

STUDY THE EFFECT OF INJECTION TEMPERATURE ON LIQUID CO₂ FLOODING.

By

GOH HOCK KIONG

FINAL PROJECT REPORT

Submitted to the Chemical Engineering Programme
in Partial Fulfillment of the Requirements
for the Degree
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved:



Mr M. Sanif bin Maulut

UNIVERSITI TEKNOLOGI PETRONAS
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June 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

 03/06/09

GOH HOCK KIONG

ABSTRACT

Injection of gas carbon dioxide is widely applied in enhance oil recovery method. This injection will normally utilized characteristic of supercritical fluid of carbon dioxide to achieve higher recovery of crude oil by displacing the crude oil to the producing well. It also reduce the viscosity of crude oil whilst enable the crude oil to flow easily to the producing well. However, the sweep efficiency of gas carbon dioxide to displace the residual oil is low due viscous fingering. Carbon dioxide flooding usually requires an operating condition of more Minimum Miscibility Pressure (MMP) to achieve a good displacement of residual oil from injection well to production well. Besides, most of the application of gas carbon dioxide injection is combine with other fluids injection such as water alternating gas (WAG), simultaneous water alternating gas (SWAG) and surfactant alternating gas (SAG). This combination of fluids injection will increase the sweep of residual oil in the reservoir and hence increase the tertiary recovery. Therefore, this study will focus on the alternative way to increase the displacement on the residual oil from the injection well to the producing well. Hence, application of injection of liquid carbon dioxide will be used to recover the residual oil. Liquid carbon dioxide will sweep the residual oil in the reservoir especially near the injection well before it vaporizes. The presence of liquid carbon dioxide displacement will help to reduce the viscous fingering due to the gas of carbon dioxide and increase the sweep efficiency. The characteristic of liquid carbon dioxide that diffuse into crude oil will reduce the viscosity of crude oil. Besides, it will reduce the interfacial tension between the carbon dioxide and the crude oil. Hence, allow crude oil to flow easily to production well. The vaporisation of liquid carbon dioxide also will help to displace the crude oil and help to carry the light component of hydrocarbon during the mass exchange. All this had contributed to the effectiveness of displacing crude oil with liquid carbon dioxide. Study on the phase behaviour of carbon dioxide with the help of carbon dioxide phase diagram need to be done to ensure the temperature of injection liquid carbon dioxide below the bubble point of carbon dioxide at desire injection pressure. The effectiveness of liquid carbon dioxide injection to increase the recovery has to be done through the experiment. Therefore, liquid carbon dioxide flooding will be done using the relative permeability system (RPS). Berea core and mineral oil has been used in this

experiment. Liquid carbon dioxide injection temperature was at ambient temperature 25 °C at injection pressure of 950psi.

From the experiment, it's found that the percentage recovery of residual mineral oil was at 20.8 % of OOIP of the berea core. This shows a significant increase in the residual oil recovery compare to the literature review of four field implementation of WAG in the reservoir can only yield the highest recovery of 17 % of OOIP. On the other hand, the temperature of injection of liquid carbon dioxide has been varied for the same injection pressure. This will help us to observe the effect of injected fluid(liquid carbon dioxide) temperature in the liquid carbon dioxide flooding. The heat of vaporization of liquid carbon dioxide increases with the decreases in the temperature. Therefore, this will lead to the increase of time require for liquid carbon dioxide to vaporized. Consequently, presence of liquid carbon dioxide to displace the residual oil in the reservoir will increase before the carbon dioxide vaporizes. Nevertheless, the validity of this principle need to be verify through the experiment. In this experiment, the injection temperature of liquid carbon dioxide has been reduce to 20 °C, 15 °C and 5 °C. It's found that the recovery of residual oil do increase from 20.8 % of OOIP at ambient temperature of liquid carbon dioxide injection to 26.1 % of OOIP at injection temperature of 5 °C. This proved that reducing the injection temperature of liquid carbon dioxide do help increase the displacement efficiency of residual oil hence increase the recovery.

In conclusion, performance of liquid carbon dioxide injection in enhance oil recovery is proven to be effective and tertiary recovery inversely proportional with the liquid carbon dioxide injection temperature.

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LIST OF ABBREVIATIONS

BOPD	- Barrel Oil Per Day
CO ₂	- Carbon Dioxide
EOR	- Enhance Oil Recovery
EUR	- Estimated Ultimate Recovery
OOIP	- Original Oil In Place
ROIP	- Residual Oil In Place
RPS	- Relative Permeability System
SAP	- Surfactant Alternating Polymer
SWAG	- Simultaneous Water Alternating Gas
WAG	- Water Alternating Gas

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The life of an oil well goes through three distinct phases where various techniques are employed to maintain crude oil production at maximum levels. The primary importance of these techniques is to force oil from the reservoir into the production well where it can be pumped to the surface. Primary recovery methods which use the natural pressure of the reservoir or the gravity, drive oil into the wellbore together with artificial lift technique such as pumps brings out about 10-20% of the original oil in place of a reservoir. To further extend the production life of a well, enhance oil recovery is applied. Injection of CO₂ is one of the few tertiary oil recovery techniques that have been practiced to increase the ultimate recovery of oil in the well. The initial practice of CO₂ in oil recovery dates back to 1952 when Whorton and Brownscombe received a patent for an oil recovery method using carbon dioxide ^[16]. There are three stages in oilfield development:

i. Primary Recovery

Oil is forced out by pressure generated from gas present in the oil. Basically this is due to the pressure different between the well bore pressure and the reservoir pressure.

ii. Secondary Recovery.

The reservoir is subjected to water flooding or gas injection to maintain a pressure that continues to move oil to the surface.

iii. Tertiary Recovery

Also known as Enhanced Oil Recovery (EOR), introduces fluids that reduce viscosity and improve flow. These fluids could consist of gases that are miscible with oil (typically carbon dioxide), steam, air or oxygen, polymer solutions, gels, surfactant-polymer formulations, alkaline-surfactant-polymer formulations, or microorganism formulations.

Carbon dioxide flooding is considered to be one of the fastest growing method in enhance oil recovery. The flooding process can occur in miscible and immiscible way to displace the residual oil in the reservoir after the water flooding. Methodology of how carbon dioxide can help to displace the residual oil will discuss further in this report.

1.2 PROBLEM STATEMENT

Carbon dioxide flooding has low sweep efficiency and hence leads to low tertiary recovery. In order to increase the recovery, the combination of other fluids with carbon dioxide has been applied in the field such as water alternating gas (WAG), simultaneous water alternating gas (SWAG) and surfactant alternating gas (SAG). Consequently, this will help to achieve a good displacement of residual oil from injection well to production well. Besides, Carbon dioxide flooding usually requires an operating condition of more Minimum Miscibility Pressure (MMP) to achieve a good displacement of residual oil from injection well to production well. In order to achieve this good displacement of residual oil from injection well to production well, the alternative way is to inject liquid carbon dioxide to displace the residual oil and also supported by the vaporisation of carbon dioxide to push the residual oil to production well. Knowing the recovery of the liquid carbon dioxide flooding, the viability of the process can be assessed.

1.3 OBJECTIVES

- i. To evaluate the performance of liquid CO₂ injection in enhancing oil recovery.
- ii. To study the effect of injection temperature on the improvement of sweep efficiency

CHAPTER 2

LITERATURE REVIEW

2.1 TYPES OF OIL RECOVERY TECHNIQUES

Recovery of oil from a reservoir can be divided into 3 phases. They are the primary, secondary and tertiary oil recovery phase as seen in the Figure 1.

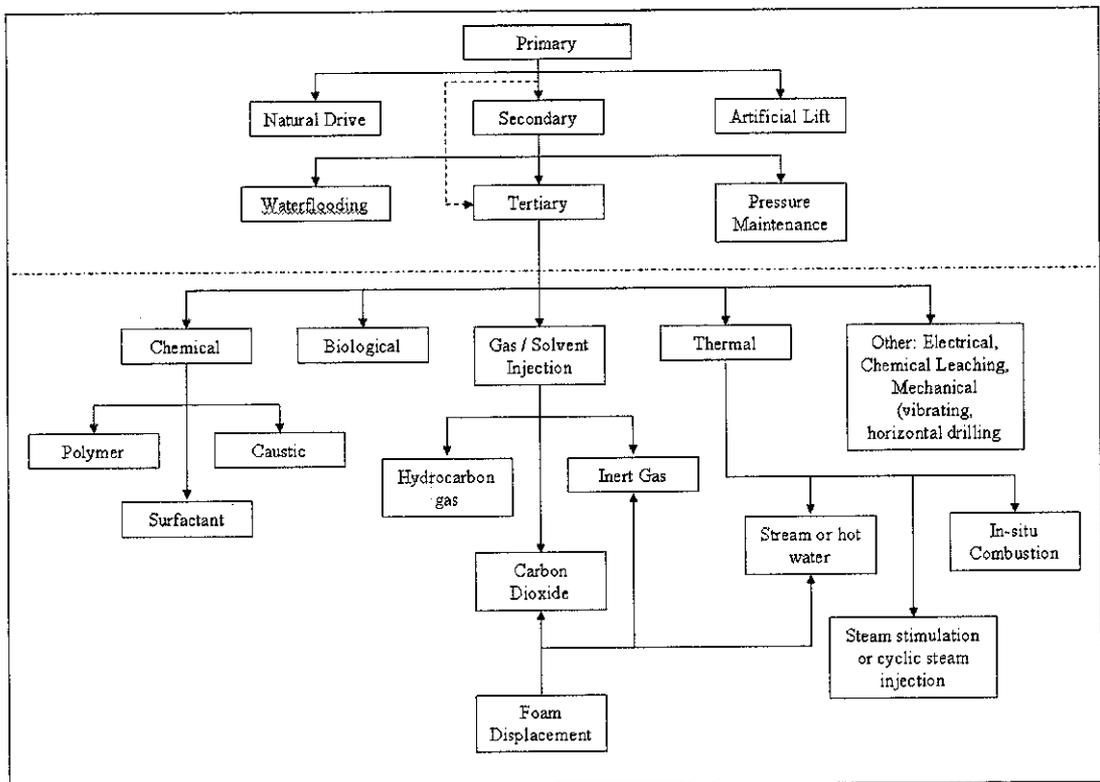


Figure 1 Oil recovery mechanism tree

Traditional primary recovery methods which use the natural pressure of the reservoir or the gravity drive oil into the wellbore together with artificial lift technique such as pumps brings out about 10-20% of the original oil in place of a reservoir. During the primary phase, reservoirs produce oil naturally due to the existence of higher pressure in the rock pores than at the bottom of the well. Natural production depends very much on the reservoir's internal energy. As oil is extracted from the reservoir, the pressure in the reservoir decreases causing the natural pressure of the reservoir to become insufficient to push the oil out of the well. Production will continue till it comes to a stage of depletion when the production rates become uneconomic. Production rates become uneconomic when cost of oil production is higher than the market price of the oil.

To further extend the production life of a well, secondary recovery phase which involves repressurizing the reservoir to drive out some of the residual oil from the primary recovery is conducted. Secondary recovery usually involves the usage of water or natural gas as an artificial drive to increase the pressure of the reservoir to drive out the residual oil. The oldest secondary oil recovery method is waterflooding as water is usually readily available and relatively less expensive. Water is pumped into the reservoir through injection wells and is forced through the rock pores sweeping the oil ahead of it towards the production well. The application of waterflooding is usually practical for recovering light to medium crude. As time passes, the percent of water being produced or water cut increases. When the cost of removing and disposing of the water exceeds the income from oil production, the secondary recovery is halted.

Injection of hydrocarbon gas or natural gas into the existing gas cap of the reservoir is another means of secondary oil recovery. The gas may be injected into the reservoir for a considerable period of time while the producing wells are shut in until the reservoir pressure is restored. Once the well is sufficiently repressurized, production is resumed. Another method is by injecting the gas as production is carried out to sustain the pressure of the reservoir. Injection of gas however requires a nearby source of inexpensive gas in sufficient volume or at times the produced natural gas is reinjected into the reservoir.

The primary and secondary recovery phase typically recover only around one third of the oil in place with the remaining two third of the oil in place left behind. Throughout the life span of a well, there will come a time where the cost of production for a barrel of oil is higher than the price the market would pay for that barrel. When such a time occurs, production of oil is halted. In the olden days, wells are abandoned with 70% of oil remaining in the ground.

With the advancement of technology, tertiary oil recovery which is also known as enhanced oil recovery (EOR) is employed to further extract oil from the reservoir thus increase ultimate oil recovery in a reservoir in a relatively more economical manner. EOR is vastly applied by many oil producing nations especially nations with reserves in the aging oil fields which are declining faster than the discovery of new oil reserves such as US and Canada ^[17]. Given declining reserves and the low probability of locating significant new oil fields, producers sought additional oil from the old reservoirs. Many techniques have been tested both in lab and in the field in hope to recover more oil. Some of the basic mechanisms employed by these techniques are:

- i. Extract oil with a solvent
- ii. Reduce interfacial tension between water and oil
- iii. increase the mobility of the displacement medium

Three of the commercially successful tertiary oil recovery are thermal recovery which involves the use of heat, chemical recovery which involves the use of polymer or surfactant and finally gas injection which uses gases such as nitrogen or carbon dioxide.

2.1.1 Thermal

Thermal methods of enhance oil recovery are the main means of recovering heavy crude oil with gravity less than 20° API, representing viscosities of 200 to 2000 centipoise (cp). Such heavy oils usually does not yield significant recovery from primary production or waterflooding thus the initial oil saturation is typically high at the initial stage of thermal recovery project ^[17]. The principle to this recovery method is to increase the temperature of the oil which in turn dramatically reduces the viscosity thus improving the mobility ratio. Two main strategies in thermal oil recovery are through injection of fluid heated at the surface (steam) or through heat production directly within the reservoir by combusting some of the oil in place.

Though the idea of heating reservoir was conceived 100 years ago, large steam drive projects began in heavy oil fields in US in the early 1950s and were followed shortly by projects in the Netherlands and Venezuela. In 1960, cyclic steam injection, also known as steam soak or “huff and puff” was discovered accidentally during a Venezuelan recovery project. Cyclic steam injection uses a single well for both injection and production. This recovery method involves the injection of steam into the well for a period of time (a few days to a few weeks) and then the well is shut in for several days to a month. This period of time is known as the soak period. After this the well is open for production for up to 6 months and then the whole process is repeated. The steam injected heats the rock and fluids surrounding the wellbore and simultaneously provides some drive pressure. As production resumes the steam has condensed and oil and water are produced.

The disadvantage of this huff and puff method is that only the reservoir near the wellbore is stimulated hence the process is often followed by continuous steam injection to drive oil toward a separate production well. Reservoir pressure as determined by the depth constraints the steamflooding process. The higher the pressure the reservoir is, the more fuel is required to generate higher temperatures on the surface such that the saturated steam required for efficient steamflood is attained. Higher temperature also leads to greater heat losses.

Apart from viscosity reduction, steam distillation of lighter component of the oil which forms a solvent bank ahead of the steam is another important recovery mechanism. Other factors affecting the flood displacement efficiency are thermal expansion, solution gas drive and miscible and emulsion drive.

Thermal recovery may face complications when a combination of numerous technical problems which may cause the project to be uneconomical, inefficient or even dangerous. Heat losses in various areas such as wellbore, rocks around the reservoir, connate water and gas cap may defeat the process. Surface equipments as well as the downhole tubing below 1500ft have to be insulated. Thermal expansion may damage the downhole equipment and cause cement failure. As steam is very reactive, pipe corrosion and scaling, mineralogical dissolution or reprecipitation, clay swelling and changes in permeability may be caused. Furthermore the higher mobility of steam as compared to oil overrides the oil and channeling through the thief zone. The high cost of air pollution byproduct control is also one of the concerns.

In-situ combustion, also known as fireflooding is a different means of thermal recovery, burning a portion of the crude oil by injecting air or oxygen. Compressed air is injected into a high gravity and high pressure reservoir with the expectation that the oxygen within the air will react with the fraction of reservoir oil at elevated temperature to produce CO₂. The resulting flue gas mixture provides mobilization force to the oil downstream of the reaction region, weeping it to the production wells. Being thermally more efficient than steam, fireflooding is a more popular thermal recovery technique as it has no depth restriction and is well suited to relatively thin reservoir sand. In practice however it is not that simple as it incurs an exorbitant price, and the process is extremely complicated and difficult to predict or control.

2.1.2 Chemical

Chemical oil recovery methods enhance oil recovery through the application of chemicals such as polymers, surfactants and alkalis. These substances are mixed with water or some other chemicals prior to injection.

One of the most commonly used chemical enhancement process is polymer flooding usually accompanied by waterflooding. This is due to its application simplicity and relatively low investment cost. Though polymer flooding increases recovery by about 5%, it can yield solid profits under the right circumstances. Viscosity of water is increased improving its mobility ratio through the addition of high molecular weight polymers. Some polymers are capable of reducing the aqueous phase permeability without changing the relative permeability of the oil which can greatly improve the waterflood volumetric sweep efficiency. Polymer concentration are 100 to 1000 parts per million (ppm) and treatment may require injection of 15 to 25% PV over several years followed by waterflooding. Polymers when gelled or crosslinked with metallic ions can improve the performance in sweep profile control. This is done by plugging the high conductivity zones or minor fractures that degrade the sweep efficiency. Some of the main setbacks of polymer flooding are the low injection rate due to the degradation in viscosity at high temperatures, intolerance to salinity, polymer deterioration from shear stress caused by pumping, flow through tubulars and perforations and long term instability in the reservoir environment.

Another form of chemical is surfactant flooding. This mode of flooding is also known as the detergent flooding, micellar polymer or microemulsion flooding. Low concentration of surfactants in water is used to reduce interfacial tension between oil and water. Though the idea of surfactant flooding dates back to the 1920s, serious research and field trials were not initiated until 1970s. Surfactant flooding might be one of the riskiest EOR methods as it involves the most difficult design decisions, requiring large capital investments and is greatly affected by reservoir heterogeneities. A surfactant flood must be designed for specific crude oil in a specific reservoir taking into account factors such as salinity, temperature, pressure and clay content ^[18]. Generally surfactant flooding is carried out in multiple slugs.

Surfactant performance is optimal over a narrow range of salinity and is subject to adsorption and retention through ionic exchange with reservoir rocks. To overcome the situation, the first slug may be a preflush water solution. Second of around 10 to 30% PV contains surface active agent, hydrocarbons, electrolyte and cosolvent, usually alcohol. This is followed by a slug of polymer-thickened water for mobility control and finally waterflood ^[17].

2.1.3 Gas or Solvent Injection

One of the fastest growing EOR process is through gas or solvent injection. This process involves injection of solvents such as liquefied petroleum gas (LPG), nitrogen, carbon dioxide (CO₂), flue gas (mainly nitrogen and CO₂), alcohol and natural gas.

The objective of solvent injection is to fully mix with the residual oil to overcome capillary forces and at the same time increase oil mobility. The displacement that occurs from the injection of gas or solvents can be miscible or immiscible. A miscible displacement occurs when the injected gas or solvent forms a single phase solution with oil when in contact with oil. Miscibility is only possible when the minimum miscible pressure (MMP) which is the minimum pressure for miscibility to occur is attained. Immiscible displacement occurs when solvent do not form a single phase with oil as it has not attained the MMP.

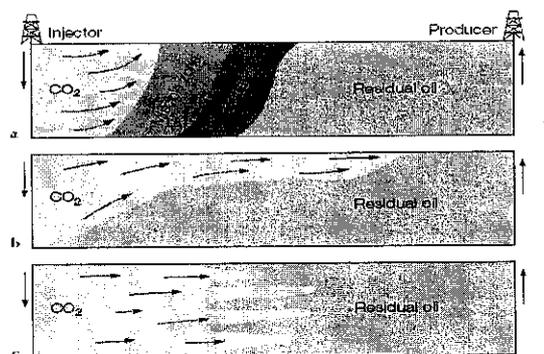


Figure 2 Phase behavior and flow dynamic in miscible flooding.(a) for ideal performance, (b) during the influence of fluid density,(c) in setting of viscosity contract which produces viscous fingering^[17]

A major problem with miscible gas flood is the adverse mobility ratio caused by the low viscosity of the injected gas relative to oil. The adversity in mobility ratio results in unstable flood front between the gas and oil allowing viscous fingering to form and to propagate through the oil, leaving much of the hydrocarbon uncontacted. To mitigate the occurrence of viscous fingering, water alternate gas (WAG) technique was introduced. In WAG, water and gas are injected into the well alternately with the design parameters being the timing and the water to gas ratio. Through WAG, mobility of gas is greatly reduce by the introduction of water. However, gravity segregation is said to compromise on the effectiveness of the WAG process. The performance of most of the EOR techniques experience adverse mobility complications between the oil and the injected substance. One of the remedy to this problem is by dispersing the gas bubbles in liquid creating foam. Foam is capable of reducing the reservoir gas permeability to less than 1% of its original value ^[17]. Foams are being tested by industry to improve the vertical and areal sweep of efficiency of CO₂ injection projects. Foams has been applied in to improve the mobility ratio between the CO₂ and reservoir crude. Foam tests have been conducted at SACROC, Rangely, Wartz and Seminole. Considering the magnitude of the potential for increasing recovery it is likely that the industry will continue to work on developing effective foams for use in CO₂ injection projects ^[5]. Some of the problems encountered include rapid changes in foam stability and quality as it migrates away from the injection well, abnormal high injector-to-producer pressure differentials required for propagation and foam breakdown in small pores.

2.2 FIELD TEST ON CARBON DIOXIDE FLOODING

About 80 field trials of CO₂ flooding have undertaken (Leonard,1986). About 30 of this field were done in immiscible way. The CO₂ flooding in immiscible way also improves the recovery though it's not as much as compare with miscible flooding. The two earliest project were not pilot project but were commercial project. These project started in 1972 in SACROC and Crossett^[5]. Below are the important parameter of reservoir and fluid properties of field ^[11].

Average porosity	: 9.41 %
Average permeability	: 3.03mD
Initial reservoir pressure	: 3122psi
Reservoir temperature	: 130 °F
Oil viscosity	: 0.35cP
Oil gravity	: 41 °API

The WAG ratio is 5:1 causes the ultimate incremental oil recovery of 7.5% of OOIP.

The project was successful and give high incremental in oil recovery. From that experienced, application of CO₂ flooding in EOR was done in oilfield. CO₂ flooding conducted at Slaughter Estate Unit in Slaughter field in West Texas (Adam and Rowe, 1981; Rowe el al.1981). The test was in San Andres carbonate. Enhance oil recovery attributable to CO₂ flooding was 14.9% of the original oil in place. The ultimate incremental recovery was projected to be 20% of the original oil in place^[5]. The test also conducted in Wasson Denver Unit in San Andres formation at depth 5100ft(Bremer,1982). The residual oil saturation was 40% after the waterflooding. CO₂ injected rate was 1.7-2.8Mcf/day. This was follow by injection of additional slug of 65000ppm chloride brine. The recovery was estimated 17% of original oil in place^[5]. Another example of CO₂ flooding done in the oil field was in the Little Creek Field in southern Mississippi at depth of 10750ft.

Reservoir parameters were:

Porosity	: 23.4%
Permeability	: 33mD
Initial oil saturation	: 44%
Residual oil saturation	: 21%
Reservoir temperature	: 248 °F
Oil gravity	: 39 °API
Oil viscosity at bubble point	: 0.3cP

The total pilot oil production was projected around 30-35% of original oil in place ^[5]. Therefore, the effectiveness of CO₂ flooding in recovering significant fraction of the oil left as residual after water flooding is being proven from all the fields that mentioned above. After that, CO₂ floods has been used successfully throughout several areas in the US, especially in the Permian Basin. Besides, 13% of OOIP being recovered from sandstone reservoir of Lost Soldier Tensleep field through the application of CO₂ (WAG) ^[12]. Below are recovery of oil from primary to tertiary recovery in Lost Soldier Tensleep field and its reservoir parameters^[12] :

Primary recovery	: 19.9 % of OOIP
Secondary recovery	: 24.4% of OOIP
Tertiary recovery CO ₂ (WAG)	: 13% of OOIP
Ultimate recovery	: 57.3 %
Permeability	: 31mD
Reservoir pressure	: 1600psi
Oil gravity	: 35 °API

Table 1 Summary of CO₂ flooding in the field

Field	% recovery of OOIP
SACROC	7.5
Slaughter	14.9
San Andres	17.0
Lost Soldier Tensleep	13

From the field test, it's proven that oil recovery responses to CO₂ injection occurred within six to eight months after start-up. It's also proven that when injection flow rate gradually increase, the production also will increase. For example at this field, the injection flow rate of gas CO₂ increase from 65 MMCFD to 90MMCFD causes the rise in oil production from 10000 BOPD to 11000BOPD.

Outside the US, CO₂ floods have been implemented in Canada, Hungary, Turkey, Trinidad and Brazil [6]. Besides, the simulation published by SPE 107163 shows that the injection of water and CO₂ in the form of WAG and SWAG process increase oil recovery to 60% of OOIP compare to 30% OOIP for pure water and CO₂ injection.

As of January 2005, the estimated oil-in-place from producing field in Malaysia stand at about 17 Bstb with estimated ultimate recovery(EUR) of 5.62 Bstb [7]. This translates to an average recovery factor of 33% for producing field in Malaysia. Petronas had realized the importance to further increase the recovery factor and so far has been pursuing EOR implementation in the field aggressively. To date,a full field review WAG application in Dulang field is already at its final stages of implementation. Reinjection of WAG which uses carbon dioxide gas at well B16 increase the pressure and reduce GOR and water cut. Oil rate increase from 105 BOPD to 300 BOPD [7].

Meanwhile, in Barunia RV2 reservoir, pilot feasibility was carried out using 2001 reservoir simulation model with the updated production pressure. Continuous, simultaneous and water-alternating-gas(WAG) injection was studied using this

composition model. Model predicted that immiscible gas injection with continue simultaneous water injection at 3200 psi (approximate reservoir pressure at the time of study) with 5 MMscf/day injection rate could yield 2.7 MMstb incremental recovery within 20 years. Current plan is to implement an observation well in this field. [7].

Therefore, base on the two field study in Malaysia, it show positive sign in increase uses of CO₂ in EOR process. The graph in figure 5 in the appendix show expected incremental oil reserve from EOR process in Malaysia.

2.3 CARBON DIOXIDE FLUID PROPERTIES

Carbon dioxide is effective in improving oil recovery for two reasons : density and viscosity. At high pressure, carbon dioxide forms a phase whose density is close to that of a liquid, even though its viscosity remains quite low. Under miscible condition, the specific gravity of this dense carbon dioxide typically is 0.7 to 0.8 g/cm³, not much less than for oil and far above that of gas such as methane, which is about 0.1 g/cm³. Dense- phase carbon dioxide has the ability to extract hydrocarbon components from oil more easily than if it were in the gaseous phase. The viscosity of carbon dioxide under miscible condition (0.05 to 0.08cp) is significantly lower than that of fresh water (0.7cp) or oil (1 to 3cp) [1]. Although the low viscosity of the gas relative to the oil can be detrimental to sweep, carbon dioxide can improve recovery by reducing the oil viscosity

2.4 BEREA SANDSTONE

In this experiment, berea sandstone will be use as core which assimilate our reservoir rock. For over 25 years, the Petroleum Industry has been using Berea Sandstone as the sandstone test material of choice. The Berea Sandston has excellent, uniform material properties. Researchers throughout the world have performed thousands of core flooding tests using the Berea Sandstone to characterize the oil production in

other sandstone reservoirs during primary, secondary, and tertiary oil flooding. The chemical compositions of the Berea Sandstone are well known and are as follows:

Table 2 Chemical composition of the Berea Sandstone ^[13].

Silica	SiO ₂	93.13%
Alumina	Al ₂ O ₃	3.86%
Ferric Oxide	Fe ₂ O ₃	0.11%
Ferrous Oxide	FeO	0.54%
Magnesium Oxide	MgO	0.25%
Calcium Oxide	CaO	0.10%

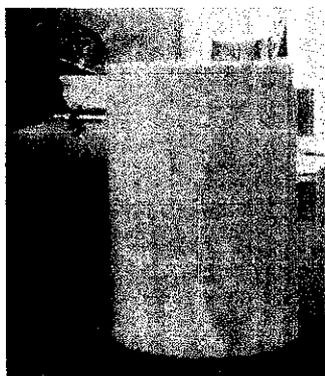


Figure 3 Berea sandstone

2.5 MINERAL OIL

Mineral oil or liquid petroleum is a by-product in the distillation of petroleum to produce gasoline and other petroleum based products from crude oil. It is a transparent, colourless oil composed mainly of alkanes (typically 15 to 40 carbons) and cyclic paraffin, related to white petroleum. It has a density of around 0.8 g/cm³ and viscosity of around 3cp ^[15]. In this experiment, the product of mineral oil is bought from Sigma- Aldrich and the material safety datasheet is attached in the appendix.

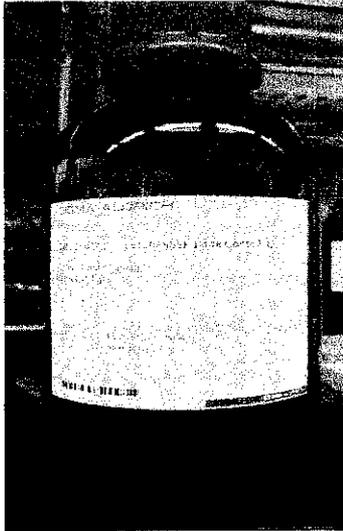


Figure 4 Mineral oil

2.6 BRINE

The brine will be used to saturate the core to assimilate salinity of Iraqi oil reservoir. Below are the compositions of brine:

Table 3 Brine Composition ^[9]

Component	Concentration (g/L)
Calcium Chloride (CaCl ₂)	0.5
Sodium Chloride (NaCl)	8
Magnesium Chloride (MgCl ₂)	0.6
Potassium Chloride (KCl)	0.4

2.7 TECHNICAL SCREENING GUIDE

Table 4 Technical Screening Guide for carbon Dioxide Flooding ^[1]

TECHNICAL SCREENING GUIDE	
Crude Oil	
Gravity	>26°API (preferably >30°)
Viscosity	<<15CP (preferably <10CP)
Composition	High percentage of intermediate hydrocarbons (C ₅ -C ₁₂) especially C ₅ – C ₁₂
Reservoir	
Oil saturation	>30%PV
Type of formation	Sandstone or carbonate with minimum fracture and high permeability streak
Net thickness	Relatively thin unless formation is steeply dipping
Average permeability	Not critical if sufficient injection rates can be maintained
Depth	Deep enough to allow high enough pressure (>about 2000ft) pressure required for optimum production (minimum miscibility pressure, MMP) ranges from about 1200 psi for high gravity (>30°API) crude at low temperature to over 4500psi for heavy crude at higher temperature
Temperature	Not critical but pressure required increases with temperature

2.7.1 Factor Affecting the Macroscopic Displacement Efficiency

i) Reservoir characteristics

a) Average Depth

The average depth of the reservoir has important influence on both the technical and economical aspects of an enhanced oil recovery. Technically, a shallow reservoir creates restraint on the injection pressure as it has to be ensured that the pressure exerted on the reservoir is less than fracture pressure. Economically, the cost of oil recovery is directly proportional to the depth. This is because as the depth of the reservoir increases, the compressor power to run the drill will require higher power.

b) Dip

This characteristic applies more for immiscible flooding rather than miscible flooding. The recovery of hydrocarbon from a porous medium is greater when gravity plays a part than when it does not. Gravitational forces are truly effective in reservoirs containing highly permeable sands in which the dip is unusually large. For horizontal beds, the critical velocity is zero, injected water will form tongue at the base of the bed and the injected gas will form an umbrella at the top of the bed. These phenomena cause rapid breakthrough of the injected fluid at the production well.

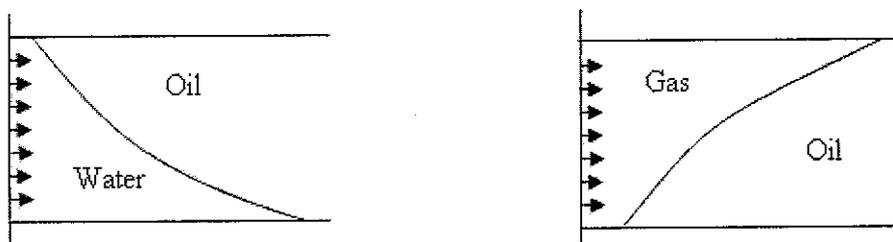


Figure 5 Tongues by water and umbrella formed by gas

c) Homogeneity

To achieve high recovery there should be no impediment to fluid flow within the reservoir. Probable impediments encountered may be of tectonic or stratigraphic nature of the reservoir such as faults and unconformities. In faulted and fissured reservoirs and those with high permeability streaks, channelling allows the displacing fluid to bypass some of the oil in place and leads to a low recovery factor.

d) Petrophysical Properties

The petrophysical properties include porosity, permeability, relative permeability, capillary pressure and the wettability properties of the reservoir. Porosity is the percent volume of the rock that is a pore space. The formulation for porosity is given as the ratio of the void volume over the void space. The higher the porosity and the higher the residual oil saturation at the end of the natural recovery phase, the more attractive the enhanced oil recovery will become. Permeability is a property which denotes the flow ability within the reservoir rocks. It dictates how well the pores in the reservoir rocks are connected. Generally high permeability is good. Very low permeability reduce the effectiveness of both water and CO₂ floods due to low injectivity. However, the higher the permeability, the greater the chance that the natural recovery will be so high that any enhanced oil recovery would be uneconomic. At the same time, very thick high permeability reservoir especially those highly vertically fractured reservoir would present CO₂ migration and low sweep efficiency problem due to gravity segregation ^[2]. The permeability distribution depends highly on the degree of homogeneity within the reservoir. The capillary effects on recovery efficiency depend on the rate of production. Occasionally, it is beneficial as it helps maintain a uniform front between two immiscible fluids in a heterogeneous porous medium. However, it is often detrimental as it traps oil within the pores.

2.7.2 Factor Affecting the Microscopic Displacement Efficiency

i) Fluid Properties

The fluid properties of the reservoir oil and the injected carbon dioxide play an important role in governing the phase behavior of the system. The lower the viscosity of the fluid and the decrease of the interfacial tension between the displacing fluid and the displaced fluid increase the capillary number and decrease the residual oil saturation, hence increasing the microscopic displacement efficiency.

ii) Saturation History of a Rock-Fluid System

The initial oil saturation before the carbon dioxide flooding takes place depends on whether the oil recovery by carbon dioxide is a secondary or a tertiary oil recovery. If prior to the carbon dioxide flooding, waterflooding has been implemented, the presence of the additional water saturation would result in a tendency to bypass oil at the microscopic level.

iii) Solvent Flow Rate and Residence Time

Molecular diffusion plays a vital role in residual oil recovery on the micro or pore scale. Diffusion path lengths in porous media vary widely in a range of values and depend on factors such as pore geometry, microscopic and macroscopic heterogeneities, fluid properties and rock wettability. The amount of time in which the carbon dioxide has been moving through the reservoir is known as the residence time. Large residence time allows the diffusion between carbon dioxide and oil to interact effectively. Improved microscopic displacement efficiency at lower solvent flow rates or with a longer residence time is attributed to the diffusion of the solvent to otherwise unrecoverable oil which is subsequently recovered by stripping or swelling. In addition to that large scale bypassing resulting over time resulted from gravity segregation as well as from reservoir stratification and unfavorable mobility ratios affect microscopic displacement efficiency.

2.7.3 Advantages of CO₂ Flooding EOR

The greatest difference compared to other gases is that CO₂ can extract heavier components up to C₃₀. The solubility of CO₂ in hydrocarbon oil causes the oil to swell. CO₂ expands oil to a greater extent than methane does. The swelling depends on the amount of methane in the oil. Because the CO₂ does not displace all of the methane when it contacts a reservoir fluid, the more methane there is in the oil, the less is the swelling of oil. CO₂ has the following characteristics in a flood process:

- It promotes swelling. CO₂ will soluble in the crude oil. Hence, the crude oil will increase in volume (expand).
- It reduces oil viscosity. Miscibility of CO₂ (low viscosity) with crude oil cause the reduction in crude oil viscosity. This phenomenon enables the crude oil flow more easily because the dissolution of CO₂ in the crude oil reduces the interfacial force between the crude oil molecules.
- It reduces oil density. Since the natural gas is heavier or denser than CO₂ then CO₂ later will displace the former that is dissolve in the crude oil, thus reducing the crude oil density.
- It can vaporize and extract portions of the oil. Upon reaching the reservoir, CO₂ will vaporize and extract the portion of the light crude (C₄-C₁₀), due to its low boiling point.
- It achieves miscibility at pressures of only 100 to 300 bar. This criterion is important in achieving the Minimum Miscibility Pressure (MMP). This is because the effectiveness of CO₂ or any other gas for EOR is dependant on achieving MMP to ensure the gas function effectively.

2.7.4 Drawback of CO₂ Flooding

Early breakthrough of CO₂ causes several problems:

- ✓ Corrosion in the producing wells

Due to the nature of CO₂ is a corrosive material when combine with water, there was uncertainty regarding the severity of corrosion. Experience indicates that corrosion has not been a severe problem

mainly because of the preventative measures taken by industry. This are such as use of corrosion inhibitors, steel wellhead and fiber glass gathering system.

✓ Production problems

The most severe production problem experience to date has been the plugging of the tubing strings by asphaltines deposition. There are also have been some problems with rod pumps gas locking and electrical submersible pump cycling when large amounts of CO₂ break through have occurred. Overall production problems have not been a major factor and have been minimized by an active well monitoring program.

The early breakthrough of CO₂ is a major concern. Majority of oil being recovered after breakthrough. This is due to the poor mobility ratio between carbon dioxide and oil with the resulting frontal instabilities further with impaired heterogeneity of reservoir such as fractures, channel or high permeability streaks. Therefore, substantial amount of oil is bypassed by the injected fluid (CO₂) due to reservoir heterogeneities, fractures and permeability variations. This lead to poor volumetric sweep efficiency. Sometimes, the injected CO₂ flow to the path of high permeability zones and brought the gas CO₂ to the surface of well before incremental of oil recovery occurred(early breakthrough). Besides, the displacement of oil in the reservoir is unstable because of viscosity of displacing fluid(CO₂ gas) is less than the viscosity of displaced fluid (oil). As a result, viscous fingering occurred.

Different techniques have been investigated for improving the overall efficiency of CO₂ flooding process. Most of these methods attempt made to improve the mobility ratio between CO₂ and oil by either affecting the relative permeability of CO₂ or increasing the viscosity of CO₂. Example of the method are : water alternating gas(WAG),simultaneous water/gas injection(SWAG),surfactant alternating gas(SAG),gel placement and viscosified CO₂ process. Nevertheless, these method s also do pose significant effects in reducing the efficiency of CO₂ recovery because the dynamic miscibility zone is destroy whenever others fluid is injected with CO₂.

CHAPTER 3

PROJECT WORK SCOPE

3.1 THEORY OF LIQUID CARBON DIOXIDE DISPLACEMENT

Injection of liquid CO₂ will displaced the crude oil from the pores of the rocks. There are two mechanisms that help liquid CO₂ displaced the crude oil in the reservoir rock. The liquid CO₂ come in contact with crude oil, sufficient quantity of liquid CO₂ contacted with crude oil will help liquid CO₂ to push the crude oil from the pores of the rocks (piston-like displacement). This is due to the pressure difference nearby injection well with the reservoir pressure. On the other hand, CO₂ will diffuse into the crude oil when it comes in contact with the crude oil. Therefore, the interfacial tension between CO₂ and crude oil also decrease. On the other hand, the diffusion of CO₂ into oil will cause the crude oil to swell. Consequently, the volume of the crude oil will increase and hence reduce the density of the crude. This occurred base on the density formulae :

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Due to the mass of the crude oil is constant and the increase of the volume of crude oil due to the swelling effect causes reduction in the density of crude oil.

The swelling factor increase with the increase in CO₂ content.

$$\text{Swelling factor} = \frac{\text{Volume of reservoir fluid} + \text{Dissolved CO}_2}{\text{Volume of reservoir fluid}}$$

Apart from the condition of crude oil swell, an inter-phase exchange of mass also take place between the two fluids. Initially, CO₂ diffuse in the crude oil, releasing dissolved gas as vapour phase (rich in methane and less viscous than reservoir fluid). This lean gas move forward more rapidly than CO₂ swollen reservoir fluid thus reducing the mobility ratio and give stable and increase the efficiency in recovery. The CO₂ saturated reservoir fluid is again contacted with fresh CO₂ and phase exchange of heavier hydrocarbon take place and this process occur repeatedly until no further vaporisation from resulting viscous reservoir fluid takes place.

On the other hand, the temperature of injection CO₂ fluid will give an impact on the recovery of the crude oil. There is always maximum temperature of CO₂ to ensure it's in liquid form at certain pressure. Therefore, lowering the injection temperature of CO₂ will cause longer liquid CO₂ contact with the crude oil and this will increase the time for the CO₂ liquid to vaporize. Consequently, this will increase the sweep efficiency of liquid CO₂. Nevertheless, the effectiveness of lowering down the injection temperature will be clarified or proved through the experiment.

In conclusion, the displacement of crude oil by using liquid CO₂ occurred in two ways that are the vaporisation of liquid CO₂ in the reservoir and through the pushing effect of liquid phase of CO₂ when liquid CO₂ in contact with the fluid at the reservoir (piston-like displacement). Varying the injection temperature of liquid CO₂ will affect percentage recovery of crude oil. Therefore, this will help to increase the sweep efficiency in enhance oil recovery.

3.2 METHODOLOGY OF LIQUID CARBON DIOXIDE EXPERIMENT

Flow chart of experiments to be conducted:

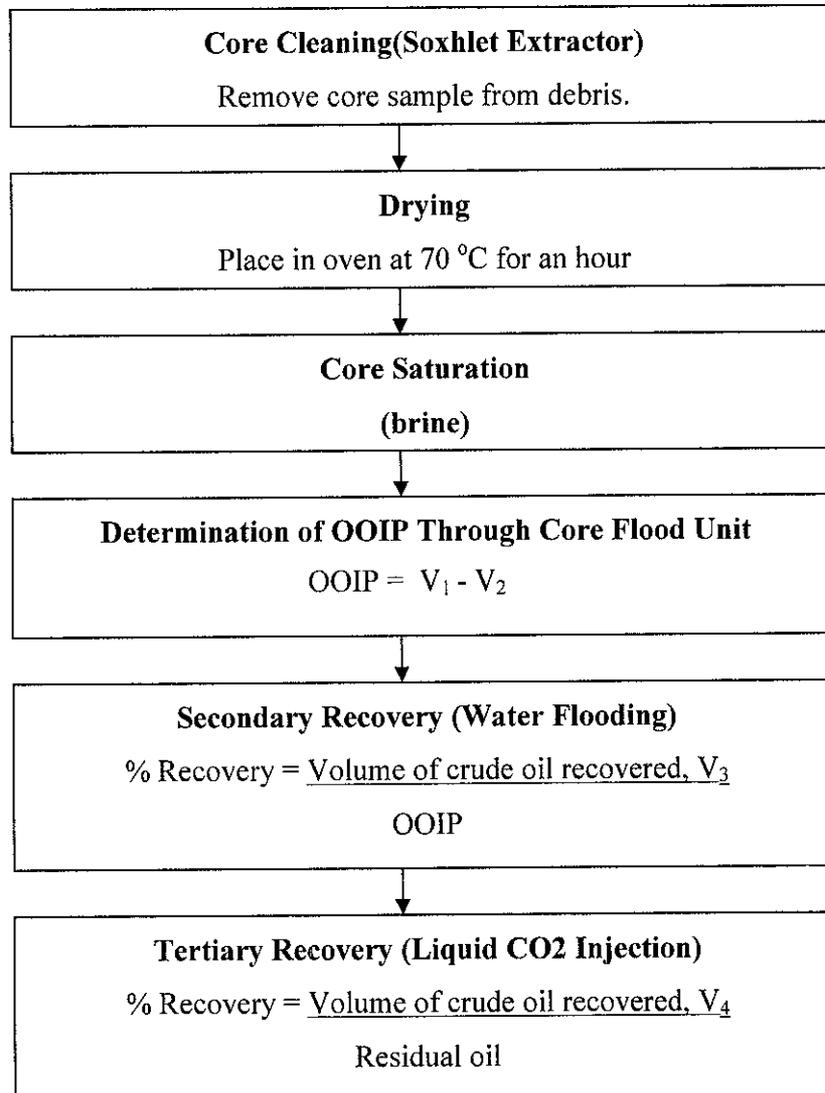


Table 5 Data for each parameter in the experiment

Parameter	Volume (mL)
Crude oil injection	V_1
Crude oil collected	V_2
Crude oil recover from water flood	V_3
Crude oil recover from CO ₂ injection	V_4

3.2.1 Core cleaning

The core samples need to be clean to remove all the debris and dust inside and also to clean the core sample from oil, water and any other materials. The cleaning process is done in the specific equipment namely Soxhlet Extractor. Using some solvent (Toluene), the core samples were left in the Soxhlet Extractor for about one day to fully removed the unnecessary particles inside the core samples.

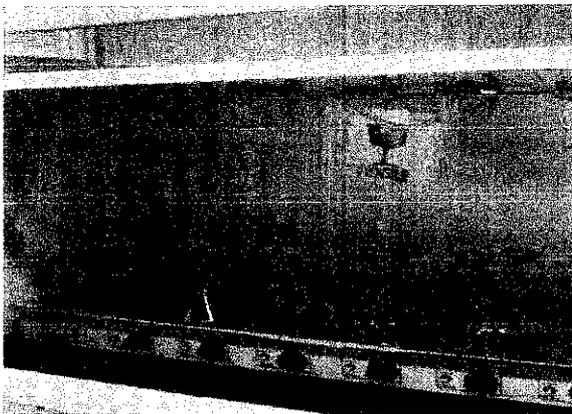


Figure 6 Mineral oil

3.2.2 Drying

The core has to be placed inside oven for drying purposes at 70°C for an hour. This drying is use to remove all the fluid that remain inside the pore of the core.

3.2.3 Core saturation

The berea core will be saturated with brine for at least six hours. This is to ensure all the pore spaces of the berea core have been fill with brine that represent the reservoir fluid composition.

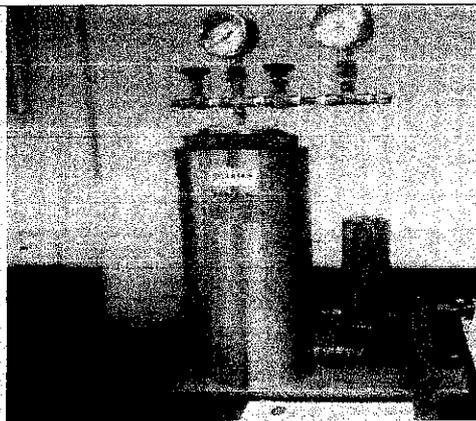


Figure 7 Manual saturator

3.2.4 Determination of OOIP Through Core Flood Unit

An amount of mineral oil will be injected into core in the Relative Permeability System(RPS). The Original Oil In Place (OOIP) is determine by deduction of the amount of fluid injected into core with the amount of fluid come out from the sample point.

OOIP = Volume of mineral oil injected, V_1 - Volume of mineral oil collected, V_2

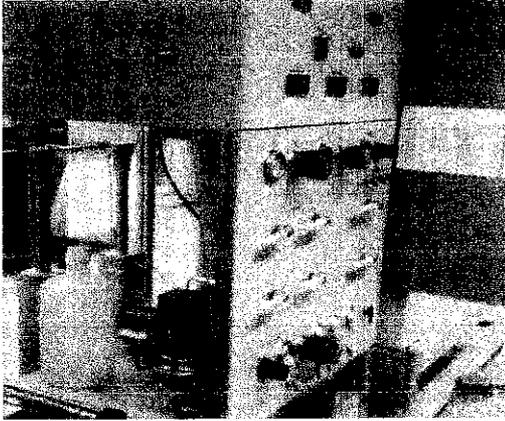


Figure 8 Relative Permeability System

3.2.5 Secondary recovery (water flooding)

Brine is used as fluid to displace the mineral oil from the core. Injection of brine is stop once there is no more crude oil come out from the sample point over a certain period of brine injection (only brine coming out). The percentage of secondary recovery can be calculated using formulae below:

$$\% \text{ Recovery} = \frac{\text{Volume of mineral oil recovered, } V_3}{\text{OOIP}}$$

3.2.6 Tertiary recovery (liquid CO₂ injection)

Gas CO₂ is transfer from CO₂ gas cylinder to accumulator 1. The gas will be compressed to pressure around 950psi to ensure the existence of liquid CO₂. The inlet pressure to core compartment will be adjusted to 950psi which is equal to the compressed gas CO₂ pressure. This will ensure the liquid CO₂ is injected into the core sample to recover the remaining oil inside the core. The condition for liquid CO₂ injection at 950psi is done base on the phase diagram on next page.

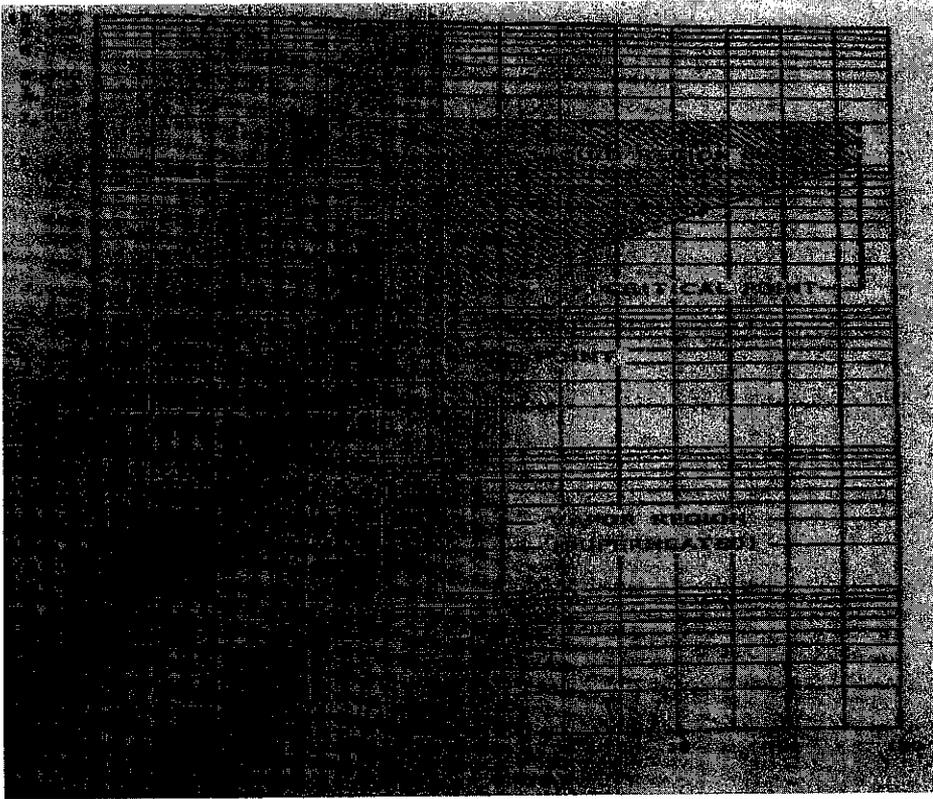


Figure 9 Carbon Dioxide Phase Diagram^[1]

At 950psi, the boiling point for CO₂ is 27°C. Booster pump will be used to pump the liquid CO₂ into core and the flow rate of liquid CO₂ flow into the core will be measure by flow meter in unit(ml/min). The flow rate will be set at 3ml/min for every fluids injection into the core. The flow rate of CO₂ can be control by using the valve at each outlet of accumulator. The recovery of mineral oil will be observed at the sample point. Small measuring cylinder will be use to collect the recovered mineral oil.

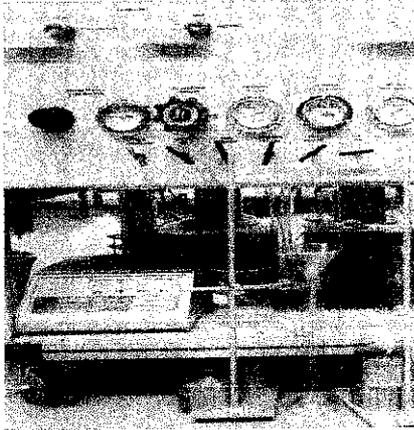


Figure 10 Sample point

For the case of varying injection temperature of liquid CO₂. The temperature of accumulator need to be cool down at interval of 5 °C from the boiling point of CO₂ at the same injection pressure condition. This can be done by placing the accumulator inside a cold basin by conditioning the water to desire temperature. The accumulator and the condition water will reach equilibrium over certain period of time. The temperature inside the accumulator is assumed to be the same as the temperature of the condition water. In the mean time, the core holder need to be heat up to the desire temperature to simulate the reservoir temperature. This can be done by placing the core holder into hot water bath basin for about 15 minutes to reach equilibrium. Once the liquid CO₂ has been compressed with the desire temperature, then proceed with the step of liquid CO₂ injection. Observe and measure the amount of recovered mineral oil at the sample point.

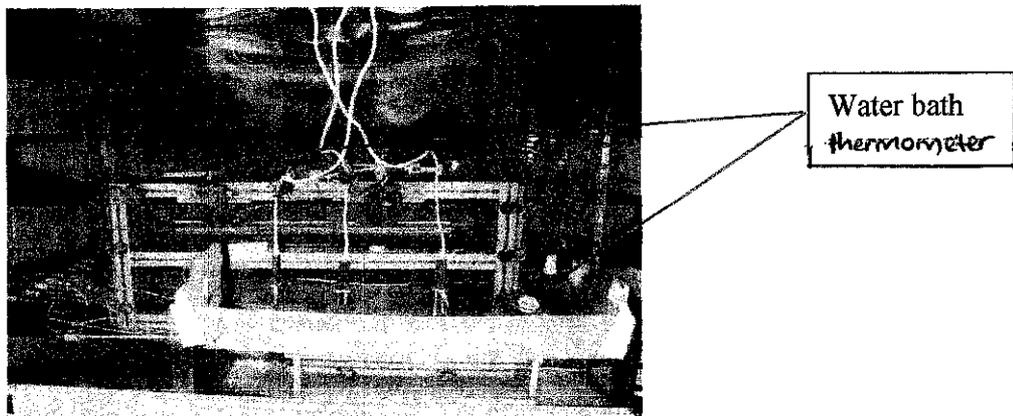


Figure 11 Hot and cold water bath.

The percentage of tertiary recovery can be calculated using formulae below.

$$\% \text{ Recovery} = \frac{\text{Volume of crude oil recovered, } V_4}{\text{Residual oil}}$$

Core Flood unit is shown in the schematic diagram below :

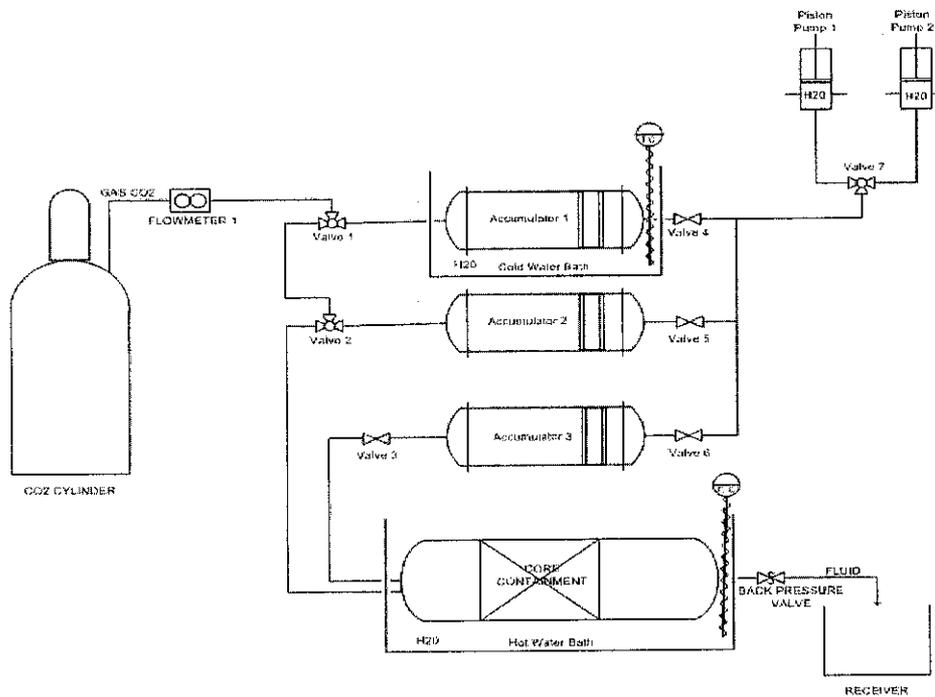


Figure 12 Schematic Diagram of Relative Permeability System(RPS)

Summary of steps of liquid CO₂ injection.

1. Condition the hot and cold water bath to the desired reservoir temperature and injection temperature consecutively. Hot water bath at 70 °C and cold water bath at 25 °C.
2. Transfer the gas CO₂ from CO₂ cylinder into accumulator 1.
3. Compress the gas CO₂ to pressure of 950psi to convert the phase of gas CO₂ into liquid CO₂.
4. Fill the accumulator 2 with mineral oil and accumulator 3 with brine.
5. Inject the brine into the core at flow rate of 3ml/min. This first injection is to determine the absolute permeability of Berea core. Stop the injection after an hour.
6. Inject the mineral oil at flow rate of 3ml/min into the core and calculate the OOIP of the core. Stop injection after an hour.
7. Inject the brine at flow rate of 3ml/min into the core and calculate the percentage of secondary recovery. Stop the injection when there is no more mineral oil recovered from the injection. At this time, core is ready for tertiary recovery.
8. Use the booster pump to pump the liquid CO₂ from accumulator to the core compartment. Set the flow rate of liquid CO₂ injection at 3ml/min.
9. Observe and collect the recovery of mineral oil at the sample point by using 50ml measuring cylinder.
10. Stop the injection when there is no more mineral oil recovered from the sample point. (Observe when there is no more fluid coming out from sample point after 20 minutes of injection since the last drop of fluid)
11. The collected sample of fluid in the measuring cylinder is allowed to settle for 12 hours for the complete separation of fluids (two layers of fluid because of the difference in density)
12. Tabulate the result of the experiment.
13. Repeat the above steps for difference in injection temperature of liquid CO₂ at 20 °C, 15 °C, 5 °C. This will enable us to quantify the relationship of the injection temperature of liquid CO₂ with the tertiary recovery.

CHAPTER 4

RESULT AND DISCUSSION

4.1 RESULT

Effective Core Porosity = 13.84%

Absolute Permeability = 205mD

Pore Volume = 26ml

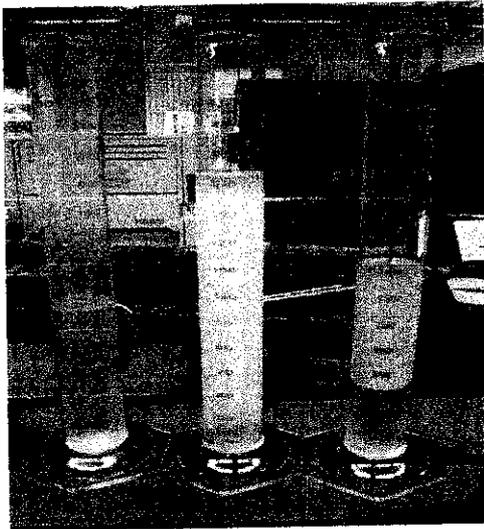


Figure 13 Effluent at $T_{injection}$ 25°C

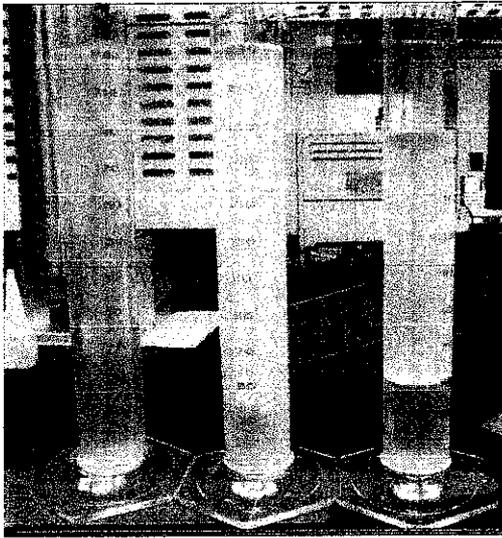


Figure 14 Effluent at $T_{\text{injection}} = 20^{\circ}\text{C}$

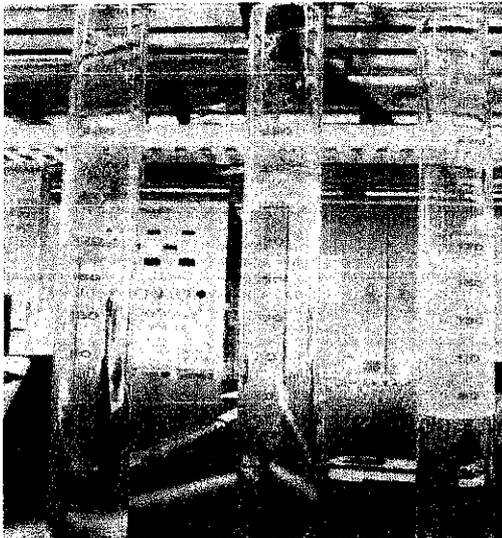


Figure 15 Effluent at $T_{\text{injection}} = 15^{\circ}\text{C}$

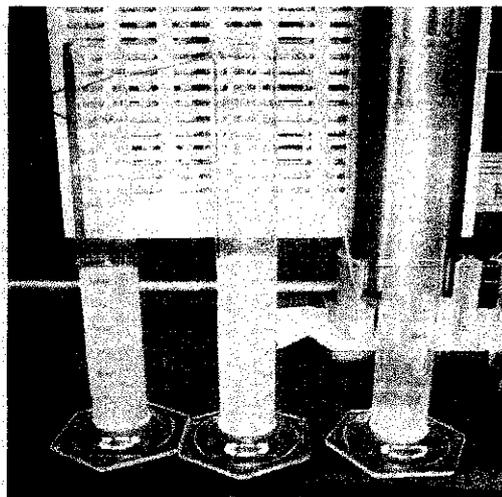


Figure 16 Effluent at $T_{\text{injection}} = 5^{\circ}\text{C}$

At temperature, $T = 25\text{ }^{\circ}\text{C}$

Volume of mineral oil injected, V_1	= 180 ml
Volume of mineral oil collected, V_2	= 156 ml
Volume of mineral oil recovered (secondary), V_3	= 13 ml
Volume of mineral oil recovered (tertiary), V_4	= 5 ml
Original Oil In Place (OOIP)	= 180 ml – 156 ml
	= 24 ml
% Secondary Recovery	= $\frac{13\text{ ml} \times 100\%}{24\text{ ml}}$
	= 54.2 %
Residual Oil in Place (ROIP)	= 24 ml - 13 ml
	= 11 ml
% Tertiary Recovery	= $\frac{5\text{ ml} \times 100\%}{11\text{ ml}}$
	= 45.5 % of ROIP
% Tertiary Recovery	= $\frac{5\text{ ml} \times 100\%}{24\text{ ml}}$
	= 20.8 % of OOIP

At temperature, $T = 20\text{ }^{\circ}\text{C}$

Volume of mineral oil injected, V_1	= 180 ml
Volume of mineral oil collected, V_2	= 156 ml
Volume of mineral oil recovered (secondary), V_3	= 14 ml
Volume of mineral oil recovered (tertiary), V_4	= 5 ml
Original Oil In Place (OOIP)	= 180 ml – 156 ml
	= 24 ml
% Secondary Recovery	= $\frac{14\text{ ml} \times 100\%}{24\text{ ml}}$
	= 60.6 %
Residual Oil in Place (ROIP)	= 24 ml - 14 ml
	= 10 ml
% Tertiary Recovery	= $\frac{5\text{ ml} \times 100\%}{10\text{ ml}}$
	= 50 % of ROIP
% Tertiary Recovery	= $\frac{5\text{ ml} \times 100\%}{24\text{ ml}}$
	= 20.8 % of OOIP

At temperature, $T = 15\text{ }^{\circ}\text{C}$

Volume of mineral oil injected, V_1	= 180 ml
Volume of mineral oil collected, V_2	= 157 ml
Volume of mineral oil recovered (secondary), V_3	= 13 ml
Volume of mineral oil recovered (tertiary), V_4	= 6 ml
Original Oil In Place (OOIP)	= 180 ml – 157 ml
	= 23 ml
% Secondary Recovery	= $\frac{13\text{ ml} \times 100\%}{23\text{ ml}}$
	= 56.5 %
Residual Oil in Place (ROIP)	= 23 ml - 13 ml
	= 10 ml
% Tertiary Recovery	= $\frac{6\text{ ml} \times 100\%}{10\text{ ml}}$
	= 60 % of ROIP
% Tertiary Recovery	= $\frac{6\text{ ml} \times 100\%}{23\text{ ml}}$
	= 26.1 % of OOIP

At temperature, T = 5 °C

Volume of mineral oil injected, V_1	= 180 ml
Volume of mineral oil collected, V_2	= 160 ml
Volume of mineral oil recovered (secondary), V_3	= 12 ml
Volume of mineral oil recovered (tertiary), V_4	= 5 ml
Original Oil In Place (OOIP)	= 180 ml – 160 ml
	= 20 ml
% Secondary Recovery	= $\frac{12 \text{ ml} \times 100\%}{20 \text{ ml}}$
	= 60 %
Residual Oil in Place(ROIP)	= 20 ml - 12 ml
	= 8 ml
% Tertiary Recovery	= $\frac{5 \text{ ml} \times 100\%}{8 \text{ ml}}$
	= 62.5 % of ROIP
% Tertiary Recovery	= $\frac{5 \text{ ml} \times 100\%}{20 \text{ ml}}$
	= 25 % of OOIP

Table 6 Summary of secondary and tertiary recovery at different temperature.

Injection Temperature (°C)	OOIP (ml)	Recovered Mineral oil from Waterflood (ml)	Volume of Residual Oil (ml)	Recovered Mineral oil from CO ₂ (ml)	% Recovery of Waterflood	% Recovery of ROIP	% Recovery of OOIP	Total % Recovery of OOIP
25	24	13	11	5	54.2	45.5	20.8	75.0
20	24	14	10	5	60.6	50	20.8	81.4
15	23	13	10	6	56.5	60.0	26.1	82.6
5	20	12	8	5	60	62.5	25.0	85.0

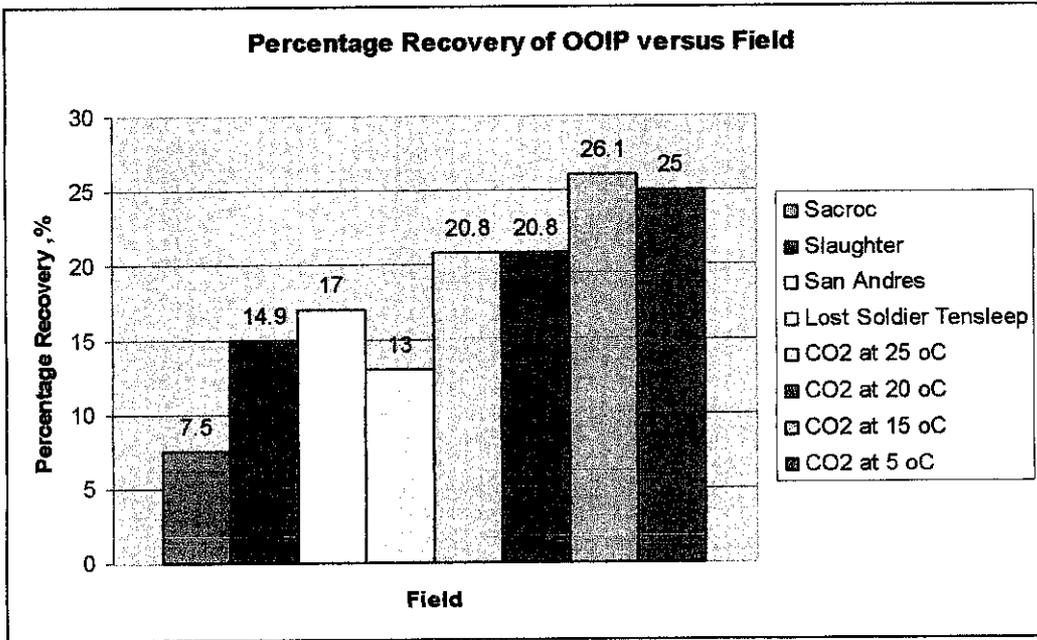


Figure 17 Tertiary recovery from OOIP in various fields(WAG) and different liquid CO₂ injection temperature ^{[11][12]}.

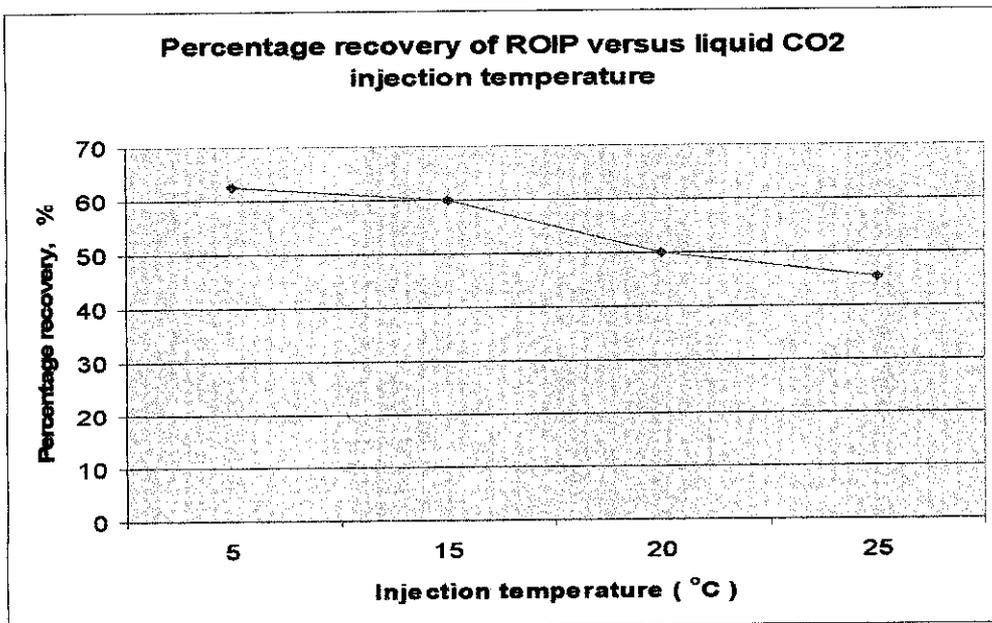


Figure 18 Tertiary recovery from ROIP at various liquid CO₂ injection temperature.

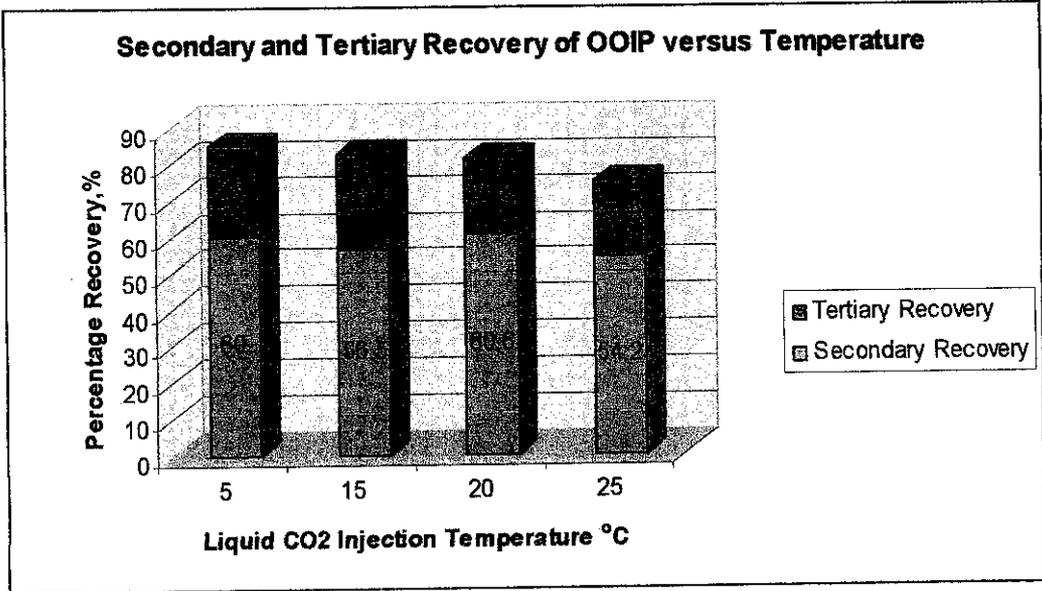


Figure 19 Total recovery from OOIP through the secondary and tertiary method.

4.2 DISCUSSION

1. Figure 1 shows the tertiary recovery from OOIP in four fields using WAG and different liquid CO₂ injection temperature. It's clearly seen that using liquid CO₂ for the injection in the tertiary recovery has been proved to be more effective than WAG and give a significant increase in recovery from OOIP. An average of liquid CO₂ injection yield an average tertiary recovery of 23.2% from the OOIP whereas from the four fields of WAG application for the tertiary recovery, the highest yield recovery at San Andres field is only at 17 % from the OOIP. It had around 6 % tertiary recovery rise through this application of liquid CO₂ injection. If we convert the percentage rise into volume of crude oil that being recovered, it give large volume of additional residual crude oil can be recovered from the existence reservoir.

Let say we take an example of a reservoir with 1 billion barrel OOIP. Below tertiary recovery from this reservoir with WAG application and the additional volume of residual crude oil recovered from the CO₂ application.

$$\begin{aligned} \text{Tertiary recovery at 17\% (WAG)} &= 17\% \times 1 \text{ Bbbls} \\ &= 170 \text{ MMbbls} \end{aligned}$$

$$\begin{aligned} \text{Tertiary recovery at 23.2 \% (CO}_2\text{)} &= 23.2\% \times 1 \text{ Bbbls} \\ &= 232 \text{ MMbbls} \end{aligned}$$

The additional volume of residual crude oil recovered through the liquid CO₂ application is 62 MMbbls.

$$\begin{aligned} &= 232 \text{ MMbbls} - 170 \text{ MMbbls} \\ &= 62 \text{ MMbbls} \end{aligned}$$

Therefore, if this 62 MMbbls of additional residual oil recovered through the application of liquid CO₂ injection is sell at the current crude oil price at around USD\$40/bbl. It give us additional huge amount of profit.

In addition, the increase of tertiary recovery through the application of liquid CO₂ proved the principle behind this displacement that is the double effect of displacement. The first displacement is through the contact of liquid CO₂ displaced the residual mineral oil inside the berea core. Due to the high temperature condition in the berea core holder which assimilate the reservoir temperature of around 160 °F, the injected liquid CO₂ will started to vaporize and this vaporization causes the expansion of the gas volume. Consequently, the expansion of the gas displaced residual mineral oil in the berea core. Therefore, from the result of this injection of liquid CO₂, we can conclude that this injection of liquid CO₂ help to reduce or to the extent of completely remove the viscous fingering effects which happen during gas CO₂ injection.

2. Figure 2 shows that the tertiary recovery from ROIP increases with decrease in liquid CO₂ injection temperature. The increase in recovery is highly due to longer existence of liquid CO₂ phase in the core. This is due to lower injection temperature of liquid CO₂ which causes more time for the liquid to be completely change phase to become gas once it flow into the core compartment where the temperature is much higher around 70 °C. Another words, the time required to reach boiling point of liquid CO₂ at the injection pressure is longer when higher temperature gradient between the injection temperature of liquid CO₂ and the temperature condition in the core. From the trend of the graph, there is maximum tertiary recovery from the ROIP by lowering the injection temperature of liquid CO₂. The recovery will be the same beyond the lowest injection temperature of liquid CO₂ which give the maximum tertiary recovery from the ROIP. At this point of time, we should look on broader picture of the reservoir volume which is much larger compare to the core that being used in the experiment. Therefore, the increase in few percent from ROIP by lowering down the injection temperature of liquid CO₂ give a significant rise to the recovery of residual oil. On the other hand, petroleum industries tend to evaluate and discuss the effectiveness of the tertiary recovery base on recovery from OOIP. The next page is an example shows the significant increase in tertiary recovery from ROIP and OOIP when the temperature of injection is being reduced. Assuming that the primary and secondary recovery from the OOIP is 400MMbbls.

Injection liquid CO₂ at 25°C = 45.5% of ROIP

OOIP = 1 Bbbls

ROIP = 600 MMbbls

Residual oil recovered = 273 MMbbls

Recovery from OOIP = $\frac{0.273 \text{ Bbbls} \times 100\%}{1 \text{ Bbbls}}$

= 27.3%

Injection liquid CO₂ at 25°C = 50% of ROIP

OOIP = 1 Bbbls

ROIP = 600 MMbbls

Residual oil recovered = 300 MMbbls

Recovery from OOIP = $\frac{0.3 \text{ Bbbls} \times 100\%}{1 \text{ Bbbls}}$

= 30%

Therefore, it give a significant increase of residual oil recovery from 273 MMbbls to 300MMbbls is observe from this reservoir if we reduce the injection temperature of liquid CO₂ from 25°C to 20°C. The percentage recovery from the OOIP also increases around 3%. Therefore, lowering the injection temperature of liquid CO₂ is a must go process to implement to increase the residual oil recovery.

3. Figure 3 shows the total recovery from OOIP through the secondary and tertiary method. The total recovery from OOIP increases with the decreases in injection temperature of liquid CO₂. This again proved the relationship of the injection temperature of liquid CO₂ with the tertiary recovery. The increase in tertiary recovery can help to increase the total recovery from the OOIP even though the core had different secondary recovery. This can be seen from the result in the table below:

Table 7 Percentage recovery from OOIP at two different injection temperature.

Percentage Recovery from OOIP	Injection temperature at 15 °C	Injection temperature at 20 °C
Secondary Recovery, %	56.5	60.6
Tertiary Recovery, %	26.1	20.8
Total Recovery, %	82.6	81.4

The difference in secondary recovery indeed does affect the total recovery in a reservoir. This differences can be due to ineffectiveness in the injection, difference in an average waterflood injection pressure and the difference of core condition after each recycle of the core being use in the experiment. Nevertheless, application of low injection temperature of CO₂ can offset the loss in the variation or inconsistency in secondary recovery which at the end of the day will affect the total recovery in a reservoir. This is also applicable in the field test where application of liquid CO₂ injection at low injection temperature will help to recover more residual oil in place in the reservoir. Hence, increase the total recovery from OOIP for that particular reservoir.

4. In this experiment, gas CO₂ was compressed to constant pressure at 950psi inside the accumulator for every difference in injection temperature. The highest injection temperature is at atmospheric condition which is 25°C. Base on the phase diagram, the bubble point pressure at this temperature is 900psi. Therefore, the compression of gas CO₂ to 950psi will cause gas CO₂ to become liquid CO₂. Theoretically, this has proven the existence of liquid CO₂ inside the accumulator for every injection of CO₂ as the temperature of injection is set to lower for each new injection temperature while maintaining the gas CO₂ compression to constant pressure that is 950psi. Another evidence of existence of liquid CO₂ inside the core is the quick pressure builds up inside the core. The effluent mixtures will only come out from outlet point when the pressure inside the core exceeds the setting of backpressure valve which set at 945 psi. From the observation, the effluent come out from the outlet point is in bathes mixtures of gas and liquid droplet and this occurred repeatedly. After every bathes of effluent mixtures discharge from the outlet, the pressure inside the core will drop to around 900psi and the continuous liquid CO₂ injection will build up the pressure to exceed the setting backpressure of 945 psi. The presence of liquid CO₂ in the injection process help to recover the pressure drop and raise the pressure above the setting backpressure within few seconds. Contrary, it will take few minutes for the continuous gas CO₂ injection to raise the pressure above the backpressure after each discharge of effluent batch from the outlet. Therefore, this is the clear evidence of existing of liquid CO₂ with the continuous liquid CO₂ injection inside the core despite the high temperature inside the core.

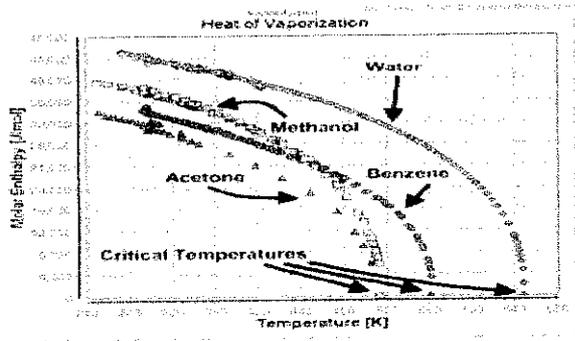


Figure 20 Figure molar enthalpy versus temperature

5. In addition to the effect of lowering the injection liquid CO₂ temperature in the recovery, this discussion will be focused on the enthalpy of vaporization, (ΔH , Btu/lb), also known as the heat of vaporization or heat of evaporation. This is the energy required to transform a given quantity of a substance into a gas and in this case is transform liquid CO₂ into gas CO₂. As shown in the above graph, the heat of vaporization is temperature-dependant and their relationship is inversely proportional. Therefore, the lower the injection temperature of liquid CO₂, the higher the enthalpy of vaporization. Consequently, it will lengthen the time require to vaporize the all liquid CO₂. Let us assume the heat transfer, (Q, btu/s) from the reservoir to the injection liquid CO₂ is constant. The heat of vaporisation at two different injection temperature of liquid CO₂ :

At 25 °C = 3.85 Btu/lb ^[1]

At 20 °C = 14.07 Btu/lb. ^[1]

The heat transfer rate is assumed to be at 10 Btu/s at the reservoir. Therefore the time require to vaporize a pound of liquid CO₂ is as follows:

At 25 °C = $\frac{3.85 \text{ Btu/lb}}{10 \text{ Btu/s}}$
= 0.385 s

$$\begin{aligned}
 \text{At } 20^{\circ}\text{C} &= \underline{14.07 \text{ Btu/lb}} \\
 &10\text{Btu/s} \\
 &= 1.41 \text{ s}
 \end{aligned}$$

The time require to vaporize a pound of liquid CO₂ at 20 °C is 1.025 seconds more than to vaporize a pound of liquid CO₂ at 25 °C. Therefore, longer time will require to vaporize the liquid CO₂ when we inject the liquid CO₂ continuously from the surface into the reservoir in the larger scales as the amount of CO₂ being injected is larger. Hence, this will increase the chances of having more liquid CO₂ displacement to displace the residual oil in the reservoir. The liquid CO₂ displacement of residual oil will help to increase the displacement efficiency as this will reduce the effect of viscous finger of gas CO₂. After the liquid displacement of CO₂, the liquid CO₂ will vaporize and this gas expansion will help to displace the residual oil in the reservoir. This both actions of displacement will occurred repeatedly with continuous injection of liquid CO₂.

CHAPTER 5

RECOMMENDATION AND CONCLUSION

5.1 RECOMMENDATION

1. Fabrication of vacuum bottle at the outlet of RPS equipment is advisable to collect all the effluent that being discharge from it. This is to ensure accuracy in the result of recovery for every injection of liquid CO₂. This is because there's some light components of the residual oil will be carry out by gas CO₂ that coming out from the outlet. Gas oil ratio experiment will be conducted on the recovered gas and oil inside the vacuum bottle to find out the total amount of hydrocarbon in the gas phase. This amount of hydrocarbon gas recovered will be added with the total liquid residual oil that has been recovered. Therefore, this will increase the accuracy of the recovery of residual oil at varying injection of liquid CO₂.
2. The effect on the injection rate of liquid CO₂ should take into consideration. Further studies and experiment need to be conducted to determine the relationship of the recovery with the effect of injection rate of liquid CO₂.
3. Economic analysis need to be conducted to determine recovery of capital investment with the application of liquid CO₂ in the field. The additional tertiary recovery of residual oil from the application of liquid CO₂ injection has to be feasible to overcome the additional cost of equipments such as compressor and chillers need to be installed on the surface prior to the injection of liquid CO₂. The breakeven analysis for economic acceptability for ultimate injection temperature of liquid CO₂ need to be conducted too. This will give highest yield on the rate of return on the investment prior to select the injection temperature of liquid CO₂.

4. The experiment can further conduct using sand pack. The porous sand should be pack inside Perspex of certain thickness. The fabrication of the Perspex need to make properly for specialize dealer to ensure it can sustain the high injection pressure of liquid CO₂. Application of sand pack can help us to observe the behaviour of liquid CO₂ flow through the sand pack and how the liquid CO₂ and its vaporization from liquid to gas can help to sweep the residual oil in the sand pack.

5. The accuracy of result obtain from the experiment can be checked with the reservoir simulator such as Eclipse. The berea core properties will be use to key into the reservoir simulator and simulation can be run with the same injection and flow rate of liquid CO₂ to observe the flow of liquid CO₂ and the changes reservoir fluids concentration from injection well to production well over time. Besides, the effect of injection flow rate of liquid CO₂ can be simulate using the software to determine the injection flow rate effect in tertiary recovery. Hence, it will give strong evidences of the effectiveness of using liquid CO₂ flooding, the effect of injection liquid CO₂ temperature and the injection flow rate in tertiary recovery.

5.2 CONCLUSION

Base on the phase diagram study of CO₂, CO₂ will be in liquid phase at 950 psi with the bubble point temperature of 82 F or 27 °C. Therefore, the highest injection temperature in this experiment is at 25 °C. This is to ensure the injection of CO₂ is in the liquid phase. The reduction of liquid CO₂ injection temperature increases the tertiary recovery. The tertiary recovery through the application of liquid CO₂ injection give greater recovery of OOIP compare with the conventional method of WAG application by using gas CO₂ injection.

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APPENDIX A

TYPICAL CO₂ FLOODING

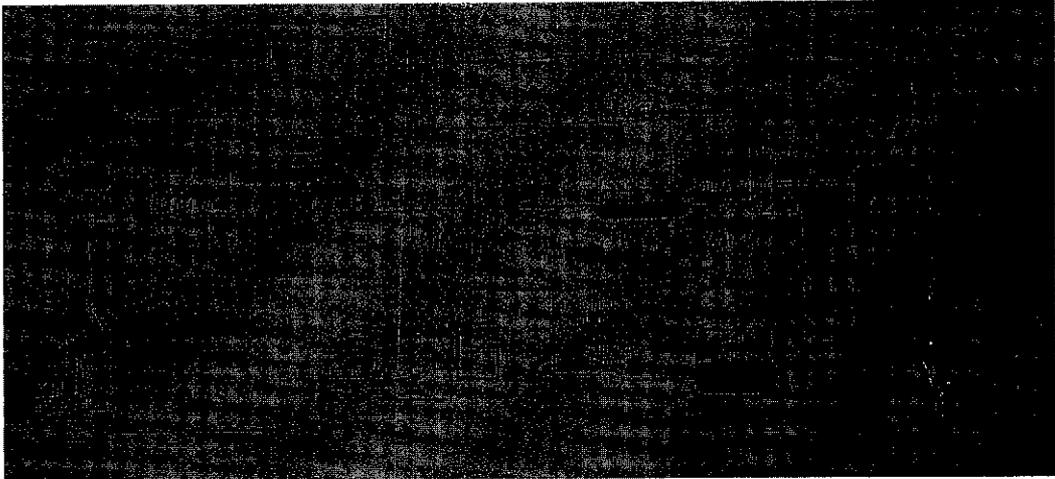


Figure 21 Typical CO₂ flooding operation [1]

CARBON DIOXIDE FLOODING

This method is a miscible displacement process applicable to many reservoirs. A CO₂ slug followed by alternate water and CO₂ injections (WAG) is usually the most feasible method.

Viscosity of oil is reduced providing more efficient miscible displacement.

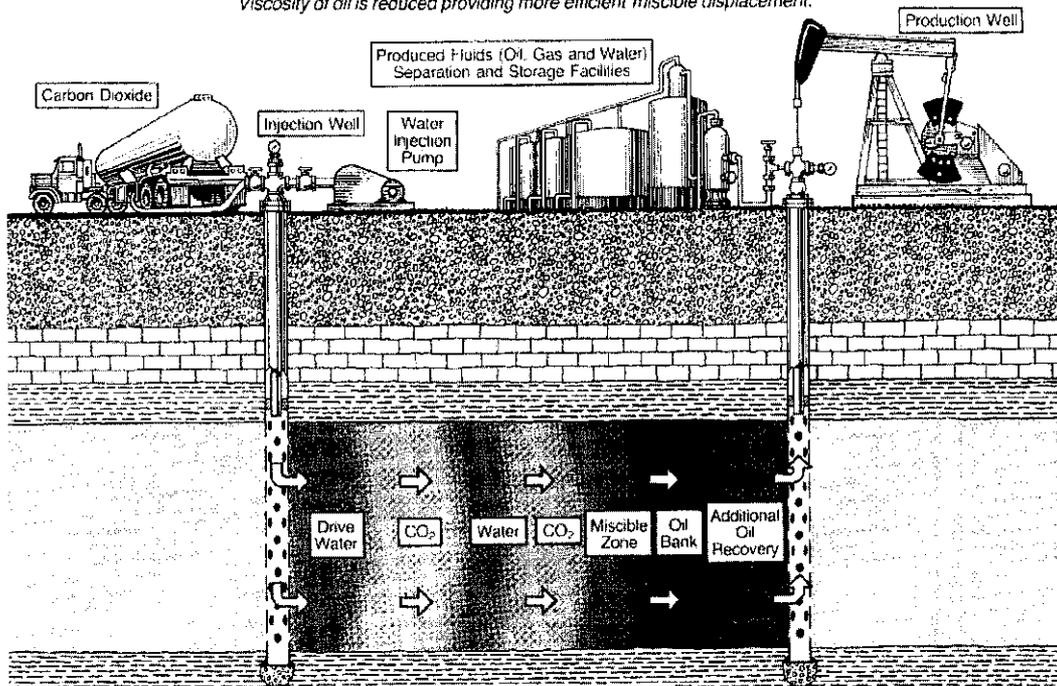


Figure 22 Carbon Dioxide Flooding [3]

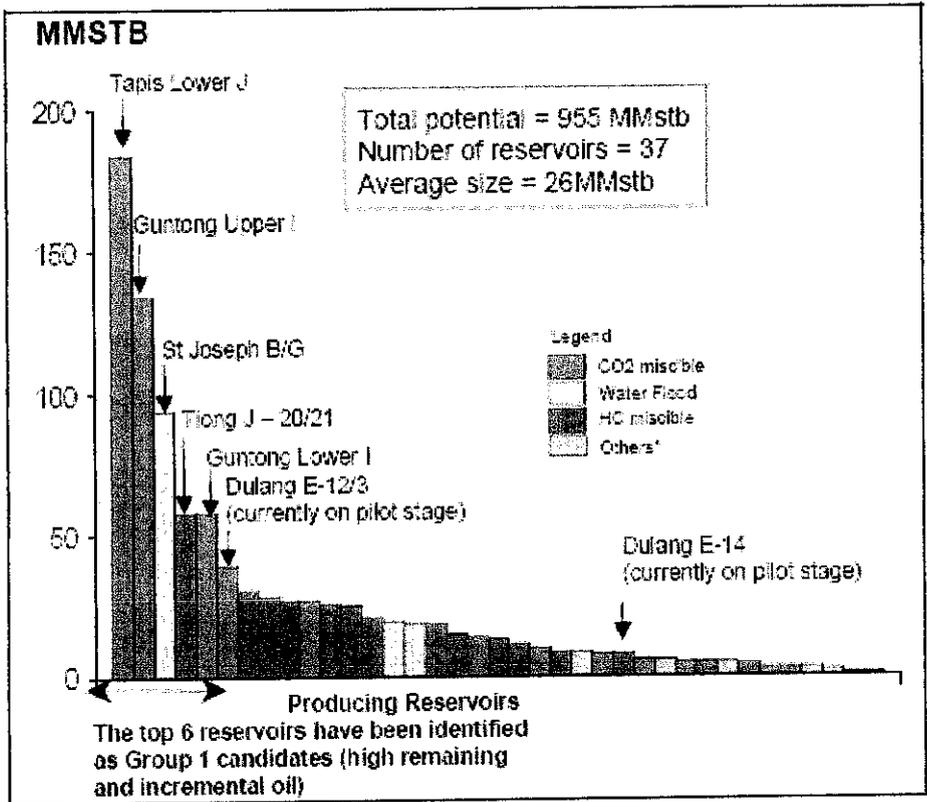


Figure 23 Expected Incremental oil reserve from EOR process in Malaysia [7]

APPENDIX B
MSDS OF MINERAL OIL

Material Safety Data Sheet

Date Printed: 17/JUN/2004

Date Updated: 13/MAR/2004

Version 1.2

According to 91/155/EEC

1 - Product and Company Information

Product Name MINERAL OIL, WHITE, LIGHT
Product Number 330779
Company Sigma-Aldrich Pte Ltd
#08-01 Citilink Warehouse
Singapore 118529
Singapore
Technical Phone # 65 271 1089
Fax 65 271 1571

2 - Composition/Information on Ingredients

Product Name	CAS #	EC no	Annex I Index Number
MINERAL OIL	8042-47-5	232-455-8	None

Synonyms Drakeol * Kaydol * Parol * Peneteck * Slab oil
(Obs.) * White mineral oil

3 - Hazards Identification

SPECIAL INDICATION OF HAZARDS TO HUMANS AND THE ENVIRONMENT

Not hazardous according to Directive 67/548/EC.

4 - First Aid Measures

AFTER INHALATION

If inhaled, remove to fresh air. If breathing becomes difficult, call a physician.

AFTER SKIN CONTACT

In case of contact, immediately wash skin with soap and copious amounts of water.

AFTER EYE CONTACT

In case of contact with eyes, flush with copious amounts of water for at least 15 minutes. Assure adequate flushing by separating the eyelids with fingers. Call a physician.

AFTER INGESTION

If swallowed, wash out mouth with water provided person is conscious. Call a physician.

5 - Fire Fighting Measures

EXTINGUISHING MEDIA

Suitable: Water spray. Carbon dioxide, dry chemical powder, or appropriate foam.

SPECIAL RISKS

Specific Hazard(s): Emits toxic fumes under fire conditions.

SPECIAL PROTECTIVE EQUIPMENT FOR FIREFIGHTERS

Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and eyes.

6 - Accidental Release Measures

PROCEDURE(S) OF PERSONAL PRECAUTION(S)

Exercise appropriate precautions to minimize direct contact with skin or eyes and prevent inhalation of vapors.

METHODS FOR CLEANING UP

Absorb on sand or vermiculite and place in closed containers for disposal. Ventilate area and wash spill site after material pickup is complete.

7 - Handling and Storage

HANDLING

Directions for Safe Handling: Avoid inhalation. Avoid contact with eyes, skin, and clothing. Avoid prolonged or repeated exposure.

STORAGE

Conditions of Storage: Keep tightly closed.

8 - Exposure Controls / Personal Protection

ENGINEERING CONTROLS

Safety shower and eye bath. Mechanical exhaust required.

GENERAL HYGIENE MEASURES

Wash thoroughly after handling.

PERSONAL PROTECTIVE EQUIPMENT

Hand Protection: Protective gloves.
Eye Protection: Chemical safety goggles.

9 - Physical and Chemical Properties

Appearance	Physical State: Liquid	
Property	Value	At Temperature or Pressure
pH	N/A	
BP/BP Range	N/A	
MP/MP Range	N/A	
Flash Point	N/A	
Flammability	N/A	
Autoignition Temp	N/A	
Oxidizing Properties	N/A	
Explosive Properties	N/A	
Explosion Limits	N/A	
Vapor Pressure	N/A	
SG/Density	N/A	
Partition Coefficient	N/A	
Viscosity	N/A	
Vapor Density	N/A	
Saturated Vapor Conc.	N/A	
Evaporation Rate	N/A	
Bulk Density	N/A	

Decomposition Temp.	N/A
Solvent Content	N/A
Water Content	N/A
Surface Tension	N/A
Conductivity	N/A
Miscellaneous Data	N/A
Solubility	N/A

10 - Stability and Reactivity

STABILITY

Stable: Stable.

Materials to Avoid: Strong oxidizing agents.

HAZARDOUS DECOMPOSITION PRODUCTS

Hazardous Decomposition Products: Carbon monoxide, Carbon dioxide.

HAZARDOUS POLYMERIZATION

Hazardous Polymerization: Will not occur

11 - Toxicological Information

RTECS NUMBER: PY8047000

SIGNS AND SYMPTOMS OF EXPOSURE

Ingestion of large doses will produce a laxative effect and may be irritating to the digestive tract. Aspiration into lungs will cause lipid pneumonia. To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

ROUTE OF EXPOSURE

Skin Contact: May cause skin irritation.

Skin Absorption: May be harmful if absorbed through the skin.

Eye Contact: May cause eye irritation.

Inhalation: May be harmful if inhaled. Material may be irritating to mucous membranes and upper respiratory tract.

Ingestion: May be harmful if swallowed.

CHRONIC EXPOSURE - CARCINOGEN

Result: This product is or contains a component that is not classifiable as to its carcinogenicity based on its IARC, ACGIH, NTP, or EPA classification.

IARC CARCINOGEN LIST

Rating: Group 3

12 - Ecological Information

13 - Disposal Considerations

SUBSTANCE DISPOSAL

Contact a licensed professional waste disposal service to dispose of this material. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber. Observe all federal, state, and local environmental regulations.

14 - Transport Information

RID/ADR

Non-hazardous for road transport.

IMDG

Non-hazardous for sea transport.

IATA

Non-hazardous for air transport.

15 - Regulatory Information

COUNTRY SPECIFIC INFORMATION

Germany

WGK: 1

16 - Other Information

WARRANTY

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Inc., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale. Copyright 2004 Sigma-Aldrich Co. License granted to make unlimited paper copies for internal use only.

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