

**Kinetics of Polymer Retention in Porous Media and its Influence in Enhanced
Oil Recovery (EOR) Applications**

by

Lukman Bin Sani

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JULY 2010

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CERTIFICATION OF APPROVAL

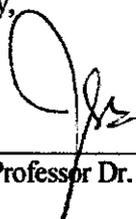
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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,



(Associate Professor Dr. Isa Bin Mohd Tan)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2010

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.



LUKMAN BIN SANI

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ABSTRACT

A research project consisting of experimental studies has been planned and executed successfully to generate information required for the performance of enhanced oil recovery (EOR) by chemical flooding employing polymer. This paper ultimately covers the theoretical and the experimental works, which include the studies of adsorption kinetics and equilibrium characteristics of the polymer on reservoir rocks and its flooding performance. This research is particularly interesting with huge opportunities to learn on how the performance of polymers for enhanced oil recovery (EOR) can be remarkably enhanced, by introducing surfactant and alkali to polymer backbone, which allows the new class of modified polymers to have more promising oilfield application.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

According to recent reports, current estimates set the total oil reserve amounts of the world to a total of 1950 gigabarrels (gb) with a margin of error no greater than 10 %.¹ Currently, the rate of oil consumption is 27 gb per year, and is expected at 42 gb per year in the year 2020. At the current rate of consumption some current predictions suggest that oil will run out in about 50 years.²

Current oil prices have renewed interests in more economical means of acquiring trapped residual oil. Therefore, the interest in EOR has been high in recent years compared to previous. Primary oil recovery, performed by pumping action, nets 15-20 % of the oil in a well and secondary oil recovery, performed by water flooding, nets an additional 15-25% of the oil.³ Used in fields that exhibit heavy oil, poor permeability and irregular faultlines, EOR entails changing the actual properties of the hydrocarbons, which further distinguishes this phase of recovery from the secondary recovery method.

While waterflooding and gas injection during the secondary recovery method are used to push the oil through the well, EOR applies steam or gas to change the makeup of the reservoir. Whether it is used after both primary and secondary recovery have been exhausted or at the initial stage of production, EOR restores formation pressure and enhances oil displacement in the reservoir.

¹ Aleklett, K., Nyoljekris för dörren, *Svenska Dagbladet*, 2002, April 24, p. 5.

² Emerson, T., The Thirst for Oil, *Newsweek the International Newsmagazine*, 2002, April 8, p.32-35

³ Jönsson, B., Lindman, B., Holmberg, K. and Kronberg, B., 19. *Microemulsions for Oil and Soil Removal in Surfactants and Polymers in Aqueous Solution*, John Wiley & Sons, Chichester, 2001, p. 382-385.

1.2 PROBLEM STATEMENT

When petroleum reservoirs are depleted by natural drive mechanisms due to decreasing reservoir pressure, only a small fraction of the oil can be produced (30-40%). Implementing a secondary recovery, water flooding, would still not produce all the recoverable oil present in the reservoir.

The interest in chemical flooding utilising polymer for enhanced oil recovery (EOR) has grown enormously but developments to address few weak areas have been quite limited especially on the polymer retention in porous media. Numerous papers, patents and proceedings have been published on the selection of polyacrylamide as one of the most widely used polymers in chemical flooding despite of its reported defects in several oilfield applications.

This exploratory research is thus focused on polymer retention, through quantification and modelling of the effect of polymer adsorption on reservoir rocks to help understand its phenomenon better. The data gathered from the studies of adsorption mechanism through adsorption kinetics and equilibrium characteristics are then modelled and best fitted. The polymer flooding performance is further evaluated by core flood technique.

1.3 OBJECTIVES AND SCOPE OF STUDY

The aim of the project is to conduct a study that will utilise the experimental means available at Universiti Teknologi PETRONAS in which the main objectives are:

- To study the concept and principles of Enhanced Oil Recovery and the role of polymer
- To investigate the adsorption mechanism through the kinetic studies and equilibrium characteristics of polymer on the reservoir rocks
- To validate how much more oil can be obtained by polymer incorporation

This research project is comprised of experimental studies, coupled with relevant engineering analyses to represent the findings more accurately.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION TO ENHANCED OIL RECOVERY

Oil production is separated into three phases: primary, secondary and tertiary, which is also known as Enhanced Oil Recovery (EOR). Primary oil recovery is limited to hydrocarbons that naturally rise to the surface, or those that use artificial lift devices, such as pump jacks. Secondary recovery employs water and gas injection, displacing the oil and driving it to the surface. The way to further increase oil production is through the tertiary recovery method or EOR. Although more expensive to employ on a field, EOR can increase production from a well to up to 75% recovery.

2.2 TYPES OF EOR TECHNIQUES

EOR consists of injecting a displacing fluid into injection wells in order to displace the oil and gas in a reservoir towards producing wells. There are many types of EOR techniques and suitable for different conditions of reservoir.

The first type of EOR technique is the thermal process, where a hot invading face, such as steam or hot water or a combustible gas, is injected, in order to increase the temperature of the oil and gas in the reservoir and facilitate their flow to the production wells, by increasing the pressure and reducing the resistance to flow.

Another EOR technique consists of injecting a miscible phase with the oil and gas into the reservoir in order to eliminate the interfacial tension effects. The miscible phase can be a miscible hydrocarbon, CO₂ or an inert gas.

Finally, the last EOR technique is the so called chemical flooding, where it is a combination of alkaline-surfactant-polymer (ASP), surfactant-polymer or polymer alone when they are injected into the reservoir. The polymer is used to improve the sweep efficiency of the invading fluid by changing the mobility ratio between the invading fluids versus the displaced fluid (oil).

The surfactant is present to change the wettability of the formation rock and to reduce the interfacial tension. On the other hand, the alkali is used to create the in-situ petroleum soaps to reduce the use of foreign surfactants and to reduce the adsorption of surfactant for economic reasons.

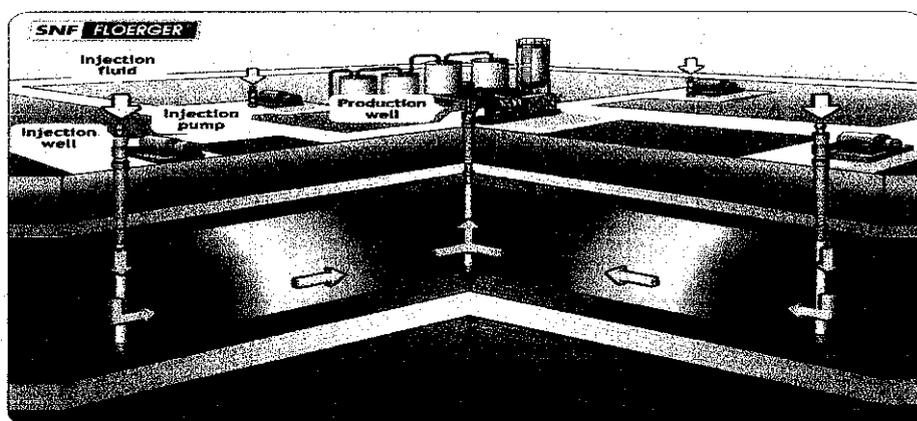


Figure 1: Schematic of Chemical Flooding

However, this study is concentrated on the chemical flooding employing modified polymer as we have the flexibility to go into microscopic level to alter its structure, to tailor it to our industrial needs. With the use of modified polymer, that is, by adding either an alkaline or surfactant chemical or both, in a polymer flood will scour residual oil from the rock, resulting in higher oil recovery than with polymer alone.

But of course this comes with a great challenge to prepare the formulations as clean as possible to ensure smooth injectivity into the reservoirs. Therefore, with the right amount of challenge and huge opportunities to learn, this has been the reason why this research is appealing, and benefiting the accessibility of the equipments and resources required to conduct the experiments.

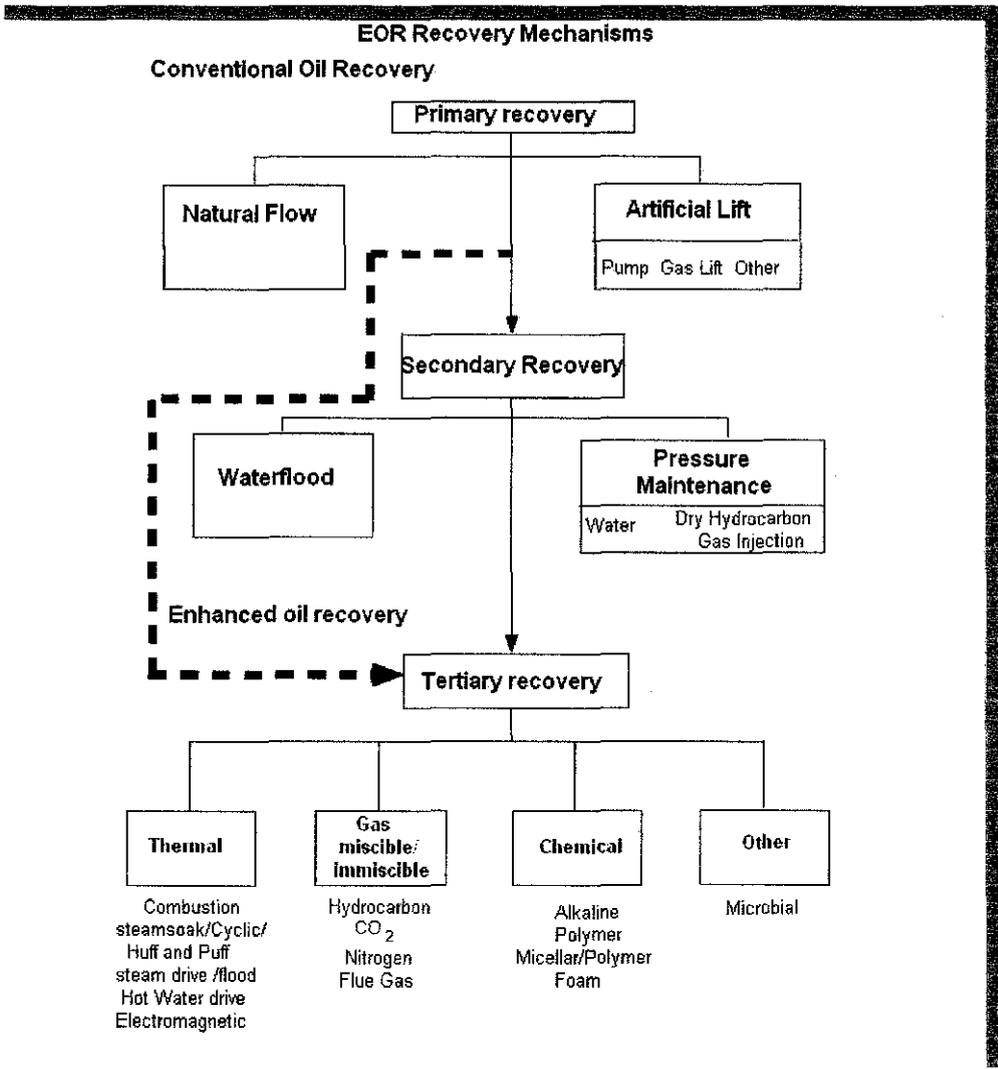


Figure 2: Summary of oil recovery methods

2.3 CHARACTERISTICS OF POLYMER FLOODING

Water soluble polymer used for EOR may be divided into two groups: polymers that are produced synthetically and polymers that are natural products from wood, seeds etc or those produced by bacteria or fungi, which are essentially polysaccharides.

2.3.1 Background of Synthetic Polymers

Polyacrylamides, (*abbreviated as PAM*) are water soluble polymers which are produced by manufacturers in many ways for different purposes, for instance as emulsifying agent in oil recovery. The monomer acrylamide is a compound derived from acrylic acid. The most important representatives of the chemical group that acrylic acid belongs to are;

$\text{CH}_2 = \text{CH} - \text{COOH}$	acrylic acid
$\text{CH}_2 = \text{CH} - \text{CN}$	acrylnitril
$\text{CH}_2 = \text{CH} - \text{COOR}$	acrylic acid ester
$\text{CH}_2 = \text{CH} - \text{CONH}_2$	acrylamide
$\text{CH}_2 = \text{CH} - \text{CHO}$	acrolein

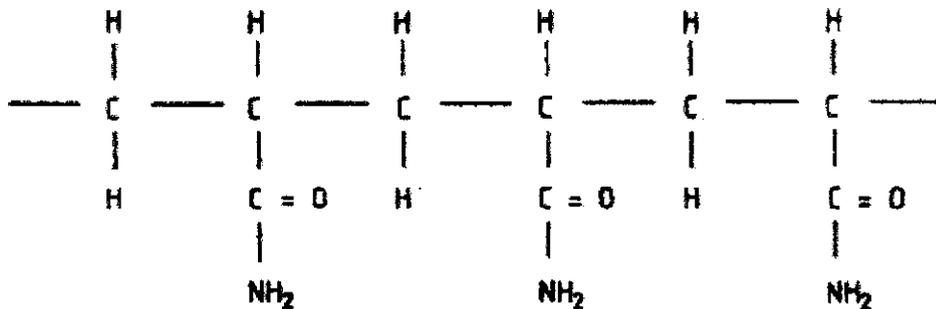


Figure 3: Structure of PAM (not hydrolyzed)

The molecular weight of polyacrylamides is between 1×10^6 and 8×10^6 g/g-mol. The size of the molecules is about 0.1 - 0.3 μm (UNSAL et. al, 1979). It is well known that high equivalent molecular weight surfactants are adsorbed preferentially on the rock surface while the lower equivalent molecular weight surfactants show very little adsorption (Akzo Nobel, 2006).

By hydrolysis in a caustic water solution some of the CONH_2 groups react to form carboxyl groups (COOH). The degree of hydrolysis is an important parameter which determines the properties of polyacrylamide in aqueous solutions as used in enhanced oil recovery. The carboxyl groups dissociate in an aqueous solution. The structure of a polyacrylamide molecule is as shown in Figure 4 below.

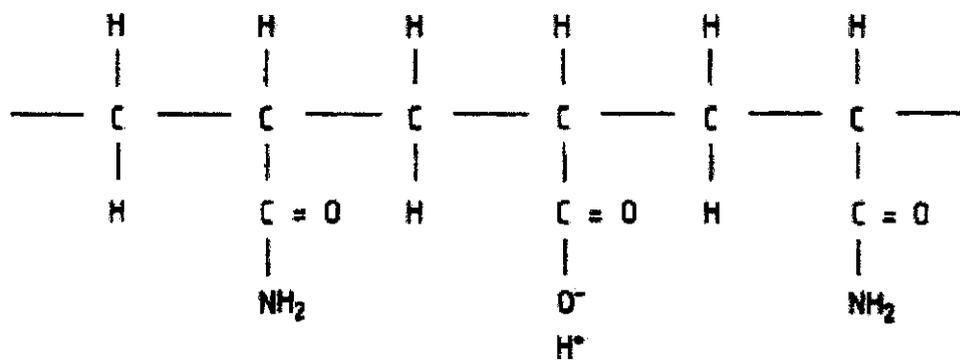


Figure 4: Molecular structure of partially hydrolyzed polyacrylamide

The structure above is representative for a polyacrylamide with a 25% of hydrolysis. The negative charges of the dissociated carboxyl groups interact in a pure, distilled water solution so that the repulsion of the charges having the same polarity keep the molecule chain in a more or less stretched form.

This produces a molecule coil in solution that assumes the largest volume possible in the solution (together with bounded solvent in the molecule coil), what results in a high viscosity yield. If only a low amount of cations is present in the water, the negative charges of the oxygen are compensated and the molecule tends to curl, so that it assumes a smaller volume in the solution.

With higher amounts of divalent cations the molecules may be cross-linked by this mechanism, so that a gel may form if the polymer concentration is high enough, or molecular aggregates are formed that fall out of solution. The configuration of a polymer molecule in solution is illustrated in Figure 5.

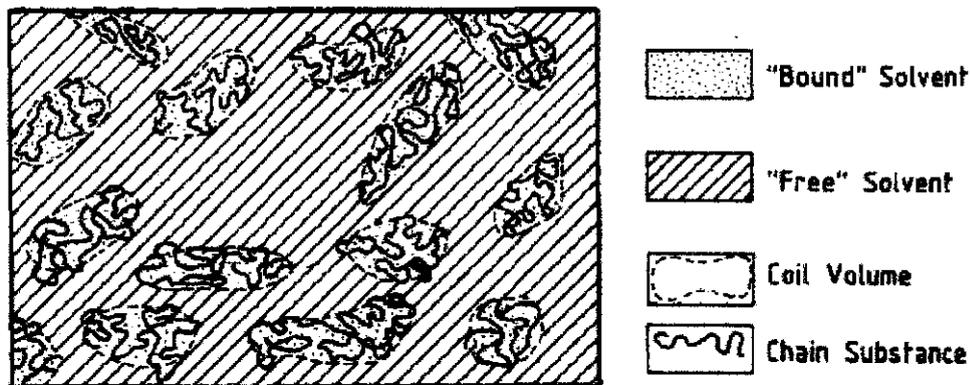


Figure 5: Illustration of a coiled polymer molecule in solution (Vollmert, 1980)

The percentage of acrylic acid in the molecule chain gives the degree of hydrolysis. Most products used for EOR have degrees of hydrolysis of 25% - 30%. But products having degrees of hydrolysis approximating zero are also available.

These products do not exhibit as strong sensitivity to salts as products of a high degree of hydrolysis do. They may be used for preconditioning reservoirs as mentioned. But one must keep in mind that a higher concentration of these products is needed, and that during flooding in a reservoir some hydrolysis always takes place which may change the chemical character of the product.

2.4 POLYMER RETENTION IN POROUS MEDIA

Water-soluble polymers are displacement fluids; there may be interactions between the transported polymer molecules and the porous medium. These interactions will cause the polymer to be retained by the porous medium and will lead to the formation of a bank of injection fluid wholly or partially denuded of polymer, this bank of fluid will have a viscosity which is much lower than the injected polymer solution and this will lead to a reduction in the efficiency of the polymer flood. This polymer retention on the porous medium may cause some reduction of the rock permeability. There are three main retention mechanisms of polymer solutions flow through porous media and they are:

1. Polymer adsorption
2. Mechanical entrapment
3. Hydrodynamic retention

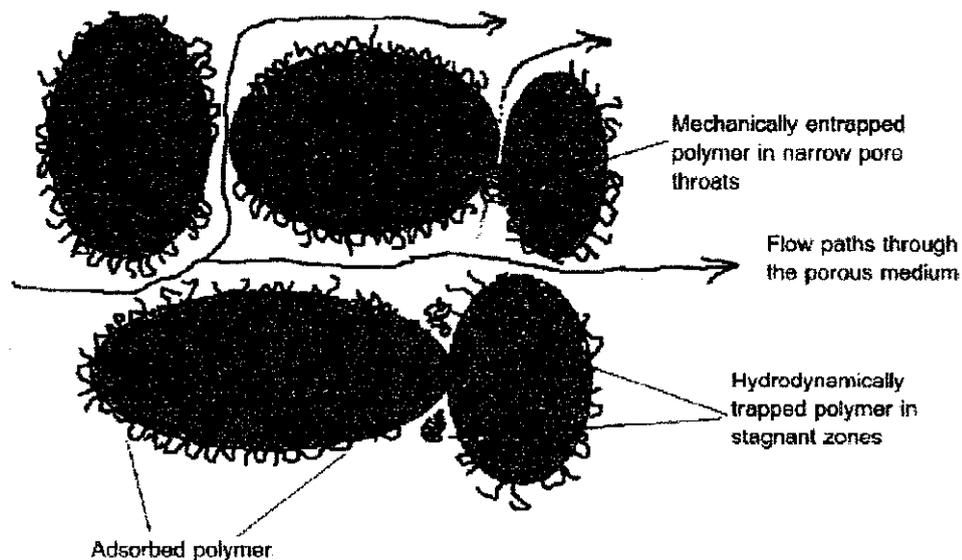


Figure 6: Polymer retention mechanisms in porous medium

2.4.1 Polymer Adsorption

Adsorption refers to the interaction between the polymer molecules and the solid surface, this interaction causes polymer molecules to be bound to the surface of the solid mainly by physical adsorption which means a relatively weak bond between the surface adsorbent (rock) and the adsorbed (polymer), and the forces between both of them are electrostatic force. Adsorption is the only mechanism that removes polymer from the bulk solution. The concentration of polymer in the flood water decreases and thus the viscosity of the displacing phase decreases.

This phenomenon has been repeatedly observed in polymer flooding is the removal of polymer from solution by adsorption on the reservoir rock. The amount of polymer lost from a bank may be large or small, depending on the nature of polymer and rock surface. Polymer molecule can be adsorbed by rock surface or trapped within small pores.

Polymer retentions vary with polymer type, molecular weight, polymer concentration, rock composition, permeability, brine salinity, brine hardness, flow rate, and temperature. Adsorption isotherms give at a particular constant temperature, the dependence of the amount adsorbed in the equilibrium concentration. Polymer adsorption influences polymer flooding, due to adsorption, the polymer solution loses its viscosity during propagation.

2.5 CHALLENGES IN POLYMER FLOODING

Despite of its wide use as a method of oil recovery, however PAM suffers from some of the worse defects when it is put into application. It cannot be used in water of high salinity especially at raised temperature, and easily degrade through oxidation. As there is no lipophilic groups that exist in its molecule structure PAM cannot emulsify the oil–water system, which limits its oil recovery capability. In order to reduce the oil–water interfacial tension and enhance the emulsification to improve the displacement efficiency, the binary flooding systems of PAM-surfactant or PAM-surfactant-alkali tertiary combination were developed. [1-3]

However, for these combined systems, the use of a large amount of surfactant leads to a high cost, and the presence of alkali causes problems such as the separation of oil from water and waste water treatment. [4] To overcome these difficulties, the right formulation of each component employed in the chemical flooding should be intensively studied to increase the interface activity, improve the emulsification ability, and enhance the viscosity.

Another important aspect to look for is the low salt tolerance, which can be improved by observing the hydrolysis degree of PAM (determined by acrylic acid) and this shall be acknowledged in great details in the findings later. As the higher polymer molecular weight, the higher the viscosity solution it will produce and this may create injectivity problems and usually are more susceptible to shear degradation, which may ultimately result in an unsuccessful application.

As also mentioned before that high molecular weight of modified PAM would result in high adsorption on the reservoir rock, hence a detailed adsorption study is needed to address this. The current application employs the classical solution, of either to add sacrificial agents into the formulation, or pre-flood the reservoir with sacrificial agents. It is also possible to adjust the molecular spectrum (equivalent molecular weight distribution) of the formulation to minimize the adsorption.

CHAPTER 3: METHODOLOGY

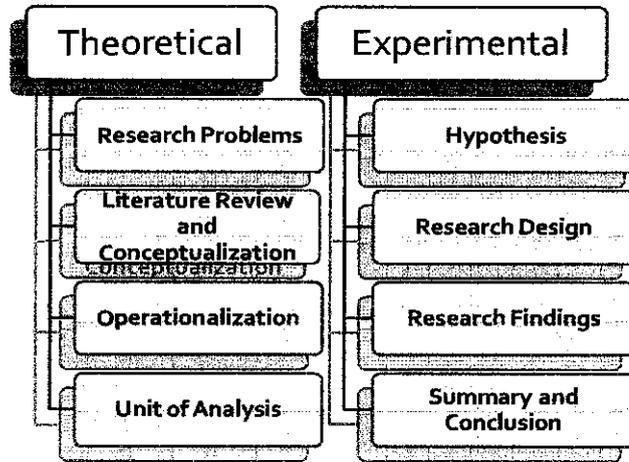


Figure 7: Flow of project methodology

Theoretical

1. The purpose of research: exploratory and explanatory – to quantify the effect of polymer adsorption on the reservoir rocks and its flooding performance for enhanced oil recovery.
2. Literatures relevant to the research problem, research design or hypothesis; analyse few concepts related to research project (adsorption kinetics and equilibrium, sweep efficiency)
3. Refer to the following chapter of methodology.
4. Find the unit of analysis within the research scope (i.e. adsorption capacity, initial rate of adsorption, isotherms).

Experimental

1. Justify hypothesis in terms of a theoretical framework or from prior researches.
2. Observation and data collection: Identify the problems and investigate if there is any interaction between them (i.e. from theoretical analysis and consultation).
3. Document the findings of the study.

3.1 MATERIALS

3.1.1 Polymer

As the allotted timeframe for the research works is quite limited, therefore it is foreseeable that full studies starting from synthesizing and characterising could not be realised. In this regard, the research has been assisted by few PhD candidacies as well as advices from UTP Enhanced Oil Recovery (EOR) Centre. The three types of polymer that prepared earlier by a PhD candidate, Mr. Ayman Abo Jabal, were used as a starting point for this research to investigate on retention phenomenon as well as on flooding performance employing polymer.

The three types of polymer are;

1. Polyacrylamide, PAM
2. Anionic Polyacrylamide, APAM
3. Copolymerised polyacrylamide – acrylic acid, CO-PAM-AA (will be represented by COPAM afterwards)

Polyacrylamide PAM is prepared by polymerising acrylamide monomer that can also be readily cross-linked, while APAM 2.5% (% refers to modified percentage) is synthesized by free radical polymerisation and initiated by potassium persulphate (KPS) as initiator, purchased from Aldrich Chemical Company. It is further added by alkali (Sodium dihydrogen phosphate, NaH_2PO_4) and grafted by surfactant SDS (Sodium dodecylsulphate, $\text{C}_{12}\text{H}_{25}\text{NaSO}_4$). While COPAM 2.5% is prepared by the same steps for APAM 2.5% but it is further co-polymerised with acrylic acid.

3.1.2 Adsorbent

As a prerequisite for successful screening to employ polymer flooding, sandstone is preferred over limestone formation as the former has the higher permeability, making it more feasible to recover more oil. Sandstone is used in the static adsorption experiment where it is collected from Civil Engineering Department. Samples were air dried for 24hrs followed by oven drying at 105°C for 24hrs. The dried sandstone samples were sieved into three distinctive sizes of 0.25mm, 0.5mm and 1mm to resemble different contact arrangement, relevant for adsorption kinetics and equilibrium studies.

3.2 EXPERIMENTAL PROCEDURES

The expected results from this research will provide quantitative parameters describing the conditions under which polymer can potentially enhance oil recovery. The laboratory works will be consisting of two parts:

PART 1: Adsorption Kinetics and Equilibrium Characteristics

PART 2: Performance Testing (Core flooding)

3.2.1 Static Adsorption Test

The objective of this test is to quantify and model the effect of polymer adsorption on reservoir rocks by varying;

- polymer concentration
- size of sandstone granules
- constant variables: mass of sand stone (g), temperature and pressure

The sandstone is first sieved into three distinct sizes of 0.25mm, 0.5mm and 1mm to resemble different packing of solid. Likewise, three types of polymer are diluted into different concentrations of 2000 ppm, 1000 ppm and 500 ppm. The following sets of formulations are then prepared and injected into the test tubes.

Table 1: Trial 1 – Sample preparation for the effect of sandstone size towards adsorption

Size of sandstone = 1mm Mass of sandstone = 2g	Size of sandstone = 0.25mm Mass of sandstone = 2g	Size of sandstone = 0.5mm Mass of sandstone = 2g
(1) PAM: 2000 ppm, 2mL	(4) PAM : 2000 ppm, 2 mL	(7) PAM : 2000 ppm, 2 mL
(2) APAM: 2000 ppm, 2mL	(5) APAM: 2000 ppm, 2mL	(8) APAM: 2000 ppm, 2mL
(3) COPAM: 2000 ppm, 2mL	(6) COPAM: 2000 ppm, 2mL	(9) COPAM: 2000 ppm, 2mL

Table 2: Trial 2 – Sample preparation for the effect of polymer concentration towards adsorption

Size of sandstone = 0.5mm Mass of sandstone = 2g	Size of sandstone = 0.5mm Mass of sandstone = 2g	Size of sandstone = 0.5mm Mass of sandstone = 2g
(10) PAM: 2000 ppm, 2mL	(13) PAM : 1000 ppm, 2 mL	(16) PAM : 500 ppm, 2 mL
(11) APAM: 2000 ppm, 2mL	(14) APAM: 1000 ppm, 2mL	(17) APAM: 500 ppm, 2mL
(12) COPAM: 2000 ppm, 2mL	(15) COPAM: 1000 ppm, 2mL	(18) COPAM: 500 ppm, 2mL

All the test tubes are then brought into an oven in order to simulate reservoir temperature of 90°C with sampling taken for every intervals of 5, 10, 20, 30, 60, 90 and 120 minutes. The small drops of sample are analyzed for their refractive indices for further calculation of kinetics and equilibrium modeling. The refractive indices obtained directly from refractometer are then converted to concentration values by plotting them based on the established literature.

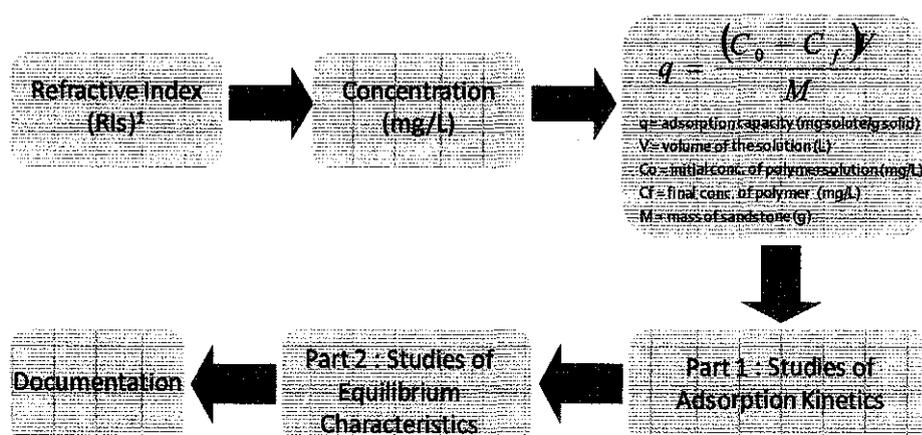


Figure 8: Flow of Adsorption Studies

3.2.2 Porosity and Permeability Test and Core Saturation

Before the core can be used in any experiment, it needs to undergo special cleaning procedures. The core sample is first washed and cleaned by using Soxhlet Extractor. Toluene is used as the fresh solvent to extract the crude oil remained in the core rock. The toluene solvent is boiled to allow it to condense and drip onto the sample in the thimble. Once the solvent reaches the top of the siphon arm, the solvent and extract are siphoned back into the lower flask. The solvent reboils, and the cycle is repeated until the sample is completely extracted, and the extract is in the lower flask. The core is then dried in an oven at 100°C for 24 hours. The petrophysical characteristics of the core are needed and vital for core flooding experiment; therefore it is characterized by employing PoroPerm System with confining pressure of 300 psi (2068.4 kPa) at room temperature. Core saturation with brine is conducted a day before the core flooding experiment can begin and is carried out in vacuum saturator.

3.2.3 Core flooding

The experiment is carried out with the objective to study and quantify the effect of polymer (polymer flooding) as tertiary recovery in EOR application. Water flooding that exists as the secondary recovery in the real application however is studied as well and served as a comparison to polymer flooding. The performance for each flooding is tested using Relative Permeability System, RPS 8310-1000 HPHT where the brine is first injected with flow rate, $Q = 3 \text{ mL/min}$, $P_{in} = 2000 \text{ psi}$ (13789.5 kPa), $T = 90^\circ\text{C}$. On the display panel, pressure drop ($P_{in} - P_{out}$) is observed to ensure that injection is stable before changing the fluid injection. A constant permeability line is also a good indicator that the core is ready for next fluid injection. Secondly, crude oil is injected with a lower flow rate than that of brine, $Q = 1.5 \text{ mL/min}$ to ensure that oil is slowly saturating the pore spaces inside the core. The brine that flushed out during the injection of crude oil implies the amount of crude oil that enters the core's pore spaces and then is collected in a graduated cylinder for measurement. Thirdly, after the system is stable, brine is again injected with the same flow rate, $Q = 3 \text{ mL/min}$ and as a result of displacement, the oil displaced by brine is then measured and therefore the performance of water flooding can be evaluated. Lastly, the polymer is injected into the core and any amount of displaced oil is observed. The displaced oil is then collected and measured; hence the performance of polymer flooding on top of water flooding can be quantified. The core sample finally is taken out from the service and is measured for its mass.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 ADSORPTION EXPERIMENTS

The polymer-reservoir rock interaction was evaluated. Literature is unanimous when considering the importance of the polymer injection process adsorption for petroleum recovery. This is the main parameter controlling the process and it is necessary, therefore, it would be known and quantifiable previously in the laboratory in order to support the design and evaluation steps.

The adsorption may be separated into the mechanical retention (irreversible) and physicochemical adsorption (reversible). The irreversible adsorption is associated with polymer molecule sizes related to the pore throats. This can be easily determined by the mass balance in a conventional porous flow test.

On the other hand, the physico-chemical or reversible adsorption, which is related to chemical and physico-chemical characteristics of the polymer and the rock, is not so easy to be experimentally measured by flow tests. One of the options discussed in literature is to perform that determination in a static way.

Generally, adsorption can be quantified by;

$$q = \frac{(C_0 - C_f)V}{M}$$

q = adsorption capacity (mg solute/g solid)

V = volume of the solution (L)

C_0 = initial conc. of polymer solution (mg/L)

C_f = final conc. of polymer (mg/L)

M = mass of sandstone (g)

Table 3: Trial 1- Effect of sandstone size towards adsorption (Vary: size of sandstone (1mm, 250µm, 500µm), Constant: polymer concentration, 2000 ppm and mass of sand stone, 2g)

Sample No.	0 min	5 mins	10 mins	20 mins	30 mins	60 mins	90 mins	120 mins
1	1.3472	1.3413	1.3414	1.3416	1.3416	1.3414	1.3411	1.3409
2	1.3445	1.3415	1.3413	1.3413	1.3413	1.3415	1.3407	1.3404
3	1.3445	1.3413	1.3412	1.3412	1.3413	1.3406	1.3407	1.3405
4	1.3472	1.3414	1.3418	1.3417	1.3417	1.3419	1.3409	1.3394
5	1.3445	1.3414	1.3416	1.3416	1.3417	1.3417	1.3417	1.3415
6	1.3445	1.3414	1.3399	1.3416	1.3411	1.3421	1.3422	1.3425
7	1.3472	1.3414	1.3405	1.3416	1.3398	1.3405	1.3408	1.3390
8	1.3445	1.3414	1.3414	1.3414	1.3415	1.3399	1.3414	1.3419
9	1.3445	1.3412	1.3348	1.3415	1.3412	1.3404	1.3411	1.3415

Based on Concentration versus Refractive Index Plot, the data were evaluated by the linear equation derived for each polymer type;

$$\text{PAM: } y = 143270x - 190989$$

$$\text{APAM: } y = 225648x - 301364$$

$$\text{COPAM: } y = 212139x - 283252$$

Sample No.	Ci (ppm)	0 min	5 mins	10 mins	20 mins	30 mins	60 mins	90 mins	120 mins
1	2000	2024.3440	1171.8875	1193.3780	1227.7628	1226.3301	1197.6761	1143.2335	1124.6084
2	2000	2024.2490	1336.0226	1304.4318	1290.8930	1290.8930	1351.8179	1166.7866	1101.3486
3	2000	1977.3711	1290.0407	1277.3124	1260.3412	1287.9193	1145.7862	1164.8787	1122.4509
4	2000	2024.3440	1196.2434	1243.5225	1242.0898	1229.1955	1263.5803	1126.0411	909.7034
5	2000	2024.2490	1329.2531	1374.3827	1369.8698	1381.1522	1376.6392	1392.4346	1347.3050
6	2000	1977.3711	1309.1332	995.1675	1353.6824	1241.2487	1461.8733	1487.3300	1550.9717
7	2000	2024.3440	1190.5126	1070.1658	1217.7339	968.4441	1067.3004	1100.2525	852.3954
8	2000	2024.2490	1317.9707	1331.5096	1324.7402	1340.5355	970.4726	1308.9448	1099.0922
9	2000	1977.3711	1270.9482	-86.7414	1332.4685	1260.3412	1101.2370	1251.8557	1338.8327

Table 4: Trial 2 - Effect of polymer concentration towards adsorption (Vary: polymer concentration: 2000ppm, 1000ppm, 500ppm, Constant: size of sandstone, 0.5mm and mass of sand stone, 2g)

Sample No.	0 min	5 mins	10 mins	20 mins	30 mins	60 mins	90 mins	120 mins
10	1.3472	1.3414	1.3405	1.3416	1.3398	1.3405	1.3408	1.3372
11	1.3445	1.3414	1.3415	1.3414	1.3415	1.3399	1.3414	1.3404
12	1.3445	1.3412	1.3348	1.3415	1.3412	1.3384	1.3411	1.3322
13	1.3392	1.3374	1.3380	1.3374	1.3374	1.3363	1.3351	1.3350
14	1.3394	1.3383	1.3386	1.3382	1.3379	1.3384	1.3362	1.3379
15	1.3402	1.3387	1.3393	1.3384	1.3385	1.3362	1.3376	1.3380
16	1.3372	1.3365	1.3368	1.3366	1.3351	1.3351	1.3347	1.3345
17	1.3382	1.3364	1.3365	1.3368	1.3362	1.3362	1.3364	1.3365
18	1.3374	1.3366	1.3372	1.3365	1.3366	1.3360	1.3352	1.3361

Based on Concentration versus Refractive Index Plot, the data were evaluated by the linear equation derived for each polymer type;

$$\text{PAM: } y = 143270x - 190989$$

$$\text{APAM: } y = 225648x - 301364$$

$$\text{COPAM: } y = 212139x - 283252$$

Sample No.	C _i (ppm)	0 min	5 mins	10 mins	20 mins	30 mins	60 mins	90 mins	120 mins
10	2000	2024.3440	1190.5126	1070.1658	1217.7339	968.4441	1067.3004	1100.2525	852.3954
11	2000	2024.2490	1317.9707	1331.5096	1324.7402	1340.5355	970.4728	1308.9448	1099.0922
12	2000	1977.3711	1270.9482	-86.7414	1332.4685	1260.3412	1101.2370	1251.8557	1338.8327
13	1000	879.8167	623.1634	700.5292	613.1345	624.5961	466.9991	293.6424	279.3154
14	1000	873.4442	625.2314	679.3869	598.1536	532.7157	645.5397	149.1141	519.1768
15	1000	1058.8092	732.1151	857.2771	670.5948	687.5659	214.4960	498.7622	594.2248
16	500	597.3748	492.7877	530.0379	509.9801	293.6424	283.6135	237.7671	206.2477
17	500	602.6666	182.9613	203.2696	282.2464	149.1141	137.8317	194.2437	223.5779
18	500	464.8200	282.3804	422.3922	265.4093	286.6232	167.8254	-1.8858	191.1607

4.1.1 Adsorptive Behaviour of Polymer

Table 5: Trial carried out in 1mm sandstone

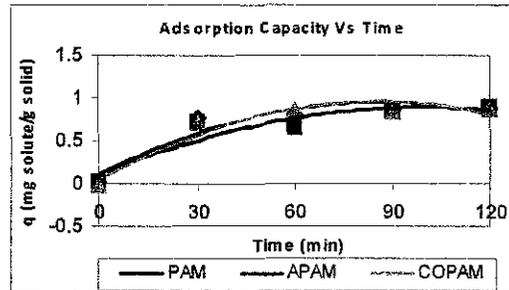


Table 6: Trial carried out in 0.25mm sandstone

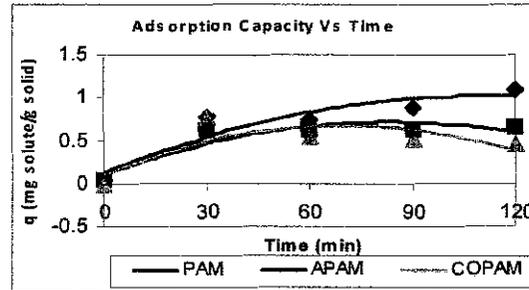
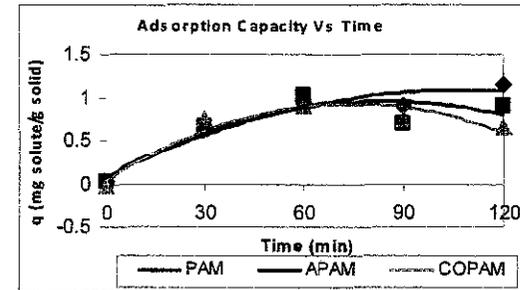


Table 7: Trial carried out in 0.5mm sandstone



In this study, the aim is to quantify and subsequently identify which of these three classes of polymer is ideal for an oilfield application. There were three runs for which a), b) and c) were carried out at a constant initial concentration of 2000 ppm at reservoir-simulated temperature of 90°C with sampling taken for every intervals of 5, 10, 20, 30, 60, 90 and 120 minutes. The difference in the packing of medium did not influence the adsorptive behaviour for each of the polymer classes. COPAM was adsorbed the least because of the augmentation with alkali that it has, as reported widely that alkali has the capability to reduce the adsorption effect of polymer solution on the reservoir rocks.

4.1.2 Effect of Concentration towards Adsorption

Table 8: Adsorption of PAM on 0.5mm

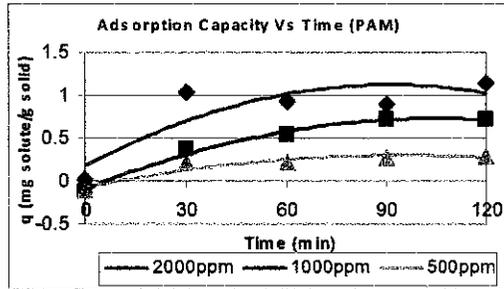


Table 9: Adsorption of APAM on 0.5mm

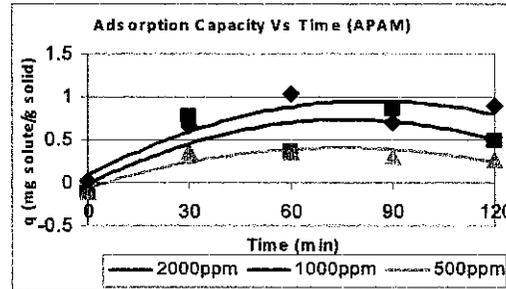
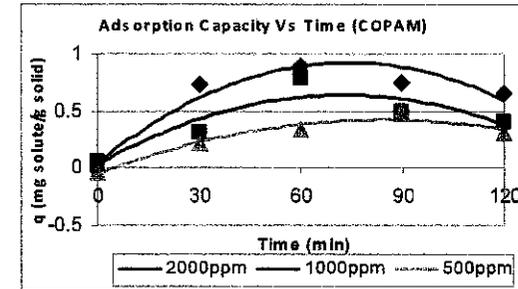


Table 10: Adsorption of COPAM on 0.5mm



Nine samples from different runs were matched to investigate the relation of concentration towards adsorption. The constant parameters were the polymer class and the sandstone packing size while concentration was varied from 2000 ppm, 1000 ppm to 500 ppm throughout all runs. The pattern shown is unanimous despite of the difference in the classes of polymer used with the highly concentrated polymer adsorbed mostly. This suggests the direct proportionality between adsorption capacity and concentration that can be found from the literature.

4.1.3 Effect of Sandstone Grain Size towards Adsorption

Table 11: PAM at 2000 ppm

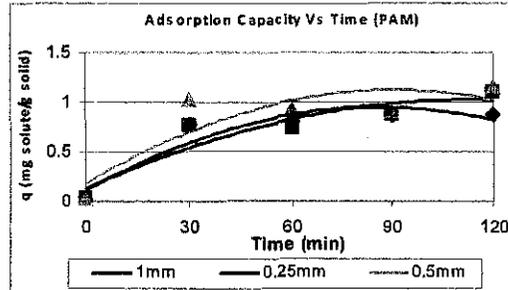


Table 12: APAM at 2000 ppm

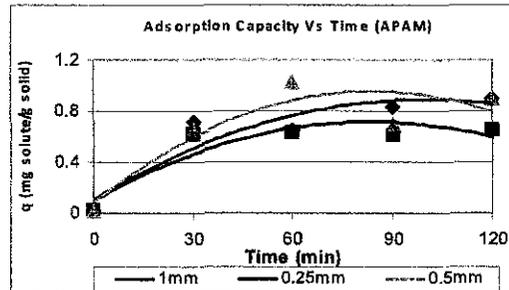
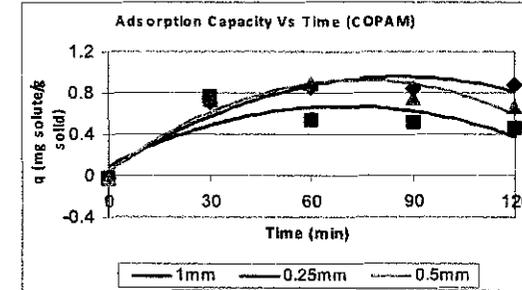


Table 13: COPAM at 2000 ppm



These runs were carried out to study how different grain size of sandstone affects adsorption. The concentration for PAM, APAM, and COPAM was kept constant at 2000 ppm while varying the grain size of adsorbent (sandstone). Theoretically, finer grains offer higher adsorption capacity, since the larger contact area, the higher adsorption (adsorption is faster; 0.25mm>0.5mm>1mm of sandstone grain size). Based on the experiments carried out, the adsorption capacity is insensitive towards the different grain sizes tested. Slight changes should be made to the values of the selected grain size so that they are properly distanced, and therefore the effect of adsorption could be seen more clearly if there is any.

4.2 ADSORPTION KINETIC MODELS

Both pseudo first- and second-order adsorption models are used to describe the adsorption kinetics data. In both models, all the steps of adsorption such as external diffusion, internal diffusion, and adsorption are lumped together, and the overall adsorption rate is proportional to either the driving force (as in the pseudo first-order equation) or the square of the driving force (as in the pseudo second-order equation).

Pseudo first-order model:

$$\ln(q_e - q_t) = \ln q_e - kt$$

where;

k = adsorption rate constant (min^{-1})

t = adsorption time

q_e = adsorption capacity at equilibrium

Pseudo second-order model:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

where;

k = adsorption rate constant ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)

$kq_e^2 = h$ ($\text{mg}/\text{g}\cdot\text{min}$) = initial rate of adsorption

Table 14: The comparison of first-order and second-order rate constant and correlation coefficients for different concentrations

Pseudo-first order kinetic model				Pseudo-second order kinetic model			
Concentration (ppm)	Polymer	$k_1 (min^{-1})$	R^2	qe^2	c	$k_2 (g/mg.min)$	R^2
2000	PAM	1.80E-03	0.01	1.32	3.59	0.21	0.96
	APAM	4.00E-04	0.00	0.81	3.21	0.38	0.93
	COPAM	2.50E-03	0.50	0.44	6.72	0.34	0.98
1000	PAM	9.50E-03	0.07	0.52	21.17	0.09	0.92
	APAM	3.30E-03	0.03	0.23	9.62	0.45	0.79
	COPAM	1.50E-02	0.46	0.16	5.46	1.11	0.90
500	PAM	7.50E-03	0.07	0.09	31.91	0.36	0.96
	APAM	1.17E-02	0.50	0.08	19.49	0.67	0.98
	COPAM	1.49E-02	0.47	0.10	14.65	0.72	0.86

Using the pseudo first-order model, $\ln (q_e - q_t)$ was plotted against t for three different classes of polymer (PAM, APAM, COPAM) at 2000 ppm and 90°C. The adsorbent used was 0.5mm sized sandstone. The first order rate constant (k_1) was determined experimentally from the slope (not shown in the figure). The values of rate k_1 and R^2 are presented in Table 14.

The first order rate constants for APAM and COPAM exhibited a notable increase with decreasing concentration except for PAM. The correlation coefficients obtained at every concentration however, are less than 0.5.

Using the pseudo second-order equation, t/q was plotted against t , and second-order rate constant, k_2 was calculated from the equilibrium uptake value, q_e determined from the slope and intercept. The values of k_2 and q_e were also presented in the Table 14.

As shown in the table, the rate constant for second order kinetic model for APAM increased as the concentration decreasing. The correlation coefficients obtained at various concentrations used were more than 0.79. Both adsorption constant rates were generally affected by the decreasing of concentration. These suggest that each of the sorption process can be described more ideally using the second-order kinetic model with fairly high correlation coefficients.

4.3 EQUILIBRIUM CHARACTERISTICS

An adsorption model is required to predict the loading on the adsorption matrix at a certain concentration of the component. The two general adsorption isotherms that can be used to describe the equilibrium adsorption relation are the well-known monolayer Langmuir and empirical Freundlich model.

1. Langmuir Isotherm

The Langmuir adsorption isotherm has been widely applied to many adsorption processes. It has produced good agreement with a wide variety of experimental data for adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogeneous sites in the adsorbent. Moreover, when a site is occupied by a solute, no further adsorption can take place at that site.

The rate of adsorption to the surface should be proportional to a driving force and area. The driving force is the concentration in the solution, and the area is the amount of bare surface. The Langmuir equation relates solid-phase adsorbate concentration, the uptake, to the equilibrium liquid concentration at a fixed temperature. The equation was developed by Irving Langmuir in 1916 (Langmuir, 1916). The Langmuir equation is expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{bq_{\max}} \frac{1}{C_e}$$

where

- q_e = quantity adsorbed
- q_{\max} = maximum quantity adsorbed
- C_e = equilibrium aqueous concentration
- b = Langmuir equilibrium constant

2. Freundlich Isotherm

Freundlich (Freundlich, 1906) developed an empirical equation to describe the adsorption process. His development was based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. Freundlich demonstrated that the ratio of the amount of solute adsorbed onto a given mass of an adsorbent to the concentration of the solute in the solution was not constant at different solution concentrations.

This isotherm does not predict any saturation of the adsorbent by the adsorbate; thus, infinite surface coverage is predicted mathematically, indicating multilayer sorption of the surface (Rawajfih and Nsour, 2006). The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. This equation can be rearranged in the linear form by taking the natural logarithm of both sides as:

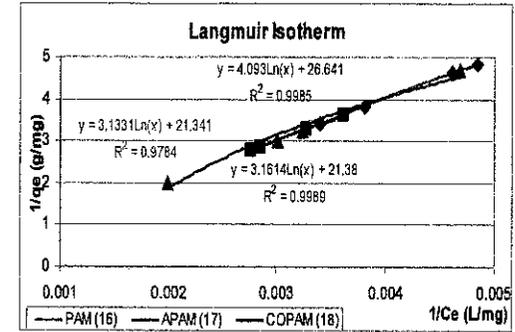
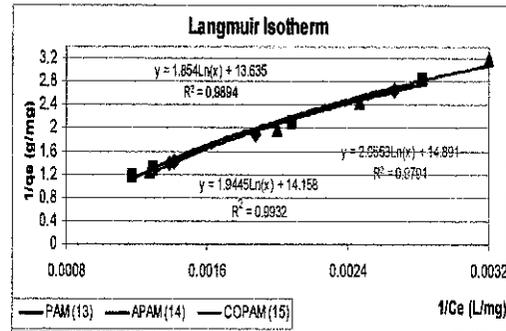
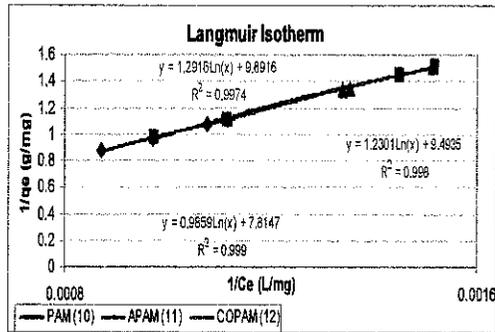
$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e)$$

where

- K_f = Freundlich equilibrium constant and n = constant, are determined experimentally

4.3.1 Best-fitting Langmuir Isotherm

Table 15: Various Langmuir fitting for samples 10 - 18



4.3.2 Best-fitting Freundlich Isotherm

Table 16: Various Freundlich fitting for samples 10 - 18

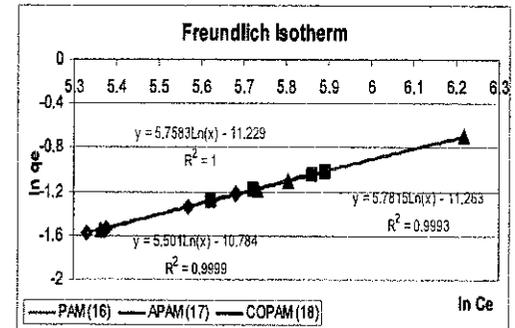
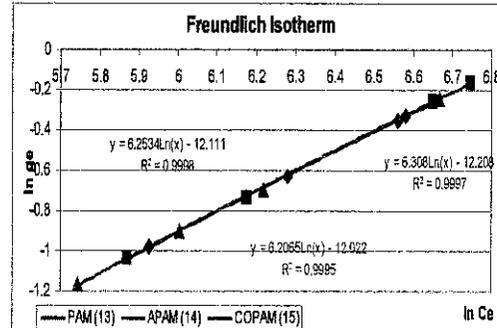
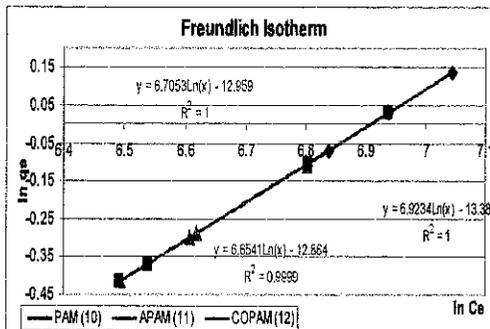


Table 17: Parameters of Langmuir model fitted to adsorption data

		Langmuir Isotherm				
Concentration (ppm)	Polymer	q_{max}	$1/q_{max} = c$	$1/bq_{max} = m$	b (L/g)	R^2
2000	PAM	0.128	7.815	0.986	7.926	0.9990
	APAM	0.105	9.494	1.230	7.718	0.9980
	COPAM	0.101	9.892	1.292	7.658	0.9974
1000	PAM	0.071	14.158	1.945	7.281	0.9932
	APAM	0.073	13.635	1.854	7.354	0.9894
	COPAM	0.067	14.891	2.055	7.245	0.9791
500	PAM	0.038	26.641	4.093	6.509	0.9985
	APAM	0.047	21.380	3.161	6.763	0.9989
	COPAM	0.047	21.341	3.133	6.812	0.9784

Table 18: Parameters of Freundlich model fitted to adsorption data

		Freundlich Isotherm				
Concentration (ppm)	c	K_f (L/g)	R^2	$1/n = m$	n	
2000	-13.380	1.55E-06	1.0000	6.923	0.144	
	-12.959	2.35E-06	1.0000	6.705	0.149	
	-12.564	3.50E-06	0.9999	6.654	0.150	
1000	-12.110	5.50E-06	0.9998	6.253	0.160	
	-12.208	4.99E-06	0.9997	6.308	0.159	
	-12.022	6.01E-06	0.9995	6.207	0.161	
500	-10.184	3.78E-05	0.9999	5.501	0.182	
	-11.229	1.33E-05	1.0000	5.758	0.174	
	-11.263	1.28E-05	0.9993	5.782	0.173	

The amount of polymer adsorbed can be estimated from the difference in refractive indices. Data were fitted to Langmuir and Freundlich models and applicability of the isotherm equations was compared by judging the correlation coefficients, R^2 . The best-fitted parameters together with regression coefficients for the three types of polymer are given above.

The data obtained from the adsorption of three types of polymer were fitted to the Freundlich model by plotting $\ln q_e$ versus $\ln C_e$. The linear plot obtained has a slope that has the value of $1/n$ and y intercept that is $\ln K_f$. K_f is a constant in the Freundlich model which is related to the bonding energy. K_f can be defined as an adsorption or distribution coefficient and represents the quantity of adsorbate (polymer) adsorbed onto adsorbents (sandstone) for a unit equilibrium concentration. As seen in Table 18, the K_f values of PAM are the highest (0.0000378 L/g) when present in low concentration (500 ppm), while APAM and COPAM values are more or less identical.

The slope $1/n$, ranging between 5.5 - 6.9 L/g, is a measure for the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is indicative of cooperative adsorption. Furthermore, a relatively slight slope (and hence a high value of n) indicates that the adsorption is good over the entire range of concentrations studied, while a steep slope (and hence small n) means that adsorption is good at high concentration but is much poorer at lower concentrations. Therefore, the polymer adsorption on sandstone involves cooperative adsorption ($1/n = 6.7$) based on Table 18.

Adsorption data fitting to Langmuir isotherm was achieved by plotting $1/q_e$ versus $1/C_e$ which yields a slope of $1/(b q_{max})$ and an intercept of $1/q_{max}$. Langmuir isotherm provides an insight into the adsorption grade by means of its b and q_{max} parameters. The value of b is homologous to Freundlich isotherm and indicates the adsorption capacity of the adsorbent to the respective solutes: the greater the b or K_f , the greater the q_e value.

The b values are recorded to fall within the range of 6.51 - 7.93 L/g, with similar pattern found in the Freundlich model, that PAM has again recorded the highest adsorption capacity (7.93 L/g) when placed in contact with sandstone. However, it would be infeasible to deduce any absolute relation that might exist between the polymer type and its concentration towards adsorption capacity, b as the latter values of the three polymer types are identical.

Maximum amount absorbed, q_{max} represents the maximum amount of the polymer adsorbed. As seen from Table 17, q_{max} values are higher for PAM, than those of APAM and COPAM with the latter being the lowest. However, as it is the case with n values of the Freundlich model, the q_{max} values of the polymer are more or less identical.

According to the values of correlation coefficients, R^2 , it can be deduced that the Freundlich model represents the adsorption data reasonably better. Correlation coefficients fall in the range of 0.9993 -1.0 for Freundlich-fitting while they range in between 0.9784-0.9999 for the Langmuir-fitting.

Based on the results obtained on polymer adsorption, it seems that adsorption depends largely on the adsorbent properties including chemical (mineralogical and organic) composition. The low affinity of SDS (surfactant augmented in APAM, COPAM) on sandstone is attributed mainly to repulsion forces between sandstone and surfactants. This is because soils in aqueous solutions often obtain negative charges on the surface thus; maintain repulsion with anionic surfactants.

Adsorption of a nonionic polyacrylamide is commonly thought to involve hydrogen bonding. Hydrogen bonding (also known as hydrophobic bonding) is weaker than electrostatic interactions. Hydrophobic bonding can also be important for adsorption on solids that possess a fully or partially hydrophobic surface. In this case, surfactant molecules can adsorb flat on the hydrophobic sites on the solid.

Another influential factor is the clay minerals and organic matter which are available in sandstone. Polymer adsorption by soils/sediments depends on the type of surfactant augmented and the soil properties. In this case, the results of different trials employing anionic (APAM, COPAM) and nonionic polyacrylamide (PAM) on sandstone have revealed the significance of compositions towards their adsorptive behaviors.

4.4 CORE ANALYSIS

Porosity, ϕ is the amount of void spaces in a rock and a measure of how much hydrocarbon the rock will hold. The porosity is computed as the ratio of pore volume to the bulk volume of core sample and given in percentage, %. While permeability is a measure of flow capacity and depends on continuity of pore spaces. However, it has no unique relationship with porosity. Permeability, k varies directly with the rate of fluid flow through a given rock, the pressure applied, the area open to flow and varies inversely with the viscosity of the fluid flowing and the length of porous rock.

The length and diameter of the cylindrical core sample is 60.62 mm and 37.84 mm respectively. Test is conducted to evaluate the porosity and permeability utilizing PoroPerm System at Building 15. The results for both porosity and permeability are laid out below.

Table 19: Physical properties for core rock sample

Sample No.	Core Dia (mm)	Core Length (mm)	Bulk Vol (cc)	Weight (g)	Grain Volume (cc)	Pore Volume (cc)	Grain Density (g/cc)	Bulk Density (g/cc)	Effective Core Porosity (%)	Date Time of test
1	37.84	60.62	68.17	136.32	53.60	14.57	2.54	2.00	21.376	23/09/201 14:43:03

Sample No.	Room Tem (°C)	Confining Pressure (kPa)	Atmospheric Pressure (kPa)	Bulk Vol (cc)	Pore Vol (cc)	Air Permeability (mD)
1	26	2068.43	101.35	68.17	14.57	181.89

4.5 FLOODING PERFORMANCE

The flooding performance is started by quantifying the effect of water injection or typically known as water flooding for oil recovery. The parameters simulating reservoir conditions are applied to the run where the inlet pressure, P_{in} is set at 2000 psi (13789.5 kPa), temperature T at 90°C (similar to adsorption testing), and overburden pressure P_{ovb} at about 3500 psi (24131.7 kPa). To imitate the reservoir natural mechanism, the brine is injected first into the core, followed by crude oil and brine again and this is called water flooding or the secondary driving mechanism to drive oil to the surface. Polymer formulation is then added to the list to enhance the oil recovery factor, RF that one could expect from the production.

Table 20: Comparison between water flooding and polymer flooding towards oil recovery

Sample No.	Effective Core Porosity (%)	Mass of Core Rock Sample (g)		Volume of Crude Oil (cm ³)		Oil Recovery Factor, RF (%)
		Initial	After Oil Saturation	OOIP	RO	
1	21.38	136.32	148.47	14.89	5.8	38.93
2	21.38	136.32	148.47	14.89	2.5 / 8.3	16.78 / 55.72

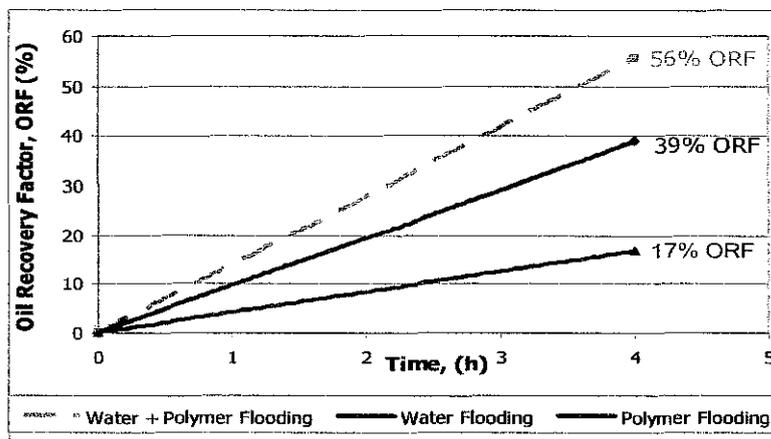


Figure 9: Different flooding packages and their effect towards oil recovery factor, RF

Based on the results obtained, water flooding has been successful in recovering 39% of original oil in place (OOIP) which is in good agreement with the projected range in literatures (30 – 40%). By using water injection and crude oil flow rate of 3 mL/min and 1.5 mL/min respectively, the water slowly travels through the pore spaces thus displaces the oil to enhance the oil recovery. The original oil in place, OOIP calculated above, 14.897 cm³ is confirmed and found in good agreement with the amount of brine that flushed out during crude oil invasion to the core sample, which is about 15 cm³.

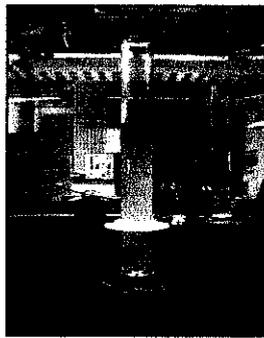


Figure 10: Recoverable oil after water flooding

By employing polymer flooding, it can be observed that the oil recovery factor, RF is enhanced by 17%, led to an amount of 56% total oil recovery throughout the run. Polyacrylamide, PAM with concentration of 2000 ppm is used to viscosify the water to be near to oil viscosity, therefore, improving the sweep efficiency of displacing fluid (water) and displaced fluid (oil).



Figure 11: Recoverable oil after polymer flooding

The polymer is injected at a lower rate of 1.5 mL/min to find its way and move through the interconnected pores to displace oil, however as Angsi crude oil exists as waxy oil in room temperature, therefore it is noticeable that the collection tubing experienced plugging, hence affecting the accuracy of the result. Two heaters were placed into the water container to soothe out the flow of fluid through the tube as it is very important not to have thermal shock during the experiment. This is the only survived method to maintain the temperature the fluid receives inside the system as opposed to tube insulation method, which is failed as it traps more water vapours, hence cools off the tube even more. This waxy plug issue is one of the main concerns, as it had caused the build up of pressure of up to 3000 psi (20684.3 kPa).

CHAPTER 5: CONCLUSION AND RECOMMENDATION

Works presented above support the notion that polymer incorporation has potentials in recovering more oil from the reservoir. However historical works on kinetics of polymer retention on reservoir rocks are inconclusive and poorly modeled. Thus this report has met its objective; that is to document the polymer adsorption behavior, its kinetics as well as its equilibrium characteristics when subjected to reservoir conditions.

The effect of polymer flooding has been successfully studied, in which polymer increases water viscosity by retarding its mobility and matches that of oil viscosity thus improving sweep efficiency. The adsorption kinetics model is important as it predicts the loading behavior on the adsorption matrix at a certain concentration of the component. As a result, the adsorption data are better fitted by pseudo second order kinetic model, judging by the correlation coefficients, R^2 . In addition, the equilibrium characteristics of polymer adsorption on the rocks have been modeled as well. These data were found to fit the Freundlich Isotherm better, which assumes surface heterogeneity and that; there are multiple layers of adsorption sites to fill. Last but not least, the oil recovery factor has improved by another 17% with polymer incorporation, leading to an amount of 56% of total oil recovery throughout the run.

Realizing that the retention phenomenon of polymer is quite significant, therefore it is hoped that further studies will be employed in the area of noble polymer synthesis, with ultimate goal to minimize this retention effect between the polymer and the reservoir rocks.

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APPENDIX

A: Summary of reservoir screening criteria for polymer flooding application

PARAMETER	CRITERIA FOR POLYMER FLOODING
Reservoir Depth	500 – 300ft below seabed
Pressure	Up to 3000 psi (20684.3 kPa)
Reservoir type	Sandstone, Carbonate
Temperature	Up to 120°C
Oil viscosity	10 to 200 cp
Salinity	35000ppm Total Dissolved Solid (TDS)

B: Sample of calculation for Oil Recovery Factor, RF

API GRAVITY

$$^{\circ}\text{API} = \frac{141.5}{\gamma_{\text{oil}}} - 131.5$$

Given specific gravity for Angsi Crude Oil, $\gamma_{\text{oil}} = 0.8156$

Therefore, $^{\circ}\text{API} = \frac{141.5}{0.8156} - 131.5 = 42^{\circ}\text{API}$

OIL DENSITY

$$\gamma_{\text{oil}} = \frac{\rho_{\text{oil}}}{\rho_{\text{water}}}$$

Given $\rho_{\text{water}} = 1 \text{ g/cm}^3$

Therefore, $\rho_{\text{oil}} = 0.8156 \times 1 \text{ g/cm}^3 = 0.8156 \text{ g/cm}^3$

FLUID VOLUME

$$\rho = \frac{m}{v}$$

v = volume of the fluid

m = mass of the fluid

ρ = density of the fluid

OIL RECOVERY FACTOR, RF

Given

Sample No.	Effective Core Porosity (%)	Mass of Core Rock Sample (g)		Volume of Crude Oil (cm ³)		Oil Recovery Factor, RF (%)
		Initial	After Oil Saturation	OOIP	RO	
1	21.376	136.32	148.47	14.897	5.8	38.93

The oil remains in the core sample can be computed from the mass difference of initial core and after oil saturation, hence;

$$m = 148.47 - 136.32 = 12.15 \text{ g of oil remains}$$

The volume of original oil in place, OOIP is then,

$$v = \frac{12.15 \text{ g}}{0.8156 \text{ g/cm}^3} = 14.897 \text{ cm}^3$$

After no more oil is flushed out or after for about 4 hours, the recovered oil, RO is collected and measured, that is 5.8 cm³, therefore

$$\text{Oil Recovery Factor, RF} = \frac{\text{Volume of Recoverable Oil, RO}}{\text{Volume of Original Oil in Place, OOIP}} \times 100\%$$

$$\text{Hence, RF} = 5.8 \text{ cm}^3 / 14.897 \text{ cm}^3 = 38.93\%$$