Laboratory Investigation on the Effects of Different Types of Surfactants on the Wettability Characteristics of Malaysian Coal for CBM Study

by

Nor Azalina binti Mohd Razlin

14961

Project dissertation submitted in partial fulfilment of

The requirements for the

Degree of Engineering (Hons)

(Petroleum Engineering)

JANUARY 2015

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

…………………….

(Dr. Saleem Qadir Tunio)

Project Supervisor

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.

Written by,

……………………………

(Nor Azalina binti Mohd Razlin, 14961)

ABSTRACT

Application of surfactant in CBM production has been steadily recognised. Surfactant acts as a wetting agent which helps to lower surface tension of coal bed groundwater, thus decreasing reservoir pressure to allow CBM production. For surfactant consequence enhancement, biosurfactant is introduced to ECBM towards better cost and environmental effect, other than its significant advantages over synthetic surfactants such as lower toxicity, higher biodegradability, better environmental capability, higher foaming and better thermal range. Unlike conventional reservoirs, dewatering process has to be done firsthand in ECBM in order to desorb CBM from coal micropores. Wettability alteration is necessary to increase coal surface hydrophobicity for more efficient dewatering process. However, biosurfactant application in hydrocarbon production is still in laboratory scale for ECBM wettability investigation, thus the information regarding biosurfactant effectiveness in Oil and Gas field is still ambiguous. There are some biosurfactants that have been applied for EOR application. However, researches done for biosurfactant application for ECBM are very few. In this project, the performance of SDS and AOS (synthetic surfactants) in comparison to betaine anhydrous (vegetal biosurfactant) for its potential use in ECBM application for coalbed reservoir is compared. The comparison is based on wettability factor between the surfactants and the coal surface. The synergistic effect between each surfactant to one another is also studied. Results show that betaine anhydrous have exceptional contact angle (27.19^{o}), and the lowest wetting angle is achieved through the synergistic effect between betaine anhydrous and SDS 1.0 wt% (23.38^{o}). The result shows that wettability performance of betaine anhydrous is as equal or better than AOS and SDS, and its applicability in ECBM is recommended based on cost comparison.

ACKNOWLEDGEMENT

First of all I would like to thank to Allah, The Most Beneficent, The Most Merciful, for all His guidance and blessings throughout my learning process in turning this project into a reality.

I would like to thank my family for their endless love, encouragement, and support throughout my final year. Heartfelt gratitude and appreciation to my Final Year Project (FYP) supervisor, Dr. Saleem Qadir Tunio for his continuous help and encouraging in gaining invaluable experience for this project. Also to my co-supervisor, Dr. Muhammad Ayoub for his guidance and invaluable technical knowledge for this project. I would also like to thank Mr. Mudassar for making me understand more about my research.

Last but not least, I would also like to express my deep gratitude to my colleagues especially Essam, Hanis, Hidayatul and Thiban. Thank you for your companionship and moral support. Last but not least, my greatest appreciation goes to those who have assisted me directly or indirectly starting from the beginning of the project. All of the experiences and lessons obtain shall not be wasted and hopefully, which will lead me to be a successful and flexible Petroleum Engineer.

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NOMENCLATURES

AOS : Alpha olefin sulphonate
C : Liquid Concentration
$C_5H_{11}NO_2$: Betaine Anhydrous (molecular formula)
CBM : Coalbed methane
ECBM : Enhanced coalbed methane
EOR : Enhanced oil recovery
IFT : Interfacial tension
Mtoe : Million tonnes of oil equivalent
pH : Potential hydrogen
pH_{pzc} : Potential hydrogen point of zero charge
sp . : Species
SDS : Sodium dodecyl sulphate
V : Liquid volume

CHAPTER 1

INTRODUCTION

1.1 Background Study

Natural gas comes from fossil fuels formation when intense heat and pressure are exposed to the layers of buried living organisms, for example humans, animals, plants, and microorganisms (Ferdian, 2012). The main structure of hydrocarbon gas mixture is methane, other than that it also consists of other higher alkanes, nitrogen, carbon dioxide and hydrogen sulphide.

Natural gas is a powerful source of energy as it can be utilized for a lot of daily important usage. Some of the applications are including electricity generation, heating and cooking. Both Halliburton (2008) and Ernst and Young (2010) agree that the key reasons for the stepping up of natural gas to become a mainstream energy resource are because natural gas provides cleaner energy, more affordable and they are more abundant.

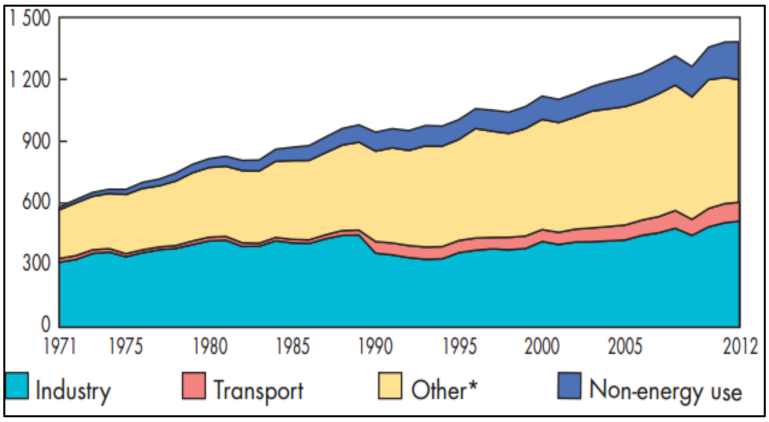


Figure 1. Global natural gas consumption by sector (IEA, 2014)

Figure 1 shows global natural gas consumption in the past from 1970 until 2012. Due to the importance of this energy, the demand has increased significantly over the last 40 years (IEA, 2014). In 2012, the consumption primarily used for other sectors such as agriculture and residential (43.4%) followed by industry purposes (36.5%).

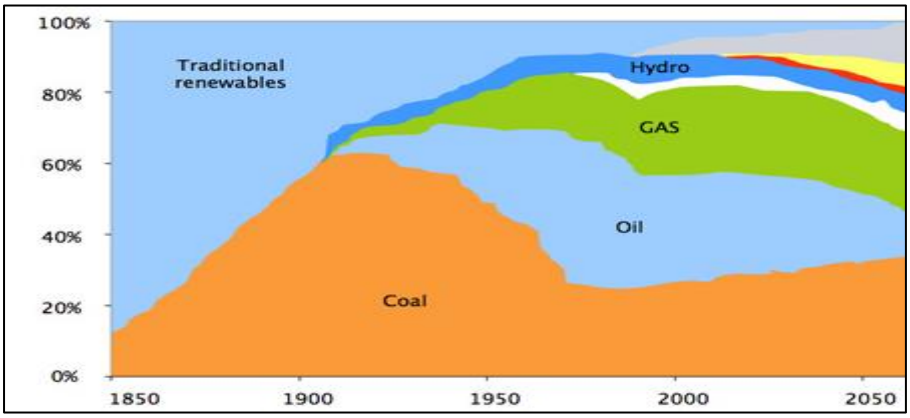


Figure 2. Global history and projected energy consumption from 1850-2050. (Ichorcoal, 2014)

Figure 2 shows the world energy consumption and predicted global consumption of natural gas until year 2050. Based on the graph, natural gas shows steady growth from 3.2% in 1925 to 22% by 2050. Natural gas consumption starts to take up more than 20% of the global energy consumption since 1990 (Ichorcoal, 2014). Natural gas extraction method can be divided into 2 parts, which are conventional and unconventional gases. Conventional gases are the gases are found in large permeable sandstone reservoir, thus having an easier extraction process via conventional drilling techniques. On the other hand, unconventional gases are the gases that are found in low permeability reservoir. There are two sub-types of unconventional gases, which are CBM and shale gas.

CBM and groundwater are the main constituents in coal-bed pores. 95% of the gas is primarily methane, whereas the remaining 5% constitutes of other heavier hydrocarbons such as ethane and propane (Halliburton, 2008). This project will focus on methane production in coal-bed, which is generally known as CBM.

Kuuskraa (1989) and Ferdian (2012) explain that in coal-bed, methane gas is adhered to the coal surface. The methane lines inside the pore of the solid matrix of the coal. The groundwater adds the adhesion tension between methane and coal surface by the presence of the hydrostatic pressure. The adsorbed methane can be released off from the solid coal matrix if the CBM is depressurized by extracting the groundwater.

1.2 Problem Statement

The use of synthetic surfactant to complement ECBM has been steadily recognised. Surfactant acts as a wetting agent which helps to lower surface tension of CBM groundwater and increasing the contact between CBM and the groundwater (Ferdian, 2012).

Wettability alteration is necessary to increase coal surface hydrophobicity for more efficient dewatering process. CBM attaches to the porous surface of the coal at molecular level and are held in place by the hydrostatic pressure exerted by groundwater surrounding the coalbed. Usually, surfactant will be injected to be mixed with groundwater near the downhole end of the well to maximize water removal for better gas recovery. If dewatering is not done effectively, the CBM production will not be optimized because some of the CBM that is stored in the coal micropores cannot be produced efficiently.

The use of biosurfactants in oil reservoirs has steadily garnered attention in hydrocarbon production field due to its environmental and financial friendly to either the mother Earth or the oil companies themselves. Other than that, biosurfactants also prove significant advantages over synthetic surfactants such as lower toxicity, higher biodegradability, better environmental capability, higher foaming and better thermal range (Torres et al, 2011). Due to its new discovery in Oil and Gas Industry, biosurfactants development in this particular field is still on laboratory scale. On top of that, smaller attention is given to the application of such additive to gas production, particularly in shale and coal-bed reservoirs. It can be seen in very few journal papers relates to the application of biosurfactants in ECBM recovery. This causes limited information on the effectiveness of biosurfactants in CBM production.

1.3 Objectives and Scope of Study

The challenges to be brought upfront for this project are:

1) To compare the feasibility of biosurfactants and synthetic surfactants in CBM reservoirs in term of wettability.
2) To study surfactant synergistic effect on contact angle.
3) To relate surfactant contact angle on coal surface with adsorption.

The study will be done for coal-bed application. Coal with sub-bituminous rank from Sarawak will be used for this study. Types of surfactants in this project refer to the materials that made up the surfactants are divided into two categories which are biosurfactant and synthetic surfactants. Three different surfactants, which consists of 1 biosurfactant and 2 synthetic surfactants will be compared in this experiment study, which are betaine anhydrous, SDS and AOS respectively. The surfactant polar heads are concentrated on anionics and amphoterics only.

CHAPTER 2
CRITICAL LITERATURE REVIEW

2.1 CBM

CBM is the type of unconventional natural gas that can be found in coal beds. CBM is colourless and odourless. Roughly 95% of CBM composition is made from methane (CH_4). Other gases present in CBM with its relative mole percentage can be referred in Table 1. CBM reservoirs usually have low to very low permeability, that is roughly ranging between 5mD to a few nanoDarcy scales (Ferdian, 2012). CBM is considered as a 'sweet gas' due to its lack of hydrogen sulphide. CBM is generally filled with groundwater, and the hydrostatic pressure keeps CBM adsorbed on the coal surface. CBM is acknowledged quickly to be a potential natural gas after a few outburst and explosions in coalfields (Ernst & Young, 2010).

Table 1. CBM Composition. (Hewitt, 1984)

Component	Composition Mary Lee Seam Warrior Basin (Mole %)
Methane	96.2
Ethane	0.01
Carbon Dioxide	0.1
Nitrogen	3.4
Hydrogen	0.01
Helium	0.26
C_{3+}	0.71

It is well known as a byproduct during coalification process. Open ventilation of CBM to the environment exposes a serious safety risk due to the fact that methane gas is highly flammable and may explode in the presence of a spark or flame. Because of this, a lot of effort has been put to vent the gas away as a part of coal mining operation. In more recent times, the technology has been developed to utilize CBM for natural gas use (Conrad, 2006). This statement is seconded by WORC (2003) and Jing (2013) whereby countries such as China and United States encourage CBM production respectively for this matter. The alternatives include the provision of tax credits to unconventional gas producers and restrictions in price uplifting.

CBM is a preferred gas production alongside coal mining as it can reduce methane ventilation to the environment, which can cause global warming. In addition, coal mining safety can be enhanced.

2.2 CBM Hydrocarbon Storage

Hydrocarbon gas storage mechanism between coal beds and conventional reservoirs are in contrast of each other. Instead of occupying void spaces between the grain spaces, the methane is held to the surface of the coal mainly by adsorption in micropores. This ability enables methane to be stored in the reservoir of less than 2.5% porosity value, which in turn enables the coal bed to store larger volume of gas compared to conventional reservoirs (Halliburton, 2008). A better illustration to the massive volume of gas entrapped in CBM is that 1 lb of coal has a surface area of 55 football fields, or 1 billion sq ft per ton of coal. A good coal-bed well can reserve two to three times more gas than a sandstone reservoir that has 25% porosity and 30% water saturation (Kuuskraa, 1989). However, according to Ernst and Young (2010), CBM reservoirs can hold up to five times more natural gas than conventional reservoirs. It must be because of the different quality of the coal, as mentioned by Al-Jubori et al. (2009). The gas content depends on the coal's rank, which is a measure of the organic matter's quality and thermal maturity. The phases of coal maturation in terms of gas volume are described in Figure 3.

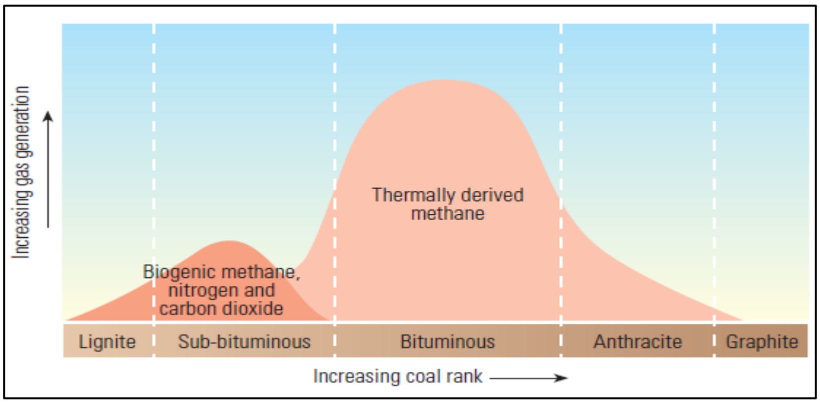


Figure 3. CBM Gas maturity phase in terms of gas generation (Al-Jubori et al., 2009)

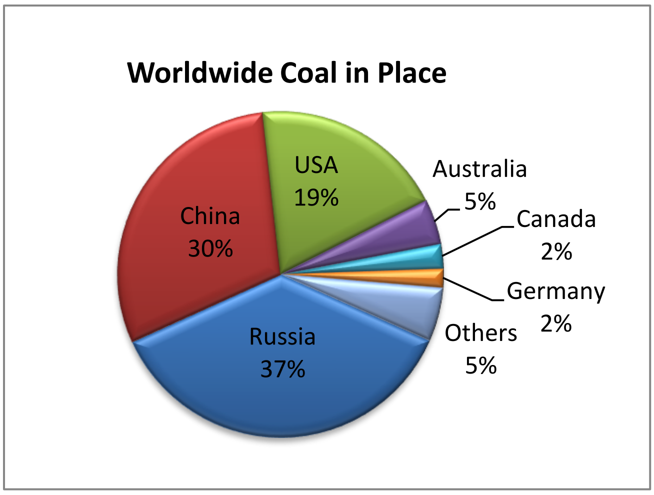


Figure 4. Worldwide coal in place (Boyer, Kelafant, & Kruger, 1992)

According to Conrad (2006), it is reported that 400 trillion cubic feet of CBM reserve is extractable, with Russia and China as the main CBM producers as shown in Figure 4.

2.3 Coal Bed Structure and Production

There is a big difference between CBM and conventional natural gas reservoir structure. For conventional gas reservoir, it mainly consists of porous sandstones with impermeable cap rock. The gas is kept under high pressure and can be produced at high flow rate, often without the necessity to pump. On the other hand, CBM is not as conventional since the reservoir is structurally weak.

Studies made by Palmer, Moschovidis, and Cameron (2005) and Conrad (2006) reported that while hydraulic fracturing is proven to be successful in some production application, it is not specifically proven for CBM wells. Due to this, careful production design has to be implemented in order to prevent formation damage. CBM pressure reduction is possible by extraction of groundwater. CBM is adsorbed, or is loosely held on the coal surface. The gas can easily drop off to the reservoir pressure reduction. Dewatering is needed to extract CBM which is dominantly adsorbed between the matrices. The extraction period can take place from between a few months until a few years depending on maturity level and groundwater content that is made up from the coalification process itself. CBM will desorb when the pressure is sufficiently reduced, which in turn increasing CBM production rate over time. Figure 5 shows CBM production stage at a single well.

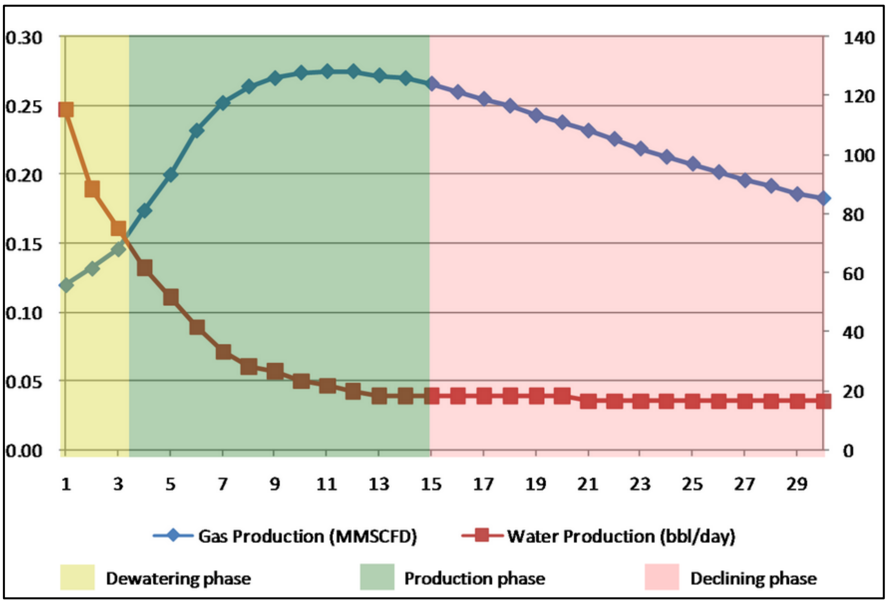


Figure 5. CBM Production Stage (Ferdian, 2012)

Ferdian (2012) thoroughly explains that there are three stages of CBM production stage which are dewatering phase, production phase and declining phase. Production period takes up long period with relatively smaller production plateau when compared with conventional reservoirs. Also, the declining rate takes up until more than ten years, making CBM as a natural gas production with a long lifetime.

To extract the gas, the hole is first drilled with a steel-encased hole into the targeted CBM. As the groundwater is pumped out from the coal bed, the coal bed pressure decreases. The process then forces the gas to desorb and to be produced. The produced gas will be sent to the compressor station and natural gas pipelines. On the other hand, the groundwater is either reused into isolated formations, released into streams, used for irrigation, or sent to evaporation pond. Due to the presence of impurities in the groundwater that can affect health, the groundwater is treated first before it is released to the environment.

Coal bed structures are made of matrix and fractures (cleats). CBMs consist of dual porosity system, which is micro and macro pores as shown in Figure 6. The micro pores exist in the matrix whereas macro-pores consist of cleats. There are two types of cleats, which are face cleats and butt cleats. Face cleats are continuous to the CBM and act as the main flow channel whereas butt cleats are discontinuous channels and perpendicular to the face cleats. Upon entering the cleats, the gas will flow obeying Darcy’s Law, where the mass flow is dependent upon pressure gradient. However, for CBM of more than 2000 metres, the cleats will close as a result of overburden pressure acting on the structurally weak coal-bed. Dewatering phase is necessary to bring the reservoir pressure down to a threshold value for methane desorption.

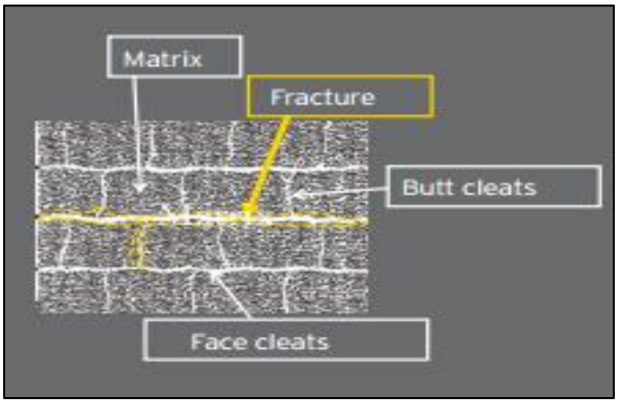


Figure 6. CBM dual porosity system (Ernst & Young, 2010)

2.4 Application of Surfactants in ECBM

The relatively weaker structure of CBM is mentioned previously by Conrad (2006). Due to this, more gentle approach to CBM production must be applied in order to prevent formation damage, which can in turn reduce well producibility than to increase them. One of the methods is by altering reservoir wettability. This approach can be done by surfactant flooding.

The surfactants decrease the IFT between gas and groundwater, which in turn decreasing the viscosity of the trapped gas and to release the retained gas in the rocks to move along with the flushed water. The presence of surfactant increases CBM production at earlier stage, thus increasing gas sweep efficiency and saving production cost.

The success of surfactant application in ECBM has been acknowledged. In laboratory scale, Baharuddin (2013) shows that the volume of gas production is more with surfactant injection, as seen in Figure 7. On a larger scale, the analysis done by Nimerick et al. (1991) prove that the proper usage of additives containing surfactants can lead to significant improvements in methane and water production in coal bed reservoirs by dewatering improvement.

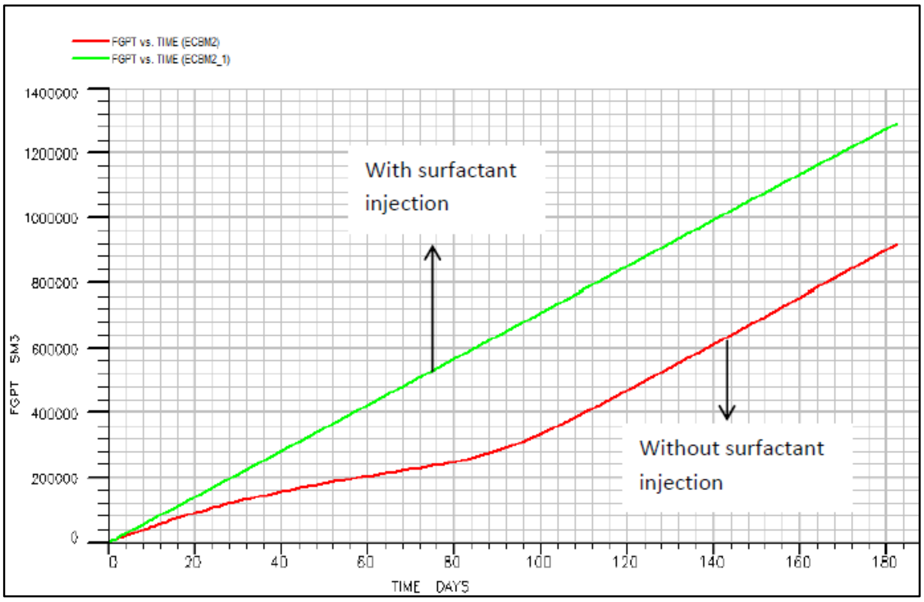


Figure 7. CBM Field gas production total vs time/ days (Baharuddin, 2013)

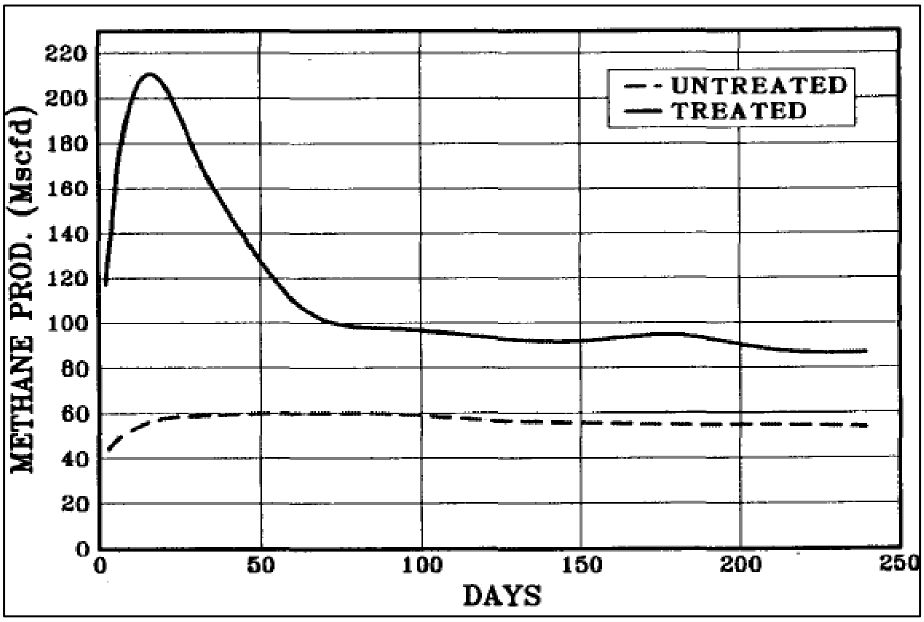


Figure 8. CBM production from a well treated with an additive containing surfactant vs untreated offset well (Nimerick, Hinkel, England, Norton, & Roy, 1991)

This high on demand alternative is currently using synthetic chemical surfactants. The surfactants can cause hazards to the environment as it is toxical and non-biodegradable. Fortunately, there are currently vigorous researches done for surface active biosurfactants that take new fermentation and economic factors into account (Torres et al, 2011).

Biosurfactants can be defined as surface-active compounds that are produced by living cells. Recently, researches regarding biosurfactants applications in ECBM have been rigorously made. Both Sineriz et al (2001) and Torres et al (2011) agree that biosurfactants comprise of selective advantages over synthetic surfactants such as lower toxicity, higher biodegradability, better environmental capability, higher foaming and better thermal range.

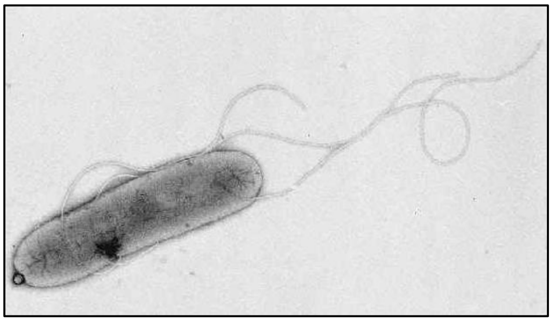


Figure 9. Pseudomonas sp. (ASCR, 2006)

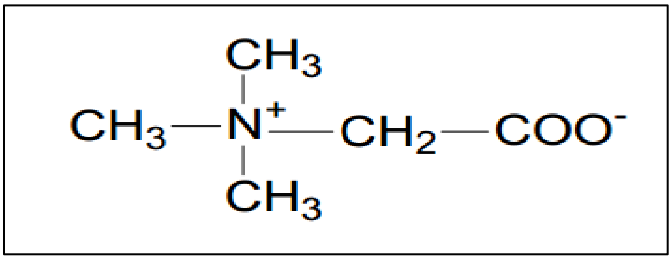
There are two types of biosurfactants, which are microbial biosurfactants and vegetal biosurfactants. Some of the microbial surfactants are still under laboratory scale. The surfactants include rhamnolipids produced by *Pseudomonas sp*., the biosurfactant produced by *Bacillus licheniformis* and surfactin produced by *Bacillus subtilis*. On the other hand, vegetal biosurfactants include guar and locust bean gums, lecithine, saponine and tannin. Although the cost of some bio-surfactants are expensive, studies done by Rodrigues and Teixeira (2008) prove that inexpensive raw materials can be utilised for biosurfactant production. The following table shows the microbial biosurfactant types that can be produced from low cost raw materials. It is to be noted that the biosurfactants listed are of general usage and not specifically proven for ECBM usage to date.

Table 2. Selected microbial surfactants by inexpensive raw materials (Mukherjee et al,2006)

Low cost or waste raw material	Biosurfactant type	Microbial stain
Rapeseed oil	Rhamnolipids	*Pseudomonas sp.*
Babassu oil	Sophorolipids	*Candida lipolytica*
Turkish corn oil	Sophorolipids	*Candida bombicola*
Sunflower oil	Lipopeptide	*Serratia marcescens*
Waste frying oils	Rhamnolipids	*Pseudomonas aeruginosa*
Oil refinery wastes	Glycolipids	*Candida antartica* and/or *Candida apicola*
Cassava flour wastewater	Lipopeptide	*Bacillus subtilis*

In this project, betaine anhydrous is used for vegetal biosurfactant. It is also known as trimethylglycine, with molecular formula of $C_5H_{11}NO_2$. Betaine anhydrous was first discovered in the 19th century in the juice of sugar beets (*beta vulgaris*), especially in its shoots and roots (McCue & Hanson, 1992). In medical field, betaine anhydrous is considered as a powerful biosurfactant and is normally used to lower homocysteine levels which can prevent diseases such as osteoporosis, cardiovascular thrombosis, skeletal abnormalities and ocular deformities (South, 2007; EMEA, 2008). Betaine anhydrous appears either as white crystals or a crystalline powder with a weak characteristic odour. It is freely soluble in water and is hygroscopic, where it is able to absorb and retain water molecules from the surrounding environment. Betaine has good functionality in ECBM whereby it is able reduce the oil/water IFT to ultra-low for alkaline-free combination flooding (Li et al., 2012).

Figure 10. Sugar beets. (NDSU, 2013)



$$CH_3-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2-COO^-$$

Figure 11. Betaine anhydrous molecular arrangement. (EMEA, 2008)

Wettability is a measure of a liquid ability to form interface between solid surfaces. In this project, anions and amphoteric surfactants are tested to study which of these type of surfactants can increase the coal surface hydrophobicity, thus decreasing gas contact angle to coal surface. The concept of contact angle to wettability can be further understood by referring to Figure 12.

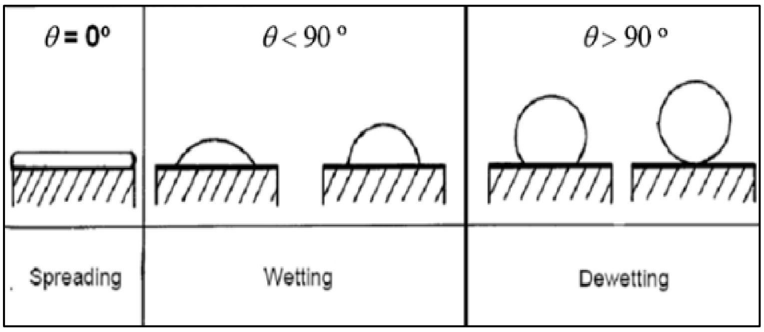


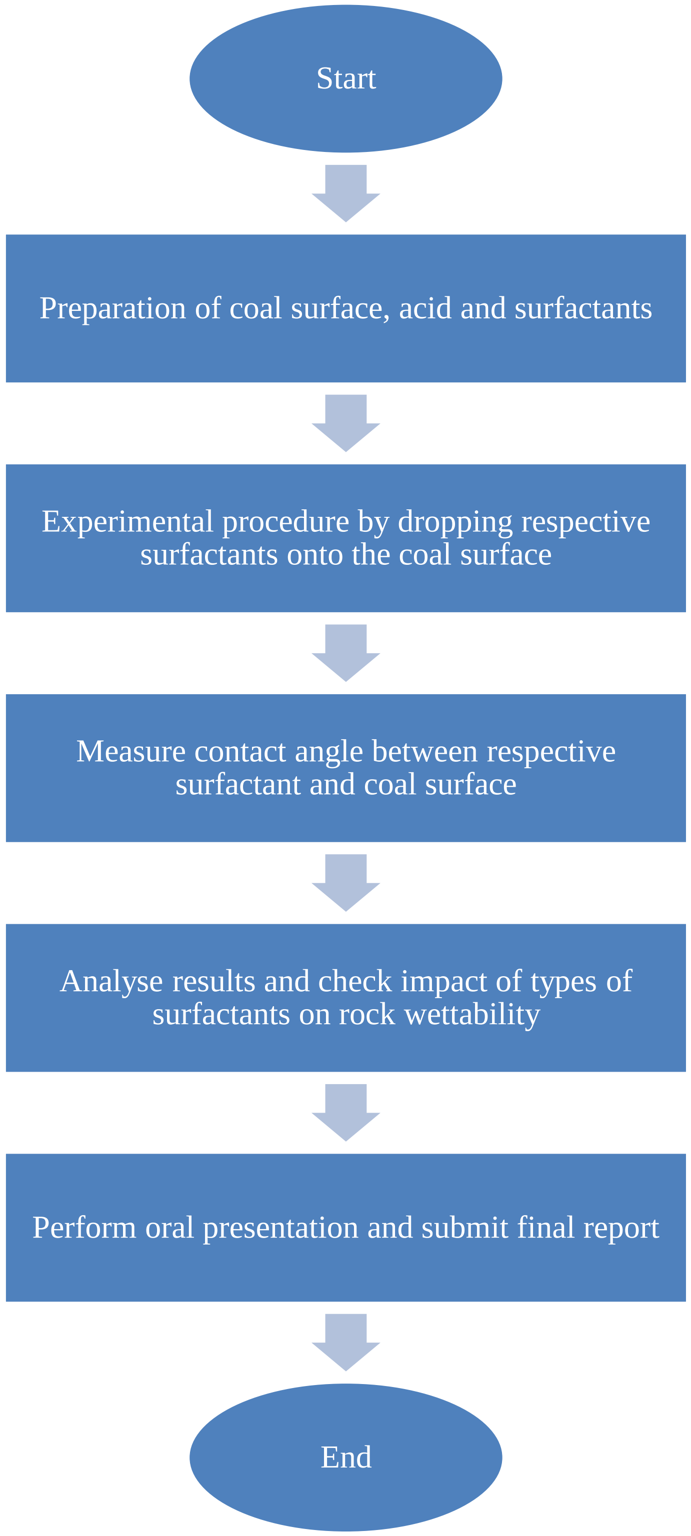
Figure 12.CBM Concept of contact angle to wettability. (Adhesives.org, 2014)

On the other hand, synergistic effect comes from the Greek word *synergos*, meaning ‘working together’. In this project, each of the surfactants will be mixed together with each other to observe the interaction between surfactants to the wetting angle, whether the combination will have a positive effect or negative effect.

CHAPTER 3

METHODOLOGY

3.1 Methodology Flow Chart



3.2 Apparatus and Materials

1. Hammer
2. Chisel
3. Rock polisher
4. Syringe
5. Digital Single Lens Reflex Camera
6. On-screen protractor
7. Coal sample (Sub-bituminous rank)
8. Surfactants
    i. Betaine anhydrous (bio, amphoteric)
    ii. SDS (synthetic, anionic)
    iii. AOS (synthetic, anionic)

3.3 Experimental Procedure

3.3.1 Coal sample preparation

1. The fracture orientation of coal bulk is identified by its physical appearance.
2. Coal bulk is carefully broken down using hammer and chisel parallel to its fracture orientation.
3. The coal samples are polished using rock polisher until the sample is flat and there are no fractures on the coal sample surface.

Figure 13. Coal sample preparation. Left: some of the coal samples after hammered. Right: samples are polished using rock polisher.

3.3.2 Surfactants Preparation

1. 20ml of 1% betaine anhydrous is prepared. 10ml of the solution is diluted to 0.5% by using the dilution formula:

$$C_1V_1 = C_2V_2$$

where

C_1: Initial concentration or molarity, fraction

V_1: Initial volume, ml

C_2: Final concentration or molarity, fraction

V_2: Final volume, ml

Incorporating the formula,

$$V_2 = \frac{(0.005)(10ml)}{(0.01)}$$

$$V_2 = 5ml$$

∴ 5ml of 1% betaine anhydrous and 5ml of distilled water is mixed in measuring cylinder to create 10ml of 0.5% betaine anhydrous.

2. The procedure is repeated with SDS and AOS.

3.3.3 Experimental Methodology

1. A flat sub-bituminous coal surface sample is prepared. The sample is put on a smooth surface.
2. A drop of betaine anhydrous is dropped on the coal sample.
3. A close up image of the experimental setup is captured with a digital single lens reflex camera.
4. The contact angle between the surfactant and the coal surface is measured from the image with an on-screen protractor. The wetting angle is measured by subtracting 180^o from the contact angle. Step 1-3 are repeated to get average surfactant contact angle. Fresh coal sample is used to prevent surfactant contamination.
5. The result is tabulated.
6. The procedure is repeated with different AOS and SDS.

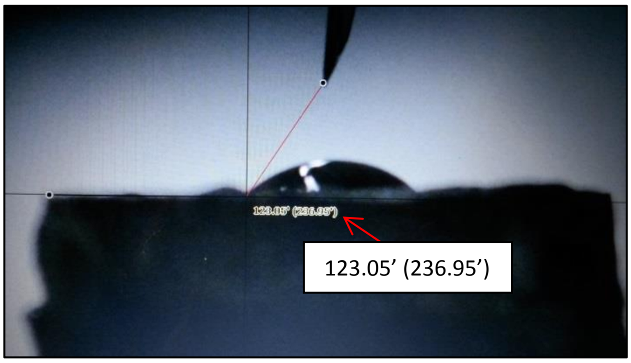


Figure 14. Measuring surfactant contact angle.

3.4 Project Timeline

The project timeline is divided into 2 parts (FYP1 and FYP2). The scheduled timeliness of this project is as follows. Due to unavoidable circumstances, the project started 9 weeks later than the expected tentative:

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
1	Selection of Project Topic	🟦	🟦						Mid-Semester Break			🟩																				
2	Preliminary Research Work		🟦	🟦	🟦	🟦							🟩	🟩																		
3	Submission of Extended Proposal Defence						●							🟩																		
4	Proposal Defence									🟦	🟦				🟩																	
5	Project Work Continues											🟦	🟦	🟦	🟩																	
6	Submission of Interim Draft Report														🟩●																	
7	Submission of Interim Report															🟩●																
8	Project Work Continues																🟩	🟩	🟩	🟩	🟩	🟩	🟩									
9	Submission of Progress Report																						🟩									
10	Poster Exhibition																									🟩						
11	Submission of Final Draft																											🟩				
12	Viva																													🟩		
13	Submission of Hardbound Copies																															🟩

● Suggested milestone
🟦 Suggested Process
🟩 Actual Process

3.5 Project Milestone

By the end of the planned weeks for both FYP1 and FYP2, I should be able to achieve the milestones:

Milestones	Week
Early research development 1. Research background 2. Scope of study	12
Middle Research Development 1. Detailed Research 2. Theory Development 3. Data Gathering 4. Data Testing 5. Theory Testing 6. Experimental Study	20
Final Research Development 1. Result analysis 2. Results finalization 3. Documentation Completion	30

CHAPTER 4

RESULTS AND DISCUSSION

The result of the experiment is as tabulated:

Table 3. Experimental result tabulation.

Sample name	Sample concentration (wt%)	Sample number	Run	Angle (°)		Average Angle (°)	
				Contact	Wetting	Contact	Wetting
AOS 1%	1.0	1	1	154.61	25.39	155.14	24.86
AOS 1%			2	159.6	20.4		
AOS 1%			3	151.21	28.79		
AOS + SDS 1%	1.0	2	1	148.95	31.05	152.95	27.05
AOS + SDS 1%			3	153.57	26.43		
AOS + SDS 1%			4	156.32	23.68		
Betaine 1%	1.0	3	4	150.44	29.56	152.81	27.19
Betaine 1%			6	155.27	24.73		
Betaine 1%			7	152.71	27.29		
SDS 1%	1.0	4	1	143.83	36.17	148.56	31.44
SDS 1%			2	154.13	25.87		
SDS 1%			3	147.73	32.27		
Betaine + AOS 1%	1.0	5	2	145.88	34.12	145.00	35.00
Betaine + AOS 1%			3	145.59	34.41		
Betaine + AOS 1%			5	143.54	36.46		
Betaine + SDS 1%	1.0	6	1	159.69	20.31	156.62	23.38
Betaine + SDS 1%			2	157.64	22.36		
Betaine + SDS 1%			3	152.54	27.46		
Betaine 0.5%	0.5	7	2	145.79	34.21	151.69	28.31
Betaine 0.5%			3	156.71	23.29		
Betaine 0.5%			4	152.56	27.44		
AOS 0.5%	0.5	8	1	138.78	41.22	139.26	40.74
AOS 0.5%			2	136.19	43.81		
AOS 0.5%			6	142.82	37.18		
SDS 0.5%	0.5	9	1	140.89	39.11	142.41	37.59

In this study, 9 samples are tested with several numbers of runs. The runs values are selected based on the comparison of wetting angles proximity of each runs to increase accuracy. The wetting angle is obtained by subtracting contact angle from the flat surface angle (180°), whereas the average of the wetting angles are obtained from averaging the three selected runs.

For CBM experiment, anionic and amphoteric surfactants are chosen because of the feasibility of the surfactants type in coalbed methane. According to Jazeyi et al (2014), the net charge of most typical rock surfaces is strongly dependent on the rock pH level. Depending on the rock type, the surface net charge is measured based on the rock's point of zero charge (pHpzc); pH values above pHpzc has positive net surface charge whereas pH values below pHpzc has negative net surface charge. Coalbed groundwater pHpzc was achieved at pH 5.2, whereas its pH value is reported to be around pH 6.5 – 8.5 (Flores, 2013). Thus, it confirms that coalbed has a positive net surface charge. Anionics and amphoterics are known to have negative head groups, which will favour electrostatic attraction between the coalbed surface and the surfactant head. Later on, the second patch of these surfactants may be adsorbed by the surfactant tail-tail interaction. The second patch's outer parts are the hydrophilic heads, which will be suitable for the coalbed groundwater environment (Flores, 2013). Also, the electrostatic attraction between the coalbed surface and the surfactant will not block the coal fractures and cleats.

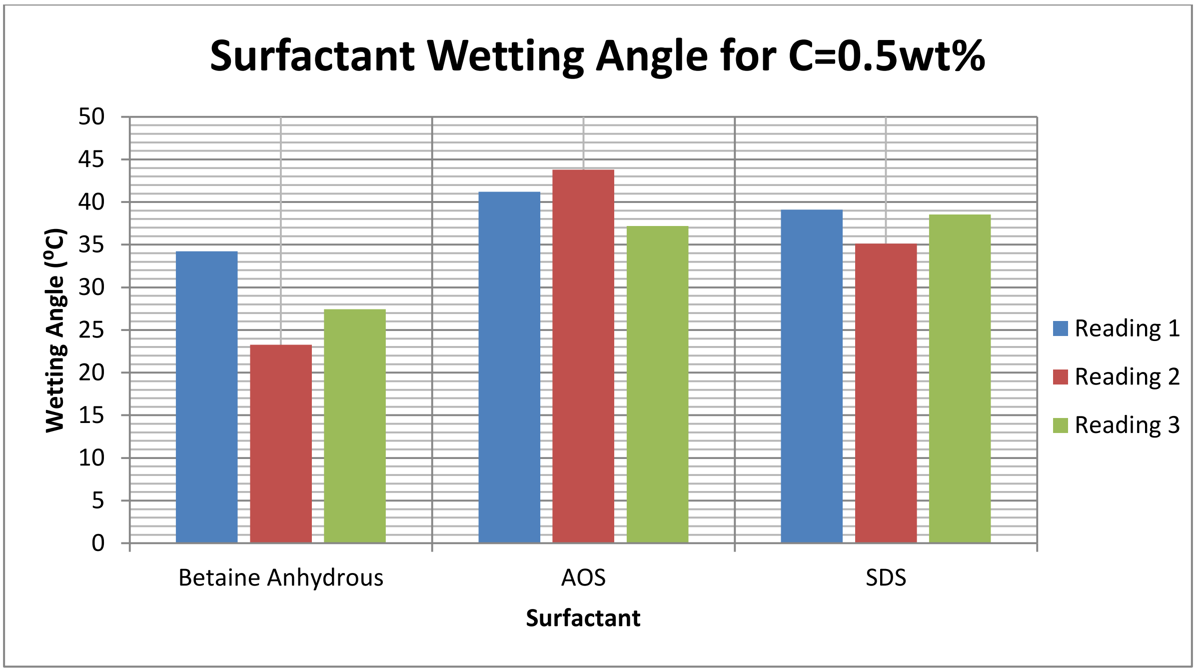


Figure 15. Graph of surfactant wetting angle for concentration=0.5wt%.

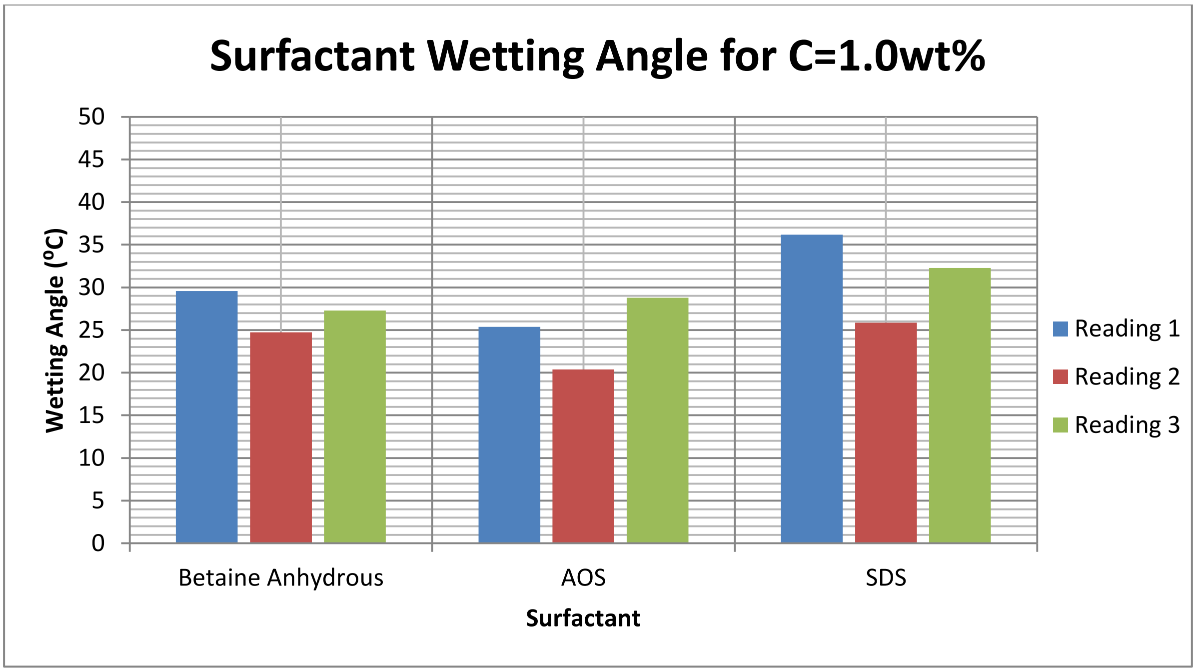


Figure 16. Graph of surfactant wetting angle for concentration=1.0%.

Based on the results, it can be seen that all of the surfactant samples wetting angles are less than 90^0. Thus, all of the surfactants show a good potential for CBM surfactants as it implies that the surfactants have well interacted with the coal sample. In another word, the wetting of the surface is very favourable as the liquid of the same volume spreads over larger area of the surface. The phenomena is supported by Yuan and Lee (2013) for their statement that higher surface tension tends to minimise the surface area by making the drop spherical. According to

Nalewaja, Goss, and Tann (1998), lower contact angle on target surface signifies lower surface tension.

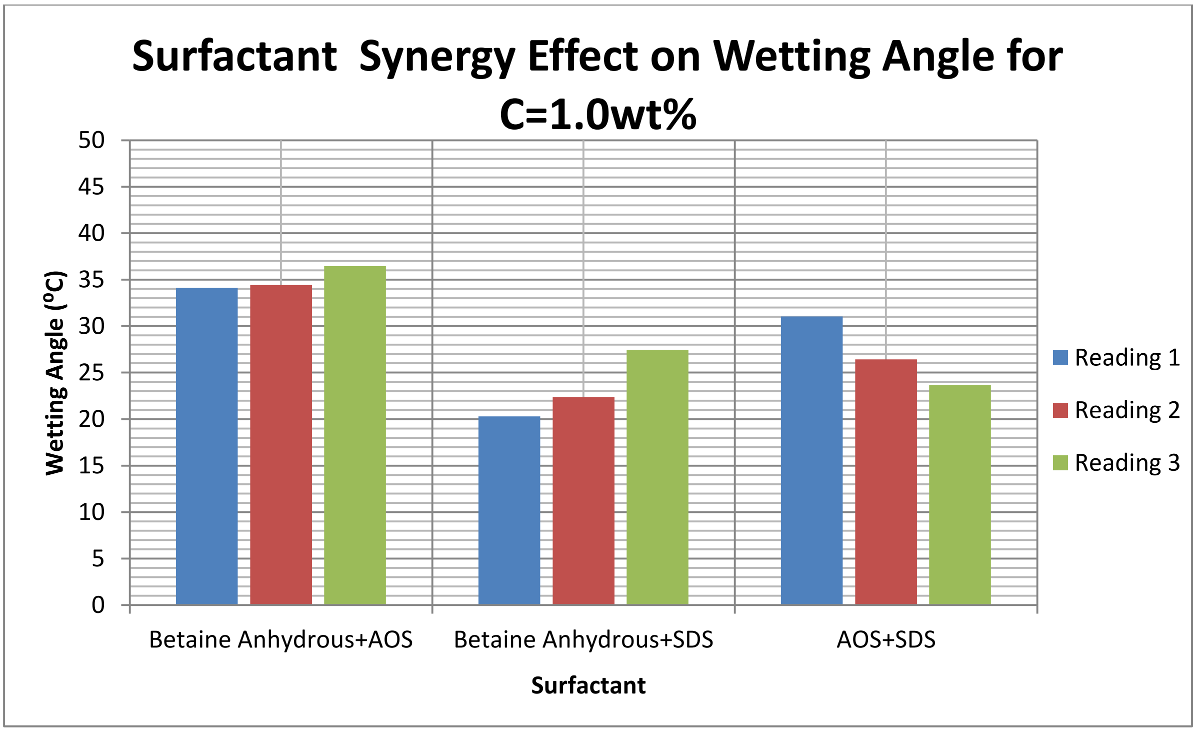


Figure 17. Graph of surfactant synergy effect on wetting angle for concentration=1.0%.

Furthermore, an important observation to be considered is that the higher surfactant concentration, the lesser the contact angle between surfactant and coal sample. This finding relates to the collision theory whereby when suitable particles of reactant hit each other, only a few percentages of the collisions will cause noticeable chemical change. Thus, the more concentrated is the surfactant, the higher the colliding possibilities. This will in make it easier to achieve activation energy for reaction to happen. Higher reaction is depicted in this project by the smaller contact angle produced on the coal surface.

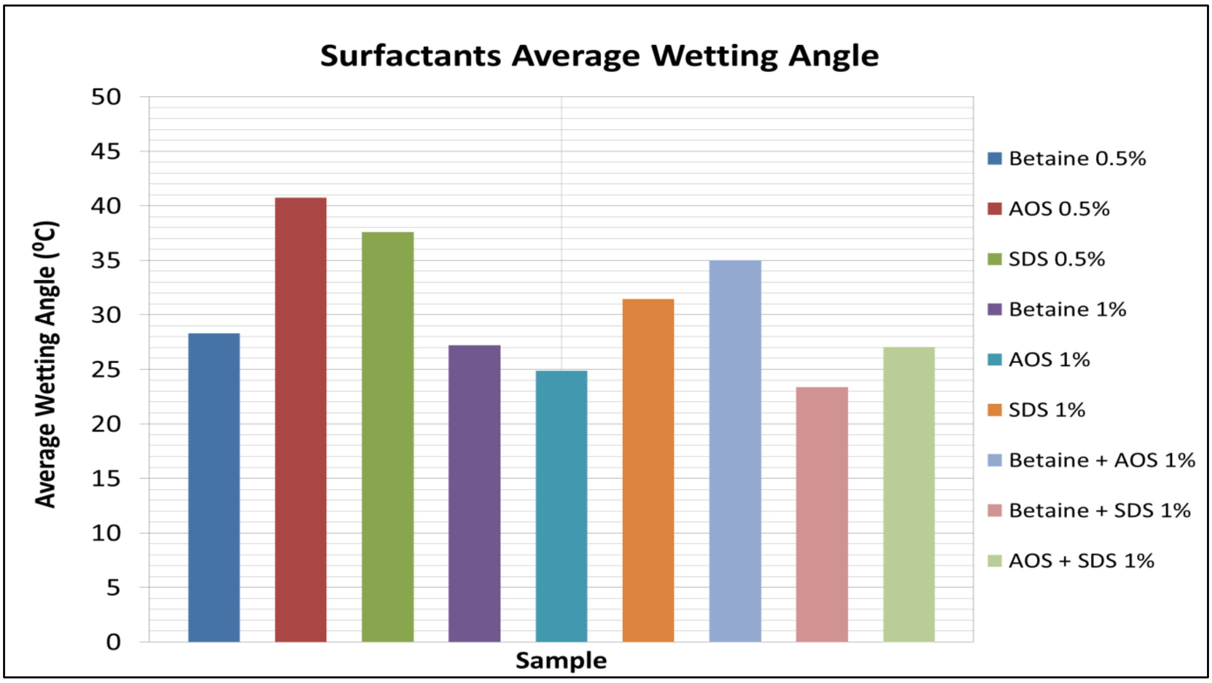


Figure 18. Graph of wetting angle for concentration=0.5wt% and 1.0% with and without synergy effect.

Other than that, it is also noticeable that when betaine anhydrous 1.0 wt% shows satisfying result even when it is used alone (27.19^0). This contact angle is comparable with AOS 1.0% (24.86^o) and SDS 1.0 wt% (31.44^o). The lowest wetting angle is achieved through the synergistic effect between betaine anhydrous and SDS 1.0 wt% (23.38^o), whereas the highest wetting angle comes from SDS (37.59^o). This condition is favourable since it can increase the mixability between the surfactant and the groundwater to be flushed up to the surface, thus allowing the gas to desorb from the coalbed at a faster rate (Baharuddin, 2013).

One interesting result obtained from the experiment is that the synergistic effect between surfactants may not be necessarily efficient. The summary of the synergistic effect on contact angles is summarised in Table 4. SDS with betaine anhydrous shows a good synergistic effect as the combination of both surfactants further reduces surfactant contact angle (23.38^o) than by using SDS (31.44^o) and betaine anhydrous alone (27.19^o). Similar case can be seen from the synergistic effect between SDS and AOS. However, when betaine anhydrous is mixed with AOS, the wetting angle significantly increases (27.19^o). It shows that the combination of both surfactants is not compatible to achieve lower wetting angle.

Table 4. Synergistic effect between surfactants of 1.0 wt% in term of wettability

Surfactant/Wetting angle	Betaine Anyhydrous 1.0%	AOS 1.0%	SDS 1.0%
Betaine Anhydrous 1.0%	27.19	35.00	23.38
AOS 1.0%	35.00	24.86	27.05
SDS 1.0%	23.38	27.05	31.44

As an addition, one more factor to be considered for surfactant application in the coalbed is the surfactant price. Market price of these three surfactants is as shown below. It can be seen that betaine anhydrous has a significant lowest cost.

Table 5. Surfactant market price based on 100g weight (Mukherjee et. al, 2006)

Surfactant name	Price per 100g
Betaine anhydrous	$31.82
SDS	$355.00
AOS	$57.91

CHAPTER 5

CONCLUSION AND RECCOMENDATION

Anionics and amphoterics are chosen as surfactants in the coalbed reservoirs due to its electrostatic feasibility to the coalbed pores. Moreover, the experimental study shows that all the three tested surfactants show contact angle less than 90° which indicates good reaction between the coalbed and the surfactant. Higher surfactant concentration yields to lesser contact angle which abides to the collision theory, and that the lowest wetting angle is achieved through the synergistic effect between betaine anhydrous and SDS 1.0 wt% (23.38°). However, synergistic effect between surfactants may be constructive or destructive.

Generally, betaine anhydrous, which is a biosurfactant is a potential candidate to be used as surfactant in CBM reservoir based on its contact angle and economic feasibility, which are equal or better than SDS or AOS. Betaine anhydrous is also considered as a good selection as it is more biodegradable.

For ECBM study enhancement, it is recommended to investigate the effectiveness of other superior biosurfactants that have been proven to be highly capable on the other fields such as rhamnolipids by *pseudomonas aeruginosa sp.* and surfactin by *bacillus subtilis sp*. Also, it would be a great extension to investigate biosurfactant IFT performance comparing to synthetic surfactants.

REFERENCES

Adhesives.org. (2014). Wetting: The Physics Behind Wetting.

Al-Jubori, A., Johnston, S., Boyer, C., Lambert, S. W., Bustos, O. A., Pashin, J. C., & Wray, A. (2009). Coalbed methane: clean energy for the world. *Oilfield Review, 21*(2), 4-13.

ASCR (Producer). (2006). Retrieved from http://www.biomed.cas.cz/gim_em/data/tem1_eng.html

Baharuddin, M. H. N. b. (2013). *Study on the Effect of Acid Injection with Surfactants on Malaysian coals for CBM Study.* Universiti Teknologi PETRONAS.

Boyer, C., Kelafant, J., & Kruger, D. (1992). Diverse projects worldwide include mined, unmined coals. *Oil and Gas Journal;(United States), 90*(50).

Conrad, G. (2006). Apparatus and Method for Increasing Well Production Using Surfactant Injection: Google Patents.

EMEA, T. E. M. A. (2008). European Public Assessment Report for betaine

anhydrous (Cystadane®). *678*.

Ernst, & Young. (2010). Shale gas and coal bed methane: Potential sources of sustained energy in the future.

Ferdian, F. (2012). Coalbed Methane - Langmuir Isotherm. Retrieved from https://coalbedmethane.wordpress.com/

Flores, R. M. (2013). *Coal and Coalbed Gas: Fueling the Future*: Newnes.

Halliburton (Producer). (2008). Coalbed Methane: Principles and Practices. Retrieved from http://www.halliburton.com/public/pe/contents/Books_and_Catalogs/web/CBM/CBM_Book_Intro.pdf

Hewitt, J. (1984). Geologic overview, coal, and coalbed methane resources of the Warrior Basin--Alabama and Mississippi.

Ichorcoal. (2014). Future Energy. from http://www.ichorcoal.com/sustainability/future-energy/?type=98

IEA. (2014). 2014 Key World Energy Statistics (pp. 34). Paris, France: IEA.

Jing, M. (Producer). (2013). China: New State Council opinion encourages coalbed methane (CBM) development. Retrieved from http://www.mondaq.com/x/270430/Mining/New+State+Council+opinion+encourages+coalbed+methane+CBM+development

Kuuskraa, V. A. (1989). Coalbed methane sparks a new energy industry. *Oil & Gas Journal, 87*(41), 49-&.

Li, N., Zhang, G., Ge, J., Zhang, L., Liu, X., & Wang, J. (2012). Ultra-low interfacial tension between heavy oil and betaine-type amphoteric surfactants. *Journal of Dispersion Science and Technology, 33*(2), 258-264.

McCue, K. F., & Hanson, A. D. (1992). Salt-inducible betaine aldehyde dehydrogenase from sugar beet: cDNA cloning and expression. *Plant Molecular Biology, 18*(1), 1-11.

Mukherjee, S., Das, P., & Sen, R. (2006). Towards commercial production of microbial surfactants. *Trends in biotechnology, 24*(11), 509-515.

Nalewaja, J. D., Goss, G. R., & Tann, R. S. (1998). *Pesticide Formulations and Application Systems: Eighteenth Volume* (Vol. 18): ASTM International.

Nimerick, K., Hinkel, J., England, K., Norton, J., & Roy, M. (1991). *Design and Evaluation of Stimulation and Workover Treatments in Coal Seam Reservoirs.* Paper presented at the SPE Eastern Regional Meeting.

Palmer, I. D., Moschovidis, Z. A., & Cameron, J. R. (2005). *Coal failure and consequences for coalbed methane wells.* Paper presented at the SPE Annual Technical Conference and Exhibition.

Rodrigues, L., & Teixeira, J. (2008). Biosurfactants production from cheese whey.

ShamsiJazeyi, H., Verduzco, R., & Hirasaki, G. J. (2014). Reducing adsorption of anionic surfactant for enhanced oil recovery: Part I. Competitive adsorption mechanism. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 453*, 162-167.

SigmaAldrich. (2012). Product Information on Surfactin from Bacillus subtilis.

Sineriz, F., R.K.Hommel, & Kleber, H.-P. (2001). Production of Biosurfactants. *Production of Biosurfactants, V*.

South, C. (2007). Clayton's Health Facts: Betaine Anhydrous.

Torres, L., & et al. (2011). Comparison of bio-and synthetic surfactants for EOR. *Journal of Petroleum Science and Engineering, 76*(1), 6-11.

Williams, D. A., Looney, J. R., Conway, M. W., & Swenson, R. A. (1995). Stimulation of coalbed methane production: Google Patents.

WORC (Producer). (2003). Coalbed Methane Developmet: Boom or Bane for Rural Residents?

Yuan, Y., & Lee, T. R. (2013). Contact angle and wetting properties *Surface science techniques* (pp. 3-34): Springer.