Branched alcohols from renewable resources for reducing the MMP of CO_2 - crude oil systems

By

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Dissertation submitted in partial fulfilment of
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Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
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Approved

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August 2011

CERTIFICATION OF ORIGINALITY

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

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ABSTRACT

Miscible displacement by carbon dioxide (CO_2) is a method to increase oil recovery. This technique is a very economical method in enhanced oil recovery (EOR), especially in CO_2-crude oil reservoir. It maintain reservoir pressure and also reduce oil viscosity. One of the most important parameters that should be known to utilise CO_2 miscible displacement is minimum miscibility pressure (MMP). MMP is the pressure at which CO_2 will achieve miscibility with the oil. Alcohol is well known as a co-surfactant in reducing interfacial tension (IFT) which is a direct parameter in reducing MMP. There are intensive researches on branched alcohol surfactants such as branched alcohol propoxylate sulphate. Branch alcohol may also reduce IFT better compare to straight chain alcohol surfactants. Yet, alcohol can only be used as the main IFT reducing agent if it can be produced cheaply. This paper focuses on synthesis of branched alcohol from Jatropha oil. However, due to the unavailability of reactant needed, final step of synthesizing branched alcohol cannot be done. But, the research is still continued with alkoxyl FAME since it shows potential for use as additives to reduce MMP due to alcohol branch attached. For the first step of synthesizing, transesterification of jatropha oil, 87% fatty acid methyl ester (FAME) yield was achieved. Next step of epoxidation FAME and alcohol addition to the epoxide FAME is done and expected to have 83.5% (Campanella, et al. 2008) and 100% (Smith. et al. 2009) conversion respectively. The effect of products on CO_2-crude oil MMP is then determined using Vanishing Interfacial Technique (VIT). The result shows MMP reduced to 1990 psia from 2240 psia when alkoxyl FAME Jatropha is mixed with Dulang crude oil at 60°C. Alkoxyl FAME Jatropha shows greater effect in reducing MMP compare to alkoxyl FAME Palm, 11.6% reduction compare to 4.46% reduction. Alkoxyl FAME Jatropha also shows better result compare to 2-methyl butan-2-ol in reducing MMP, 11.6% and 5.8% reduction respectively. This happened because alkoxyl FAME Jatropha mainly consists of highly branched alcohol FAME structures (65.86%) which result to higher polarity. This higher polarity affects the CO_2 capacity to form interaction with the crude oil, thus lower the MMP. Meanwhile for alkoxyl FAME Palm, it mainly consists of FAME structures without alcohol branched (52.69%). And eventhough FAME structures with alcohol branched (47.31%) are present, it only mainly made up of single alcohol branched FAME. This make alkoxyl FAME Palm less in polarity.

Therefore, the ability of alkoxyl FAME Palm to reduce MMP is lower than alkoxyl FAME Jatropha. For 2-methyl butan-2-ol, lower polarity compare to alkoxyl FAME Jatropha is resulted from lesser branched alcohol. As conclusion, alkoxyl FAME synthesized from Jatropha oil have the ability in reducing MMP for CO_2 – crude oil systems, and gives better result compare to alkoxyl FAME from Palm oil and 2-methyl butan-2-ol.

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CHAPTER 1: INTRODUCTION

1.1 Background Study

Highest economical recovery factor is always the main objective for a reservoir engineer when working on their project. Primary and secondary recovery can only extract 20% - 40% reserve in the reservoir. However, by introducing Enhanced Oil Recovery (EOR) techniques, they can extract up to 30% - 60% of the total reservoir (US Department of Energy, 2011). EOR purpose is not only to restore formation pressure, but also to improve oil displacement or fluid flow in the reservoir, by reducing interfacial tension and viscosity.

One of the widely used EOR methods is miscible gas injection displacement, and carbon dioxide (CO_2) is often used as the injected gas due to its inert characteristic, cost and abundant supply, moreover in CO_2-crude oil system. For this method, pressure above Minimum Miscibility Pressure (MMP) must be achieved. In a study by Hui (1995) shows that the estimated MMP CO_2 for Malaysian crude is between 2300-4380 psig. Interfacial tension is a direct parameter in measuring MMP. This method will allow the injected gas to form a single phase solution with the oil in place so that oil mobility is increased to ease production from the reservoir (Donaldson, et al. 1985 and Green and Wilhite 1998).

Miscibility between fluids can be achieved in two ways; first contact miscibility or multiple contact miscibility. For CO_2 and oil case, it is usually multiple contact miscibility. Components of oil and CO_2 transfer back and forth until the oil-enriched CO_2 cannot be distinguished from the CO_2-enriched oil (Perry, et al. 2002). Thus CO_2 becoming more soluble into the oil. This mass transfer between CO_2 and oil continues until there is no distinguishable in fluid properties terms. At this point, it results to one phase hydrocarbon.

Study by Quesheng, et al. (2003) shows that alcohol has a polar and non-polar part, which classifies them as a semi polar solvent. Oil and CO_2 are both non-polar. Oil and CO_2 will mix with the carbon based end of alcohol molecules, the non-polar end. When alcohol is injected into the reservoir along with CO_2, alcohol will lower the

MMP between CO_2 and crude oil composition in the reservoir by reducing the Interfacial Tension (IFT), because alcohol will enhance the solvating power and polarity of CO_2, caused by the formation of special interaction between solute and co-solvent molecule.

For a branched alcohol to be used as surfactant, they must be able to be mass produced and economically competent. One way of reducing branched alcohol production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and by-products of refined vegetables oils. This fatty acid will then be converted into branched alcohol. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive branched alcohol. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative. With no competing food uses, this characteristic turns attention to Jatropha *curcas*, which is readily grown in tropical and subtropical climates across the developing world (Hanny and Shizuko 2007).

1.2 Problem Statement

1. Alcohol as Surfactant

   Alcohol used in the industry (eg: alcohol ethoxylates) is very expensive. The current price for one gallon of alcohol is approximately USD 6.90. Often, alcohol is only used as a co-surfactant instead.

2. High Minimum Miscibility Pressure (MMP)

   MMP explain the concept of lowest pressure for a displace fluid (CO_2 in this case) to achieve miscibility with the crude oil. For miscible displacement to occur, displacing fluid will be injected at pressure higher than MMP. But, fracture pressure of the reservoir need to be consider. Injecting pressure above this fracture pressure will cause the unwanted fracturing to the reservoir (Martin, et al. 1992 and Perry, et al. 2002).

1.2.1 Problem Identification

In order to yield high amounts of branched alcohol from jatropha oil, an in-depth study to determine the most suitable method is needed. From all the options reviewed, process which involves transesterification, epoxidation, alkoxylation, and ester reduction was selected. MMP will then be estimated using VIT method, where estimation of IFT = 0 (MMP is achieved) is done from extrapolation of IFT versus pressure plot. The reduction of MMP will be compared to the results of 2-methyl butan-2-ol and Palm oil product, which also undergo the same process.

1.2.2 Significance of Project

This project is beneficial for oil and gas industry because it allows the usage of branched alcohol as surfactant instead of co-surfactant by means of finding a way of producing branched alcohol from renewable resources such as jatropha oil. This project also improves the current EOR-CO_2 miscible displacement technique because it can reduce MMP.

1.3 Objectives

1. **To produce branched alcohol from renewable resources**

   A designated methodology to produce branched alcohol from jatropha oil is already identified. Percentage of product yield is the main factor for determination of appropriate method.

2. **To estimate MMP by means of IFT measurement to prove effect of branched alcohol.**

   MMP is achieved when IFT approaches zero. The condition of IFT = 0 is impossible to achieve. Therefore, VIT method is used, where MMP is estimated from extrapolation IFT versus pressure plot (Ayirala and Rao, 2006).

1.4 Scope of Study

- Production of branched alcohol from Jatropha and Palm oil using 4 synthesizing steps; transesterification, epoxidation, alkoxylation, and ester reduction.
- Investigate effect in MMP reduction for both products and 2-methyl-2-butanol.

1.5 Relevancy and Feasibility of Study

1.5.1 Relevancy of Study

This study is an improvement to the current CO_2 miscible displacement technique. This is relevant to the industry since this technique is widely used in the current Exploration and Production (E&P) project. This research could provide a way of reducing MMP by using branched alcohol as surfactant, and it can be produced in a cheap large scale from abundant renewable resources.

1.5.2 Feasibility of Study within the Scope and Time Frame

All the objectives were achieved within the given time frame, except for conversion into final product with alcohol as main functional group. However, final synthesized product from this research is attached with alcohol branch, which make the investigation on the effect of branched alcohol on MMP is possible.

Main objective in producing branched alcohol from renewable resources is achievable if students are given some procurement time in buying their reactants.

CHAPTER 2: LITERATURE REVIEW

2.1 Alcohol as Surfactant

Alcohol has been known for their ability to act as a surfactant. In surfactant EOR technique, the basic physics behind them is that the residual oil are dispersed as micron-sized ganglia, trapped by high capillary forces within the porous media. Increasing the fluid flow viscous forces or decreasing the capillary forces holding the oil in place are required before the oil can be pushed through the pore throats and sent on to a production well (Wu, et al. 2005). For this to succeed, ultra low IFT is needed (0.001mN/m).

Branched alcohol propoxylated sulfates have emerged to be a good type of surfactant for oil removal. Propoxylated sulfate surfactant has been shown to create middle-phase micro emulsions versus crude oils, and presumably achieve low interfacial tension (Aoudia, et al. 1996). Another study demonstrated branched chain alkyl group to have lower IFT than those with straight chain alkyl group (Rosen, et al. 2005).

In the study done by Wu, et al. (2005), 18 different branched alcohol propoxy sulfates are selected, of the Alfoterra® mn (m=1,2,3,4,5,6; n=3,5,8) series supplied by Sasol Corporation.

Below is the data showing the result of branched alcohol propoxylated of Alforterra been use as surfactant to reduce IFT:

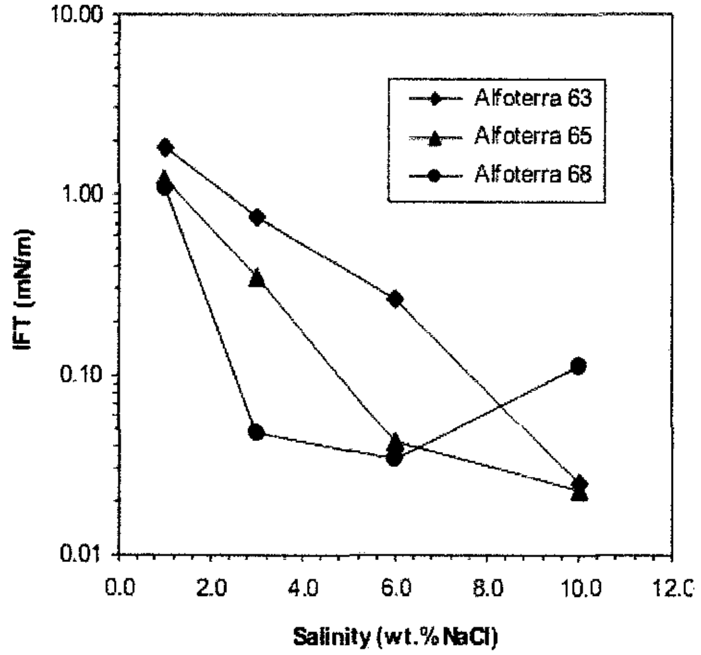


Figure 1: IFT result of Alfoterra 63, 65 and 68 at low concentration (0.2 wt. %) in various salinity (Oil phase: n-octane, room temperature) (Wu, et al. 2005)

Table 1: Result of IFT of Alfoterra surfactant

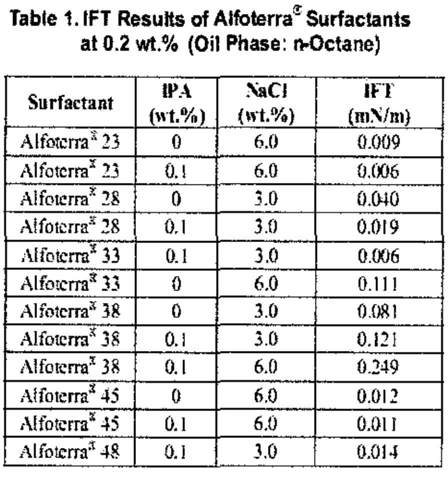


Table 1. IFT Results of Alfoterra® Surfactants at 0.2 wt.% (Oil Phase: n-Octane)

Surfactant	IPA (wt.%)	NaCl (wt.%)	IFT (mN/m)
Alfoterra® 23	0	6.0	0.009
Alfoterra® 23	0.1	6.0	0.006
Alfoterra® 28	0	3.0	0.040
Alfoterra® 28	0.1	3.0	0.019
Alfoterra® 33	0.1	3.0	0.006
Alfoterra® 33	0	6.0	0.111
Alfoterra® 38	0	3.0	0.081
Alfoterra® 38	0.1	3.0	0.121
Alfoterra® 38	0.1	6.0	0.249
Alfoterra® 45	0	6.0	0.012
Alfoterra® 45	0.1	6.0	0.011
Alfoterra® 48	0.1	3.0	0.014

IPA: iso-propanol .

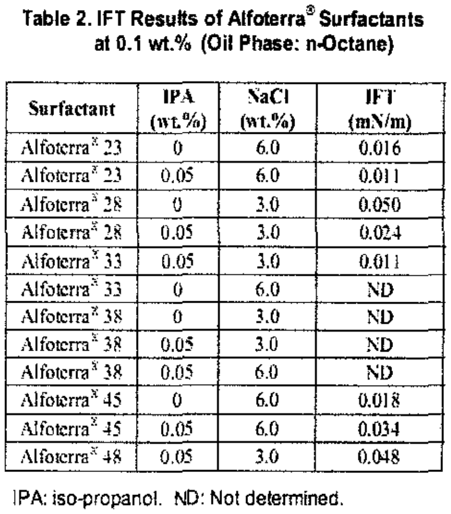


Table 2. IFT Results of Alfoterra® Surfactants at 0.1 wt.% (Oil Phase: n-Octane)

Surfactant	IPA (wt.%)	NaCl (wt.%)	IFT (mN/m)
Alfoterra® 23	0	6.0	0.016
Alfoterra® 23	0.05	6.0	0.011
Alfoterra® 28	0	3.0	0.050
Alfoterra® 28	0.05	3.0	0.024
Alfoterra® 33	0.05	3.0	0.011
Alfoterra® 33	0	6.0	ND
Alfoterra® 38	0	3.0	ND
Alfoterra® 38	0.05	3.0	ND
Alfoterra® 38	0.05	6.0	ND
Alfoterra® 45	0	6.0	0.018
Alfoterra® 45	0.05	6.0	0.034
Alfoterra® 48	0.05	3.0	0.048

IPA: iso-propanol. ND: Not determined.

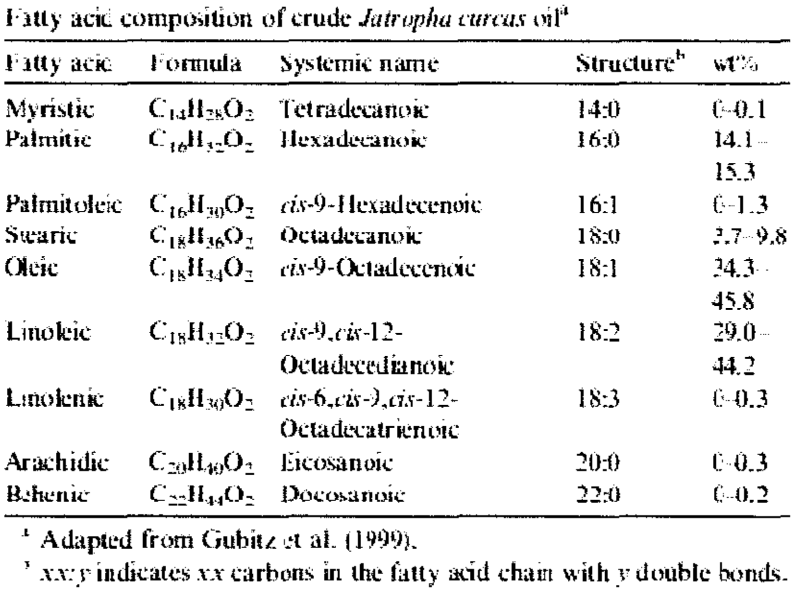
These studies give strong foundation in the effectiveness of branched alcohol in reducing IFT, which is the direct parameter to indicate reduction of MMP.

2.2 Jatropha *curcas* L.

Jatropha oil is a product from Jatropha *curcas L.* seed. It grows in tropical and subtropical climates across the developing world. This inedible vegetable oils is a promising candidate of being main biodiesel source (Campanella, et al. 2008) since it have no competing food uses unlike palm oil which main function is for cooking oil.

Oil contents, physiochemical properties, fatty acid composition and energy values of Jatropha were investigated (Openshaw, 2000), and it is considered as toxic substance. Jatropha is chosen as the candidate oil for this research due to high content of unsaturated fatty acid components.

Table 2: Fatty Acid composition of crude Jatropha curcas oil [Akintayo, 2004]



Fatty acid composition of crude *Jatropha curcas* oil[a]

Fatty acid	Formula	Systemic name	Structure[b]	wt%
Myristic	$C_{14}H_{28}O_2$	Tetradecanoic	14:0	0–0.1
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0	14.1–15.3
Palmitoleic	$C_{16}H_{30}O_2$	*cis*-9-Hexadecenoic	16:1	0–1.3
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:0	2.7–9.8
Oleic	$C_{18}H_{34}O_2$	*cis*-9-Octadecenoic	18:1	24.3–45.8
Linoleic	$C_{18}H_{32}O_2$	*cis*-9,*cis*-12-Octadecedianoic	18:2	29.0–44.2
Linolenic	$C_{18}H_{30}O_2$	*cis*-6,*cis*-9,*cis*-12-Octadecatrienoic	18:3	0–0.3
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0	0–0.3
Behenic	$C_{22}H_{44}O_2$	Docosanoic	22:0	0–0.2

[a] Adapted from Gubitz et al. (1999).

[b] *xx:y* indicates *xx* carbons in the fatty acid chain with *y* double bonds.

From the table, Jatropha *curcas* oil mainly consists of linolenic and oleic fatty acid. Both components are made up of 2 and 1 unsaturated double bond respectively. These bonds can be replaced with alcohol branch that will the effect of branching in reducing IFT.

2.3 Guerbet Alcohol

Ethanol and other biomass fuel (straight chain alcohol) can be generated from renewable resources such as wheat straw, corn stover, soft wood, and sugarcane bagasse (Mousdale, 2008). But for this project, the main interest is to produce branched alcohol in a simple and cheap way.

Guerbet's method provides a way in producing branched alcohol from alcohol of natural origin, at high temperature and with catalysts. Branched alcohol produced will have twice the molecular weight of the original alcohol minus one mole of water. Guerbet alcohol tends to be more expensive than other types alcohols when produced in high purity. High cost is mainly due to stripping off unreacted monomer alcohol to produce high purity.

However, inexpensive Guerbet alcohol (GA) can be prepared by aiming for a less quantitative conversion during the alcohol dimerization process. The resultant blend will be 85-95% GA and the remaining will be monomer alcohol.

Even though Guerbet's method is a relatively easy method, synthesis of straight chain alcohol from renewable resources itself require complex setup and apparatus. Therefore instead of applying this method, synthesis of branched alcohol straight from renewable resources becomes the main study of interest.

2.4 Branched Alcohol Synthesis from Palm Oil

Smith, et al. (2009) has documented optimal condition for epoxification for synthesis of saturated fatty acid from oleic acid of palm oil. Epoxification must be performed at a constant 60°C on a temperature controlled hotplate/stirrer (Smith, et al. 2008) with peroxyformic acid or peroxyacetic acid. This reaction is monitored over a 24h period to determine optimum residence time. Acid catalyst is required to optimize acid recovery from this method. Residual acid and peroxide used is then neutralised using sodium bicarbonate, several water washes and anhydrous sodium sulphate for drying.

For alcohol branching of saturated fatty acid, addition of alcohol is needed. Alcohol (eg: propanol or butanol) addition is performed in a glass reaction apparatus on a hotplate at 60°C. Sulfuric acid 2 wt% is used as catalyst, and reaction is monitored for batch time of 6h. Residual catalyst and alcohol will be removed by repeated water washes and phase separation followed by drying over anhydrous sodium sulphate and filtration (Smith, et al. 2009).

Smith, et al. (2009) also studied the effects of temperature, catalyst concentration and effect of molar ratio of alcohol used on conversion of epoxy butyl biodiesel.

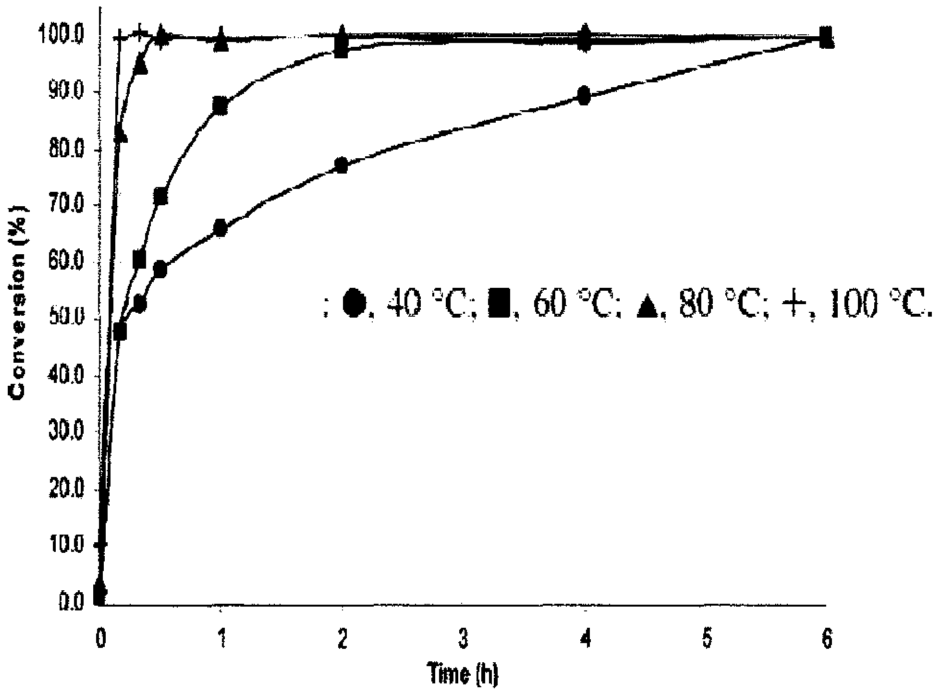


Figure 2: Effect of temperature on conversion of epoxy butyl biodiesel

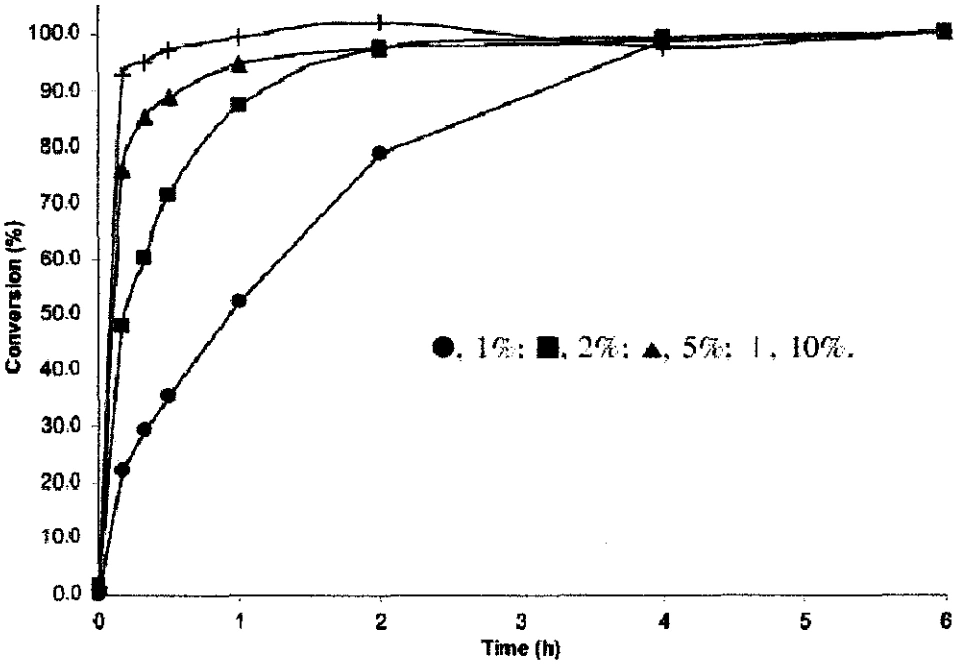


Figure 3: Effect of Catalyst concentration on conversion of epoxy butyl biodiesel

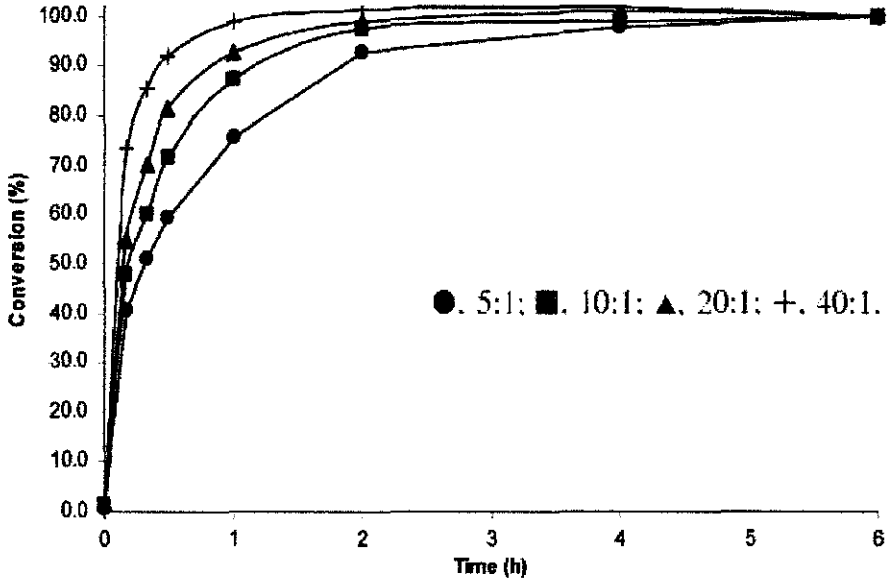


Figure 4: Effect of molar ratio of butanol on conversion of epoxy butyl biodiesel

Knowledge on these 3 parameters is essential for designing optimal methodology in branching of saturated fatty acid with alcohol.

Lastly, a method of converting fatty carboxylic acid into alcohol must be identified. Most common method for reducing carboxylic acid into alcohol is using Lithium Aluminium Hydride ($LiAlH_4$). This reaction is a difficult process to do and often requires heating in tetrahydrofuran solvent for completion. $LiAlH_4$ is also not safe to handle since it is very reactive, and this chemical is relatively expensive. Alternatively, borane tetrahydrofuran complex (BH_3/THF) can be used to reduce carboxylic acid into alcohol. Reaction of an acid with BH_3/THF occurs rapidly at room temperature, and the procedure is often preferred to reduction with $LiAlH_4$ because it is relatively easy, safe and specific. The specificity of BH_3/THF is important so that the alcohol branch of the chemical produced earlier will not be reduced by this reducing agent (McMurry, 2004).

2.5 CO_2 Miscible Displacement

Miscible displacement can be classified as first contact miscible (FCM) and multiple contact miscible (MCM) on the basis of how the miscibility is achieved between oil and injected fluid. For CO_2 displacement, miscibility is achieved by multiple contacts miscible. Multiple-contact processes are classified as vaporizing-gas (lean gas) displacement, condensing and condensing/vaporizing-gas (enriched-gas) displacement (Green and Wilhite, 1998).

CO_2 displacement behaviour is analogous to the vaporizing process under some conditions of proper pressure, temperature and composition, but it is more complex. According to Green and Willhite (1998), in the vaporizing-gas process, the composition of the injected gas is modified as it moves through the reservoir so that it becomes miscible with the original reservoir oil. That is, the injected fluid is enriched in composition through multiple contacts with the oil, during which intermediate components in the oil are vaporized into the injected gas. Under proper conditions, this enrichment can be such that the injected fluid of modified composition will become miscible with the oil at some point in the reservoir. From that point on, under idealized conditions, a miscible displacement will occur (Green and Wilhite, 1998).

Theoretically for miscibility to occur, the interfacial tension (IFT) between the two fluids will be zero (Ayirala and Rao, 2006). Gas is considered miscible in the fluid or solvent if both gas and fluid can assume a single phase. The basic of this phenomenon is, mass will be transferred between the gas and the solvent. According to Lee, et al. (1988), the mass transfer mechanism involved is vaporizing gas drive. CO_2 is a lean gas which will strip the liquid which is rich in intermediate and heavy hydrocarbons until the gas has similar composition with the solvent and become miscible.

Knowledge on this matter is crucial for better understanding in CO_2 miscibility displacement. One of the research objectives is to investigate MMP for miscibility between CO_2 and crude oil. Therefore, basic understanding for the whole process in reservoir is needed.

2.6 Minimum Miscibility Pressure (MMP)

MMP is the lowest pressure needed for the displacing fluid (CO_2 in this case) to achieve miscibility with the crude oil. CO_2 miscibility in oil is a function of both temperature and pressure, but pressure is the main concerned for isothermal reservoir. When the contact between CO_2 and oil occurs with little or no reservoir mixing, the pressure at which miscibility happens is defined as the thermodynamic minimum miscibility pressure (thermodynamic MMP) (Perry. et al, 2002). As CO_2 becomes miscible with the crude oil, it will reduce the viscosity of the oil hence increasing its mobility towards the producing well. Miscibility of CO_2 will also reduce the density between the fluids.

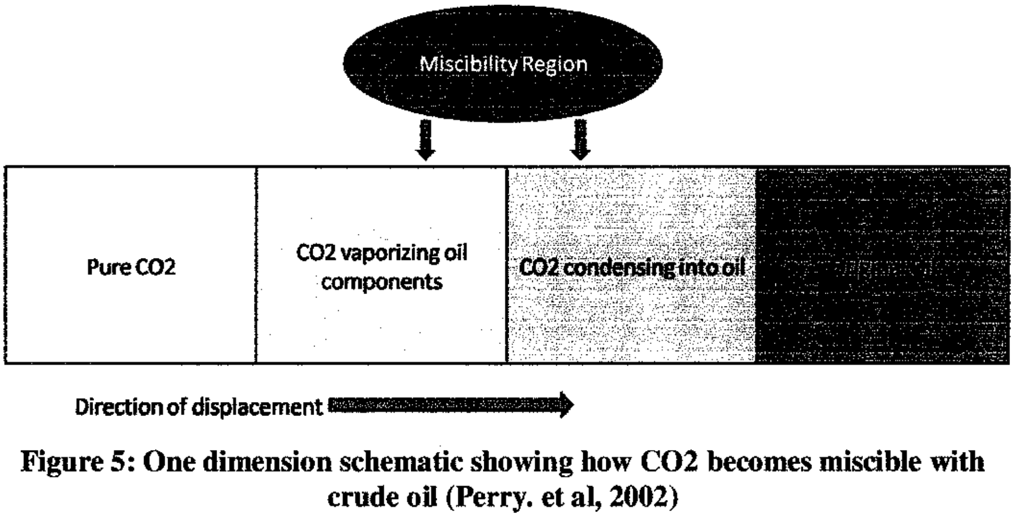


Figure 5: One dimension schematic showing how CO2 becomes miscible with crude oil (Perry. et al, 2002)

Along the displacement direction, CO_2 concentration reduced, therefore some of the oil remain unvaporized and stays as residual oil. Subsequent contact with fresh CO_2

will slowly vaporize these heavier components. Because of the additional vaporization, the residual oil saturation after CO_2 flooding is considerably less than the residual oil saturation after waterflooding (Perry. et al, 2002).

Based on this study, MMP is well defined, and recovery of reservoir oil is enhanced by means of decreasing residual saturation.

2.7 Surface/ Interfacial Tension

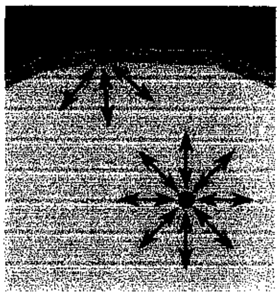


Figure 6: Diagram of the forces on two molecules of a fluid (blue) interfacing with another fluid (black) (Snacks, 2010)

When two immiscible fluids are in contact, the fluids are separated by a well-defined interface, which are only a few molecular diameters in thickness. In the middle of liquid phase, a fluid molecule will be pulled at every direction whereas at the interface of the two fluids, there is an imbalance between the forces. This would create a barrier between the fluids from becoming miscible (denoted by the dark blue line in Figure 1). High values of the surface tension means the molecules tend to interact strongly. Lower values mean the molecules do not interact as strongly and will easily become homogeneous.

Interfacial tension is described as a measurement of energy on the barrier separating the two phases. IFT can be measured using the pendant drop method. They have the dimensions of force per unit length (Newtons/meter or Dynes/cm).

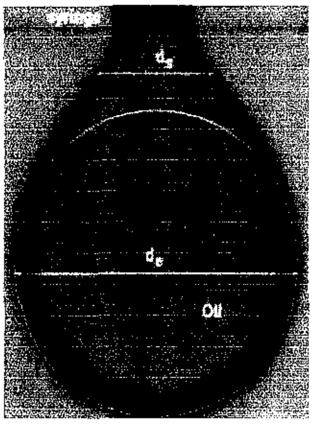


Figure 7: An illustration of the pendant drop method

Using the pendant drop method (Figure 2), the geometry of a drop is analysed optically. A drop is generated from the end of a capillary needle in a bulk fluid at reservoir conditions (Pressure and Temperature). With a calibrated and accurate video lens system, the complete shape of the drop is captured and analysed with software. Then, the Laplace equations of the analysis are solved numerically over its complete shape to get the IFT.

2.8 CO_2 Density

Since IFT measurement process requires bulk density of CO_2 for varying temperature, calculation beforehand is needed. The density for every temperature is obtained based on real gas equation:

$$PV = \frac{m}{M} zRT$$

Where;

P = pressure
V= volume
m = mass of gas
M = molecular weight
Z = correction factor
R = universal gas constant
T = temperature

Based on the above equation, density of CO_2 is tabulated:

Table 3: CO2 density at varying pressure

Pressure (psia)	Density (g/cc)
1000	0.152105
1100	0.175840
1200	0.202752
1300	0.240000
1400	0.269530
1500	0.311250
1600	0.360000
1700	0.412780
1800	0.464909
1900	0.511780
2000	0.551300

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

Research methodologies for this study are divided into two parts;

1. Branched alcohol synthesis from jatropha oil.
2. CO_2-crude-branched alcohol oil MMP estimation using VIT method.

3.1.1 Synthesis Branched Alcohol from Jatropha Oil

Procedure

Procedure 1: Acid Value Determination

a) 1 drop of phenolphthalein and 0.1M NaOH is added into 50 ml ethanol.
b) The mixture is then added into 5g of sample (jatropha oil).
c) Shake the mixture.
d) 0.1M NaOH is added dropwise into the mixture until the colour of the mixture turn to pink.
e) Volume of NaOH needed to change the colour is taken.
f) Acid value is then calculated using:

$$\%\,acid\ value = \frac{volume\ of\ NaOH\ \times 28.2}{weight\ sample}$$

g) If acid value is >2%, proceed with Procedure 2.

Procedure 2: Acid Pre-treatment

a) Oil is poured into reaction glass and heated to 50°C.
b) Solution of H_2SO_4 (1% w/w) in methanol (60% w/w) is heated to 50°C.
c) The solution is added into the reaction glass. The temperature is maintained at 50°C in water bath.
d) The mixture was allowed to react for 2 hours.
e) The mixture is then poured into separation funnel and allowed to settle overnight.
f) Procedure 1 is repeated to check the new acid value.
g) If acid value is $\leq 2\%$, proceed with Procedure 3.

Procedure 3:Base Catalyzed Transesterification

a) 1 mol of oil is poured into reaction glass and heated to 60°C in water bath.

b) Solution of $NaCH_3O$ (0.5% w/w) in 7 mol of methanol is prepared without heating.

c) The solution is added into the reaction glass.

d) The mixture was allowed to react for 2 hours.

e) The mixture is then poured into separation funnel and allowed to settle overnight.

f) Separate the glycerol at bottom layer from fatty acid methyl ester at top layer.

g) FAME is water washed several times to remove residual methanol, base and glycerol.

h) Methyl ester is analysed using Gas Chromatography Mass Spectroscopy (GCMS).

Procedure 4: Epoxidation (Smith. et al,2008 and Smith. et al,2009)

a) 1 mol of FAME and 0.5 mol formic acid is poured into reaction glass and heated to 40°C in water bath.

b) Afterwards, 2 mol hydrogen peroxide, H_2O_2 (35 wt% aq) was added drop by drop for 1 hour and the reaction mixture was held at constant temperature and under stirring for 11.5 hours.

c) After reaction completion, washed with a solution of sodium bicarbonate (5 wt%), next with water until complete elimination of acidity in the organic phase, and last with NaCl (5 wt%). The final product was then dried in rotary evaporator.

d) The product is analysed using GCMS.

Procedure 5: Alkoxylation of Epoxide FAME

The above product is then undergo propanol addition for branching purposes. The expected product is Alkoxyl FAME (FAME with propanol branch)

a) 1 mol of oil is poured into reaction glass and heated to 60°C.
b) Solution of H_2SO_4 (2% w/w) is mixed into 10 mol of 2-propanol.
c) The solution is added into the reaction glass. The temperature is maintained at 60°C in water bath.
d) The mixture was allowed to react for 2 hours.
e) The mixture is then poured into separation funnel and allowed to settle overnight.
f) Residual catalyst and 2-propanol were removed by repeated water washes and phase separation followed by drying over anhydrous sodium sulphate and filtration.
g) The product is analysed using GCMS.

3.1.2 CO_2-crude-branched alcohol oil MMP estimation using VIT method

MMP estimation is obtained experimentally using IFT-700. Pendant drop method is used in this experiment because of condition where density of crude oil used in this research is higher than the density of CO_2. MMP is then estimated from the result obtained using VIT method.

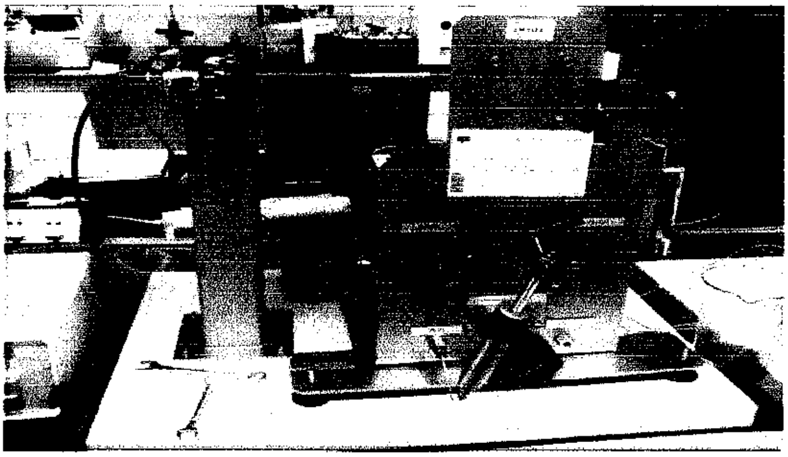


Figure 8: IFT 700

Procedure

a) Samples of alkoxyl FAME Jatropha, alkoxyl FAME Palm, 2methyl butan2ol mix with Dulang crude oil is prepared.
b) Sample of Dulang crude oil is also prepared for base case experiment.
c) Density for each sample is measured.
d) IFT is then measured using IFT 700 device.

Procedure of using IFT 700 device is included in Appendix.

3.1.3 Density Measurement

For IFT 700 to measure IFT, fluid density is needed. Density will be measured using Anton Paar DMA 45 instrument.

Procedure

a) Device is turned on.
b) All the fluids that need to be measured are prepared.
c) Using the device, the measured fluid is suck into the device.
d) Density reading within 30°C - 40°C temperature is then taken.
e) Density at 60°C is then obtained from extrapolation.
f) Clean the device using solvent or ethanol.
g) Repeat procedure from step d for different chemical.

3.2 Project Work Flow

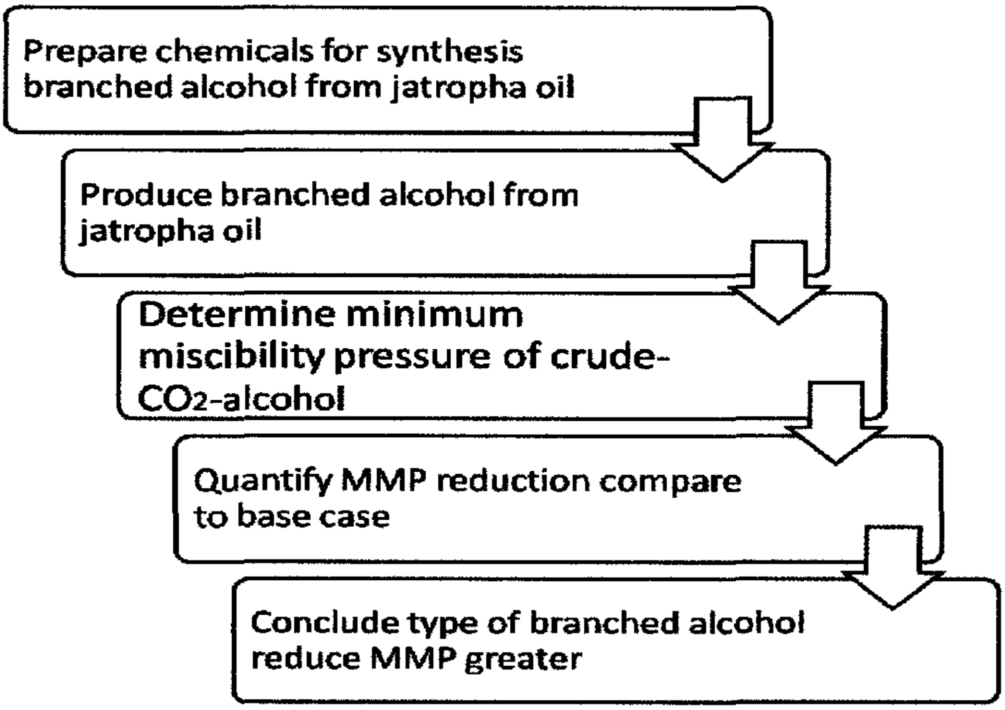


Figure 9: Flow diagram of Project work flow

3.3 Equipment and Tools

This project is divided into two parts, first synthesizes branched alcohol and second is MMP determination experiments. Synthesize branched alcohol was done at Chemical Block at Block 3 (Petrochemical Lab). Lot of beaker, reaction glass, were used along the experiment. Other tools and equipment used included thermometer, retort stand, condenser, separating funnel, fume hood, oven and measuring cylinder.

For the second part of the experiment, main equipment used was IFT 700 device, together with minor used of oven, fume hood and beakers.

CHAPTER 4: RESULTS & DISCUSSION

4.1 Branched Alcohol Synthesis from Jatropha Oil

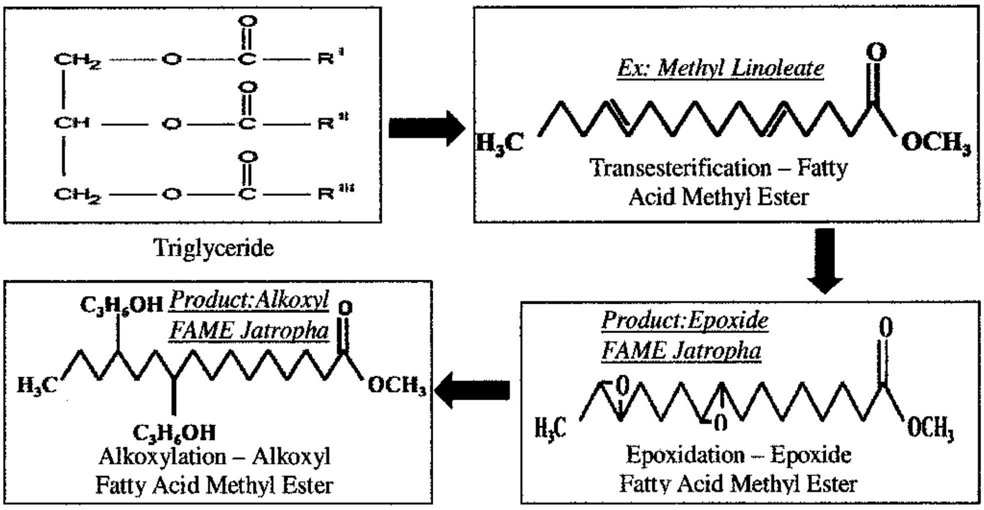


Figure 10: Overall chemical reaction

4.1.1 Acid Value Determination

For Jatropha *curcas* seed oil, continuous exposure to light and improper storage will cause the oil to damage due to various chemical reactions such as hydrolysis, polymerization and oxidation. These damages alter the physical and chemical properties of the oil. Free fatty acid (FFA) has been found to increase due to the hydrolysis of triglycerides with presence of moisture and oxidation process (Hanny and Shizuko, 2007). FFA is an unwanted property in the oil because it will not be converted into fatty acid methyl ester (product of Procedure 3) due to formation of soap instead. FFA formation in jatropha oil is easily occur due to higher concentration of unsaturated fatty acids, which are mainly made up of linoleic acid (up to 44%) and oleic acid (up to 45%).

Acid value determination experiment shows jatropha oil used in this experiment contained 14.3% FFA. This value need to be reduced to $\leq 2\%$. This is done by procedure 2: Acid Pretreatment.

4.1.2 Acid Pretreatment

Main objective of this step is to reduce FFA content in the Jatropha oil. The ratio of methanol-oil used is taken from a study conducted by Hanny and Shizuko (2007). It shows the value of methanol needed is 60% w/w. It was reported that to get completely FFA esterification, the experiment must be done at reaction temperature 50°C and the acid H_2SO_4 to oil ratio 1% w/w (Ghadge and Raheman, 2005 and Veljkovic. et al, 2006).

The product yield is then tested for FFA content using Procedure 1. FFA content reduces to 1.7% after acid pretreatment.

Example of experiment:

Oil weight: 35.00g
Methanol weight: 21.00g
H_2SO_4 weight: 0.35g

Result:

i. During mixing, milky colour appeared.
ii. After mixture is settled, 2 distinguishable layers appeared. The bottom layer is taken to be treated Jatropha oil.
iii. Run procedure 1 to test on new acid value.
iv. New acid value obtain is 1.7% instead of 14.7% before treatment.

4.1.3 Base Catalyzed Transesterification

Table 4: Analytical result of components of FAME for Jatropha & Palm Oil

Fatty Acid Methyl Ester	Jatropha (%)	Palm (%)
Methyl Laurate	0.10	0.41
Methyl Myristate	0.07	1.12
Methyl Palmitate	14.92	34.50
Methyl Palmitoleate	0.66	0.18
Methyl Stearate	8.64	6.30
Methyl Oleate	40.58	41.30
Methyl Linoleate	34.70	15.36

Qualitative and quantitative analysis result of methyl ester components in Jatropha and palm oil transesterification product are presented in Table 4. The table indicates that the FAME from Jatropha contained mainly methyl oleate (40.58%) and methyl linoleate (34.70%) which are comparable to fatty acid composition in jatropha feedstock. As for palm oil, it mainly contained methyl oleate (41.30%) and methyl palmitate (34.50%). FAME yield was 82% and 85% for Jatropha and palm oil respectively

This result is in line with the main objective of producing branch alcohol. High amount of unsaturated fatty acid allow for more alcohol branching. Since Jatropha FAME contained 34.70% methyl linoleate which have 2 unsaturated bond, and 40.58% methyl oleate which have 1 unsaturated bond, the alcohol branch will become dominant in the mixture.

Example of experiment:

Palm Oil weight: 160.22g

Methanol weight: 42.82g

$NaCH_3O$ weight: 0.81g

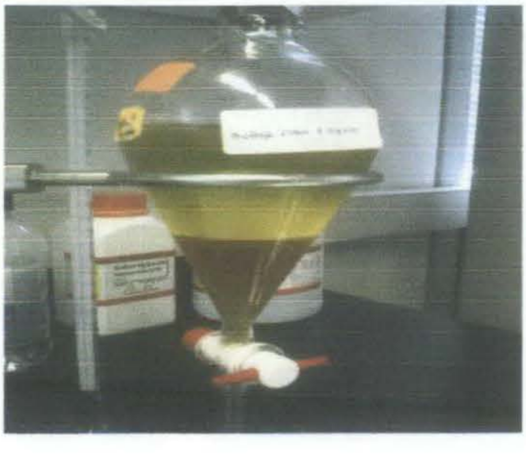
Result:

i. 2 distinguish layer is observed. Top layer is methyl ester and bottom layer is glycerol.

ii. Several water wash is needed to increase purity and remove residual methanol and catalyst.

iii. Percentage of methyl ester recovered = 94%

iv. Product is analysed by GCMS.



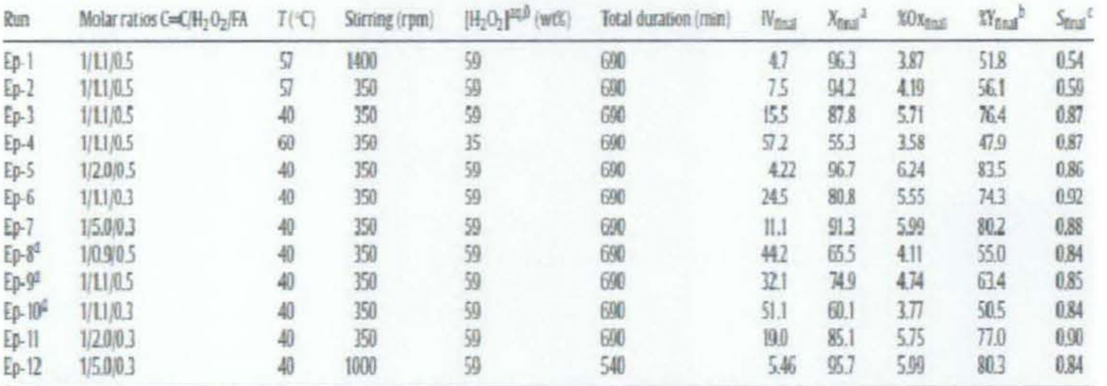
2 distinguish layer of methyl ester and glycerol appeared.

Using water bath technique and condenser to retain evaporized alcohol

4.1.4 Epoxidation of FAME

Epoxidation of FAME is done using *Performic acid generated in-situ* technique. It was reported this technique have high conversion rate at 40°C reaction temperature, 2 mol hydrogen peroxide H_2O_2 (60wt%) and 0.5 mol formic acid for 1 mol of FAME (Campanella. et al, 2008) .

Table 5: Epoxidation of soybean FAME with performic acid generated in-situ from formic acid and hydrogen peroxide



Run	Molar ratios C=C/H_2O_2/FA	T (°C)	Stirring (rpm)	$[H_2O_2]^{aq,0}$ (wt%)	Total duration (min)	IV_{final}	X_{final}[a]	$\%Ox_{final}$	$\%Y_{final}$[b]	S_{final}[c]
Ep-1	1/1.1/0.5	57	1400	59	690	4.7	96.3	3.87	51.8	0.54
Ep-2	1/1.1/0.5	57	350	59	690	7.5	94.2	4.19	56.1	0.59
Ep-3	1/1.1/0.5	40	350	59	690	15.5	87.8	5.71	76.4	0.87
Ep-4	1/1.1/0.5	60	350	35	690	57.2	55.3	3.58	47.9	0.87
Ep-5	1/2.0/0.5	40	350	59	690	4.22	96.7	6.24	83.5	0.86
Ep-6	1/1.1/0.3	40	350	59	690	24.5	80.8	5.55	74.3	0.92
Ep-7	1/5.0/0.3	40	350	59	690	11.1	91.3	5.99	80.2	0.88
Ep-8[d]	1/0.9/0.5	40	350	59	690	44.2	65.5	4.11	55.0	0.84
Ep-9[d]	1/1.1/0.5	40	350	59	690	32.1	74.9	4.74	63.4	0.85
Ep-10[d]	1/1.1/0.3	40	350	59	690	51.1	60.1	3.77	50.5	0.84
Ep-11	1/2.0/0.3	40	350	59	690	19.0	85.1	5.75	77.0	0.90
Ep-12	1/5.0/0.3	40	1000	59	540	5.46	95.7	5.99	80.3	0.84

[a] Percent conversion of double bonds calculated as $X = [(IV^0 - IV)/IV^0] \times 100$. The initial iodine value (IV^0) was 129.6.

[b] Percent oxirane oxygen yield $= [(\%Ox)/(\%Ox_t)] \times 100$, where $\%Ox_t$ represents the theoretical %Oxirane for IV^0: $\%Ox_t = \{(IV^0/MW_{I_2})/[100 + (IV^0/MW_{I_2})MW_O]\}MW_O \times 100 = 7.4$.

[c] Oxirane oxygen selectivity $= [(\%Ox)/(\%Ox_t)] \times [IV^0/(IV^0 - IV)]$.

[d] Organic solvent (heptane) added: molar ratio C=C/heptane = 1/2. See text for details.

Expected epoxide FAME conversion for both Jatropha and Palm oil is 83.5%. For the experiment which have been done, hotplate used is unable to maintain temperature at 40°C. Therefore the reaction temperature is altered to 50°C, which is the minimum temperature that can be maintain by the hotplate. It was reported, temperature increases are significantly detrimental for achieving high oxirane numbers, as the selectivity to ring-opening reactions increases. Therefore it is expected the epoxide FAME produce will have slightly lower oxirane number.

Another problem for this experiment is the concentration of hydrogen peroxide used. The suitable concentration is 60wt%, but hydrogen peroxide available is only 35wt% concentration. Therefore, some alteration on the procedure need to be done to suit this limitation, but lower oxirane number is again expected.

Example of Experiment

Jatropha oil weight: 50.0g
Performic acid weight: 33.1g
Formic acid weight: 4.61g

Result:
Jatropha Epoxide FAME

i. Epoxide produced have slightly lighter orange colour compare to Jatropha FAME.
ii. Yield 47.91g (from 50.0g) with expected conversion of 83.5%.

4.1.5 Alkoxylation of Epoxide FAME

The objective of this step is to attach alcohol chain (2-propanol) to the oxyrane ring opening. There are 4 parameters that effect the conversion of epoxy FAME, which are temperature, catalyst and molar ratio of 2-propanol and time. The optimum condition were investigated (Smith. et al, 2009) and it was concluded the reaction temperature is at 80°C, 2wt% H_2SO_4 and 40:1 molar ratio of alcohol over a period of 1h.

The main byproducts of this reaction are the aforementioned glycol and the keto form as a result of rearrangement of oxirane, as reported by Rios. et al, (2005). Glycol and keto formation must be kept at minimum and parameters that control this formation is reaction temperature, catalyst and molar ratio. That is why the experiment must be designed at the optimum condition

But due to equipment limitation and limited alcohol available, the experiment was conducted at 60°C and 10:1 molar ratio. But this condition is compensated by increasing the reaction time to 6 hours. The conversion rate of **100% after 6 hours reaction** is expected (Smith. et al, 2009). But significant increase in glycol and keto formation is expected by this condition.

Example of Experiment

Epoxide FAME Jatropha weight: 56.51g
2-propanol weight: 97.00g
H_2SO_4 weight: 1.13g

Result:

i. Formation of one product is observed (Alkoxyl FAME + 2-propanol residue + impurities).
ii. Several water washing is needed to completely remove the residue alcohol, acid catalyst and other impurities.
iii. Other purification techniques cannot be done due to either equipment or chemicals inavailability.

4.2 IFT Measurement for MMP Estimation

4.2.1 Density Measurement

Table 6: Density for samples

Sample °C Temperature	Crude Oil + Alkoxyl FAME Jatropha (g/cc)	Crude Oil + Alkoxyl FAME Palm (g/cc)	Crude Oil + 2methyl butan-2-ol (g/cc)	Crude oil (g/cc)
30	0.8615	-	-	-
33	0.8595	0.8562	-	-
35	0.8583	0.8541	-	-
38	0.8553	0.8528	-	-
60	**0.8366**	**0.8346**	**0.7660***	**0.8020***

***density is obtained from Nafis, (2011)**

4.2.2 CO_2 Density

Table 7: CO2 density at varying pressure

Pressure (psia)	Density (g/cc)
1000	0.152105
1100	0.175840
1200	0.202752
1300	0.240000
1400	0.269530
1500	0.311250
1600	0.360000
1700	0.412780
1800	0.464909
1900	0.511780
2000	0.551300

4.2.2 Interfacial Tension Result

Table 8: Summary of all IFT measurement result

Sample / Pressure, Psia	Crude Oil + Alkoxyl FAME Jatropha	Crude Oil + Alkoxyl FAME Palm	Crude Oil + 2methyl butan-2-ol*	Crude oil*
1200	8.02	8.00	10.5	14.12
1400	6.31	6.24	7.99	10.26
1600	3.56	4.36	5.1	7.06
1800	3.24**	3.05	4.02	6.66
2000	-	-	-	3.12
MMP (Psia)	**1990**	**2140**	**2110**	**2240**

****measurement was conducted at 1700psi**

Interfacial Tension Measurement

IFT measurements were done at pressure within 1200 to 2000 psia and at constant temperature of 60°C. For every run, 10 minutes interval was given in order to stabilize pressure inside the cell and give clearer view for camera since fogging environment often created when CO_2 is injected into the cell in order to attain the required pressure. For every run, data obtained is corresponded to angle of the drop shape which is use for IFT measurement by the equipment. Only the data with the biggest angle is taken, since IFT reading is most accurate at this point.

a) INTERFACIAL TENSION BETWEEN CO_2 AND CRUDE OIL.

Table 9: Pressure, angle and IFT table (crude oil)

Pressure (psia)	Angle	IFT (mN/m)
1200	98.63	14.12
1400	105.15	10.26
1600	98.1	7.06
1800	101.64	6.66
2000	95.33	3.12

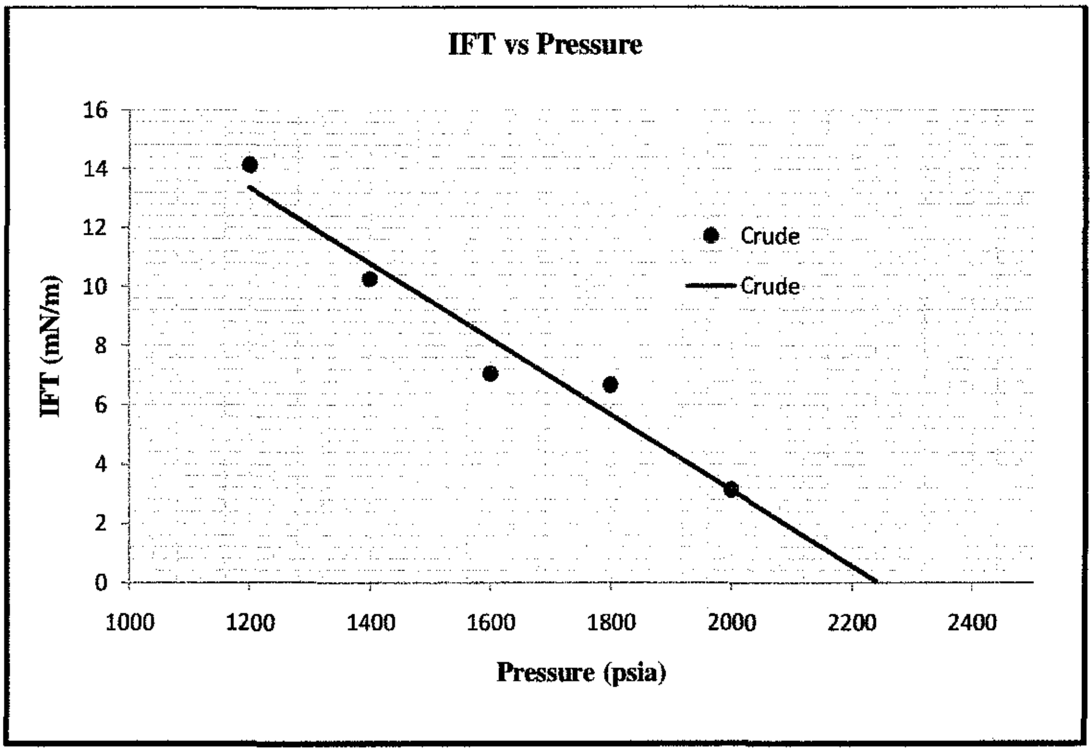


Figure 11: IFT vs Pressure graph (CO2 and Crude oil)

From the above result, an almost linear trend can be seen from Figure 11. Extrapolation to IFT at 0 mN/m gives pressure 2240 psia. Thus, MMP for crude oil in CO_2 without any surfactant is 2240 psia.

b) INTERFACIAL TENSION BETWEEN CO_2 AND CRUDE OIL WITH ALKOXYL FAME JATROPHA

Table 10: Pressure, angle and IFT table (crude oil & Alkoxyl FAME Jatropha)

Pressure (psia)	Angle	IFT (mN/m)
1200	101.08	8.02
1400	108.1	6.31
1600	90	3.56
1700	93.82	3.24
2000	-	-

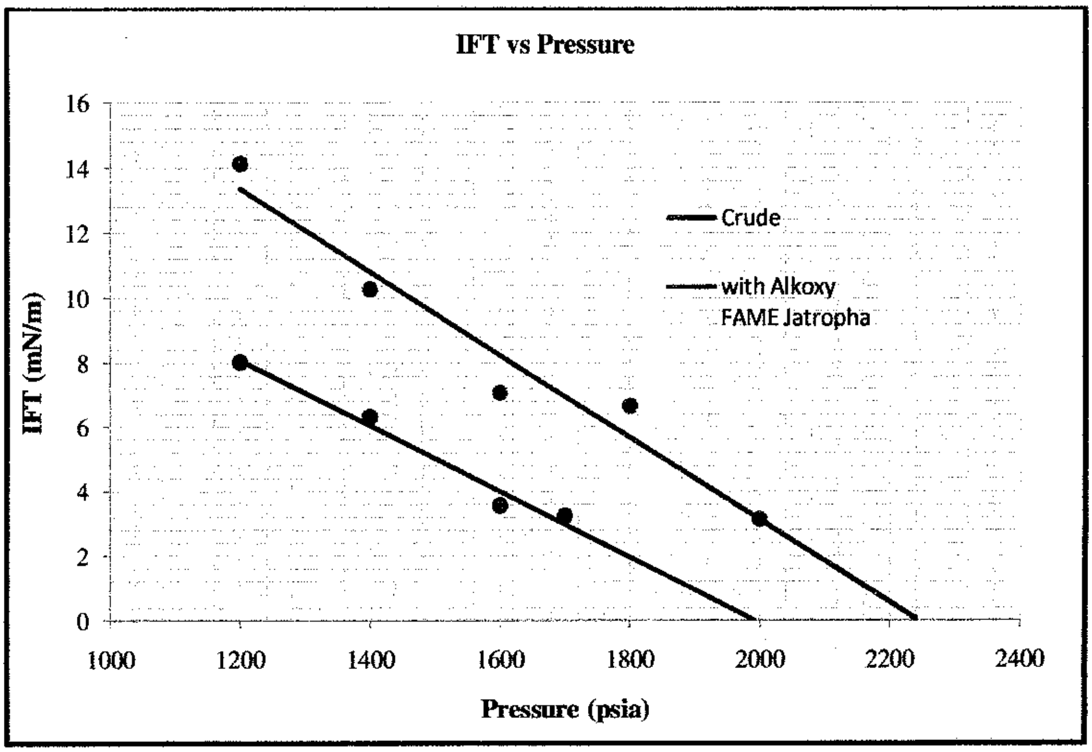


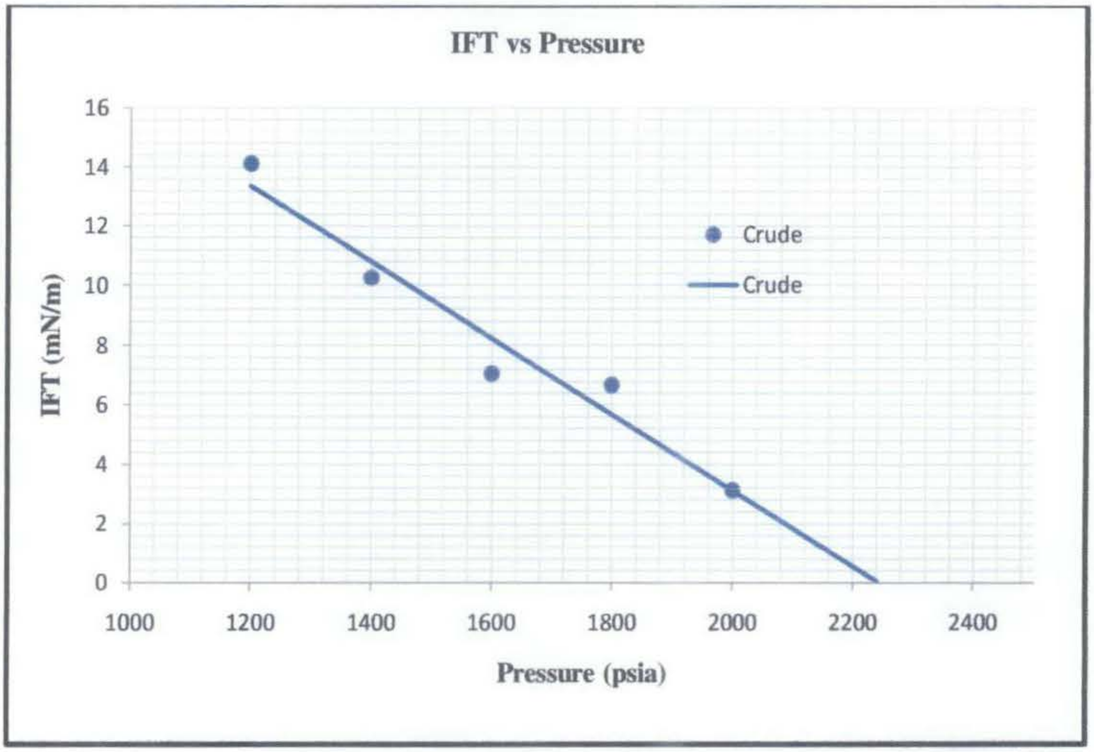
Figure 12: IFT vs Pressure graph (CO2 and Crude oil with Alkoxyl FAME Jatropha)

From the above result, an almost linear trend can be seen from Figure 12. Extrapolation to IFT at 0 mN/m gives pressure 1990 psia. Thus, MMP for crude oil with Alkoxyl FAME Jatropha as surfactant in CO_2 is 1990 psia.

a) INTERFACIAL TENSION BETWEEN CO_2 AND CRUDE OIL.

Table 9: Pressure, angle and IFT table (crude oil)

Pressure (psia)	Angle	IFT (mN/m)
1200	98.63	14.12
1400	105.15	10.26
1600	98.1	7.06
1800	101.64	6.66
2000	95.33	3.12



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b) INTERFACIAL TENSION BETWEEN CO_2 AND CRUDE OIL WITH ALKOXYL FAME JATROPHA

Table 10: Pressure, angle and IFT table (crude oil & Alkoxyl FAME Jatropha)

Pressure (psia)	Angle	IFT (mN/m)
1200	101.08	8.02
1400	108.1	6.31
1600	90	3.56
1700	93.82	3.24
2000	-	-

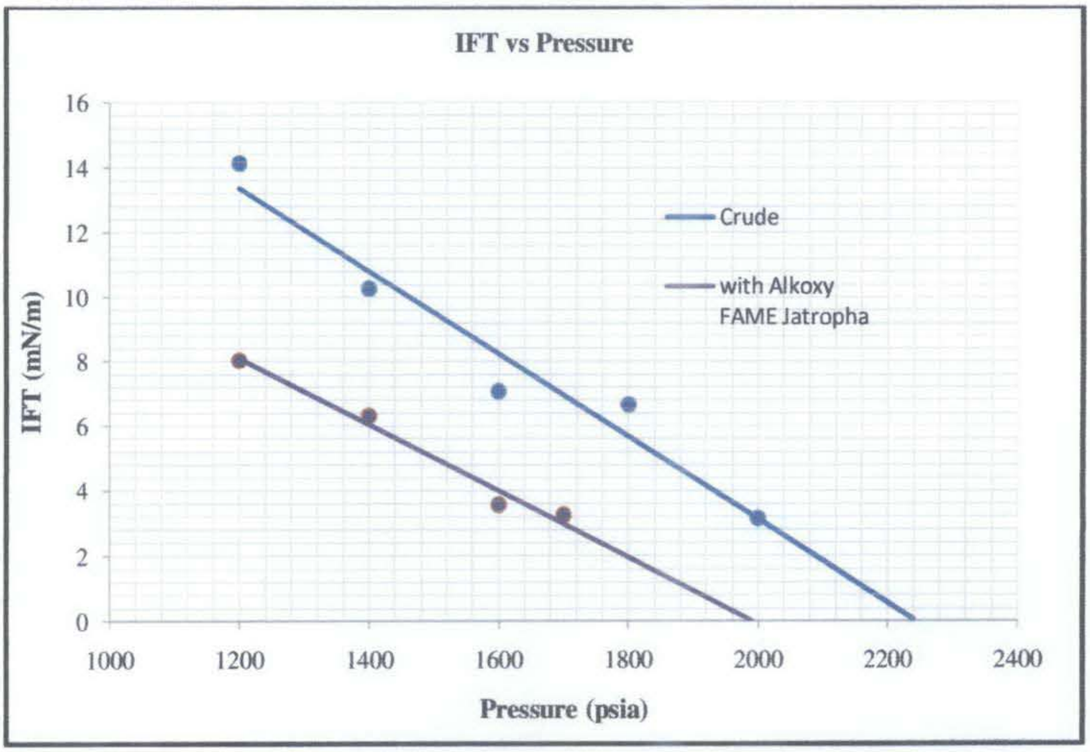

Figure 12: IFT vs Pressure graph (CO2 and Crude oil with Alkoxyl FAME Jatropha)

From the above result, an almost linear trend can be seen from Figure 12. Extrapolation to IFT at 0 mN/m gives pressure 1990 psia. Thus, MMP for crude oil with Alkoxyl FAME Jatropha as surfactant in CO_2 is 1990 psia.

c) INTERFACIAL TENSION BETWEEN CO_2 AND CRUDE OIL WITH ALKOXYL FAME PALM

Table 11: Pressure, angle and IFT table (crude oil & Alkoxyl FAME Palm)

Pressure (psia)	Angle	IFT (mN/m)
1200	108.43	8.00
1400	105.62	6.24
1600	104.86	4.36
1800	104.56	3.05
2000	-	-

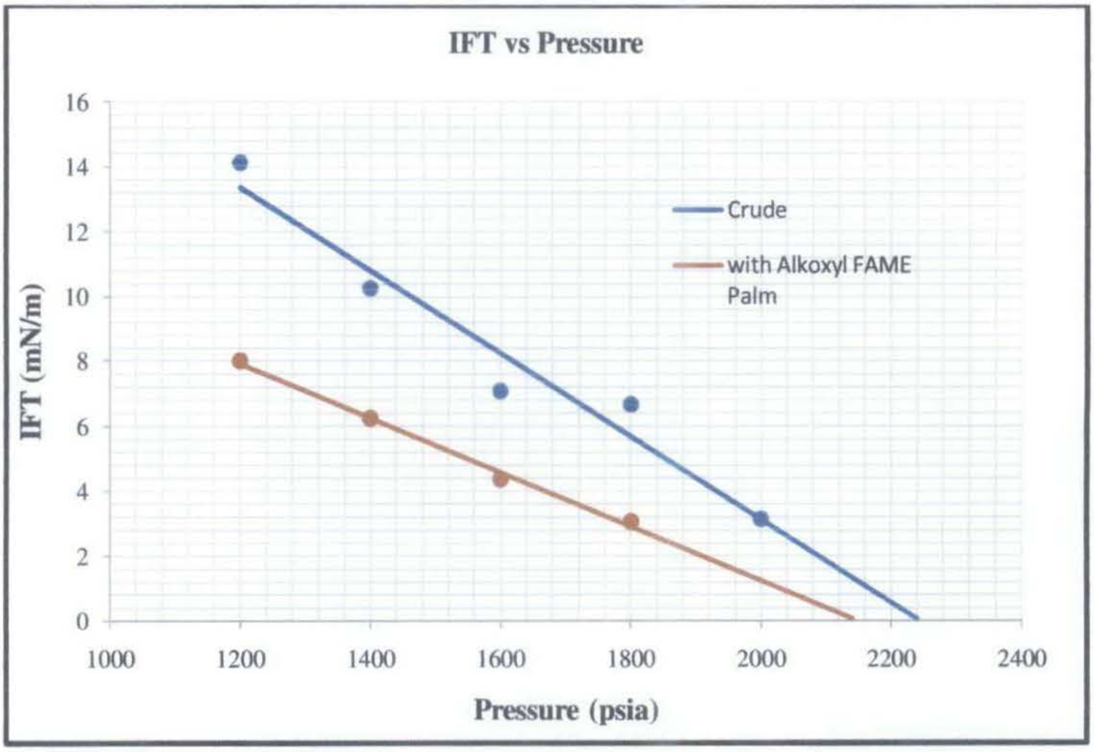

Figure 13: IFT vs Pressure graph (CO2 and Crude oil with Alkoxyl FAME Palm)

From the above result, an almost linear trend can be seen from Figure 13. Extrapolation to IFT at 0 mN/m gives pressure 2140 psia. Thus, MMP for crude oil with Alkoxyl FAME Palm as surfactant in CO_2 is 2140 psia.

d) INTERFACIAL TENSION BETWEEN CO_2 AND CRUDE OIL WITH 2-METHYL BUTAN-2-OL

Table 12: Pressure, angle and IFT table (crude oil & 2-methyl butan-2-ol)

Pressure (psia)	Angle	IFT (mN/m)
1200	99.05	10.5
1400	105.94	7.99
1600	97.71	5.1
1800	104.87	4.02
2000	-	-

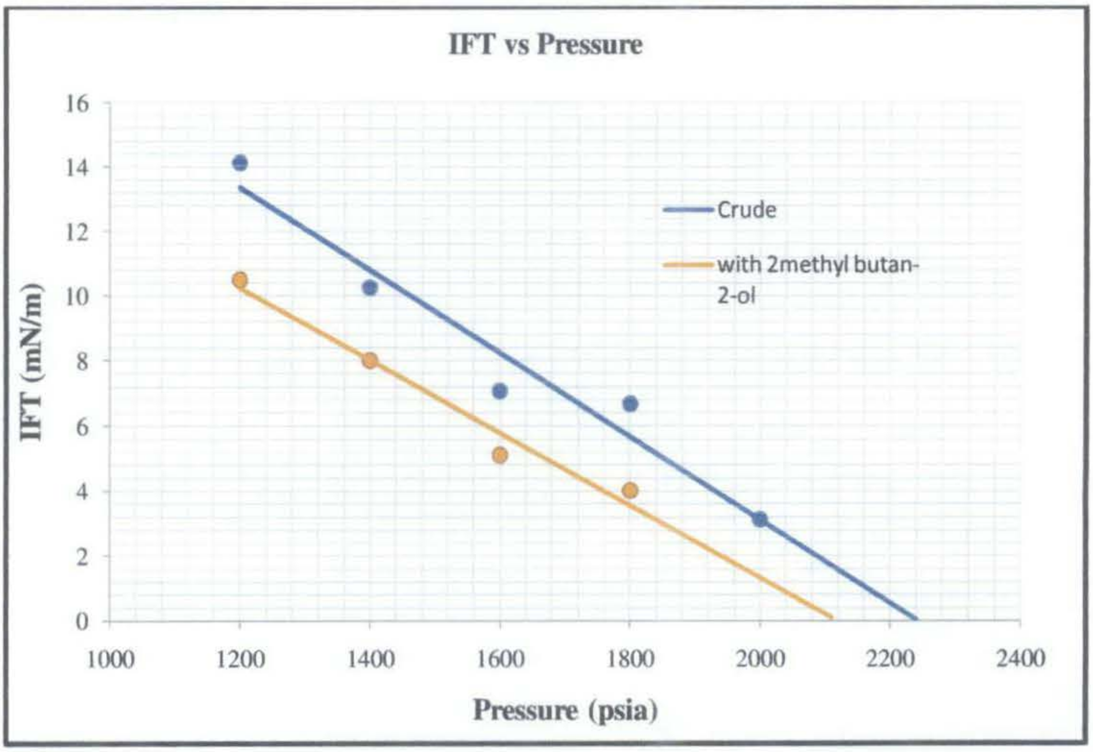

Figure 14: IFT vs Pressure graph (CO2 and Crude oil with 2-methyl butan-2-ol)

From the above result, an almost linear trend can be seen from Figure 14. Extrapolation to IFT at 0 mN/m gives pressure 2110 psia. Thus, MMP for crude oil with 2-methyl butan-2-ol as surfactant in CO_2 is 2110 psia.

4.2.3 Interfacial Tension Discussion

Interfacial tension and surface tension is somewhat similar since a cohesive force is involved. However, in interfacial tension, the main forces involved are adhesive forces (tension) between the liquid phase of one substance and either a solid, liquid or gas phase of another substance. The interaction occurs at the interfaces of both substances. In this research, it is between CO_2 (gas) and crude oil with surfactant (liquid). For MMP determination, it is said MMP is achieved at IFT = 0 (Ayirala and Rao_6, 2006).

IFT measurements were carried out with 0.5:1 surfactant to crude oil ratio. This ratio was chosen because it gives optimum condition for IFT reduction (Nafis, 2011) when alcohol is used as the surfactant.

Alkoxyl FAME Jatropha were tested at pressure 1200 psia until 1700 psia. From the data, there is 11.6% MMP reduction. At low pressure (1200 & 1400 psia), the difference in IFT is bigger compare to higher pressure where IFT difference becoming less significant. This is the result from different CO_2 behaviour at high pressure where it already enters supercritical state.

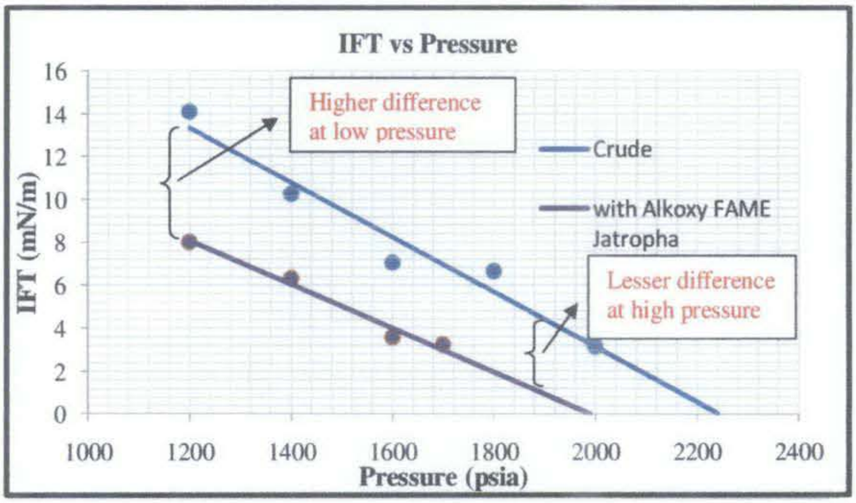

Figure 15: Alkoxyl FAME Jatropha - Pressure & IFT reduction relationship

For 2-methyl butan-2-ol, it was tested at pressure 1200 to 1800 psia. The result shows 5.8% reduction in MMP. This reduction is far less than reduction by Alkoxyl FAME Jatropha. From GCMS result, 65.86% Alkoxyl FAME Jatropha are made of FAME with alcohol branched. These structures are highly branched compare to 2-

methyl butan-2-ol. This in turn result to higher polarity for Alkoxyl FAME Jatropha compare to 2-methyl butan-2-ol. This lower polarity of 2-methyl butan-2-ol affects the CO_2 capacity to form interaction with the crude oil (Quesheng. et al, 2003).

However, 2-methyl butan-2-ol gives more uniform IFT reduction along the incline pressure compare to alkoxyl FAME Jatropha. This is likely due to main functional group effects. Alcohol is the main functional group for 2-methyl butan-2-ol as compare to ester for alkoxyl FAME Jatropha. This makes the polarity of the 2-methyl butan-2-ol stable along the increasing pressure. Thus change in CO_2 behaviour somewhat a bit compensated by this stable polarity.

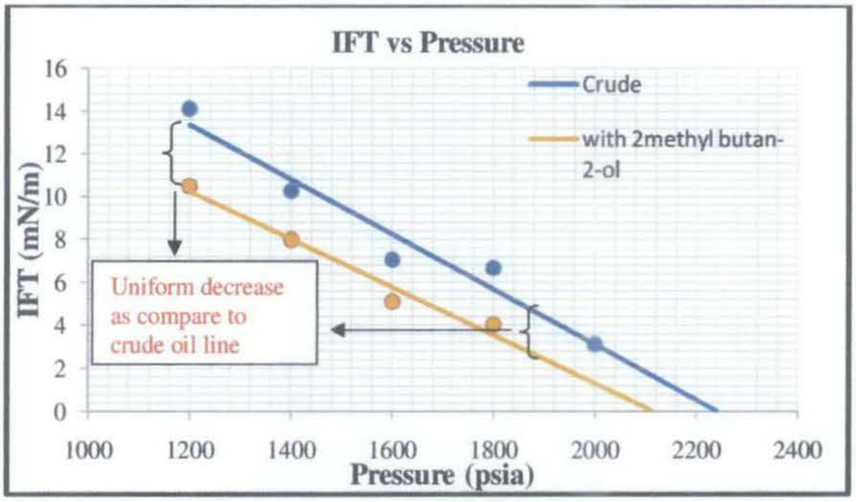

Figure 16: 2-methyl butan-2-ol - Pressure & IFT reduction relationship

Finally, for Alkoxyl FAME Palm, the MMP reduction is 4.46% which is the lowest among all the surfactant used. This is due to the fact that this surfactant contained the lowest 2-propanol branched concentration (47.31% which mainly consist of low branched structures). Alkoxyl FAME Palm also shows high IFT reduction at low pressure, but this reduction become lesser as pressure is increases. This proves the effect of CO_2 on alkoxyl FAME ability in reducing IFT, where the reduction become lesser as pressure is increases.

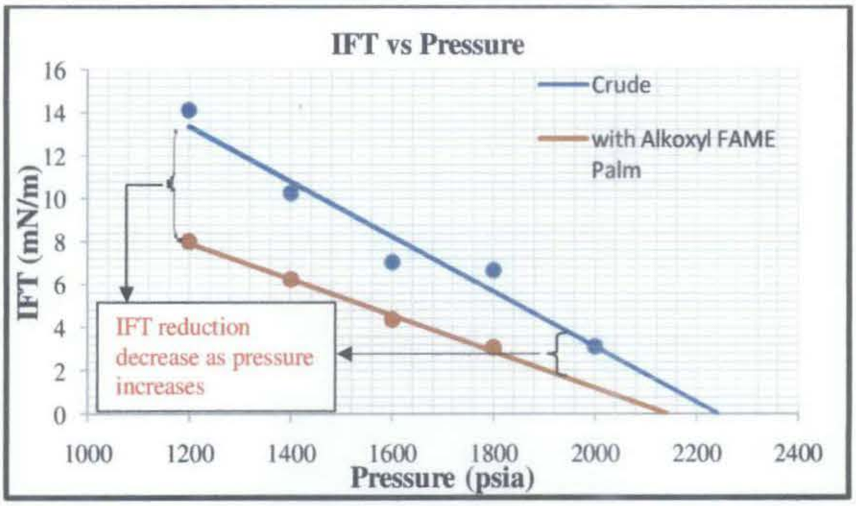

Figure 17: Alkoxyl FAME Palm - Pressure & IFT reduction relationship

REFERENCES

1. "Fats, oils, and oilseeds (fa or equivalent): World Production, 1999-2000 / 2002-2003" Agricultural Statistics 2004. United States Department of Agriculture

2. A. Campanella, C. Fontanini, M. A. Baltanas " High yield epoxidation of fatty acid methyl esters with performic acid generated in-situ" 2008, INTEC, ELSEVIER

3. Akintayo, E.T , 2004 " Characteristic and composition of *Parkia biglobossa* and *Jatropha curcas* oils and cakes" Biosource Technology 92, 307-310

4. Alsahmi, N., "Alcohol as an additive to increase CO_2 and crude oil miscibility", UTP FYP, 2011, Universiti Teknologi PETRONAS

5. Anthony J. O' Lenick, Jr – *A Review of Guerbet Chemistry*

6. Aoudia, M., Wade, W., and Weerasooriya, "Optimum microemulsions formulated with propoxylated Guerbet alcohol and propoxylated tridecyl alcohol sodium sulfates" *J. Dispersion Sci. Technol., 16, 115-135, 1996*

7. Ayirala, S.C. and Rao, D.N. (2006). Comparative Evaluation of a New MMP Technique. *SPE 99606, SPE/DOE Symposium on Improved Oil Recovery*

8. Ayirala, SC., Rao, D.N. and Casteel, J. (2003). New Comparison of Minimum Miscibility Pressures Determined From Gas-Oil Interfacial Tension Measurements with Equation of State Calculations. *SPE 84187, SPE Annual Technical Conference*

9. Clinton F. Lane, Hal L. Myatt, John Daniels, and Harvey B Hopps "Organic Synthesis Using Borane Methyl Sulfide Reduction of Aromatic Carboxylic Acids in the Presence of Trimethyl Borate" Aldrich Boranes, Inc, Milwaukee, Wisconsin 53233 (1974)

10. David M. Mousdale, "Biofuels - *Biotechnology, Chemistry, and Sustainable Developtment"*, (2008)

11. Don W. Green & G. Paul Willhite "Enhanced Oil Recovery" SPE Textbook Series Vol 6 (1998)

12. Elsharkawy, A.M., Poettmann F.H. and Christiansen, R.L. (1992). Measuring Minimum Miscibility Pressure: Slim Tube or Rising Bubble Method?. *SPE 91918, SPE/DOE Symposium on Enhanced Oil Recovery*

13. Enhanced Oil Recovery, Donaldson, E.C, Chilingarian and Yen, page 200, Feb 1985

14. Enhanced Oil Recovery, Green D.W and Wilhite G.P, 1998

15. Enhanced Oil Recovery/CO_2 Injection, using the US Department of Energy website, from http://www.fossil.energy.gov/programs/oilgas/eor/index.html

16. Ghadge, S. V, Raheman, H., 2005 "Biodiese production from mahua (Madhuca indica) oil having high free fatty acids. Biomass Bioenergy 28, 601-605.

17. Gubitz, G.M., Mittelbach, M., Trabi, M., 1999 "Exploitation of tropical oil seed plant *Jatropha curcas* L" Bioresource Technology 67,73-82

18. Hanny Johanes Berchmans, Shizuko Hirata "Biodiesel Production from Crude Jatropha curca L.sees oil with a high content of free fatty acids" Elsevier (2007)

19. Holm, L.W. and Josendal, V.A "Mechanisms of Oil Displacement by Carbon Dioxide", paper SPE 4736 presented at SPE-AIME Symposium on Improved Oil Recovery, Tulsa, Oklahoma, 22-24 April (1974). JPT (December 1974): 1427-1438

20. John McMurry "Organic Chemistry" Thomson Brooks/Cole, Cornel University (2004)

21. Luo, K. and Chen, G. (2001). Application of the Gas-Oil Interfacial Tension to Determine Minimum Miscibility Pressure. *PETSOC 2001-135, Canadian International Petroleum Conference*

22. Martin, F.D. and Taber, J.J. "*Carbon Dioxide Flooding*", paper SPE 23564, Journal of Petroleum Technology (April 1992): 396-400

23. Nor Idah, K., Zahidah M.Z., Noraini A. and DM Anwar Raja. (1999). New Experimental Approaches in Minimum Miscibility Pressure (MMP) Determination. *SPE 57286, SPE Asia Pacific IOR Conference*.

24. Openshaw, K., 2000 "A review of *Jatropha curcas:* An oil plant of unfulfilled promise" Biomass and Bioenergy 19, 1-15

25. P.C. Smith, Y. Ngothai, Q.D. Nguyen, B.K O'Neill "Alkoxylation of Biodiesel and its impact on low temperature properties" School of Chemical Engineering, University of Adelaide, 2008.

26. Paul C. Smith, Brian K. O'Neill, Yung Ngothai and Q. Dzuy Nguyen "Butoxylation of Butyl Biodiesel: Reaction Conditions and Cloud Point Impact" School of Chemical Engineering, University of Adelaide, 2009.

27. Perry M. Jarrel, Charles E. Fox, Michael H Stein and Steven L Webb "*Practical Aspect of CO_2 Flooding*", Monograph Volume 22 SPE Henry L Doherty Series (2002)

28. Quesheng Li, Zeting Zhang, Chongli Zhong, Yancheng Liu, Qingrong Zhou "Solubility of solid solutes in supercritical dioxide with and without cosolvent" Science Direct Fluid phase equilibria 207(2003)183-192

29. Rosen, M.J., Wang, H., Shen, and Zhu, Y. "Ultralow Interfacial Tension for Enhanced Oil Recovery at Very Low Surfactant Concentrations", *Langmuir,* 21, 3749-3756, 2005

30. Veljkovic, V.B.,Lakicevic, S.H., Stamenkovic, O.S., Todorovic, Z.B, Lazic, K.L, 2006 "Biodiesel production from tobacco (Nicotiana tabacum L) seed oil with a high content of free fatty acids, Feul 85, 2671-2675

31. Y. Wu, P. Shuler, M. Blanco, Y. Tang and W.A Goddard, "*A Study of Branched Alcohol Propoxylate Sulfate Surfactants for Improved Oil Recovery*" Paper 95404-MS (2005)

32. Zhou, D and Orr, Jr.F.M. *"Analysis of Rising Bubble Experiments to Determine Minimum Miscibility Pressure"*, paper SPE 30786 presented at SPE Annual Technical Conference and Exhibition, Dallas, 22-25 October (1995). SPE Journal (March 1998): 19-25

APPENDIX

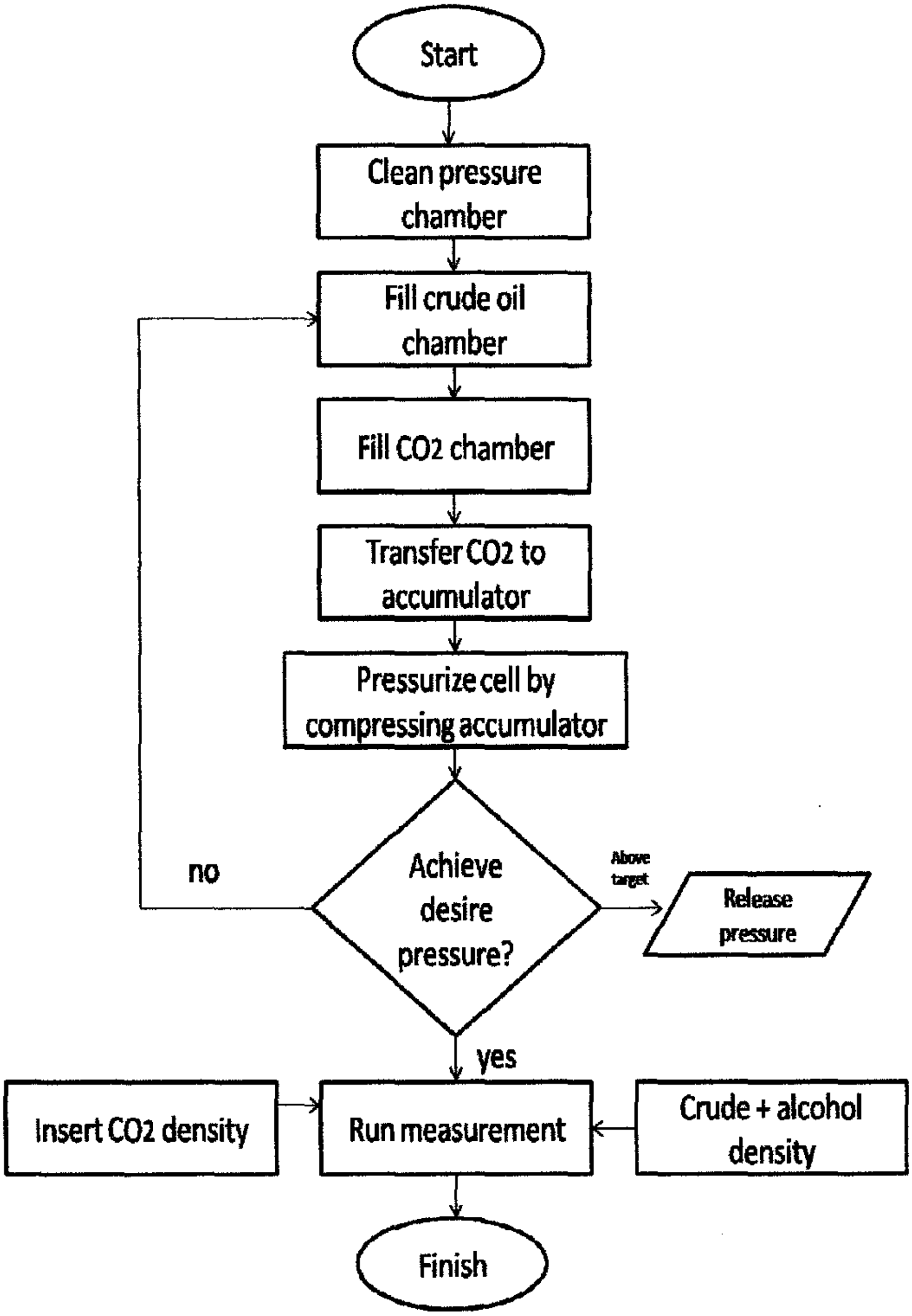

Figure 18: Flow diagram of IFT measurement

Table 13: Dulang crude oil composition

Component	**Sep Gas (MOL%)**	**Sep Oil (MOL%)**	**Wellstream (MOL%)**
CO_2	49.93	0.196	20.743
N_2	0.13	0.094	0.109
C_1	34.8	1.168	15.062
C_2	5.88	0.984	3.007
C_3	4.71	1.301	2.71
i-C_4	1.72	0.548	1.032
n-C_4	1.41	0.463	0.854
i-C_5	0.71	0.208	0.415
n-C_5	0.5	0.13	0.283
C_6	0.21	4.823	2.917
C_7	0	4.827	2.833
C_8	0	2.189	1.285
C_9	0	4.209	2.47
C_{10}	0	4.016	2.357
C_{11+}	0	74.844	43.923
Total	100	100	100

FINAL YEAR SEMESTER (May 2011)

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1.	Collect chemicals and apparatus involve	■							Mid-semester break								
2.	Exp 1: Esterification of jatropha oil	■	■	■													
3.	Exp 2: Epoxidation of fatty acid		■	■													
4.	Exp 3: Branching of saturated fatty acid			■	■	■											
5.	Exp 4: Synthesis alcohol from fatty acid					■	■	■									
6.	Submission of Progress report									■							
7.	Exp on IFT									■	■	■	■	■			
8.	Pre-EDX												■				
9.	Submission of Draft report													■			
10.	Submission of Dissertation														■		
11.	Submission of Technical Paper														■		
12.	Oral Presentation															■	
13.	Submission of Project Dissertation (Hard bound)																■

Figure 19: Final Year Project Gantt chart

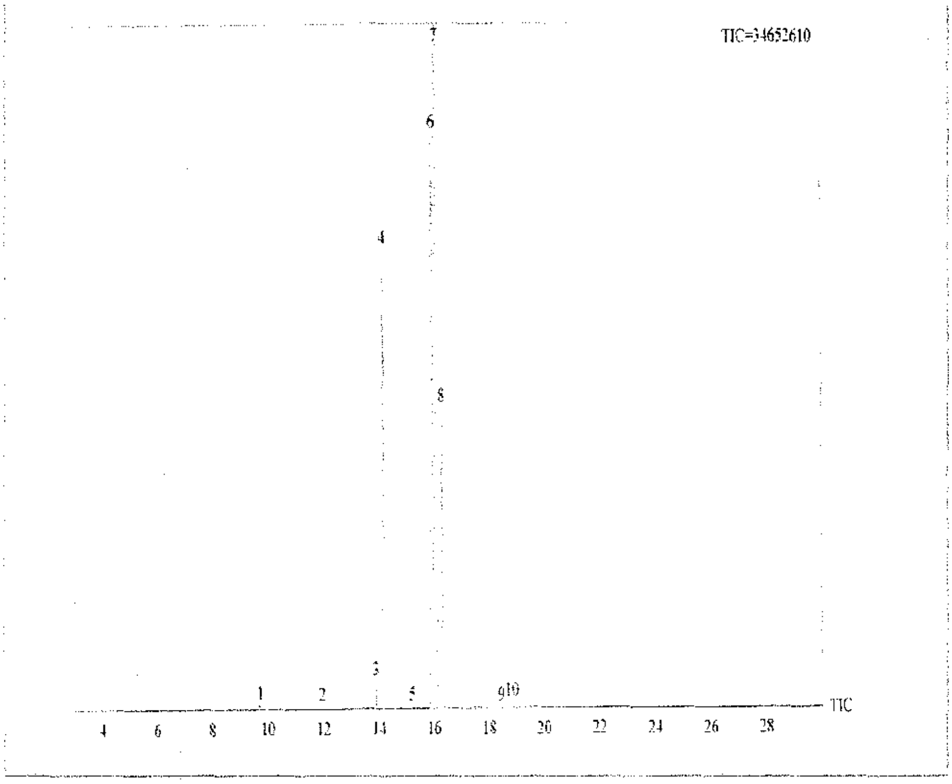

Figure 20: GCMS Result for FAME Jatropha

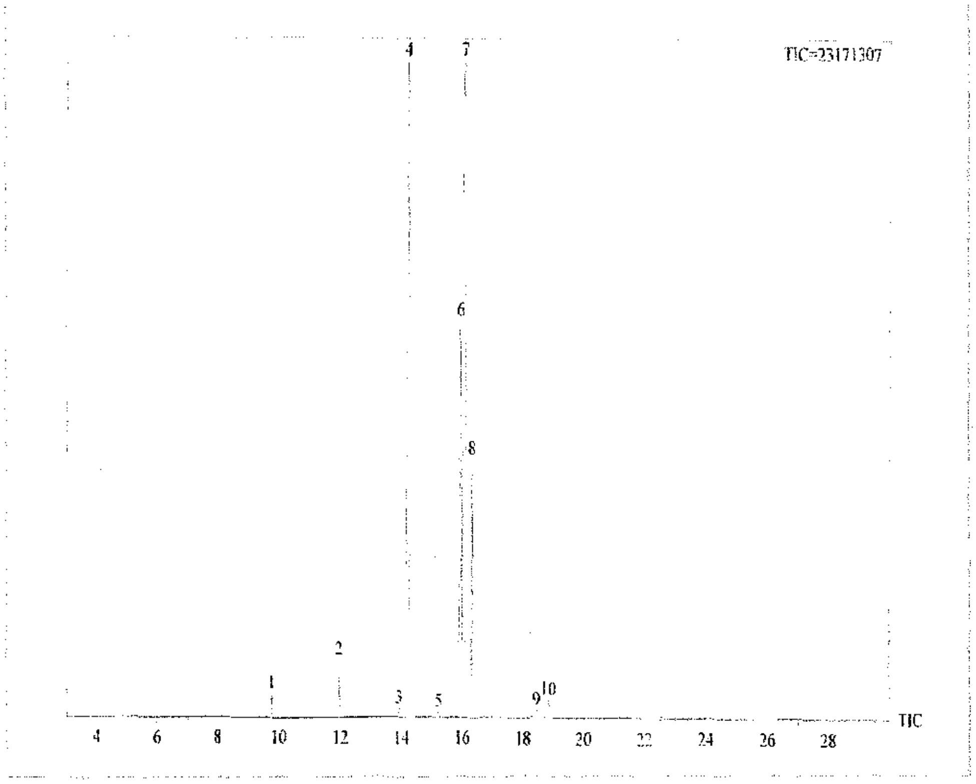

Figure 21: GCMS Result for FAME Palm

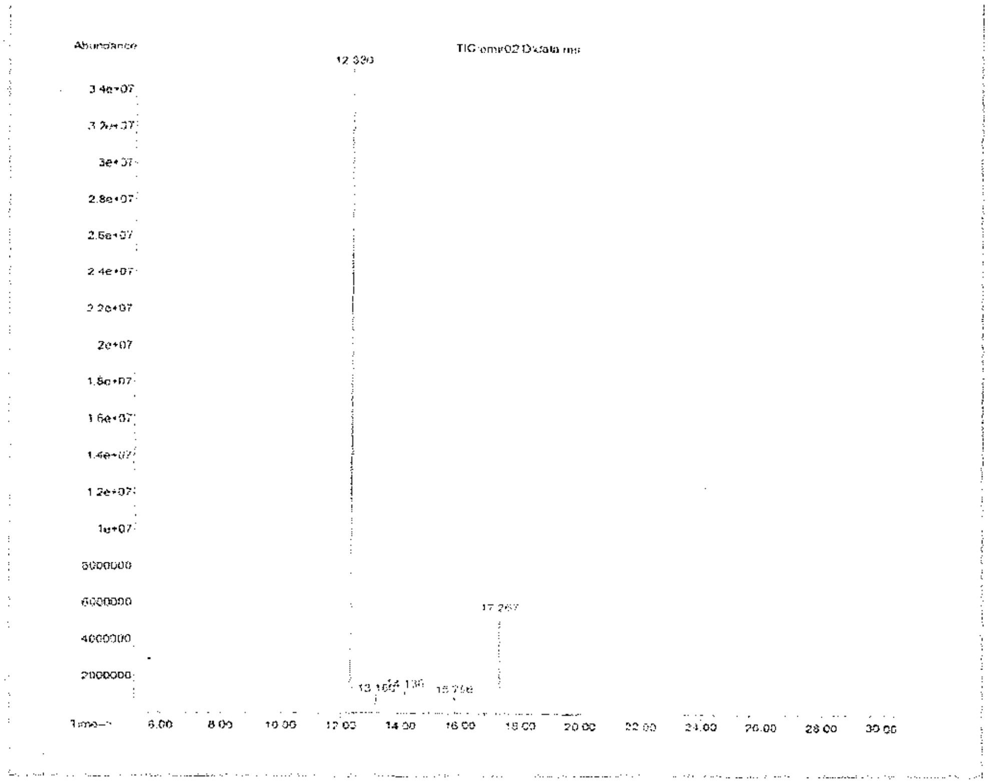

Figure 22: GCMS for alkoxyl FAME Palm

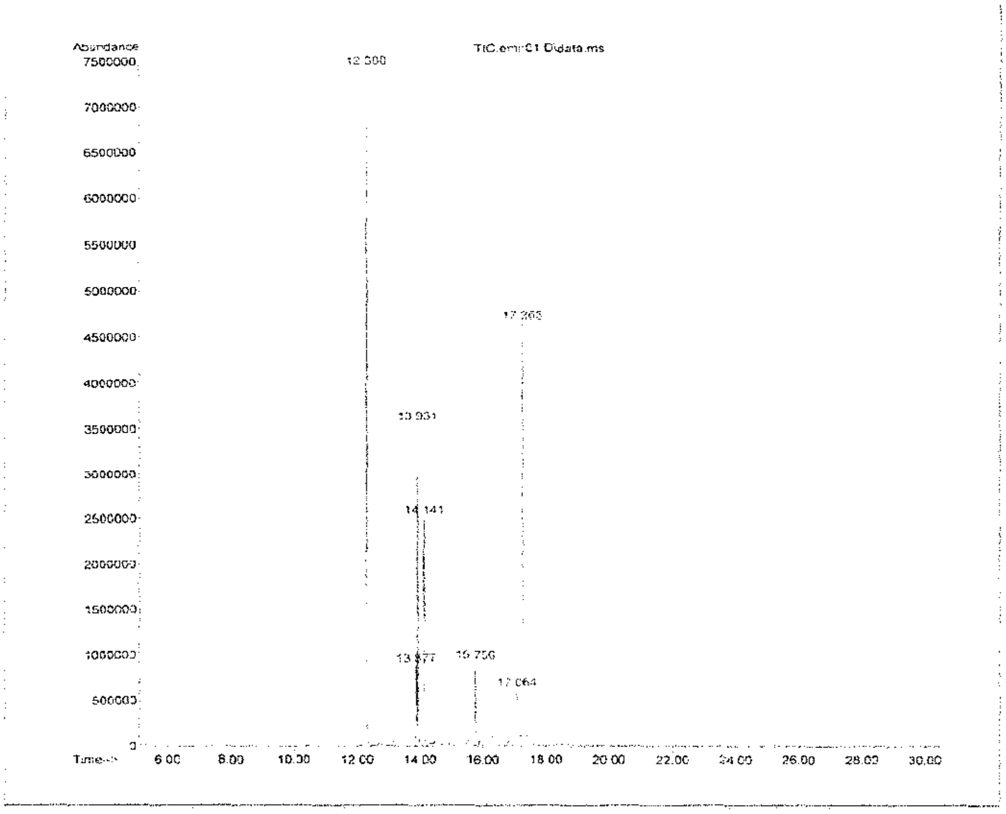

Figure 23: GCMS for alkoxyl FAME Jatropha

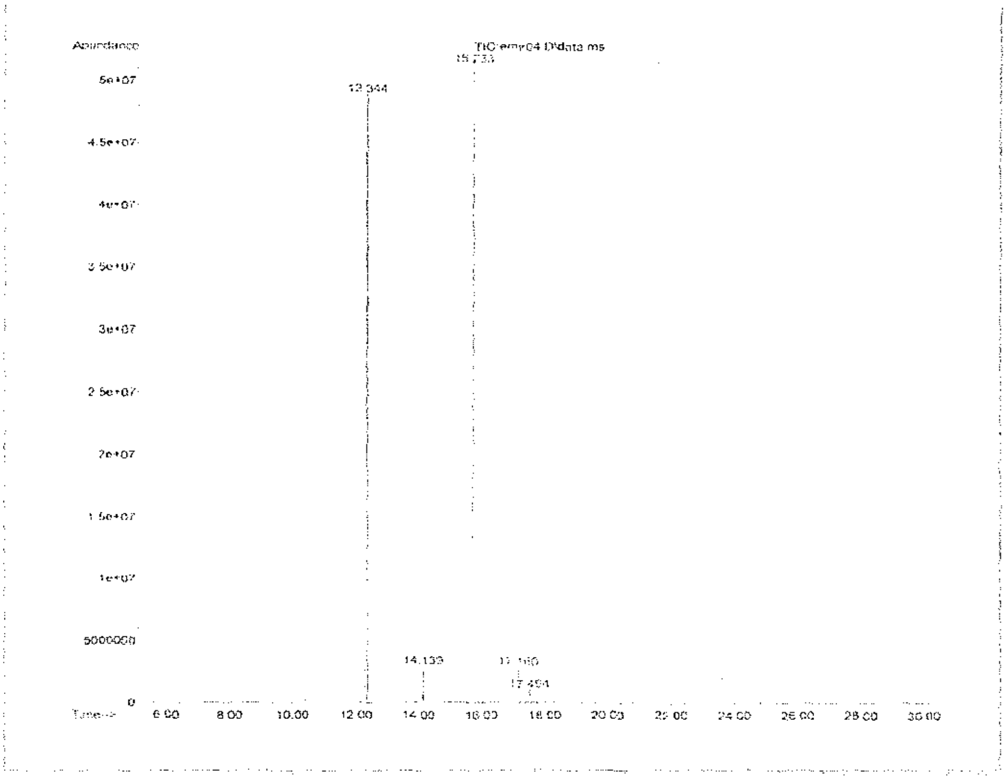

Figure 24: GCMS for epoxide FAME Palm

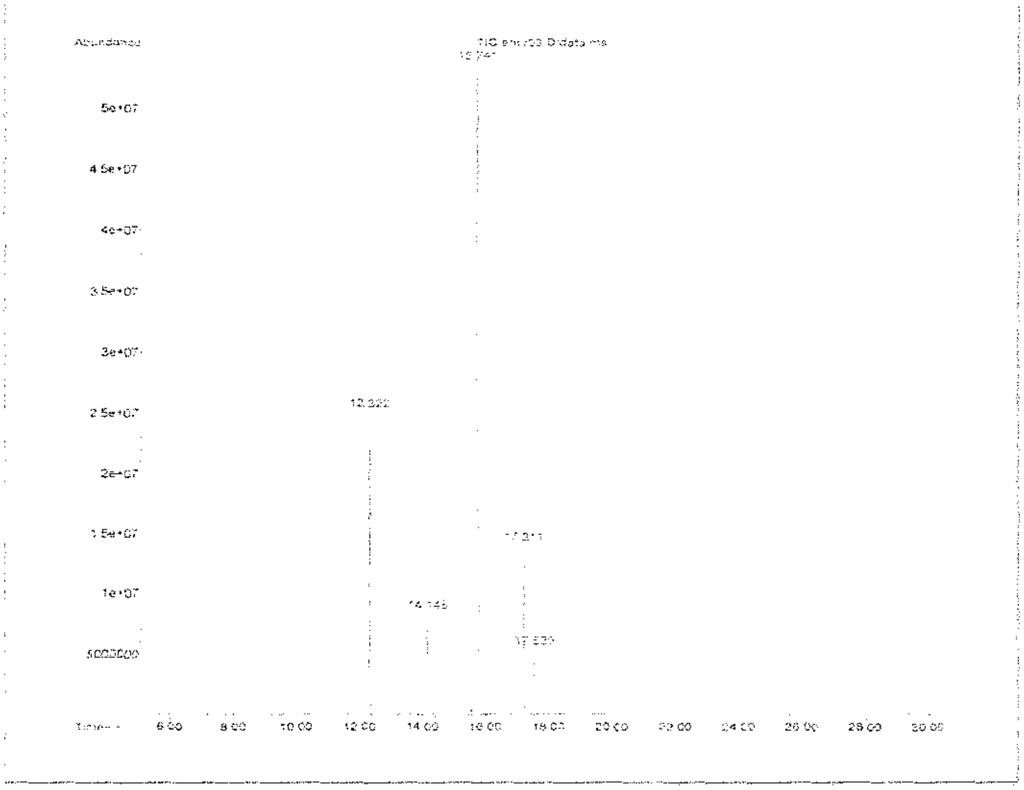

Figure 25: GCMS for epoxide FAME Jatropha

CO_2 – crude oil IFT results

Table 14: IFT result at pressure = 1200psia

Tension	Angle
14.12	98.63
14.06	98.41
14.06	98.36
14.27	98.25
14.07	98.22
13.84	97.82
13.92	96.96
14.12	96.91
13.72	96.25
13.91	96.13
13.78	96.06
13.97	95.69
13.8	95.52
13.47	94.18
13.53	93.78
13.66	93.44
13.62	93.05
13.49	90
13.43	90
13.79	90

Table 15: IFT result at pressure = 1400psia

Tension	Angle
10.26	105.15
10.25	105.26
10.25	104.9
10.24	105.28
10.18	105
10.14	104.78
10.14	104.22
10.12	104.2
10.1	104.7
10.1	104.64
10.1	104.17
10.07	104.83
10.07	104.66
10.07	104.58
10.05	104.64
10.03	104.54
10	103.37
9.99	104.47
9.97	104.15
9.93	103.31

Table 16: IFT result at pressure = 1600psia

Tension	Angle
7.06	98.1
7.35	97.53
6.86	97.05
7.09	97.03
6.93	96.67
6.92	96.65
6.83	96.45
7.2	96.39
7.04	96.17
7.08	95.83
6.8	95.52
7.02	95.51
6.83	95.4
6.72	95.13
6.84	94.76
7	94.41
7.06	94.08
6.99	93.87
6.86	90
6.83	90

Table 17: IFT result at pressure = 1800psia

Tension	Angle
6.66	101.64
6.47	100.81
6.54	100.35
6.34	100.3
6.44	100.26
6.38	100.2
6.37	100.16
6.45	100.13
6.54	100.07
6.32	99.68
6.28	99.64
6.2	99.26
6.38	99.24
6.33	99.22
6.15	99.19
6.29	98.61
6.24	98.5
6.23	98.27
6.15	98.06
6.1	95.23

Table 18: IFT result at pressure = 2000psia

Tension	Angle
3.12	95.33
3.1	90
3.05	90
3.09	90
3.14	90
3.29	90
3.18	90
3.17	90
3.02	90
3.17	90
3.23	90
3.21	90
3.25	90
3.21	90
3.05	90
3.19	87.04
3.17	86.41
3.21	86.13
3.15	85.48

CO_2 – crude oil with alkoxyl FAME Jatropha IFT results

Table 19: IFT result at pressure = 1200psia

Tension	Angle
8.02	101.08
7.97	101.07
7.99	100.97
7.98	100.9
7.99	100.65
8.01	100.6
8	100.54
8.01	100.32
7.95	100.18
7.95	99.71
7.94	99.7
7.95	99.7
7.96	99.67
7.96	99.6
7.94	99.45
7.93	99.41
7.95	99.41
7.95	99.1
7.9	98.84
7.96	98.74

Table 20: IFT result at pressure = 1400psia

Tension	Angle
6.31	108.1
6.33	108.01
6.1	107.18
6.13	107.13
6.12	106.71
5.92	106.48
5.93	106.48
5.96	106.25
6.04	106.15
6.01	106.12
5.84	106.05
6.07	106.02
5.94	105.75
5.92	105.74
5.98	105.53
5.97	105.5
5.91	105.38
5.9	105
5.94	104.98
5.65	103.09

Table 21: IFT result at pressure = 1600psia

Tension	Angle
3.56	90
3.53	90
3.53	90
3.55	90
3.56	90
3.62	90
3.47	90
3.64	90
3.62	90
3.59	90
3.57	90
3.6	90
3.58	90
3.62	90
3.53	90
3.56	90
3.61	90
3.56	90
3.55	88.87
3.57	88.22

Table 22: IFT result at pressure = 1700psia

Tension	Angle
3.12	93.82
3.1	93.42
3.05	92.97
3.09	91.99
3.14	90
3.29	90
3.18	90
3.17	90
3.02	90
3.17	90
3.23	88.61
3.21	88.5
3.25	87.75
3.21	86.86
3.05	86.54
3.19	85.96
3.17	85.7
3.21	85.29
3.15	85.25

CO_2 – crude oil with alkoxyl FAME Palm IFT results

Table 23: IFT result at pressure = 1200psia

Tension	Angle
8	108.43
7.96	108.17
7.9	108.07
7.95	107.98
7.78	107.7
7.71	107.64
7.79	107.48
8.07	107.43
7.74	107.25
7.85	107.12
7.73	107.11
7.67	107.02
7.88	107
7.64	106.93
7.62	106.83
7.47	106.82
7.81	106.6
7.72	106.46
7.43	106.3
7.44	105.11

Table 24: IFT result at pressure = 1400psia

Tension	Angle
6.24	105.62
6.06	105.02
6	104.66
5.82	103.94
5.86	103.73
5.93	103.47
5.71	103.36
5.76	103.28
6.05	103.12
6.08	103.07
5.78	102.57
5.73	102.35
5.77	102.29
5.94	102.29
5.65	102.26
5.97	101.44
5.79	100.7
5.43	100.65
5.8	100.54
5.65	99.59

Table 25: IFT result at pressure = 1600psia

Tension	Angle
4.36	104.86
4.29	104.36
4.21	104.25
4.3	103.87
4.3	103.67
3.94	102.53
4.1	102.5
3.83	102.16
4.24	102.14
3.98	102.09
3.96	101.84
3.93	101.47
3.87	101.26
3.8	99.84
3.77	99.24
3.76	99
3.74	98.99
3.6	97.18
3.59	96.49
3.72	96.18

Table 26: IFT result at pressure = 1800psia

Tension	Angle
3.05	104.56
3.11	103.84
3.09	103.76
3.06	103.03
2.93	103
2.82	102.78
2.97	101.98
2.86	101.83
2.93	101.63
2.87	101.54
2.88	101.07
2.71	100.55
2.72	100.37
2.7	100.01
2.63	99.36
2.73	99.28
2.56	98.8
2.71	98.69
2.59	97.51

CO_2 – crude oil with 2-methyl butan-2-ol IFT results

Table 27: IFT result at pressure = 1200psia

Tension	Angle
10.5	99.05
10.5	98.17
10.57	98.83
10.58	98.35
10.59	96.89
10.48	97.17
10.53	95.89
10.61	97.12
10.59	95.64
10.6	95.47
10.47	95.7
10.53	92.57
10.54	94.71
10.71	93.91
10.38	93.79
10.6	94.31
10.37	90
10.51	90
10.67	93.45
10.63	90

Table 28: IFT result at pressure = 1400psia

Tension	Angle
7.99	105.94
8.02	105.71
7.63	104.88
7.16	104.46
7.82	104.33
7.31	103.86
7.14	103.65
7.36	103.53
6.89	102.94
6.9	102.83
7.08	102.3
6.68	101.94
6.41	100.64
6.17	100.25
6.11	99.93
6.16	99.73
5.23	96.29
5.54	95.4
4.49	90
4.89	90

Table 29: IFT result at pressure = 1600psia

Tension	Angle
5.1	97.71
4.96	97.18
5	95.98
4.89	94.58
4.89	94.16
4.86	93.99
4.99	93.61
4.83	93.12
4.78	91.87
5.06	91.59
4.86	91.25
4.76	90
4.77	90
4.91	90
4.87	90
4.96	90
4.9	90
4.86	90
5.04	90
4.78	86.88

Table 30: IFT result at pressure = 1800psia

Tension	Angle
4.02	104.87
4.13	104.07
3.95	103.1
3.89	103
3.81	102.33
3.74	102.28
3.89	102.07
3.84	101.95
3.73	101.78
3.81	101.59
3.71	101.59
3.8	101.53
3.69	101.23
3.63	101.05
3.63	100.95
3.61	100.24
3.6	100.17
3.55	99.95
3.56	99.68