

## DETERMINATION OF MINIMUM MISCIBILITY PRESSURE IN SUPERCRITICAL REACTOR USING OIL SATURATED SAMPLE

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The main parameter for the determination if CO<sub>2</sub> injection can be applied for a specific oil field is a Minimum Miscibility Pressure (MMP), the lowest pressure for which a gas can develop miscibility through a multi contact process with a given reservoir oil at the reservoir temperature. The oil formation to which the process is applied must be operated at or above the MMP. Before field trial this parameter is to be determined at the laboratory traditionally in a slim tube or raising bubble experiments. In order to investigate the MMP, we suggest another method by using a supercritical reactor *Spe-ed SFE* and the oil saturated natural rock samples. The clean chalk sample was saturated with oil from the Dan field under vacuum. The CO<sub>2</sub> gas was injected to the extractor vessel with the sample in it at increasing pressure. The oil displaced such way was collected and measured. The volume of extracted oil was plotted against the increasing pressure. The form of the graph is similar to that of obtained from the slim tube experiment or the solubility of the chemicals in supercritical carbon dioxide. Following the breakover point criterion the MMP read from the plot is equal to 20 MPa at 80°C. Chromatographic analysis of the oil samples extracted at various pressure values showed that the spectra for the pressure values below 20 MPa differ from the spectra for all the values of pressure above it. This allows the distinction of the MMP value based on the shape of chromatogram.

### 1. INTRODUCTION

After application of the conventional methods of oil recovery which include natural drive mechanisms and water injection, 2/3 of oil deposits on the average in the world remain in the subsoil. If to calculate the entire oil amount left behind in the abandoned oil fields during the whole history of petroleum development, and recover, there will be enough oil for quite a long period of time. To extract additional oil many tertiary methods exist. One of them is an injection of carbon dioxide in the oil formation. Carbon dioxide at supercritical conditions is often used for the extraction of the valuable chemical substances from solids, especially from aromatic, medicinal, and spice plants (Souza et al.,) due to its classification as a green technology, strong solvent properties and applicability at intermediate temperatures. Wider implementation of the CO<sub>2</sub> injection as an oil recovery method will also contribute more in the reduction of green house effect representing how utilization of carbon dioxide can be combined with the rational usage of natural resources and the saving of energy sources. In the petroleum industry CO<sub>2</sub> gas should be injected into the oil saturated layer above the pressure called minimum miscibility pressure (MMP) to provide effective oil extraction. As a complex compound the oil is miscible with carbon dioxide through multiply contact miscibility when light and intermediate fractions are involved in the extraction of heavier fractions. In this process, the CO<sub>2</sub> first mixes with the intermediate fraction of the oil and form a new mixture with a composition that is miscible with more of the heavy components until eventually the two fluids are completely miscible. When the miscibility between carbon dioxide and oil is achieved, the viscosity of the oil reduces, which makes it flow faster and easier.

Before any field operations are started the value of this effective pressure should be found through the laboratory experiments. The traditional ways of Minimum Miscibility Pressure (MMP) determination in the petroleum industry are raising bubble apparatus and slim-tube specially designed for this purpose. In raising bubble experiment the process of miscibility is observed visually in a glass chamber when carbon dioxide begins to interact with oil. Miscibility visually looks as the differences between two component systems disappear. It was noted that the interpretation of the results from this experiment is complicated and requires participation of an experienced observer (Stalkup, 1992).

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For slim tube experiment 12m spiral tube is filled with sandstone or glass beads and saturated with oil. The carbon dioxide is injected at increasing pressure. The oil recovered such way is collected, measured and plotted as a function of operating pressure. In the early literature, MMP was the pressure at which ultimate recovery approached 100%. In the later literature, MMP was determined as a breakover point on the plot of the oil recovery versus pressure (Orr, 1982). Above that breakover point, the increase of pressure doesn't contribute in significantly higher oil recovery. The breakover point criterion not always signifies most effective displacement and achievement of full miscibility. Other operators define MMP as a combination of the two criteria: breakover point and the oil recovery of 80-90 %.

Many authors underlined the complexity of oil extraction by carbon dioxide from carbonate rocks due to the complexity of the porous structure of the carbonates. In the sandstones porous space is more like a system of channels. But in the chalk rocks the pores are poorly interconnected; there can be also isolated pores inside the rock matrix. At high porosity up to 40%, permeability is low, just 0-20 mD. In this connection, if even miscibility between oil and carbon dioxide would be achieved, 80-90% of the oil recovery could be not reached. Due to that, in our studying, we shall determine MMP only as a breakover point.

Both equipments, raising bubble apparatus and slim tube, are not widely available. For studying the miscibility phenomena we applied the high pressure reactor *Spe-ed SFE* which often can be found in the universities, where they are used for investigation of the supercritical effects and catalytic conversions. Within the range of pressures up to 60 MPa and temperatures up to 240°C the analyst can accomplish a wide range of extractions.

The results of our various experiments obtained with oil saturated chalk samples, as extracted from the oil reservoir as saturated with the oil at the laboratory, showed that supercritical extractors are also reliable instrument for the determination of the most effective pressure and also applicable for the oil similarly as such equipment is used for the studying of extractions of naphthalene, caffeine and other chemical substances. The subject of the investigation was the oil saturated chalk because many of the North Sea oil reservoirs are located in the chalk rocks. The crude oil used was from Halfdan field.

The purpose of the studying was to find out the characteristic distinctions of the effective pressure in the graph of oil recovery versus pressure (breakover point) and to check whether these distinctions can be seen at chromatograms of the extracted oil.

## 2. MATERIAL AND METHODS

### 2.1 Preparation of the sample

A cylindrical sample was prepared from the clean tight chalk rock excavated from a deep mine. Its geometrical parameters were measured, and the bulk volume of the sample was calculated by equation  $V_b = \pi/4D^2L$ . The sample was first placed in an oven for 24 hour in order to remove the moisture. The dry and clean sample was weighed and placed in the saturation apparatus as shown in Figure 1. Laboratory set up was made in order to perform the saturation process. Oil was introduced from one side of the flask, and the vacuum was created by mean of vacuum pump. The sample remained 24 hours in the same tight flask to achieve proper saturation. After the saturation the excess liquid was blot-off and removed, the sample was weighed. Then the weight of the saturation liquid was calculated by subtracting the dry weight from saturated weight of the core.

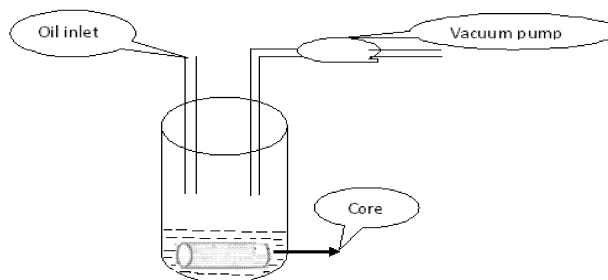


Fig.1 Setup for the saturation of chalk sample with oil.

## 2.2 Equipment operation

The extraction experiments were conducted using **Spe-ed SFE** equipment. The schematic diagram below in Fig.2 shows the layout of equipment. The reactor is a thick stainless steel tube of 100 ml volume to be closed tightly from both ends by cap-ends. The sample under studying was vertically placed in the reactor and put in the oven at the temperature of 80°C to simulate reservoir temperature. Through the hole in the bottom cap-end the carbon dioxide is injected into the reactor from the gas pump until it reaches planned pressure value. Then the valve is closed for 30 minutes for extraction period.

Afterwards the inlet valve was closed, the vent and outlet valves opened to let the extracted oil to be collected through the Control and Collection module (C&C module on the figure) which is used for an easy collection of residues into collection tubes via outlet valves. After that the valve opens the upper cap-end for the collection of the extracted oil in the test tube during 15 minutes.

Such way the extraction was repeated from the pressure value of 10 MPa till 37 MPa with the interval of pressure in 2-3 MPa to avoid the influence of pressure oscillation. The collection tubes were weighed before and after oil collection to determine the weight of extracted oil.

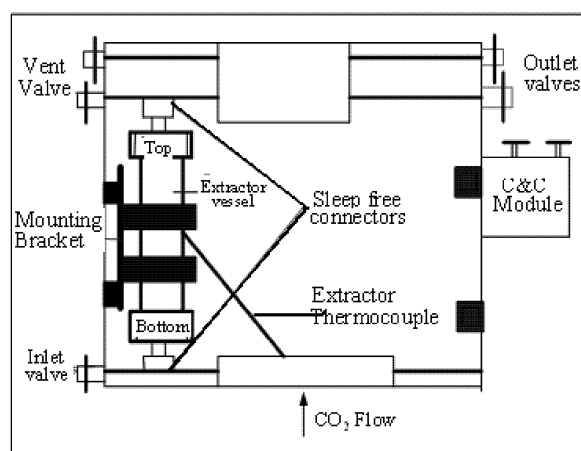


Fig.2 Schematic diagram of supercritical reactor **Spe-ed SFE**.

## 3. RESULTS AND CALCULATIONS

### 3.1 Determination of MMP

The graph obtained through the experiment following above mentioned procedure is shown in Fig.3. The oil recovery grows gradually firstly to the values of 12-14 MPa where they form a kind of step. Such sharp increase in recovery as the pressure approaches the critical value of 7.3 MPa for CO<sub>2</sub> is typical of supercritical systems (Smith et al., 2005). Then the oil amount extracted sharply grows to the breakover point which is according to the definition made by Orr (1982) is a criterion for MMP determination. Above the breakover point, the volume of extracted oil at the higher pressure values does not increase. Thus, the MMP for the oil in investigation is 20 MPa at the temperature of 80°C.

### 3.2 Calculation of MMP

The difference in experimental and numerical approaches made a lot of different values. A large number of models as experimental as well as numerical were created by various authors. For the accurate modeling the precise composition of the oil is needed including all heavy components. The presence of the light components decreases MMP value. Precise composition of our experimental oil was unknown, and it was degassed. For that

reason, only Orr and Metcalfe model based solely on the value of temperature was used to evaluate the order of the expected value:

$$MMP_{pure} = 1833.717 + 2.2518055T + 0.01800674 * T^2 - \frac{10349.93}{T} \quad (1)$$

For the reservoir temperature of 80°C degrees (176 °F) applied for the extraction experiment,  $MMP_{pure} = 18.8$  MPa. This value is not precisely what we derived from the experiment as it was obtained for the stock tank oil with the gas present but quite close.

### 3.3 Porosity calculation

The density of oil measured in the laboratory was equal to 0.8025g/cm<sup>3</sup>. The initial weight of core before saturation  $W_i = 16.81$  gm. The final weight of core after saturation with oil was  $W_f = 21.65$  gm. The total volume of the oil which the chalk adsorbed was 6.031 cm<sup>3</sup>.

For the porosity calculation the following data are firstly needed to be calculated:

The volume of the porous space:

$$V_p = (W_f - W_i) / \rho_o = 6.031 \text{ cm}^3 \quad (2)$$

The bulk volume:

$$V_b = \pi r^2 L = 15.061 \text{ cm}^3, \quad (3)$$

where the radius  $r = 1.181$  cm and the length  $L = 3.44$  cm of the cylinder.

$$\text{Porosity was calculated as } F = (V_p / V_b) * 100 = 40.04\% \quad (4)$$

The value of porosity of 40.04% is in a good agreement with the known data.

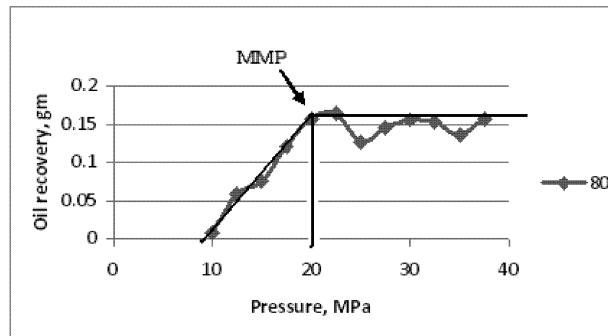


Fig.3 The graph for the determination of Minimum Miscibility Pressure (MMP).

### 3.4 Calculation of oil recovery

The total oil displaced from the sample was 1.4624 gm. By using the value of density the volume of oil extracted after treating was calculated to be 1.822 cm<sup>3</sup>. Therefore, the percentage of oil recovery during the period of the whole experiment for the time of interaction of 30 minutes was 29 %.

#### 4. CHROMATOGRAPHIC ANALYSIS

The oil samples extracted at different pressure values differed in colour and viscosity. Till the value of 18 MPa the oil samples are more viscous and brownish than at the values of 18 and 20 MPa where the oils are water-like and very light, becoming again darker and more viscous with the pressure increasing till 37 MPa.

All the oil samples collected from supercritical extraction experiment were studied with chromatograph GCMS. The capillary column VF-5ms 30Mx0.25MM was used. Following the standard procedure, in order to carry out analysis, the oil samples collected have been diluted in the test tubes with pentane and put for chromatographic analysis. The chromatograms were registered till 27 minutes of retention time showing the presence of carbon groups from C10 to C25.

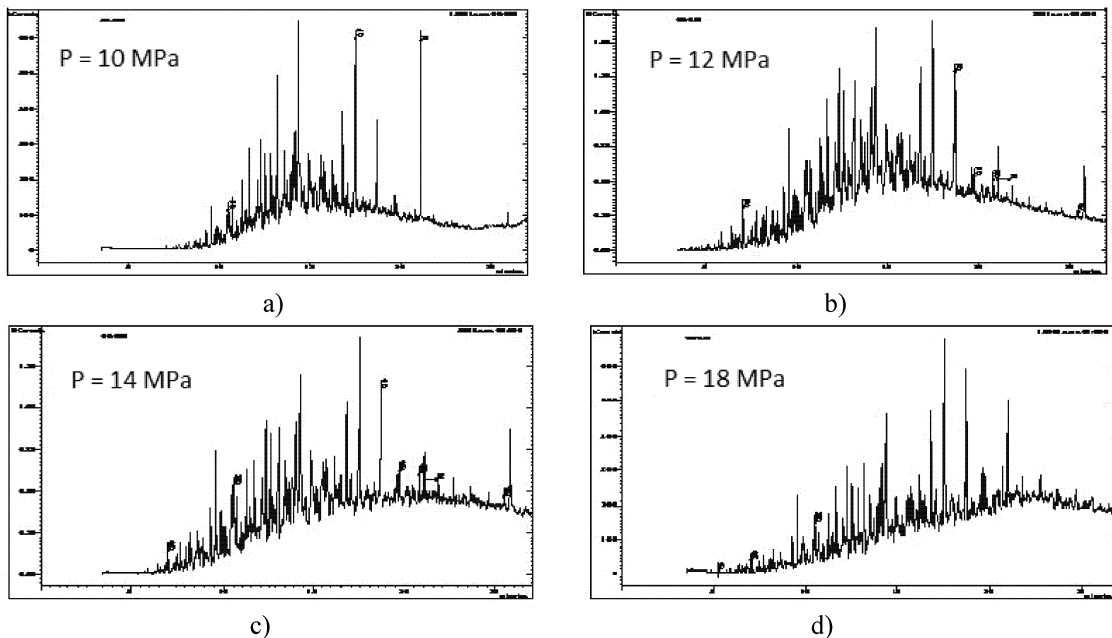
The chromatograms of oil samples for a specific pressure values are shown below in Figure 4. The chromatograms are recorded for 12 different pressure values. The shapes of spectra differ for different pressure values. For the pressure values of 10 and 12 MPa the spectra have a shape of a fold locating between retention time of 10 and 21 minutes with the approximate centre of the fold at the retention time equal to 15 minutes matching C15 (Fig.4a,b). No peaks are observed for C20 to C25 in the range of retention time 20-27 minutes.

Further the conditional centre of the fold shifted to the retention time of 19 minutes at 14 MPa (Fig.4c). The spectrum grows in the range of retention time from 10 to 19 minutes, slightly declining from 21 minutes to the end of spectrum from C20 to C25. The shape of the spectrum is asymmetrical; it has a convex shape of a left side at the retention time in the range of 10-19 minutes with uplifted right side.

For the pressure values of 18 and 20 MPa the spectra have similar look with only difference that the conditional centres are at 22 and 23 minutes of retention time correspondingly. Till those points the spectra grow straight up declining slightly at the end (Fig.4d, e). The shapes of both spectra are linear from the left sides and uplifted right sides.

The spectrum of the chromatogram for the pressure of 22 MPa grows straight up to the point matching 25 minutes of retention time. The part of spectrum between 25 and 27 minutes of retention time is horizontal (Fig.4f).

At all the other chromatograms matching to the pressure values from 22 to 37 MPa associated with miscible displacement in our experiment, the spectra in chromatograms grow almost in a straight line starting from approximately 7 minutes in the whole range of recorded retention time sometimes even creating convexes in the intervals of retention time between 14 and 23-24 minutes at the highest pressures as it is shown for 32 and 37 MPa (Fig.4j, l).



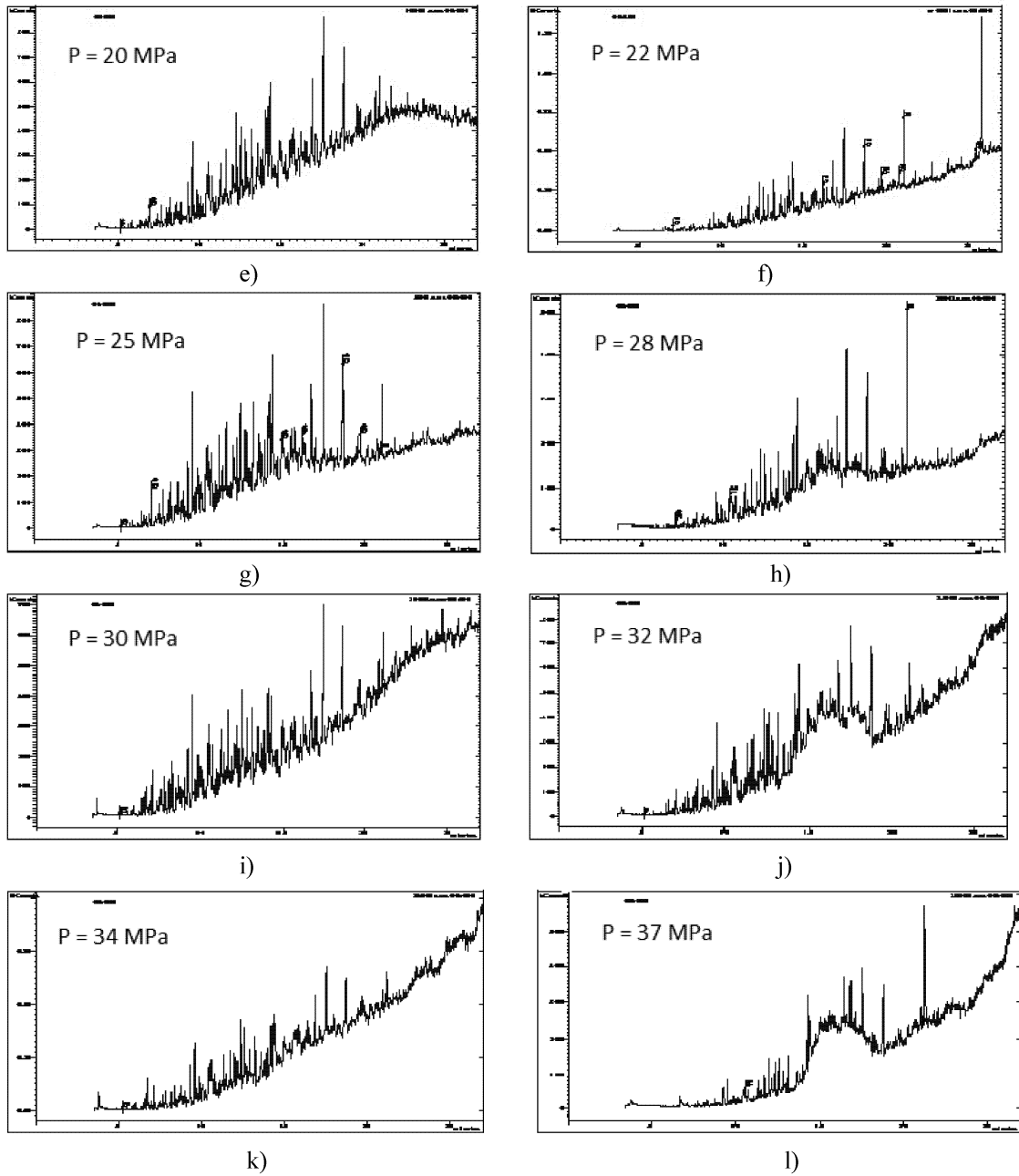


Fig.4 Chromatograms obtained from the oil samples extracted at the varies pressure values: a) pressure 10 MPa; b) pressure 12 MPa; c) pressure 14 MPa; d) pressure 18 MPa; e) pressure 20 MPa; f) pressure 22 MPa; g) pressure 25 MPa; h) pressure 28 MPa; i) pressure 30 MPa; j) pressure 32 MPa; k) pressure 34 MPa; l) pressure 37 MPa.

The experiment following above described procedure was repeated four times. The oil samples were placed in chromatograph in a random order to exclude the influence of other factors like column bleeding.

## 5. DISCUSSION

There is a considerable difference of opinion reported in literature on the effect of packing material and flooding rate on oil recovery and MMP. Some say that the packing material has no effect, while others maintain that porosity has no effect but the permeability however influences the injection rate during flooding. Especially the complexities of the porous space of the carbonate rocks are underlined. For our experiments we used natural chalk samples to model the process of supercritical extraction close to the North Sea oil reservoir conditions.

The shape of our experimental graph of the amount of oil extracted from the oil saturated chalk in the process of carbon dioxide injection as a function of operating pressure is similar to the plots from miscibility experiments conducted in slim tubes (Yellig and Metcalfe, 1980), pressure/composition diagrams (Stalkup, 1992; Turek, 1980) for oil, solubility of the chemicals like naphthalene (McHugh and Paulaitis, 1980) and others in supercritical carbon dioxide. Generally, the graphs from all the above mentioned analysis, showing also the amount of the chemical substance soluble or extracted as a function of pressure, demonstrate firstly the gradual growth till the specific pressure above which the curve does not grow substantially. This allows implementing such graphs for the determination of the most efficient pressure for the extraction of the chemicals by carbon dioxide which in our case is a Minimum Miscibility Pressure of CO<sub>2</sub> injection for the oil field operations. Based on this similarity, when the equipment specially designed for the MMP determination is absent, any high pressure extractor like used for our experiments can be also applied. However, it needs to note that for the oil being a complex compound when the next pressure value was set, some amount of lighter fractions which possibly could participate in multiply-contact was extracted during extraction at the previous pressure value. In big volumes the absence of some amount of these fractions could be not noticeable but for the samples of very small size, that can probably affect the MMP value. In the period of extraction totally only 29 % of oil was extracted. In the absence of visual cell, it is impossible to verify if full miscibility occurred.

On the other hand, the particularity of the MMP value of 20 MPa determined from the experiment is confirmed by chromatographic analysis. The whole extraction process is clearly reflected in the chromatograms showing how the heavier hydrocarbon fractions gradually were involved in extraction. At the lowest pressure values, the chromatograms have a symmetric folded shape. At gradually growing pressures, the right side of the spectra is also growing up, and the centre of the symmetry of the fold is moving to the higher values of retention time. For the pressures above 20 MPa the lighter and intermediate components contacted heavier components in miscibility process. At 22 MPa, the next after breakover point from the graph of extraction experiment, the end of the right side of the spectrum is horizontal. Even the amount of oil recovered at 22 MPa to some extent is bigger than at the previous value. All the chromatograms at the pressures higher than the breakover point are characterized with the sharply, almost linearly uplifting right sides demonstrating that the heavier hydrocarbon fractions are more and more extracted with elevating pressure values. For the given oil, the chromatograms obtained can serve as the patterns for the determination of MMP as they have very distinctive, well recognizable look.

## 6. CONCLUSIONS

Supercritical extractor *Spe-ed SFE* can be applied for the studying of miscibility phenomena. Instead of only oil or artificially simulated porous media like sand or glass beads, the natural rock samples can be used.

The value of the breakover point used for the determination of MMP for the oil from Halfdan field at the temperature of 80°C is equal to 20 MPa.

The chromatographic analysis confirmed the distinction of breakover point. The spectra in all the chromatograms fitting the pressure values above 20 MPa have growing up right side in the range of 10-27 minutes of retention time. The shapes of all chromatograms clearly reflect the whole extraction process.

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