ASPHALTENE FLOW BAHAVIOR IN PRESENCE OF CARBON DIOXIDE (CO_2) GAS IN POROUS MEDIA

By

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JAN 2011

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.

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ABSTRACT

CO_2 injection is one of efficient enhanced oil recovery (EOR) methods among gas flooding. However, it may change the reservoir fluid properties and cause some problems such as asphaltene precipitation. Asphaltenes are components of petroleum whose behavior and structure change with pressure, temperature and oil composition. For this project, it will concentrate on the precipitation of asphaltene due to CO_2 injection process for enhanced oil recovery purposes. The asphaltenes turn into solid form and separate from the rest of the liquid oil. Unwanted asphaltene precipitation is a serious concern to the petroleum industry because asphaltenes plug up well bores, decrease production and could cause adverse affect on the oil recovery. Once these problems occur, it will need high investment of time and money to remove the asphaltene deposits from wells, transfer lines and storage facilities. To understand the mechanism of asphaltene deposition is necessary to develop effective engineering practice for minimizing the formation damage and to design the treatment program for restoring well productivity. Study shows that the amount of asphaltene precipitation is depend on the CO_2 concentration. Same goes to reduction in rock porosity and permeability. Therefore this project will review on the Asphaltene flow behavior in presence of CO_2 gas in porous media and how it will cause problem to the well by developing mathematical considering the relationship of CO_2 concentration with the asphaltene precipitation, porosity and permeability reduction problems during CO_2 flooding for Malaysia crude oil.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Asphaltenes are among the least understood deposits occurring in the oil field. They are thought to be the byproduct of complex hetero-atomic aromatic macro-cyclic structures polymerized through sulfide linkages. The deposition of asphaltenes has been observed in a large number of locations in producing wells and associated transfer and storage facilities. Some of these depositions occur at locations of particular interest, which include well chokes, casing perforations, formation rock, the vacuum side of pumps, storage tanks and well tubing.

Certain techniques intended to enhance the recovery of petroleum result in the problem of asphaltene deposition. A particularly striking example of this is true is in the widespread usage of CO_2 flooding. Carbon dioxide (CO_2) gas injection is one of the tertiary recovery techniques that have been applied in oil and gas industry to extract oil from the reservoir. Carbon dioxide (CO_2) gas could increase oil recovery by means of swelling, evaporating and lowering oil viscosity. In the displacement front, injected gas may become enriched by the oil components and gas may dissolve into reservoir oil. CO_2 injection from industrial plants emission also provides another beneficial opportunity due to the added value of dealing with global warming and reducing Green House Gas emission by CO_2 sequestration and as storage oil/gas reservoirs.

However, this technique results in significant amounts of asphaltene deposition and might cause serious problem to the petroleum industry. This project focuses on the relationship between CO_2 concentration with the percentage of asphaltene precipitation and reduction in rock porosity and permeability. Also will relate it on how it will cause problem to the well.

1.2 PROBLEM STATEMENT

Asphaltene is one of the components of crude oil that can precipitate as solids during the field handling of crude oil or even downhole. The deposition of such solids can be so significant that they foul equipment surfaces and cause cessation of flow and/or extreme difficulty in initiating flow. Some of the factors that may cause asphaltene precipitation are temperature and pressure changing and also the most concern in this project is the existence of carbon dioxide (CO_2).

CO_2 gas injection is one of the main approved technologies that are being applied in future developments during both secondary and tertiary stages of oil recovery. Occasionally, in the initial investigation of the oil recovery process, the potential of asphaltene precipitation occurring during gas injection (CO_2) is either overlooked or not anticipated, seemingly due to two reasons. Either the asphaltene content of the reservoir is negligible or the reservoir had no asphaltene problem during the primary production phase. Often, operators are confounded and taken by surprise when they experience injectivity problems due to the manifestation of serious asphaltene precipitation soon after the gas injection project has started.

For this reason, careful attention and a systematic approach are required for investigating asphaltene precipitation problems during a CO_2 injection project at the earliest stage of the planning. This is because, once the asphaltene precipitation occurs, it causes severe permeability and porosity reduction and wettability alteration, changing relative permeability in the reservoir and in the severe cases plugging the wellbore and surface facilities. Remedial measures such as chemical treatments and work over operations are disruptive and expensive.

1.3 OBJECTIVES

The objectives of this research are:

- To investigate asphaltene flow behavior in presence of CO_2 gas in porous media.
- To study and understand the characteristics of asphaltene in the crude oil.
- To investigate formation damage and permeability reduction in the reservoir due to asphaltene precipitation during CO_2 gas injection process.
- To develop mathematical model considering the relationship of CO_2 concentration with the asphaltene precipitation, porosity and permeability reduction problems during CO_2 flooding.

1.4 SCOPE OF STUDY

The scope of this study is to do research about the flow behavior of asphaltene in presence of Carbon Dioxide gas during the oil recovery process mainly in Enhanced Oil Recovery (EOR). Based on the understanding of the behavior of asphaltene once CO_2 is injected, a mathematical model using EOS method considering asphaltene precipitation is presented and an oil field scaled numerical simulator is developed to predict for asphaltene precipitation problems during CO_2 flooding.

Mathematical model will be developed by using Malaysia crude oil data. From the data given, the mathematical modeling was developed to see the relationship between CO_2 concentration with percentage of asphaltene precipitation and rock porosity and permeability reduction.

1.5 FEASIBILITY OF PROJECT WITHIN SCOPE AND TIME FRAME

The first phase (FYP-1) of the project involves the literature review on the background knowledge and previous related work on asphaltene precipitation during CO_2 gas injection. I focused more on the investigation of asphaltene flow behavior in presence of CO_2 gas in porous media during tertiary recoveries – EOR (CO_2 gas injection).

The second phase (FYP-2) of project involves on developing mathematical modeling considering the relationship of CO_2 concentration with the asphaltene precipitation, porosity and permeability reduction problems during CO_2 flooding. This mathematical model is then implemented with the field data (Malaysia crude oil). Result obtained has been analyzed and compared the mathematical model with the experiment data.

CHAPTER 2: LITERATURE REVIEW

During the lifetime of an oil reservoir, oil production is usually implemented in two phases, if economical, three phases. The primary phase is categorized by natural flow that force and push production oil to the surface. However, years by years over the lifetime, the pressure will fall, thus insufficient underground pressure to force oil to the surface. Thus we need to be implemented secondary recovery, which water and gas is injected to displace oil making it much easier to drive it to production wellbore. Next phase is the tertiary recovery as we known as Enhance Oil Recovery (EOR).Enhanced oil recovery (EOR) refers to the reservoir process that recover oil not produced by secondary processes.

Good number of these projects involves certain kinds of CO_2 gas injection [1]. CO_2 flooding appeared in 1930's and had a great development in 1970's [2]. CO_2 flooding has become a leading EOR technique for light and medium oils [3]. One of the major problems that confront reservoir/production engineers considering a miscible CO_2 flooding project is the need to assess the likelihood of Asphaltene precipitation [4].

2.1 ENHANCED OIL RECOVERY (EOR)

EOR is defined as any method that increases oil production by using techniques or materials that are not part of normal pressure maintenance or water flooding operations [5]. Enhanced oil recovery through the injection of CO_2 as a tertiary recovery mechanism, preferably after water flooding, is one mechanism with which to recover more oil, extend the field life and increase the profitability of the fields.

In general, EOR technologies fall into three groups of the following categories:

- Gas miscible recovery
- Chemical flooding
- Thermal recovery

But for this project is focusing on Gas miscible recovery which is CO_2 gas

2.1.1 EOR by CO_2 Gas Flooding

CO_2 flooding has proven to be among the most promising EOR methods, especially in the US because it takes advantage of available, naturally occurring CO_2 reservoirs. CO_2 gas is injected above minimum miscible pressure such that gas becomes miscible on oil in the formation. Viscosity of oil is reduced providing more efficient miscible displacement.

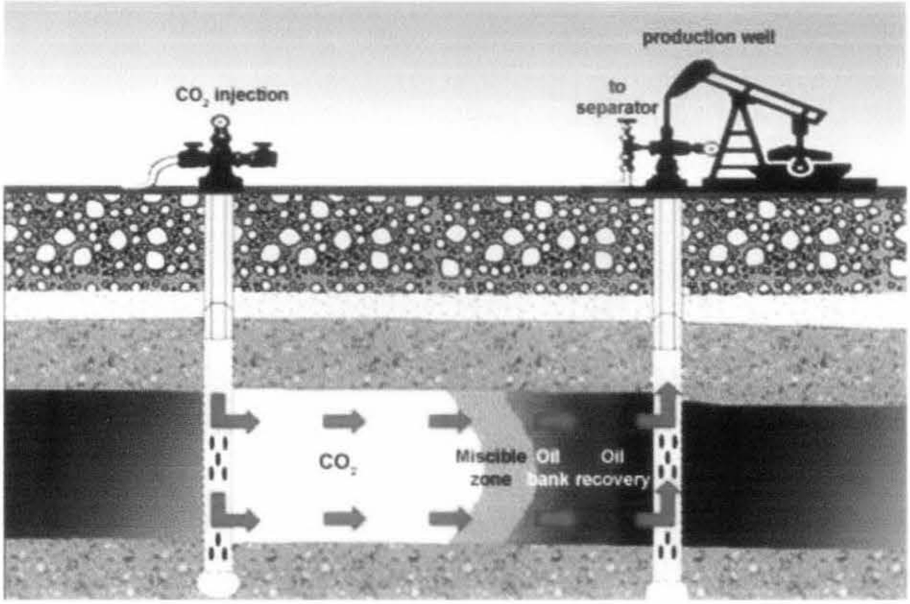


Figure 2.1: The process of CO_2 flooding

An advantage to use CO2 in EOR is that the pressure required for achieving dynamic miscibility with it is lower than the pressure required for dynamic miscibility with other gases such as a natural gas, flue gas or nitrogen [6]. Successful EOR operations are routine business in USA and can serve as example. Currently, about 71 of the 84 projects of CO2 applications for EOR worldwide projects are not carried out specifically for reducing GHG. The amount of enhanced oil being produced from these CO2, EOR projects averages 206,000 bbl/day [7].

2.1.2 Sources of CO_2

There are three main sources of CO_2 [1]:

- Natural sources of CO_2 such as those in the Permian basin of the USA and Hungary
- CO_2 separated during the manufacture of hydrogen or ammonia
- CO_2 produced from combustion processes.

This third source has been the subject of significant technology development activities over the last few years with a range of alternative processes evaluated and developed to varying levels of maturity [9]. Current countries of high potential of CO_2-EOR application depends mostly on the second and the third sources due to the lack of large natural CO_2 resources.

2.1.3 Advantages and disadvantages of CO_2 flooding

The greatest difference compared to other gases is that CO_2 can extract heavier components up to C_{30}. The solubility of CO_2 in hydrocarbon oil causes the oil to swell. CO_2 expands oil to a greater extent than methane does. The swelling depends on the amount of methane in the oil. Because to CO_2 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.

The main disadvantage of CO_2 flooding is the injected into the oil formation can induce flocculation and **deposition of asphaltene**. This can cause numerous production problems with a detrimental effect on the permeability and oil production.

2.2 WHAT IS ASPHALTENE

2.2.1 Definition

Asphaltenes are the most heavy and polar components in crude oil. Polarity of asphaltenes is due to the presence of hetero-atoms and condensed aromatic rings.

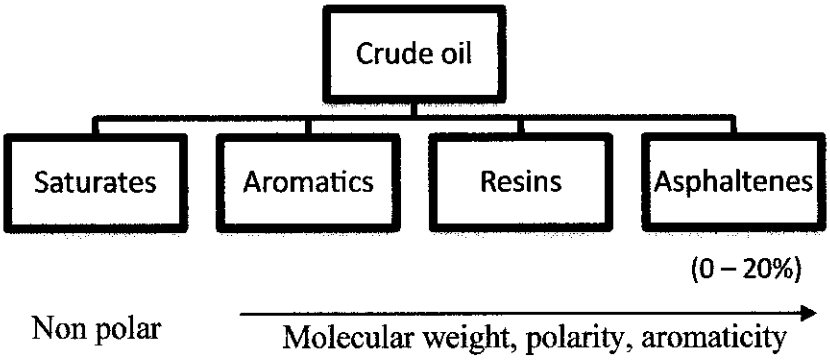


Figure 2.2: Components of crude oil

The classical definition [10] of asphaltenes is based on the solution properties of petroleum residuul in various solvents and is shown schematically in figure 3.

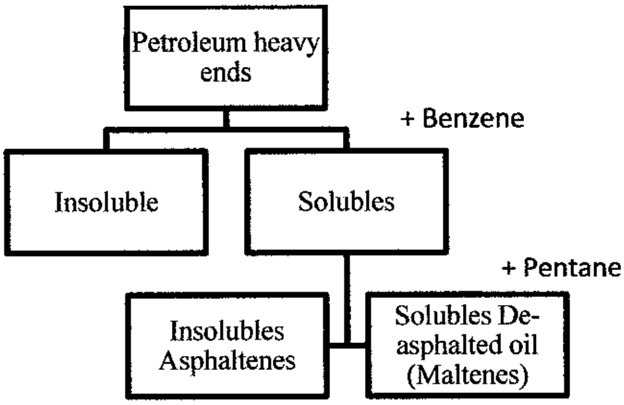
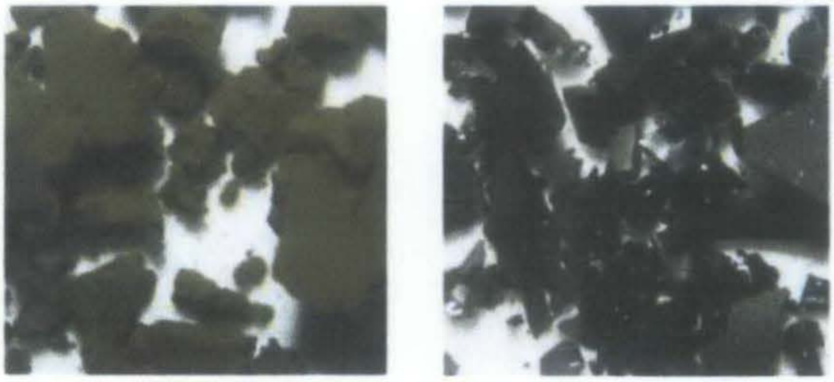


Figure 3: Separation of asphaltenes from petroleum residuum

Asphaltene are the crude oil components that meet some procedural definition. A common definition is that asphaltenes are the material that is (1) insoluble in n-pentane (or n-heptane) at a dilution ration of 40 parts alkane to 1 part crude oil and (2) re-dissolves in toluene. [11]



(a) n- C5 asphaltenes (b) n-C7 asphaltenes

Figure 4: Example of the appearance (magnified about 15 times) of asphaltenes separated from Mars-P crude oil with an excess of (a) n- pentane (n- C5) and (b) n-heptane (n-C7).

2.2.2 Typical asphaltene molecular properties

Below are typical molecular properties for asphaltene:

- H/C = 0.8 – 1.4
- Molecular weight : depends on solvent and concentration; monomer = 500-1000, while micelles = 1000-5000
- Heteroatoms: acting as polar functional group
  S = 0.5-10 wt%; N = 0.6-2.6 wt%; O = 0.3-4.8 wt%
- Metal elements: Ni, V, Fe

2.2.3 Structure and Chemistry of Asphaltene and Resins

Asphaltenes are not crystallized and cannot be separated into individual components or narrow fractions. Thus, the ultimate analysis is not very significant, particularly taking into consideration that the neutral resins are strongly adsorbed by asphaltenes and probably cannot be quantitatively separated from them. Not much is known of the chemical properties of asphaltenes. Asphaltenes are lyophilic with respect to aromatics, in which they form highly scattered colloidal solutions. Specifically, asphaltenes of low molecular weight are lyophobic with respect to paraffins like pentanes and petroleum crudes terms of chemical structure and elemental analysis as well as by the carbonaceous sources. [12]

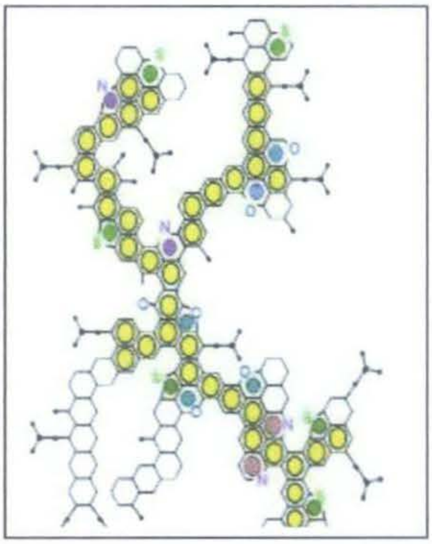


Figure 5: Molecular structure of asphaltene proposed for Maya crude (Mexico) by Altamirano, et al. [IMP Bulletin, 1986]

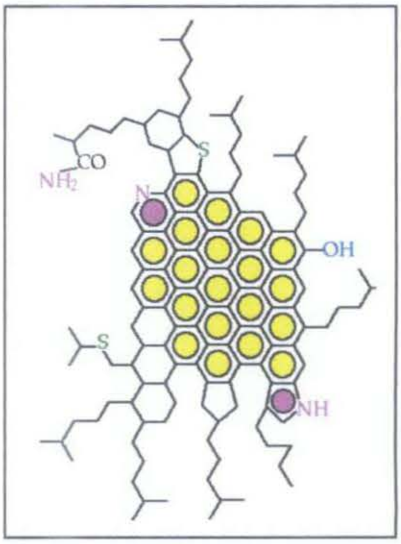


Figure 6: Molecular structure of Asphaltene Proposed for 510C Residue of Venezuelan Crude by Carbognani [INTEVEP S.A. Tech.Rept., 1992]

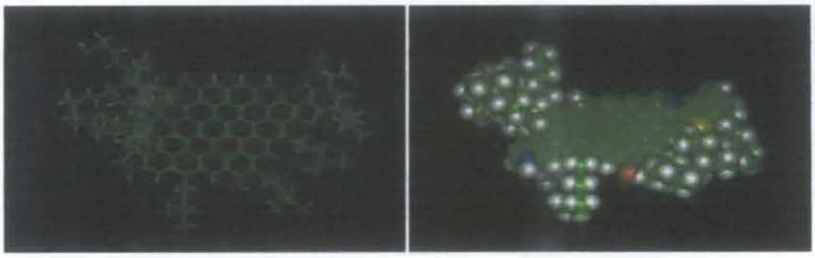


Figure 7: 3D Picture of Carbognani's Model of Venezuelan Crude Asphaltene Molecule (Courtesy of Prof.J.Murgich)

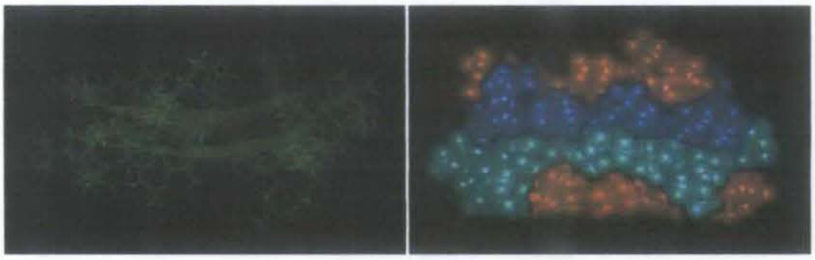


Figure 8: Flocculation/ Aggregation of Venezuelan Crude Asphaltene Molecules (Courtesy of Prof. J. Murgich)

Flocculation and aggregates of asphaltene can be caused due to the addition on non-polar solvents such as CO_2.

2.3 WHEN DO ASPHALTENES CAUSE PROBLEMS

Asphaltenes can cause problems in oil production, transportation, and processing. In many cases the deposits can be formed in the reservoir, in the well tubing and can be carried through the flow lines and into the separators and other downstream equipment. At normal reservoir conditions, the Asphaltene, resins, maltenes, and oil phase are in thermodynamic equilibrium. This equilibrium can be disturbed by a number of factors such as pressure reductions, change in temperature, change in crude oil chemical compositions, addition of miscible gases (CO_2) and liquids to the oil as applied in various EOR techniques. But for this project is focusing on the asphaltene precipitation in presence of CO_2 gas in porous media.

2.3.1 Carbon Dioxide (CO_2) flooding

The injections of CO_2 often cause the asphaltenes to precipitate within a very short period. The asphaltene flocculation/precipitation is depending on the CO_2 gas concentration.

2.3.1.1 Asphaltene colloidal properties and CO_2 mechanism

Asphaltenes in solution in the crude oil have been regarded by many researchers as a colloidal system [13]. Several investigators have observed that Asphaltenes carry an intrinsic charge that may be positive or negative depending on the oil composition. The highly polar resins act as peptizing agents for Asphaltenes and are attracted by their charge. They are absorbed by Asphaltenes and act as protective layer and hold the Asphaltene in the oil. Both asphaltenes and resins have a tendency to aggregate with each other. The degree of aggregation depends on the aromaticiy and the chemical composition of the oil. These resins and Asphaltenes together are called micelles as shown in figure 9 below.

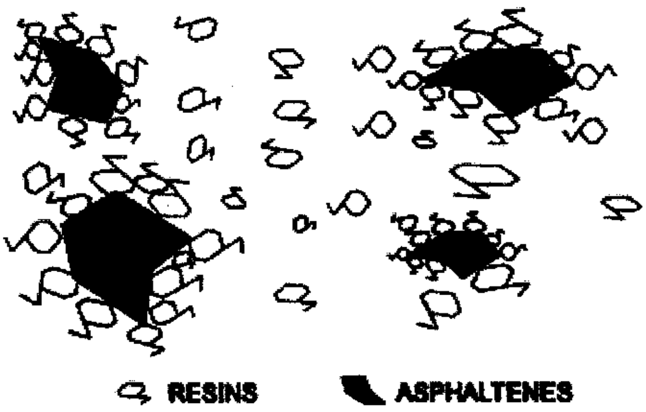


Figure 9: peptization of Asphaltenes by resins [13, 14]

During CO_2 gas injected into the reservoir, it will cause resin to solute in the CO_2, it will become lesser support to the Asphaltene, resulting in asphaltene and resin molecules **precipitating** out of the oil. Precipitation corresponds to the formation of a solid phase from thermodynamic equilibrium. Because of the high polarity of the asphaltene, the particles will go to each other and flow as suspended particles and will cause **flocculation.** Then **deposition** begins with adsorption of flocculated asphaltene particles into larger aggregates. Deposition of solid asphaltenes causes a reduction of solid asphaltenes causes a reduction of the pore space available for fluids. It is important to note that asphaltene flocculation and deposition are two separate phenomena. It is possible to have flocculation without substantial in situ deposition.

2.3.1.2 Deposition mechanisms

Based on the experimental observation [15], three main mechanisms contribute in asphaltene deposition and reduction in rock permeability. They are the surface deposition, the pore throat blocking and the entrainment of asphaltene deposits [16].

1. **Surface deposition:** adsorption of asphaltene particles on the surface of the pores causes gradual pore blocking. Surface deposition rate coefficient (α: 1/sec) is defined as the parameter that accounts for the ability of surface deposition mechanism to decrease the permeability. Deposition of fine particles in single-phase flow by surface deposition rate is directly proportional to the concentration of fine particles and for multiphase flow, the surface deposition rate is directly proportional to the concentration of suspended asphaltene precipitates, C_A, the porosity, Ø and liquid saturation, S_l.

2. **Pore throat plugging:** asphaltene particles mechanically bridge the pore throats. Pore throat plugging rate coefficient (Y_i: $\frac{1}{meter}$) shows the amount of contribution of pore throat plugging mechanism in deposition and permeability reduction.

3. **Entrainment:** as long as deposition continues, pressure drop along the core increases and a shear stress begins to develop. When pressure drop increase sufficiently, shear stress breaks up the layer of deposited asphaltene and a certain amount of the deposited asphaltene is drifted away by the fluid stream resulting in a temporary permeability increase. Entrainment rate coefficient (β:$\frac{1}{meter}$) shows the power of entrainment process in permeability improvement. Entrainment rate of asphaltene deposits is directly proportional to the amount of asphaltene deposits, E_A, and the difference between the

actual interstitial velocity and the critical interstitial velocity necessary for asphaltene deposition mobilization. If the interstitial velocity is larger than critical velocity, this mechanism affects the asphaltene deposition. Therefore, the value of each mechanism shows the ability of that mechanism in asphaltene deposition and permeability reduction.

2.4 THE EFFECTS OF ASPHALTENE PRECIPITATION DURING CO_2 GAS INJECTION

Any action of chemical, electrical or mechanical nature that depeptizes the asphaltene micelle leads to flocculation and precipitation of asphaltenes from the crude oil. After flocculation, the asphaltenes aggregates may be brought into contact with the possible retention site on the rock surface. They either deposit at the surface or are carried away by the flowing stream. The deposition process is therefore a sequence of the following mechanisms [17]:

- The contact of asphaltene aggregate with the rock surface
- The adsorption of asphaltene aggregate on the rock surface
- The possible breaking away or the desorption of previously adsorbed asphaltene

The factors which control adsorption of asphaltenes or resins on mineral surfaces are:

- Chemical and structural nature of the rock mineral substrate
- Asphaltene and resin content on the crude oil
- Brine pH and composion
- Pores shape and distribution
- Pressure and temperature

Once the asphaltene flocculation and deposition occurs, it can severely reduce permeability and alter wettability.

2.4.1 Where does asphaltene deposition occur?

Asphaltene deposition can occur during the production and processing of oils and can pose a serious problem. In many cases the deposits can be formed in the reservoir, in the well tubing and can be carried through the flow lines and into the separators and other downstream equipment.

2.4.1.1 Inside the reservoir

2.4.1.1.1 Effect of asphaltene precipitation on rock porosity and permeability

Changes in rock porosity and permeability may result from the asphaltene precipitation. Reactions between reservoir oil, brine, formation rock and CO_2 most probably will lead to dissolution of rock minerals resulting in an increase in the formation permeability, pore size distribution and the effective porosity. Precipitation of asphaltene in the reservoir however leads to an opposite effect; reduce in porosity and permeability. Asphaltene precipitation might reduce the porosity and permeability of the rock because it is believed that asphaltene particle size and salt aggregates are larger or the same size as the rock pore throats [1]. Thus, it will plug the pore spaces inside the rock. The reduction of porosity and permeability of rock can be seen from below figures:

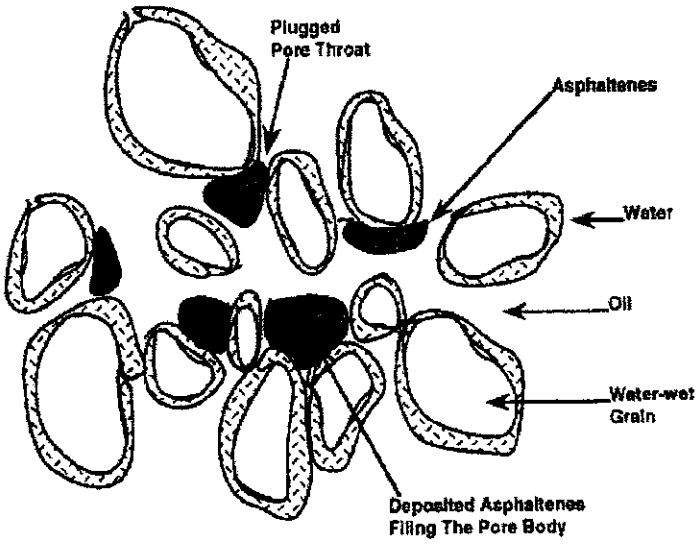


Figure 10: In situ asphaltene deposition causing physical blockage

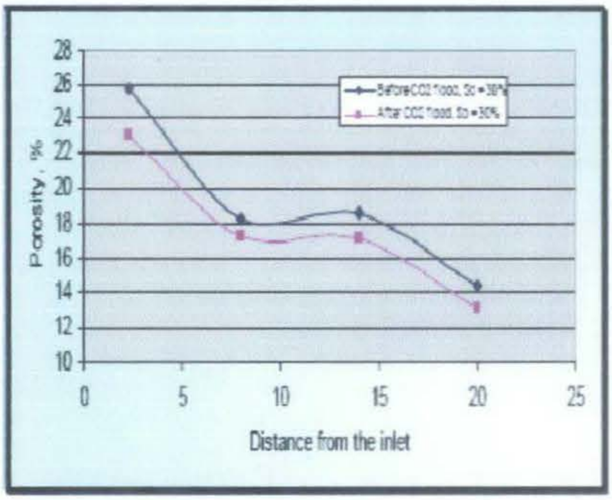


Figure 11: (Ref. SPE 104630) Reduction in rock porosity after CO_2 flooding

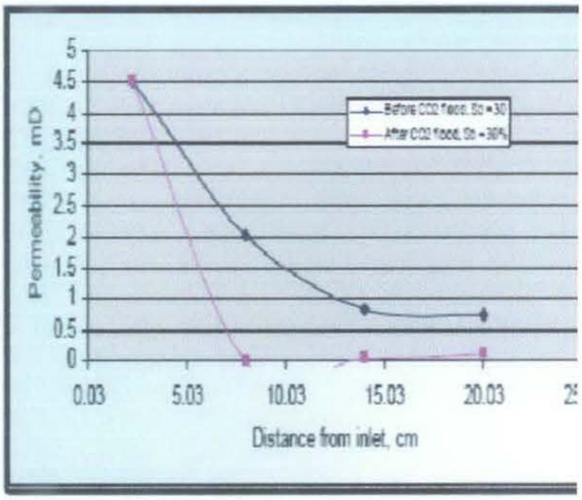


Figure 12: (Ref.SPE 104630) Reduction in rock permeability after CO_2 flooding

2.4.1.1.2 Effect of asphaltene on reservoir wettability

Researchers [19] reported that when asphaltene content in the crude oil exceeds 4.6 wt%, the wettability of sandstone cores would change from water wet to oil wet and that would produce lower oil recovery. Other researchers [20] confirmed this and reported that a significant increase in oil wet conditions takes place close to the onset of asphaltene precipitation. This will plug well bores and flow lines. This was experienced with four of five studied oil samples indicating the possibility of change in system wettability at conditions of asphaltene instability. This can be seen clearly from figure 13:

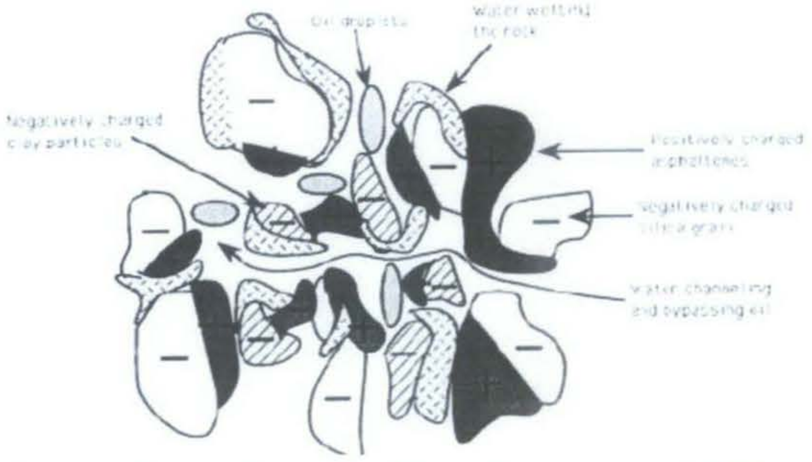


Figure 13: Asphaltenes adsorbed on the rock, causing wettability changes

2.4.2.2 Well Bores and tubing

Perhaps the place where the asphaltene problem is most acute is in the well bores and well tubing. In many instances the asphaltene deposits plug the wells and result in production losses. To compensate for these losses the pressure is reduced at the well head until it cannot be reduced any further. Production losses lead to increased costs and well clean-ups from asphaltene deposition can adversely affect the economics of the oil recovery project. Besides added cost, asphaltene deposition inside the wells has the potential of serious accidents. For example, the malfunction of the down hole safety valves and other valves inside the well can lead to very serious consequences. In one case a blow out of the asphaltene plug resulted in the shooting of highly asphaltenic sour crude oil into the air.

2.5 OIL FIELD TREATMENT METHOD

Asphaltene depositions are common in a very large number of producing wells throughout the world, and their cost to the producers is significant. Therefore, the removal or treatment of damaged media's is an essential issue that needs to be investigated and discussed for prevention of oil production restriction. Conventional and recent techniques for treatment of asphaltene deposition can be categorized into 3 main groups which are **chemical treatment, mechanical treatment, and thermal treatment [23].** This remedial procedure requires considerable investments in time, solvent, and lost production. Often the depositions are so severe that the well's production rate falls from thousands of barrels per day to zero [21]

2.5.1 Chemical treatment

Chemical methods are the most popular ones for asphaltene treatment since they can be used to treat depositions in wellbore hole and/or into the producing formations. Chemical treatment falls into three major classes:

i. **Solvent treatment**: Solvents [25] such as toluene and xylene is normally used to dissolve deposits of asphaltene.
ii. **Asphaltene Detergents**: detergents are a class of surface-active agents. They are used to break up the asphaltene deposits and also prevent them from reagglomerating back.
iii. **Crystal modifiers**: they are polymers used to alter wax crystal growth by disrupting nucleation, crystallization, or modification of the paraffin crystals.

For all types of chemical treatments, environmental safety and personal exposure hazard concern should be considered, which produce additional disadvantages and restrictions for many chemical-treatment materials.

2.5.2 Mechanical treatment

Normally this method is used to remove asphaltene deposits from flow lines, producing tubing, and pipelines. These methods include rod scrapers, wireline scrapers, flow line scrapers, free-floating piston scrapers, "pigging" flow lines and wirelining tubing. The mechanical method advantages are good cleaning is assured and minimal formation damage may take place. However, it has some advantages which are:

i. Expensive treatments and restricted to production facilities but not to producing formation
ii. Application is limited to equipment involved and time
iii. Danger of fishing of tools which may be lost in the hole
iv. May plug the perforations and increase the stability of oil-in-water emulsions

2.5.3 Thermal treatment

This category of treating methods includes hot oiling, bottom hole heaters, water, or steam, and the use of heat-liberating chemicals.

i. **Hot oiling**: injecting hot oil to remove asphaltene deposits from a well. Hot oiling causes formation damage and is not good if large deposits are accumulated
ii. **Downhole heaters**: the downhole heater represent a continuous source of heat which can be used to melt asphaltene or paraffin deposits in the wellbore or on the tubing for a period of time after which the melted material can be pumped up to the surface with oil production. This technique has the following shortcomings: hindered by economics, maintenance cost of heating system, and availability of electric power
iii. **Using Heat-Liberating Chemicals**: involves pumping down a mixture of equi-molar concentrations of ammonium chloride and sodium nitrate. A buffer is used to delay the exothermic reaction until the fluid reaches the bottom-hole with a large quantity of nitrogen gas. However, the disadvantages of this method are; it is very expensive in comparison to conventional thermal methods, and the process must be designed and closely monitored by a chemist on location.

2.5.4 Additional treatments

Other methods of treating the asphaltene deposition are also been applied which are:

i. **Bacteria treatment**: bacteria is mixed with biocatalyst. Also, biocide was used to control the sulfate-reducing bacteria (SRB) growth. It is important to show that bacteria treatment is limited to wells producing water and it suffers from the difficulty to control the process.
ii. **Production techniques and Facilities Modifications** to Reduce Deposition: Manipulation of production technique [24] may help to reduce asphaltene deposition.

iii. **Combination** of two or more treatments: many problems of asphaltene deposition require using a combination of two or more of the previous methods for getting the solution, such as using hot chemicals which combines thermal and chemical methods.

2.6 FIELD EXAMPLES

Asphaltene precipitation during oil recovery is a well known problem and occurs in many areas throughout the world. This precipitate can form a sludge and can plug well bores, pipes and processing equipment. In some cases it can also lead to closure of a particular field. This problem has been there for many years and numerous chemical products are available for cleaning.

2.6.1 Greeley and Ventura Fields, California

The precipitation of asphaltenes has been observed even before the introduction of gas flooding projects during the early period of crude oil production in the Greeley field of California. It was reported that asphaltic bitumen granules were observed in an oil and gas separator on a producing well. They found that the asphaltic material was deposited in the well tubing and was carried to the well head and into the processing equipment.

In the Ventura field in California [25] significant problems occurred during the early production stages of the wells. Deposition of asphaltenes was partly responsible for the plugging of well bores and tubing. During the early production period the oil was circulated to prevent and reduce the asphaltene problem. This was thought to be beneficial because it diluted the crude oil and reduced the tendency of asphaltenes to precipitate. Numerous solvents were also tried but they were not very successful. Among the solvents used were toluene, pyridine and carbon disulphide.

The author reports that the problems at the Ventura field diminished after the bottom hole pressure decreased and fell below the bubble point pressure of the crude oil. At this time many wells were redrilled and the wells have produced free from asphaltenes problems since the early 1970's.

2.6.2 Little Creek Field, Mississippi

Asphaltene deposition also occurred in the well tubing in the Little Creek CO2-flooding EOR pilot plant study in Mississippi [25]. No such problem was observed during the primary and secondary recovery history of this field. The deposition is thought to have been caused by CO_2 which in the presence of water has an acidizing effect on the reservoir. Well stimulation and acidizing fluids have a damaging effect in wells that produce asphaltenic crude oils since the acid can cause asphaltene deposition as well as well bore damage. Attempts to remove the deposited asphaltenes were often unsuccessful and in some cases permanently damaged the well. Tuttle suggested that the crude oil and the well stimulation fluids should be tested for compatibily before any well stimulation operations are conducted. In cases where asphaltenes had already precipitated, mechanical cleaning techniques were found to be the most effective.

2.6.3 Hassi Messaod Field, Algeria

Asphaltene deposits were observed in the well tubing from the early stages of production of the Hassi Messaoud field [26]. Wells often lost 20 to 25% of wellhead pressure in 15 to 20 days, causing considerable loss in production. To prevent these deposits a program for cleaning the tubing with a solvent was established. The profile and volume of deposit were determined by successive gauge rings and the amount of solvent for cleaning was determined. These profiles provided clues to the temperature and pressure conditions at the point of deposition and the evolution of the shape of the deposit. They observed that the point in the tubing most conducive to deposition was where the pressure was just under the bubble point. Based on these observations, Hasket and Tartera [26] estimated that the problems would be largely controlled if the wells were produced at low wellhead pressures. Application of this idea has greatly reduced the asphaltene deposition problems and the number of tubing washed required.

CHAPTER 3: METHODOLOGY

3.1 PROJECT FLOW

The overall project work will follow the chart below:

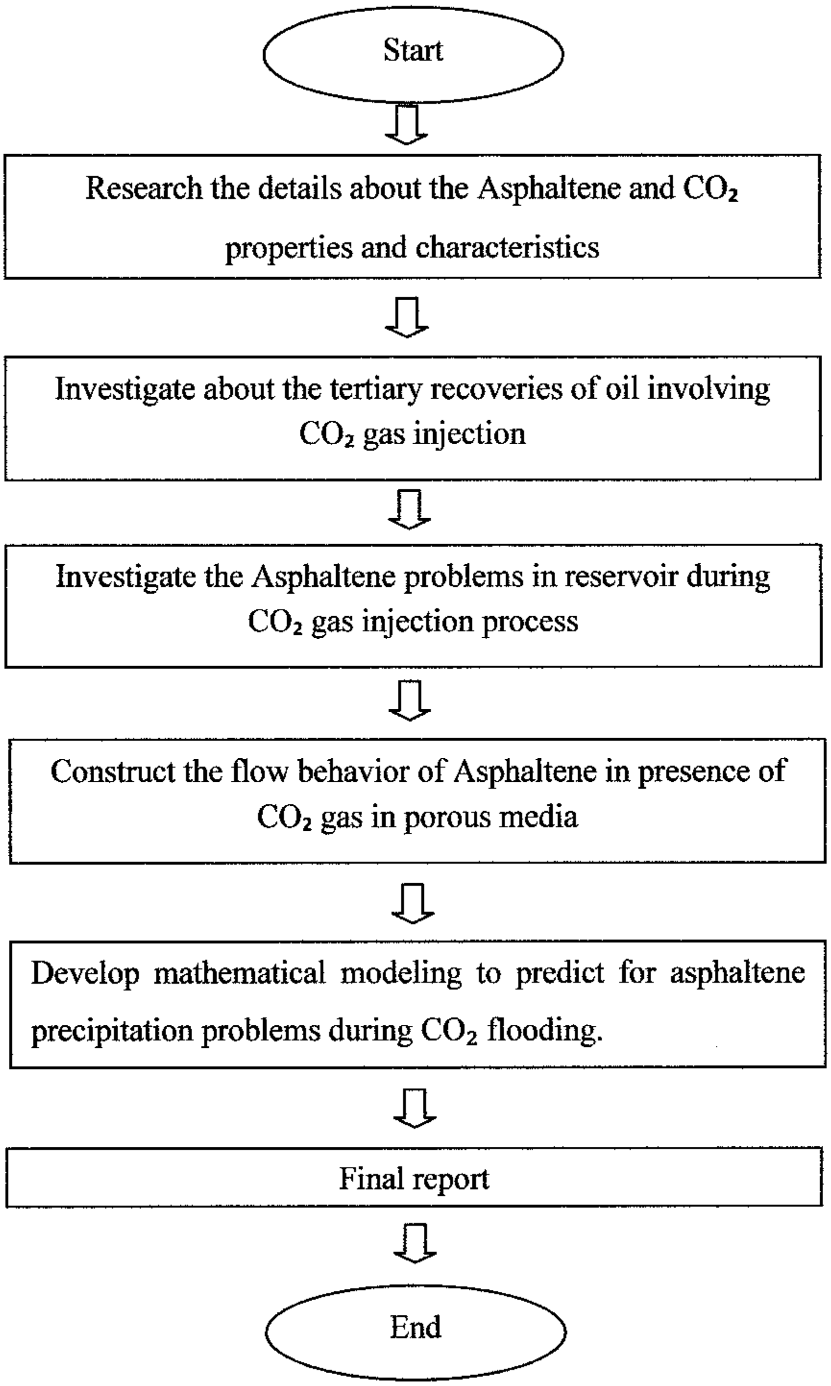


Figure 14: Project Work Flow

3.2 PROJECT ACTIVITIES

3.2.1 Develop mathematical model

The mathematical models developed are the relationship between CO_2 concentrations with:

i. **Weight percentage of asphaltene precipitation**

$$C_{oo} = -a_1 C_{co2}^3 + a_2 C_{co2}^2 - a_3 C_{co2} + a_4$$

ii. **Rock porosity reduction**

$$\emptyset = (\emptyset_0 - \sum \Delta\emptyset)$$

$$\sum \Delta\emptyset = (\delta_{ao} + \delta_{ao}^*) - (\delta_{0ao} + \delta_{0ao}^*)$$

iii. **Rock permeability reduction**

$$k = f_p k_0 \left(\frac{\emptyset}{\emptyset_0}\right)^n$$

The details on the equation will be explained in details under chapter 4, result and discussion

3.2.2 Implement field data with mathematical equation

The laboratory data is for Malaysia crude oil. From the data given, the relationship between CO_2 concentration with asphaltene precipitation, porosity and permeability reduction was developed. Then from here I plot the graph to see the relationship and do analyze the result.

The overall summary modeling work flow will follow the chart below:

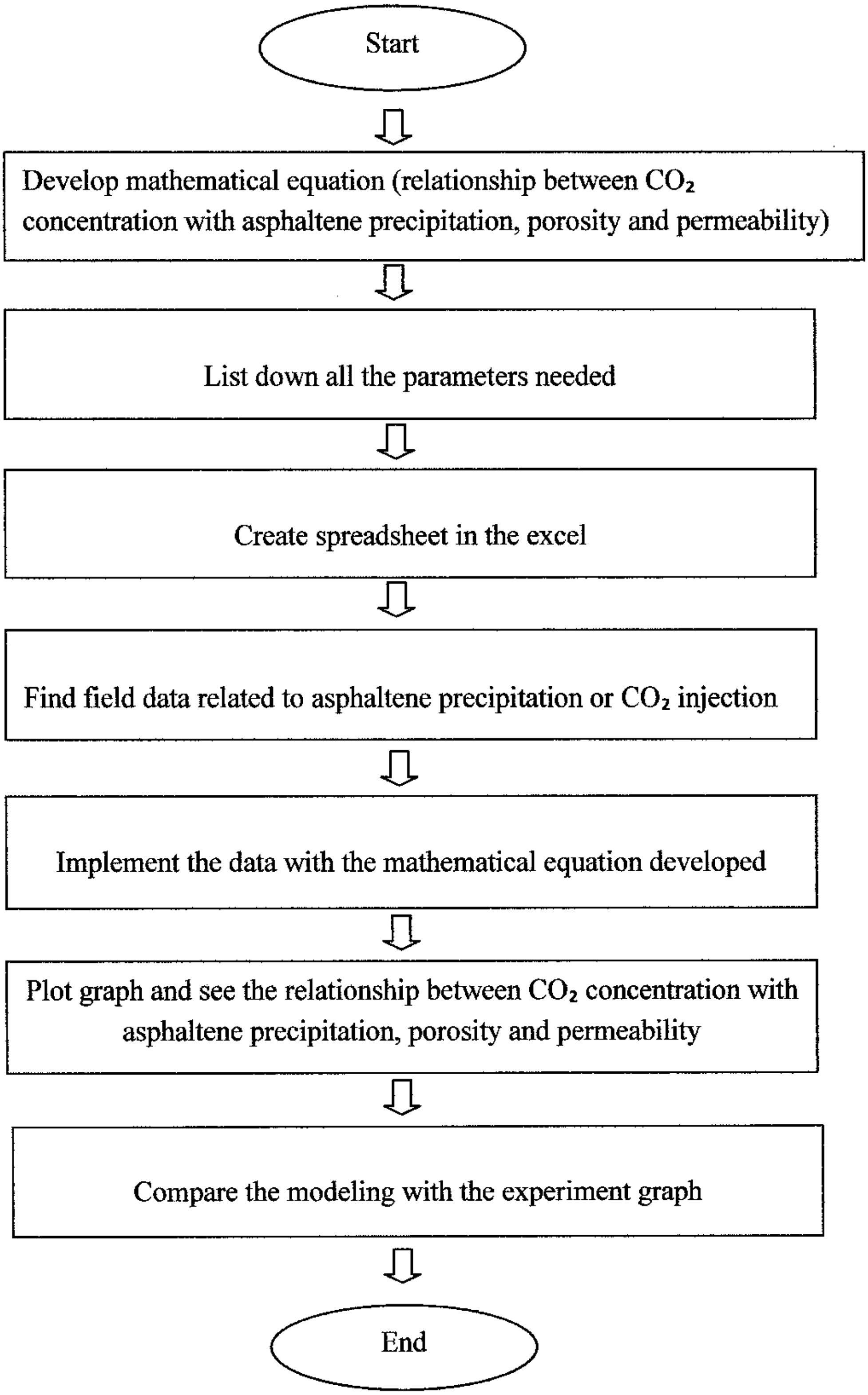


Figure 15: Summary Modeling work flow

3.3 TOOLS

The tools that have been used are as follows:

- **Microsoft excel 2007:**

  For this project I will do the modeling by using excel.

- **Information Resource Centre:**

  The library is the source of information that can be used to extract important information for this project. The main focus of research is at the journal section and the available book. Information gained from this location is of the properties of asphaltene and CO_2.

- **Online journal reviews:**

  Online journals can be found on the internet. Among the site to find journals are like OnePetro and ScienceDirect. Most of the journals available are SPE paper and PETSOC paper. The SPE paper is really helpful cause most of the paper was wrote by experienced people and have field background.

3.4 PROJECT PLANNING

No	Detail/Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14	15
1	Develop mathematical equation	🟩	🟩	🟩				Mid-Semester Break									
2	List down all the parameters needed				🟩												
3	Find field data				🟩	🟩	🟩										
4	Implement the data with the mathematical equation developed				🟩	🟩	🟩										
5	Plot and see the result						🟩		🟩								
6	Submission of Progress Report II									🟥							
7	Prepare poster										🟩	🟩					
8	Pre- EDX presentation										🟩	🟥					
9	Prepare for oral presentation											🟩	🟩	🟩			
10	Oral presentation														🟥		
11	Final report submission to supervisor															🟥	
12	Hardbound copies submission																🟥

Figure 16: Project planning

CHAPTER 4: RESULT AND DISCUSSION

4.1 FINDINGS

4.1.1 The Principles of asphaltene precipitation during CO_2 flooding

Asphaltene is the heaviest component in crude oil and it is generally in soluble state in oil reservoirs before production. Either in the process of CO_2 miscible or immiscible flooding, the solubility of CO_2, asphaltene precipitation is an adverse for it leads to formation damage and wettability alteration. Raj. K. Srivastava and Sam S. Huang et.al [15] studied the behaviors of asphaltene deposition during CO_2 flooding by experimental approach. At the operating conditions of 16MPa and 59-61°C, they have the relations between the CO_2 concentration and asphaltene flocculated for Weyburn oil samples. Asphaltene flocculated from oil can be expressed as:

$$C_{oo} = -a_1 C_{co2}^3 + a_2 C_{co2}^2 - a_3 C_{co2} + a_4 \;\ldots\ldots\ldots\; (C > C_{onset}) \text{ ------- } (1)$$

$$C_{oo} = 0 \;\ldots\ldots\ldots\ldots\ldots\; (C \leq C_{onset})$$

Asphaltene flocculated from oil may be suspended in oil and may be absorbed on pore surfaces or captured by pore throats. Asphaltene in soluble state will flow with oil flow in porous media. According to reference [16], we can draw a pressure vs CO_2 concentration chart to describe the ratio of asphaltene flocculated to total asphaltene in oil (Figure 12).

According to Figure 17, supposing the solubility of asphaltene in oil is C_s, the ratio of asphaltene flocculated to total asphaltene in oil is R_{af}, then the percentage of asphaltene flocculated in oil phase is

$$C_{oo} = C_s R_{af}(P, C_{co2}) \text{ ------------------ } (2)$$

Where P is pressure, C_{co2} is mole concentration of CO_2 in oil phase.

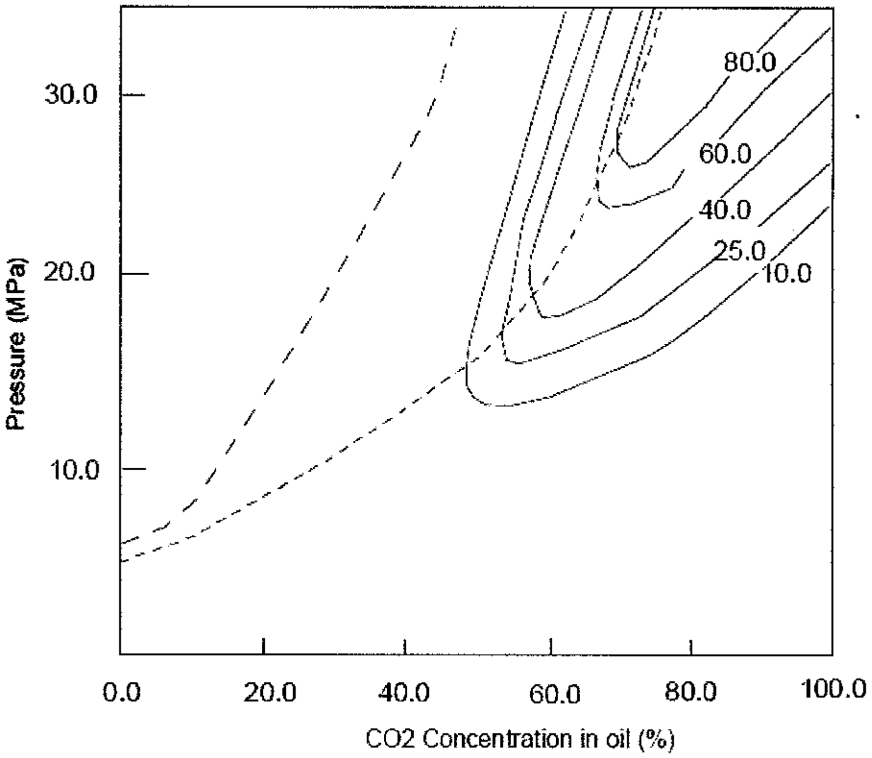


Figure 17: Pressure vs CO_2 concentration chart used for predicting asphaltene flocculation in oil (isothermal system)

Mathematical model

The mathematical model is based on the following assumptions:

1) The fluids in porous are four components and three phase
2) The model is three-dimensional and isothermal
3) Consider the compressibility of reservoir rock and fluids
4) The flows in porous media are assumed to follow Darcy's law
5) Asphaltene precipitation and its effects on porosity, permeability and wettability are considered
6) Three liquid phases are Newtonian fluids
7) Both capillary and gravity forces are considered
8) CO_2 and natural gas can be dissolved in oil and water
9) There is no water component in oil
10) There is no oil component in water

4.1.2 Thermodynamic Equilibrium

The precipitated asphaltene is represented as a pure solid while the oil and gas phases are modeled with an EOS with volume shift parameters. Let n_c be the number of components in the oil and gas phases and n_c be the index of the asphaltene component. The equations for thermodynamic equilibrium of oil, gas and solid are described in the following [27].

4.1.2.1 Asphaltene Precipitation Model

$$ln\, f_{ig} - \ln f_{io} = 0, \quad i = 1, 2, 3, \ldots.., n_c$$

$$\ln f_s - \ln f_{n_{c0}} = 0$$

Where f_{io} and f_{ig} are the components fugacities in the oil and gas phases calculated with an EOS, and f_s is the pure solid fugacity given by:

$$\ln f_s = \ln f_s^* + \frac{v_s(p-p^*)}{R\,T} \text{--------------------} (3)$$

From above equation, f_s and f_s^* are respectively the fugacities of pure solid asphaltene at pressure p and p^*, v_s is the molar volume of pure solid asphaltene, R is the universal gas constant and T is the temperature. There is solid precipitation if:

$$\ln f_{n_{c0}} \geq \ln f_s$$

4.1.2.2 Asphaltene Flocculation Model

Irreversibility of solid precipitates is modeled by allowing solid S_1 to be transformed via simple reversible chemical reaction into another solid, S_2. This can be viewed as the flocculation of smaller asphaltene particles into larger aggregates. The reaction may be written as follows [28]:

$$S_1 \leftrightarrow S_2$$

The reaction rate for the formation of S_2 is:

$$r = k_{12} C_{S1,0} - k_{21} C_{S1,0} \text{ --------------- } (4)$$

Note that S_2 can go back into the solution by first becoming S_1 through the reverse reaction, and then dissolving into the oil phase through thermodynamic equilibrium.

4.1.2.3 Asphaltene Deposition Model

An equation relating asphaltene deposition rate to the primary physical deposition processes (adsorption, pore throat plugging and entrainment) was presented by Wang and Civan [29]. In fact, they modified Gruesbeck and Collin's theory of plugging and non- plugging [30]. The discretized form of the deposition rate equation is:

$$\frac{V_{S_2^d}^{n+1} - V_{S_2^d}^{n}}{\Delta t} - \alpha C_{S_2^f}^{n+1} \emptyset^{n+1} + \beta V_{S_2^d}^{n+1} \left(v_0^n - v_{cr,0} \right) - \Upsilon . u_0^n C_{S_2^f}^{n+1} = 0 \text{ ----------------- } (5)$$

The surface deposition rate coefficient α is a positive constant and is dependent on the rock type. The entrainment rate coefficient β is set to zero when the interstitial velocity is less than critical velocity. The pore-throat plugging coefficient ϒ is set to zero if the average pore throat diameter is larger than some critical values.

When asphaltene is included, equation (6) is added to the flow equations for deposited solid S_2 and transport of solid S_2.

$$\Delta T_0^m y_{is2}^m (\Delta p^{n+1} - \Upsilon_0^m \Delta D) + V \emptyset S_0 r + q_i^{n+1} - \frac{V}{\Delta t} (N_i^{n+1} - N_i^n) = 0 \text{-------------} (6)$$

$$i = 1,2, \ldots \ldots , n_c$$

The unknowns are pressure, moles of hydrocarbon and water components, K-values, moles of S_1, and S_2, and moles deposited S_2.

4.1.3 Continuity Equation

4.1.3.1 The governing equations for multiphase flows in porous media

Since the flows of oil (o), water (w) and gas (g) in porous media follow Darcy's law, the governing equations for describing multiphase Newtonian flows are given by the following equations [31]:

i. **Water component**

$$div\left(\frac{kk_{rw}}{B_w\mu_w}\rho_w grad\Phi_w\right)+q_w=\frac{\partial}{\partial t}\left(\frac{\emptyset\rho_w S_w}{B_w}\right) \text{ -------- } (7)$$

ii. **Oil component**

$$div\left(\frac{kk_{ro}}{B_o\mu_{omix}}\rho_o grad\Phi_o\right)+q_o=\frac{\partial}{\partial t}\left(\frac{\emptyset\rho_o S_o}{B_o}\right) \text{ -------- } (8)$$

iii. **Natural gas and CO_2 component**

$$div\left(f_{vif}\frac{kk_{rg}}{B_g\mu_g}\rho_g grad\Phi_g+\frac{kk_{ro}R_{sio}}{B_o\mu_{omix}}\rho_o grad\Phi_o+\frac{kk_{rw}R_{siw}}{B_w\mu_w}\rho_w grad\Phi_w\right)+$$

$$q_{gi}=\frac{\partial}{\partial t}\left[f_{vif}\emptyset\left(\rho_g\frac{S_g}{B_g}+\rho_o\frac{R_{sio}S_o}{B_o}+\rho_w\frac{R_{siw}S_w}{B_w}\right)\right] \text{ ------------- } (9)$$

$$i = natural\ gas, CO_2$$

For flow of the three-phases of oil, water and gas, the sum of the saturations of oil, water and gas is equal to 1.

$$S_o+S_w+S_g=1$$

The summary of fraction of component in gas phase is equal to 1.0

$$\sum f_{vif} = 1$$

The three parameters regarding potentials are defined as:

$$\Phi_o = P_o + \gamma_o . h \text{ ------- } (10)$$

$$\Phi_w = P_w + \gamma_w . h = P_o + P_{cwo} + \gamma_w . h \text{ ----- } (11)$$

$$\Phi_g = p_g + \gamma_g . h = P_o + P_{cgo} + \gamma_g . h \text{----- } (12)$$

Where:

f_{vif} = mass fraction of component i

t = time

q = production or injection rate of a component

S = saturation

μ = viscosity

P = pressure

k = absolute permeability

k_r = relative permeability

B = volume factor of fluid

Ø = porosity of porous media

R_s= solution gas-oil ratio

γ = specific gravity of fluids

h = distance from reference level

Pc = capillary force

4.1.3.2 Transport of asphaltene in soluble state in porous media

Transport of asphaltene in soluble state flow in porous media can be described mathematically by convection-diffusion equation

$$\frac{\partial}{\partial x}\left(u_{xomix}C_s - \emptyset S_o D_{xs}\frac{\partial C_s}{\partial x}\right) + \frac{\partial}{\partial y}\left(u_{yomix}C_s - \emptyset S_o D_{ys}\frac{\partial C_s}{\partial y}\right) + \frac{\partial}{\partial z}\left(u_{zomix}C_s - \emptyset S_o D_{zso}\frac{\partial C_s}{\partial z}\right) + \emptyset S_o \frac{\partial C_s}{\partial t} + R_{Loss} + Q_s = 0 \text{ ------- } (13)$$

Where:

C_s = solubility of asphaltene in oil

D = diffusivity of asphaltene

R_{Loss} = the flocculated rate of asphaltene from soluble state in oil; x,y and z are three space dimensions

Q_s= rate of change of asphaltene caused by a source/sink terms

4.1.3.3 Transport of flocculated asphaltene in porous media

Flocculated asphaltene suspended in the oil phase or be adsorbed on pore walls. In as much as the asphaltene suspended is small enough in size, diffusion should be also considered. Thus, considering Brownian diffusion effects in the process of asphaltene migration in porous media, the continuity equation for asphaltene in oil phase can be expressed as by modifying the equation [32]

$$\frac{\partial}{\partial x}\left(u_{xomix}C_{ao} - \emptyset S_o D_{xao}\frac{\partial C_{ao}}{\partial x}\right) + \frac{\partial}{\partial y}\left(u_{yomix}C_{ao} - \emptyset S_o D_{yao}\frac{\partial C_{ao}}{\partial y}\right) + \frac{\partial}{\partial z}\left(u_{zomix}C_{ao} - \emptyset S_o D_{zao}\frac{\partial C_{ao}}{\partial z}\right) + \emptyset S_o\frac{\partial C_{ao}}{\partial t} + R_{ao} + Q_{ao} = 0 \text{ --------------- } (14)$$

Where:

C_{ao}= volume concentration of flocculated asphaltene in oil phase

D= diffusivity of asphaltene

R = the netting asphaltene change rate on the pore surfaces; x,y and z are three space dimensions

Q = the rate of change of asphaltene volume described by a source/sink term

Hydrodynamic forces can release the asphaltene adsorbed on pore walls. Asphaltene deposition on pore surfaced will occur when the onset of asphaltene precipitation reached and pore throats may also capture asphaltene solid particles when the size of solid asphaltene is large enough comparing to the diameters of pore throats of porous media. According to the mechanisms of asphaltene change on pore surfaces or at pore throats, the R_{ao} in equation (14) can further be written as

$$R_{ao} = R_{hao} + R_{dao} + R_{pao} \text{ ---------- } (15)$$

Where:

R_{hao} = asphaltene release rate from pore wall by hydrodynamic forces

R_{dao} = the deposition rate on pore surfaces

R_{pao} = the capture rate at pore throats

$R_{hao,} R_{dao} R_{pao}$ can be defined as:

$$R_{hao} = -\propto_{hao} \partial_{ao}(v_o - v_{oc})$$

$$R_{dao} = \propto_{dao} v_o C_{ao}$$

$$R_{pao} = \propto_{pao} V_o C_{ao}$$

Where:

v_{oc} = critical flow velocity of oil phase for asphaltene release from pore surface by hydrodynamic forces

$\propto_{hao}$= rate constant for the release of asphaltene by hydrodynamic forces

∂_{ao}= volume of asphaltene deposited on pore surfaces per unit bulk volume

$\propto_{dao}$= rate constant for asphaltene deposition on pore surfaces when asphaltene deposition onset arrives

$\propto_{pao}$= capture rate constant of asphaltene at pore throats when asphaltene deposition onset arrives

4.1.4 Evaluation for porosity and absolute permeability

Generally, the pore bulk volume is regarded as being slightly compressible and permeability is regarded as a constant [33, 34]. However, the asphaltene release from pore surfaces, the adsorption on pore surfaces, and blocking at pore throats in the process of asphaltene migration may lead to the changes in local porosity and permeability. The instantaneous porosity is expressed by

$$\emptyset = (\emptyset_0 - \sum \Delta\emptyset) \text{ ------------ } (16)$$

Where $\sum \Delta\emptyset$ denotes the variation of porosity by release and retention of asphaltene in porous media, and it is expressed by

$$\sum \Delta\emptyset = (\boldsymbol{\delta_{ao}} + \boldsymbol{\delta^*_{ao}}) - (\boldsymbol{\delta_{0ao}} + \boldsymbol{\delta^*_{0ao}}) \text{ ---------- } (17)$$

Where:

$\boldsymbol{\delta_{ao}}$= volume of asphaltene deposited on the pore surfaces per unit bulk volume

$\boldsymbol{\delta^*_{ao}}$= the volume of asphaltene trapped at the pore throat per unit bulk volume

0 = initial time

If $\sum \Delta\emptyset$ is greater than 0, the retention of asphaltene is dominant, and the porosity will decrease, (i.e $\emptyset < \emptyset_0$). If $\sum \Delta\emptyset$ is less than 0, the release of asphaltene is dominant, and the porosity will increase.

The change in permeability in this study is caused by asphaltene release and mobilization. Modifying Kozeny Equation, taking into account the asphaltene plugging effect, and according to the study of Liu [35], the expression for instantaneous permeability changed by release and retention of asphaltene is given by:

$$\boldsymbol{k = f_p k_0 (\frac{\emptyset}{\emptyset_0})^n} \text{ -------------------- } (18)$$

Where:

k_0= initial permeability

$\emptyset_0$= initial porosity

k = instantaneous local permeability of porous media

$\emptyset$ = porosity of porous media

n = index number range from 2.5 to 3.5

f_p= permeability modification factor

A flow efficiency factor, f_p, is defined as the fraction of the original cross-sectional area open for flow. According to Ju's expression [36], the flow effiency factor, f_p, as a linear function of the volume of asphaltene entrapped at pore throats, is given empirically by

$\boldsymbol{f_p = 1 - \propto_{feao}\ \delta^*_{ao}}$, where $\propto_{feao}$ is the coefficient of flow efficiency.

4.2 NUMERICAL RESULTS AND DISCUSSIONS

4.2.1 Asphaltene precipitation

This section will discuss the mathematical modeling developed for Malaysian crude oil. It will cover the relationship between CO_2 concentration with asphaltene precipitation, porosity and permeability. Below is the laboratory data for Malaysian crude oil:

Table 1: Asphaltene precipitation (wt %)

CO_2 (mol %)	Asphaltene precipitation, lab (wt %)
20	0
22	0.503
40	0.703
70	1.36
85	1.75

This experiment was conducted at pressure and temperature of 3008 psia and 204°F. To have a better picture below is the plot of asphaltene precipitation (wt %) vs CO_2 concentration (mol %):

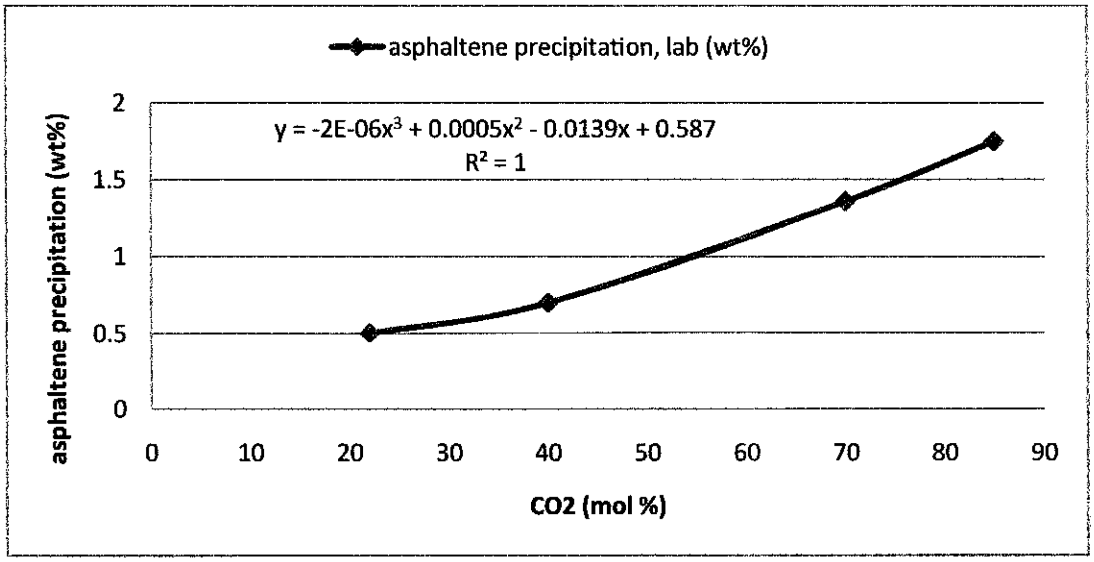


Figure 18: Cumulative asphaltene precipitation with different % mol of CO_2 at 3008 psia and 204°F

From figure 18, as we can see that asphaltene starts to precipitate at the concentration of 22% mol of CO_2 and increases slowly until 40% mol CO_2. After 40% mol CO_2 there was a linear increase of asphaltene precipitation with amount of injected CO_2. According to Srivastava study [37] the onset point for asphaltene flocculation for Weyburn reservoir was in the range of 39-46 mol % CO_2 concentration. The flocculation increased linearly with CO_2 concentration after the onset. This is because, it is believes that as the CO_2 gas injected into the reservoir, it will cause resin to solute in CO_2, it will become lesser support to the asphaltene, resulting in asphaltene and resin molecules precipitating out of the oil. Therefore, as we increase the concentration of CO_2 more resin will solute in CO_2 resulting in more asphaltene precipitate out of the oil due to lesser support of the resin.

From figure 18, mathematical equation can be developed using trend line of polynomial order 3. This is corresponding to equation no (1) stated in the finding above. The relationship between asphaltene precipitation and CO_2 concentration can be modeled as:

$$\boldsymbol{C_{oo} = -2x10^{-6}C_{co2}^{3} + 0.0005C_{co2}^{2} - 0.0139C_{co2} + 0.587} \text{------------ } \mathbf{(19)}$$

By using equation (19), we can predict the amount of asphaltene precipitation at any CO_2 concentration. Next is the graph for both experimental and mathematical modeling for this Malaysian crude oil:

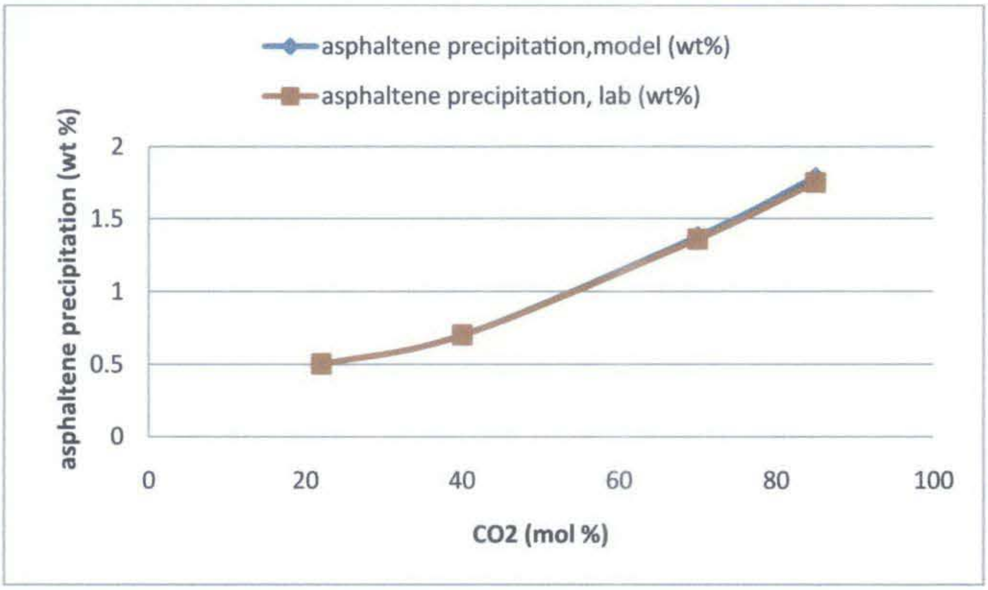


Figure 19: comparison between lab and modeling data

From figure 19, there is not much different between mathematical modeling with the experiment data. Therefore equation (19) is valid to use to predict asphaltene precipitation for this Malaysian crude oil for the specific field in the future or maybe it can be first estimation for any area nearer to the field. However each type of crude oil has its own different properties that might have some influence on asphaltene precipitation too. Therefore, at present the mathematical modeling is limited to case study only not be a general study yet. This can be proved by looking at the asphaltene precipitation reported for Weyburn Reservoir [37]. Figure 20 shows the same shape as figure 19, as the concentration of CO_2 is increase; the % of asphaltene precipitation also will be increased. However the value will be different since as stated above each type of crude oil will have different properties and this might affect the asphaltene precipitation.

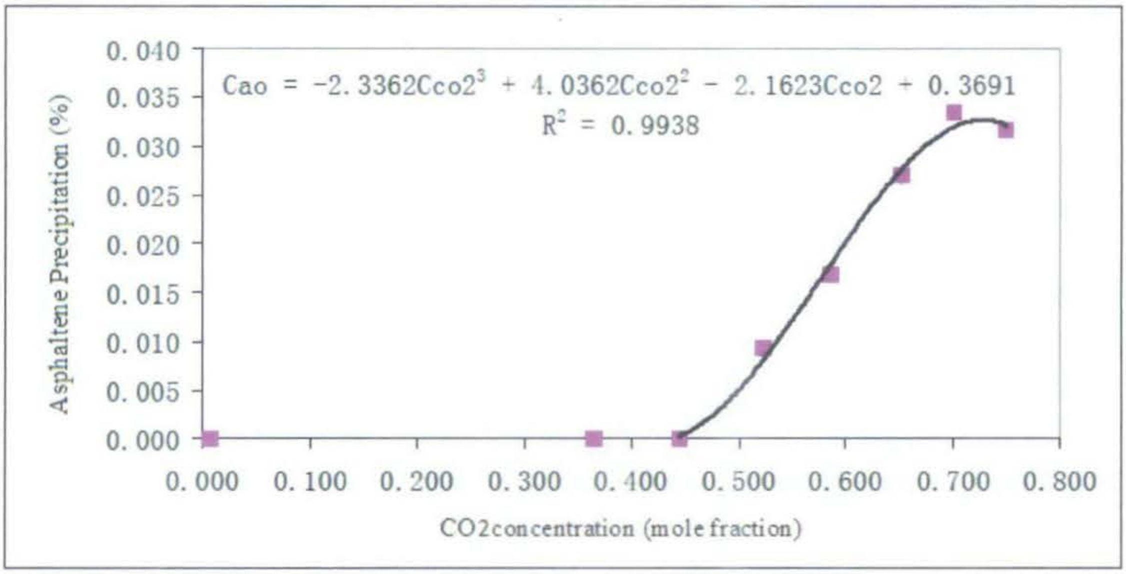


Figure 20: the relations between CO_2 concentration and asphaltene precipitation for Weyburn reservoir.

4.2.2 Porosity and permeability reduction

Below is the main parameters given for this Malaysian crude oil field:

Table 2: parameters of the field

Parameters	Value
Initial porosity	19 %
Initial permeability	70 mD
Oil viscosity	0.3 cp
Initial asphaltene content of oil	0.117 wt%
Asphaltene density	1.19 g/mL
$\propto_{feao}$	110

4.2.2.1 Porosity reduction

The porosity reduction can be calculated by using equation (16):

$\emptyset = (\emptyset_0 - \sum \Delta\emptyset)$ and $\sum \Delta\emptyset = (\boldsymbol{\delta_{ao}} + \boldsymbol{\delta^*_{ao}}) - (\boldsymbol{\delta_{0ao}} + \boldsymbol{\delta^*_{0ao}})$.

The porosity reduction was tabulated below:

Table 3: Porosity reduction

Asphaltene precipitation (wt %)	Volume asphaltene precipitation (cm^3)	Fraction of deposited asphaltene/bulk volume	Porosity (%)
0	-	-	19.0000
0.503	2.515	0.002515	18.7485
0.703	3.515	0.003515	18.6485
1.36	6.800	0.006800	18.3200
1.75	8.75	0.00875	18.1250

From the porosity calculated in table 3, graph porosity vs CO_2 concentration was plotted:

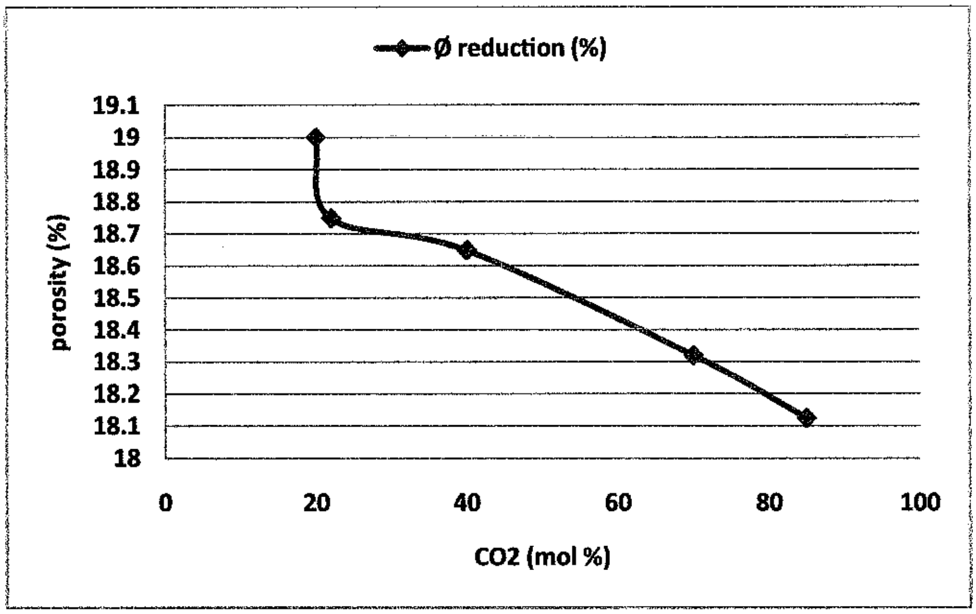


Figure 21: Reduction in rock porosity after CO_2 flooding

As can see from above figure 21, the rock porosity is tending to reduce due to the asphaltene precipitation. This is because it is believed that asphaltene particle size and salt aggregates are larger or the same size as the rock pore throats. Thus, it will plug the pore spaces inside the rock. Therefore it will reduce the porosity of the rock as we know the definition of porosity is pore volume of the rock over total bulk volume.

4.2.2.2 Permeability reduction

The permeability reduction can be calculated by using equation (18):

$$k = f_p k_0 (\frac{\emptyset}{\emptyset_0})^n$$

The permeability reduction was tabulated below:

Table 4: permeability reduction

CO2 (mol%)	Asphaltene precipitation, lab (wt%)	Ø reduction (%)	δ_{ao}	f_p	K reduction (mD)
20	0	**19**			**70**
22	0.503	18.7485	0.002515	0.72335	48.650276
40	0.703	18.6485	0.003515	0.61335	40.595446
70	1.36	18.32	0.0068	0.252	15.812997
85	1.75	18.125	0.00875	0.0375	2.2787808

From the permeability calculated above, graph permeability vs CO_2 concentration was plotted:

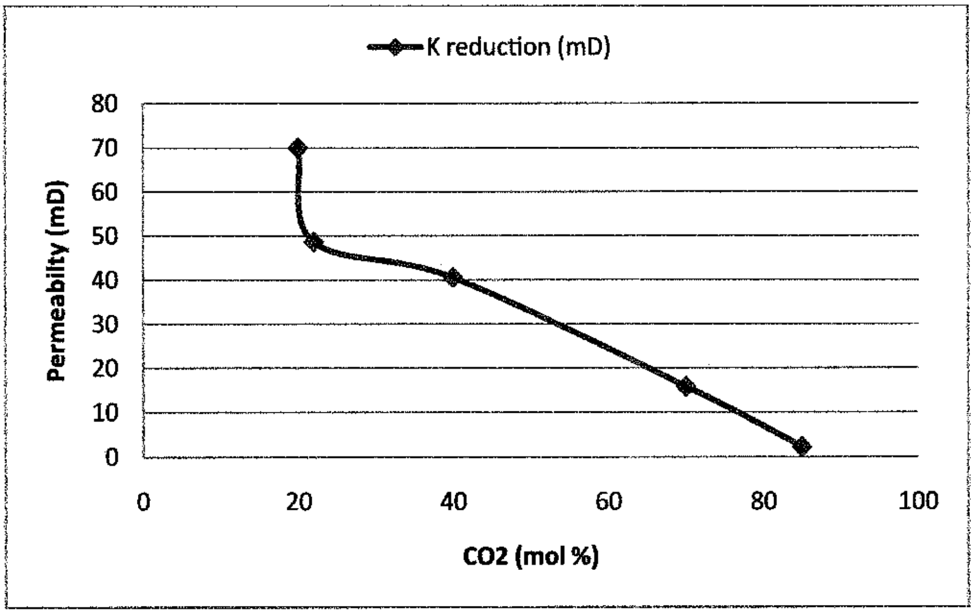


Figure 22: Reduction in rock permeability after CO_2 flooding

As can see from above figure 22, the rock permeability is tending to reduce due to the asphaltene precipitation. This is because the pore spaces in the rock were plugged by the small particles of asphaltene. Thus the pore spaces are not interconnected to each other thus it will decrease the ability of the rock to transmit fluid. Next is the combination of rock porosity and permeability reduction:

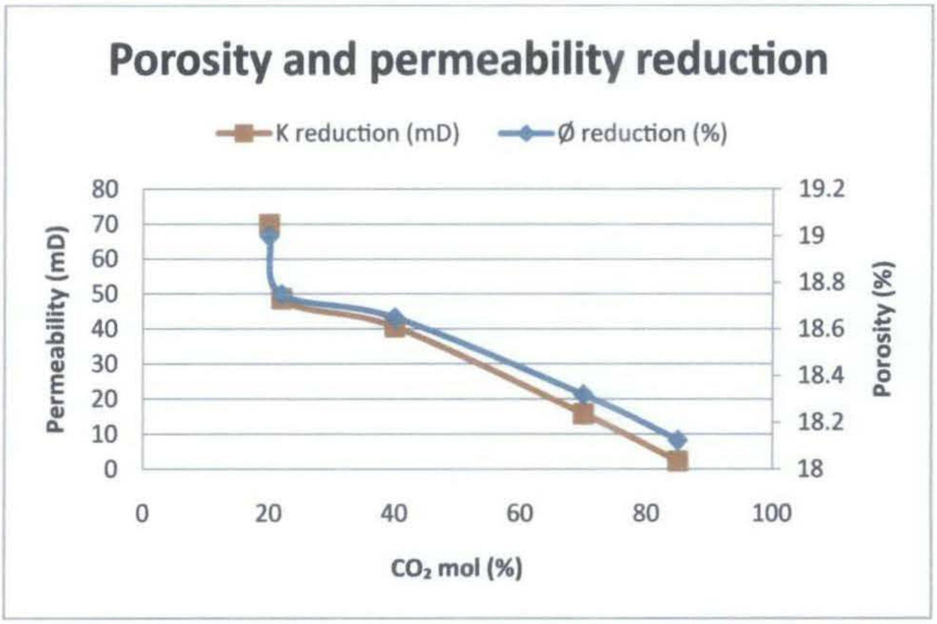


Figure 23: Reduction in rock porosity and permeability reduction after CO_2 gas injection

The shape of rock porosity and permeability reduction is almost the same because permeability is always correlated with the porosity. This is because permeability is the measurement of a rock's ability to transmit fluids. In or order to allow the fluid to move, the pore volume must be interconnected to each other. Normally, as the porosity decrease, the permeability will decrease as well.

Abdulrazaq et.al [38] reported in their study on carbonate formation, the porosity and permeability of the rock is reduced after CO_2 flooding:

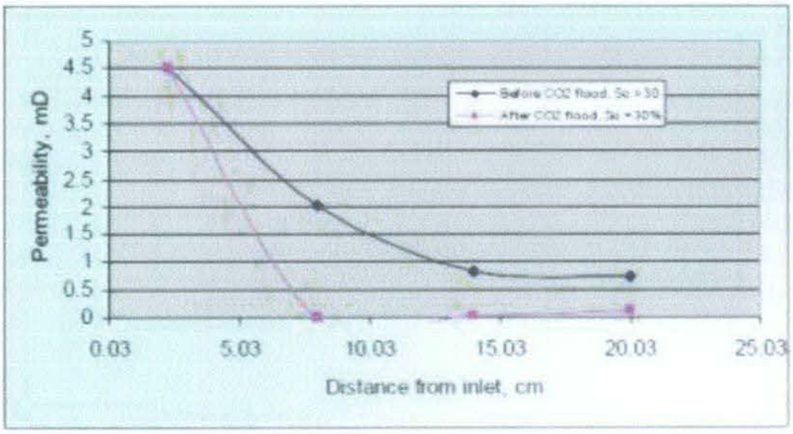


Figure 24: permeability reduction after CO_2 flooding [38]

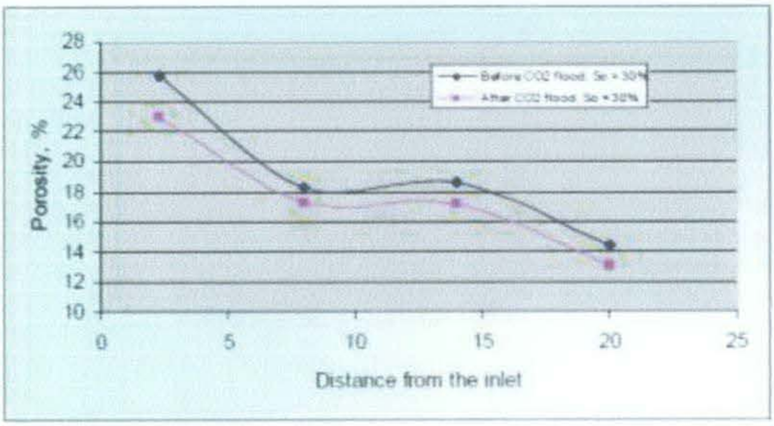


Figure 25: porosity reduction after CO_2 flooding [38]

This reported observation suggests that there is no specific value for finding porosity and permeability reduction based on CO_2 concentration. It is depending on the type of rock for that specific field. Therefore, at present the asphaltene precipitation study is limited to case study only and could not be a general study yet.

CHAPTER 5: CONCLUSION

5.1 CONCLUSION

As a conclusion asphaltene content in the Malaysia crude oil starts to precipitate at the concentration of 22% mol of CO_2 and increases slowly until 40% mol CO_2. This shows that the amount of asphaltene precipitation is depending on the CO_2 concentration. Also shows that quite significance amount of porosity and permeability reduction due to the asphaltene precipitation. This is because the pore spaces in the rock were plugged by the small particles of asphaltene. There is no specific value for finding porosity and permeability reduction based on CO_2 concentration. It is depending on the type of rock for that specific field as well.

Precipitation of asphaltene is really a serious problem since it can cause plugging of reservoir formation, wellbore, tubing and production facilities. As it is difficult to control and remedy the effects asphaltene precipitation (such as severe permeability reduction and wettability alteration) within the reservoir, a prior investigation into the characteristics and impact of asphaltene precipitation during CO_2 injection is crucial and critical to the design of a successful CO_2 injection project. Therefore the topic is worth to be explored since many tertiary recoveries – EOR projects are in the design or implementation stage in many parts of the world to help meeting this extra global oil demand.

For this project have been achieved all the objectives stated in chapter 1(background) which is first investigating asphaltene flow behavior in presence of CO_2 gas in porous media. As stated in this report earlier, once we injecting CO_2 gas in the reservoir it might affect the stability of the oil components which are asphaltene and resins. Once this happen, it will cause asphaltene to precipitate, flocculate and the worst case is it will cause deposition. This deposition may reduce the porosity and permeability of the rock, thus will lower the percentage of oil recovery. Asphaltene deposition not only lead to formation damage but also in worse case will cause well plugging. Second is to study and understand the characteristics of asphaltene in the crude oil. Lastly is developing mathematical modeling considering the relationship of CO_2 concentration with the asphaltene precipitation, porosity and permeability reduction problems during CO_2 flooding. This is the main objective for this project which has been shown in the result and discussion section. The comparison between experiment results with mathematical model results for asphaltene precipitation also shown.

5.2 RECOMMENDATION

These are some of the recommendations to further enhance this study in future work:

i) If possible get the values of porosity and permeability of the rock right after the CO_2 injection. Then compare it with the model and from here can know either the model is valid or not.

ii) Do the experiment on the core sample to see the reduction of porosity and permeability after inject CO_2 gas at specific temperature and pressure.

iii) Look at how asphaltene precipitation will be affected by the pressure and temperature changes instead of just looking at CO_2 concentration.

iv) Investigate on how the amount of asphaltene content in the crude oil will affect the precipitation at the constant CO_2 concentration.

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APPENDIXES

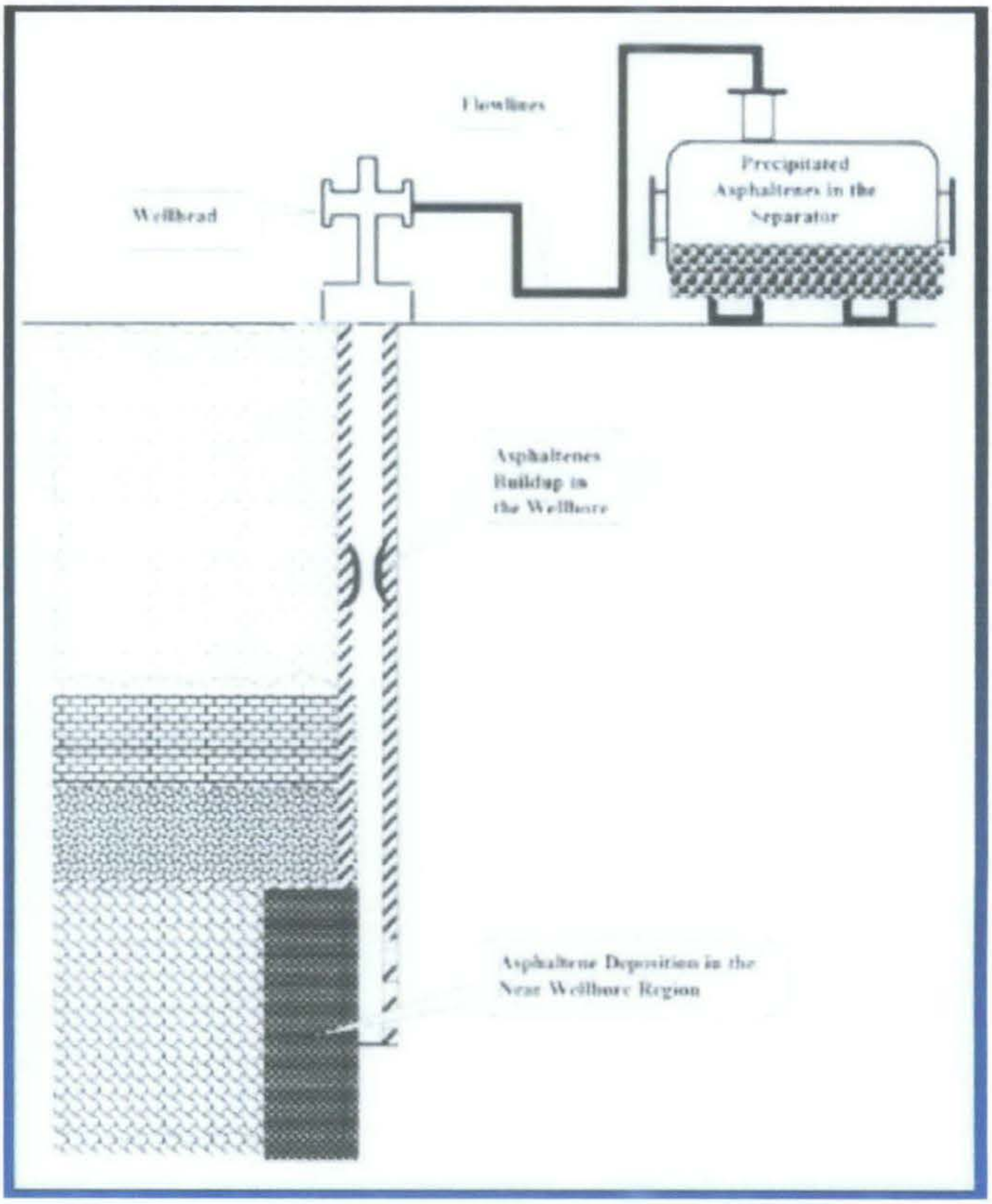

Figure 26: Asphaltene precipitation in the wellbore

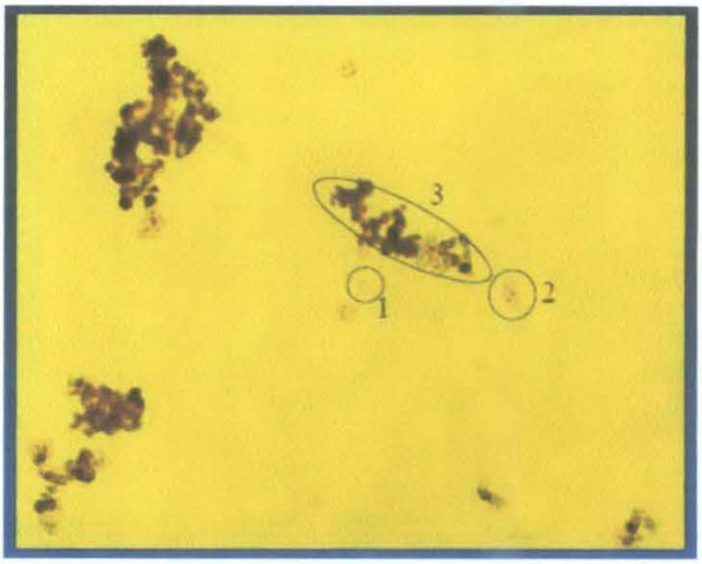

Figure 27: Asphaltene flocculates under microscope

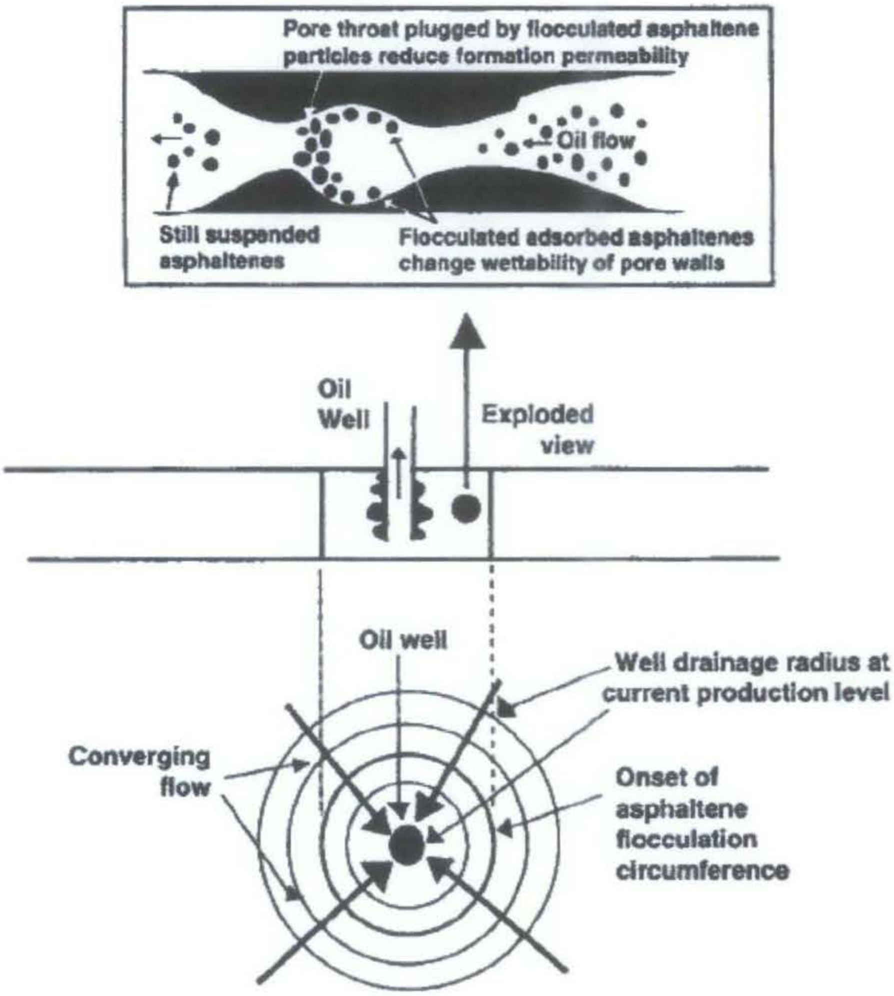

Figure 28: Asphaltene flocculation and deposition near a producing well