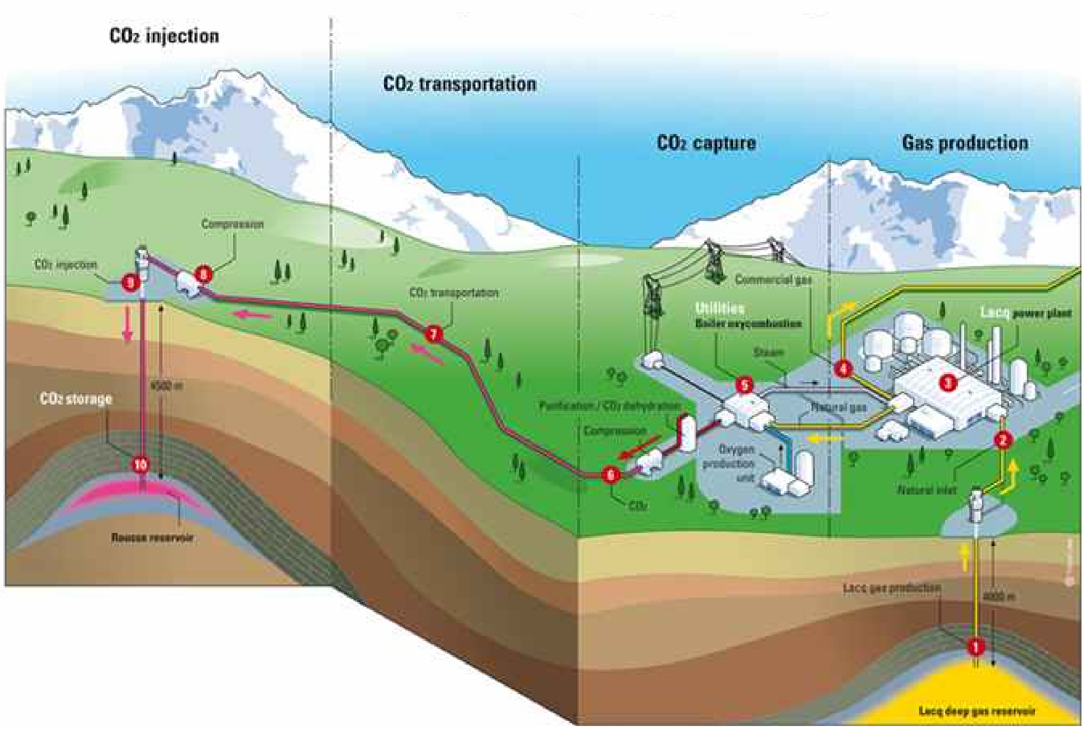

Experimental studies of Carbon dioxide Injection for enhanced Oil Recovery Technique

M.Sc Oil and Gas Technology

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Abstract

The main purpose of this thesis report is to investigate the possibility of Carbon dioxide injection for Enhanced Oil recovery and to calculate the potential of oil recoveries from North Sea chalk samples.

A number of parameters affect the minimum miscibility conditions, including chemical compositions of the oil and the injection gas, and the reservoir temperature. It is also believed that physical dispersion can locally have some impact on the minimum miscibility conditions.

The process of achieving miscibility at the minimum miscibility conditions can be different, depending on the compositions of the displacing and displaced fluids and the reservoir temperature.

Detailed experiments have been performed on supercritical extractor at high pressure and temperature. In total 9 experiments have been performed using cylindrical core samples and cubical core samples with temperature range of 50, 60 and 70°C.

To analyze the displacement of the crude oil through carbon dioxide flooding, minimum miscibility pressure determination is important parameter. The oil recovery grows sharply till the value of 180 MMP, and the highest volume of extracted oil occurred at the pressure of 180 bars. That indicates that this value is a MMP.

Volume of oil displaced from chalk samples using CO_2 injection plotted against pressure gave the minimum miscibility pressure (MMP), the value determining the applicability of gas injection to the oil field. Additionally, volumetric calculations were calculated to show the recoveries ratios. The recoveries ratios for cubical and cylindrical samples were calculated from 26% to 55 percent%, with a pressure range of 100 to 430 bars.

Oil samples after extracted from supercritical extraction unit were visualised, and it was found at lower values of pressure, when first sample was extracted at 100 bar, it was viscous and was difficult to move. With the increasing pressure values samples extracted were observed less viscous and were able to move, which is indication of decrease in viscosity and mobility ration with fresh carbon dioxide, continuously injecting into the core samples. At the value of minimum miscibility pressure at (180bar) the viscosity of extracted oil was observed, that corresponds to water viscosity. Porosity of cubical and cylindrical core samples was found 36%, saturating with oil and saturating with water was found 39%.

The samples of oil obtained at different temperatures and pressures have been analyzed in gas chromatograph apparatus to check the types of hydrocarbons extracted at every specific pressure. At lower pressure value carbon dioxide displaced lighter hydrocarbons and it can be seen in the trends taken from gas chromatography unit. When pressure started increasing the heavy hydrocarbons can been seen on the chromatograms.

Thermogravic analyzer (TGA) has been performed to find loss in weight of oil with respect to time, and its found that in loss in weight was 45% in first sample because it was injected with delayed time, but second sample which was injected without any loss of time, loss in weight was about 42%.

GULRAIZ KHAN --

Acknowledgement

I would like to express my profound gratitude and deep sense of indebtedness to my learned guide supervisors Svetlana N. Rudyk, Erik G. søgraad for their able guidance, generous help and valuable suggestions for the accomplishment of this task.

I would also like to recognise here the cooperation and support shown by the library and lab staff during the project work.

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Preface

This report contains experimental studies based on minimum miscibility pressure determination by using supercritical extractor high pressure unit. The report consist two parts, theoretical part which explains briefly on EOR techniques, and carbon dioxide capture, transportation and underground storage and injection. Further minimum miscibility concepts have been explained using ternary diagram and phase diagram for North Sea reservoir temperature and pressure conditions. Basic petrochemical properties and important terms used has been explained briefly.

Experimental section of the report consist of four parts, In Part A porosity calculation with oil and water saturated core samples from Danish North sea has been found. Core samples dried were divided into cylindrical and cubical dimensions and saturated core samples were further used in supercritical extractor apparatus. Thermo gravimetric Analysis (TGA) has been carried out to find loss of weight of oil with respect to time. The supercritical extractor has been used to extract oil in contact with pure Carbon dioxide. Crude oil sample has been taken from Danish North sea, Halfdan oil field. Graphs have been drawn between Saturation pressure and oil displaced to observe MMP values. Oil samples collected has been analyzed in Gas chromatography unit. Finally recovery percentage calculations based on different experiments has been find out.

All figures are numbered at bottom and tables are numbered at top. References can been found at the end of report and has been represented by superscript letters(^{R}) .The list of appendix can been found at the end of this report in Appendix list, A, B, and C.

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CHAPTER 1

1. INTRODUCTION

1.1 Introduction and analysis

Oil and gas consists of porous rocks covered by impermeable cap rock, which is often dome shape in location that prevents further migration of hydrocarbon. After more than a century of Petroleum exploitation, thousands of oil and gas fields are approaching the ends of their economically productive lives. Production in most of the oil fields includes three stages namely, primary, secondary and tertiary, or enhance oil recovery. During the primary recovery, the natural pressure of the reservoir or the gravity drive oil into the well bore and artificial lift technique, but only 10 to 25% of the reservoir original oil in place is produced. Secondary methods are used to re pressure the reservoir and drive out the remaining oil. Water is usually used as it is available and cheapest; through water flooding process it is pumped to maintain the required pressure of reservoir. Water flooding is effective in all reservoirs, and typically recoveries are 25 to 45% after primary recovery. Injection of hydrocarbon based gas into existing gas cap is also used to recover the oil.

In most field only a portion of Original Oil in Place is recovered using standard recovering extraction methods. Primary oil recovery (pumping oil with no pressure artificial membrane), and secondary, where field is flooded with water, will recover 20-40% of the oil originally found in the reservoir. EOR has potential to increase the oil field ultimate recovery of oil up to 60%, and extend oilfield by decades.

Carbon dioxide can be used in a process know as EOR to recover more oil. When CO_2 is injected for EOR it contacts oil that cannot be produced conventially and causes it to swell and becomes less viscous, if the subsurface rock is to be thought as sponge-like with pores containing the oil, and then swelling of the oil helps to push the portion of oil out of pores. The reduced viscosity then improves the flow of oil to the production wells. This technique is called CO_2-EOR is well established. If the CO_2 is used then stored in the oil reservoir, EOR has the potential to become an environmentally attraction option as well as economical.

Depleted oil and gas fields have a number of attracted features as Carbon dioxide storage reservoirs.

- Exploration costs would be small
- The reservoirs are proven traps, known to have held liquids and gases for million of years.
- There is the potential to re-use some parts of hydrocarbon production equipment to transport and injected CO_2.

Most of the CO_2 extracted from natural reservoirs, but some is captured from natural gas plants and ammonia plants. In addition, much of the technology for the transport and storage of gases is well established and in the wide spread use. Large volumes of CO_2 are routinely transported in pipelines. The global potential for the storage CO_2 in depleted oil and gas field and underground resources at a cost of less than 20$/ton of CO_2.

Underground storage of CO_2 used for EOR recovery is one of the most promising and economic ways to effect the geological storage of CO_2.

1.2 Project Objective

The main objective of this report is to know about the CO_2 injection for the purpose of enhanced oil recovery and to get knowledge about projects related to EOR in mature and depleted oil and gas reservoirs. To understand Gas injection and miscibility concepts briefly and further phase behaviour of reservoir fluids using ternary diagram system.

CO_2 injection system, also called enhanced oil recovery system, is a procedure used to extract maximum oil amount. This system is performed through injecting natural gases like carbon dioxide to the oil wells.

The main objective of the CO_2 injection is to stimulate the oil droplets that are inside the oil reservoir rock. MMP is achieved by lowering the viscosity of the oil to make it flow easily to the surface. is CO_2 a fluid which has the density of a liquid and the viscosity of a gas. is CO_2 easy to meter and pump, so it is the ideal tool to be used in the enhanced oil recovery system. CO_2 is the perfect solvent for oil. It can move oil from the reservoir much more efficiently than water.

To calculate the minumum miscibitly pressure(MMP) is important part of this study, the minumum pressure at which miscible recovery takes place. This minimum dynamic miscibility pressure depends upon several factors, such as compostion of injected gas, reservoir temperature and pressure, charactrestics of in place fluids. The key objectives of experimental based analysis are summerized as fallows.

- To study the minimum miscibilty concepts in detail by using ternary diagram and phase behavoir of supercritical fluid.
- To calculate the value MMP of Carbon dioxide in supercritical high pressure unit, and furthur analyse the samples in Gas Chromatography unit for hydrocarbon identification.
- Thermogravic analysis of samples to measure weight loss of material with respect to time.

1.3 Problem analysis

The displacement of crude oil by supercritical carbon dioxide miscible flooding at certain temperature and pressure which effects the miscibility process was analysed in detail in this project. The crude oil sample, and core sample was taken from Halfdan oil field(North sea reservoir).

Sample of crude oil was collected at 180bar pressure and 53.8 ^oC. the layout diagram of task and approach to towards the results are shown in figure below.

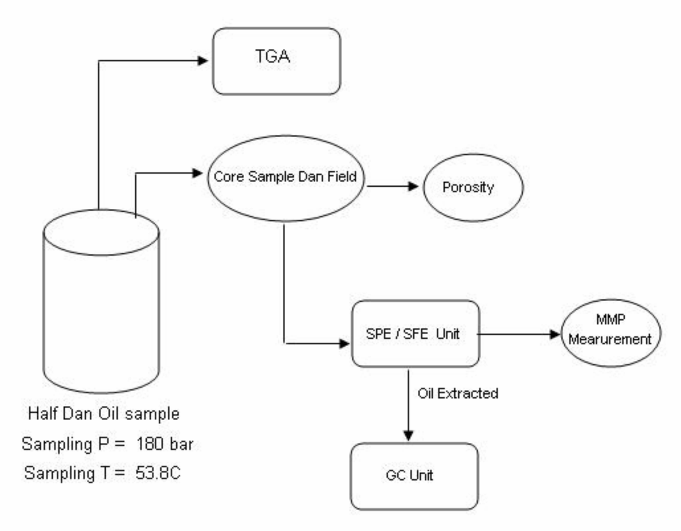


Figure 1:Layout of Experimental and working setup

The work performed on carbon dioxide injection for EOR is an extension of previous research work carried out in Aalborg University, Esbjerg. So all the drawbacks and experimental techniques has been considered during this project.

In order to investigate the minimum miscibility concepts the core sample has been dried in over at 105 ^oC, for 24 hours and then was saturated with oil sample using the vacuum unit. Porosity of sample was analysed after saturating it with oil and water as well. Then core sample was used in **Spe SFE** apparatus to recover oil using supercritical CO_2.

Thermo gravimetric analysis has been taken out to find how much weight of oil is loss with respect to time scale. Two sample of crude oil has been taken to analyse in TGA unit at 900 ^oC.

The samples extracted from supercritical units are then analysed in Gas chromatography unit to find out the presence of hydrocarbons.

CHAPTER 2

2. ENHANCED OIL RECOVERY

2.1 Introduction

Enhanced oil recovery (EOR) is defined as "the recovery of oil by injection of a fluid that is not native to the reservoir." EOR is a means to extend the productive life of depleted and uneconomic oil field. It is usually practiced after recovery by other, less risky and more conventional methods, such as pressure depletion and water flooding, have been exhausted. When primary and secondary recoveries starting depleted we go towards the Enhanced Oil recoveries methods.

Not all reservoirs are amenable to EOR. Effective screening practices must be employed to identify suitable candidates. As part of the screening, discounted cash-flow projections are routinely performed to assess profitability. At the core of these projections is an estimate of recovery performance. In the initial screening studies, invariably, performance predictions from numerical simulation studies are not yet available.

Therefore, other methods usually empirical are needed to estimate future performance.

2.2 EOR Methods

All of currently available EOR is based on one or more of two principles: increasing the capillary number and/or lowering the mobility ratio, compared to their water flood values. Increasing the capillary number means, practically speaking, reducing oil-water interfacial tension. The mobility may be reduced by increasing water viscosity, reducing oil viscosity, reducing water permeability or all of the above.

EOR processes are divided into four categories: thermal, gas, chemical, Microbial flooding, gas miscible recovery and other summarizes the main processes within each category. The processes are typically defined by the nature of their injected fluid. For instance, gas EOR includes hydrocarbon miscible/immiscible and CO_2 miscible and immiscible processes.

Thermal EOR processes

- Steam flooding
- Cyclic steam stimulation
- In-situ combustion
- Hot water flooding
- Steam-assisted gravity drainage

Gas EOR processes

- Hydrocarbon miscible/immiscible
- CO_2 miscible
- CO_2 immiscible
- Nitrogen
- Flue gas (miscible and immiscible)
- Gravity drainage

Chemical EOR processes

- Micellar-polymer
- Polymer
- Caustic/alkaline
- Alkaline/surfactant

Other EOR processes

- Carbonated water flood
- Microbial
- Electromagnetic heating

2.2.1 Thermal EOR Methods

Thermal methods lower mobility ratio by decreasing oil viscosity. Since the effect of temperature is especially pronounced for viscous crude, these processes are normally applied to heavy crudes. This "niche" is actually quite large world wide, consisting of more in-place hydrocarbon than light crudes. An approximate classification of viscous crude oils based on reservoir conditions viscosity is as follows:

Viscosity less than 1,000 cp heavy crude
1000 to 100,000 cp tar sand
100,000 to 1,000,000 cp bitumen or oil shale

Besides being aimed at viscous crudes, thermal methods will be successful if there is a rigorous heat management procedure in place. This means that heat losses are to be minimized as much as possible. Heat loss sources are:

1. Losses to rock and water - minimized by restricting application to reservoirs with small water saturation, large porosities or small shale content.

2. Losses to surface equipment - normally the smallest heat loss source, this is minimized by insulating surface lines and minimizing line length.

3. Losses to well bores - minimizing well bore heat loss is done by restricting application to shallow reservoirs. Heat loss in this manner can be controlled by insulating down hole tubulars, generating heat down hole, using in-situ combustion, injecting the steam at high rate or evacuating the production casing.

4. Losses to adjacent strategy - minimizing this form of heat loss means minimizing the producing life of the field (normally done with small well spacing) or Restricting application to thin reservoirs.

2.2.1.1 Cyclic Steam Stimulation.

CSS is also known as steam soak, or huff and puff. In this process steam is injected into a well bore out to a heated radius of a few tens of meters. Then the original steam injector is converted to a producer and a mixture of steam, hot water, and oil produced. CSS is the most common steam injection process today. Most of the time most of the wells are producers: there are no dedicated injectors. CSS is often used as a precursor to steam drive.

2.2.1.2 Steam Drives.

Also known as steam flooding, in this process steam is injected into dedicated wells and the fluids driven to a separate set of producers. Combined CSS and steam drives often recover more than 50% of the original oil in place. This combination is the first commercial EOR process and has been so since the mid 50s. Perhaps more than 2 billion barrels of oil have been produced in this manner to date.

2.2.1.3 In-situ Combustion

This process is an attempt to extend thermal recovery technology to deeper reservoirs and/ or more viscous crudes. In recent years it has become known as high-pressure air injection. In-situ combustion recovers 10-15% of the original oil in place.

2.2.2 Gas EOR Methods

These methods are capillary number increasing methods. They are also called solvent flooding, miscible-gas flooding or simply gas flooding. The injecting can be dry gas, Enriched gas (hydrocarbon miscible), CO_2, nitrogen or flue gas, or combinations of these.

Solvent methods recovery oil by mass transfer. For some processes, the mass transfer of intermediate hydrocarbon components is from the crude to the solvent (vaporizing gas drive) and for others the transfer is from the solvent to the crude (condensing or rich gas drives). CO2, nitrogen or flue gas are vaporizing gas drives and hydrocarbon miscible drives are the latter. In all cases it is the intermediate component, the component that is doing the transferring, that is key.

If the reservoir pressure is large enough (or if there is sufficient intermediate content at the current pressure), the mass transfer will result in a mixture that is miscible with the crude, in which case the predominant recovery mechanism is a miscible displacement. In a miscible displacement, interfacial tension vanishes and capillary number becomes infinite. Failing this, the displacement will be immiscible. Immiscible displacements are not as efficient as miscible displacements but may still recover oil by swelling, viscosity reduction or permeability increase, or pressure build up. CO2 and enriched hydrocarbons tend to be miscible solvents; nitrogen and flue gas tend to be immiscible. Miscible displacements in the laboratory result in nearly 100% ultimate oil recoveries.

Field-scale displacements recover much less, primarily because the solvent tends to be more mobile that the oil/water mixtures they are displacing, which leads to bypassing of the solvent around or through the oil. Bypassing is the result of reservoir heterogeneity and viscous instability between two fluid fronts. Some types of heterogeneity can result in substantial mixing in the reservoir and a loss of miscibility.

The bypassing can be eliminated or at least reduced by co-injection of water with the solvent (the WAG process), conducting the flood in a gravity stable mode and/or using foams to reduce the gas mobility.

2.2.3 Chemical EOR Methods

These methods are increasing capillary number processes (micellar-polymer, caustic/alkaline) or mobility ratio processes (polymer). All are based on injecting one or more chemicals into a reservoir to bring about the aforementioned changes.

2.2.3.1 Polymer Flooding

Polymer methods consist of injecting an aqueous phase (water, orbrine) into which has been dissolved a small amount of a polymeric thickening agent. The thickening agent increases water viscosity and in some cases lowers the permeability to the phase to bring about the lowered mobility ratio. Polymer methods do not increase capillary number.

Primarily because of its small cost, there have been more polymer floods done than any other type of EOR process. Unfortunately most of these were take advantage of an artificial taxing policy in the US and not to recover much incremental oil. With the lapsing of the policy and the collapse of the oil price in the mid 80s, these projects virtually disappeared, giving way to a variation of the process based on polymer gels. With the restoration of the oil price, interest has picked up, especially because of the significant reported successes in the Chinese Daqing Field. Polymer processes have historically recovered about 5% of the original oil in place and taken about 1 lbm of polymer to produce an incremental barrel.

2.2.3.2 Micellar Polymer Flooding

Micellar-polymer processes are similar to polymer process but with the addition of a surfactant to the injection. The surfactant reduces oil-water interfacial tension making this process both a mobility ratio decreasing and a capillary number increasing process. This process virtually disappeared in the low price environment of the 80s but is experiencing revitalization, though as yet there are no current field projects. MP processes recover about 15% of the original oil in place, but they are not economical at oil prices less than about 30$/bbl.

2.2.3.3 Alkaline Flooding

Caustic/alkaline processes are an attempt to use the interfacial tension lowering properties of natural surfactants that exist in many crudes. A highly interesting innovation with this process is the use of a small amount of co-surfactant in the so-called alkaline surfactant process. Field experience is immature, but initial report suggest that incremental oil can be recovered for 20-25$/bbl.

2.2.4 Other EOR Methods

2.2.4.1 Microbial Enhanced Oil recovery

MEOR is known as tertiary oil recovery. Recovering Microbial Enhanced Oil Recovery (MEOR) is the use of micro organisms to retrieve additional oil from existing wells, thereby enhancing the petroleum production of an oil reservoir. In this method, selected natural micro organisms are introduced into oil wells to produce harmless by-products. These process help to mobilize the oil and facilitate oil flow, they allow a greater amount to be recovered from the well.

2.2.4.2 Gas Injection or hydrocarbon miscible injection

Oil displacement by CO_2 injection depends on the phase behaviour of CO_2 and crude oil mixtures that are strongly dependent on reservoir temperature, pressure and crude oil composition. These mechanisms range from oil swelling and viscosity reduction for injection of immiscible fluids (at low pressures) to completely miscible displacement in high-pressure applications. In these applications, more than half and up to two-thirds of the injected CO_2 returns with the produced oil and is usually re-injected into the reservoir by various means.[R1]

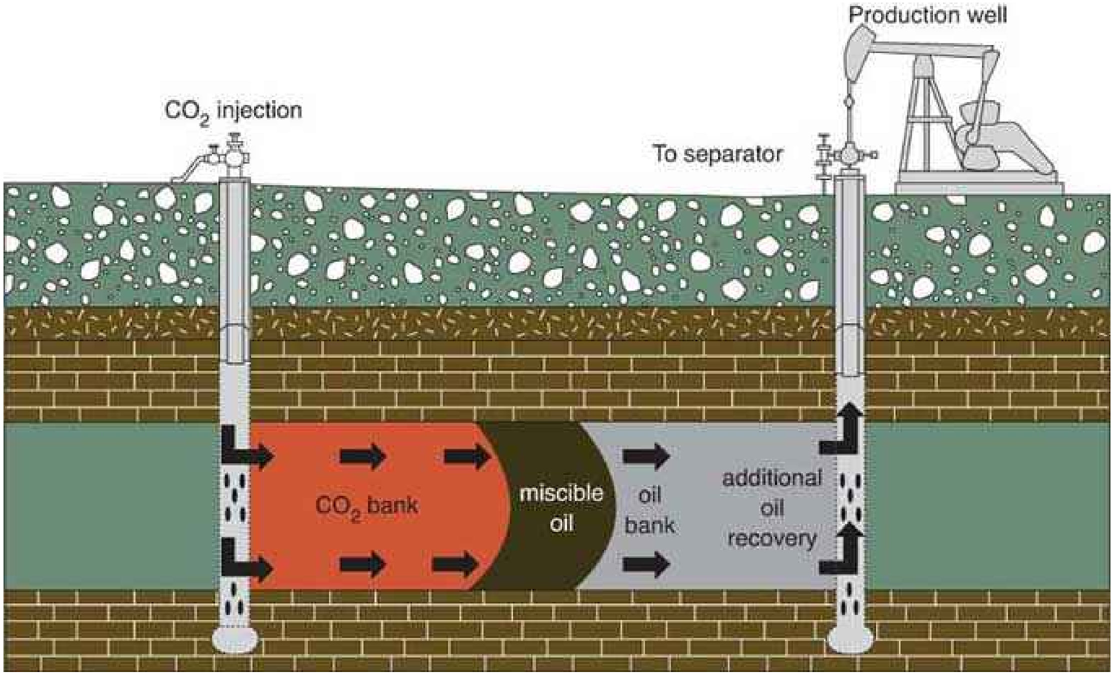


Figure 2: CO2 injection for enhanced oil recovery

2.3 CO_2 Injection Prospects

Carbon dioxide increase recovery from 7% to 15% after conventional water-flooding. CO_2 vaporizes or extracts hydrocarbons from the crude as heavy a the gasoline and gas/oil fractions. Vaporization occurs at temperatures where the fluid at the displacement front CO_2—rich gas, and extraction occurs at temperatures where the fluid at the displacement front is CO_2 -rich liquid.

The pressure required for achieving dynamic miscibility with CO_2 is usually significantly lower than the natural gas, flue gas and nitrogen. This is major advantage of the CO_2 miscible process because miscibility can be achieved at attainable pressures in a bread spectrum of reservoir.

CO_2 injection is useful because of the following reasons.

- Carbon dioxide injection extracts heavier compounds C_{15} – C_{30}
- The CO_2 solubility in oil causes swelling which enhance recovery.
- It reduces the interfacial tension between oil and water.
- Expansion of oil in this case is large extent in this case else than the methane and flue gases etc.
- CO_2 is soluble in water at high pressure as compared with other gases.
- Miscibility is attained low pressure as compared to other gases.

On the other hand CO_2 has some disadvantages like corrosion problems, and scale formation as well. Carbon dioxide flooding compared with water flooding results the low viscosity of CO_2 relative to that of oil. For example at most reservoir temperature of 110 °F, CO_2 is viscosity is about 0.03 cp at 1500 psi, where at 2500 psi, the viscosity is about 0.06 cp. The low viscosity of CO_2 causes the mobility ratio in most CO_2 floods to be unfavourable. The density of oil and CO_2 are similar at many reservoir conditions, which tends to minimize, although not necessarily eliminate, segregation between these fluids in reservoirs that have not been water flooded. In reservoir that have been water flooded or have had water injected with CO_2 to counteract the effects of viscosity ratio and permeability, the density contrast between water and CO_2 may cause segregation.

Before starting the details of injection of Carbon dioxide into suitable reservoir at required temperature and pressure, it is important to explain its caputre,tranportation by different means and storage. CO_2 capture and injection into depleted oil fields reduce the Green house gases (GHG) emissions while extending the economic life of aging oil fields.

2.4 Carbon dioxide Capture and Storage

The capture and geological storage of CO_2 is a process that consists of separating and recovering the CO_2 from process gases or flue gases at large industrial installations, then transporting it and injecting it into a suitable underground formation for storage.

There are three main steps involved in the process (i.e., capture, transport and storage), CO_2 must be separated from the other constituents (mainly water vapour and nitrogen).
Yet this step is crucial for at least two reasons:

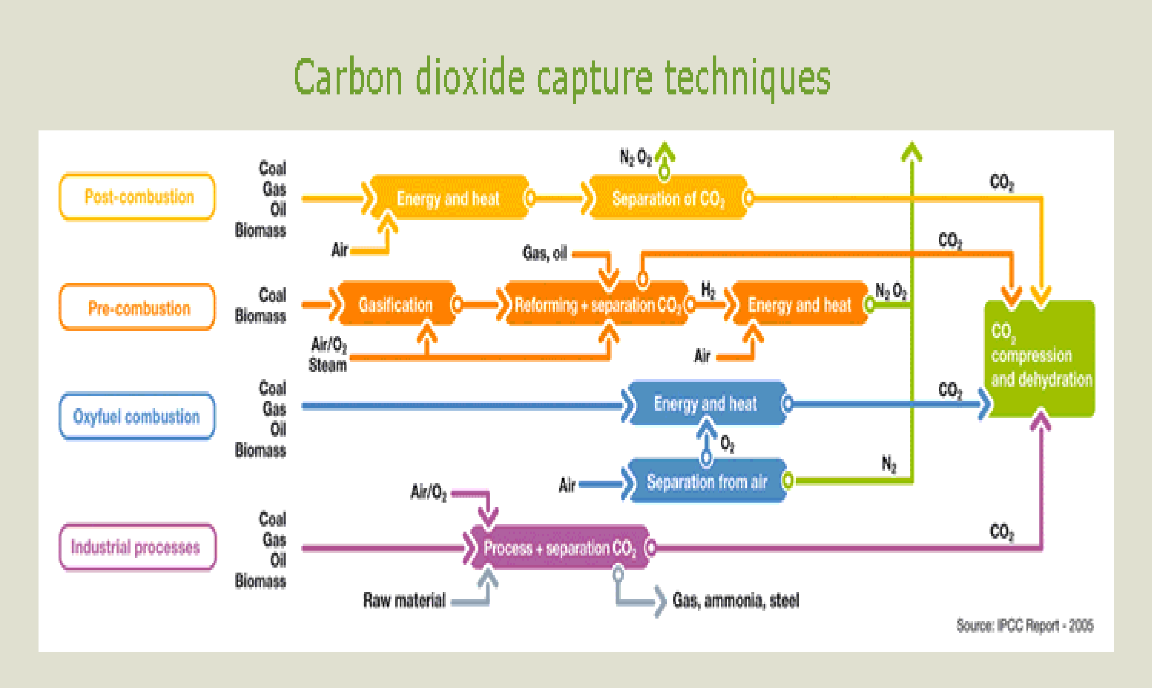
- Combustion gases contain an average of 3 to 15% CO_2, so removing the CO_2 reduces the volume that must be transported, and therefore the associated costs;
- Only a limited number of formations meet the specifications for CO2 storage, so isolating the CO2 is a means of optimizing the available storage capacity.

2.4.1 Carbon dioxide Capture techniques

There are three main techniques to capture dioxide as follow.
According to the type of installation, CO2 capture may take place at three different stages, termed post-combustion, precombustion, or oxyfuel combustion decarbonisation. Each of these techniques is at a different stage of maturity and offers its own advantages and drawbacks (cost, energy consumption, etc.).

- Post-combustion decarbonisation is the most mature, but also the most costly of the three techniques, and is appropriate for existing installations. It involves separating the CO_2 contained in combustion gases, usually by means of a liquid solvent such as mono ethanol amine (MEA).
- Pre-combustion decarbonization yields two separate concentrated streams of hydrogen and CO2, thereby facilitating CO2 capture. The process consists of treating the fuel either with steam and air (steam reforming) or with oxygen (partial oxidation) to produce a synthesis gas that contains mainly carbon monoxide (CO) and hydrogen, a potential energy carrier that generates no CO2 emissions. A second step converts the CO in the presence of water (H2O) then separates the resulting CO2 for capture and storage.

Oxyfuel combustion decarbonization is still in the pilot phase. This technique yields a combustion gas highly concentrated in CO2 (between 80% and 90% by volume) and could constitute a suitable retrofit technology for existing installations. The process uses high-purity oxygen instead of air for combustion, the main difficulty being to extract the oxygen from the air. Due to the high cost of this separation step, a “chemical looping” process is being investigated in which the oxygen supply is derived from a reaction involving a metal oxide, using metal particles such as iron filings, which would serve as the oxygen carrier from air to fuel.



Source: IPCC Report - 2005

Figure 3 :CO2 Capture Techniques

2.4.2 Carbon dioxide transport options.

CO_2 can be transported by pipelines. The CO_2 must then be pressurized to at least 73 bar to reach a supercritical state and a high density, giving it properties similar to the liquid state.

When transport distances exceed 500 to 1,000 km (the threshold varies according to the source quoted), transport by ship is considered a more economical option. In this case, CO_2 is transported in the liquid state under conditions comparable to those of LPG (liquefied petroleum gas) transport.

2.4.3 Various types of geological storage

A portion of the captured CO_2 can be reused by the food and chemical industries. However, the needs of industry fall far short of the quantities potentially recoverable.

Although the various possible options for geological storage are at different stages of maturity, all solutions will have to store the CO_2 at sufficient depth (more than 800 meters) in order for the gas to reach the supercritical state and thus occupy the smallest possible volume.

- Storage in depleted oil and natural gas reservoirs. This type of storage offers numerous advantages, the most significant being that the cap rock is impermeable and well known. Indeed, natural reservoirs have proven their capacity to contain hydrocarbons for several million years. Moreover, CO_2 storage in this type of formation is a practice which, although not widespread, is at least known to the oil and gas industry, which already injects CO_2 into oilfields to reduce crude oil viscosity, improve mobility and thereby boost the recovery rate – a technique known as Enhanced Oil Recovery (EOR). Finally, some of the infrastructure in place for exploration and production of crude oil (such as pipes and wells) can be reused for CO_2 storage operations, thereby helping to control costs. However, reservoirs are not always located near the source of CO_2 emissions; nor is the available storage capacity sufficient to meet all needs.
- Storage in unminable coal beds. In this option, the coal bed is not used as a reservoir, but stores the CO_2 by absorption of the gas. Provided the coal bed is adequately covered over by impermeable cap rock, this technique would allow not only storage of CO_2 but also methane recovery (ECBMR – Enhanced Coal Bed Methane Recovery). However, present understanding of this type of storage is still incomplete.
- Storage in saline aquifers. There are numerous such aquifers located in sedimentary basins, with areas of up to several thousand square kilometers. They can be either offshore or onshore. Formed of porous, permeable rock often saturated with brackish water or brine that is unfit to drink, these aquifers are potential storage sites for considerable quantities of CO_2, provided they are at a sufficient depth (> 800 meters) and have overlying impermeable layers. However, extensive work is still needed to gain better knowledge of these aquifers.[R3]

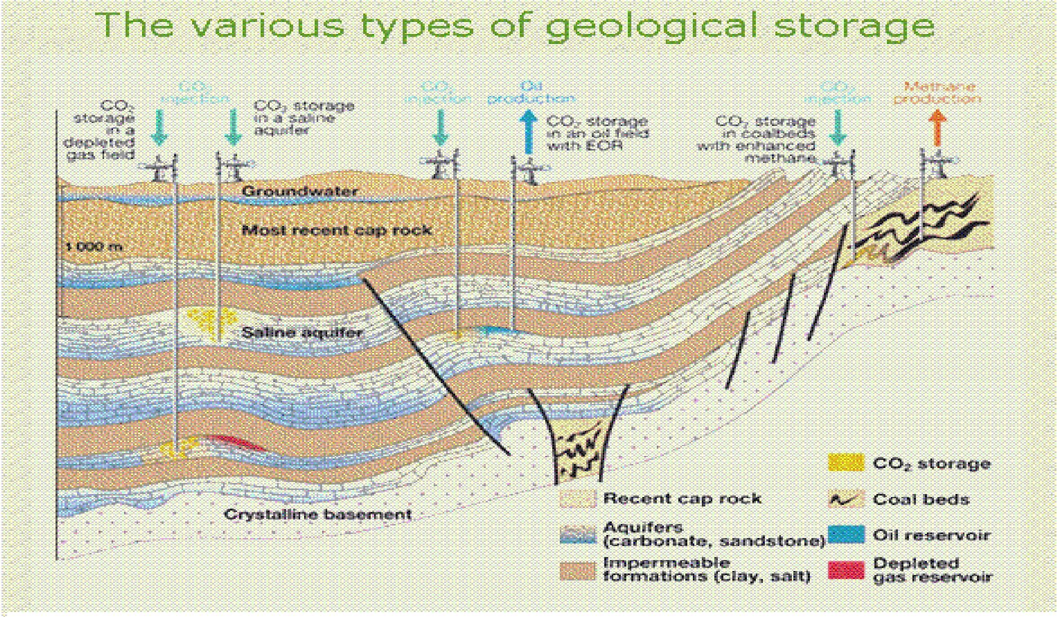


Figure 4: Various types of Geological storage of Carbon dioxide

2.4.4 Physical Properties Of Carbon Dioxide

Critical point

Critical temperature : 31 °C
Critical pressure : 73.825 bar
Critical density : 464 kg/m^3

Triple point

Triple point temperature : -56.6 °C
Triple point pressure : 5.185 bar

Molecular Weight

Molecular weight : 44.01 g/mol

Gas density

1.013 bar and 15 °C : 1.87 kg/m^3

Compressibility Factor (Z)

(1.013 bar and 15 °C) : 0.9942

Specific gravity (1.013 bar and 21 °C) : 1.521

The densities of oil and CO_2 are similar at many reservoir conditions, and, depending on the particular temperature, pressure, and oil composition, CO_2 can be either less or more dense than reservoir oil.
The figures no 3 and 4 shows the compressibility factor and density of pure CO_2 vs. temperature and pressure.
In figure 4, with pressure about 70 bar and 40 ^{o}F compressibility is about 0.2 while it is increasing at higher pressure values with increasing temperature values.
In figure 5, density of Carbon dioxide is varying with increase of temperature and pressure, and at high value of pressure 10000 Psia (690 bar) density is about 10 g/cm^3, which is almost constant with increase in temperature. R4

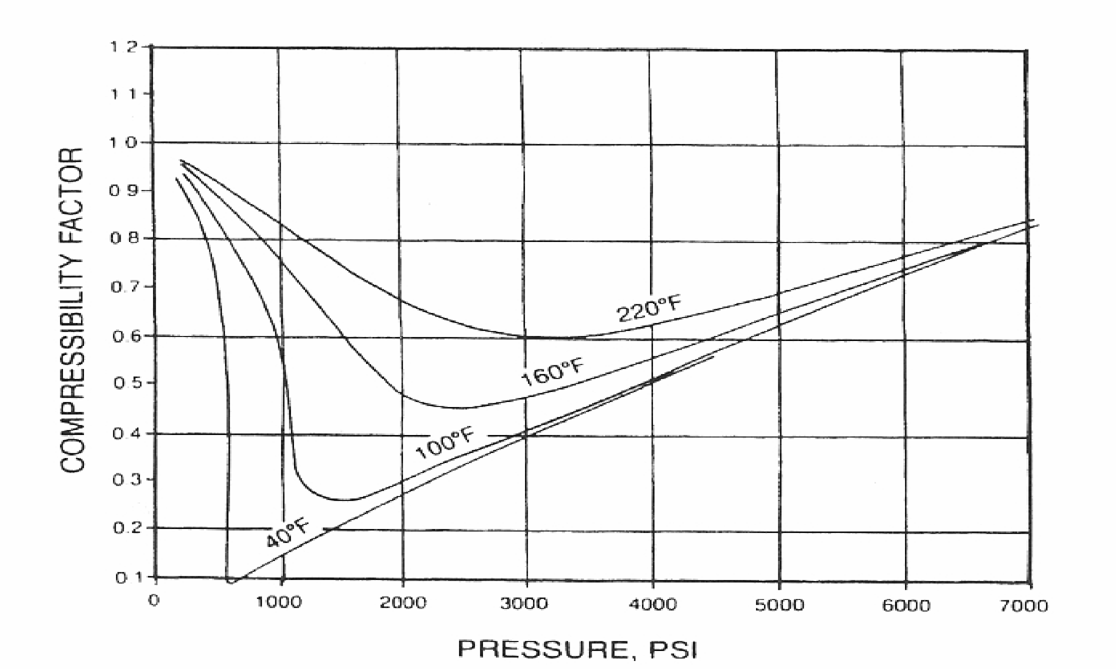


Figure 5: Compressibility factors for CO2

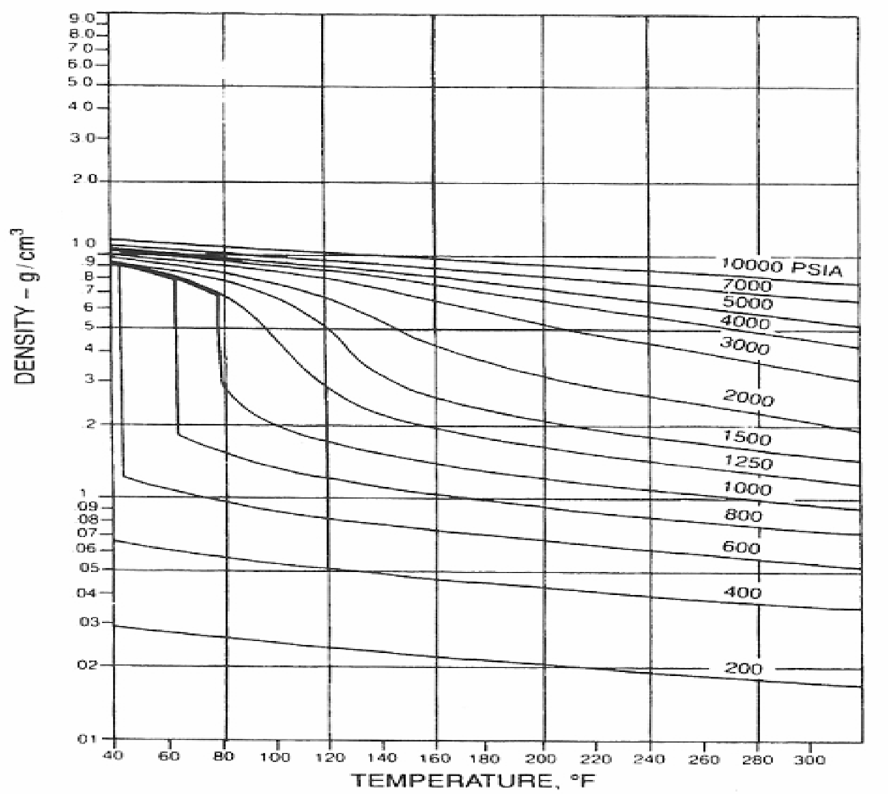


Figure 6: CO2 density versus temperature at various pressures

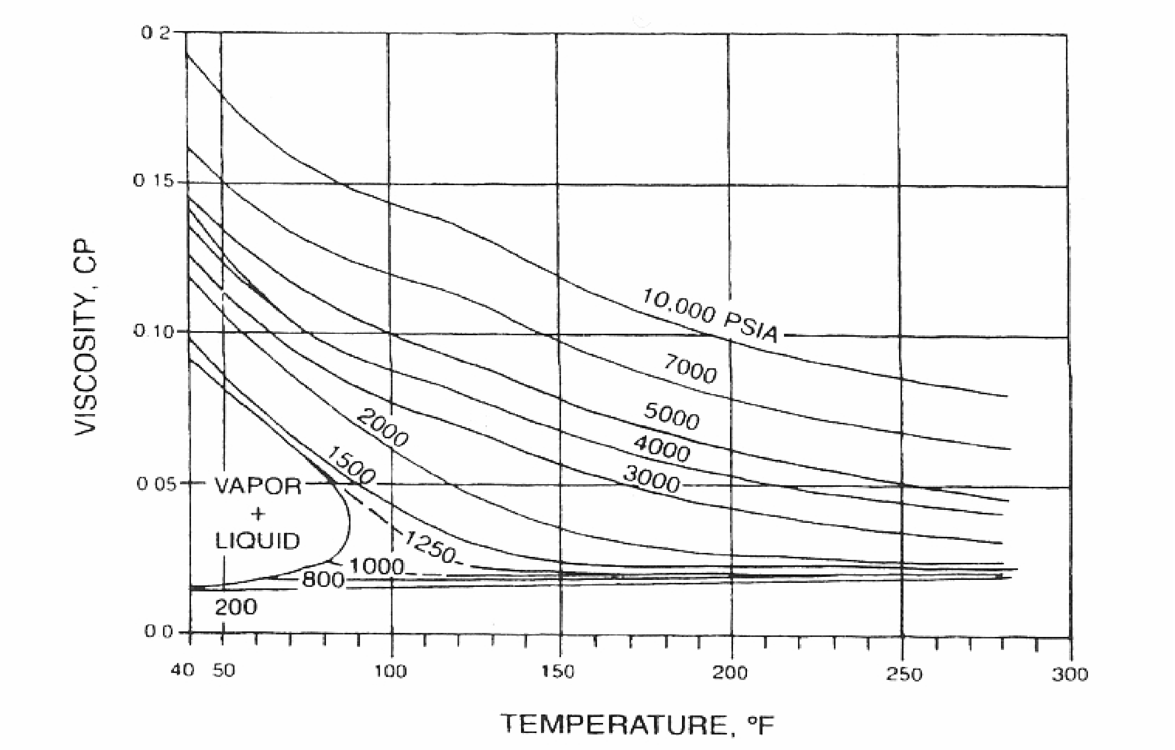


Figure 7: Viscosity of CO2

Figure 6 shows the viscosity of pure CO_2 versus temperature and pressure. Temperature is very interesting in miscible flooding; CO_2 viscosity is more gas-like than liquid-like.

In the figure we can see that in the range of MMP at pressure of about 1100 Psia (75 bar) there is vapor-liquid phase, but if we increase temperature further then viscosity of Carbon dioxide is decreasing.

Carbon dioxide is a partially soluble in water, and a portion of the CO_2 injected in a miscible flood will be dissolved , either by the water injected either CO_2 for mobility ration improvement. This reduces the volume of the CO_2 vailable for miscible displacement of the oil. Figure 7 gives the solubility of CO_2 in fresh water. CO_2 solubilty increases with pressure but decreases with increasing tempreture.

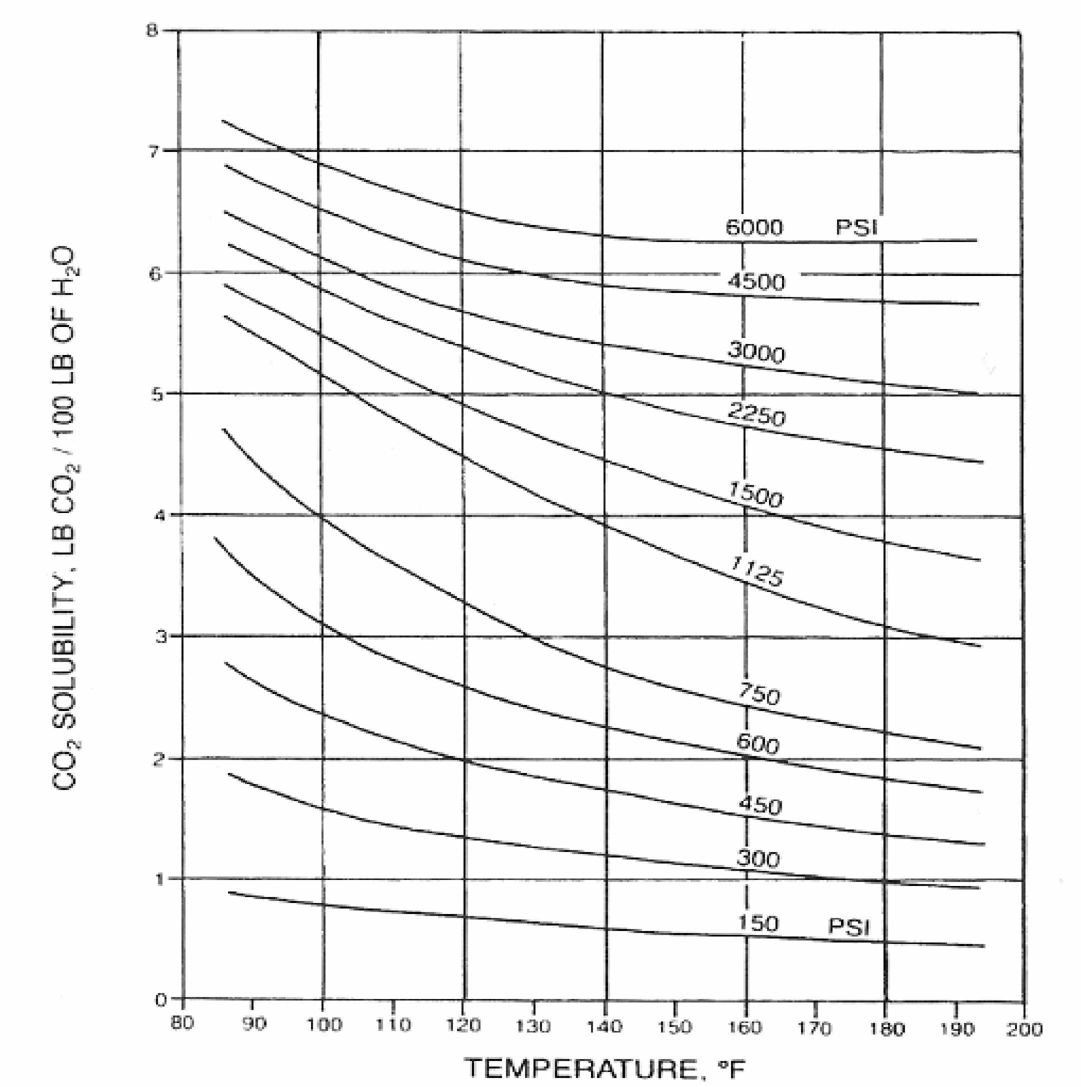


Figure 8: Effect of temperature and pressure on the solubility of CO2 in water

Solubility in brine decreases with increasing salinity of the brine, as shown in figure 7.
Water also is soluble in CO_2. Before transporting CO_2 in a pipeline or reinjecting it in an oilfield flood, enough water must be removed by drying to prevent condensation and corrosion in lines.

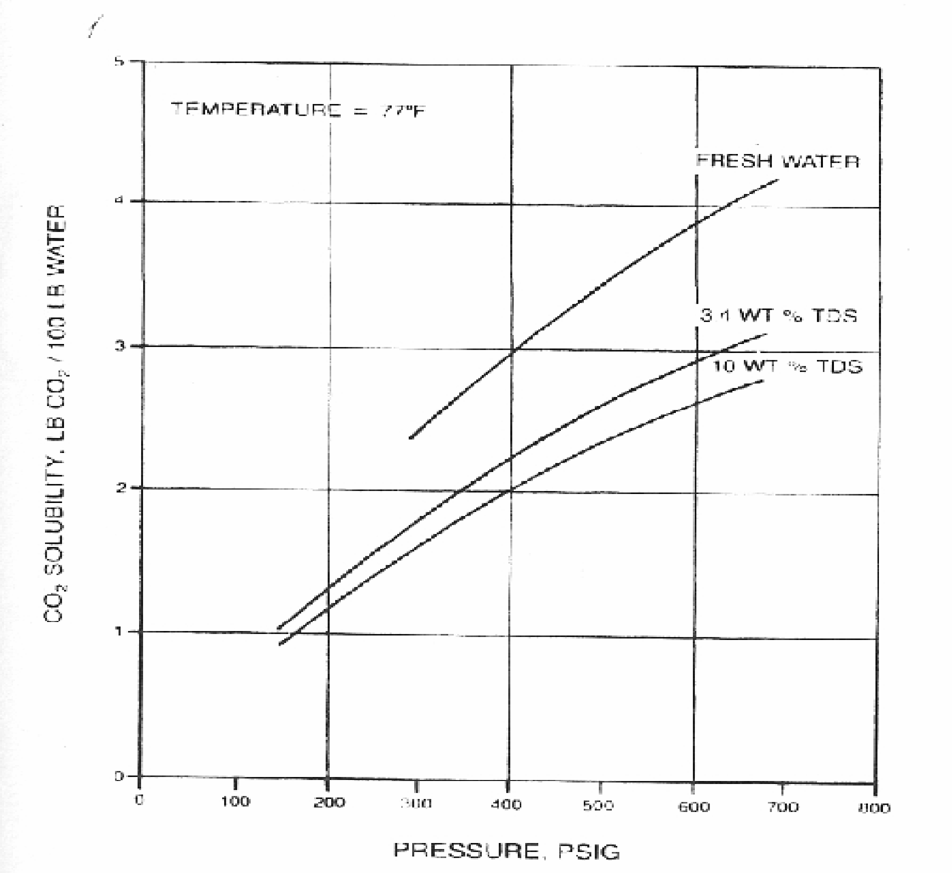


Figure 9: Effect of salinity on CO2 solubility in water

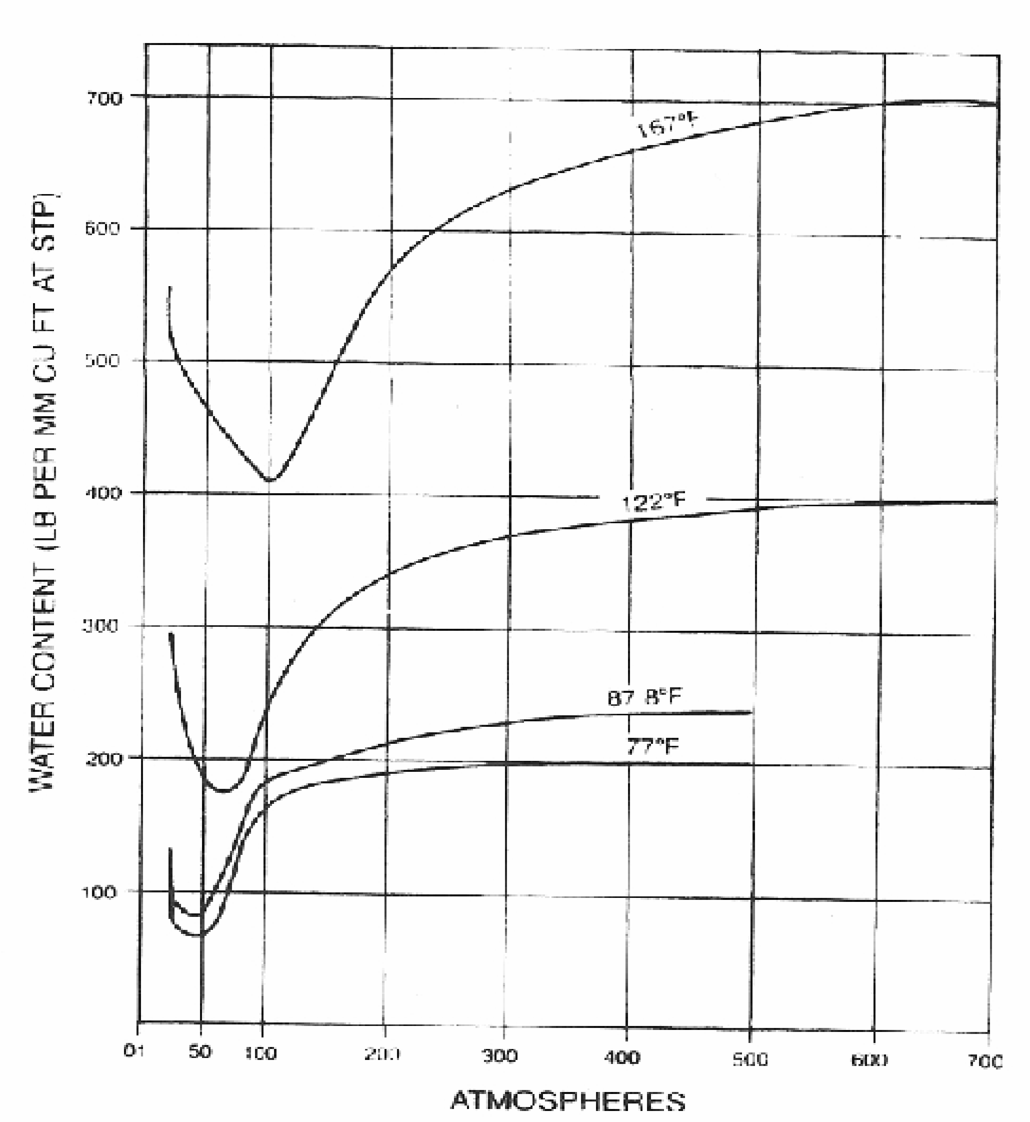


Figure 10: Water vapour content of CO2 at saturation

Figure 10 shows solubility of water in CO_2 for a range of temperatures and pressures. When water is present, CO_2 hydrates can form at appropriate temperatures and pressures. So before transporting CO_2, hydrate should be removed.

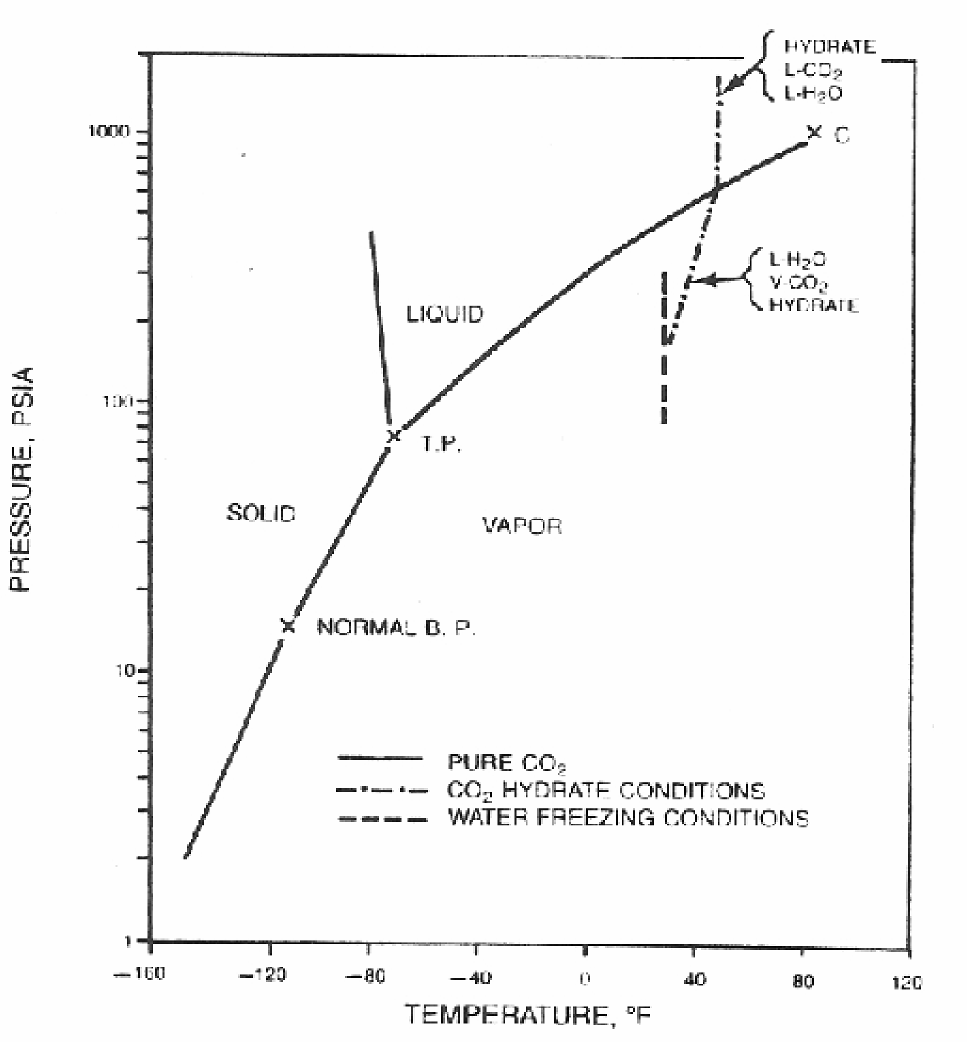


Figure 11: : Phase behaviour of CO2 and CO2/water mixtures

Phase behaviour and thermodynamics properties of pure CO_2 are shown in the figure above, showing temperature and pressure conditions necessary for the coexistence of two phases: vapor/liquid, vapor/solid (dry ice), or liquid/solid. The triple point, where all three phases coexist, occurs at – 70 ^{o}F and 75 Psia. CO_2 hydrates can occur at a temperature as high as 50 ^{o}F if pressure is greater than 650 Psia. Hydrates formation can be troublesome at valves and chokes where pressure is reduced suddenly and CO_2 cools because of expansion.

Examples of Carbon dioxide injection projects in the world.

- Weyburn (Canada): injection of CO_2 into an oil reservoir and EOR.
- In-Salah (Algeria): storage in an onshore aquifer.
- Sleipner (Norway): separation of CO2 from a natural gas field and storage in an offshore saline aquifer.

CHAPTER 3

3. CO_2 MISCIBLE FLOODING

3.1 Introduction

A number of petroleum reservoirs have been reported [1–9] worldwide exhibiting continuous compositional variations with depth. The mole fraction of the lighter components decreases with depth, while the mole fractions of the heavier components increase from the top to the bottom of the reservoir. The fluid at the GOC is neither an oil nor a gas, but a critical mixture. The saturation pressure of this mixture is the critical pressure at the reservoir temperature and also is the maximum saturation pressure of the entire fluid system.

Miscible gas flooding projects normally require extra investments if the reservoir pressure needs to be maintained or the injection gas needs to be enriched. Consequently, to optimize the economy of the project, miscible gas injection strategy will always be compared with less costly immiscible gas injection.

The objective of this study is to define the miscibility conditions for the fluid system as a whole and to investigate the possibility of developing miscibility at pressures lower than the maximum saturation pressure by enriched gas injection.

Carbon dioxide is used for the purpose of multiple contact and dynamic miscibility due to the following reasons.

- Reduction of oil viscosity and increasing mobility ration
- Oil swelling
- Extraction or vaporization of oil into the CO_2 rich phase
- Reduction in residual oil saturation due to reduction in CO_2 oil interfacial tension.

3.2 Identification of CO_2 with Miscibility Flooding Potential

For a reservoir to be a CO_2- miscible flooding candidate, miscibility pressure must be attainable over a significant volume of the reservoir. Miscibility pressure for CO_2 often is significantly lower than the pressure required for miscibility with natural gas, flue gas or nitrogen are limited because high pressure required for dynamic miscibility is unattainable in many reservoirs. CO_2 miscibility can be attainable at shallower depths for a much wider spectrum of oils than is possible with the other gases.

CO_2 miscibility will not be attainable in all reservoirs. Generally reservoirs shallower than 2500 ft are not the candidates because at this shallow depth even a relatively low miscibility pressure usually cannot be attainable without fracturing the reservoir. Miscibility pressure increasing with decreasing API oil gravity, and reservoirs containing oil with gravities lower than about 27^o API generally will not be CO_2- miscible candidate because of a high miscibility pressure requirement.

Oil viscosity and reservoir heterogeneity also determine the suitability of a reservoir for CO_2 flooding. Because CO_2 has a low viscosity, the viscosity ratio with reservoir oils invariably will be unfavourable; and, because of this the mobility ratio of the displacement will be unfavourable unless the CO_2 relative permeability is sufficiently reduced by alternative water injection. Semisolid or heavy-liquid precipitation or other factors to keep the mobility ratio favourable. An unfavourable mobility ratio adversely affects the sweep out and can has hasten CO_2 slug destruction in the gas-driven slug process by viscous fingering. For these reasons reservoirs containing oil of relatively high viscosity are not suitable candidates for CO_2 miscible flooding. In hydrocarbon-miscible flooding, severe reservoir heterogeneity causing excessive production of CO_2 is to be avoided. Although some CO_2 production is to be expected even in the best-performing floods and although compression and re injection of produced CO_2 may be economically sound in specific projects, sever channelling cause by extreme stratification or fracturing can reduce the ratio oil recovered per gross cubic foot of CO_2 injected to an uneconomical value, and reservoirs with these characteristics should be avoided. Water floods history, geology, logs and well transient tests can be indications of reservoir heterogeneity.

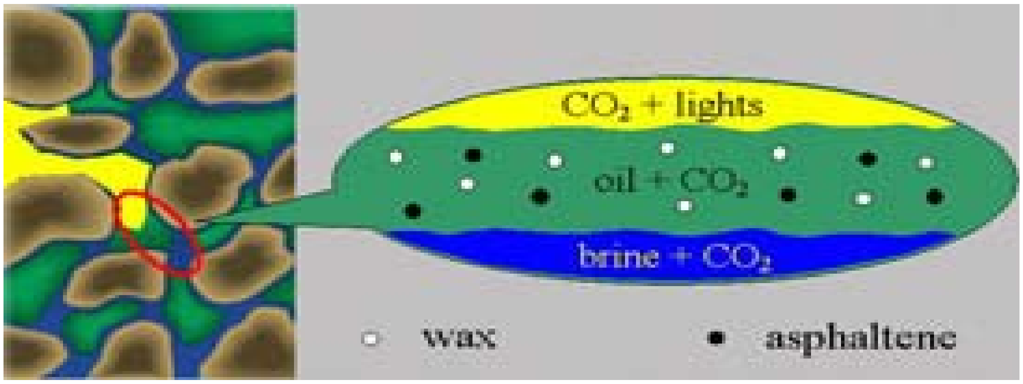


Figure 12: Graphical presentation of Carbon dioxide using for Enhanced Oil Recovery

With the hydrocarbon-miscibility processes, economic factors determine the minimum oil saturation that is acceptable for CO_2 flooding. However, as rough guideline, oil saturation should not be less than about 20% PV in those portions of the reservoir that will be swept miscibility.

3.3 Minimum miscibility

The minimum conditions at which the resulting mixture of two fluids mixed together at any proportion is homogeneous in compositions and identical in intensive properties (e.g. density and viscosity).

3.4 Miscibility concepts

A number of parameters affect the minimum miscibility conditions: including chemical compositions of the oil and the injection gas, and the reservoir temperature. It is also believed that physical dispersion can locally have some impact on the minimum miscibility conditions. The process of achieving miscibility at the minimum miscibility conditions can be different, depending on the compositions of the displacing and displaced fluids and the reservoir temperature. Some fluids may become miscible upon the first contact; the process is called first-contact miscible. Some fluids are not first-contact miscible, but can achieve miscibility through continuous contact by interphase mass transfer. These fluids are multicontact. miscible. For hydrocarbon reservoirs, the multi-contact miscible process usually is the common one occurring in actual field operations.

Different multi-contact miscible mechanisms have been proposed and studied in the literature [11, 12] based on the nature of compositions of the two fluids and pressure and temperature: first contact miscibility, multiphase contact miscibility, vaporizing gas drive (VGD), condensing gas drive (CGD) and condensing/vaporizing gas drive (C/V).

The phase behaviour of three component mixture (L: Light, I : intermediate, H: Heavy) at constant temperature and pressure is show in figure… by a ternary diagram. Each corner of the triangular diagram represents a components as pure 100 %, while all binary pictures are on the lines connecting the two corners, e.g. , point D. Any point within ternary diagram represents a three component mixture, e.g., Point M and its composition is determined are mixed, the overall mixture lies on the line connecting the two fluids, which is called the dilution or operating line , and its position can be determined by the lever rule.

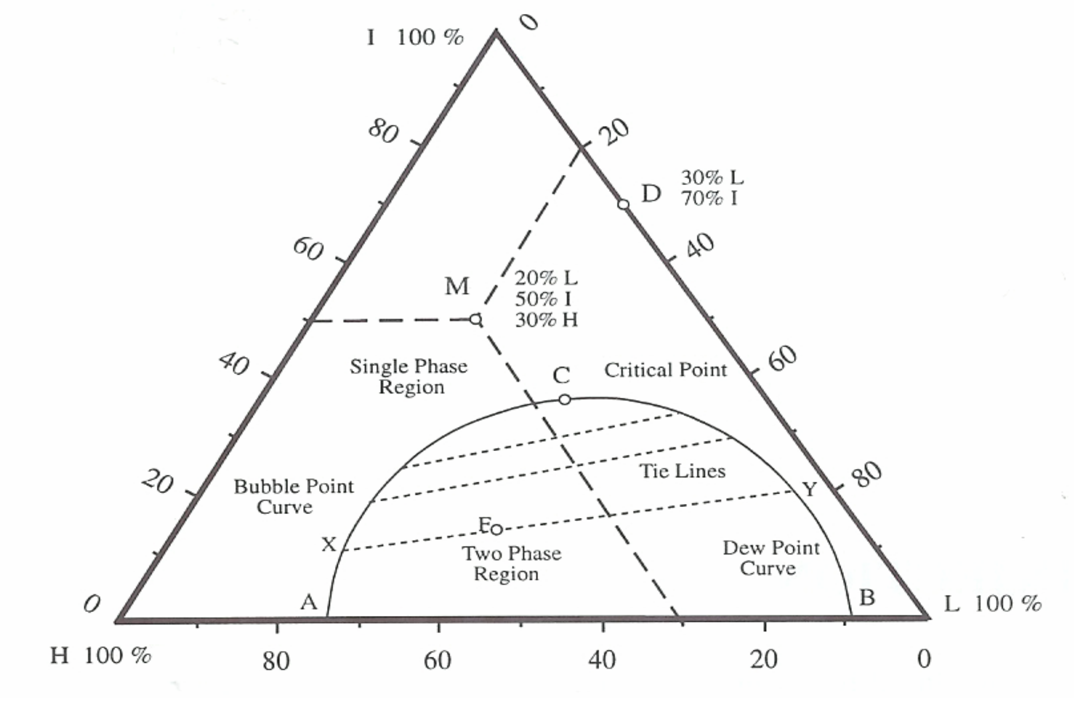


Figure 13: Ternary diagram of fluid phase equilibria at constant pressure and temperature

The phase envelope is shown by the curve ACB in figure 13. Any mixture, F, inside the two phase envelope forms a vapour phase, Y , and a liquid phase, X , at equilibrium, lying on the phase boundary curve. The line XY, connecting the two phases at equilibrium is known as the tie line. The left side of the curve, AC, represents saturated liquids, i.e. the bubble point curve, whereas the right hand side, CB, represents saturated gases, i.e. the dew point curve. The two parts of the curve converge at the critical point C, also know a s the plait point. Any mixture outside the phase envelope is a single phase under-saturated fluid. Phase envelopes, and the associated tie lines, at different pressures can be shown on the same diagram, where increasing the pressure generally results in the shrinkage of the phase envelope. A ternary system may form more than two phases, or have a number of isolated two-phase regions, but the diagrams shown in Figure 12,resembles most of the practical cases, and adequate for describing the miscibility concepts.

Two fluids are considered to be miscible, when they form a single phase at all proportions, at constant pressure and temperature. It is evident that any two fluids with operating line not crossing each the two phase region within the phase envelope are miscible.

3.4.1 First Contact Miscibility

Figure 13 shows that an injection gas comprised only of I is miscible when contacted with oil B, whereas Gas A is not, however, miscible either by enrichment with I to A’ or by raising the system pressure to shrink the phase envelope as shown by the dashed phase envelope. When the injection gas and reservoir oil, mixed at any ratio, form a single phase, they are called *first miscible contact.* First contact miscibility can be achieved only for highly rich gases, or at very high pressures for lean systems.

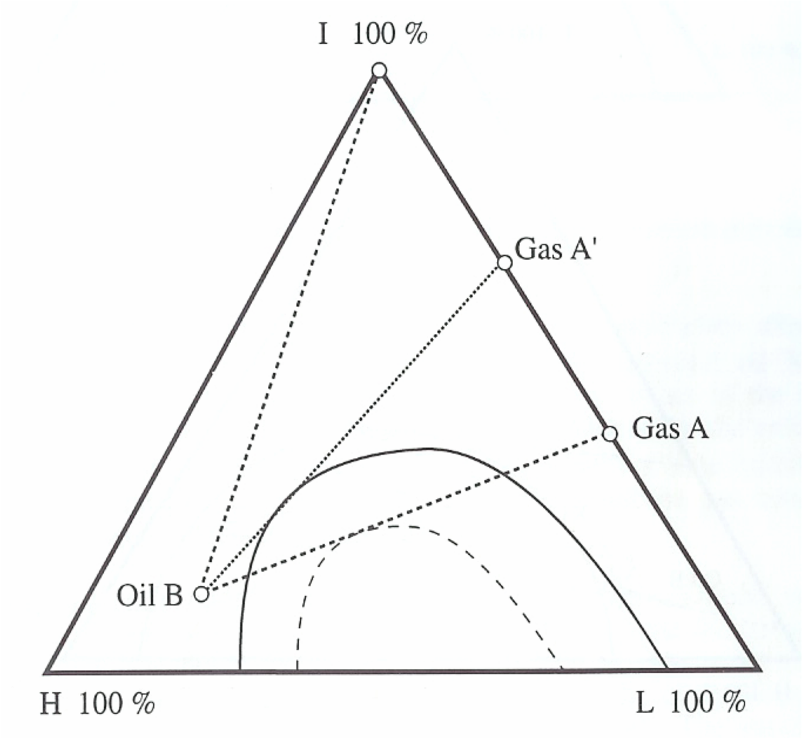


Figure 14: First contact miscibility

3.4.2 Condensing / Vaporizing Miscibility Mechanism

The condensing/vaporizing gas drive for enriched gas injection was first proposed and verified by experiments and numerical simulations by Zick [13] in 1986. Interphase mass transfer of the intermediate components is the key process of the mechanism. Later, analytical theory [14] for the combined condensing/vaporizing mechanism was developed. It can be argued that condensing/vaporizing gas drive is the most common mechanism developed in miscible gas injection field projects as injection gases usually contain somewhat light- and heavier-intermediate components.

A typical condensing/vaporizing gas drive shows the following characteristics:

1. Development of a miscible front characterized by converged phase densities and other intensive fluid properties. Interfacial tension at the front is extremely low and this is the direct indication of achieved miscibility.

2. Two regions identified on each side of the miscible front. The region upstream of the miscible front is dominated by strong vaporization of heavy components of the reservoir oil. The region downstream of the miscible front is strongly dominated by condensation of intermediate components of the injection gas.

3. Component K-values (ratio of composition of the component in vapour phase to the composition of the component in the liquid phase) tend to converge at the near miscible front and then diverge downstream.

It has been reported that miscible displacement of oils and/or gas condensates can develop through a condensing/vaporizing mechanism at a pressure far below saturation pressure if the injection gases are sufficiently rich in intermediate components [15] or CO_2 [16]. For saturated oil reservoirs or depleted gas condensate reservoirs, if the C/V mechanism exists and an oil bank develops at and above the C/V minimum miscibility conditions, the oil saturation behind this front approaches zero.

3.4.3 Vaporizing gas drive

Any injection gas which is not miscible with an oil at first contact, may achieve miscibility during multiple contacts by getting enriched through vaporizing the intermediate fractions of oil. The process, known as the vaporizing gas drive (VGD) is conceptually shown in Figure…..

The injection gas, L, comprised of the light fluid, after contacting Oil, A, forms two equilibrated phases of liquid X_1, and gas Y_1, with an overall mixture F_1. Note that the gas phase, Y_1, is the original gas L after it has picked up some intermediate and heavy fractions from the oil phase. The gas phase, Y_1, moves forward and makes further contacts with the fresh oil and progressively becomes richer particularly in the intermediates, as shown by Y_2, Y_3.... The gas ultimately becomes miscible with oil at C, that is , where the tangent line at the critical point, which is the critical tie line with zero length, goes through the oil composition.

The above injection gas, pure L, however, doesn't attain multiple contact miscibility with Oil B, as the enrichment of the advancing gas is limited by the tie line X_2' Y_2' (limiting tie line) which , if extended, goes through Oil B. It is evident that the miscibility cannot be achieved when the oil composition and the phase envelope are at the same side of the critical point tangent line(critical tie line extension). The vaporizing gas drive miscibility for oil B can be achieved, however, by raising the pressure sufficiently to shrink the phase envelope, as shown by the dotted boundary. The pressure at which the critical tie line goes through the oil is the minimum required pressure to achieve miscibility, hence, called *the minimum miscibility pressure* (MMP). At MMP, the limiting tie line becomes the critical tie line as the gas phase enriches through multiple contacts with the original oil attaining the critical composition.

In the vaporizing gas drive , the miscibility is achieved at the front of the advancing gas, the gas composition varies gradually from that of the injected gas till reaching the critical composition. Then it miscibility displaces the original reservoir oil in a piston-type manner. No phase boundary exists within the transition zone.

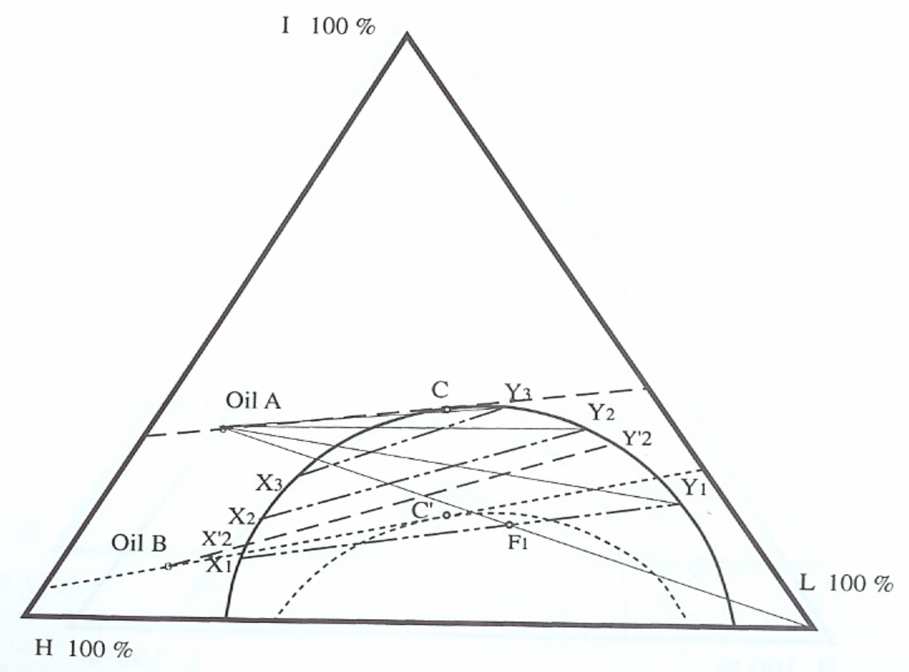


Figure 15: Schematic phase diagram of vaporizing gas drive at minimum miscibility pressure

The gas composition appears to have no effect on achieving the miscibility state in the vaporizing gas drive as it is fully controlled by the oil phase as shown in the figure above.

3.4.4 Condensing gas drive

A rich gas, not forming first contact miscibility with an oil, can however, achieve multiple contact miscibility through condensing its intermediate fractions to the oil as shown conceptually in figure 15 the process is called the *condensing gas drive*(CGD) is described below.

The rich gas A forms two phases, gas , Y1, and oil, X1 , in the equilibrium after contacting the reservoir oil. The gas phase move forward and leaves the enriched oil X_1, behind to be contact with fresh gas A, resulting in an oil even richer in the intermediates as shown by X_2 and X_3…

This process goes on and the oil is enriched to the extent that is finally acquiring the composition of the critical oil at C. At this point it will be miscible with gas A. The pressure at which the critical tie line extension gas composition, is the minimum required pressure to achieve miscibility (MMP).

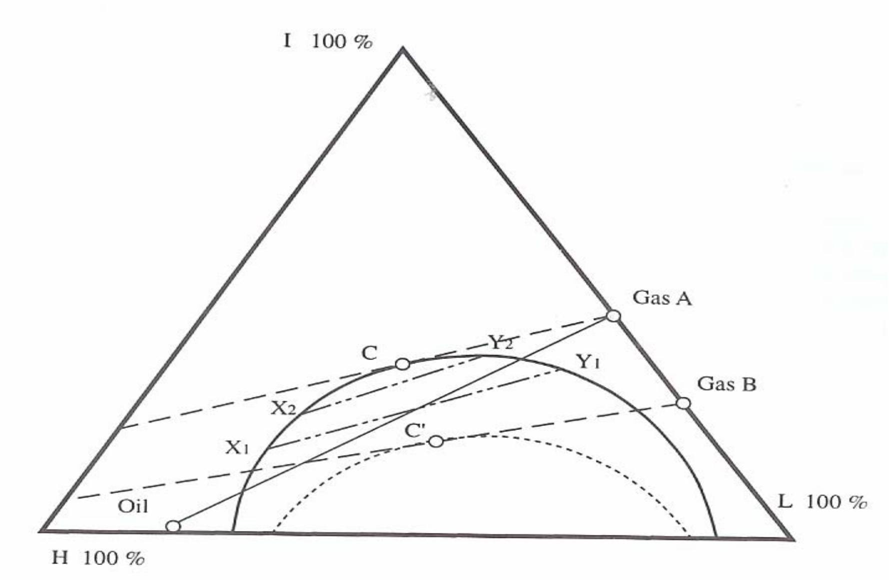


Figure 16: Condensing gas drive phase diagram at minimum miscibility pressure

At MMP, the oil phase enriched in the intermediate though multiple contacts with the injection gas attain the critical composition, with the limiting tie line become the critical tie line. The injection Gas B, which is leaner in the intermediates than Gas A, does not form miscibility, at the current pressure, as the enrichment of the oil is limited to the composition of the tie line extending through the injection gas composition (limiting tie line). The miscibility, however, can be achieved by raising the pressure to shrink the phase envelope as shown by the dotted curve.

The original oil composition has no effect on achieving the miscibility state in the condensing gas drive, as it is controlled by the injection gas composition. Hence, instead of raising the pressure to achieve miscibility, the injection gas may be enriched. The enrichment level at which the critical tie line extension goes through the injecting gas composition is called the minimum miscibility enrichment (MME).

In the condensing gas drive, the miscibility is achieved at the injection point. The injection gas displaces the critical fluid, in a piston type manner, with the liquid composition varying gradually to that of the original oil. No phase boundary exists within the transition zone.

3.4.5 Miscibility in Real Reservoir Fluids

The ternary phase diagram of a multiple component reservoir fluid is often expressed by representing the fluid with three pseudo components. It is common to group C_1, and N_2 as the light (L), CO_2, H_2S, and C_2-C_6 as the intermediate (I), and C_{7+}, as the heavy (H) fraction.

The conceptual discussion on multiple contact miscible processes, using the ternary diagram, is not strictly valid for real reservoir fluids, and the diagram should not be used generally in the design of real processes. The basic idea of multiple contact miscibility through mass exchange between the phases, and the requirement of attaining the critical composition, are all valid for real systems. However, the existence of a large number of components in a real reservoir fluid provides additional possibilities for compositional variations, and achieving miscibility. In the following discussion, the miscible is referred to the condition where miscibility can just be achieved , that is at MMP. At higher pressures, the miscibility well obviously be achievable.

The injected rich gas does not generally contain heavy fractions which are present in the oil. Hence the injection gas enriches the oil in light intermediate range, it strips the heavier fractions. The reservoir oil in contact with the fresh gas initially becomes lighter, but as it contacts more gas and loses only some of its lighter heavies, over all it tends to get enriched in very heavy fractions and thus becomes less similar to the injection gas.

Figure 16 shows variation of measured component groups in the oil phase at the injection point for North Sea oil. As the oil is contacted with additional rich gas, the concentration of C_{7+} is decreased, apparently lightening the oil in its path towards achieving the condensing miscibility. An examination of the heavy end , e.g., C_{20+} shows this fraction has increased due to vaporization of the lighter heavies. This oil cannot become miscible with the fresh injection gas. The phase envelope, as determined by measuring the compositions of equilibrated phases at the injection point and also at the gas front in a laboratory test, is shown in Figure…

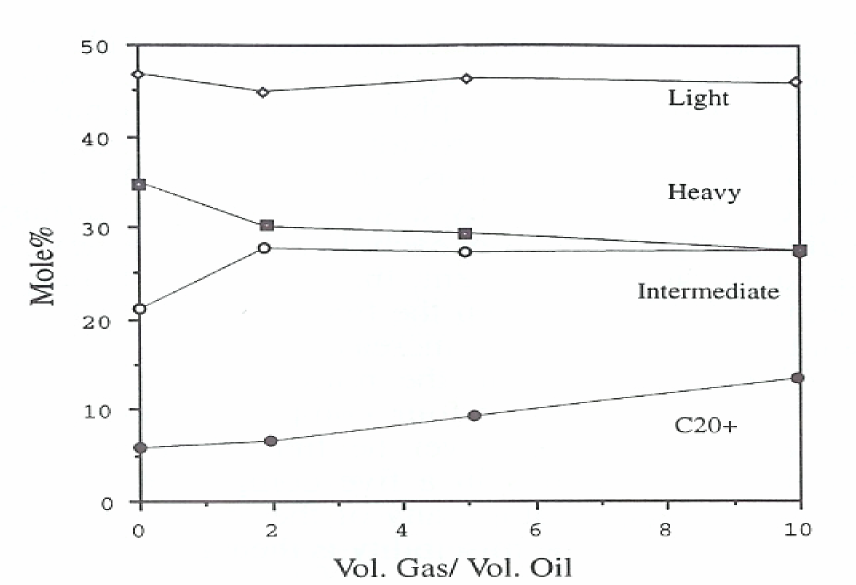


Figure 17: Variation of component groups in contacted oil at injection point with the ratio of injected gas volume to contacted oil volume.

Note that the bubble point and the dew point curves initially converge, demonstrated by shortening tie line lengths, and then diverge.

As the forward moving gas becomes richer in heavy fractions, it vaporizes less of these compounds while losing intermediates to the oil. At favourable conditions the combined vaporization/condensation process results in a state within the transition zone where the compositional path goes through the critical point, achieving miscibility. This can be a combination of the condensing process at the front, and the vaporizing process at the tail. This process , is called the condensing/vaporizing gas drive, was reported by Zick (1) in 1986, and detailed by Stalkup in 1987.

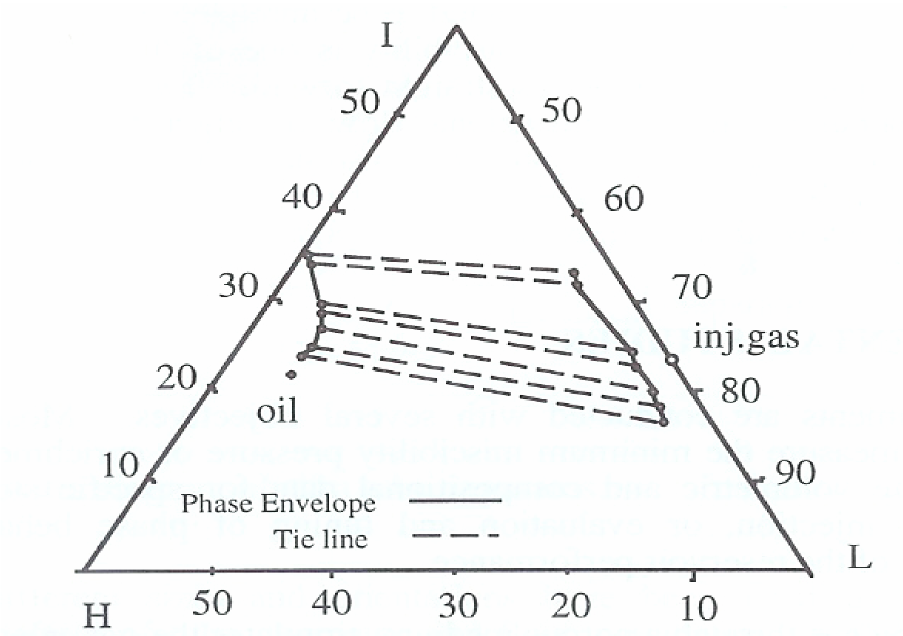


Figure 18: Phase diagram of a North Sea oil and rich injection gas determined experimentally during contact experiment

The multiple contact miscibility in multiple component systems is achieved in a dynamic process; hence, it can be affected by other factors additional to the fluid phase behaviour. The compositional path depends on other mechanisms such as multiphase fluid convection and dispersion in porous media. The two limiting critical tie lines, that is, those with extensions going through the original oil and the injection gas, depends only on the original fluids. Hence, the miscibility conditions can be determined by phase behaviour considerations only, if the miscibility is achieved by either vaporizing or condensing gas drive mechanisms. Otherwise, the critical tie line, hence miscibility, depends on the local fluid mixture composition influenced by flow factors.

3.5 Factors effecting MMP

The main factors affecting the miscibility are the reservoir fluids composition, injection gas composition, reservoir temperature and pressure.

3.5.1 Reservoir fluid composition

Carbon dioxide is more miscible with the lighter hydrocarbons present in a reservoir fluid, and gradually less miscible with increasing molecular weight. Therefore larger the fraction of the lighter components in the oil, the lower the CO_2 MMP. Similarly larger the fraction of the heavy components in the oil, the higher the CO_2 MMP. Carbon dioxide can attain the miscibility with the heavier

3.5.2 Reservoir temperature and pressure

For CO_2 flooding, higher reservoir temperatures result in higher MMPs. Therefore deeper, hotter reservoirs need higher MMPs. As pressure increases, miscibility of the injection gas and the reservoir fluid increases. Higher injection pressure will give a greater oil recovery. Above the MMPs the increase in oil recovery will not be as great with an equivalent increase in injection pressure as it below the MMP, and thus, a break over in the oil recovery-pressure relation is observed at the MMP. Due to this, gas floods are often operated near the MMP.

3.5.3 Effects of Pressure on Phase Behaviour

When CO_2 is used as the solvent, four mechanisms may adversely affect oil recovery as pressure is reduced.

- The ability of CO_2 to extract components from crude oil decreases as pressure decreases.
- Interfacial tension between the CO_2-rich phase and crude oil increases as the pressure decreases, making displacement of crude oil less efficient.

- At lower pressures, less CO_2 will dissolve in oil to increase oil volume, and oil recovery due to swelling will be reduced.
- Lower CO_2 solubility also results in less oil viscosity reduction at lower pressures.

3.5.4 Injection gas composition

Methane and nitrogen are less miscible with reservoir fluids than CO_2. There are some common impure components found in the injection gas. Certain impurities, such as H_2S and SOx, could contribute toward attaining CO_2/oil miscibility at lower pressures. The presence of C_1 and N_2, however, could increase the MMP and having more of these components in the injection gas will increase MMP. Ethane or heavier alkanes and hydrogen sulphide are more miscible with reservoir fluids. Having these components in the injection gas brings MMP down.

3.6 Conclusion and recommendations for Carbon dioxide flooding

The viability of a CO_2 flood in areas of any oil field is dependent on the following general conditions:

- The reservoir is continuous and is well sealed to prevent excessive solvent loss to other zones.
- The reservoir pressure is greater than minimum miscibility pressure.
- The spacing between wells are optimized to allow efficient use of the CO_2 and to maintain effective flood control.
- The CO_2 flood should be designed to optimize the volumes of CO_2 required to produce the oil, since CO_2 represents a large operating cost component of the project.

3.7 Considerations for CO_2 EOR

A successful implementation of CO_2 flooding in any oil field requires a detailed engineering approach that addresses not only the technical issues, but also undertakes a thorough optimization study. A detailed and comprehensive understanding of real field is required for conducting winning CO_2 flooding projects. As part of our all-inclusive approach to successful field implementation of CO_2 flooding, the following technical challenges will be addressed in order to optimize the field operations:

- Improving performance of CO_2 flooding
- Early breakthrough of injected CO_2
- Viscous fingering and low volumetric sweep efficiency
- Asphaltinic and solid particles precipitation
- Injectivity loss
- Wettability and relative permeability alteration
- Potential corrosion issues
- Achieving and maintaining miscibility
- Effect of temperature of injected CO_2 on reservoir

CHAPTER 4

4. PETROPYSICAL PROPERTIES OF NORTH SEA RESRVOIR

4.1 Introduction

In the North Sea, chalk became a reservoir for oil and gas by a combination of fortunate circumstances. Shortly after burial, chalk in general has a high porosity, but a low permeability. It is a micropore reservoir. For fluids to enter the pore space, pressure is necessary. North Sea Chalk hydrocarbon fields are all located over thick areas of Kimmeridge and Oxford Clay source rocks, on structures which grew during the Tertiary. Structural growth caused fracturing allowing hydrocarbons, which were generated from as early as Oligocene times onwards, to build up in the fracture systems within structural closures in the Chalk. In this way hydrocarbons were able, by their buoyancy or by the pressure generated from the shales below, to enter the chalk reservoir. In areas where Paleocene sands are present, a closed pressure system was not found and no saturation of the Chalk was possible. Chalk is composed of the debris of coccolithophorids, which being composed of low magnesium calcite, is of great chemical stability. Burial diagenesis does not start until approximately 1000 m below surface. In the case of North Sea Chalk reservoirs, diagenesis, which will normally reduce porosity from approximately 50% at the sea bed to 10% at between 3000 and 4000 m burial depth, is arrested by three factors:

1) The pressure generated, which partially or wholly supports the overburden, thus reducing or preventing pressure solution.
2) Oil or gas in the pore space which as a chemically inert fluid also largely prevents pressure solution.
3) Magnesium ions present in sea water and in greater concentrations in the pore waters of up-domed beds overlying Zechstein evaporites, poison sites of nucleation of calcite, retarding diagenesis. [R5]

4.2 Rock properties

An aggregate of minerals or organic matter (in the case of coal, which is not composed of minerals because of its organic origin), or volcanic glass (obsidian, which forms a rock but is not considered a mineral because of its amorphous, non crystalline nature) Rocks can contain a single mineral, such as rock salt and certain limestone (calcite), or many minerals, such as granite.

The physical characteristics of reservoir rocks that enable them to store fluids and to allow fluids to flow through them. The main properties of interest are rock porosities and permabilities.

4.3 Porosity

Sand grains and particle carbonate materials that make up sand stone and line stone reservoir usually never fit together perfectly due to the high degree of irregularity in shape. The void space created throughout the beds between grains, called pore space or interstice, is occupied by fluids (liquids and/or gases). The porosity of a reservoir rock is defined as the fraction of the bulk volume of the reservoir that is not occupied by the framework of the reservoir. This can be expressed in mathematical form as

$$\phi = \frac{V_b - V_{gr}}{V_b} = \frac{V_p}{V_b} \qquad (4.1)$$

Where

ϕ = porosity, fraction

V_b = bulk volume of the reservoir rock

V_{gr} = Grain volume

V_p = pore Volume

According to this definition, the porosity of porous materials could have nay value, but the porosity of most sedimentary rocks is generally lower than 50%.

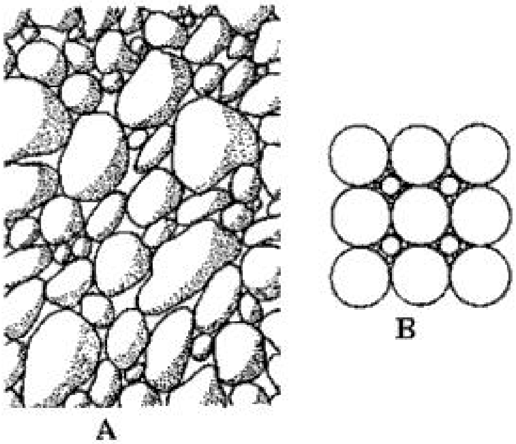


Figure 19: Collection of (a) different sized and shaped sand grains and (b) spheres illustrating a cube packing three grain sizes.

4.4 Petrophysics

4.4.1 Engineering classification of Porosity

During sedimentation and lithification, some of the pore spaces initially developed became isolated from the other pore spaces by various digenetic and catagenetic process such as cementation and the compaction. Thus, many of the pores will be interconnected, whereas other will be completely isolated. This lead to two distinct categories of porosity, namely, total (absolute) and effective , depending upon which pore spaces are measured in determining the volume of that sample, regardless of whether or not those void spaces are interconnected. A rock may have considered absolute porosity and yet have no fluid conductivity for lack of pore interconnections. Examples of this are lava, pumice stone, and other rocks with vesicular porosity.[R6]

4.4.1.1 Effective Porosity

The effective porosity, p_e, also called the kinematic porosity, of a porous medium is defined as the ratio of the part of the pore volume where the water can circulate to the total volume of a representative sample of the medium.

The definition of effective (kinematic) porosity is linked to the concept of pore fluid displacement rather than to the percentage of the volume occupied by the pore spaces. The pore volume occupied by the pore fluid that can circulate through the porous medium is smaller than the total pore space, and, consequently, the effective porosity is always smaller than the total porosity. In a saturated soil system composed of two phases (solid and liquid)

where

(1) V_s is the volume of the solid phase,

(2) $V_w = (V_{iw} + V_{mw})$ is the volume of the liquid phase,

(3) V_{iw} is the volume of immobile pores containing the water adsorbed onto the soil particle surfaces and the water in the dead-end pores,

(4) V_{mw} is the volume of the mobile pores containing water that is free to move through the saturated system, and (5) $V_t = (V_s + V_{iw} + V_{mw})$ is the total volume, the effective porosity can be defined as follows:

$$p_e = \frac{V_{mw}}{V_t} = \frac{V_{mw}}{V_s + V_{mw} + V_{iw}} \tag{4.2}$$

4.4.1.2 Absolute porosity

The total (absolute) porosity of a porous medium is the ratio of the pore volume to the total volume of a representative sample of the medium Assuming that the soil system is composed of three phases -- solid, liquid (water), and gas (air) -- where V_s is the volume of the solid phase, V_l is the volume of the liquid phase, V_g is the volume of the gaseous phase, $V_p = V_l + V_g$ is the volume of the pores, and $V_t = V_s + V_l + V_g$ is the total volume of the sample, then the total porosity of the soil sample, p_t, is defined as follows:

$$p_t = \frac{V_p}{V_t} = \frac{V_l + V_g}{V_s + V_l + V_g} \tag{4.3}$$

Porosity is a dimensionless quantity and can be reported either as a decimal fraction or as a percentage. Table 3.1 lists representative total porosity ranges for various geologic materials

Table 1:Range of Porosity of different materials

Range of Porosity Values	
Soil Type	Porosity, p_t
Unconsolidated deposits	
Gravel	0.25 - 0.40
Sand	0.25 - 0.50
Silt	0.35 - 0.50
Clay	0.40 - 0.70
Rocks	
Fractured basalt	0.05 - 0.50
Karst limestone	0.05 - 0.50
Sandstone	0.05 - 0.30
Limestone, dolomite	0.00 - 0.20
Shale	0.00 - 0.10
Fractured crystalline rock	0.00 - 0.10
Dense crystalline rock	0.00 - 0.05
Source: Freeze and Cherry (1979).	

4.4.2 Permeability

Permeability is the property of the porous medium that measures the capacity and ability of the formation to transmit fluids. The rock permeability, k, is a very important rock property because it controls the directional movement and flow rate of the reservoir fluids in the formation. This rock characterization was first defined mathematically by Henry Darcy in 1856. In fact , the equation that defines permeability is terms of measurable quantities is called Darcy's law. Darcy developed a fluid flow equation that has since become one of the standard mathematically tools of petroleum engineers. If a horizontal linear flow of an incompressible fluid is established through a core sample of length L and across section of area A, the governing equation is defined

$$V = -\frac{K}{\mu}\frac{dP}{dL} \qquad (4.4)$$

Where
V = apparent fluid flowing velocity cm/sec
k = proportionality constant, or permeability, Darcy
μ = Viscosity of the flowing fluid, cp
$\frac{dP}{dL}$ = pressure drop per unit length, atm / cm

The velocity, V in above equation (4.4) is not the actual velocity of the flowing velocity but is apparent velocity determined by divining the flow rate by cross sectional area across which the fluid is flowing

$$V = \frac{q}{A} \qquad (4.5)$$

Therefore, by putting the value of V in the main equation and it can be re written as

$$q = -\frac{KA}{\mu}\frac{dP}{dL} \qquad (4.6)$$

Where

q = flow rate through the porous medium, cm^3/sec
A = cross sectional area across which flow occurs, cm^2

Thus, when all other parts of equation (4.6) have values of unity, k has a value of one Darcy.
One Darcy is a relatively high permeability as the permeability of most reservoir rocks are less than one Darcy. In order to avoid use of fractions in describing permeability, the term milli Darcy is used. As the term indicates, one milli Darcy, i.e., 1 md, is equal to the one thousandth of one Darcy.

The negative sign in equation (4.6) is necessary as the pressure increases in one direction while the length incases in opposite direction.

By applying the integration over the geometry such as pressure points P_1 and P_2 across the length of the core sample the equation (4.6) can be solved as

$$q\int_0^L dL = -\frac{KA}{\mu}\int_{P1}^{P2} dP \qquad (4.7)$$

$$qL = -\frac{KA}{\mu}\left(P_2 - P_1\right) \qquad (4.8)$$

$$qL = \frac{KA}{\mu}\left(P_1 - P_2\right) \qquad (4.9)$$

$$q = \frac{KA}{\mu}\frac{\Delta P}{L} \qquad (4.10)$$

Above equation (4.10) is the conventional linear flow equation used in the fluid flow calculations. Relative permeability for the two phase flow considering water and oil can be developed by extending Darcy's equation for single flow. Hence in this case the equation (4.6) can be written in the form

$$q_w = -\frac{K_{rw} A}{\mu_w} \frac{dP_w}{dL} \tag{4.11}$$

$$q_o = -\frac{K_{ro} A}{\mu_o} \frac{dP_o}{dL} \tag{4.12}$$

Where

q_w, q_o = flow rate of the water and oil through the porous media cm^3/sec

K_{rw} , K_{ro} = Relative permeability of water and oil respectively, Darcy

μ_w, μ_o = Viscosities of water and Oil (cp)

$\frac{dP_w}{dL} \frac{dP_o}{dL}$ = pressure drops in fluids phases per unit length, atm / cm

Hence the equation 4.11 and 4.12 used to describe the relationship between the flow rate pressure gradient for each phase at each of the various saturation occurring within the reservoir..

4.4.2.1 Determination of Permeability

The determination of this rock property is an important property in assessing the reservoir ability to transmit the fluid store in it. Laboratory estimates of water / oil relative permeability are conventionally determined by using two methods, Steady state or unsteady state. The steady state method consist of establishing a constant fractional flow of oil and water along the length of the core. The saturation of the core and pressure drop across the core is determined at each imposed fractional flow.

The determination of relative permeability using the unsteady state method consist of injecting only the displacing phase while monitoring the production of both phases and the pressure drop across core sample for duration of test.

4.4.3 Saturation

Saturation is another important rock property. Saturation is defined as that fraction, or percent of the pore volume occupied by a particular fluid (oil , gas or water). This property is expressed mathematically by the following relationship.

Fluid saturation total = (volume of the fluid) / (pore volume)

Applying the above mathematical concept of saturation to each reservoir fluid gives

$$S_o = \frac{Volume\ of\ oil}{pore\ volume}$$

$$S_G = \frac{Volume\ of\ gas}{pore\ volume}$$

$$S_W = \frac{Volume\ of\ water}{pore\ volume}$$

Where

S_o = Oil saturation

S_G = Gas saturation

S_w = Water saturation

Thus all saturation values are based on pore volume and not on the gross reservoir volume.
The saturation of each individual phase ranges between zero to 100%. by definition the sum of saturations is 100%, therefore

$$S_o + S_G + S_w = 1 \qquad (4.13)$$

4.4.3.1 Residual Oil saturation

During the displacement process of the crude oil system from the porous media by water or gas injection there will be some reaming oil left that is quantitatively characterized by a saturation value that is larger than the crude oil saturation. This saturation value is called residual oil saturation. (Sor) The term residual saturation is usually associated with the non wetting phase when it is being displaced by wetting phase.

4.4.3.2 Average saturation

Proper averaging of saturation dada requires that the saturation values be weighed by both the interval thickness hi and interval porosity f. The average saturation of each reservoir is calculated from the following equations

$$S_o = \frac{\sum_{i=1}^{n} \phi_i h_i S_{oi}}{\sum_{i=1}^{n} \phi_i h_i} \qquad (4.13)$$

$$S_w = \frac{\sum_{i=1}^{n} \phi_i h_i S_{wi}}{\sum_{i=1}^{n} \phi_i h_i} \qquad (4.13)$$

$$S_G = \frac{\sum_{i=1}^{n} \phi_i h_i S_{Gi}}{\sum_{i=1}^{n} \phi_i h_i} \qquad (4.13)$$

Some of these rock properties are calculated in the lab and used in the calculation in the coming chapter.

CHAPTER 5

EXPERIMENTAL WORK SECTION A

5. DETERMINATION OF POROSITY OF CORE SAMPLES BY SATURATION METHOD

5.1 Introduction

This part consist of series of experiments, which is divided in four parts in which core sample of chalk sample has been taken from north sea reservoir has been taken. The core sample was saturated with oil and water to find out the porosity, further TGA analysis has been performed to determine a crude oil thermal stability and its fraction of volatile components by monitoring the wt% change with respect to time that occurs as a oil sample is heated.

Purpose of these basic experimental work was to observe CO_2 effect on oil and core sample with using it high temperature and high pressure.

5.2 Determination of porosity of core samples by saturation method

Porosity of sample is defined as percentage of the bulk volume of a rock that is not occupied by minerals. These pores or gaps can be filled with fluids, typically in deep rocks this fluid is salty water but it can be also oil or gas, like methane or CO2. Porosity has been found out in laboratory to estimate the oil amount available in core sample, which was used future to calculate the recovery efficiency.

Core sampling method was used to saturate the North Sea chalk samples which were further used in MMP calculations. [R7]

5.2.1 Core sampling saturation procedure

The core sampling saturation procedure was used in order to find out porosity, Four samples of Cubical shape have been taken with almost equal dimensions and weight, similarly four samples of cylindrical shape(equal weight and dimensions) has been saturated These samples were placed in air tight glass flask. In which crude oil was introduced carefully from the top to saturated samples as shown in the figure. The vacuum pump is attached to flask to create vacuum. The samples were placed in vacuum created flask for 48 hours. Core samples were removed and weighted; increase in weight of sample was measured carefully.

The samples were used for MMP determination in supercritical extractor at high pressure and temperature.

Figure 20: Saturation setup for chalk core sample

5.3 Crude oil specification used for saturating Chalk samples.

Offshore sample field:	Half Dan
Sampling point:	Outlet V-3 v02 (Export GOE)
Sampling Time/ Date:	18:00 / 05-08-2008
Sampling Pressure:	180 Bar
Sampling Temperature:	53.8 ºC

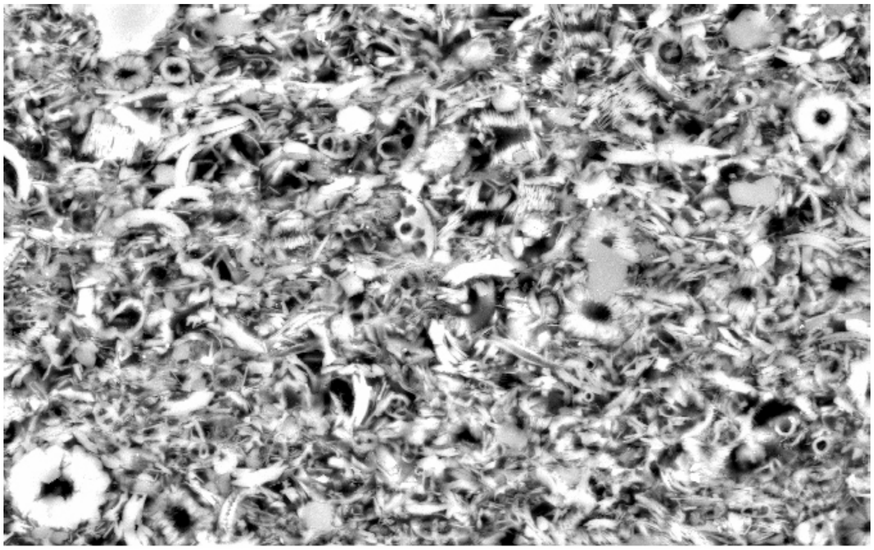


Figure 21: Chalk sample from North Sea with porosity of 37.9% and permeability 0.7 mD [R8]

5.4 Procedure for calculating porosity

The laboratory procedure for finding porosity has been carried out for regular cubical and cylindrical samples, which is described as follows.

5.4.1 Regular core samples

- Calculation of bulk volume is simply measuring the length, width and height in case of cubic core as

  $V_b =$ L.W.H

- Weight core and dry in dryer at 105 ^{o}C for 24 hours.
- After saturating the sample under vacuum condition for 2 days it is taken out and weighed again, and subtract the dry weight of sample gives the volume of oil saturated.

5.5 Porosity measurement:

Porosity is defined as measure of the storage capacity, ratio of pore volume to the total volume (bulk volume). Porosity has been measured for both cylindrical and cubic samples saturated with oil and water. Sample dimensions and weight calculation before saturation and after saturation has been explained below.

5.5.1 Porosity calculation cubical core sample saturated with Oil

The chalk samples from North Sea were prepared in 2 dimensional types, cubical and cylindrical.

The samples were weighed and were dried at 105 ºC in an oven for 24 hours. Loss in weight after drying shows moisture contacts have been removed from samples. Then samples were saturated with crude oil from North Sea in a vacuum flask for 48 hours. Regular cubical sample porosity is then calculated in the fallowing way.

Bulk volume = V_b= L.W.H= 15.76 cc
Pore Volume = (Wf-Wi)/Density of saturated oil
Density of saturated oil= 780kg/m^3=0.78 g/cc
Initial wt of core before saturation = Wi = 23.1767 g
Final wt of core after saturation = Wf = 27.6618 g
After putting values V_p = 5.7496 cc
Porosity = (Vp/Vb)* 100
= 36.48 %

5.5.2 Porosity calculation of regular cylindrical samples saturated with oil

Volume of Cylinder = pi * radius^2 * height
Where Height = 3.84 cm
And diameter = 3.91 cm
Radius of cylinder = r = D/2 = 1.955 cm
Bulk volume = 15.366 cc
Pore Volume = (Wf-Wi)/Density of saturated oil
Density of saturated oil= 780kg/m^3=0.78 g/cc
Initial wt of core before saturation = Wi = 24.7612 g
Final wt of core after saturation = Wf = 29.1804 g
After putting values Vp= 5.6654 cc
Porosity = (Vp/Vb)* 100
=36.8%

5.5.3 Porosity calculation of Cylindrical samples saturated with water

Volume of Cylinder = pi * radius^2 * height
Where Height = 3.84 cm
And diameter = 3.91 cm
Radius of cylinder = r = D/2 = 1.955 cm
Bulk volume = 15.366 cc
Pore Volume = (Wf-Wi)/Density of saturated oil
Density of saturated oil= 1000kg/m^3=0. 1g/cc
Initial wt of core before saturation = Wi = 24.7612 g
Final wt of core after saturation = Wf = 30.7612 g
After putting values Vp= 6.0812 cc
Porosity = (Vp/Vb)* 100
=39.57%

5.5.4 Procedure

The chalk samples from North Sea were prepared in 2 dimensional types, cubical and cylindrical.

The samples were weighed and were dried at 105 ºC in an oven for 24 hours. Loss in weight after drying shows moisture contacts have been removed from samples. Then samples were saturated with crude oil from North Sea in a vacuum flask for 48 hours. Porosity and MMP measurements were carried out on these core samples.

Table 2: Cubical samples weight and dimensions after drying at 105 ºC for 24 hours.

Sample no.	Weight (grams)	Length(cm)	Breadth (cm)	Height (cm)
1	23.1767	4	2.42	2.9
2	22.0519	4	2.37	3
3	27.1610	4.3	2.181	2.742
4	19.0342	4	2.489	3

Table 3: Weight of Cubical core samples after saturation and extraction.

Sample no.	Wt after saturation(gm)	Wt after extraction(gm)	Length(cm)	Height (cm)	Breadth (cm)
1	27.6618	23.2144	4	2.9	2.42
2	26.8715	22.1105	4	3	2.37
3	32.8925	27.2113	4.3	2.742	2.181
4	22.5586	19.1031	4	3	2.489

Table 4:Cylindrical regular core samples after drying at 105 ºC for 24 hours.

Sample no.	Weight (grams)	Length(cm)	Diameter (cm)
5	24.7612	3.84	3.91
6	25.2382	3.97	3.83
7	25.1861	3.86	3.93
8	22.9870	3.72	2.26

Table 5: Cylindrical core samples after saturation and extraction.

Sample no.	Wt after saturation(gm)	Wt after extraction(gm)	Length(cm)	Diameter (cm)
5	29.1804	25.099	3.84	3.91
6	29.9389	25.8207	3.97	3.83
7	29.265	25.7111	3.86	3.93
8	25.265	23.5819	3.72	2.26

Table 6: Cylindrical regular core samples after saturating with water for 24 hours.

Sample no.	Weight (grams)	Length(cm)	Diameter (cm)
5	30.76	3.84	3.91
6	30.28	3.97	3.83
7	30.27	3.86	3.93

CHAPTER 6

EXPERIMENTAL WORK SECTION B

6. THERMO GRAVIMETRIC ANALYSIS (TGA)

6.1 General Description

Thermo gravimetric analysis (TGA) is an analytical technique used to determine a material thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air, an inert atmosphere such as Helium, Nitrogen or Argon. Measurement is also carried in a lean oxygen atmosphere (1 to 5 % O_2 in H_2 or He) to slow down oxidation.
In the experiment performed, Nitrogen was used as medium.

In most cases, TGA analysis is performed in an oxidation atmosphere (air or oxygen and inert gas mixtures). Maximum temperature was selected so that specimen weight becomes stable at the end of experiment.
When TGA analysis is carried out there is sudden weight loss in the start as most of hydrocarbons are volatile, so if we look in the plot then we can see that with the increase of temperature accompanied by sudden loss of a significant fraction of the sample mass.

Equipment used for Thermo Gravimetric Analysis has been placed in Aalborg University Esbjerg, in material Laboratory. Equipment setup has shown in figure below.

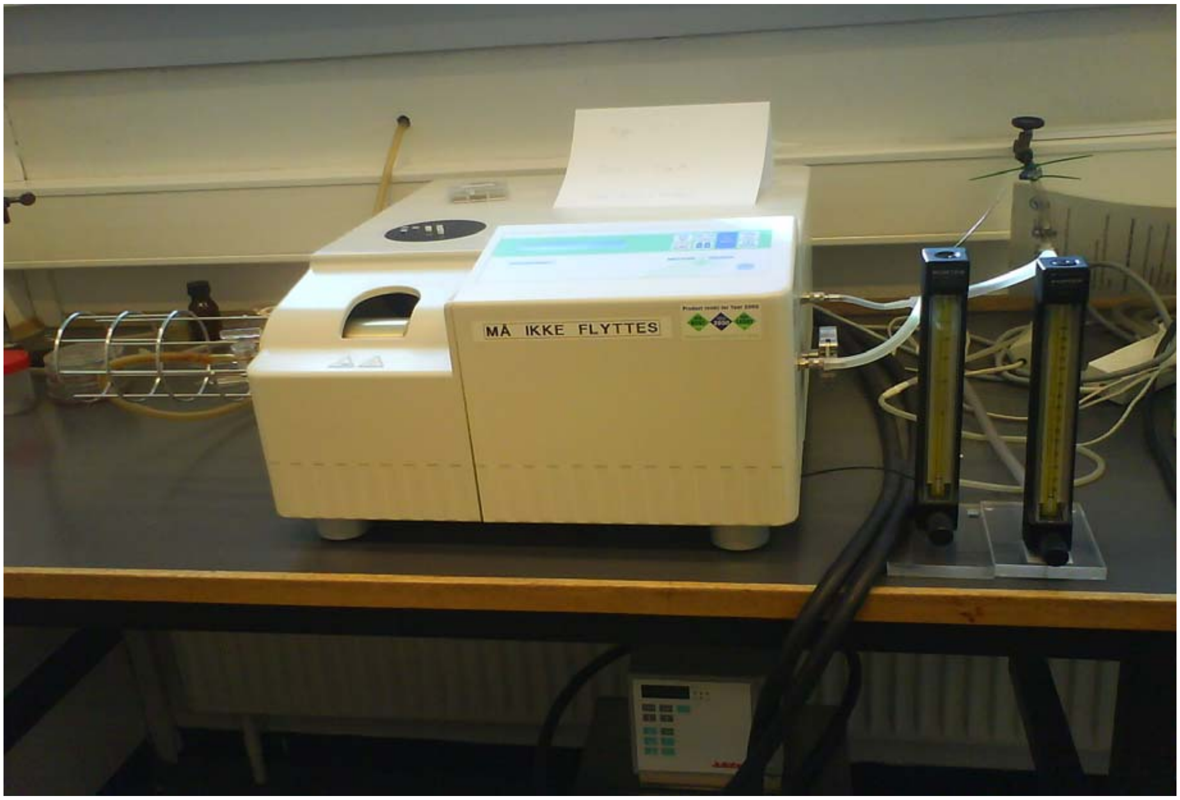


Figure 22: TGA Apparatus

6.2 Characteristics and properties measured by TGA.

Thermo gravimetric equipment is used to investigate the weight gain or weight loss of material, amount of oil present, structural water release, carbonate decomposition, structural decomposition, gas evolution, sulphur oxidation and fluoride oxidation.

Therefore weight loss of crude oil sample has been found, because same crude oil has been used to saturate the core sample. Core sample has been used in Supercritical extractor at high temperature and pressure, so it's better idea to calculate to weight loss, so we can know that how the volatile component of given crude oil sample effects the results.

6.3 Operating Principle of TGA

A sample of the test tube material was placed into a alumina cup that is suspended from an analytical balance located outside the furnace chamber. The balance is at zero reading in the start, and sample cup is heated according to a predetermined thermal cycle. The balance is sending the signal to the computer for storage, along with the sample temperature and elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis.

6.4 Experiment on crude oil sample.

Two experiments have been performed on crude oil sample. In first experiment it was found there was delayed in time, when sample was put on alumina cup, to enter it in the furnace chamber. So there was rapid loss of weight in the start, as more volatile component went out of it.

In second experiment the sample was put on alumina cup and was entered in the furnace chamber without any loss of time. In both cases sample was heated in presence of nitrogen as burning gas, at about 900 ^{o}C. The indication of results shows that in the first case there was loss of weight of approximately 45 %, while in second experiment 42 % loss in weight was found. All plots and values of temperature change with loss of weight, with respect to time can be found in appendix A, can be found in CD ROM as well.

CHAPTER 7

EXPERIMENTAL WORK SECTION C

7. MINIMUM MSCIBILITY ANALYSIS BY SUPER CRITICAL EXTRACTOR

7.1 Introduction

This section gives the description of experimental analysis, performed on North sea chalk core sample saturated with crude oil from Halfdan oil field. Samples were saturated for 48 hours and used to investigate the minimum miscibility pressure in Supercritical Extractor unit at high pressure and temperature.

Super critical fluid carbon dioxide was used to extract the oil as it increases the mobility ratio and decrease the viscosity of most saturated alkanes as compared to other gas injection enhanced oil recoveries. Minimum miscibility pressure (MMP) is lowest possible pressure at which Carbon dioxide can develop multi contact miscibility. Series of experiments were performed at different pressure and temperatures using super critical extractor to find the Minimum Miscibility pressure and recovery ratios.

Figure 23: Supercritical CO2 Equipment

7.2 Use of Apparatus [R8]

The SFE apparatus may be used for extractions, impregnations and reactions in supercritical CO_2.

7.3 Reactors used in the SFE equipment

There are two different reactor types for the SFE equipment. These are a 24 ml reactor and a 100 ml reactor, both stainless steel and usable up to 10.000 psi / 600 bar.

In my case I used the 100ml reactor, description of the reactor is given as below.

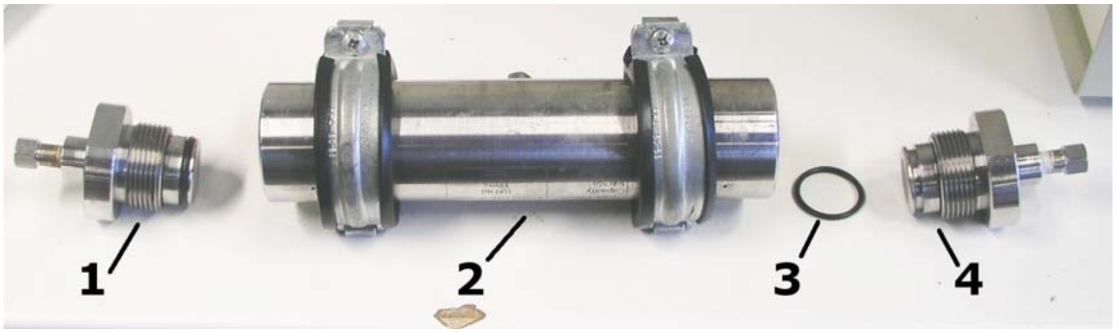


Figure 24: Reactor used in SFE equipment

1: Assembled end-cap, containing seals as well on both ends.
2 : Reactor and mounting, used to put samples and having mounting ends to install inside the Oven
3: Gasket or seals to avoids unwanted pressure leakage and temperature.
4: End-caps.

The reactor end-caps are tightened by hand; no tools are needed to ensure they are sealing the reactors tightly. Seals were used with some lubricants to ensure that to put and remove easily.

7.4 Operation

The pictures on the below show the actual SFE equipment. In order to understand the operation of the SFE we should be follow the steps given below, because use of equipment cannot be understand without following these steps.

The assembled reactor is placed in the oven (1) by hanging it on the studs (2) on the right side of the oven wall. The tubing (3) and (4) is connected to the reactor and tightened with tools, to ensure proper sealing. The thermocouple (5) is then fastened on the reactor by inserting it under the bands holding the reactor in place. This will measure the outside temperature of the reactor during the experiment. Close the oven.

Ensure that the inlet (6), outlet (7), release (8) and metering valves (9) are closed before proceeding to turn on the equipment by the switches (10)(11)

The temperature is set at the temperature controls using the following method, which is used for all set point on the equipment.

1. Press SP.
2. Use the forward and backward keys indication to move the digit indicator (a small blinking dot).
3. Use the upward and downward keys to change the digit.
4. Press SP to end set point change.

These steps are completed for both oven (12) and valve temperature (13), and take care that the valve temperature is approximately 20 °C above the desired reactor temperature to ensure no precipitation in the outlet system (7) (9). However the valve temperature (13) should not be raised above 120 °C, in cases where oven temperature (12) is above 100 °C the valve temperature (13) will be kept at 120 °C. The vessel temperature (14) cannot be set, but only measured; hence the oven temperature (12) is used to set/control the vessel temperature (14). This means that at high temperatures the oven temperature (12) needs to be set significantly higher than the desired vessel temperature (14) due to heat loss to the surroundings. Discuss your heating with one of the operators before starting your experiment series, as it is a matter of experience to be able to get a relatively fast heating.

Once temperatures are set, switch on the heating by the switches for the oven (15) and valves (16). During heating the system will not be pressurized to the desired process pressure, as the temperature increase will increase pressure in the reactor. To do this first pressurization open the CO_2 valve on the flask (22) and valve (17) to allow CO_2 to enter the system. The inlet valves (6) are then opened letting CO_2 into the system. To increase the pressure turn the knob (18) until the pressure in the system starts to increase slightly (19). Then leave the pressure at that value until the temperature of the reactor is at the desired value. Bear in mind that the temperature measured for the reactor is on the outside of the reactor and hence there should be allowed for a period of temperature stabilization across the reactor wall to ensure the inside is at a correct temperature. This period should preferably be around 15-25 minutes.

Once temperature is at the correct value the knob (18) is turned to increase the pressure to the desired conditions. From this point there are two modes of operation, either static or dynamic, both which will be explained subsequently.

Normally there are two types of operations can be followed for this equipment, but in my case I perform Dynamic operation, which is described as follows.

Supercritical Fluid Extraction (SFE) is based on the fact that, near the critical point of the Gas and solvent , its properties change rapidly with only slight variations of pressure.
The diagram below shows the SFE loop, where feed is continuously passing through the SFE vessel while interacting with gas counter- currently. The required pressure is provided by pump, which is reduced after passing through the expansion valve.

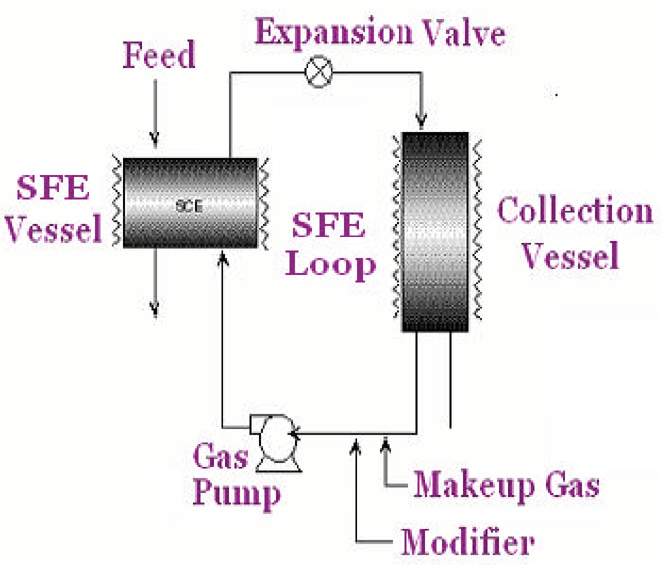


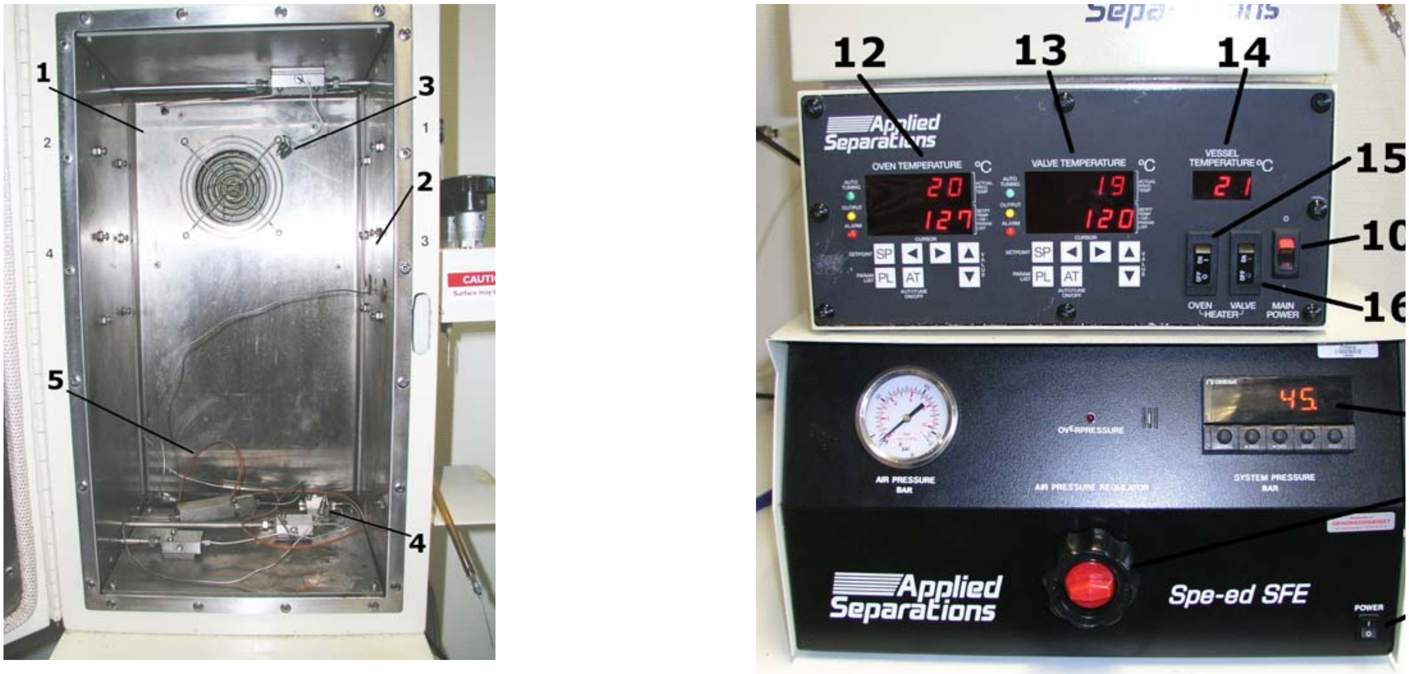
Figure 25: Supercritical extraction unit layout

7.4.1 Dynamic Operation:

During dynamic operation the outlets (7) and metering valve (9) are opened and the flow measured by inserting the flow meter tube (21) into a test tube and measuring the flow in the flow meter (20). This means new CO_2 will be introduced into the system continuously and hence the pressure needs to be watched to remain the desired range. Due to the pumping system the pressure will vary, with increasing variation at increasing pressures. This is an undesirable effect, but it cannot be circumvented. Once the experiment is completed the knob (18) it turned completely down and the inlet valve (6) is closed and the system relieved of pressure. Once the system is relieved of pressure the valves at the CO_2 flask (16), (17) are closed and the inlet valve (6) opened to remove the last CO_2 from the system.

Left side

Right side



Central unit

Controls

Figure 26: Spe-ed SFE, supercritical extractor unit

7.5 Flow measurement

In order to measure flow of gas during the experiment flow meter has been calibrated as below, which shows the correlation between flow meter and actual CO_2. flow Taking the reading on point 2 in the figure below, for example gives the flow of 2.4 l/min.

During all the experiments performed, flow meter position was kept at point 2 shown in figure.

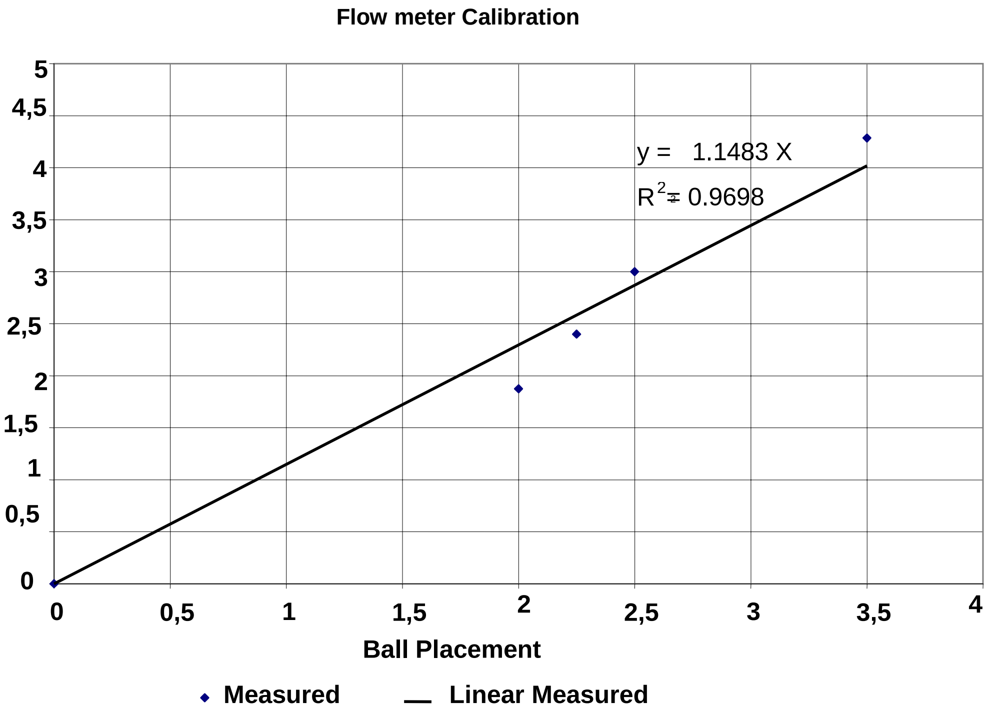


Figure 27: Correlation between flow meter and actual CO2 flow

7.6 Checklists for SFE Equipment

Checklist – Start-up

☐ The cooling bath should be at temperature of maximum 2°C.
☐ The compressed air should be connected and the valve open.
☐ All valves on the SFE are closed
☐ Inlet
☐ Outlet
☐ Metering Valve
☐ A flow restrictor is placed between the pump system and the reactor

Checklist – Shut down

☐ System is depressurized.
☐ The reactor is removed from the oven.
☐ The reactor, end-caps, and oven is clean.
☐ The CO_2 flask is closed.
☐ Valves on the SFE are open
☐ Inlet
☐ Outlet
☐ Exit valve

7.7 Specification of system

Max. Pressure:	10.000 Psi or 690 bar
Max. Temperature:	120 °C
Reactor Volumes:	100 ml
CO_2 supply:	Pressurized flask with dip pipe
Air supply:	Compressed air, 5 bar

Power:	220 V AC
Coolant:	Water
Coolant Temperature:	< 2 °C
Tubing:	1/16”

7.8 Comments and recommendations

While using the Supercritical Equipment with carbon dioxide, specification should be followed strictly as well. One should follow the following operational comments and recommendations as these are observations found during the experiment.

7.9 Measurements

7.9.1 Pump and pressure measurement

During the operation if the pump action is so fast, mean if it is not able to overcome the pressure, it means there is no CO_2 or there may be a leakage in the system. Sometimes if any of the valve like outlet or exit is opened then it should be closed.

If there is no CO_2 , then cylinder should be filled with it. If there is any leakage it should be seal or fittings where the leakage is located.

Normally it is difficult for pump to stay on the same reading, when system is working on higher pressures; it is going 10 bar above or below 10 bar the required pressure.

7.9.2 Temperature measurement

Temperature is not varying like pressure, before fix it on set point. It should be kept in mind that set point should be 1 or 2 degree Celsius above than the required temperature as there can be heat losses in a reactor. Any how by doing this way, we can get the same temperature for vessel.

7.9.3 Flow measurement.

It has been found during all these experiments flow cannot be measured exactly at high pressure values exactly, because when it is measured like more than 200 bar the ball placement on flow meter just show bubbling. Instead of moving up to point 1 or point 2 its bubbling behaviour is undesired activity.

One should be keep in mind while opening of flow and metering valve, lid on measuring test tube should be kept tightly to move the ball of metering valve up at constant level.

Similarly the plastic tube which is used to collect the oil sample should be cleaned properly as always the oil can be left in the tube, which is undesirable during the sample readings. It is highly recommended that we can get good results if using a tube with some packing material to absorb oil exactly.

7.10 Miscibility measurement by using saturated core sample

7.10.1 Miscibility Measurement by using artificially saturated cubical chalk sample at 60^{o}C, (Experiment no 1).

Chalk sample which was used for experiment was taken from Danish North sea reservoir, and saturated with crude oil from Hafldan oil field. MMP value is shown in the graph at which highest amount of oil was recovered at minimum possible pressure, while using the fixed temperature of 60 ^{o}C. Physical Parameters used during the experiment are given below.

Weight of sample after drying for 48 hours at 105 ^{o}C in oven = Wo = 23.1767 g
Weight of sample after saturation = W1 = 27.6618 g
Weight of sample after extraction= W2= 23.2144 g
Operating temp = 60 ^{o}C
Extraction time of sample with Carbon dioxide injection = 30 minutes
Operating pressure = 100 bar to 300 bar
Inlet valve and outlet valve position is fully open.
Total duration of experiment = 20 hours
Pressure difference interval = 10 bars

Table 7: Amount of oil displaced at 60°C

Tube no	Saturation Pressure (bar)	Vessel Temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	60	8.3621	8.3745	0.0124
2	120	60	8.311	8.3299	0.0189
3	130	60	8.3964	8.421	0.0246
4	140	60	8.3031	8.3346	0.0315
5	150	60	8.2974	8.299	0.0016
6	160	60	8.2622	8.3649	0.1027
7	170	60	8.3515	8.422	0.0705
8	180	60	8.263	8.4644	0.2014
9	190	60	8.4771	8.6565	0.1794
10	200	60	8.2567	8.4337	0.177
11	210	60	8.3666	8.64	0.2734
12	220	60	8.3029	8.4444	0.1415
13	230	60	8.3966	8.542	0.1454
14	240	60	8.2929	8.48	0.1871
15	250	60	8.3397	8.466	0.1263
16	260	60	8.3756	8.5013	0.1257
17	270	60	8.3345	8.4872	0.1527
18	280	60	8.2905	8.4379	0.1474
19	290	60	8.3682	8.4841	0.1159
20	300	60	8.1938	8.2248	0.031

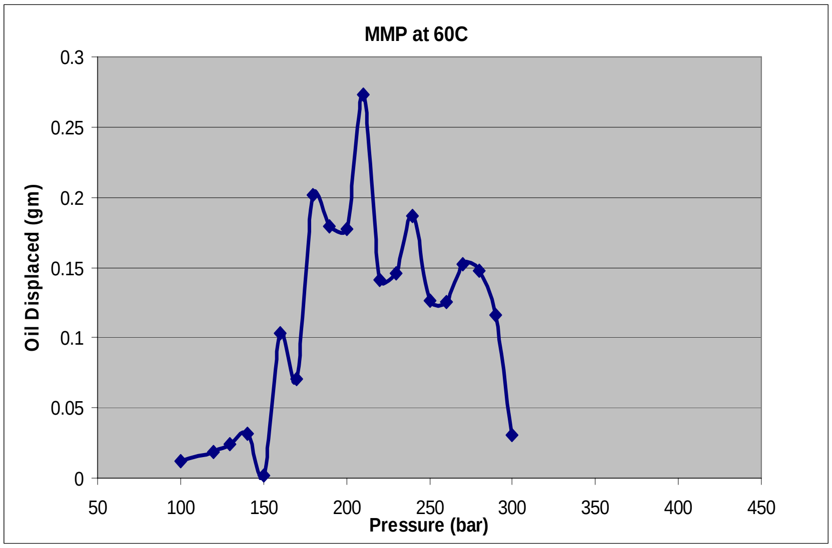


Figure 28: Amount of Oil displaced Vs saturation pressure at 60 °C

Results and Analysis

The experiment performed on saturated chalk core at 60°C with a pressure difference range of 10 bar produced reliable results. In the graph and table above, from 100bar to 150bar oil extracted amount was not reasonable, but when we switched to 160 bar the volume of oil extracted started increasing, and it continued with variation up to 220 bar. At 220 bars maximum value was attained which is indication of MMP value. At 180 bar the value was quiet good as well. The breakeven point at 220 bars doesn't signify the MMP concepts strictly but its criteria are accepted as explained in the ternary diagram.

Density of crude oil was calculated to be 0.825 g/cm^3, total amount of oil displaced by Carbon dioxide during the experiment is 2.2664 grams (2.7472 cm^3), and recovery percentage of oil is 50.96. All the tables from 2 to 9 are attached in the Appendix A:

Table 8: Recovery calculation.

Total weight of oil recovered	2.2664	gm
Density of Oil calculated	0.825	gm/cm^3
Volume of oil recovered	2.7472	cm^3
Saturated weight of chalk	27.6618	gm
Dry weight of chalk	23.2144	gm
weight of oil saturated in chalk	4.4474	gm
Percent recovery	50.96	%

7.10.2 Miscibility Measurement by using artificially saturated Cubical core sample at 70^{o}C, (Experiment no 2).

The procedure carried out during the experiment was same as performed in Experiment no.1. There is only difference in size of chalk samples and operating temperature, maximum pressure value. Purpose of experiments with different parameters, temperature, and pressure range and time interval is only to get MMP.

Weight of sample after drying for 48 hours at 105 ^{o}C in oven = Wo = 22.0519 g
Weight of sample after saturation = W1 = 27.6618 g
Weight of sample after extraction= W2= 23.2144 g
Operating temp = 70 ^{o}C
Extraction time of sample with Carbon dioxide injection = 30 minutes
Operating pressure = 100 bar to 430 bar
Inlet valve and outlet valve position is fully open.
Total duration of experiment = 30 hours
Pressure difference interval = 10 bars

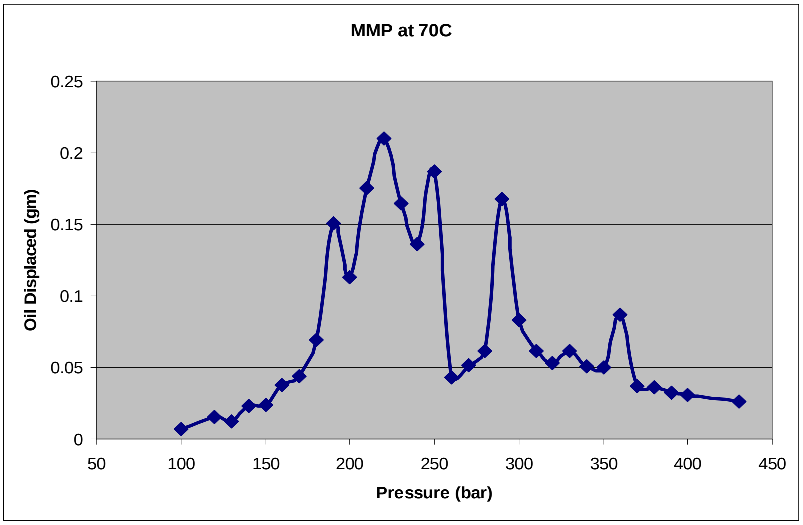


Figure 29: Amount of Oil displaced Vs saturation pressure at 70 °C

Results and Analysis

The experiment performed on saturated chalk core at 70^{o}C with a pressure difference range of 10 bar produced results which are changing with pressure. In the graph above, from 100bar to 190bar the amount of oil extracted increased first and then dropped again at 200 bar, but when we switched to 200 to 220 bar the volume of oil extracted started increasing, and reached at maximum value at 220 bar. At 220 bars maximum value was attained which is indication of MMP value. After 220 bar, the amount of oil extracted started decreasing again and up to 240 bar. After wards its value showing the zigzag results. The breakeven point at 220 bars doesn’t signify the MMP concepts strictly but its criteria are accepted as explained in the ternary diagram.

Density of crude oil was calculated to be 0.825 g/cm^3, total amount of oil displaced by Carbon dioxide during the experiment is 2.3037 grams (2.7924 cm^3), and recovery percentage of oil is 48.39%.

Table 8: Recovery measurement

Table 9:Recovery calculation

Total weight of oil recovered	2.3037	gm
Density of Oil calculated	0.825	Gm/cm^3
Volume of oil recovered	2.7924	Cm^3
Saturated weight of chalk	26.8715	Gm
Dry weight of chalk	22.1105	Gm
weight of oil saturated in chalk	4.761	Gm
Percent recovery	48.39	%

7.10.3 Miscibility Measurement by using artificially saturated Cubical core sample at 70°C, (Experiment no 3).

The procedure carried out during the experiment was same as performed in Experiment no.1 with a cubical core sample, with same operating temperature, and different pressure range up to maximum pressure value 430bar. Experiment with different parameters, temperature, and pressure range and time interval of 30 minutes duration is to observe MMP value of Carbon dioxide with given oil sample, and compare it with reservoir conditions. Pressure value was started with 100 bar with a variation of 30 bar before MMP value and after 160 bar to 220 bar pressure was changed with 20bar variation. All together experiment was performed at 13 different values. The parameters which were used during the experiments are as fallows.

Weight of sample after drying for 48 hours at 105 °C in = Wo = 27.1610
Weight of sample after saturation = W1 = 32.8925 g
Weight of sample after extraction= W2 = 27.2113 g
Operating temp = 70 °C
Extraction time of sample with Carbon dioxide injection = 30 minutes
Operating pressure = 100 bar to 430 bar
Inlet valve and outlet valve position is fully open.
Total duration of experiment = 10 hours
Pressure difference interval = 30 bar before MMP value, 20bars at MMP from 160bar-220 bar, and again 30 bar up to 430 bar.

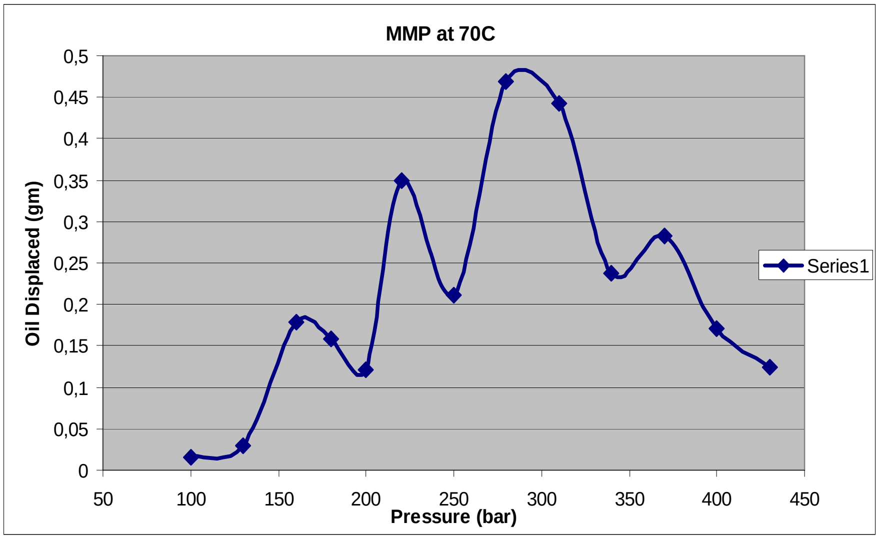


Figure 30: Amount of Oil displaced Vs saturation pressure at 60 °C

Results and Analysis

The experiment performed on cubical saturated chalk core at 70°C with a pressure difference range of 30 bar produced results which are changing with pressure. In the graph above, from 220bar the amount of oil extracted increased first and then dropped again at 250 bar, but when we switched to 280 to 310 bar the volume of oil extracted was more than at MMP value which is not required so there might be problem with Carbon dioxide flow in the extraction unit. The breakover point at 280 bars doesn't signify the MMP concepts. It should be around 180bar to 200 bar. Total amount of oil displaced by miscible displacement of Carbon dioxide during the experiment is 2.7915 grams (2.7924 cm^3), and recovery percentage of oil is 49.14, which is good amount if we compare it with other experimental values.

Table 10:Recovery measurement.

Total weight of oil recovered	2.7915	gm
Density of Oil calculated	0.825	gm/cm^3
Volume of oil recovered	3.3836	cm^3
Saturated weight of chalk	32.8925	gm
Dry weight of chalk	27.2113	gm
weight of oil saturated in chalk	5.6812	gm
Percent recovery	49.14	%

7.10.4 Miscibility Measurement by using artificially saturated Cubical core sample at 60°C, (Experiment no 4).

Amount of oil displaced versus saturation pressure is shown in graph below. Saturated core sample, of cubical dimensions was injected into the supercritical extractor unit at 60 °C. The viscosity of oil visualised was minimum as well and has been explained in the graphical figures of oil samples which were taken from extraction unit. At lower value of pressure the value of oil was more viscous, and higher value of pressure oil is less viscous, which shows indication of miscibility with Carbon dioxide. After the MMP value at 180 bar it has been observed that amount of oil displaced started decreasing. Altogether oil samples have been collected at 13 different pressure values. Important parameters used during the experiment are as fallows.

Weight of sample after drying for 48 hours at 105 °C in = Wo = 19.0342 g
Weight of sample after saturation = W1 = 22.5586 g
Weight of sample after extraction= W2 = 19.1031 g
Operating temp = 60 °C
Extraction time of sample with Carbon dioxide injection = 30 minutes
Operating pressure = 100 bar to 430 bar
Inlet valve and outlet valve position is fully open.
Total duration of experiment = 10 hours
Pressure difference interval = 30 bar before MMP value, 20bars at MMP from 160bar-220 bar, and again 30 bar up to 430 bar.

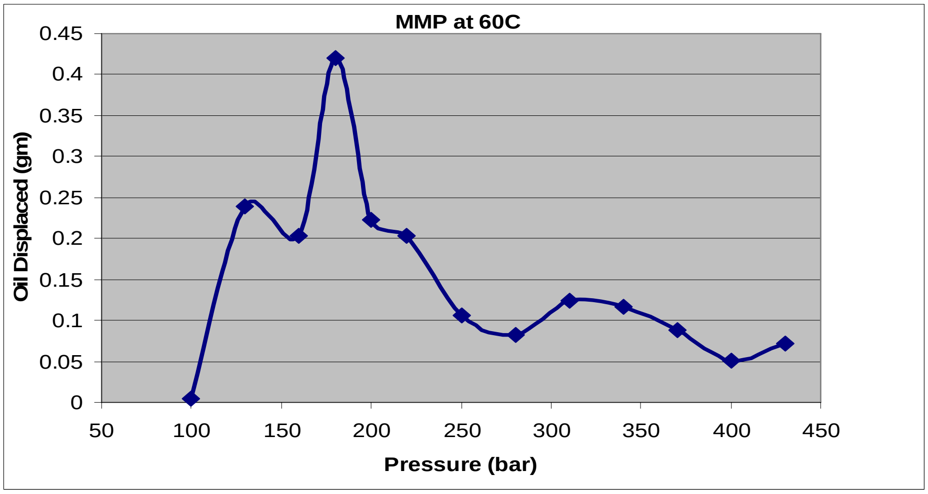


Figure 31: Amount of Oil displaced Vs saturation pressure at 60 °C

Results and Analysis

The experiment performed on cubical saturated chalk core at 60°C with a pressure difference range of 30 bar before the MMP range. Maximum volume of oil was extracted at 180 bars which follow the criteria for minimum miscibility criteria of Carbon dioxide with crude oil. The breakeven point at this 180bar completely signifies the MMP concepts which have been explained in miscibility contact angles. The interesting observation was the viscosity change, as the pressure started increasing the viscosity of oil started decreasing, which is confirmation of Carbon dioxide and oil, at 180 bar they are almost completely miscible with each other. Total amount of oil displaced by miscible displacement of Carbon dioxide during the experiment is 1.9312 grams (2.3408 cm^3), and recovery percentage of oil is 55.89, which is highest as compared to all other experimental results.

Table 11:Recovery measurement

Total weight of oil recovered	1,9312	Gm
Density of Oil calculated	0,825	gm/cm^3
Volume of oil recovered	2,3408	cm^3
Saturated weight of chalk	22,5586	Gm
Dry weight of chalk	19,1031	Gm
weight of oil saturated in chalk	3,4555	Gm
Percent recovery	55,89	%

7.10.5 Miscibility Measurement by using artificially saturated Cylindrical core sample at 60°C, (Experiment no 5).

Amount of oil displaced versus saturation pressure is shown in graph below. Saturated core sample, but with cylindrical dimensions was injected into the supercritical extractor unit at 60 °C. The viscosity of oil visualised was minimum when pressure started increasing and at 180 bar we can observe minimum viscosity of oil. At lower value of pressure the value of oil was more viscous, and higher value of pressure oil is less viscous, which shows indication of miscibility with Carbon dioxide. After the MMP value at 180 bar it has been observed that amount of oil displaced started decreasing. Altogether oil samples have been collected at 13 different pressure values, but amount of oil displaced at 280 bar and 310 bar was higher as compared to other pressure ranges.

Weight of sample after drying for 48 hours at 105 °C in = Wo = 24.9224g
Weight of sample after saturation = W1 = 29.1804 g
Weight of sample after extraction = W2 = 25.0990g
Operating temp = 60 °C
Extraction time of sample with Carbon dioxide injection = 30 minutes
Operating pressure = 100 bar to 430 bar
Inlet valve and outlet valve position is fully open.
Total duration of experiment = 10 hours
Pressure difference interval = 30 bar before MMP value, 20bars at MMP from 160bar-220 bar, and again 30 bar up to 430 bar.

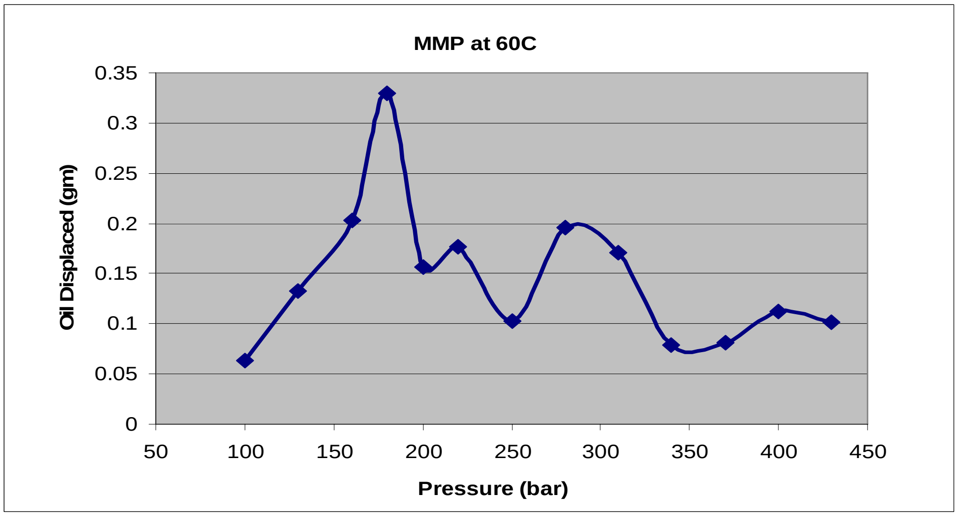


Figure 32: Amount of Oil displaced Vs saturation pressure at 60 °C

Results and Analysis

The experiment performed on cylindrical saturated chalk core at 60°C with a pressure difference range of 30 bar before the MMP range, and 20bar during the MMP range. The purpose was to compare the results with cubical core sample. Maximum volume of oil was extracted at 180 bar which follow the criteria for minimum miscibility criteria of Carbon dioxide with crude oil. The breakeven point at this 180bar strictly signifies the MMP concepts. The interesting observation was the viscosity change, again like in cubical core sample, as the pressure started increasing the viscosity of oil started decreasing, which is confirmation of Carbon dioxide and oil, at 180 bar they are almost completely miscible with each other. Total amount of oil displaced by miscible displacement of Carbon dioxide during the experiment is 1.9041 grams (2.3080 cm^3), and recovery percentage of oil is 46.65, which is not high enough like cubical core sample at the sample temperature and pressure values.

Table 12:Recovery measurement

Total weight of oil recovered	1,9041	gm
Density of Oil calculated	0,825	Gm/cm^3
Volume of oil recovered	2,3080	Cm^3
Saturated weight of chalk	29,1804	gm
Dry weight of chalk	25,099	gm
weight of oil saturated in chalk	4,0814	gm
Percent recovery	46,65	%

7.10.6 Miscibility Measurement by using artificially saturated Cylindrical core sample at 70°C, (Experiment no 6).

Amount of oil displaced versus saturation pressure is shown in graph below. Saturated core sample, but with cylindrical dimensions was injected into the supercritical extractor unit at 70 °C. The viscosity of oil visualised was minimum when pressure started increasing and at 180 bar we can observe minimum viscosity of oil. After the MMP value at 180 bar it has been observed that amount of oil displaced started decreasing. Altogether oil samples have been collected at 13 different pressure values. It has been observed that, although maximum peak is observed at 180 bar which is corresponds to MMP value, but at 220bar and then again, from 280bar to 340bar good results have been found. The parameters which were used during the experiments are as fallows.

Weight of sample after drying for 48 hours at 105 °C in = Wo = 25.0324g
Weight of sample after saturation = W1 = 29.9389 g
Weight of sample after extraction = W2 = 25.8207g
Operating temp = 70 °C
Extraction time of sample with Carbon dioxide injection = 30 minutes
Operating pressure = 100 bar to 430 bar
Inlet valve and outlet valve position is fully open.
Total duration of experiment = 10 hours

Pressure difference interval = 30 bar before MMP value, 20bars at MMP from 160bar-220 bar, and again 30 bar up to 430 bar.

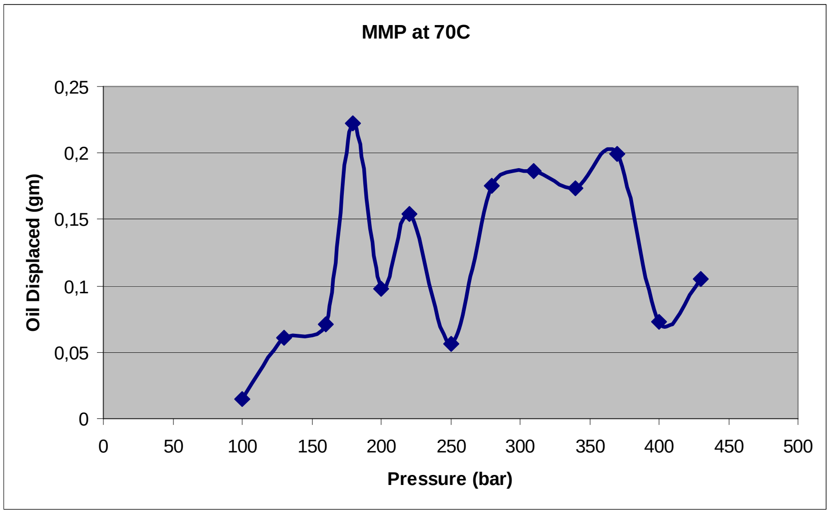


Figure 33: Amount of Oil displaced Vs saturation pressure at 70 °C

Results and Analysis

The experiment performed on cylindrical saturated chalk core at 70°C with a pressure difference range of 30 bar before the MMP range, and 20bar during the MMP range. Maximum volume of oil was extracted at 180 bar which follow the criteria for minimum miscibility criteria of Carbon dioxide with crude oil. The break over point at this 180bar strictly signifies the MMP concepts. The interesting observation was the viscosity change, again like in cubical core sample, as the pressure started increasing the viscosity of oil started decreasing, which is confirmation of Carbon dioxide and oil, at 180 bar they are almost completely miscible with each other. Recovery measurement has been shown in the below where the recovery percentage of oil is 38.59.

Table 13:Recovery measurement

Total weight of oil recovered	1.5891	gm
Density of Oil calculated	0.825	gm/cm^3
Volume of oil recovered	1.9262	cm^3
Saturated weight of chalk	29.9389	gm
Dry weight of chalk	25.8207	gm
weight of oil saturated in chalk	4.1182	gm
Percent recovery	38.59	%

7.10.7 Miscibility Measurement by using artificially saturated Cylindrical core sample at 50°C, (Experiment no 7).

Amount of oil displaced versus saturation pressure is shown in graph below. Saturated core sample, but with cylindrical dimensions was injected into the supercritical extractor unit at 50 °C. Altogether oil samples have been collected at 13 different pressure values. It has been observed that, although maximum peak is observed at 180 bar which is corresponds to MMP value. The parameters which were used during the experiments are as fallows.

Weight of sample after drying for 48 hours at 105 °C in = Wo = 24.891g
Weight of sample after saturation = W1 = 29.2650 g
Weight of sample after extraction = W2 = 25.7111 g
Operating temp = 50 °C
Extraction time of sample with Carbon dioxide injection = 30 minutes
Operating pressure = 100 bar to 430 bar
Inlet valve and outlet valve position is fully open.
Total duration of experiment = 10 hours

Pressure difference interval = 30 bar before MMP value, 20bars at MMP from 160bar-220 bar, and again 30 bar up to 430 bar.

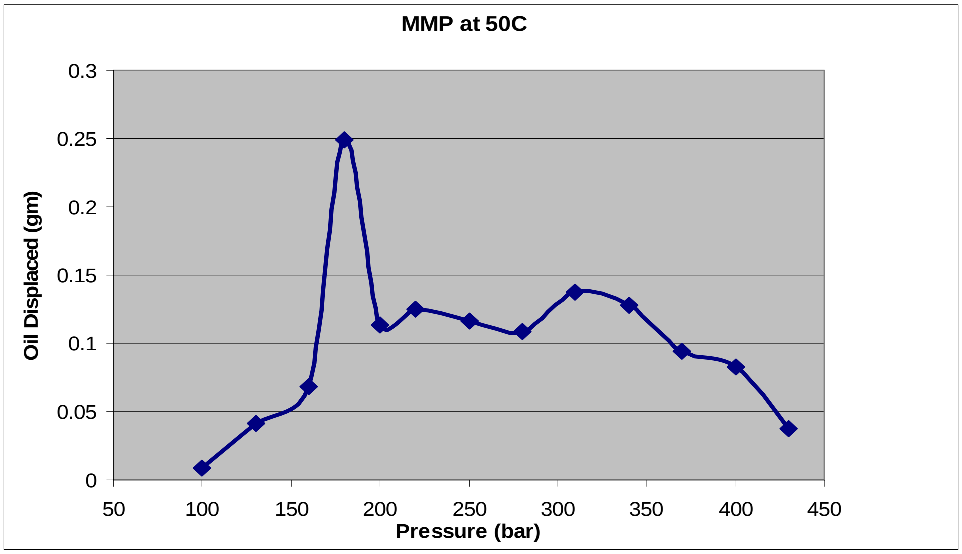


Figure 34: Amount of Oil displaced Vs saturation pressure at 50 °C

Results and Analysis

The results of the experiments are calculated in such a way that the collected amount of oil was weighed after every 30 min, and minimum miscibility pressure was predicted from the graph plotted from calculated data. Details of data tables are attached in the appendix. Plot obtained between amounts of oil extracted in grams Vs saturation pressure are shown above represents the recovery plot. Maximum amount of oil recovered was at 180 bar which corresponds the minimum miscibility pressure, and is a break over point. After MMP value the graph shows deviation and recovered amount of oil was not significant. Total amount of oil recovered was 1.3098gm (1.5876 gm/cm^3) with a percent recovery of 36.86.

Table 14:Recovery measurement

Total weight of oil recovered	1.3098	Gm
Density of Oil calculated	0.825	gm/cm3
Volume of oil recovered	1.5876	cm3
Saturated weight of chalk	29.2650	Gm
Dry weight of chalk	25.7111	Gm
weight of oil saturated in chalk	3.5539	Gm
Percent recovery	36.86	%

7.10.8 Effect on MMP by using artificially saturated core sample at different temperatures.

The saturation pressure effects the displacement of oil by supercritical carbon dioxide in two ways. Firstly these parameters affect the physical properties, viscosity and density, which affect the flow of fluid and its displacement through CO_2. Secondly there is effect of temperature and pressure on the miscibility of Carbon dioxide into the crude oil.

From the combined chart shown for three different temperatures below, the amount of oil displaced increases with increase of pressure. It is observed that initial pressure value didn't displace significant amount of oil and when pressure reached at 180bar on all three graphs with different temperatures (50,60,70) Celsius results in high efficiency of displacement. An important feature of all these trends is of course, a MMP value at certain pressure, but after that saturation pressure it is observed the amount of oil displaced was less even at increasing pressure value. This can be observed from graphs, and it was observed visually during the sample collection, that at MMP value the viscosity of extracted oil is very low and it is moveable like water. It was also observed that after MMP value even at higher pressure values the viscosity of oil started increasing which can be seen in graphs and was observed visually.

There is another important result which can be seen in all graphs that after MMP value, these falling treads tends towards the lower amount of oil, and then started fluctuating then the normal behaviour, which is indication of increasing amount of oil displaced. This was again visualized by extracted oil samples and shown in can be seen in Gas Chromatography section.

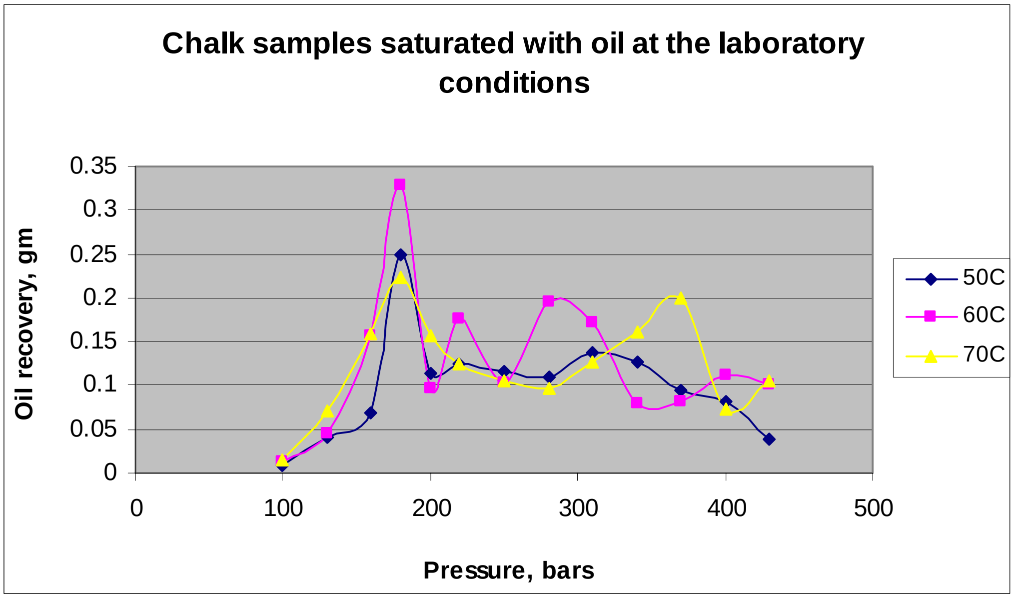


Figure 35: combined amount of oil displaces Vs saturation pressure (50, 60, and 70 °C)

The recovery percentage was higher from 100 to 180 bar, than 200 to 430 bar,i.e recovery percentage at 50°C increases 12 to 18% by increasing pressure value from 100 to 180 bar and then decreases from 14 to 6.2%.

The miscibility of supercritical Carbon dioxide increases with increasing the pressure but decreasing with the increase in temperature, which means that temperature, makes a considerable difference on the pressure at which the extraction of crude oil occurs.

Experiment no 8

Table 15: Recovery measurement

Total weight of oil recovered	0,9978	gm
Density of Oil calculated	0,825	gm/cm^3
Volume of oil recovered	1,2095	cm^3
Saturated weight of chalk	25,7983	gm
Dry weight of chalk	23,5819	gm
weight of oil saturated in chalk	2,2164	gm
Percent recovery	45,02	%

Experiment no 9

Table 16: Recovery measurement

Total weight of oil recovered	1,1607	gm
Density of Oil calculated	0,825	gm/cm^3
Volume of oil recovered	1,4069	cm^3
Saturated weight of chalk	26,7450	gm
Dry weight of chalk	22,341	gm
weight of oil saturated in chalk	4,404	gm
Percent recovery	26,36	%

Conclusion

The oil recovery grows sharply till the value of 180 MMP, and the highest volume of extracted oil occurred at the pressure of 180 bars. That indicates that this value is a MMP. As the oil is movable as it was saturated at the lab conditions and didn't yet create bonds with the rock particles, the graph forms external points at MMP – the biggest percentage of oil was extracted.

The slope of the pressure growth to the break over point grows with the temperature. It reaches break over point faster at 70 °C when at 50 °C it firstly forms a step.

7.10.9 Equilibrium confirmation by changing extraction time of samples.

The last problem which needs to find out is if the equilibrium occurs after 30 minutes. Other words, question which has to be answered is if the time of extraction affects the shape of graph and changes the value of MMP. For that purpose the same piece of chalk was saturated with oil 3 times and used for supercritical extraction during different time periods but at the same temperature of 60 °C. First time the extraction time period was 30 minutes, second – 60 minutes and the third – 90 minutes at each pressure value.

As it can be seen from the plots, the graphs for 30 and 90 minutes are similar. The 60 minutes graph shows deviation and shows highest peak at different value than for 30 and 90 minutes. The reason for that could be some technical problems with oil collection during experiment but for better confirmation this experiment is recommended to repeat again. So there is confirmation of equilibrium that change in time doesn't effect the MMP values as all these trends are similar as explained before different temperatures.

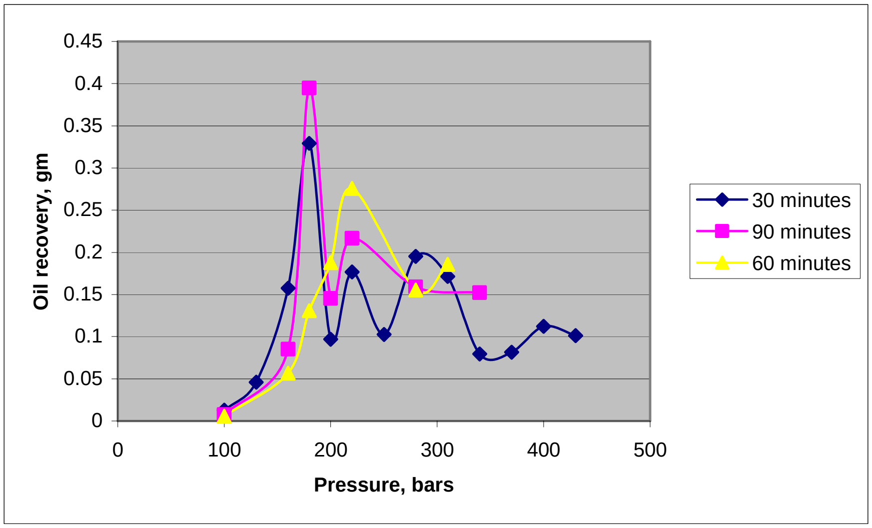


Figure 35:Amount of oil displaced Vs saturation pressure with variation of time

Note: Tables in details are attached in Appendix: B

CHAPTER 8

EXPERIMENTAL WORK SECTION D

8. GAS CHROMATOGRAPHY

8.1 Introduction

The gas composition is determined, invariably, by gas chromatography (GC). Gas chromatography is also used to oil analysis with a comparable accuracy. Oil analysis by distillation takes many days and requires relatively a large volume of sample, while gas chromatography can identify components as heavy as C_{80} in a matter of hours using only small fraction of sample fluid.[R9]

8.2 Procedure and injection of sample in GC apparatus

In order to carry out GC analysis 50 mg (0.05g) of methaylheptadecane has been taken and diluted with 100ml of pentane reagent (grade 98%). Oil samples collected from Supercritical extractor at fixed temperature and varying pressures has been diluted in test tubes so that tubes were half filled with samples.

The samples were injected into a heated zone, vaporized, and transported by a carrier gas; helium was used in the case, as it is a noble gas, into a packed column, which contained partition to put different samples. General purpose columns partition components mostly according to their boiling points; hence compounds are eluted in a similar order in distillation. The eluted compounds are carried, by the carrier gas, into a detector where the component concentration is related to the area under the detector response-time curve. Individual peaks may be identified by comparing their retention times inside the column with those of known compounds previously analyzed at the same GC condition.[R10]

8.3 Types of Detector used in GC

The most commonly used detectors are the flame ionization detector (FID) and the thermal conductivity detector (TCD). The FID is almost proportional to the mass concentration of the ionized compound. It cannot detect non-hydrocarbons such as N_2 and CO_2. TCD is used for analysis of gaseous mixtures that contain non-hydrocarbon components.[R11]

8.4 Drawback of GC

Major drawback of GC analysis is the lack of information, such as the molecular weight and density, on the identified Saturated Normal hydrocarbons (SCN) groups. The lack of molecular weight is quite limiting as the response of FID, used for oil analysis, is proportional to the mass concentration. Molecular weight data are needed, to convert mass fraction to molar basis required for compositional studies.

Figure 36: Gas chromatography unit

8.5 Results and Conclusion

Table 17: Experiment no 5, cylindrical sample

(Extracted oil) Sample no.	Temp(^{o}C)	Pressure (bar)
1	50	100
2	50	130
3	50	160
4	50	180
5	50	200
6	50	220
7	50	250
8	50	280
9	50	310
10	50	340
11	50	370
12	50	400
13	50	430

Samples of oil were injected with duration of 30 min for each sample, with a detector response of 650 counts at fixed value. Most of samples detected the hydrocarbon were in the range of C_{10}-C_{25}, when the pressure ranges were up to 310bar. When pressure increased at fixed temperature of 50 ^{o}C, the lighter components C_{10} were already distilled out from the crude oil sample leaving the heavy hydrocarbon. Another interesting observation was found during the experiment that oil extracted by Supercritical Extractor was less viscous when pressure was above 300 bars, which was further confirmed during the Chromatographs results, which shows that at higher pressure again lower ranges hydrocarbons were found C_{20}. Carbon dioxide is efficient to decrease viscosity, and increase mobility, of heavy hydrocarbons ranges up to C_{30}.

Table 18: Experiment no 6, cylindrical sample

(Extracted oil) Sample no.	Temp(°C)	Pressure (bar)
1	70	100
2	70	130
3	70	160
4	50	180
5	70	200
6	70	220
7	70	250
8	70	280
9	70	310
10	70	340
11	70	370
12	70	400
13	70	430

In this experiment at temperature of 70 °C, at 100 bars C_{12} at graph can be seen. There are C_{10} if we look in sample 2 at graph no 2 , where below this range, hydrocarbons range cannot be seen, lighter components and gases were vent off at high temperature.
Most of the chromatographs in this experiment show hydrocarbons up to C_{17} before MMP values but C_{25} can be seen on graph no. 5, which is confirmation that CO_2 can displace heavy hydrocarbon by reducing the viscosity and increasing mobility ratio.

Table 19: Experiment no 7, cylindrical sample

(Extracted oil) Sample no.	Temp(°C)	Pressure (bar)
1	50	100
2	50	130
3	50	160
4	50	180
5	50	200
6	50	220
7	50	250
8	50	280
9	50	310
10	50	340
11	50	370
12	50	400
13	50	430

At 50 °C the chromatographs, shows that in the start the hydrocarbons were found in the range of C_9-C_{19}. In the range of MMP there was no progressive change to get higher hydrocarbons. At higher pressure values, above 250bar C_{10}-C_{18} were found.

Table 20:Experiment no 8,(1 hr duration) Cylindrical sample

(Extracted oil) Sample no.	Temp(^{o}C)	Pressure (bar)
1	60	100
2	60	160
3	60	180
4	60	200
5	60	220
6	60	280
7	60	340

Interesting results were found during this experiment with 1 hour duration at 60 ^{o}C, at 100 bar and 160 bar hydrocarbons were found up to C_{19}. At 180 bar and 200 bar in the range of MMP C_{25} and higher range were found. Higher pressure after 220 bar to 340 bar also displaced C_{25} and higher.

Table 21: Experiment no 9, (1.5 hr duration, 60 oC)

(Extracted oil) Sample no.	Temp(^{o}C)	Pressure (bar)
1	60	100
2	60	160
3	60	180
4	60	200
5	60	220
6	60	280
7	60	340

When experiment was repeated at 60^{o}C with 1.5 hour duration the different results were observed, with respect to 1 hour duration. At 100-180 bar saturation pressure displaced the Hydrocarbons from C9-C25, but at higher pressure range above 200 bars didn't show the higher hydrocarbons, which is obvious.

Note: All the chromatographs trends are attached in CD-Rom as well as in the end of report in Appendix C

8.6 Visual observation of extracted oil samples at different pressures

Oil samples after extracted from supercritical extraction unit were visualised, and it was found at lower values of pressure, when first sample was extracted at 100 bar, it was viscous and was difficult to move. With the increasing pressure values samples extracted were observed less viscous and were able to move, which is indication of decrease in viscosity and mobility ration with fresh carbon dioxide, continuously injecting into the core samples. At the value of minimum miscibility pressure the viscosity of extracted oil was observed, that was corresponding to water viscosity, which can move easily. It can be shown in graphics taken as shown below.

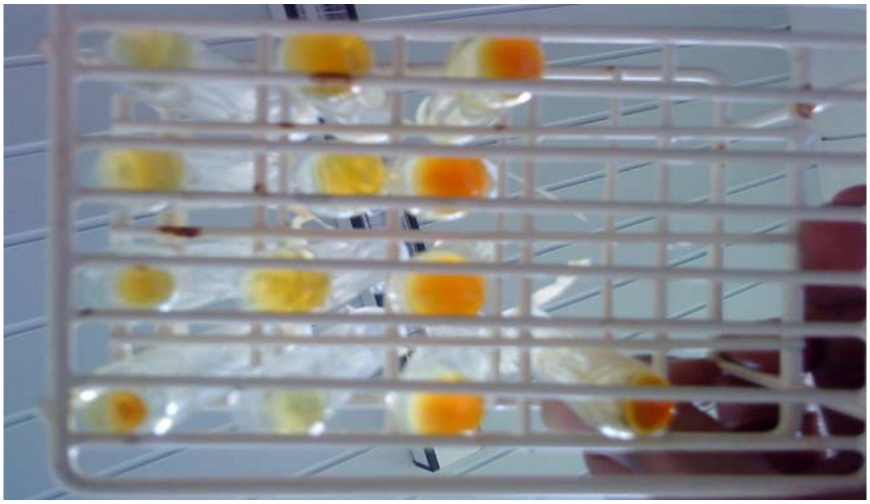


Figure 37: Visual observation of the extracted oil

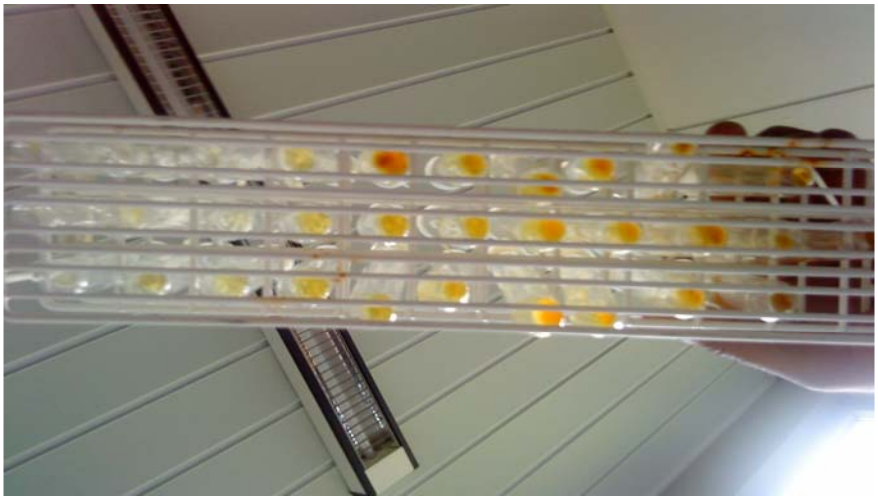


Figure 38: Visual observation of the extracted oil

CHAPTER 9

9. MISCIBILITY AND RECOVERY CALCULATION

9.1.1 Recovery calculation at different temperatures calculated during the experiments.

Recovery calculation can be carried out by using the volumetric calculation. Recovery calculations after the experiments are carried out as fallows.

From the table no.22 the total amount of oil displaced at 60°C is 2.2664 gm. Using the density of crude oil as 0.825 gm/cm3 then the total volume of oil displaced 2.7472 cm3.

Table 22: Final calculation for Oil recovery

Sample operating temperature	**Total volume of oil in sample(cm^3)**	**Total volume of extracted oil(cm^3)**	**Recovery (%)**
Core 1= 60°C	5.39 cm^3	2.7472 cm^3	50.96
Core 2 = 70°C	5.77 cm^3	2.7924 cm^3	48.39
Core 3= 70°C	6.88 cm^3	3.3836 cm^3	49.14
Core 4 = 60°C	4.18 cm^3	2.3408 cm^3	55.85
Core 5 = 60°C	4.94 cm^3	2.308 cm^3	48.33
Core 6 = 70°C	4.99 cm^3	1.9262 cm^3	38.59
Core 7 = 50°C	4.30 cm^3	1.5876 cm^3	36.86
Core 8 = 60°C	2.68 cm^3	1.2095 cm^3	45.02
Core 9 = 60°C	5.34 cm^3	1.406 cm^3	26.36

MMP calculation using correlation (R6-19)

A variety of correlations for the estimation of MMP has been developed from regression of slim tube data. Although less accurate, correlation are quick and easy to use and generally require only a few input parameters. Hence, they are very useful for fat screening of reservoir for potential CO2 flooding. they are also useful when detailed characterizations are not available.

Some MMP correlations require only the input of the reservoir temperature and the API of the reservoir fluid. Other more accurate correlations require reservoir temperature and the C2- C6 content of reservoir fluid. A few require a detail EOS characterization.

Despite evaporating the light components from the oil saturated chalk plug used, it would be interesting to compare experimental results with the results which can be found from analytical methods. The composition of original crude oil from the field of investigation was used for calculation by Yelling and Metcalfe, Glaso and Cronquist equations and simulations based on four models. I have also used the new correlation for the calculation purpose.

Yelling and Metcafe correlation

Yelling and Metcafe correlation in equation is based on reservoir only and doesn't account for oil composition. We can calculate the MMP at different reservoir temperature which we have used for our experiments by using the equation below. Bases on this correlation MMP varies from 15 to 19 Mpa approximately which is also near to experimental calculation.

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

Where T is the reservoir temperature

At T = 50C (122 F)

MMP = 2291.614 Psia, 15.98 MPa

At T = 60C (140)

MMP = 2427.97 Psia, 16.88 MPa

At T= 70C (158 F)

MMP= 2573.517 Psia, 17.80 MPa

The result shows that the MMP value is nearly closer to experimental results.

10. Discussion

Slim tube traditionally used for MMP determination in oil industry is a rare and expensive tool. Only one such device exists in Denmark and it is unavailable. our approach to use supercritical extractor for MMP determination was based on the observation that CO_2 is a very common agent used for the extraction of many substances in many industries like naphthalene, caffeine from coffee beans and asphaltenes and so on. [R13] The graphs of the solubility of such processes have all the attributes of the graphs obtained with slim tube. The supercritical reactors are often available to the universities when they are used for the studying of catalytic reactions, supercritical technologies and thermodynamic processes. In the first trial with oil-saturated core sample the graph obtained with SPE showed the same type of the curve as from the slim-tube experiment. This project was the trial to deepen and expand the basis to prove that SPE can be used for MMP determination.

R

In this project the samples of pure chalks was used instead of glass beads in slim tube. They have been saturated with the oil. This is more convenient case than to use originally oil-saturated samples because the MMP for the oil based of the oil composition can be analysed but it was not done due to the absence of time and equipment.

The plots demonstrate individualistic graphs for the different samples due to complex internal structure of the chalk matrix. The biggest difference from slim tube is that they have a peaks at MMP which is explained that the oil is movable, i.e. the oil is not trapped inside the chalk matrix. The presence of these peaks also underlines again that this pressure (180 bars for our oil) is most effective. In this project MMP is understood as the break over point at the graph and most effective pressure where the maximum of oil recovery occurred. The theoretical questions if MMP signifies full miscibility was not discussed because of the complexities of miscibility phenomena.

Normally it is difficult for pump to stay on the same reading, when system is working on higher pressures; it is going 10 bar above or below 10 bar the required pressure.

Conclusion

1) In all the experiments with cylindrical samples the MMP was determined at the same value of 180 bars with a slight dependence on temperature

2) The slope to a break over point (MMP) grows faster with growing temperature

3) Experiment with different time of extraction showed that for 30 and 90 minutes the plots obtained are identical. There is break over point at 180 bar

4) SC extractor can be used for MMP determination

RECOMMENDATIONS

During the experiments the problems encountered effects different factors, so we must consider these to improve the results. Some of recommendations are related to improve the way of experiments while some are related to the better understanding of Carbon dioxide techniques.

Temperature is not varying like pressure, before fix it on set point. It should be kept in mind that set point should be 1 or 2 degree Celsius above than the required temperature as there can be heat losses in a reactor. Any how by doing this way, we can get the same temperature for vessel.
For experiment it needs to use hard chalk samples, because soft the samples when used for saturation with given oil samples can be break (the soft samples were smashed during experiment).sample size is also important factor. Large sample size can provide better results having the more surface area of core to contact with carbon dioxide and can improve the recovery ratio of oil.

During the operation if the pump action is so fast, mean if it is not able to overcome the pressure, it means there is no CO_2 or there may be a leakage in the system. Sometimes if any of the valve like outlet or exit is opened then it should be closed. If there is no CO_2 , then cylinder should be filled with it. If there is any leakage it should be seal or fittings where the leakage is located.
Similarly the plastic tube which is used to collect the oil sample should be cleaned properly as always the oil can be left in the tube, which is undesirable during the sample readings. It is highly recommended that we can get good results if using a tube with some packing material to absorb oil exactly and precisely. A phase separator could also be attached to the control and collection modules to collect and separate the fluid phases.
It has been found during all these experiments flow cannot be measured exactly at high pressure values exactly, because when it is measured like more than 200 bar the ball placement on flow meter just show bubbling. Instead of moving up to point 1 or point 2 its bubbling behaviour is undesired activity.
One should be keep in mind while opening of flow and metering valve, lid on measuring test tube should be kept tightly to move the ball of metering valve up at constant level.

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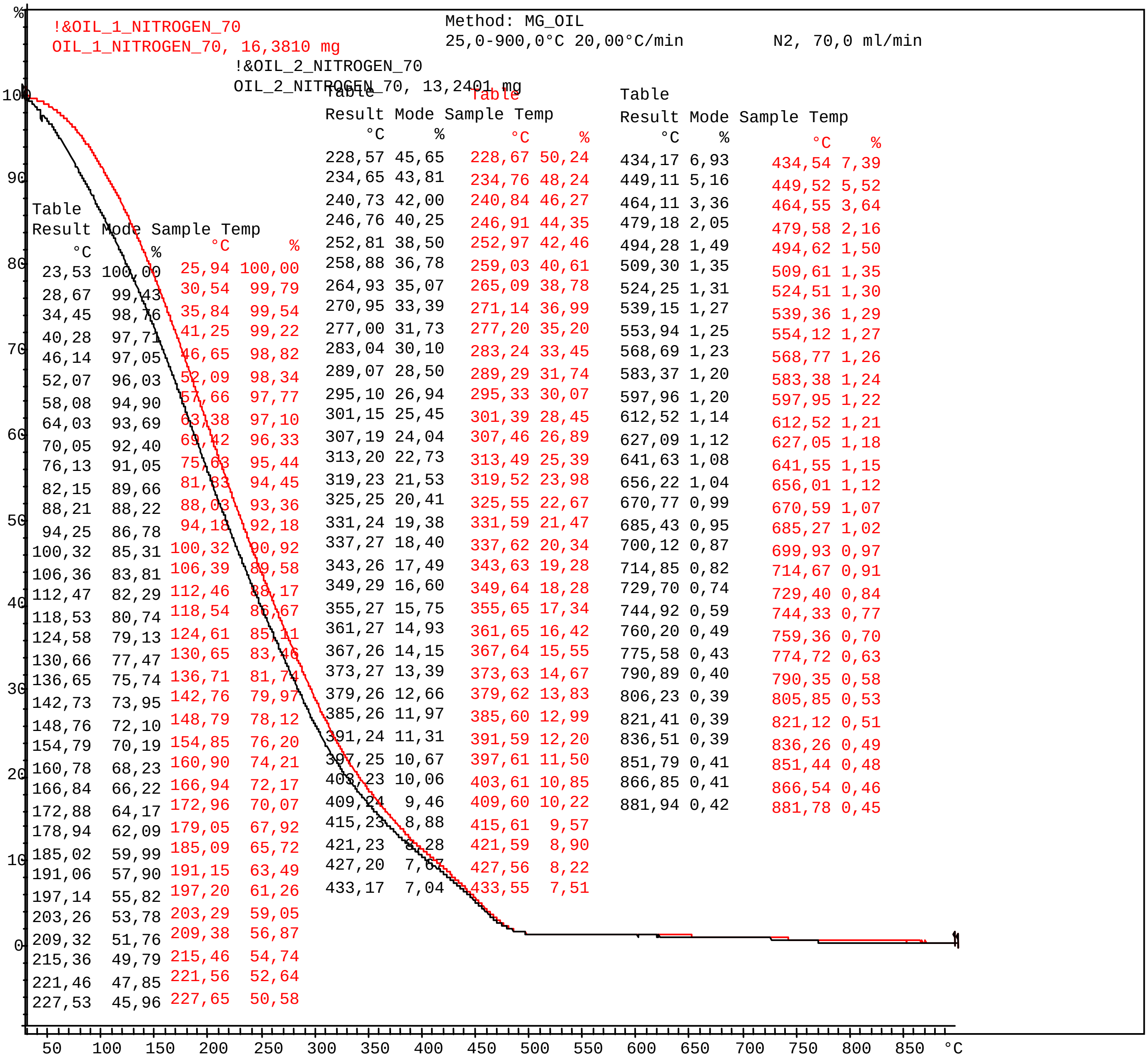
AppendixList
AppendixA

MG_OIL 13.03.2009 16:04:39



!&OIL_1_NITROGEN_70
OIL_1_NITROGEN_70, 16,3810 mg
!&OIL_2_NITROGEN_70
OIL_2_NITROGEN_70, 13,2401 mg

Method: MG_OIL
25,0-900,0°C 20,00°C/min N2, 70,0 ml/min

Table
Result Mode Sample Temp

°C	%	°C	%
23,53	100,00	25,94	100,00
28,67	99,43	30,54	99,79
34,45	98,76	35,84	99,54
40,28	97,71	41,25	99,22
46,14	97,05	46,65	98,82
52,07	96,03	52,09	98,34
58,08	94,90	57,66	97,77
64,03	93,69	63,38	97,10
70,05	92,40	69,42	96,33
76,13	91,05	75,63	95,44
82,15	89,66	81,83	94,45
88,21	88,22	88,03	93,36
94,25	86,78	94,18	92,18
100,32	85,31	100,32	90,92
106,36	83,81	106,39	89,58
112,47	82,29	112,46	88,17
118,53	80,74	118,54	86,67
124,58	79,13	124,61	85,11
130,66	77,47	130,65	83,46
136,65	75,74	136,71	81,74
142,73	73,95	142,76	79,97
148,76	72,10	148,79	78,12
154,79	70,19	154,85	76,20
160,78	68,23	160,90	74,21
166,84	66,22	166,94	72,17
172,88	64,17	172,96	70,07
178,94	62,09	179,05	67,92
185,02	59,99	185,09	65,72
191,06	57,90	191,15	63,49
197,14	55,82	197,20	61,26
203,26	53,78	203,29	59,05
209,32	51,76	209,38	56,87
215,36	49,79	215,46	54,74
221,46	47,85	221,56	52,64
227,53	45,96	227,65	50,58

Table
Result Mode Sample Temp

Table

°C	%	°C	%
228,57	45,65	228,67	50,24
234,65	43,81	234,76	48,24
240,73	42,00	240,84	46,27
246,76	40,25	246,91	44,35
252,81	38,50	252,97	42,46
258,88	36,78	259,03	40,61
264,93	35,07	265,09	38,78
270,95	33,39	271,14	36,99
277,00	31,73	277,20	35,20
283,04	30,10	283,24	33,45
289,07	28,50	289,29	31,74
295,10	26,94	295,33	30,07
301,15	25,45	301,39	28,45
307,19	24,04	307,46	26,89
313,20	22,73	313,49	25,39
319,23	21,53	319,52	23,98
325,25	20,41	325,55	22,67
331,24	19,38	331,59	21,47
337,27	18,40	337,62	20,34
343,26	17,49	343,63	19,28
349,29	16,60	349,64	18,28
355,27	15,75	355,65	17,34
361,27	14,93	361,65	16,42
367,26	14,15	367,64	15,55
373,27	13,39	373,63	14,67
379,26	12,66	379,62	13,83
385,26	11,97	385,60	12,99
391,24	11,31	391,59	12,20
397,25	10,67	397,61	11,50
403,23	10,06	403,61	10,85
409,24	9,46	409,60	10,22
415,23	8,88	415,61	9,57
421,23	8,28	421,59	8,90
427,20	7,67	427,56	8,22
433,17	7,04	433,55	7,51

Table
Result Mode Sample Temp

°C	%	°C	%
434,17	6,93	434,54	7,39
449,11	5,16	449,52	5,52
464,11	3,36	464,55	3,64
479,18	2,05	479,58	2,16
494,28	1,49	494,62	1,50
509,30	1,35	509,61	1,35
524,25	1,31	524,51	1,30
539,15	1,27	539,36	1,29
553,94	1,25	554,12	1,27
568,69	1,23	568,77	1,26
583,37	1,20	583,38	1,24
597,96	1,20	597,95	1,22
612,52	1,14	612,52	1,21
627,09	1,12	627,05	1,18
641,63	1,08	641,55	1,15
656,22	1,04	656,01	1,12
670,77	0,99	670,59	1,07
685,43	0,95	685,27	1,02
700,12	0,87	699,93	0,97
714,85	0,82	714,67	0,91
729,70	0,74	729,40	0,84
744,92	0,59	744,33	0,77
760,20	0,49	759,36	0,70
775,58	0,43	774,72	0,63
790,89	0,40	790,35	0,58
806,23	0,39	805,85	0,53
821,41	0,39	821,12	0,51
836,51	0,39	836,26	0,49
851,79	0,41	851,44	0,48
866,85	0,41	866,54	0,46
881,94	0,42	881,78	0,45

Aalborg University Esbjerg: TGA System

Appendix B

Experiment no 1

Tube no	Saturation Pressure (bar)	Vessel Temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	60	8,3621	8,3745	0,0124
2	120	60	8,311	8,3299	0,0189
3	130	60	8,3964	8,421	0,0246
4	140	60	8,3031	8,3346	0,0315
5	150	60	8,2974	8,299	0,0016
6	160	60	8,2622	8,3649	0,1027
7	170	60	8,3515	8,422	0,0705
8	180	60	8,263	8,4644	0,2014
9	190	60	8,4771	8,6565	0,1794
10	200	60	8,2567	8,4337	0,177
11	210	60	8,3666	8,64	0,2734
12	220	60	8,3029	8,4444	0,1415
13	230	60	8,3966	8,542	0,1454
14	240	60	8,2929	8,48	0,1871
15	250	60	8,3397	8,466	0,1263
16	260	60	8,3756	8,5013	0,1257
17	270	60	8,3345	8,4872	0,1527
18	280	60	8,2905	8,4379	0,1474
19	290	60	8,3682	8,4841	0,1159
20	300	60	8,1938	8,2248	0,031

Experiment no 2

Tube no	Saturation Pressure (bar)	Vessel temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	70	8,4371	8,444	0,0069
2	120	70	8,3801	8,3958	0,0157
3	130	70	8,2941	8,3064	0,0123
4	140	70	12,147	12,17	0,023
5	150	70	8,1299	8,154	0,0241
6	160	70	8,2303	8,2678	0,0375
7	170	70	8,2691	8,313	0,0439
8	180	70	8,3173	8,3864	0,0691
9	190	70	8,246	8,3966	0,1506
10	200	70	8,3156	8,429	0,1134
11	210	70	8,3056	8,481	0,1754
12	220	70	8,2239	8,434	0,2101
13	230	70	8,2662	8,4311	0,1649
14	240	70	8,3058	8,4419	0,1361
15	250	70	8,4263	8,6133	0,187
16	260	70	8,2826	8,3255	0,0429
17	270	70	8,2448	8,2961	0,0513
18	280	70	8,38	8,4413	0,0613
19	290	70	8,2276	8,395	0,1674
20	300	70	8,4526	8,5357	0,0831
21	310	70	8,2918	8,3533	0,0615
22	320	70	8,3026	8,356	0,0534

Tube no	Pressure(bar)	Vessel temp	Weight of Empty test tube(gm)	Weight of sample test tube(gm)	Oil Displaced
23	330	70	8,3394	8,401	0,0616
24	340	70	8,3122	8,3629	0,0507
25	350	70	8,3654	8,4157	0,0503
26	360	70	8,313	8,4003	0,0873
27	370	70	8,3393	8,3764	0,0371
28	380	70	8,3252	8,3612	0,036
29	390	70	8,256	8,2886	0,0326
30	400	70	8,2739	8,3049	0,031
31	430	70	8,2595	8,2857	0,0262

Experiment no 3

Tube no	Pressure (bar)	Vessel temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	70	8,2801	8,2955	0,0154
2	130	70	8,3637	8,3928	0,0291
3	160	70	8,3806	8,5585	0,1779
4	180	70	8,3338	8,4929	0,1591
5	200	70	8,381	8,5027	0,1217
6	220	70	8,2264	8,5757	0,3493
7	250	70	8,3005	8,5121	0,2116
8	280	70	8,2153	8,6845	0,4692
9	310	70	8,3018	8,7449	0,4431
10	340	70	8,2313	8,4684	0,2371
11	370	70	8,4106	8,6935	0,2829
12	400	70	8,31	8,4806	0,1706
13	430	70	8,3442	8,4687	0,1245

Experiment no 4

Tube no	Presure (bar)	Vessel temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	60	8,2569	8,2615	0,0046
2	130	60	8,3916	8,6304	0,2388
3	160	60	8,3259	8,5291	0,2032
4	180	60	8,3863	8,8067	0,4204
5	200	60	8,2685	8,4906	0,2221
6	220	60	8,315	8,5183	0,2033
7	250	60	8,2935	8,3996	0,1061
8	280	60	8,2806	8,3627	0,0821
9	310	60	8,3364	8,4604	0,124
10	340	60	8,4031	8,5201	0,117
11	370	60	8,2159	8,3038	0,0879
12	400	60	8,3	8,3505	0,0505
13	430	60	8,3825	8,4537	0,0712

Experiment no 5

Tube no	Pressure (bar)	Vessel temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	60	8,3332	8,396	0,0628
2	130	60	8,3428	8,475	0,1322
3	160	60	8,2926	8,4951	0,2025
4	180	60	8,2297	8,5589	0,3292
5	200	60	8,3275	8,4845	0,157
6	220	60	8,2429	8,4198	0,1769
7	250	60	8,4024	8,5051	0,1027
8	280	60	8,3648	8,5602	0,1954
9	310	60	8,3138	8,485	0,1712
10	340	60	8,1602	8,2396	0,0794
11	370	60	8,2554	8,337	0,0816
12	400	60	8,2949	8,407	0,1121
13	430	60	8,3861	8,4872	0,1011

Experiment no 6

Tube no	Pressure (bar)	Vessel temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	70	8,3489	8,3637	0,0148
2	130	70	8,4016	8,4624	0,0608
3	160	70	8,3189	8,3896	0,0707
4	180	70	8,3246	8,5472	0,2226
5	200	70	8,3656	8,4632	0,0976
6	220	70	8,317	8,4709	0,1539
7	250	70	8,3242	8,3801	0,0559
8	280	70	8,3575	8,5331	0,1756
9	310	70	8,3835	8,5703	0,1868
10	340	70	8,3138	8,4874	0,1736
11	370	70	11,9598	12,159	0,1992
12	400	70	8,3997	8,4723	0,0726
13	430	70	8,39	8,495	0,105

Experiment no 7

Tube no	Presure (bar)	Vessel temp	Weight of Empty Test Tube (gm)	Weight of Sample Test Tube (gm)	Oil Displaced (gm)
1	100	50	8,2416	8,2506	0,009
2	130	50	8,1568	8,1982	0,0414
3	160	50	8,2125	8,2812	0,0687
4	180	50	8,4109	8,6597	0,2488
5	200	50	8,2988	8,4119	0,1131
6	220	50	8,165	8,2898	0,1248
7	250	50	8,3707	8,487	0,1163
8	280	50	8,278	8,3868	0,1088
9	310	50	8,3339	8,4711	0,1372
10	340	50	8,2555	8,3831	0,1276
11	370	50	8,3785	8,4726	0,0941
12	400	50	8,2512	8,3336	0,0824
13	430	50	8,3268	8,3644	0,0376

Experiment no 8

Tube no	Pressure	Vessel temp	Oil displaced	Wt of test tube	Wt with oil displaced
1	100	60	0,0058	8,3342	8,34
2	160	60	0,0566	8,2094	8,266
3	180	60	0,1308	8,3198	8,4506
4	200	60	0,1878	8,2117	8,3995
5	220	60	0,2757	8,3444	8,6201
6	280	60	0,1553	8,3453	8,5006
7	340	60	0,1858	8,3177	8,5035

Experiment no 9

Tube no	Pressure	Vessel templ	Wt of empty test tube(gm)	Wt of sample test tube(gm)	Oil displaced (gm)
1	100	60	11,626	11,6335	0,0075
2	160	60	8,3364	8,4215	0,0851
3	180	60	8,3402	8,735	0,3948
4	200	60	8,427	8,5725	0,1455
5	220	60	8,3038	8,5205	0,2167
6	280	60	8,3387	8,4975	0,1588
7	340	60	8,3384	8,4907	0,1523

Appendix C