EXTRACTION KINETICS OF FATTY ACIDS ETHYL ESTERS (FAEE) FROM OIL PHASE USING AQUEOUS ETHANOL

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EXTRACTION KINETICS OF FATTY ACID ETHYL ESTERS (FAEE) FROM OIL PHASE USING AQUEOUS ETHANOL

SALINA BINTI AHMAD SAFII

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
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JUNE 2015

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature   :
Name of main supervisor   : DR MOHD SABRI BIN MAHMUD
Position   : SENIOR LECTURER
Date   : JUNE 2015

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature   :
Name   : SALINA BINTI AHMAD SAFII
ID Number   : KA11022
Date   : JUNE 2015

Dedication

Special dedication to my beloved father, mother, brothers, and sister for their love support and best wishes

ACKNOWLEDGEMENT

ABSTRACT

There is a need for alternative energy sources to replace petroleum based fuels due to the world's crude oil reserves, global warming and environmental concerns. Biodiesel is clean, biodegradable, non-toxic and renewable fuel which is considered to be the best substitution for diesel fuel. In addition, biodiesel has more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons that make it suitable as alternative fuel in transportation sector. The main issue in biodiesel production is the expensive and non-stable supply of feedstock from vegetable oils. Alternatively, waste cooking oil, tallow and non-edible oils are favourable, although they are restricted feedstock for existing conventional productions of biodiesel due to its impurities such as food residue, biopolymer, cellular remaining, dissolved water and free fatty acids which necessitate additional acidic pre-treatments. The need of extension to the current biodiesel plants resulted in a pursuit of more viable process. One of the potential methods to produce biodiesel from low grade oils and cheap bioethanol is through the extractive reactor. Since, this technique is still new, many physical properties of the oil-alcohol mixture system were not explored. In particular, extraction kinetics of fatty acid ethyl esters from reactive region using aqueous ethanol is essential in order to determine the practicality of the process of extractive reaction for biodiesel synthesis. This experiment was conducted to characterize extraction kinetics of FAEE from oil phase by using aqueous ethanol and to determine the distribution coefficient of FAEE between oil phase and aqueous ethanol. Three different oil:ethanol molar ratio which is 1:1, 1:3 and 3:1 where oil was first diluted with FAEE was used with different stirred time range between 1-20min. A settling time for the mixture was recorded and a sample was taken for concentration determination using gas chromatography (GC) analysis. It is expected that the distribution coefficient of fatty acids ethyl esters (FAEE) is higher in solvent than solution.

Keywords: biodiesel, extraction, aqueous ethanol, cooking oil, FAEE, gas chromatography

ABSTRAK

Terdapat keperluan sumber tenaga alternatif untuk menggantikan bahan api yang berasaskn petroleum berikutan daripada rizab minyak mentah dunia, pemanasan global dan keprihatinan kepada alam sekitar. Biodiesel yang bersih, mesra alam, tidak beracun dan boleh diperbaharui adalah bahan api terbaik utk menggantikan diesel. Selain itu, biodiesel mempunyai profil pelepasan pembakaran yang lebih baik seperti kurang pengeluaran karbon monoksida, habuk, dan hidrokarbon yg tidak terbakar menjadikannya sesuai sebagai alternatif dalam sektor pengankutan. Isu utama dalam pengeluaran biodiesel adalah bekalan bahan mentah daripada minyak sayuran yg mahal dan tidak stabil. Sebagai alternatif, sisa minyak masak, lemak dan minyak yg tidak boleh dimakan boleh digunakan walaupun ianya terhad bagi pengeluaran biodiesel yg sedia ada pada masa kini kerana terdapat bendasing seperti sisa makanan, biopolymer, baki sel, air terlarut, dan asid lemak bebas yang memerlukan rawatan asid tambahan. Keperluan tambahan kepada loji biodiesel yang sedia ada memerlukan lebih usaha untuk memcapai proses yang lebih berdaya maju. Salah satu kaedah yang berpotensi untuk menghasilkan biodiesel daripada minyak gred rendah dah murah adalah melalui reaktor ekstraktif. Memandangkan proses ini masih baru, banyak sifat fizikal system campuran minyak-alkohol belum diterokai. Khususnya, kinetik ekstraktif fatty acids ethyl esters dari kawasan reaktif menggunakan etanol akueus adalah penting untuk menentukan kewajaran proses tindak balas ekstraktif untuk sintesis biodiesel. Eksperimen in dijalankan untuk mencirikan kinetic ekstraktif FAEE dari fasa minyak menggunakan etanol akuos dan untuk menentukan nisbah taburan bagi FAEE diantara fasa minyak masak dah etanol akuos. Tiga nisbah molar minyak:etanol berbeza iaitu 1:1, 1:3 dan 3:1 dimana minyak dicairkan terlebih dahulu dengan FAEE dijalankan dengan berbeza masa dikacau dalam tempoh antara 1-20 minit. Masa campuran untuk setel dicatat dan sampel diambil untuk kepekatan analisis menggunakan analisis gas kromatografi. Dianggarkan bahawa pecahan FAEE lebih banayak di dalam pelarut berbanding larutan.

Kata kunci : biodiesel, ekstraktif, etanol akuos, mintak masak, FAEE, gas kromatografi

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J	Diffusion flow (mass/cm^2.s)
c	concentration of diffusing species (mol/cm^3)
dc/dx	concentration gradient
D	diffusion coefficient (cm^2/s)

Subscripts

δo	thickness of organic films
δw	thickness of aqueous films
R_O	Resistant of organic films
R_W	Resistant of aqueous films
R_i	Interface between organic and aqueous films
V_{nH}	Volume of n-heptane (ml)
V_{EO}	Volume of ethyl oleate (ml)
MW_{nH}	Molecular weight of n-heptane (g/mol)
MW_{EO}	Molecular weight of ethyl oleate (g/mol)
P_{nH}	Density of n-heptane (g/ml)
P_{EO}	Density of ethyl oleate (g/ml)

LIST OF ABBREVIATIONS

FAEE	Fatty acids ethyl esters
GC	Gas chromatography
FID	Flame ionization detector
HLPC	High performance liquid chromatography
KOH	Potassium hydroxide
EtoH	Aqueous ethanol

1 INTRODUCTION

1.0 *Motivation and statement of problem*

Nowadays, the current scenario of biodiesel production is the shortage and unstable cost of feedstock resulting in uncompetitive price of biodiesel. The main problem for current biodiesel production is high cost. According to statistics, 70% of manufacturing cost of biodiesel is from feedstock (Izah et al, 2013). Biofuel feedstock includes many crops that would otherwise be used for human consumption directly or indirectly as well as animal feed. Diverting these crops to biofuels may lead to more land area devoted to agriculture, increased use of polluting inputs resulting in higher prices. Cellulosic feedstock can also compete for resources such as land, water and fertilizer that could otherwise be devoted to food production. As a result, biofuel production may give rise to price and unstable cost of feedstock.

The dominant factor in the production process of biodiesel is the cost of feedstock while capital costs only contribute about 7% (Sani et al, 2013). Therefore, it is essential to utilize cheap feedstock to reduce the overall production cost. Waste cooking oil, animal fat and non-edible oils are potential substitutes and a pre-treatment process using acid catalyst and glycerol extraction was additionally employed in the current plant. There are many works reliable researches, implementation and useful results come to exist. The alternative feedstock must be technically acceptable, economically competitive, environmentally acceptable and easily available. Researches on biodiesel derives from waste cooking oils, animal fats and non-edible oils are being investigated to alternate vegetable oil as biodiesel feedstock.

Furthermore, the utilisation of waste cooking oil is a key component in reducing biodiesel production costs up to 60% until 90% (Kiakalaieh et al, 2013). It is because waste cooking oil is abundantly available in the local market at cheaper rate as it is not commonly used. Meanwhile, a huge quantity of waste cooking oil can be collected from restaurants and food item industry (Shahid et al, 2012). Besides that, biodiesel may also can be produced from less expensive animal fats such as inedible tallow, pork lard and yellow grease (Dhiraj et al, 2012). Animal tallow generated biodiesel offers a wide ranged of energy, environmental and economic advantage (Nelson et al, 2006)

Transesterification is one of the main solutions that have appeared as effective method for using animal fats in diesel engine. Nevertheless, without deep understanding on the equilibrium of liquid mixing during the reaction, transesterification of the low grade oils could not be realistic.

Besides that, a feedstock need a pretreatment process due to its undesired impurities to avoid rection hindrance and saponification problem occurs. Pre-treatment is the first step of biofuel process, and its quality and efficiency of pre-treatment directly affect the subsequent steps. Additionally, pre-treatment is a combination of many process. It consists of a size reduction step followed by chemical, biological or physical treatments (Tong et al, 2013). However,these combinations add extra costs to the production and make the pre-treatment process to become too slow. There are several pre-treatments method that usually used in industries such as steam explosion pre-treatment, dilute acid pre-treatment organosolv pre-treatment, and sulfite pre-treatments (Tong et al, 2013). However, organosolv pre-treatment is limited because of the high operation cost and high cost of organic solvent (Zhao et al, 2009). Tong et al, (2013) from university of Floridahas study a pre-treatment of lignocellulosic biomass for biofuels. He claimed that although pre-treatment is the first step, it is one of the most expensive parts of the entire bioethanol process (Tong et al, 2013)

 On the other hand, there is currently a need to improve the commercial feasibility of biodiesel production in order to make it an alternative to conventional biodiesel process. In brief, extractive reaction is one the reactor intensification techniques in order to overcome the reaction hindrance and saponification problems due to undesired impurities in the feedstock. For this purpose, extraction can only be sustained if the medium consistently appears as two-immiscible liquid and the solute is more soluble in the solvent. Hence, this study is essentially to characterize the solubility mechanism and extraction kinetics of fatty acid ethyl esters (FAEE) from reactive region especially at interface by using aqueous ethanol. Briefly, solvent extraction has been defined as a process for transporting materials from one phase to another phase for the purpose of separating one or more compounds from mixtures (Johnson et al, 1983). In the case of biodiesel extraction, FAEE was separated by aqueous ethanol from cooking oil. Aqueous ethanol solution is used as a solvent because of its solubility in water and glycerol that is deposited on lipase surface may be stripped from active active lipasic

sites into the aqueous phase, therefore improving enzyme activity and shifting the reaction equilibrium to the right (Chesterfield et al, 2013)

1.1 *Objectives*

The following are the objectives of this research:

i) To characterize extraction kinetics of FAEE from oil phase by using aqueous ethanol

ii) To determine the distribution coefficient of fatty acids ethyl esters (FAEE) between oil phase and aqueous ethanol

1.2 *Scope of this research*

The following are the scope of this research:

i) Palm oil and ethanol at the ratio of 1:6 at $65^{o}C$ will be used to extract fatty acids ethyl esters (FAEE) using trans esterification reaction

ii) Ethanol is used as a solvent for this experiment since it is less toxic and more excellent fuel properties compared to methanol

iii) Comparison of the result for different molar ratio of solvent on extractive performance

iv) Analysis of component using gas chromatography

1.3 *Main contribution of this work*

The following are the contributions of this work:

i) Researches on biodiesel for alternative sources of energy to replace petroleum due to environmental concern

ii) Researches on biodiesel derive from low grade oils as alternative to alternate vegetable oil as biodiesel feedstock to reduce biodiesel production cost

iii) Development of integrated process that combine different steps into one single unit through extractive reactor.

iv) Extractive reaction is one the reactor intensification techniques in order to overcome the reaction hindrance and saponification problems due to undesired impurities in the feedstock

1.4 *Organisation of this thesis*

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description about conventional technologies for biodiesel production that implies high production cost due to its operation that need purification of biofuel. This chapter also provides a brief discussion on the integration possibilities for production of biodiesel using waste cooking oil, animal fat and non-edible oil as alternative feedstock to reduce production costs. Besides that, an explanation about the use of aqueous ethanol as a solvent in extraction process is also presented. Futhermore, a general description on rate controlling role of both the chemical reactions and diffusional processes are provided. Lastly, this chapter also explain the principles of solubility and solutions, as well as a summary on previous experimental work on solubilities of various vegetable oils in solvent.

Chapter 3 gives a methodology for preparing calibration curve using GC device approach. Seven samples with different concentration used for concentration determination by FID analysis. This chapter also discuss method for preparation of FAEE. Besides that, brief explanation about methodology to do an experimental study for determination of effect of stirred time on settling time of the mixture and to determine the distribution coefficient of FAEE also presented to give understanding about extraction kinetics of FAEE from reactive region by using solvent aqueous ethanol and solubility mechanism characteristic. Extraction can only be sustained if the medium consistently appears as two-immiscible liquid and the solute is more soluble in the solvent.

Chapter 4 gives result and discussion of this experiment. The result gives an experimental kinetic data refer to a reaction rate and how this is affected by stirrer variables. This chapter also gives an understanding about extraction kinetics of FAEE from reactive region by using aqueous ethanol and solubility mechanism characteristic. It also discusses the extraction kinetics that was controlled by diffusion of FAEE occurring in proximity to the interface with added schematic diagram. Besides that, brief explanation about the distribution concentration of FAEE at both upper layer and bottom layer of mixture of oil:ethanol with different molar ratio also outlined. Lastly, this chapter also explain how different volume of aqueous ethanol will affect the distribution of FAEE in the solution and compare it.

Chapter 5 concluded the whole findings from the experiment process and some recommendation are highlighted when conducting the experiment in order to get better result in future.

2 LITERATURE REVIEW

2.1 *Introduction*

Nowadays, biodiesel that derived from biological sources such as fats and oils have received increasing attention (Dhiraj et al, 2012). Biodiesel can be used to replace petroleum. An intensified search for alternative sources of energy is essential since continuing depletion of the reserves of non-renewable petroleum, price volatility, and feedstock availability concerns (Dhiraj et al, 2002). Besides that, the combustion of petroleum based fuels has causes environmental problems. Thus, it gives impacts on the environment and human health and also threatens wild and human life. Furthermore, the emission of CO, SO_2 and NO_X as the combustion products has cause further global warming. Its part in global warming potential has increased from year by year and now bigger than those of the domestic and industrial sector (Dhiraj et al, 2002).

Biodiesel are most important liquid biofuels in transportation sectors. These biofuels can be uses as a sole fuel in motor engines and as additives in diesel and gasoline blends in other to enhance the oxygen content of such fuel (Gutierrez et al, 2009). These oxygenated blends allow the reduction of polluting gases mostly aromatic hydrocarbons and carbon monoxide (CO) (Gutierrez et al, 2009). In addition, the biodiesel is a mixture of ethyl ester of fatty acids and these ester grouos increases the oxygen content of diesel-biodiesel blend. Therefore, it can improve the combustion efficiencyof conventional follsil diesel (Gutierrez et al, 2009)

2.2 *Conventional technologies for biodiesel production*

Nowadays, the conventional technologies for biodiesel production mostly using a reactor with acid or basic catalyst and separation like distillation, centrifugation, flash evaporation, filtration and decantation that use unit operation (Sanchez, 2010). However, this operation need purification of biofuel that implies high capital investment and energy consumption leading to elevated production cost (Sanchez et al, 2010). One of the important alternative approaches for more intensive and cost effectiveness process is through the development of integrated process that combine different steps into one single unit (Sanchez et al, 2010). Moreover, Gutierrez et al (2009) has been study the integration possibilities for production of biodiesel using a single source of biomass as a feedstock. He claimed that the integration of material flows between

ethanol and biodiesel production lines allowed a reduction unit energy costs down to 3.4%, whereas the material and energy integration leaded to 39.8% decrease of those costs.

Extraction of biodiesel from oil phase using aqueous ethanol is the crucial method in order to imply low capital investment in production of biodiesel. The reactive exraction is an integrated process simultaneous commbining the chemical reaction and liquid-liquid extraction (Sanchez et al, 2010). Briefly, process integration looks for the integration of all operations involve in the production of one specific product. Hence, this can be achieved through the development of integrated processes that combine different steps into one single unit (Sanchez et al, 2010). Besides that, the latter phenomenon allows the continuous removal of the reaction products favouring the direct conversion in the case of reversibel reactions like the esterification of vegetable oils with alcohol. In addition, Sanchez et al (2010), have been evaluating the possibility of applying the integration principle to the biodiesel production by extractive reaction from palm oil. Interestingly, during the esterefication of palm oil with alcohol such as methanol, the product form which is methyl esters ang glycerine generate two immiscible phases. Hence, this will makes the possible to separate removal of two products stream which is biodiesel enriched in extract streams and glycerine enriched in raffinate streams. In this way, the principle of reaction-separation integration can be applied in the production of ethyl esters using palm oil ad even castor oil (Sanchez et al, 2010)

2.3 *Solvent in extraction process*

Aqueous ethanol is used as a solvent in extraction process to produce bioethanol. Fuel ethanol is the most employed liquid biofuel worldwide (Gutierrez et al, 2009). Moreover, a broad variety of plants materials containing the sugars required for fermentation process can be utilized for fuel ethanol production like sugar cane juice and cane or beet molasses. Starchy materials are also used for these purposes (Gutierrez et al, 2009). Besides that, ethanol can be produced from linocellulosic biomass as well. The lignocellulosic biomass is considered as the most promising feedstock at misterm for ethanol production due to its availability and low cost (Gutierrez et al, 2009). In addition, the extraction of palm oil has generates significant amount of lignocellulosic residues which can be used as a feedstock for ethanol production. If the integration of production line for processing both palm oil linocellulosic biomass is considered, hence

the synthesis of an integrated technological scheme for biodiesel is feasible. It is because it will reduce the production cost since there is no need to purchased ethanol because ethanol can be produced within the same process.

2.4 *Solvent extraction kinetics*

The kinetics of solvent extraction is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species that control the chemistry of the extraction process (Rydberg et al, 2004)

2.4.1 *Rate-Controlling Role of the Chemical Reactions*

For solvent extraction systems, there are two additional complications. First, the chemical reactions can take place in two bulk phases, since it dealing with two immiscible liquid layers. Second, the chemical reactions can occur in the two-dimensional region called the liquid-liquid interface that separates the two immiscible liquids (Rydberg et al, 2004)

2.4.2 *Rate-Controlling Role of the Diffusional Processes*

In order to understand the dependence of the extraction kinetics on the rate of diffusion of chemical species that participate in the extraction reaction, there is a need to distinguish between diffusion in the bulk phases and diffusion through the thin layers adjacent to the interphase. When two phases are vigorously stirred, it is possible to describe interfacial diffusion by assuming the existence of two stagnant thin layers of finite thickness located on the aqueous and organic side of the interface. This model of interphase is extremely useful for describing extraction kinetics that is controlled by diffusion occurring in proximity to the interface. (Rydberg et al, 2004)
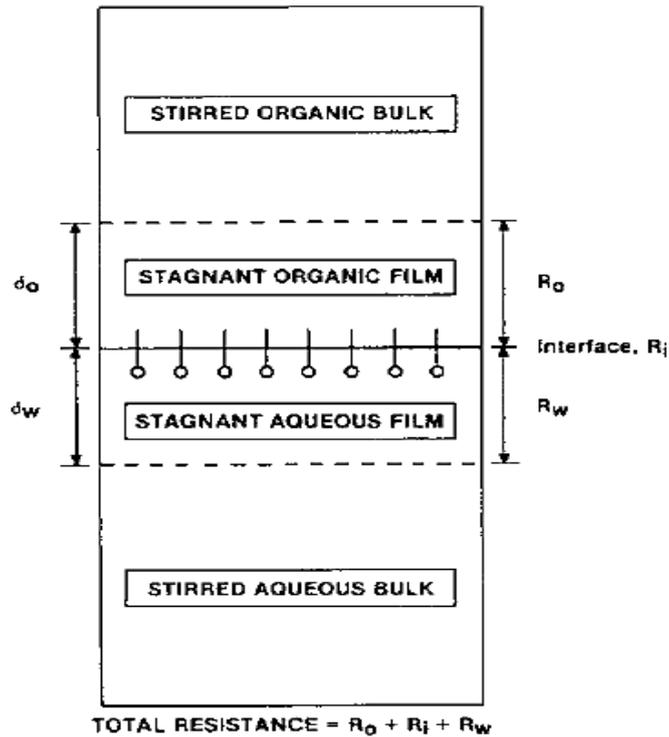
Figure 1 Interfacial diffusion films. (Rydberg et al, 2004)

Figure 1 shows interfacial diffusion films and δo and δw are the thickness of the organic and aqueous films, respectively. The presence of an adsorbed layer of extracting molecules at the interface is also shown in the figure. The thickness of both organic and aqueous films depends on the stirring rate of the two phases. The higher the rate of mixing, the lower the thickness of the diffusion film. In addition, even when dealing with the most efficiently stirred systems, the chemical species that have to be transported to or away from the interface for the extraction reaction to take place always have to diffuse through the diffusion films. The time required for this often can be comparable or longer than that required for the actual chemical changes in the extraction. As a consequence, diffusion through these films controls the overall kinetics of extraction. Experience has shown that film diffusion is the predominating rate-controlling factor in many practical extraction processes. (Rydberg et al, 2004)

2.4.3 *Diffusion*

Diffusion is irreversible process by which matter spontaneously moves from a region of higher concentration to one of lower concentration. Nevertheless, when dealing with solutions containing extractable species (FAEE) and extracting regions at concentrations much lower than those of the molecules of the solvents (aqueous ethanol), diffusion is sufficiently well described by considering only those species for

which the concentrations appreciably change during the extraction reaction(Rydberg et al, 2004)

The diffusion flow, J (mass/cm^2.s) is the amount of matter that passing perpendicularly through a reference surface area during a unit time. When concentration of diffusing species, c are expressed in mol/cm^3, the correlation between the flux across a unit reference area located perpendicularly to the linear coordinate x and the concentration gradient, dc/dx will be given by the Fick's law of diffusion, that is

$$J = - \frac{Ddc}{dx}$$

Where D (cm^2 /s) is the diffusion coefficient of the species and is independent of concentration. (Rydberg et al, 2004)

2.5 *Principles of solubility and solutions*

Solvent extraction is the distribution of solute between two liquids that must not be completely mutually miscible. The distribution of a solute depends on its preference for one or other liquid which is closely related to its solubility in each one of them. Thus, the general subject of solubility is highly relevant to solvent extraction. In solution, the solutes particles interact with solvent molecules and also, provided the concentration of the solute is sufficiently high with other solute particles. These interactions play the major role in the distribution of a solute between the two liquid layers in liquid-liquid distribution systems. (Rydberg et al, 2004)

2.5.1 *Solvent miscibility*

Solvent extraction takes places through the distribution of solutes between two practically immiscible liquids. For a separation to be carried out by solvent extraction, the solute has to transfer from one region of space to another such region, which is physically separated from the first. In phase region, the solute is dissolved uniformly in a liquid at all points under the same pressure. (Rydberg et al, 2004)

2.5.2 *Solubilities in ternary systems*

Ternary systems of interest to solvent extraction are generally two-phase systems, but occasionally ternary systems that consist of a single phase must be considered. It is customary to depict such a system at a given temperature on a triangular phase diagram,

where a composition is indicated by a point in an equilateral triangle. (Rydberg et al, 2004)
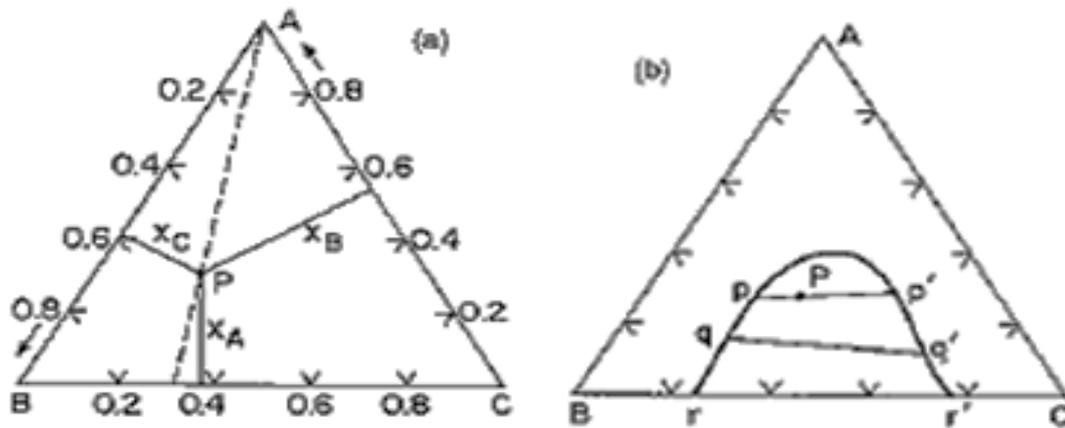
Figure 2 Ternary Phase Diagram with Components A, B And C. (Rydberg et al, 2004)

The figure 2(a) shows a homogeneous system. The composition at point P is being given by the length of the line. This distance represents the corresponding mole fractions. The dashed line shows the changes occurring when solvent A is added (upward) or removed (downward). An apex of the triangle represents a pure component (Rydberg et al, 2004)

The figure 2(b) shows a heterogeneous system, splitting into two liquid phases, with composition market with r, q, p, p', q' and r' along the phase boundary where r and r' denote the BC miscibility gap. A line on the triangular diagram encloses such a region of nominal compositions of the system. A straight tie-line connects the points on the enclosing line that corresponds to phase in mutual equilibrium. At nominal composition P, there is Pp' moles of a phase of composition p for every pP moles of one of composition p', at the two ends of the tie line (Rydberg et al, 2004).
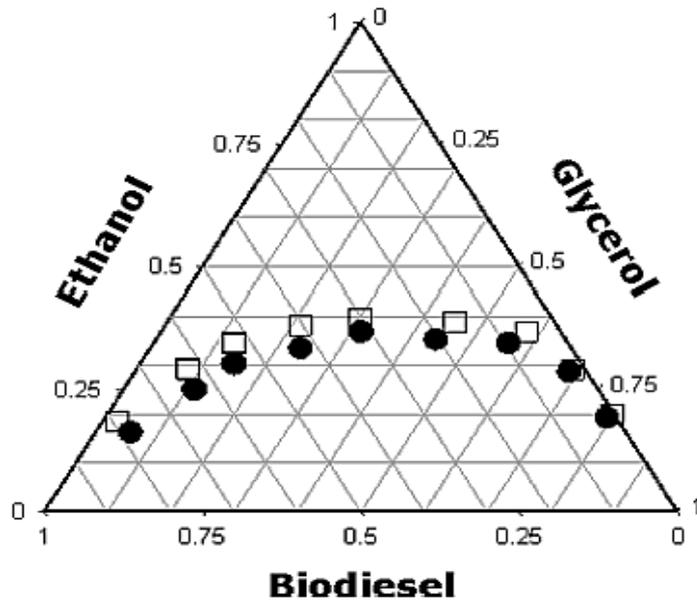
Figure 3 phase diagram of biodiesel + glycerol + ethanol at ☐ 298.15K and ● 333.15K. (Franca et al, 2009)
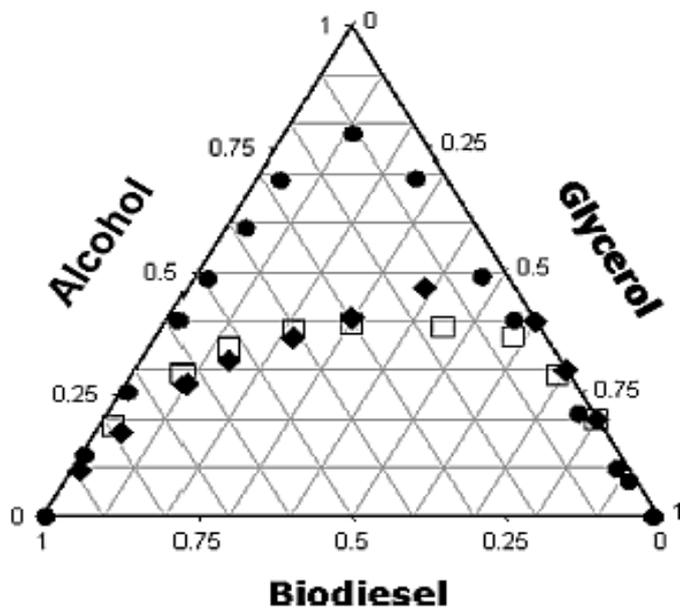
Figure 4: phase diagram of castor oil biodiesel + glycerol + ◆ methanol + ☐ ethanol at 298.15K. ● Jatropha curcas biodiesel at 298.15K. (Franca et al, 2009)

It can be observed in Figure 3 that biodiesel has greater solubility in the glycerol-enriched phase in the system containing ethanol at 298.15K. Comparing the systems with ethanol at (298.15K and 333.15K) in Figure 4, it can be observed that the solubility increases with temperature. Despite these variations, they are not significant enough to

determine phase behaviour of the systems. The alcohol concentration is the main factor that affects biodiesel product solubility. (Franca et al, 2009)
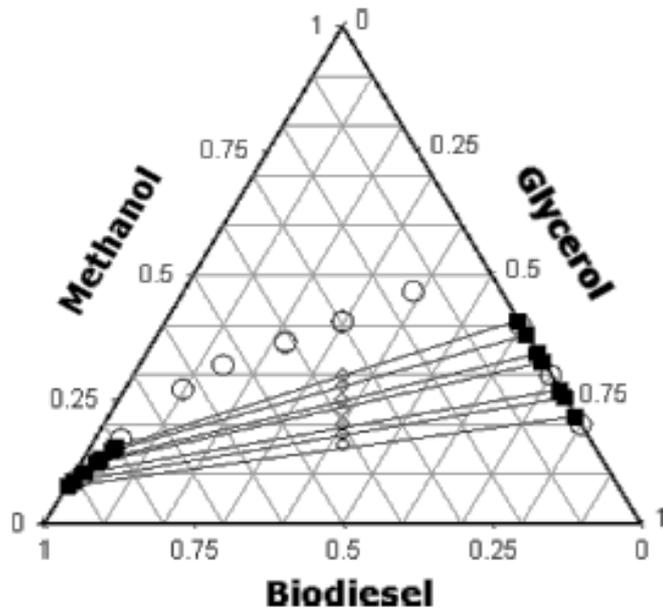
Figure 5 tie lines for the system biodiesel + glycerol + methanol at 298.15K: ⭕ bimodal; ◇ global composition and ⬛ tie line. (Franca et al, 2009)

Figure 5 shows the composition of equilibrium phases cross global composition. The solubility of glycerol in the biodiesel phase is slightly greater than that of biodiesel in the glycerol phase. (Franca et al, 2009)

2.5.3 *Solubilities of various vegetable oils in solvent*

From the analysis by Rao et al (1956), the solubility characteristics of babasu oil and coconut oil in ethanol are similar since they have similarity in chemical composition.
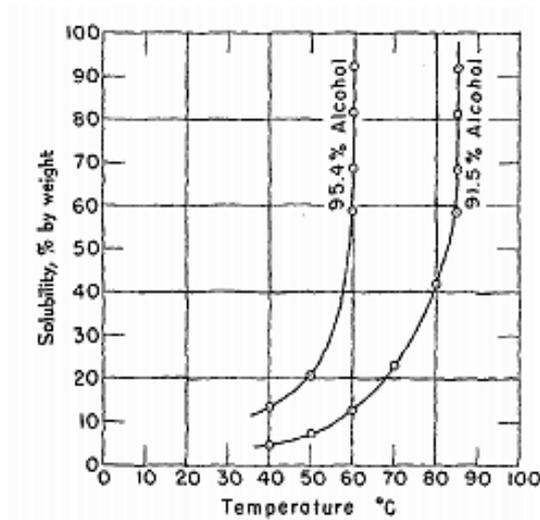
Figure 6 solubility curves for babasu oil
(Rao et al, 1956)
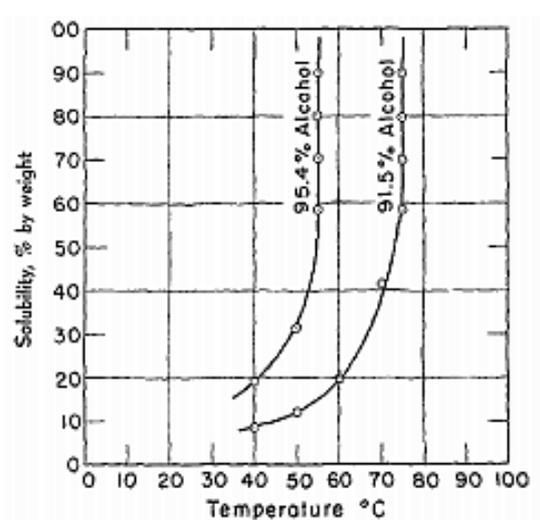
Figure 7 solubility curves for coconut oil
(Rao et al, 1956)

Figure 6 shows that babasu oil was miscible in 99.9% ethanol at 30°C while Figure 7 shows that coconut oil was miscible at 23°C. In 98.0% ethanol, miscibility was attained at 45°C for babasu oil and at 35°C for coconut oil. In 95.4% and 91.5% ethanol miscibility temperature were 60°C and 85°C for babasu oil while 55°C and 75°C for coconut oil respectively. The coconut oil was the most soluble of the six oils examined (Rao et al, 1956).
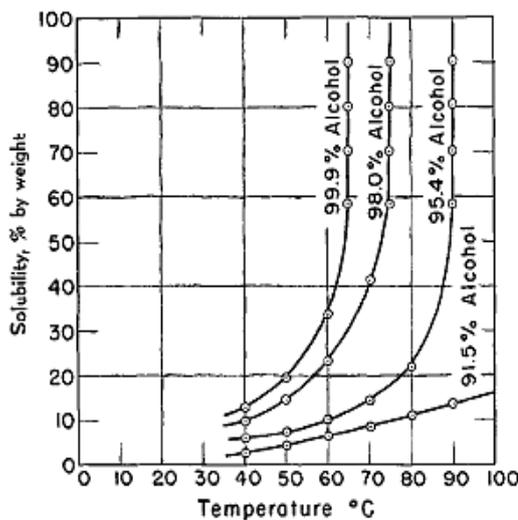
Figure 8 solubility curves for palm oil
(Rao et al, 1956)
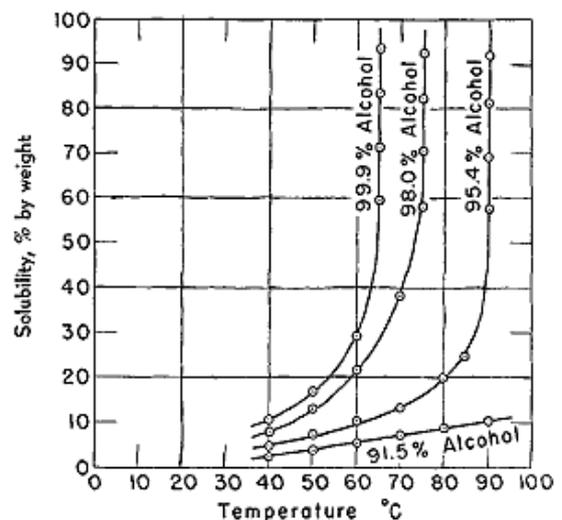
Figure 9 solubility curves for sunflower oil
(Rao et al, 1956)

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Palm oil (Figure 8) and sunflower seed oil (Figure 9) showed identical miscibility temperature in three highest concentrations of ethanol. In 99.9%, 98.0% and 95.4% of ethanol, the miscibility temperatures was 65°C, 75°C and 90°C respectively. However, in 91.5% ethanol, the solubility of sunflower seed oil was only 10.17% at 90°C compared with 13.5% for palm oil at this temperature. (Rao et al, 1956)
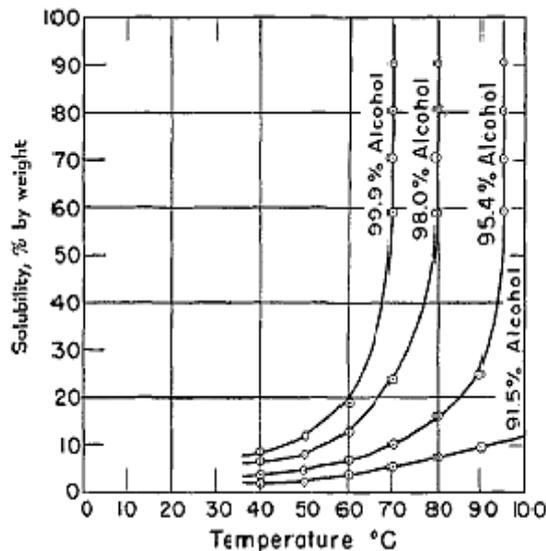
Figure 10 solubility curves for olive oil (Rao et al, 1956)
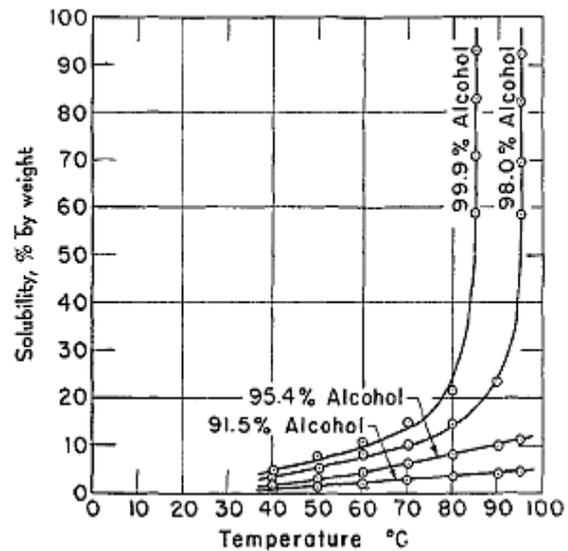
Figure 11 solubility curves for rapeseed oil (Rao et al, 1956)

Figure 10 shows that the miscibility of olive oil in 99.9%, 98.0% and 95.4% ethanol was 70°C, 80°C and 95°C respectively and in each case, it was 5% above palm and sunflower oil. The least soluble of the group was rapeseed oil (Figure 11) with miscibility in 99.9% ethanol at 85°C and in 98.0% ethanol at 95°C. The solubility in 95.4% and 91.5% ethanol at 95°C was only 11.3% and 4.9% respectively. Thus, this oil was the least soluble of the entire group. (Rao et al, 1956)

For overall, it can be seen clearly at 45°C, pure ethanol and oil is partially miscible. We deliberately want to create it to ensure extraction while the dissolve ethanol involve in reaction at low temperature. (Rao et al, 1956)

In addition, from the analysis by Kaparti et al (1959), the saturation solubility of the oils was determined from 40°C to 100°C in 85% by weight to 99% ethanol. It can be seen that the saturation solubility of vegetable oil depends on the concentration and temperature of aqueous ethanol. The solubility are very low at low temperature and

increase tremendously as the critical temperature is reached at any particular concentration and all vegetable oil such as peanut oil, mowrah oil, cottonseed oil and safflower oil has complete miscibility at 70°C in absolute alcohol(99%). As the alcohol temperature increases, the solubility temperature decreases. At 80°C, safflower oil, mowrah oil and peanut oil has complete miscibility in about 98% ethyl alcohol (Kaparthi et al, 1959).

2.6   *Summary*

Conventional technologies for biodiesel production imply high production cost due to its operation that needs purification of biofuel. This paper presents a study on the integration possibilities for production of biodiesel using waste cooking oil, animal fat and non-edible oil as alternative feedstock to reduce production costs using extractive reactor by using aqueous ethanol as a solvent in liquid-liquid extraction. Besides that, extraction kinetic depends on the rate of diffusion of chemical species that participate in chemical reaction.. Futhermore, to design efficient extraction unit to extraction unit, knowledge of the solubility of oils in solvent are necessary. For overall, it can be seen clearly at 45°C, pure ethanol and oil is partially miscible. We deliberately want to create it to ensure extraction while the dissolve ethanol involve in reaction at low temperature

3 MATERIALS AND METHODS

3.0 *Overview*

This experiment was conducted to characterize extraction kinetics of FAEE from oil phase by using aqueous ethanol and to determine the distribution coefficient of FAEE between oil phase and aqueous ethanol. This experiment was conducted with three different oil:ethanol molar ratio which is 1:1, 1:3 and 3:1 where oil was firstly diluted with FAEE. The mixture was heated and stirred with different stirred time range between 1-20min. A settling time for the mixture was recorded and a sample was taken for FAEE concentration determination using gas chromatography (GC) analysis. Graph of FAEE concentration against stirred time will be plotted and analysed.

3.1 *Introduction*

The kinetics of solvent extraction is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species that control the chemistry of the extraction process. For solvent extraction systems, there are two additional complications. First, the chemical reactions can take place in two bulk phases, since it dealing with two immiscible liquid layers. Second, the chemical reactions can occur in the two dimensional region called the liquid-liquid interface that separates the two immiscible liquids

3.2 *Chemicals*

Table 1: List of chemicals used

No	Chemicals Name	Type	Purify
1	Absolute ethanol	Liquid	99%, 0.154wt% water
2	Cooking oils	Liquid	100%
3	High performance liquid chromatography (HPLC)-grade n-heptane	Liquid	99%
4	Potassium hydroxide pellets	Solid	100%
5	Ethyl oleate	liquid	99%

3.3 *Preparation of ethyl oleate calibration curve*

3.3.1 *Samples preparations*

A sample of ethyl oleate was diluted first using n-heptane to achieve 3000ppm concentration in 3ml vial. The calculation as below:

Table 2: ethyl oleate and n-heptane specification

	Ethyl oleate	n-Heptane
Molecular weight (g/mol)	310.51	100.21
Density (g/ml)	0.87	0.684

$V_{EO} + V_{nH} = 3ml$ ……………….. (1)

$$V_{EO} = \frac{nEO(MWEO)}{\rho EO} \qquad V_{nH} = \frac{nnH(MWnH)}{pnH}$$

$$\frac{nEO}{nEO+nnH} = 0.003$$ …………………. (2)

$$V_{EO} = \frac{\frac{0.003}{0.997}nnH(MWEO)}{pEO}$$

$$\frac{\frac{0.003}{0.997}nnH(MWEO)}{pEO} + \frac{nnH(MWnH)}{pnH} = 3ml$$

$$\frac{\frac{0.003}{0.997}nnH(310.51g/mol)}{0.87g/ml} + \frac{nnH(100.21g/mol)}{0.684g/ml} = 3ml$$

Therefore, $n_{nH} = 0.02mol$
$\qquad\qquad V_{nH} = 2.93ml$
$\qquad\qquad V_{EO} = 0.02ml$

Another samples with concentration 1500ppm was prepared in 1ml vial by dilute the first sample of 3000ppm with n-heptane by using calculation as below:

M1V1 = M2V2

Where M1 = 3000ppm   V1 = x

$\qquad$ M2 = 1500ppm   V2 = 1ml

x = 0.5ml

Hence, 0.5 ml sample of 3000ppm concentration was diluted with 0.5 ml n-heptane to achieve 1500ppm concentration. Another sample with different concentration which is

1000ppm, 500ppm and 200ppm was prepared using same way. The concentration of each sample will be measured using GC analysis. A graph of area under gas chromatography curve against concentration of ethyl oleate solution was prepared

3.3.2 *Flame ionization detection (FID) analysis*

FID device was used to obtain concentration measurements of study samples. Twenty millilitre (20um) aliquots will be diluted in 1ml of n-heptane before GC analysis. External standard calibration will be used for quantification. The GC device will be fitted with a Restek MXT Biodiesel TG column (15m x 0.32mm ID x 10um) and employed both a temperature program (50-380°C) and pressure program (20-65kPa). Solvent used in this analysis were n-heptane

Figure 12 Gas chromatography device

3.4 *FAEE preparation*

A mixture of oil:ethanol with the molar ratio of 1:6 was mixed in a conical flask. The calculation as below:

$$V_{Et} + V_{oil} = 1000ml \dots\dots\dots\dots (1) \quad R_{oil:Et} = \frac{1}{6} \dots\dots\dots\dots (2)$$

$$R_{oil:Et} = \frac{noil}{nEt} = \frac{(\rho o)(Vo)(MWEt)}{(\rho Et)(VEt)(MWo)}$$

$$\frac{Vo}{VEt} = \frac{(Roil:Et)(\rho Et)(MWo)}{(\rho o)(MWEt)}$$

$$\frac{Vo}{VEt} = \frac{(\frac{1}{6})(0.78g/ml)(890g/mol)}{(0.89g/ml)(46.06g/mol)} = 2.822$$

$V_{Et} + 2.822V_{Et} = 1000ml$

$V_{Et} = 261.62ml$

$V_{oil} = 738.38m$

Then, the solution was added with a little bit 2wt% of potassium hydroxide (KOH) which is about 15g KOH to ensure that there are a reaction occurs. After that, the mixture was stirred and heated using hot plate magnetic stirrer while a condenser was assembled on top of the conical flask to condensate the mixture. The figures are as below:
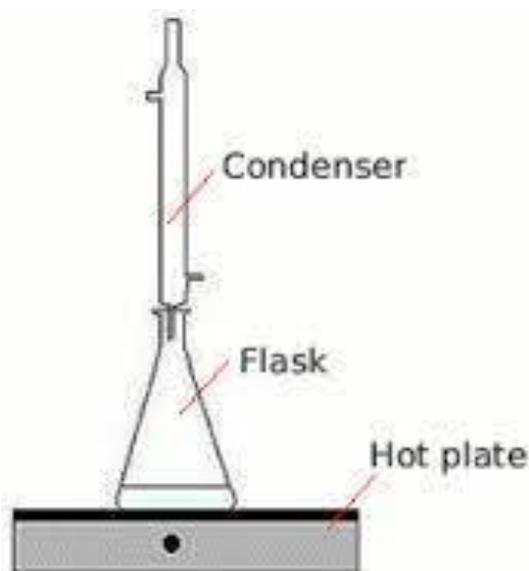
Figure 13: setup for preparation of FAEE

The set up was left for one day to ensure complete reaction. After one day, the mixture was poured into the separating funnel to separate the FAEE. The mixture was washed three times to remove any impurities as in figure below
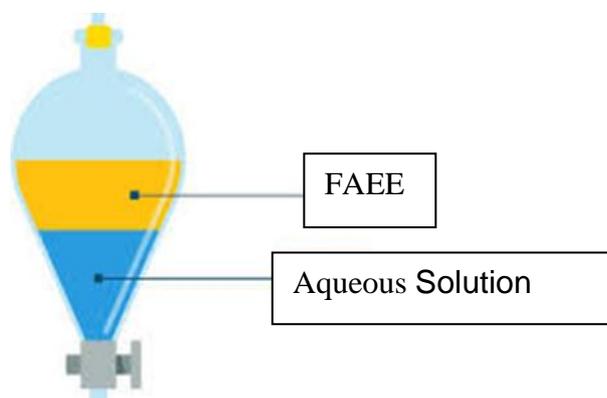
Figure 14: FAEE washing and separating procedure

3.5 *Solvent extraction kinetics experiment*

Objective: to characterize extraction kinetics of FAEE from oil phase by using aqueous ethanol

A mixture of oil:ethanol with the molar ratio of 1:1 was prepared. Before that, the oil was diluted first with FAEE using molar ratio of oil:FAEE which is 10:3. The calculation as shown below:

$V_{Et} + V_{oil} + V_{FAEE} = 50ml$ ……….. (1)

$R_{oil:Et} = \dfrac{1}{1}$ ………………….. (2)

$R_{oil:Et} = \dfrac{noil}{nEt} = \dfrac{(\rho o)(Vo)(MWEt)}{(\rho Et)(VEt)(MWo)}$ $\dfrac{Vo}{VEt} = \dfrac{(Roil:Et)(MW\ oil)(p\ Et)}{(p\ oil)(MW\ Et)}$

$\dfrac{Voil}{VEt} = \dfrac{(\frac{1}{1})(0.78g/ml)(890g/mol)}{(0.89g/ml)(46.06g/mol)} = 16.93$ $V_{oil} = 16.93\ V_{Et}$

$R_{FAEE:oil} = \dfrac{3}{10}$ ………………….. (3)

$\dfrac{Voil}{V\ FAEE} = \dfrac{(Roil:FAEE)(MW\ oil)(p\ FAEE)}{(p\ oil)(MW\ FAEE)} = \dfrac{(\frac{10}{3})(890g/mol)(0.8181g/ml)}{(0.89g/ml)(1216.02g/mol)} = 2.24$

$V_{oil} = 2.24\ V_{FAEE}$

Hence, $V_{Et} + 16.93V_{Et} + 7.56V_{Et} = 50ml$ …………. (1)

$V_{Et} = 1.96$ ml
$V_{oil} = 33.22$ ml
$V_{FAEE} = 14.82$ ml

Next, the mixture was stirred with different time ranged between 1-20minutes. The time for the reaction mixture for settlement was recorded in the as table below:

Table 3: Settling time of a mixture for different stirred time

Stirred time (min)	Settling time (min)		
	Oil:ethanol molar ratio 1:1	Oil:ethanol molar ratio 1:3	Oil:ethanol molar ratio 3:1
1			
5			
10			
15			
20			

After settlement, 20μl sample of the mixture at both layer of immiscible liquid was taken using micro pipette. Solvent n-heptane was added into the 1ml vial together with the sample. Next, its concentration was determined by using gas chromatography analysis and a graph of concentration against stirred time was plotted. The experiment was repeated using mixture of oil:ethanol with different molar ratio of 1:3 and 3:1

3.6   *Summary*

It is expected that the result from the experiment will be able to give understanding about extraction kinetics of FAEE from reactive region by using aqueous ethanol and solubility mechanism characteristic. The kinetics of solvent extraction is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species that control the chemistry of the extraction process. Extraction kinetics was controlled by diffusion of FAEE occurring in proximity to the interface. The higher the stirred time, the thickness of diffusion film was increasing resulting in the increases time for FAEE diffuse through the stagnant layers. Extraction can only be sustained if the medium consistently appears as two-immiscible liquid and the solute is more soluble in the solvent

4 RESULTS AND DISCUSSION

4.0 *Overview*

The partition of solute between two immiscible solvents is a major technique in separation, both in the laboratory and industry. All chemical reaction occurs with a certain rate. For aqueous systems, in which no redox reaction occur, equilibrium was often attained rapidly. However, the transfer of a solute from an aqueous solution to an organic solvent occurs via a phase boundary. This reaction depends on several parameters and may be quite slow. Therefore, the kinetics of solvent extractions, which is paramount importance to all industrial applications, is largely determined by the interfacial chemistry. To speed up phase transfer, there is a need to maximize the interfacial surface by violent stirring.

4.1 *Solvent extraction kinetics*

Table 4: Settling time of a mixture for different stirred time

Stirred time (min)	Settling time (min)		
	Oil:ethanol molar ratio 1:1	Oil:ethanol molar ratio 1:3	Oil:ethanol molar ratio 3:1
1	3.32	2.03	2.18
5	3.58	5.08	3.00
10	4.00	5.37	5.10
15	5.28	10.26	13.29
20	17.08	18.13	24.50

The experimental kinetic data refer to a reaction rate and how this is affected by stirrer variables. The kinetics of solvent extraction is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species that control the chemistry of the extraction process. Table 4 shows the settling time of a mixture for different stirred time ranged between 1-20 min for three different oil:ethanol molar ratio.
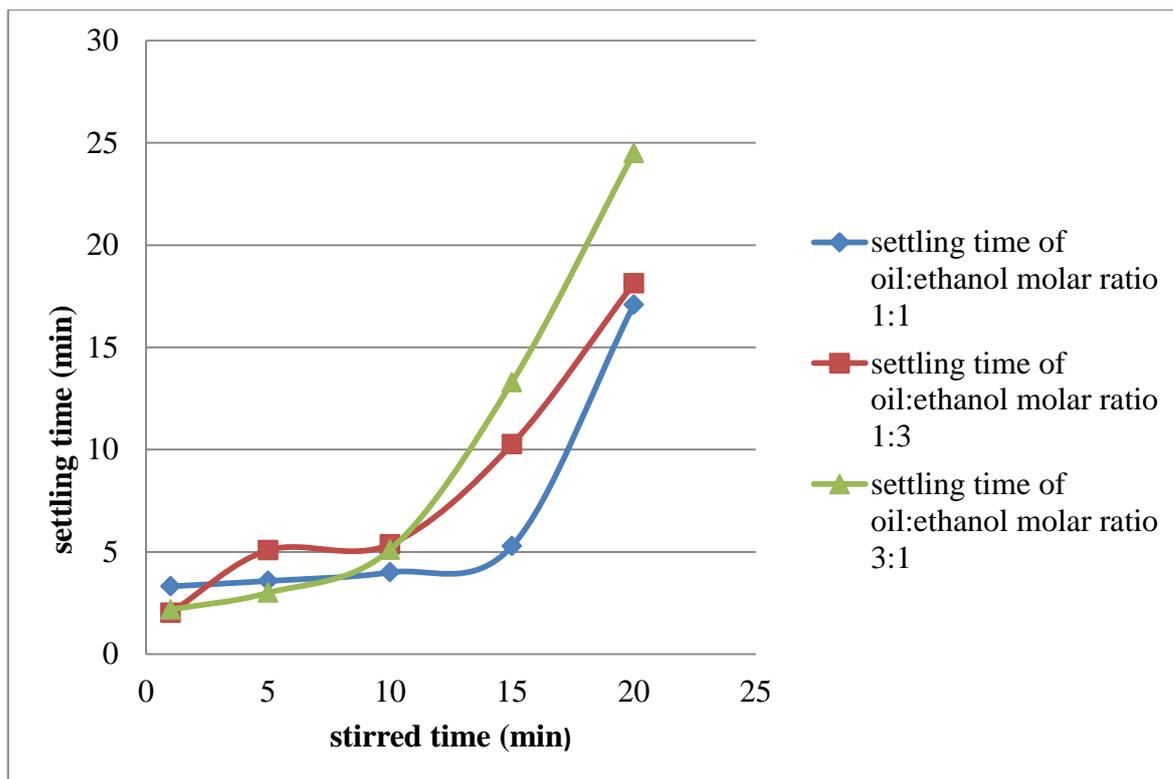
Figure 15: graph of settling time for different oil:ethanol molar ratio against stirred time

Figure 15 shows the settling time for different oil:ethanol molar ratio which is 1:1, 1:3 and 3:1 after being stirred for different time interval. For all molar ratios, the settling time of the mixture was increasing with the increasing of stirred time. From the graph, we can see that the settling time for 3:1 molar ratio was increasing slightly between stirred time 1-10 minutes. Then it was increasing rapidly until 20 minutes stirred time. The settling time for the 1:3 molar ratios has followed a very similar pattern. On the other hand, the settling time for 1:1 molar ratio was increasing gradually between stirred times 1 until 15 minutes but then increasing dramatically for 20 minutes stirred time.

When the two solutions that containing extractable species which is FAEE in cooking oil and extracting reagents which is ethanol vigorously stirred, there was a reaction occur and the existence of two stagnant thin layers of finite thickness located on the aqueous and organic side of the interface. Extraction kinetics was controlled by diffusion of FAEE occurring in proximity to the interface. From the experiment, we can see that the higher the stirred time, the thickness of diffusion film was increasing. Therefore, the time for FAEE diffuse through the stagnant layers also increase and the longer it's settling time. Whenever at least one of the chemical steps of the overall

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reaction mechanism is slow enough, compared with the diffusion rate, the kinetics of extraction would depend on the rate of the slow chemical reactions.

The dependence of the kinetics on the chemical reactions in this experiment can be understood by considering that the final products of extraction process are in a chemical state different from the initial unreacted species. This is true even for the simple partition of neutral molecules between two immiscible liquid phases, where the chemical change is in the solvation environment of the extracted species. For solvent extraction systems, there are two additional complications. First, the chemical reactions can take place in two bulk phases, since this experiment are dealing with two immiscible liquids layers. Second, the chemical reactions can occur in the two-dimensional region called the liquid-liquid interface, that separates the two immiscible liquids, or in a thin volume region very close to it.

4.1.1 *Rate controlling role of the diffusional processes*

In other to understand dependence of the extraction kinetics on the rate of diffusion of the FAEE that participates in this experiment of extraction reaction, it is important to distinguish between diffusion in the bulk phases and diffusion through the thin layers adjacent to the interface. In this experiment of solvent extraction, both of the cooking oil and the solvent aqueous ethanol phases are efficiently stirred. It follows that transport of material from the bulk of the phases up to a region very close to the interface can be considered instantaneous and that diffusion in the bulk of the phases can be neglected. Nevertheless, diffusional processes can still have an appreciable influence on the solvent extraction kinetics.

When the cooking oil and aqueous ethanol are vigorously stirred, it is possible to describe interfacial diffusion by assuming the existence of two stagnant thin layers of finite thickness located on the aqueous and organic side of the interface.
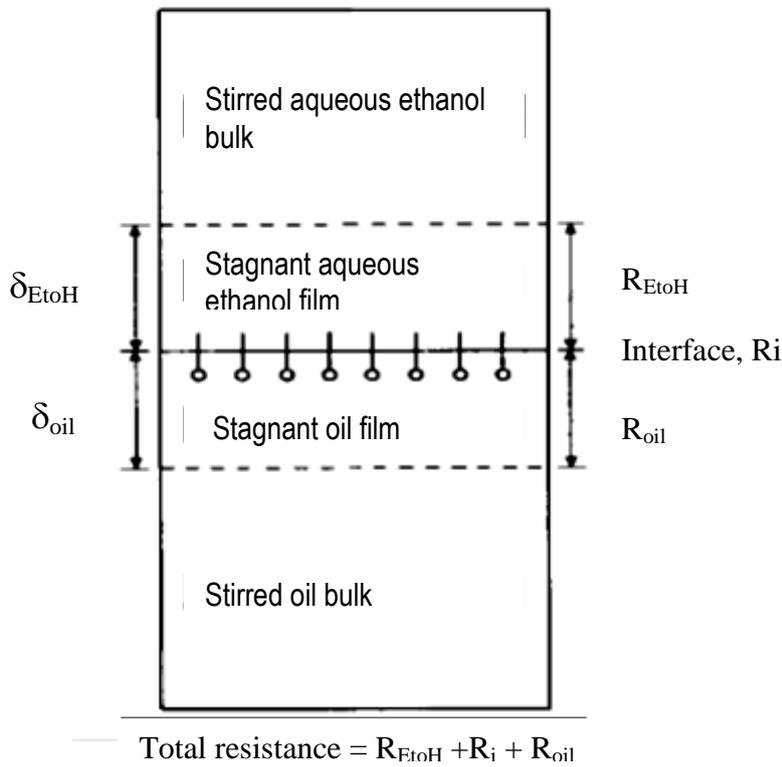
Figure 16 : The schematic diagram of this experiment's interfacial diffusion films.

The figure 16 above shows the model of the interphase of this experiment that describing this extraction kinetics that was controlled by diffusion occurring in proximity to the interphase. The δ_{oil} and δ_{EtoH} are the thickness of the cooking oil and aqueous ethanol respectively. The presence of an adsorbed layer of extracting molecules at the interface is also shown. The two-film models are used throughout this experiment. The two films are schematically described in figure 16 above, in which the presence of an interfacial absorbed layer of extracting molecules is also shown. The δ_{oil} and δ_{EtoH} represents the thickness of the cooking oil and aqueous ethanol films respectively. In these layers, both of liquid phases are considered completely stagnant.

The thickness of the diffusion films in this experiment was an inverse function of the mechanical energy dissipated into the liquid system to stir it. This means that δ_{oil} and δ_{EtoH} depend on the stirring rate of the two phases, on the geometry of the solvent extraction equipment, and of the stirrers used. For both cooking oil and aqueous ethanol phases and a fixed apparatus of this experiment, the thickness of the diffusion films was increases with increase in the rate of mixing. When dealing with the efficiently stirred

systems, the chemical species that have to be transported to or away from the interface for the extraction reaction to take place always have to diffuse through the diffusion films. The time required for this often can be comparable or longer than that required for the actual chemical changes in the extraction. As a consequence, diffusion through these films controls the overall kinetics of extraction. Experience has shown that film diffusion is the predominating rate-controlling factor in many practical extraction processes

4.2 *Extraction of FAEE from oil phase using aqueous ethanol*
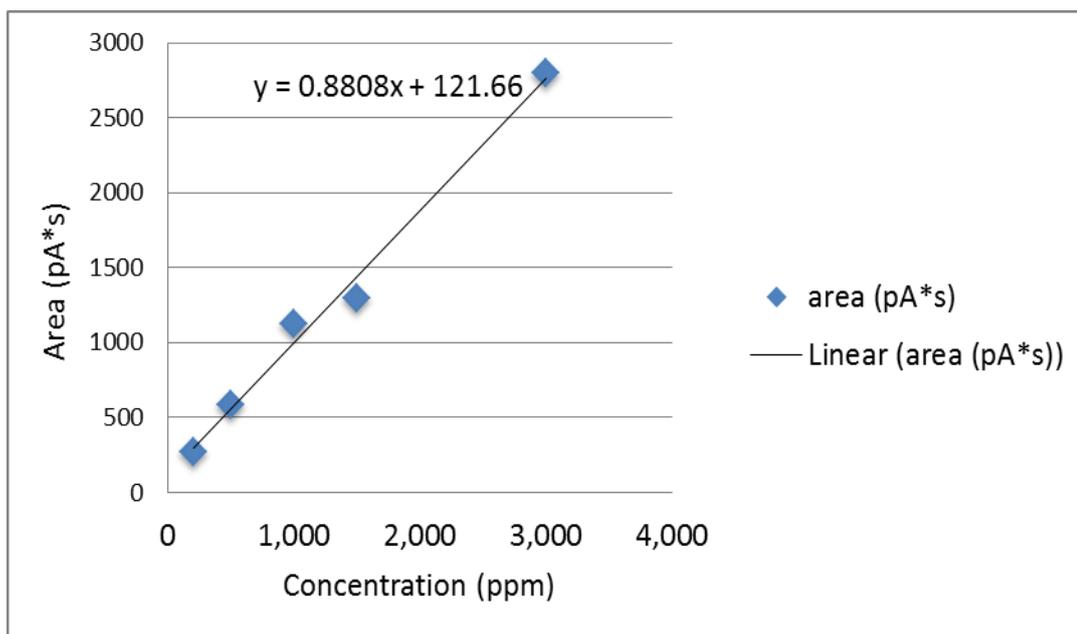
Figure 17: calibration curve of ethyl oleate

Figure 17 shows the calibration curve for ethyl oleate. Ethyl oleate with different concentration ranged between 3000 to 200ppm after diluted with n-heptane was used as standard samples. This standard sample was analysed using gas chromatography equipment to determine its area under graph of gas chromatography after analysis. This calibration curve was used as a general method to determining the concentration of a substance which is FAEE by comparing the area under gas chromatography graph to a set of standard samples of known concentration.
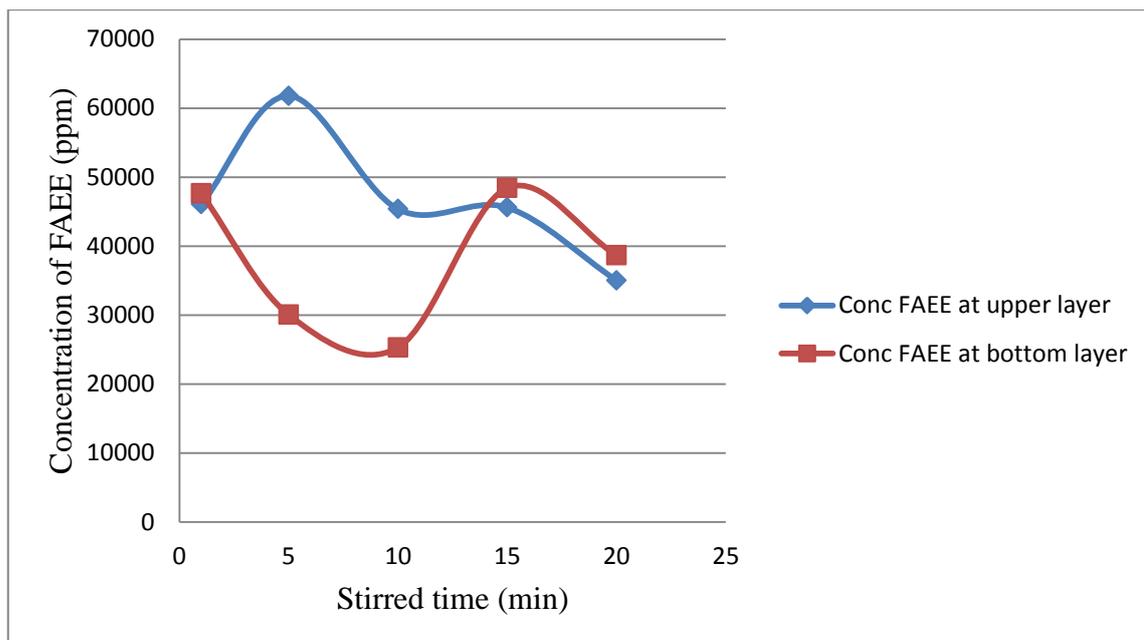
Figure 18: graph of concentration of FAEE against stirred time for molar ratio oil:ethanol of 1:1

Diffusion is sufficiently described when concentration of extractable species which is FAEE are appreciably change during the extraction reaction. Solvent extraction refers to the distribution of a solute between two immiscible liquid phases in contact with each other. Figure 18 above shows the distribution concentration of FAEE at upper and bottom layer of the solution at different stirred time for a mixture of oil:ethanol molar ratio 1:1. The aqueous ethanol is lighter and has lower density than cooking oil. So, the upper layer was aqueous ethanol while the bottom layer was cooking oil. For a separation to be carried out by solvent extraction, the solute FAEE has to transfer from cooking oil region of space to another aqueous ethanol region, which is physically separated from the first. In each such region, the solute FAEE was dissolved uniformly in a liquid and at all points under the same pressure. Such a region of space is called a phase. At equilibrium, at a constant temperature and pressure, a liquid phase is homogeneous and has the same properties in all direction.

In this experiment, the two liquid phases which is cooking oil and aqueous ethanol in contact are under the same temperature and pressure, which eventually reach mass transfer equilibrium after being stirred. From the figure, we can see that the concentration of FAEE for 1, 5 and 10 minutes of stirred time was higher in upper layer than the bottom layer of the solution. It means that the FAEE was successfully extracted from the oil phase to the ethanol phase. However, for the 20 and 25 minutes of stirred

time, it can be seen that the concentration of FAEE was slightly lower at upper layer than bottom layer of the solution. It means that the FAEE wasn't successfully extracted at this stirred time range.
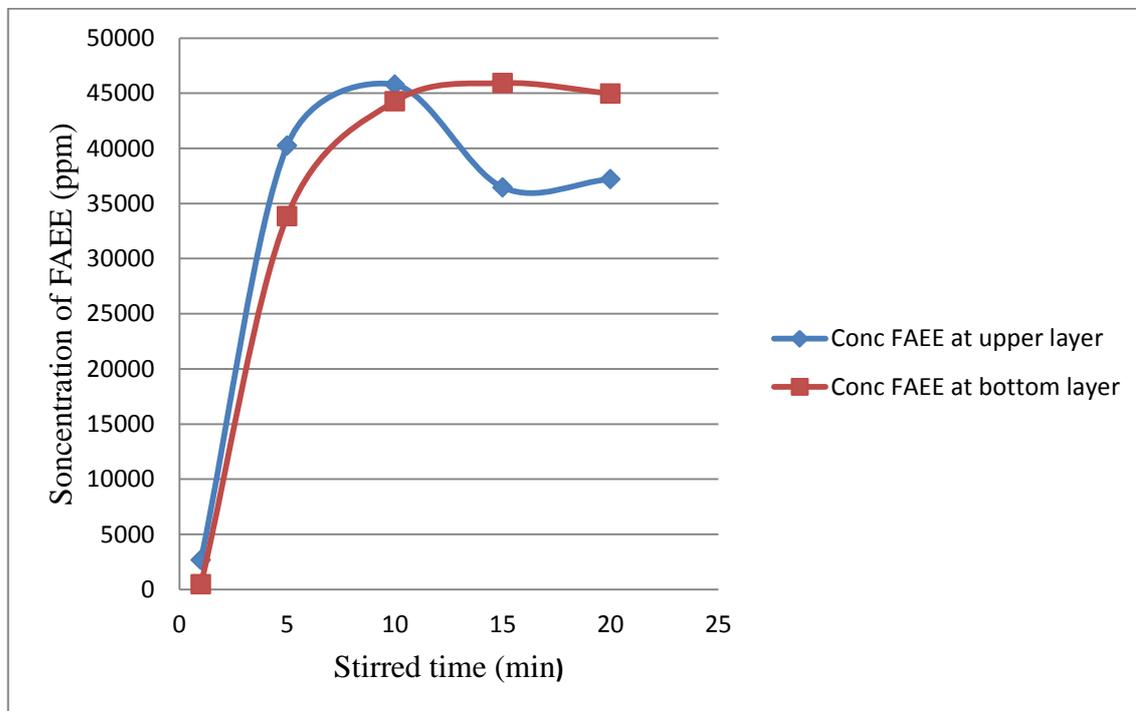
Figure 19: graph of concentration of FAEE against stirred time for molar ratio oil:ethanol of 3:1

Figure 19 above shows the distribution concentration of FAEE at upper and bottom layer of the solution at different stirred time for a mixture of oil:ethanol molar ratio 3:1. From the figure, we can see that the concentration of FAEE for 1, 5 and 10 minutes of stirred time higher in upper layer than the bottom layer of the solution. This scenario was similarly to the experiment for molar ratio oil:ethanol 1:1,the FAEE was successfully extracted from the oil phase to the ethanol phase in this range of stirred time. Meanwhile, for the 20 and 25 minutes of stirred time, it can be seen that the concentration of FAEE was slightly lower at upper layer than bottom layer of the solution. It means that the FAEE was unsuccessfully extracted.
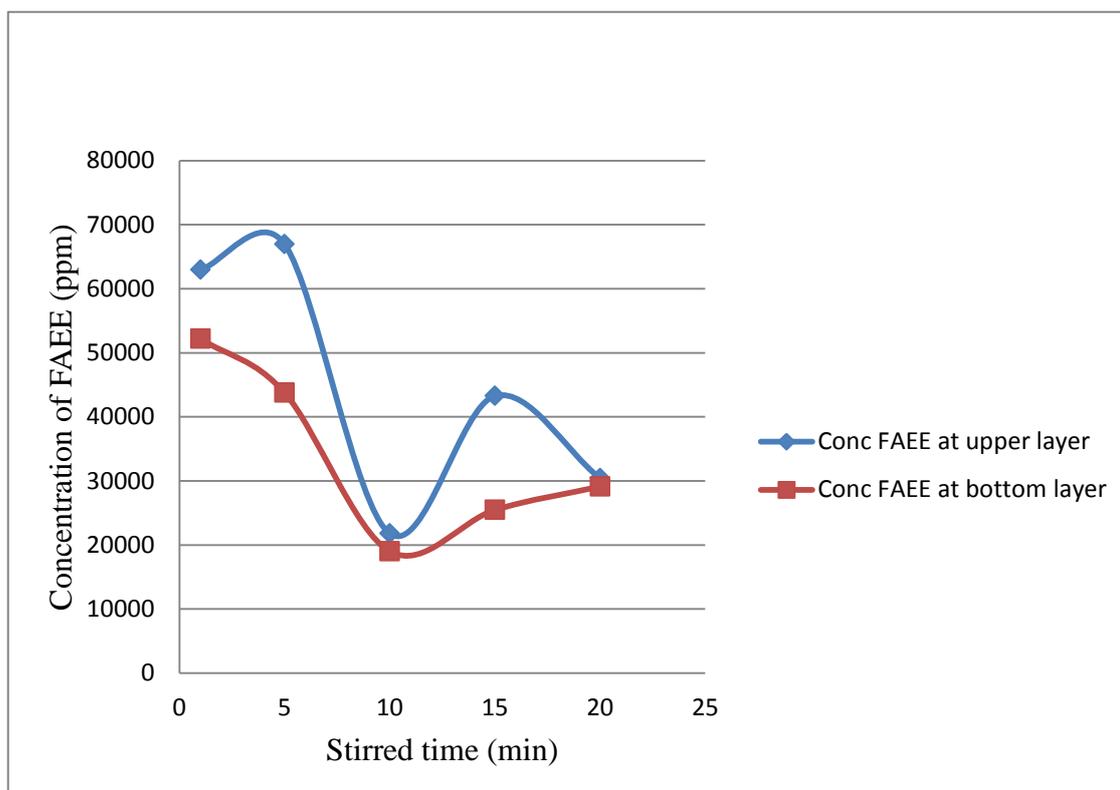
Figure 20: graph of concentration of FAEE against stirred time for molar ratio oil:ethanol of 1:3

Figure 20 above shows the distribution concentration of FAEE at upper and bottom layer of the solution at different stirred time for a mixture of oil:ethanol molar ratio 1:3. From the figure, we can see that the concentration of FAEE for all stirred time was higher in upper layer than the bottom layer of the solution. It means that the FAEE was successfully extracted from the oil phase to the ethanol phase. It can be concluded that the distribution coefficient of FAEE was higher in aqueous ethanol phase compared to oil phase for molar ratio oil:ethanol 1:3 for all stirred time range. This distribution of solute FAEE depends on its preference for cooking oil or the other liquid which is aqueous ethanol. It is closely related to the FAEE solubility in each one of them. In the solution, the FAEE molecules interact with solvent molecules and also, resulted in the concentration of FAEE is sufficiently high in the aqueous ethanol, comparing with the other cooking oil layer for all stirred time interval for this molar ratio.

By comparison, the most efficient oil: ethanol molar ratio was 1:3 because the solute FAEE was successfully extracted from oil phase region to the aqueous ethanol phase

region for all stirred time range. This result shows that an excess of ethanol was required to favour the direct reaction leading to an increased conversion by taking into account the reversibility of the extraction.

This experiment was illustrated in Figure 21 below. A separatory funnel contains two layers of liquids, one that is cooking oil layer and the other is an organic solvent which is aqueous ethanol. The aqueous ethanol is lighter and has lower density than cooking oil. So, the upper layer was aqueous ethanol while the bottom layer was cooking oil. The solute which is FAEE which initially was dissolved only in cooking oil layers, eventually distributes between the two phases after being stirred for different stirred time. When this distribution reaches equilibrium, the solute FAEE is at concentration $[FAEE]_{Oil}$ in the oil layer and at concentration $[FAEE]_{EtOH}$ in the aqueous ethanol solvent
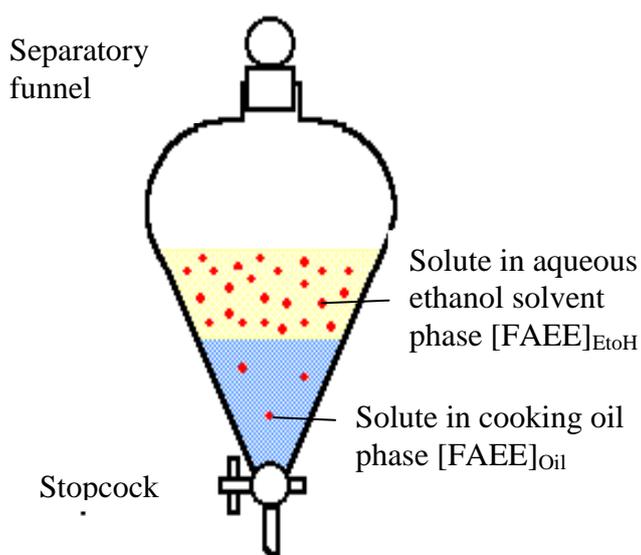
Figure 21 : A schematic representation of this experiment of solvent extraction. A solute FAEE was distributed between the upper layer and bottom layer of a mixture.

Figure 21 above shows a schematic representation of this experiment. Solutes FAEE have differing solubility's in different liquids due to variations in the strength of the interaction of FAEE molecules with those of the solvent. Thus, in this experiment of two immiscible of partially immiscible solvents, solutes FAEE become unevenly distributed between the two solvent phases and this is the basis for the solvent extraction technique.

4.3 *Summary*

The result from the experiment has given an understanding about extraction kinetics of FAEE from reactive region by using aqueous ethanol and solubility mechanism characteristic. Extraction can only be sustained if the medium consistently appears as two-immiscible liquid and the solute is more soluble in the solvent. When the two solutions that containing extractable species which is FAEE in cooking oil and extracting reagents which is ethanol vigorously stirred, there was a reaction occur and the existence of two stagnant thin layers of finite thickness located on the aqueous and organic side of the interface. Extraction kinetics was controlled by diffusion of FAEE occurring in proximity to the interface

5 CONCLUSION

5.0 *Conclusions*

Based on my experiment, it can be concluded that the kinetic of solvent extraction was controlled by the rate of diffusion of extractable species which is FAEE that occurring in proximity to the interphase of oil and aqueous ethanol layer. In addition, the FAEE that has to be transported to or away from the interface for the extraction reaction to take place always have to diffuse through the diffusion films. The kinetic data of the experiment refer to a reaction rate that affected by the stirrer variables. From the experiment, the higher the stirring time, the higher the settling time for all molar ratio of oil:ethanol. I can concluded that the thickness of the diffusion film was depends on the stirring rate of the two immiscible oil and aqueous ethanol phase. The thickness of diffusion film was increases with increase in the rate of stirring. It will lead to the increasing time for FAEE diffuse through the diffusion film of stagnant layer resulted with increasing settling time. As a conclusion, diffusion through these diffusion films controls the overall kinetics of extraction. Experience has shown that film diffusion is the predominating rate-controlling factor in many practical extraction processes. Besides that, it can be concluded form the experiment that the distribution coefficient of FAEE was higher in aqueous ethanol phase compared to oil phase for molar ratio oil:ethanol 1:3. This distribution of solute FAEE depends on its preference on aqueous ethanol phase. By comparison, the most efficient oil: ethanol molar ratio was 1:3 compared to two other oil:ethanol molar ratio which is 1:1 and 3:1 because the solute FAEE was successfully extracted from oil phase region to the aqueous ethanol phase region for all stirred time range. This result shows that an excess of ethanol was required to favour the direct reaction leading to an increased conversion by taking into account the reversibility of the extraction. The potential application of this study is to determine the integration possibilities for production of biodiesel using cooking oil as alternatives feedstock to reduce production cost using extractive reactor by using aqueous ethanol as a solvent in liquid-liquid extraction

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7 APPENDICES

Data for calibration curve: ethyl oleate

concentration (ppm)	area (pA*s)
3,000	2795.33716
1,500	1294.20532
1,000	1124.69177
500	588.83478
200	266.27536

Graph of area against concentrations of ethyl oletae

$y = 0.8808x + 121.66$
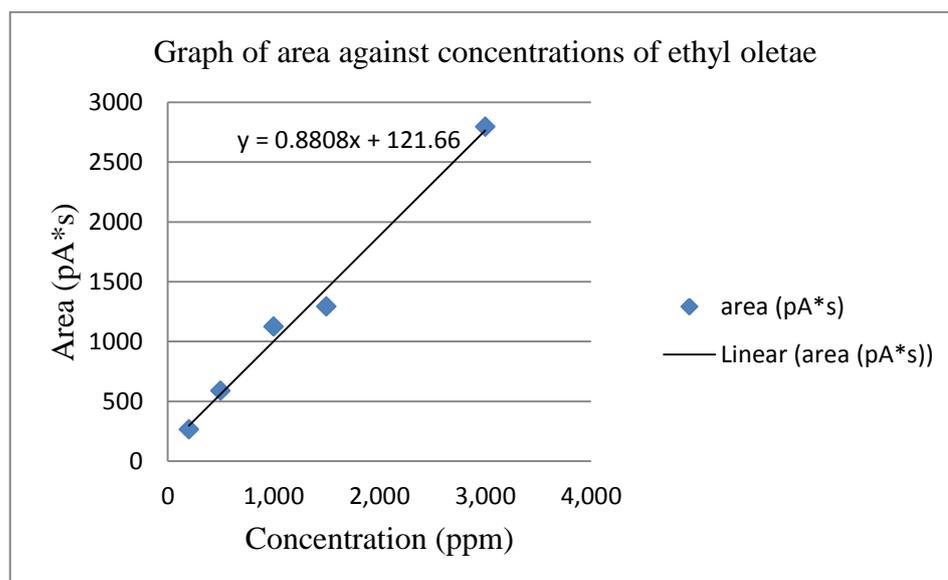
Gas chromatography results for molar ratio oil: ethanol of 1:1

Vial	Retentation time(min)	area (pA*s)	M1 (ppm)(from calibration curve)	M2 (ppm)
1min(B)	7.851	961.2356	953.1966394	47659.83197
1min(T)	7.93	932.8928	921.0181653	46050.90827
5min(B)	0.085	651.1163	601.1084242	30055.42121
5min(T)	8.109	1210.036	1235.667575	61783.37875
10min(B)	8.049	567.3205	505.9724114	25298.62057
10min(T)	8.062	920.7484	907.2302452	45361.51226
15min(B)	8.071	974.7271	968.5139646	48425.69823
15min(T)	0.079	924.7255	911.7455722	45587.27861
20min(B)	8.005	802.5505	773.0364441	38651.82221
20min(T)	7.996	738.5496	700.3742053	35018.71026

$M1V1 = M2V2$

$M1=GC$ $V1=1000ul$
$M2= X$ $V2=20ul$

stirred time (min)	Conc FAEE at upper layer	Conc FAEE at bottom layer
1	46050.90827	47659.83197
5	61783.37875	30055.42121
10	45361.51226	25298.62057
15	45587.27861	48425.69823
20	35018.71026	38651.82221

Graph of concentration of FAEE against stirred time
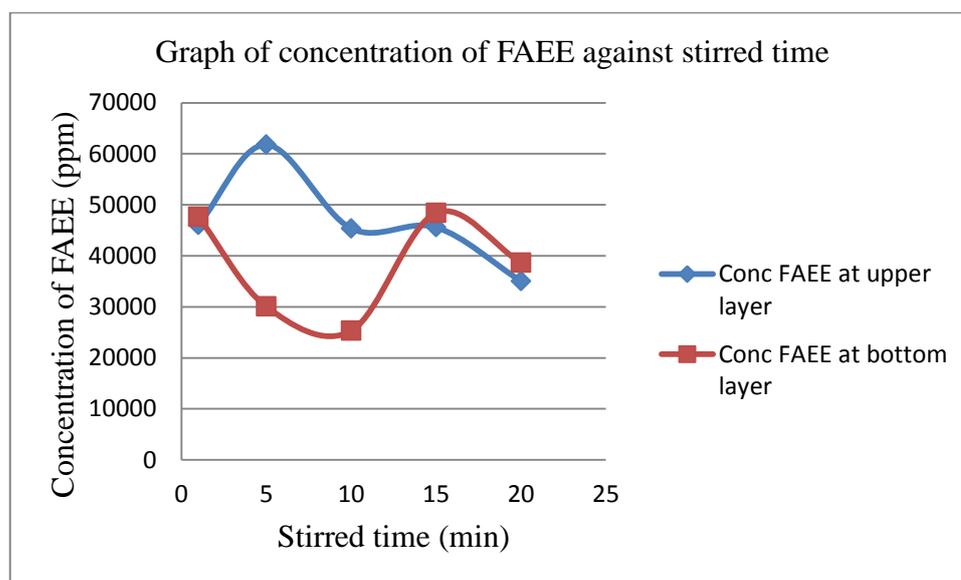
Gas chromatography results for molar ratio oil: ethanol of 3:1

Vial	Retentation time(min)	area (pA*s)	M1 (ppm)(from calibration curve)	M2 (ppm)
1min(B)	7.888	129.6656	9.089009991	454.4504995
1min(T)	7.897	168.7452	53.45731153	2672.865577
5min(B)	8.014	717.883	676.9107629	33845.53815
5min(T)	8.012	830.7733	805.0786785	40253.93392
10min(B)	8.03	901.4427	885.3118756	44265.59378
10min(T)	8.027	927.9476	915.4037239	45770.18619
15min(B)	7.96	930.5573	918.3665985	45918.32993
15min(T)	7.962	763.9344	729.1943688	36459.71844
20min(B)	7.953	913.8326	899.3785195	44968.92598
20min(T)	7.945	777.1319	744.1779064	37208.89532

M1V1 = M2V2

M1=GC   V1=1000ul
M2= X   V2=20ul

stirred time (min)	Conc FAEE at upper layer	Conc FAEE at bottom layer
1	2672.865577	454.4504995
5	40253.93392	33845.53815
10	45770.18619	44265.59378
15	36459.71844	45918.32993
20	37208.89532	44968.92598
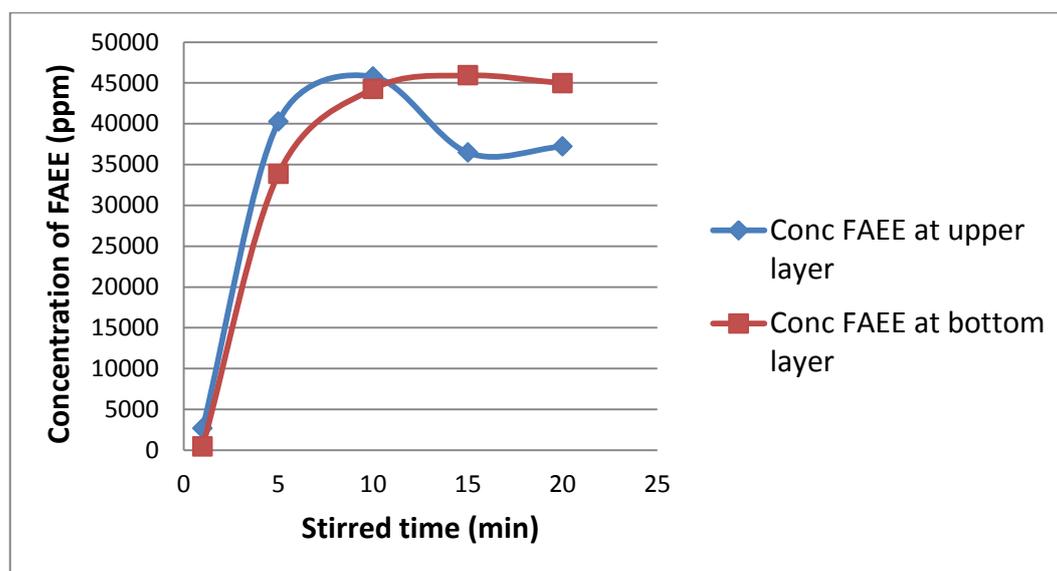
Gas chromatography results for molar ratio oil: ethanol of 1:3

Vial	Retentation time(min)	area (pA*s)	M1 (ppm)(from calibration curve)	M2 (ppm)
1min(B)	8.044	1040.7778	1043.503406	52175.1703
1min(T)	8.054	1230.415	1258.804496	62940.2248
5min(B)	8.028	892.389	875.0329246	43751.64623
5min(T)	8.04	1300.9908	1338.931426	66946.5713
10min(B)	7.964	456.3747	380.012148	19000.6074
10min(T)	7.972	505.3594	435.6260218	21781.30109
15min(B)	7.979	570.1484	509.1830154	25459.15077
15min(T)	7.991	883.6155	865.0720936	43253.60468
20min(B)	7.93	634.6193	582.3788601	29118.94301
20min(T)	7.936	657.353	608.1891462	30409.45731

M1V1 = M2V2

M1=GC   V1=1000ul
M2= X   V2=20ul

stirred time (min)	Conc FAEE at upper layer	Conc FAEE at bottom layer
1	62940.2248	52175.1703
5	66946.5713	43751.64623
10	21781.30109	19000.6074
15	43253.60468	25459.15077
20	30409.45731	29118.94301

Graph of concentration of FAEE against stirred time