon fractions at lower pressure affect the oil recovery rate at higher pressure. The first serial test was conducted with three core chalk samples of equal size and each of a weight of 9 g. The samples were naturally saturated with oil at three values of temperature of 50°, 60° and 70°C. For comparison, the second serial test was conducted with three pure chalk samples of equal size and weight of 26 g saturated with the North Sea oil under vacuum in the laboratory at the same values of temperature. The results of experiments were represented as the surfaces in the coordinates of (Pressure, Amount of extracted oil, Temperature). 3D models revealed that the deviations in the graphs are not occasional. They form wavy surfaces where the folds of waves correspond to hydrocarbon fraction of certain compositions. The highest amounts of oil at all three temperature values in both tests were extracted at 18 MPa in average, where the graphs formed peaks, but the oil was very light, which means that the heavier hydrocarbon fractions were not extracted at such pressure value.

1. Introduction

Leaving behind the heavy components of oil in the oil reservoir is often mentioned as one of the disadvantages of carbon dioxide injection method. Specific hydrocarbon fractions are extracted at certain pressures. The higher the pressure, the more fractions are extracted. Carbon dioxide is supposed to be injected at the pressure above minimum miscibility pressure (MMP) determined as a breackover point in the graph of Recovery rate versus Pressure traditionally obtained from slim tube experiment (Danesh, 2007). Above MMP, significantly higher extraction does not occur at increasing pressure. Nevertheless, some heaviest fractions can remain unrecovered at MMP. It can be questioned how to optimize the conditions of better extraction of hydrocarbon fractions at moderate pressure. Of interest is also how the extraction of lighter components, needed for achieving miscibility, affects the extraction rates at higher pressure. That can be a matter of the technological scheme to apply: either to use one fixed value of elevated pressure to extract all the fractions, which can be extracted at these conditions, or gradually to increase pressure to extract higher fraction after the lighter components
have been extracted. In this experimental study, the oil extraction was investigated at increasing pressure values to see how the shortage of lighter components extracted earlier affects the extraction of the heavier components.

2. Materials and Methods

Experimental part consisted of three serial tests: 1) with naturally oil saturated core chalk samples, 2) with pure chalk samples saturated with oil in the laboratory, 3) determination of equilibrium time.

2.1 Experimental set-up

Supercritical extractor Spe-ed SFE was used for investigations as it is described in (Rudyk et al., 2009a). The oil-saturated sample was put in the heated extractor at the fixed values of temperature. The CO₂ was injected into the reactor until it reached planned pressure value. At such pressure, the sample remained during 30 minutes for interaction between CO₂ and oil, followed by 15 minutes of collection of the extracted oil in the test tubes. Then, the pressure value was increased to the next planned value, and the procedure was repeated.

2.2 Presentation of Results

The collection test tubes were weighed before and after each test at certain pressure. The recovered amount of oil was calculated as a subtraction of the weight of collection tube before extraction test from the weight after. The amount of extracted oil was plotted versus corresponding pressure values. 3D models of both tests were performed using Rhinoceros program.

3. Experimental part

3.1. Tests with naturally oil saturated core samples

Naturally oil saturated core chalk sample from the Dan field from the depth of 2700 m was cut into three pieces of equal size and 9 g of weight each for the tests at three temperature values of 50°, 60° and 70°C in the range of pressures from 10 to 30 MPa. The results of the tests are shown in Fig.1a. The graphs have irregular shapes. The peaks matching to the highest rates of recovery were observed at 18 MPa at 50°C and 60°C, and 17 MPa at 70°C. The recovery rates in the range of pressure from 20 to 25 MPa are close in amount at all three temperatures, but the deviations in the curves do not coincide. 3D model of the process in Fig.1b shows that the curves formed a wavy surface, and that the number of peaks and bends are equal at all the temperatures. The small size of the samples and the interval of only 1 MPa between the neighboring values of pressure could make the extraction process very sensitive to influence of oscillation and other occasional effects. The distribution of oil throughout the sample can be also uneven due to the long period of preservation of the core and aging of the oil creating the deviations observed.

3.2. Tests with chalk samples saturated with oil in the laboratory vacuum set-up

The second serial test was a repetition of the first but with the bigger samples and at interval of 2-3 MPa between neighboring values of pressure. The tests were conducted
with three tight pure chalk samples of 26 g of weight each saturated with oil in a vacuum set-up in the laboratory as described in (Rudyk et al., 2009b). Maersk Oil Company provided the oil for experiment. During the time of saturation approximately 4.1-4.2 g of oil imbibed in each chalk sample. The chalk samples were investigated at 50°C, 60°C and 70°C of temperature in the longer range of pressure from 12 to 43 MPa. The graphs again formed irregular peaks and bends. The more similarity is between graphs for 50°C and 70°C. The graph at 60°C has more deviations, which do not coincide with the deviations in the curves at the other two temperature values (Fig.2a). At 18 MPa the

![Graph](image)

Fig.1. Results of the oil extraction from core samples at various pressures and temperatures(first serial test): a - 2D presentation, b - 3D model.

peaks for all the three temperatures coincide. The increase in oil recovery rates in the range of 12-18 MPa is temperature dependent. It is more gradual at 50°C and sharp at 70°C with the graph at 60°C between. The visual observation of the oil samples
extracted at various pressure values revealed that they differ in color and viscosity. Below 18 MPa, the color of the samples is yellow, but it is almost white at 18 and 20 MPa. The intensity of color also increases at further increasing pressure to dark orange at 45 MPa. During the whole process of extraction, totally 1.31 g of oil was extracted at 50°C, 1.66 g at 60°C and 1.62 g at 70°C.

Fig. 2. Results of the oil extraction from chalk samples saturated with oil at the laboratory conditions at various pressures and temperatures (second serial test): a - 2D presentation, b - 3D model.

3D model in Fig. 2b demonstrates that seemingly irregular deviations in the graphs are not occasional. They form wavy surface evidently reflecting the deviations in composition. This conclusion was supported by visual and chromatographic observations of the extracted oil samples.
3.3. Equilibrium test
To exclude the possible effect of the duration of the time of interaction on the results of experiment, the third test was conducted for the purpose to check whether 30 minutes of gas injection was sufficient to achieve equilibrium. The chalk sample of 26 g of weight used for the test at 60°C in the second serial test was saturated with oil in vacuum set-up again. The test was repeated in the range of pressure from 10 to 34 MPa at the temperature of 60°C during 90 minutes of interaction between CO₂ and oil. The graphs from previous test at 30 minutes of injection and from this test at 90 minutes were plotted together as shown in Fig.3. It is seen that 90 minutes curve follows many of the features of the deviations of 30 minutes curve. Three times longer period of interaction did not lead to the significant increment of oil recovery. Totally, 1.12 g was extracted during 30 minutes of interaction and 1.19 g during 90 minutes.

![Graph](image)

*Fig.3. Results of equilibrium test at 60°C: oil recovery at 30 minutes and 90 minutes of CO₂ injection.*

4. Discussion
The character of the graphs shown in Fig.1 and Fig.2 obtained from our extraction tests differs from the similar graphs obtained from the slim tube experiments (Firoozabadi, 1999). There can be different reasons for the formation of high peaks at 18 MPa and deviations in the curves of our experiments: equilibrium time is not achieved, aging of oil, effect of chalk matrix, effect of the size of samples, absence of lighter components extracted at previous pressures, or particularities of the phase behavior dependent on oil composition. To find out, which of those reasons lead to the formation of the mentioned above curves and peaks, several comparisons were made. The achievement of equilibrium was checked as described in paragraph 3.3 and showed that it was achieved in 30 minutes. The complexity of the structure of porous space in carbonate rocks could play role in the first test, as the oil was trapped in the rocks during long geological time, but in the second test all the oil was movable. The extraction results from the samples of different sizes (9 g and 26 g) have shown the formation of peaks in both cases. 3D models revealed that irregular deviations in the graphs form wavy
surfaces. The folds of the waves corresponding to certain hydrocarbon fractions can appear because of previous extraction of lighter components, but the peaks cannot be formed for the same reason, as the amount of oil extracted below 18 MPa was negligible. In our previous work [Rudyk et al., 2010], the experiment was performed with only oil excluding probable effect of rock matrix. At each pressure value, the new portion of oil was put in the extractor to ensure that no light components were extracted before. A similar peak was also observed at 20 MPa. Several authors [Metcalfe and Yarborough, 1979; Stallup, 1992; Ryosuke, 2009] published data about phase behavior of the oils, where the liquid-vapor phase was formed in the breakover points. That phase can contribute in higher extraction rate. Probably, the formation of peaks is a distinctive characteristic of the North Sea oil depending on composition.

5. Conclusions
1. 3D models of extraction of oil by CO2 made evident that the deviations on the graphs of Oil recovery versus Pressure match to the areas of the different oil fractions. These areas are similar from both experiments - with naturally oil saturated core samples and laboratory oil saturated chalks.
2. North Sea oils have specific feature of forming a peak at 18 MPa in the graph of Oil recovery versus Pressure.

References
Firoozabadi A., 1999, Gibbs free energy surface analysis, Thermodynamics of hydrocarbon reservoirs, 220.
Rudyk S., Spirov P., Sogaard E., 2010, Extraction of Heavy Oil by Supercritical Carbon Dioxide, CHISA, Symposium on Supercritical Fluid Applications, C6.4, Serial number 0310.