

The effect of miscibility conditions on Gas Oil Gravity Drainage; an experimental study in a simulated fractured medium using CO₂ as a displacement agent.

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1. Abstract

Production from fractured reservoirs is low because many displacing fluids sweep the fractures, but do not produce oil from the matrix blocks. In case of water-wet reservoirs it is possible to inject water that displaces the oil from the matrix blocks into the fractures. For oil-wet reservoirs water displacement is inefficient. Therefore this thesis investigates the possibility to inject high pressure gas, such as nitrogen, flue gas and CO₂. The expected mechanism is gas-oil gravity drainage, where the oil is displaced in the matrix blocks by gravity and produced in the fractures. Secondary mechanisms occurs due to dissolution of the gaseous components in the oil, which leads to swelling, IFT reduction and viscosity reduction.

The method of investigation is through experiments, where a core is placed inside a core holder with free space all around it representing the fracture. The injection point was on the top centre, whereas the production point was at the bottom centre. All injection rates were 5 ml/minute at the experimental conditions. A total of eight experiments successful experiments were performed. There were two kinds of cores, viz., with sizes of (diameter × height) of (0.03 m × 0.1 m) for core-A, and (0.04 m × 0.2 m) for core -B.

Experiments (1-3) in core-A, with carbon dioxide, nitrogen and flue gas at low (45 bar) pressures did not lead to any discernible oil production. Experiment (4) that used CO₂ at 60 bar in core A, resulted in 62% recovery. Experiment (5) used CO₂ at 80 bars also in core A resulted in 85% recovery.

Experiment 6 that used CO₂ in core B at 45 bar resulted in 38% recovery. CT scan observations showed that CO₂ entered from top in piston like displacement until capillary-gravity equilibrium was attained. Experiment 7 that used CO₂ in core B at 80 bars resulted in almost complete recovery as determined by a post-mortem observation. However only 50% of the liquids were collected, and it was inferred that the other part was produced along with the gas phase. Experiment 8 that used CO₂ in an mixture of heptane, decane and iodo-decane, resulted in a recovery of 85%. CT scan data showed that the CO₂ entered from the bottom, but there was a transition zone between the gas that entered and the initial oil.

A finite element model was developed that uses the Brinkman equation both in the fracture and the matrix for the case that we have miscible conditions. Comparison between experiment and modelling shows a qualitative agreement.

2. Introduction

2.1. Introduction

Concern about the availability of fossil resources in the next decades is growing. The production of oil fields is declining and a decline in fossil resources is expected in this century [U.S. Department of Energy, 2011]. There is therefore an increased interest in Enhanced Oil Recovery (EOR) methods as one of the options to contribute to fossil fuel production.

Global warming, often related to an increasing CO₂ content has possibly a direct relation to the fossil resources. A variety of storage options of CO₂ in the subsurface have been proposed. However, the required energy to store CO₂ in depleted hydrocarbon reservoirs, combined with the zero revenue of the process has resulted in a reserved attitude on practical viability of this method. CO₂ storage in depleted hydrocarbon reservoirs can give some, albeit limited (<15%) contribution to decrease the amount of CO₂ emitted to the atmosphere, but its economic viability is more prosperous as it may enhance the amount of recovered oil. Other factors like the capture and transport of the CO₂ in its pure form and the social (in)acceptance of the matter, has further increased the doubts on CO₂ storage in the aquifers (which are located close to inhabitant areas) and depleted oil and gas reservoirs.

Injection of CO₂ in a reservoir and thereby producing oil can be done by several methods. CO₂ can be injected in its pure form, where depending on the temperature, pressure and oil composition, it can be in different states of miscibility with respect to the oil. CO₂ can also be found in a gas mixture that is produced by many energy supplying industries as the so called “ flue gas”, which mainly consists of nitrogen (~80%) and partly of CO₂ (~20%).

Naturally-fractured reservoirs are an important source of hydrocarbon production worldwide. They contain about 20% of the world oil reserves (Saidi, 1983), while they are among the most complicated reservoirs to be produced. The biggest challenge in these reservoirs is the high permeability contrast between the oil-bearing matrix and the fracture pathways. This can result in an inefficient oil recovery from these reservoirs if the injected fluids would bypass most of the oil and be confined to the high permeable channels. Many varieties of oil displacement techniques are used worldwide (Appendix C). This thesis concentrates on one of the enhanced recovery techniques making use of different types of gas injection.

Spontaneous imbibitions has been reported to be an efficient (although slow) recovery mechanism for the fractured reservoir (Verlaan en Boerigter, 2006; Suicmez et al, 2011). However, water will imbibe from the fracture into the matrix if the capillary forces are favourable, i.e., the matrix is water wet. If the rock is non-water wet, the water invasion into the matrix is retarded.

Gas-oil gravity drainage (GOGD) has been proposed as an efficient method of oil recovery from non-water-wet fractured reservoirs. This technique relies on the density difference between the injected gas and the in-situ oil. The maximum production rate from GOGD before the gas breakthrough can be calculated from:

$$q_{max,GOGD} = \frac{k_{mat}k_{r_{og}}^0 A}{\mu_o} \Delta\rho_{og}g , \quad (1)$$

where $q_{\max, \text{GOGD}}$ (m^3/s) is the maximum drainage rate, $k_{\text{mat}}(\text{m}^2)$ is the permeability of the matrix, kr_{og}^0 , is the end-point oil-gas relative permeability, $A(\text{m}^2)$ is the cross section area of the core, μ_o is the oil viscosity ($\text{Pa} \times \text{s}$), $\Delta\rho_{\text{og}}$ (kg/m^3) is the density difference between oil in the matrix and gas in the fracture and g (m/s^2) is the acceleration due to gravity. Capillary forces will inhibit the gravity drainage performance in immiscible experiments if capillary gravity equilibrium is attained. The reduction factor is $(1 - (H_c / H_o))$ where H_c is the capillary entrance height and H_o is the oil column height (Verlaan and Boerrigter, 2006).

Injection of gas under fully miscible conditions (Appendix A) will enhance the ultimate recovery process. Under fully miscible conditions two phase flow aspects like capillary hold up is no longer relevant. The process of mixing will give a reduction in the oil viscosity and density and elimination of the interfacial tension. These effects are usually beneficial for improved recovery. The negative effect of the mixing is the decrease in the density difference between the oil and gas (Darvish et al. 2006). As stated in Eq. (1), the maximum drainage rate is linearly dependent on the density difference. The density increase of CO_2 as injection gas under miscible conditions is of great importance and possibly a limiting factor in practical application of miscible GOGD with CO_2 .

It is expected that miscible displacement experiments lead to the highest recovery by gravity drainage displacement. Immiscible experiments are likely to have a substantial lower recovery due to the presence of capillary opposing forces. The oil is capillary trapped in the matrix and the gravity drainage rates are low. Once miscibility is achieved, these capillary forces can be neglected and consequently the ultimate recovery is improved.

2.2 Objectives:

The main objective of this thesis is to quantify the transfer rate of different gases, namely CO_2 , N_2 and flue gas, to the oil bearing matrix. To achieve the objective we use drainage experiments in cores placed in a core holder with an open space around it representing the fracture. Interpretation of the experiments is facilitated by using a CT-scan and numerical modelling.

To predict the performance of a natural fractured reservoirs by gas drainage several driving mechanisms have to be simulated. Natural convection, molecular diffusion, gas oil gravity drainage and capillarity effects are all contributors in the reservoir production rate.

In the first part of the thesis we compare the effect of the different gas composition on the recovery of the oil. Elaborating on these results we focused on pure CO_2 as the displacement gas and investigated the production effect of miscibility conditions of CO_2 . The oil production by the injection of a synthetic flue gas mixture of CO_2 and nitrogen is also part of this research.

Experiments resulting in CT-images and oil recovery data combined with modelling output provide us with concrete numbers and visualization data. These methods are the foundation to achieve the research goals and provides us with comparison between theory and practice.

3. Methods

3.1 Experiments

3.1.1 Experimental Work:

Experiments can be used to simulate oil reservoir behavior on a smaller scale. In this thesis several experiments have been performed to assess the effect of miscibility on the oil recovery from fractured reservoirs. To this end, different gas compositions, including CO₂, N₂, and a synthetic flue gas composed of 20 vol.% CO₂ and 80 vol. % N₂ are applied at different pressures and thus miscibility conditions.

Besides the production rates and recovery factors of the experiments with gas injection we are also interested in the observation of the saturations in the core. With the help of a CT-scanner we get insight in the movement of the gases, which helps in the understanding of the main driving mechanisms of the oil production. We chose to visualize the key experiments for the understanding of the driving mechanisms, due to limited availability of the CT-scanner.

3.1.2. Material Properties

Bentheimer cores were used in the experiments as a porous medium. The core has a porosity of 0.21 (± 0.01) and a permeability of 1.47×10^{-12} m². For the experiments without the CT-scan a 3-component synthetic oil sample was used. This oil is composed of 30 wt% n-heptane, 30 wt% n-decane and 40 wt% hexadecane and simulates a light oil. The density at room temperature is 733 kg/m³. The density is inferred from a volume average of the component densities. The viscosity varies between 0.99-1.22 mPas (Amerighasrodashti, 2012). A synthetic flue gas composed of 20 mol% CO₂ and 80 mol% N₂ is used to mimic gas emission from power plants. All experiments were performed at room temperature. The core holder was made of PEEK (*Polyether ether ketone*). The PEEK coreholders were designed such that they can cope with pressures up to 150 bars and is capable of transmitting X-ray for CT-scanning. Rubber O-rings were used to close the system and prevent leakages and Teflon placers are used to fix the position of the core.

Different oil samples were used for the experiments under the CT-scanner. 100% n-Hexane was used for the immiscible experiment and for one of the miscible experiments. The room temperature density of n-Hexane is 654.8 kg/m³. Hexane was chosen for the miscible experiment because it has a much lower density than supercritical CO₂. The density of CO₂ at 85 bar and room temperature increases to 808 kg/m³. If the density difference would be too small, it will result in a poor visibility of the images and a decreased gravity drainage rate (Equation 1). Hexane was experimentally difficult to handle; a vast amount (~ 50%) was produced in the gas phase rather than the liquid phase. The gas phase was not collected in the experiment and therefore the recovery rate had to be calculated post mortem, based on a mass balance.

The other oil sample used for the miscible experiments has a composition of 60 wt % n-Decane, 30 wt% n-heptane and 10wt% Iodo-decane. Iodo-decane is a doping agent for the CT-scan experiments and enhances visibility of the experiments. The outcome of these experiments is shown in section Experimental results.

The first contact miscibility pressure for a CO₂-Oil system was calculated using a PVT phase behavior. The different Minimum Miscibility Pressures (MMP) can be found in Table 1 (Results and Discussion) A system pressure of 80 bars is applied to guarantee fully miscible conditions and 45 bars to guarantee immiscible conditions. A pressure of 60 bars was used for one of the experiments to simulate the near-miscible or multi-contact miscible case. An overview of experimental conditions can be found in Table 1. More information about the concept of “miscibility” can be found in Appendix B

3.1.3. Experimental procedure

The experimental procedure consists of the following steps:

1. Drill and cut the Bentheimer sandstone cores with the right dimensions. Let the cores dry in an oven for 2 days. Weigh and measure the dimensions of the dry core before saturation.
2. Place the cores inside the core holder and connect to the production and injection lines.
3. Check the system for leakages using helium. The difference between the injected helium and the bulk volume equals the fracture volume + dead volume.
4. Vacuum the system for 2 days to release all the remaining fluids and gases
5. Inject the oil sample to saturate and pressurize the core and fracture with oil. Because of the small heterogeneities of the core (oil has to flow inside all the pore space) the pressure initially decreased; therefore injection was continued until the pressure remained constant.
6. The oil in the core was determined by the difference between the injected oil and the fracture volume + dead volume (tubings).
7. Step-wise, the backpressure is applied to the desired pressure level. If this is not done in steps, the backpressure regulator can break due to an instant big pressure difference.
8. Once the pressure is constant, the desired gas is injected with a flow rate of 5 ml/min.
9. The produced oil is separated and measured by a digital balance or a fraction collector.
10. The recovery factor can be obtained from the difference of the initial oil in the sample and the produced oil out of the matrix.
11. If there is no oil produced for more than 5 hours after oil production, the gas injection is stopped. The core is weighed and from a mass balance the remaining oil is determined.

The experimental procedure under the CT-scan is similar to the steps mentioned above albeit that the scanning procedure is described here below. A scan of a core saturated with the injection gas has to be made before the start of the experiment. After this a scan of the dry core has to be made and subsequently a scan of the core fully saturated with oil. CT-images are correlated to the density difference, which is scaled to the density difference of a fully oil saturated sample and the fully gas saturated sample, Eq(2).

The experiments were done with CO₂ at different pressures. CO₂ is the only gas used by us that can be miscible and liquid at lab scale pressures (60-80bar) with the oil samples used. One experiment with CO₂ was carried out at 45 bars which is representative of an immiscible gas displacement experiment.

3.1.4. Experimental set-up: In this thesis two experimental set-ups were used. Set-up 1 (Figure 1 and Figure 2) was built inside a high pressure lab. A core with a length of 10 cm was used to simulate the porous medium. A space of 0,5 cm between the core and core holder represents the fracture.

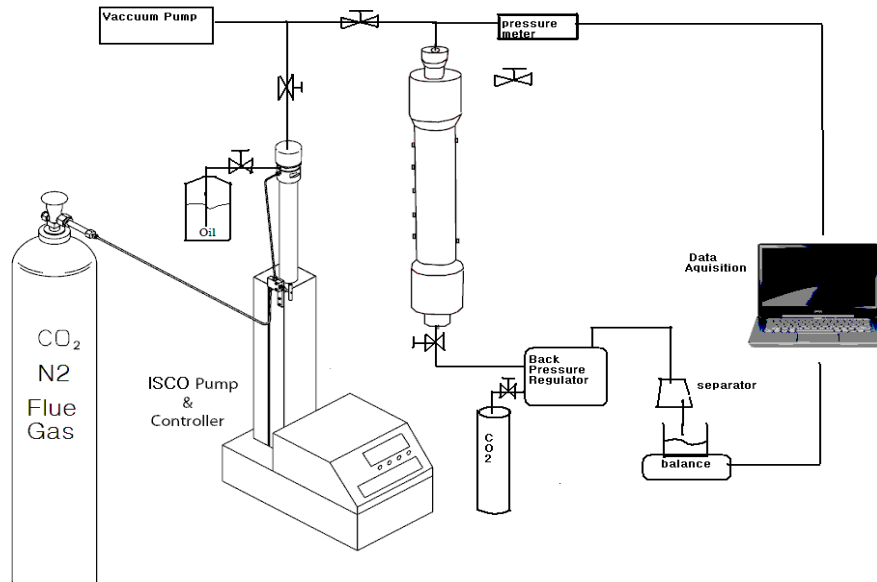


Figure 1 Experimental set-up

Two ISCO pumps were used to inject oil and the displacement agent. The pump can inject with an injection range of 0.1-107 ml/min and can attain pressures up to 500 bar. The pumps can be set for constant pressure or constant flow rate depending on the experiment that is performed.

A vacuum pump was used before every experiment to vacuum the whole system and to get rid of excess gases or residual oil. A backpressure regulator was placed to produce the oil sample between the production line and the balance. This pressure regulator uses nitrogen to keep the system under a constant pressure and only opens when the system's pressure equals the setpoint. During production, the system pressure decreases somewhat, and the backpressure regulator closes again. After production the system pressure increases due to a constant injection of the displacing agent. The backpressure regulator will only open when the system pressure builds up to the selected reference pressure. In this way the pressure becomes equal again and the produced liquid can flow into the separator. A separator is used to separate the oil and gas. A digital balance was used to measure the amount of oil that is produced. The balance together with the digital pressure gauge were connected to a data acquisition system.



Figure 2 Set up 1 A) Injection line B) Pressure transducer C) Core holder D) Production Line E) Back-pressure regulator F) Separator G) Balance H) Isco Pump controller I) Double Isco Pump J) Gas Injection K) Vacuum pump

The second set-up (Figure 3) was built to perform experiments using a CT-scan. The second core holder was fully made of PEEK which is transparent to CT. This core holder allows us to extend the length of the core to 20 cm. The fracture aperture was decreased to 2 mm. The set-ups used in the CT scan experiments and in the production experiments are very similar and are shown in Figure 2 and Figure 3. A gas booster was used to increase the CO₂ pressure higher than the minimum miscibility pressure. If we only used the ISCO-pumps for a constant pressure of 80 bars the amount of compressed gas available in a single stroke of the pump is much smaller which is not preferable.

3.1.5 CT-Scanning

CT-scanners are conventionally used for medical applications, i.e. scanning parts of the human body without damaging the tissue. Over the past few decades this technique is also applied in the petroleum engineering. CT-imaging gives insight about the transport processes conducted in the experiments described here but pose a number of experimental difficulties when the density of the in-situ fluids are comparable.

Computing Tomography (CT)- scanning is an imaging method that uses X-ray beams rotating around an object. Each time step results in four different images of four different detectors. Each image has 512 × 512 pixels. The images are converted to a 512 × 512 matrix containing the CT-coefficient numbers. These coefficients numbers are given in Hounsfield units which depicts the density change. One Hounsfield unit represents the change of 0.1% change in density with respect to



Figure 3 Set-up 2: A) Double ISCO-pump for CO₂ injection B) CT-Scanner C) Core holder D) Data acquisition E) ISCO-pump for oil injection F) Gas booster G) Bentheimer sandstone core H) Teflon placer I) Fraction Collector J) CT-scan X-ray at the middle of the core K) Core holder failure

the calibration density (Kahrobaei, 2011). The CT-numbers can be converted to the saturation of the displacement agent using the equation (Farajzadeh et al. 2009):

$$\% \text{Displacement agent} = \% \text{Produced Oil} = \frac{CT_{exp} - CT_{oil}}{CT_{displacement_agent} - CT_{oil}} \quad (2)$$

CT_{oil} is the CT-number of the core fully saturated with the oil sample, and is obtained at the beginning of the experiment. The $CT_{displacement_agent}$ scan is made before the start of the experiment. The core is fully saturated with the displacement agent. After this scan, the displacement agent is extracted and the core is vacuumed again before the experiment starts. The scan is used for the determination of the displacement agent/oil ratio. After the start of the experiment, scans are made on a regular time base and CT_{exp} values are obtained. These combined scans are the starting point for the image process.

Equation (2) is valid under the following assumptions:

- No volume is lost during the experiment
- The pore volume occupied by the displacement agent is equal to the displaced oil from that same volume for the miscible displacement.

3.1.6. Image reconstruction

The images constructed from the CT-scan are in grey-scale and can be improved with an image tool in MATLAB. The scan represents a slice obtained from the exact middle of the core, which gives the best representable image for the experiments. Every scan consists of 4 scans, each with 2.5 mm spacing. The CT-scans include the complete core holder and some surrounding extensions. The 4 scans are averaged, which results in one image file with their corresponding attenuation coefficients.

The only interesting part is the core and the fracture, therefore the image is cropped in the correct dimensions. After the cropping the contrast of the images is adjusted to highlight and improve the visualization of the transport process. A MATLAB code is used to subtract the images corresponding to the above mentioned equation and results in the images depicted in the section Results and Discussion.

Although no metal parts were used in the set-up some inconveniences are encountered due to the artifacts and noise that is displayed by the used materials. Therefore it is only possible to construct a reliable 2-D image. Inferring a 3-D image from these images is not practically possible.

4. Numerical approach

4.1. Numerical models

A numerical method to model miscible and immiscible CO₂ displacement experiments has been a challenging subject for many studies in the past. Modeling and applying the governing equations of a matrix-fracture system is complex and is still a subject of on-going research in reservoir engineering (Uleberg and Høier, 2002, Saidi, 1983).

We employed the following PDE modeling platform to simulate the fully miscible CO₂ experiments which was performed under a CT-scan:

The COMSOL 4.2a Multiphysics engineering software is used to simulate the miscible displacement experiment. COMSOL makes use of accurate geometry and meshing methods, specifying physics and visualize the results. Several predefined modules are used to describe the dilution of species in the matrix-fracture system. Brinkman's module is used for defining the transport in a radial symmetric system.

4.2 Miscible CO₂ injection in COMSOL

Understanding what happens during the transition from slow flow in porous media to fast flow in a channel is critical in many environmental cases and applied problems. This type of flow appears near rivers, estuaries, wellbores, caverns, and lava tubes, to name a few examples.

The modelling requires to connect the Stokes flow in fracture to Darcy's law in the core (matrix). Brinkman's equation even if its validity in the transition zone has been criticized allows a continuous transition between channel flow and porous medium flow. Our interest is not in the transition zone and hence we used this equation.

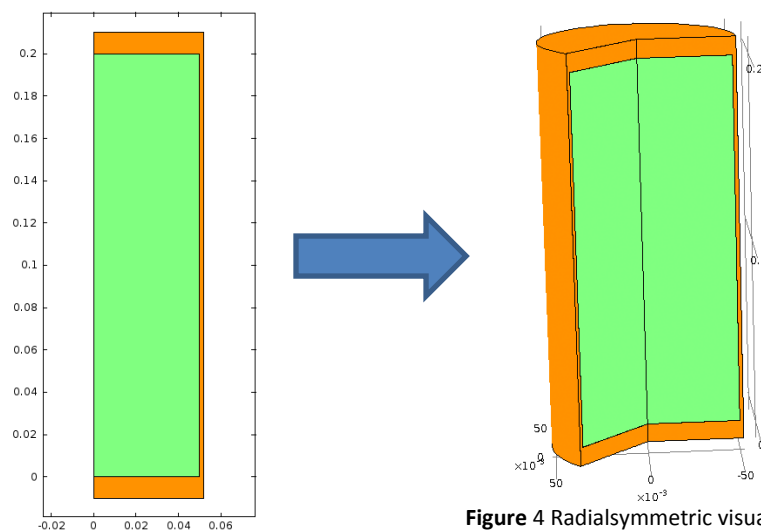


Figure 4 Radiallysymmetric visualization in COMSOL

A 2D-radiallysymmetric model in COMSOL is used to simulate a cylindrical system. This simulates the experiments, which are performed with a symmetric cylindrical sample and a evenly surrounding fracture. The correct dimensions and parameters are applied to get the initial geometry of the model depicted in Figure 4.

The two simulated regions in COMSOL are shown in Figure 4. The green part represents the matrix and the orange part represents the fracture. The parameters for the matrix properties are based on the measured values of the set-up. The parameters of the fracture are taken such that it can be representative for the set-up. The porosity is 1 and the permeability in the fracture is increased with respect to the matrix with a factor of 10^{15} . As for the diffusion coefficient, a 100 times smaller value is chosen with respect to the matrix, to represent the natural convection flows.

The COMSOL model is making use of the following equations. Each of the equations are applied on both areas.

Brinkman's equation COMSOL:

$$\frac{\rho}{\varepsilon_p} \frac{\partial u}{\partial t} = \nabla \cdot \left[-pI + \frac{\mu}{\varepsilon_p} (\nabla \cdot u + (\nabla u)^T) - \frac{2\mu}{3\varepsilon_p} (\nabla \cdot u)I \right] - \left(\frac{\mu}{\kappa_{Br}} + \beta_F |u| + Q_{Br} \right) u + F \quad (3)$$

The term on the left represents the transient term and is only used to allow some time to attain a for steady state. The first bracketed expression on the right represents the force balance of the bulk fluid and contains the pressure force, the force due to shear flow and the term due to a changing volume of the system. In our case we use incompressible flow and this term is disregarded. The second bracketed expression on the right represents the force balance in the porous medium and contains three terms. The first term represents the resistance due to Darcy flow. The second term represent the resistance due to inertia forces in the porous medium, the so-called Forchheimer term. The third term adds an additional resistance due to volume changes in the system. Finally F represents an external force, e.g., the gravity force.

$$\rho \nabla \cdot u = Q_{Br} \quad (4)$$

Transport of diluted species

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) + u \cdot \nabla c_i = R_i \quad (5)$$

The first term is the accumulation term, the second term is the diffusion term or a dispersion term, the third term is convection term. The right side allows to incorporate a source term.

The flux term can be written as

$$N_i = -D_i \nabla c_i + u c_i \quad (6)$$

At the boundary line between the fracture and the matrix, an inward flux is chosen, that equals the outward flux. The inward flux is proportional to the concentration difference between the fracture in the matrix. In this way we create an open boundary.

$$\text{Flux}_{\text{matrix}} = M (c_f - c_m) = \text{Flux} = M (c_m - c_f) \quad (7)$$

To take the effect of density into account, i.e. the driving mechanism of the flow is gravity drainage, we give each region an average density, composed of the combined densities of the oil and the displacement agent with respect to its concentration.

5. Results and discussion

5.1 Experiments

In this section all the experimental results are analysed. Table 1 lists all the performed experiments. Although some experiments have resulted in zero or little oil production and therefore have no recovery profile, the outcome of these tests contributes to a better understanding of the main recovery mechanisms. Moreover Table 1 lists the two types of experiments that were performed viz. 1) production type, where only pressure and production data (i.e., the recovery rate) and 2) CT-scan type where besides the production and pressure data, also CT-images are taken to visualize the saturation distribution inside the core. Table 1 also lists the dimensions of the set-up, pressure conditions and the chemicals that were used.

Experiment types							
Production type							
Experiment number	Displacing agent	Pressure (bar)	Core length (cm)	Core diameter (cm)	Frac. Size(cm)	Oil sample	MMP (bar)
PR1	CO ₂	45	10	3	0,5	A	61
PR2	N ₂	45	10	3	0,5	A	n/a
PR3	Flue gas	45	10	3	0,5	A	n/a
PR4	CO ₂	60	10	3	0,5	A	61
PR5	CO ₂	80	10	3	0,5	A	61
CT-Scan type							
Experiment number	Displacing agent	Pressure (bar)	Sample length (cm)	Sample diameter (cm)	Frac. Size(cm)	Oil Sample	MMP (bar)
CT1	CO ₂	45	20	5	0,2	B	60
CT2	CO ₂	80	20	5	0,2	B	60
CT3	CO ₂	80	20	5	0,2	C	67
Oil Sample							
A	30 wt% n-heptane, 30 wt% n-decane and 40 wt% hexa-decane						
B	100 wt% n-hexane						
C	60 wt% n-decane, 30 wt% n- heptane, 10 wt% iododecane						

Table 1 Experiment types

5.1.2 Production Type experiments PR1, PR2 and PR3

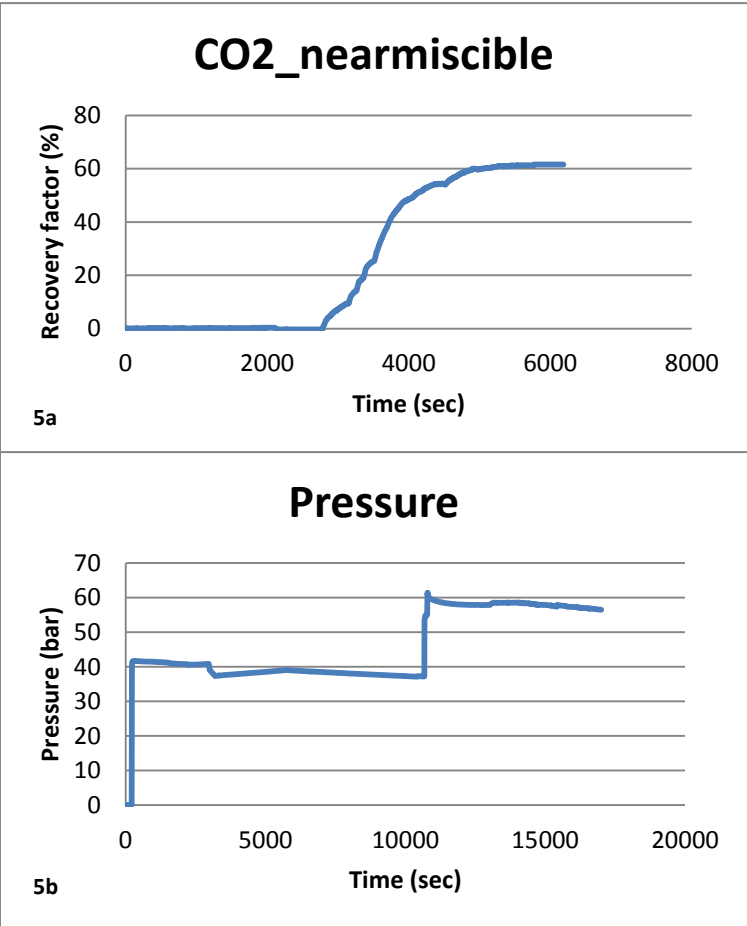
Experiment PR1, PR2 and PR3 were all performed under immiscible conditions. Although the displacement agents are different, each gas has a higher minimum miscibility pressure (Appendix A) than 45 bars. This experiment is performed to test if immiscible displacement plays a noticeable role for the production. The set-up for these experiments is shown in Figure 2. Previous experiments with immiscible CO₂ (Asghari and Torabi, 2008; Chakravarty and Muralidharan 2006) give a recovery in the range of 55-70 %.

PR1, PR2 and PR3 all showed hardly any oil production. The oil is retained in the core due to capillary hold-up. Indeed capillarity plays an important role in this system. A certain threshold pressure, which is higher than the capillary pressure, is required to drive the oil phase through the pores. The driving force of gravity drainage, which is the main contributor in these experiments cannot overcome the opposing capillary force. The capillary threshold height exceeds the core dimensions (10 cm length) and thus oil is capillary trapped in the core.

These results show that the core dimensions are of importance. Equations about the influence of capillarity on the performed experiments can also be found in Appendix B.

5.1.3 Experiment PR4

Experiment PR4 started with a pressure of 40 bars. After approximately 3 hours, no production was observed and the pressure was increased to 59 bars. CO₂ becomes liquid at 59 bars and behaves



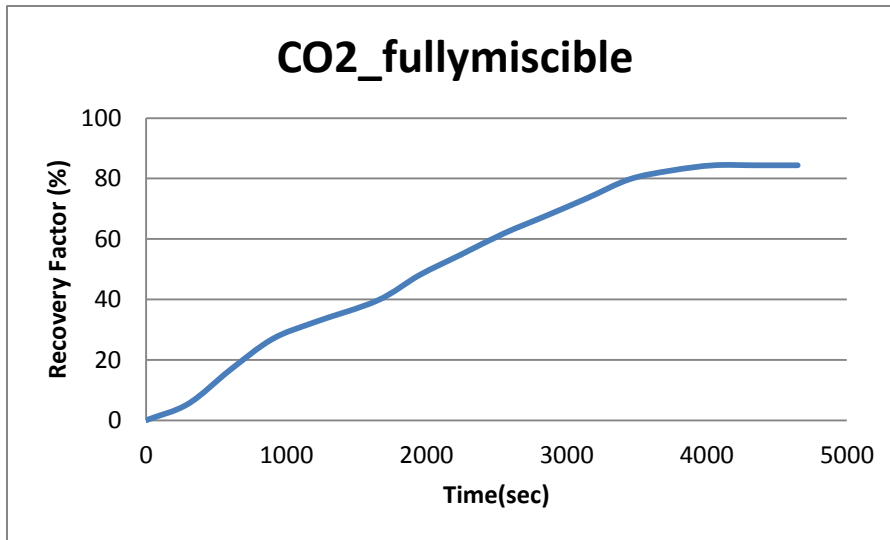
miscibly in this state. Although CO₂ becomes liquid, there is still a development of miscibility after the liquid condensation (at room temperature, i.e. below the critical temperature) of CO₂. Previous studies show three important stages in the miscibility process between CO₂ and oil (Appendix A). In this experiment developed contact miscibility conditions of CO₂ and oil are reached. Fig. 5a shows the production history and Fig. 5b represents the pressure build-up. It has to be noted that the first 7000 sec, during which the pressure was 40 bar no oil recovery was observed and therefore this period was not included in Fig. 5a, i.e t=0 corresponds to the time at which pressure was increased to 59 bar. As soon as the pressure is increased to the developed (near) miscibility pressure, the production starts and a final recovery factor of 62% is

Figure 5 Recovery profile and pressure development of Experiment PR4

reached. A reduced capillary pressure is likely to be the reason for this recovery increase. Because the experiment is performed at developed miscible conditions, there is still a two-phase transition zone and therefore the production will not increase to the same level that can be achieved with gravity drainage experiments when fully miscible pressure conditions are applied .

5.1.4. Experiment PR5

In this experiment CO₂ is used again as the displacing agent and the pressure is increased above the first contact miscibility pressure (fully miscible conditions): 80 bar. Figure 6 shows the recovery history of this experiment. The pressure is kept constant at 80 bar.



A final recovery factor of 85% is reached. The recovery profile shows the high recovery of miscible displacement. This high recovery is caused by the absence of capillary forces at miscible conditions. The oil and CO₂ are in the same phase and therefore the system it is difficult to distinguish

Figure 6 Recovery profile Experiment PR5

the interface i.e., the IFT is zero. Another advantageous side-effect with respect to the oil production is the high solubility of CO₂ in the oil sample. This solubility could not contribute in the immiscible experiments because of the capillary hold-up and penetration of carbon dioxide in the core due to diffusion is slow hence only negligible mixing occurs. In the miscible experiments it causes an increase of the production. When the CO₂ dissolves in the oil it usually causes a decrease in the oil viscosity (Prausnitz, 2004). A lower viscosity means a faster recovery because the oil feels a decreased resistance to flow (see Eq.1).

5.2.1 CT-scan type experiment CT-1

Experiment CT-1 is the first of 3 experiments using a CT-scan to visualize the processes inside of the core. In CT-scan type experiments, set-up B is used with larger core dimensions (length × diameter = 0.2 m × 0.05 m). The fracture width is decreased to 0.002 m. Similar as in the previous experiments, the recovery factor is determined, collecting the produced oil. The pressure of the experiment is held constant at 45 bars; CO₂ is immiscible at these conditions. As explained in the section Methods, it is important to keep the core holder at the same location during the complete experiment. CT-scans are made for the dry core as well as for the core completely saturated with oil and CO₂. During the experiments the core is scanned at time intervals of 10 min. Figure 7 shows the constructed images of the CT-scans with respect to time in minutes.

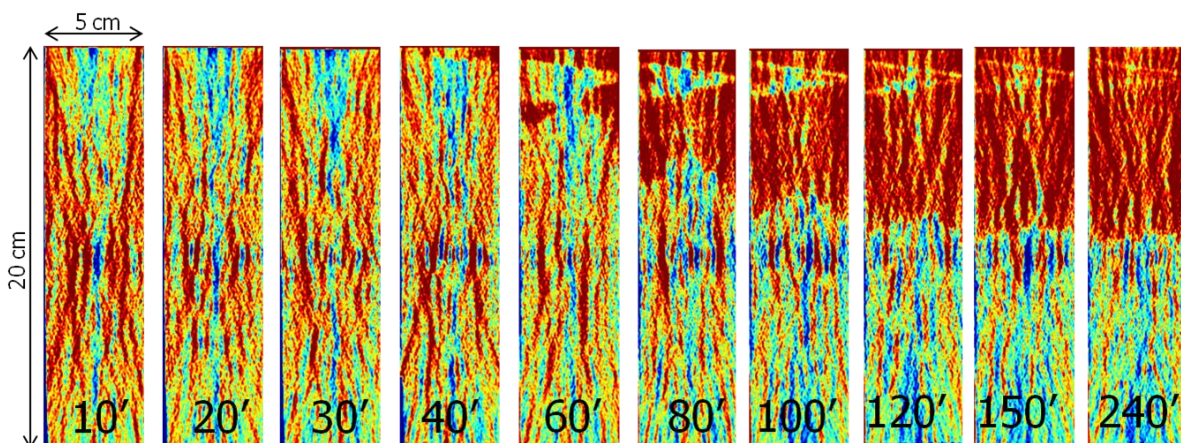


Figure 7 CT-images for immiscible CO₂ injection; Experiment CT-1

Figure 7 shows an image of the middle of the core. Four images were taken per scan, with a distance of 2.5 mm between every image. These four images were averaged and represent a one cm central slice in the core . As stated above, a thick PEEK core holder is used, combined with a sandstone core

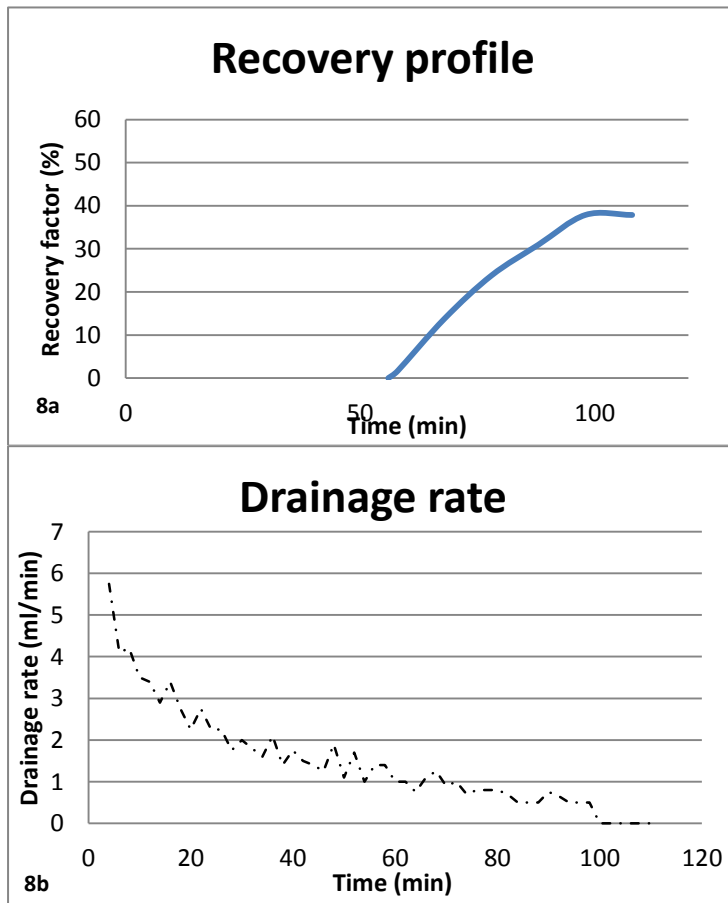


Figure 8 Recovery profile and Drainage rate Experiment CT-1

and this results in artefacts in the initial constructed image (slice) made by the CT-scan. Nonetheless these images are used because a clear trend is visible in the constructed images. The final images show a clear development of a moving red front, with a sharp (two-phase) interface, which displaces the CO₂ front piston-like.

The position of the sharp interface corresponds to the capillary height. The scanning is stopped after 240 minutes because the front is barely moving and there is hardly any production of the oil .

Unlike the previous experiments, a fraction collector is used to collect the produced oil. This gives the production rate of the experiment and can be used to calculate the total recovery .

In the first 60 min the oil from the measured fracture and dead volume is produced. The oil production from the matrix starts after 60 min. From this time onwards the recovery factor is calculated. The difference between the total amount of oil collected by the fraction collector subtracted by the measured fracture and dead volume is used for the calculation of the recovery factor i.e. the result of this subtraction is divided by the measured pore volume to come up with an ultimate recovery factor of 38%.

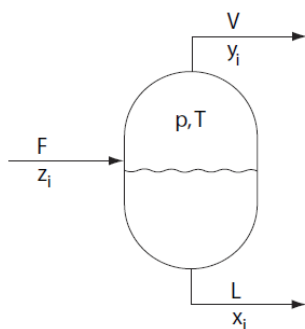
5.2.2 Experiment CT-2

Experiment CT-2 was our first experiment for the visualization of miscible CO₂ injection. Hexane is used and represents light oil. Hexane is chosen to obtain a high density difference between the oil and the CO₂ (see Material properties). The results of the experiment were different than expected for reasons to be explained below. Normally the oil is produced in its liquid phase after its passage through the backpressure regulator. In this experiment we saw the production of a vapor phase as well as an oil phase.

There are two possibilities for the vapor production. One of them is a malfunctioning of the backpressure regulator; the backpressure nitrogen gas could be produced as a by-product due to leaking. No fluctuations were observed in the backpressure regulator, so this was not the reason for gas development.

Gas production from the system itself was another possibility. After the experiment the balance data was analysed and showed that less than 50 % of the oil was produced, which is not in estimation with respect to previous experiments with miscible displacement. After the data collection, the core was taken out of the core holder and immediately placed on a balance to measure the mass after the experiment. The mass of the core after the experiment was approximately the same as the mass of the dry core which implied that there was nearly 100% recovery. Because of the mass balance, the only way to get this recovery factor is by producing the oil in the gas phase as well as the liquid phase.

A flash calculation was made to confirm this theory. Flash calculation are used for processes with vapor/liquid- equilibrium (Skogestad, 2009):



'Consider a flash where a feed F (with a composition z_i) is injected in a system with certain P, T conditions. The system is split into a vapor product (with a composition of y_i) and a liquid product L (with a composition of x_i). The material balance is written as:

$$Fz_i = Lx_i + Vy_i \quad (8)$$

In addition, the vapor and liquid is assumed to be in equilibrium',

$$y_i = K_i x_i \quad (9)$$

The equilibrium constants are computed using a flash calculation software from chemical engineering, making use of the Peng-Robinson equation of state (Peng and Robinson, 1976) to show the behaviour of n-Hexane and CO_2 under fully miscible conditions. Fig.9 shows a fast increase of n-Hexane in the vapor phase when reaching the first contact miscibility point. Under fully miscible conditions (80 bar), 50 wt% of the n-Hexane is produced in the vapor phase and therefore is not collected during the experiment. This explains the outcome of the experiment.

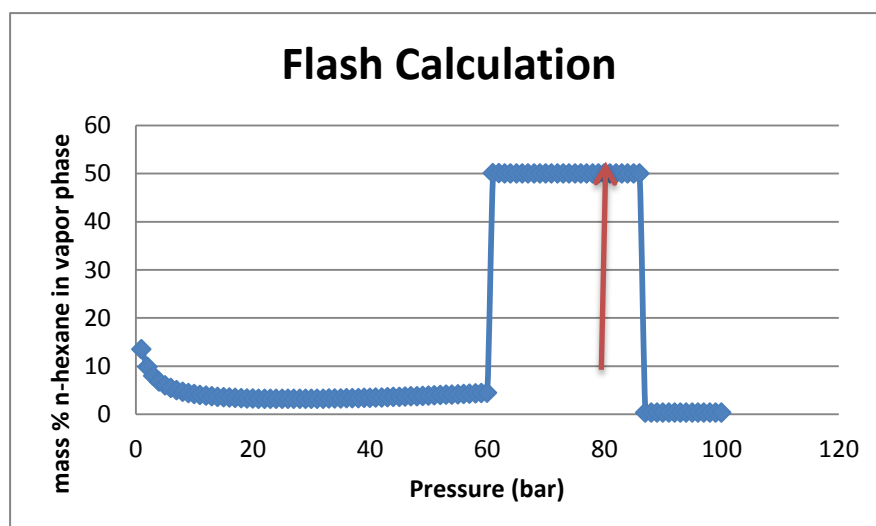


Figure 9: Flash calculation

The CT-images constructed from this experiment are not shown in this report . It was not possible to construct images that show a distinction between CO₂ and the n-hexane. The poor visibility can be caused by several factors:

- The density difference was too small to observe a clear distinction between the two components
- No doping agent was used to increase the contrast between the two components (see Experiment CT-3)
- The phase behaviour resulting in the production of the oil in the gas phase

5.2.3 Experiment CT-3

Experiment CT-3 was our second miscible displacement experiment visualized by the CT-scan. The pressure was well above the Minimum Miscibility Pressure (MMP) and therefore the conditions are fully miscible. Figure 10 shows the ultimate recovery factor of the experiment (80%). Figure 11 shows the pressure development. There were some difficulties performing the experiment. The

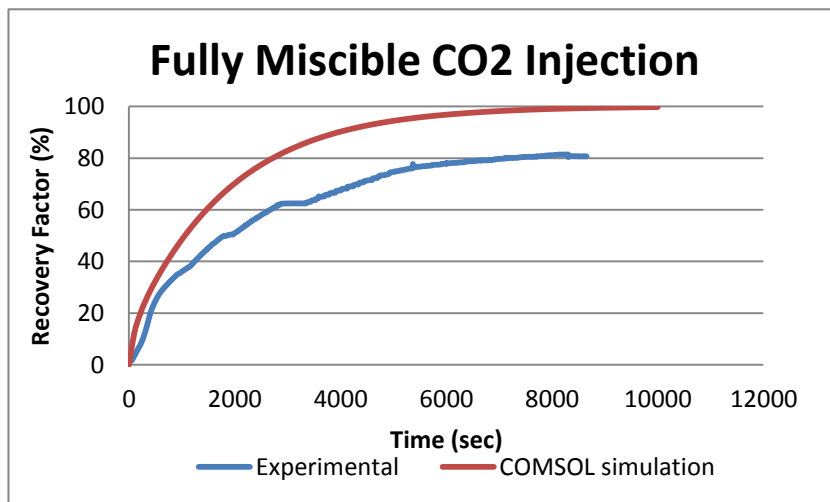


Figure 10 Experimental and numerical recovery profile Experiment CT-3

backpressure regulator had to be replaced during the experiment. Normally a regulator with a rubber section is used to regulate the pressure. CO₂ in supercritical phase has the unfavourable ability to diffuse into this rubber section. As a consequence of this diffusion, the rubber gets ruptured and the backpressure valve becomes unusable. The system was

closed and the CO₂ injection was stopped for a short time. Another type of backpressure regulator was installed to complete the experiment. This regulator did not have a rubber section, but was a spring loaded pressure regulator adjusted to a reference pressure of approximately 80 bars. As is illustrated in the pressure development graph, the new backpressure was installed after approximately 40 min. The disadvantage of this type of backpressure regulator lies in the pressure window that developed during the test. The oscillation increased to a pressure window of

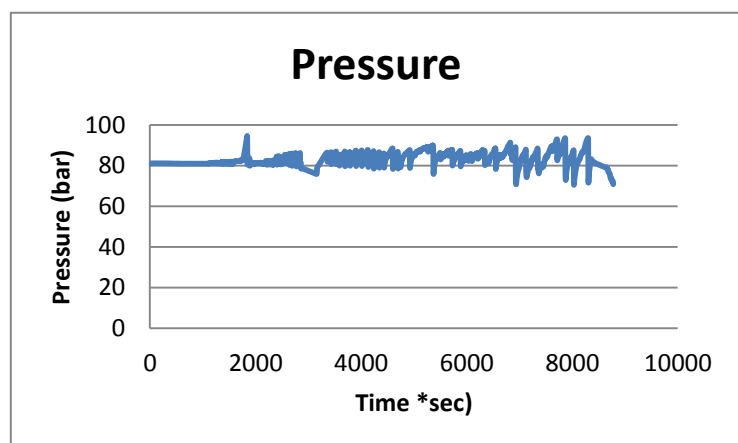


Figure 11 Pressure development Experiment CT-3

around 15 bars (75-90bars). Although this is not preferable, the pressure stayed far above the desired MMP of 67 bars and thus in the fully miscible region. The experiment had to be stopped after approximately 2.5 hr. for several reasons. The production was reduced to a slow rate and the big pressure oscillation caused unstable production and small amounts of oil spill occurs due this sudden oscillation of the pressure; oil is thereby released with a bigger force than the phase separator can handle.

The numerical recovery profile is also plotted in Figure 10. The experimental ultimate recovery is approximately 20% lower than the numerical data. The slope and time scale of the recovery process show a similar trend. After 8000 seconds the oil production is stopped. The drainage rate is fast in the first 2000 seconds and the cumulative production attains an asymptotic value. The model input data rely on gravity drainage, viscosity and density changes. The heterogeneity of the porous medium is not included in the model. These processes can cause the difference of 20% less recovery; the oil can be trapped or slowed down. The previously mentioned early breakdown of the experiment combined with the possible oil sample production in the gas phase (see experiment CT2) and minor oil spills are believed to be responsible for measuring less than 100% recovery. All the same, based on these observations the modelling outcome gives a reasonable and qualitative approximation.

One of the most important goals was to see the development of the CO₂ into the core and this is seen in the time interval of the experiment in which CT images were collected. The scanning process is identical to the immiscible experiment, subtracting the images from the oil saturated sample with the images fully saturated with CO₂. Figure 12 shows the CT-images of the experiment at the time in minutes indicated below Fig. 12.

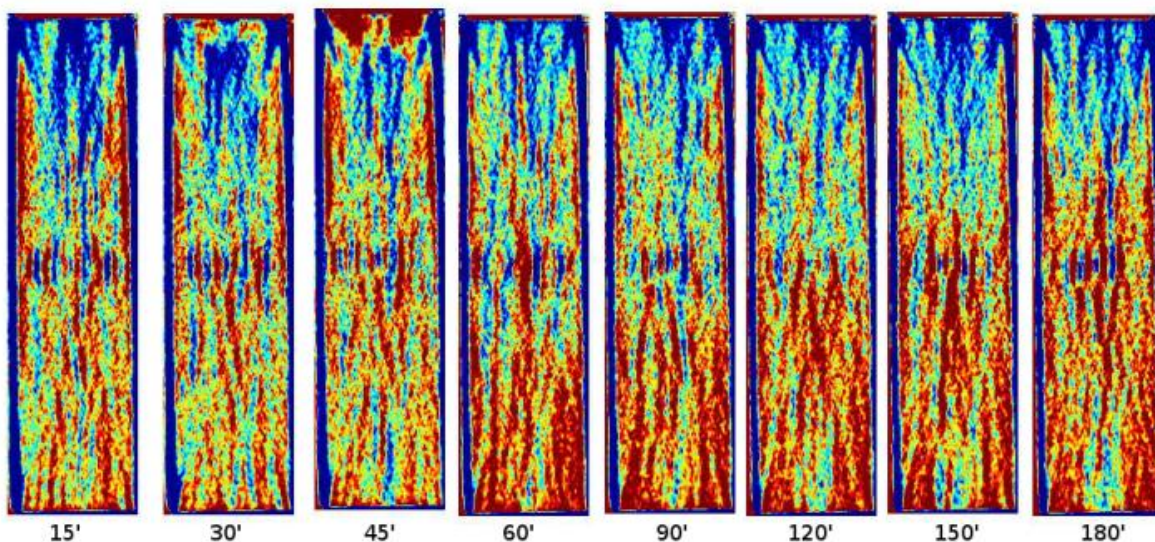


Figure 12 CT-images for fully miscible CO₂ injection; Experiment CT-3

Although these images are not as clear as the images from the miscible experiments, probably caused by a smaller density difference, a definite trend of a moving red front from the bottom side is visible. As in the immiscible experiment, this red front represents the CO₂. Unlike the immiscible experiment there is no sharp interface between CO₂ and oil. Because of the state of miscibility, CO₂ and oil are in the same phase. Instead of a piston-like displacement there is a transition zone between the oil and the CO₂.

Another main difference compared to the immiscible experiments is the density difference of the mixture. CO₂ in a miscible state has a density of approximately 808 kg/m³ as compared to a density of 744 kg/m³ of the oil mixture. One would expect that due to gravity, the CO₂ enters the core from the bottom instead of from the top. This is exactly the trend observed looking at the CT-images.

6. Conclusions

- It is possible to study experimentally the transfer of gaseous components in the fracture to the oil in the matrix (core) under miscible conditions. The study shows the difference in performance between miscible, nearly miscible and immiscible conditions. Eight experiments were performed under a variety of conditions.
- The lowest recovery is observed at immiscible conditions due to capillary forces in the core between the gaseous phase in the fracture and the liquid phase in the core.
- The dimensions of the core during immiscible experiments are of importance. The oil in cores with a size of (length × diameter = 0.1 m × 0.03 m) is trapped in the capillary hold-up zone and therefore is not produced whereas in cores with a size of (length × diameter = 0.2 m × 0.05 m) gravity forces become important and lead to a recovery of 38%.
- The highest recoveries were observed for fully miscible conditions. Recoveries in the range of 85-100% were observed. A recovery of 62% was observed when the system was under developed miscibility conditions.
- CT-scans give an adequate visualization of the saturation distribution inside the core during high pressure gas injection. Although noise and artefacts of the core and core holder do not give an unambiguous picture, the images show a distinction between the displacement agent and the oil.
- When performing miscible experiments with CO₂ injection, a doping agent has to be used to increase the contrast between the components which have now a substantially lower density difference than the fluids in the immiscible experiments.
- CT-scans show that immiscible experiments show a piston-like displacement from the top side of the core whereas fully miscible experiments, show a transition zone between the oil and CO₂ developing from the bottom side of the core.
- A numerical simulation in COMSOL using Brinkman's equation in a matrix-fracture system shows a qualitative agreement with the experiments.
- Gravity drainage, capillary hold-up and mixing are the main mechanisms responsible for the ultimate recovery of the performed experiments.

The EOR method of gas injection to increase the oil recovery relies on the miscibility of the specified gas-oil system. Gas injection is normally used to maintain the reservoir's pressure but it can also contribute to the recovery. The contribution is due to the mass transfer between the two phases. For example, if the system's phases becomes completely miscible, the liquid-vapor interface will vanish. The system's efficiency can increase up to 100% due to a lack of interfacial tension and the detachment of oil drops in the system's pore space.

To describe a certain phase system we have to apply Gibb's rule phase rule:

$$F = C - P + 2$$

where F= the degrees of freedom

C= the number of components

P= the number of phases present in the system.

To illustrate Gibb's phase rule, Figure 13 gives an example of the phase diagram of CO₂.

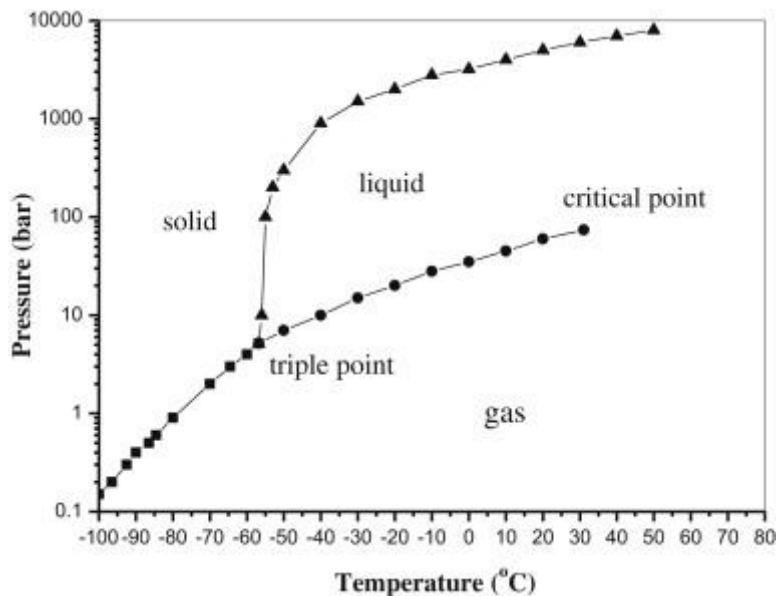


Figure 13 Phase diagram CO₂

CO₂ in its pure form will give a C-value of 1. If we consider that CO₂ can be in three phase-stages (solid, liquid and gas phase), the value of P can vary. P = 1 will describe a one phase system, where P=2 will lie on the line between 2 phases. Only on the triple point we have a three-phase system with P=3.

P= 1 will result in 2 degrees of freedom and therefore a certain system have to be described with 2 variables (P,V, or T). P=2 will result

in 1 degree of freedom, and it results in a dependence of two variables. If one wants to increase the Temperature, the Pressure has to change with a dependent amount to stay in the two-phase region. P=3 this will result in 0 degrees of freedom. Figure 12 shows that the triple point is fixed at a certain temperature and pressure. All variables have to be fixed at a certain position, there is no freedom to change and 3 phases will be present at that specific state.

For ternary systems, consisting of three components we have C=3 and F=5-P. When the system consists of only one phase F=4. A combination of the pairs (P,V), (P,T) or (T,V) together with two relative mass fractions(x₁,x₂) is used to describe the system. Note that the third mass fraction is

(1-x₂-x₁). If the system is in a two phase region, only 3 variables are needed. For practical reasons the (P,T) pair is chosen together with 1 mass fraction.

If the three components are mixed at a certain pressure and will result in a two phase region, the mixture will split in two phases with its own composition; two mass fractures. One of the mass fraction is given for the gas-phase composition and the other for the liquid-phase composition. They are connected with so-called tie lines, which are uniquely determined in experiments. This tie-line has a point which gives its overall composition (bulk composition). Note that if we take point B in Figure 14, mass fractions X and Y are determined uniquely and only the Temperature and Pressure are needed to describe the system according to Gibb's phase rule.

This research' experiments cope with several phase/composition systems. Injecting gas into a saturated (multi-component) oil sample will result in a multi-phase and multi-component system . These systems can become too complex and therefore we chose to focus ourselves on two or three component systems only. Working with a multi-component oil, the system is described with a ternary diagram, shown in Figure 14, with every (pseudo)component at the corner. The ternary diagram is made on a constant pressure and temperature. The white part with the tie lines inside is the two-phase envelope, both gas and liquid phases are present in here. This white part decreases in size, when the pressure increased.

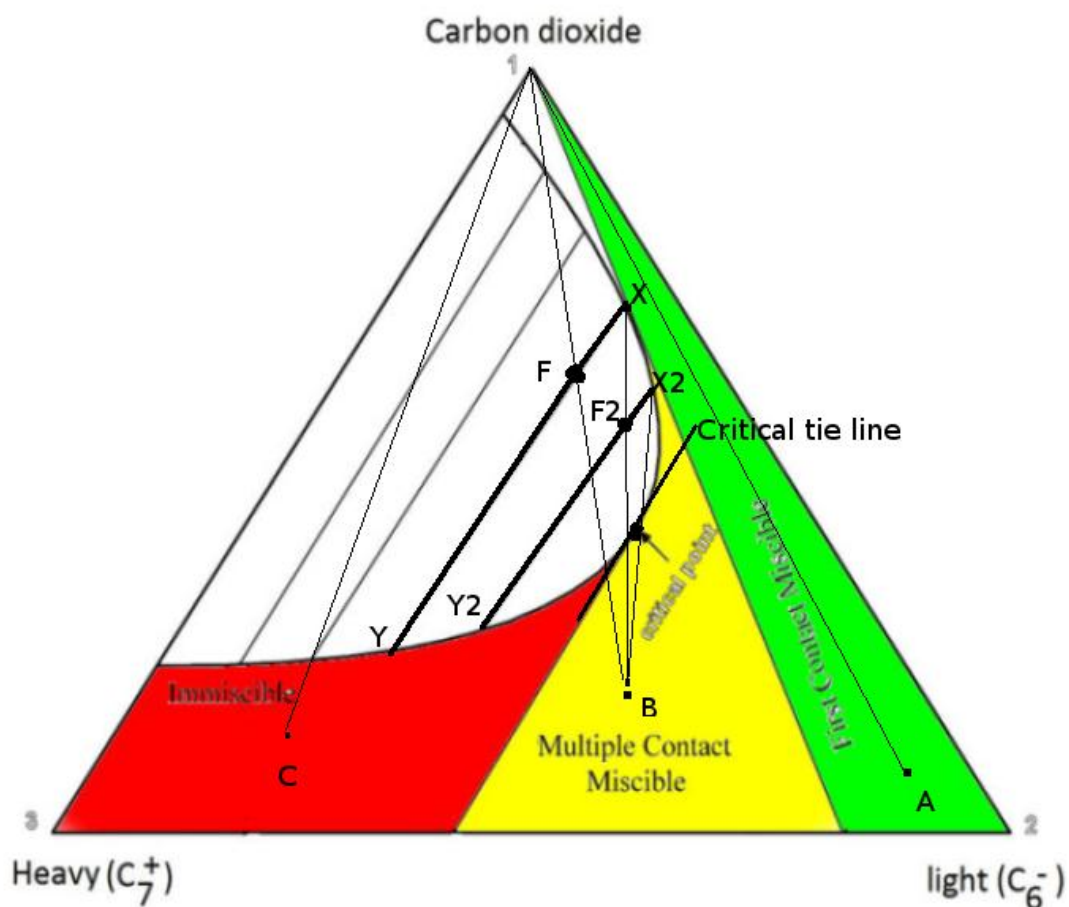


Figure 14 Ternary diagram CO₂-Oil

To illustrate the different miscibility stages, CO₂ is taken as the injection gas. A light and heavy component-term represent the oil sample. Three different oil composition (A,B and C) are taken to simulate the different miscibility paths. The components of Fig. 13 are similar to the the experiments and therefore Fig. 13 can be used to explain the concept of the miscibility stages in our experiments.

Figure 14 shows that a binary mixture of light and heavy oil always remains in the 1-phase region. A binary mixture of light component oil and CO₂ will also result in a 1-phase system whereas a binary mixture of Heavy component and CO₂ will result in a 1-phase system only when mixed within a limited ratio. Oil A simulates a light oil with a small amount of heavy components. When we draw a line to simulate contact between oil A and the CO₂, it will never cross the two phase region and therefore the system always remains 1-phase and is called *fully miscible*.

The line drawn between oil B and CO₂ crosses the two phase region. In the two phase region it originally forms a mixture of overall composition F, containing a gas composition X and a liquid composition Y. Note that the gas phase X, is the original gas CO₂, enriched with light and heavy components where the liquid phase Y is enriched in CO₂. The fresh oil B then contacts with the 'new' gas composition X and the same process will take place with an new overall composition and two enriched gas/liquid compositions. The gas is getting enriched during this process till the tie lines reach the critical tie line. After the multiple contacts the overall composition contains only of 1 phase and is described as a miscible process from that moment. This process is called *multi contact miscibility* or *developed miscibility* and is of importance in this thesis.

The critical tie line bounds the region for miscibility as is shown in Figure 14. Oil B lies in the immiscible region. Multiple contacts with 'new' gas composition will never move past the critical point and tie line and therefore the process is called *immiscible*. The only way to force the system miscible, is to increase the pressure and decrease the two-phase envelope. If the oil sample is situated on or on the right side of the critical tie line of the new phase envelope, it can become miscible with the CO₂*.

* This Appendix is based on the chapter "Ternary gas\oil displacement " in the book " Theory of Gas Injection Processes " by Franklin M. Orr Jr. and can include citations.

7.2 Appendix B Concept of capillary forces during immiscible experiments.

The immiscible experiments performed in this study, two phases are present viz. 1) a liquid phase representing the oil and 2) a gas phase representing the displacement agent. Cohesive and adhesive forces appear on the contact of these phases, resulting in a pressure difference across the interface (Mayer and Hassanizadeh, 2000). The definition of this pressure difference is defined as the capillary pressure p_c :

$$P_c = P_{nw} - P_w$$

where p_{nw} is the non-wetting phase pressure and p_w is the wetting phase pressure. In the immiscible experiments P_{nw} is equivalent to P_{CO_2} whereas P_w is equivalent to P_{oil} . At equilibrium the pressure difference of the interface is balanced by the interfacial tension, given by Laplace's equation of capillarity (Mayer and Hassanizadeh, 2000) and is furthermore explained as a function of porosity and permeability by Hagoort, 1970:

$$p_c = \frac{2\sigma}{r'} = \sigma \sqrt{(\phi/k)}$$

where σ is the interfacial tension (mN/m), and r' is the radius of curvature for a hemispherical interface. A certain threshold capillary is therefore needed to drive a non-wetting phases (the CO_2) through the oil saturated pores. ϕ is the porosity (-) and k is the permeability (m^2)

The capillary pressure head, for a an air-water system is determined in terms of an equivalent height of a water column. The density of air is often neglected and this results in the following capillary head definition:

$$h_c = \frac{p_c}{\rho_w g}$$

The estimation of a CO_2 -Oil is different than the previous equation. One can't neglect the density of the pressurised CO_2 . The adjusted equation for our system will be given by:

$$h_c = \frac{(\sigma \sqrt{(\phi/k)})}{\Delta\rho g}$$

where $\Delta\rho = \rho_{oil} - \rho_{CO_2}$

7.3 Appendix C Worldwide EOR potential in fractured reservoirs

Worldwide numbers of oil production and reserves are used to obtain a better insight in the potential of EOR. The volume of the Original Oil In Place (OOIP) gives an indication about the efficiency of the currently used oil recovery techniques. Table 2 (Godic et al. 2011) lists up the 54 world largest oil basins accounting 95% of the worlds estimated ultimate recovery (EUR) oil potential.

Region Name	Total OOIP (MMBO)	Basin Count	Primary/Secondary Production (MMBO)			
			Cum Production	Reserves	EUR	% of OOIP
Asia Pacific	236,480	8	42,218	35,473	77,691	33%
Central and South America	358,240	7	63,444	48,131	111,575	31%
Europe	145,842	2	26,550	23,252	49,802	34%
Former Soviet Union	751,158	6	109,428	145,342	254,770	34%
Middle East and North Africa	2,205,843	11	215,997	521,987	737,984	33%
North America/Non U.S.	155,718	3	30,157	23,649	53,806	35%
United States	595,700	14	173,500	15,871	189,371	32%
South Asia	22,663	1	3,375	5,065	8,440	37%
Sub-Saharan Africa and Antarctica	150,372	2	22,363	25,877	48,240	32%
Total	4,622,017	54	687,032	844,647	1,531,679	33%

Table 2 Worldwide oil reserves and potential

These oil fields have an estimated amount of 4.662 billion barrels of oil that already is discovered. From this 4.662 billion barrels, 687 billion is already produced by primary and secondary production. This gives an EUR of 1.531 billion barrels of and that corresponds to an average recovery of 33% of the OOIP. The 67%, meaning 3.090 billion barrels of oil that is left behind is a target for EOR.

The undiscovered reserves of oil is still a matter of debate. Countries as Saudi Arabia and Iraq produce their oil from only a small number of fields while they discovered but not developed over 50 fields each. Estimations from the U.S.G.S. show that there is an additionally number of 8700 billion barrels of undiscovered oil in place which would provide around 5800 billion barrels for EOR purposes. From the numbers it becomes clear that the potential of this tertiary recovery methods is of great interest.

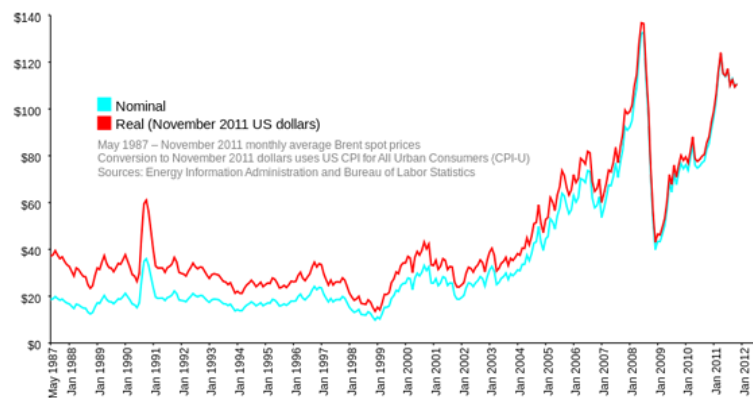


Figure 15 World's Brent Oil price

Combined with an increased oil price shown in Fig. 15, the necessary research fund is available. The oil recovery process in EOR projects can be described in three phases. Primary recovery is first applied. The oil comes out of the reservoir by natural drive mechanisms, water influx, gas cap drive and gravity drainage. Gas re-injection or water flooding are secondary recovery techniques. These techniques are for improved production rates as well as maintenance of the reservoir pressure. Tertiary recovery also known as EOR is the classification for all techniques used after the secondary recovery.

EOR is divided in three categories: thermal, chemical or solvent methods.

Thermal methods: The method used mostly worldwide is thermal EOR. The injection of steam and hot soak are methods to decrease the oil viscosity and therefore the oil can flow out more easily.

Chemical methods: Chemical flooding by the injection of surfactants or polymers is used to get a higher viscosity ration between water and oil during a water drive. Viscous fingering and water coning are prevented. The interfacial tension between water and oil can also be reduced by surfactant injection. This reduction makes oil that is trapped by capillarity pressure mobile again and available for production.

Solvent methods: Solvent injections are primary used to mix with the reservoir oil and thereby reduce the viscosity and density of the oil and reduce the interfacial tension between. Liquid solvents like pentane and hexadecane (Kahrobaei, 2011, Berg et al. 2010) help to improve miscible displacement recovery. Gases can also be used as solvents. Certain gases like CO₂ have a minimal miscibility pressure (MMP) from which the gas is miscible with the oil.

Natural fractured reservoirs are responsible for almost 20% of the global hydrocarbon reserves that can be produced. To forecast the production rate of these reservoirs is among the most challenging topics of the oil and gas industry.

In natural fractured reservoirs there is big difference between the fracture and the matrix. Many carbonate reservoirs, with usually low permeabilities, owe their production to these fractures. Fractures are a result of rock failure due to geological stress changes induces by tectonics or litostatic pressure changes. In geological terms, a fracture is any planar or curvi-planar discontinuity that results from the process of brittle deformation in the earth's crust. Planes of weakness in rock respond to changing stresses in the earth's crust by fracturing in one or more different ways, depending on the direction of the maximum stress and the rock type (Djebbar and Donaldson, 2012). A fraction can have a positive or negative effect on fluid flow depending on the connection with the matrix and its pathway in the reservoir rock.

To predict the performance of a natural fractured reservoirs by gas drainage several driving mechanisms have to be simulated. Natural convection, molecular diffusion, gas oil gravity drainage and capillarity effects are all contributors in the reservoir production rate.

7. Acknowledgments

I want to thank professor Ruud Schotting for the contact with Delft University of Technology. I want to thank Rouhi Farajzadeh for creating a research in my line of interest, combining CO₂ storage with EOR. Special thanks go to professor Hans Bruining, for the very useful evening meetings at his place, finalizing the thesis and help me with the understanding of the most important mechanisms and the modelling described in this thesis. I want to thank all technicians who contributed in the preparing of the experiments and data acquisition.

At last I want to thank Amin Amerighasrodashti, who was my main supervisor. He learned me how to prepare an experimental set-up from the beginning and taught me never to give up when an experiment failed. He reviewed my thesis from the beginning and gave me very useful advice in making this whole project successful.

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