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PRODUCTION OF BIODIESEL FROM PALM OIL IN SUPERCRITICAL METHANOL

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งานวิจัยนี้ศึกษาการผลิตไบโอดีเซลจากน้ำมันปาล์มด้วยปฏิกิริยาทรานสเอสเทอริฟิเคชั่นที่สภาวะเมทานอลเหนือวิกฤติ เริ่มโดยทดลองการเกิดปฏิกิริยาในถังปฏิกรณ์แบบกะที่สภาวะต่างๆ คือในช่วงอุณหภูมิของปฏิกิริยา 250-300 องศาเซลเซียส และสัดส่วนโดยโมลของเมทานอลต่อน้ำมันปาล์มในช่วง 6:1-45:1 เวลาที่ใช้ในการทำปฏิกิริยาอยู่ในช่วง 10-240 นาที จากผลการทดลองแสดงให้เห็นว่าเปอร์เซ็นต์ของเมทิลเอสเทอร์เพิ่มขึ้น เมื่ออุณหภูมิ อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันปาล์มและเวลาที่ใช้ในการทำปฏิกิริยาเพิ่มขึ้น และพบว่าสภาวะที่ดีที่สุดที่ใช้ในการทำปฏิกิริยาผลิตเมทิลเอสเทอร์คือ ที่อุณหภูมิ 300 องศาเซลเซียส และอัตราส่วนโดยโมลของเมทานอลต่อน้ำมันปาล์มที่ 45:1 โดยเปอร์เซ็นต์เมทิลเอสเทอร์ที่ได้ที่สภาวะนี้ มีค่าเท่ากับ 85 เปอร์เซ็นต์ หลังจากใช้เวลาในการทำปฏิกิริยา 80 นาที จากการศึกษาจลนพลศาสตร์ พบว่าลักษณะของปฏิกิริยาทรานสเอสเทอริฟิเคชั่นเป็นปฏิกิริยาอันดับหนึ่ง และมีค่าพลังงานกระตุ้นของปฏิกิริยา เท่ากับ 86 กิโลจูลต่อโมล กรณีการศึกษาผลของตัวทำละลายร่วม (ทูโลอีน เบนซีน และ เฮกเซน) ที่เติมลงไปในปฏิกิริยา เพื่อเพิ่มผลได้ของไบโอดีเซล จากผลการทดลองพบว่า เมื่อเติมทูโลอีนและเบนซีนเข้าไปในปฏิกิริยา จะช่วยเพิ่มผลได้ของไบโอดีเซลที่ผลิตได้เมื่อเทียบกับปฏิกิริยาที่ไม่เติมตัวทำละลายดังกล่าว ส่วนในกรณีของเฮกเซนกลับทำให้ได้ผลได้ไบโอดีเซลลดลงในเกือบทุกสภาวะที่ทำการทดลอง นอกจากนี้ยังมีการการศึกษาการเกิดปฏิกิริยาทรานส์เอสเตอริฟิเคชั่นในกระบวนการแบบต่อเนื่องของน้ำมันปาล์มกับเมทานอลและตัวทำละลายเบนซีนและทูโลอีน ที่อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันปาล์มที่ 25:1 โดยเติมตัวทำละลาย 50% โดยปริมาตรของน้ำมัน พบว่าเวลาของปฏิริยามีผลต่อผลได้ของไบโอดีเซล และจากการทดลองนี้ สรุปได้ว่า ระบบของปฏิกิริยาเมื่อได้รับการปรับปรุงแล้วทั้งแบบกะและแบบต่อเนื่องจะมีศักยภาพ และสามารถใช้ในการผลิตไบโอดีเซลจากกระบวนการทรานส์เอสเทอริฟิเคชั่นของน้ำมันปาล์มในเมททานอลวิกฤตยวดยิ่ง

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This study examines non-catalytic transesterification of palm oil in supercritical methanol. First, the reaction was carried out in a batch reactor at various temperatures between 250–300 °C, the molar ratio of methanol to palm oil in range 6:1-45:1, and the reaction time between 10-230 min. The results demonstrated that the percent of methyl ester increased with increasing reaction temperature, molar ratio of methanol to palm oil, and reaction time. It was found that the best condition to produce methyl ester was at 300 °C and molar ratio of methanol to palm oil of 45:1. At this condition the percentage of methyl ester produced was 85 %, after 80 min reaction time. The first order kinetic was found to give suitable description of the reaction rate, and the activation energy of palm oil was estimated to be 86 kJ/mol. In addition, in this study, the effect of co-solvents (toluene, benzene and hexane) was examined and the results indicated that toluene and benzene could potentially be used as co-solvents in the reaction system, as they enhanced the production of biodiesel compared with the reaction without co-solvents. On the other hand, hexane was found to decrease the production yield for most of the conditions tested. Lastly, the continuous biodiesel production in a tubular flow reactor was evaluated at 300 °C, with toluene and benzene used as co-solvents. In this experiment, the percent by volume of solvent to oil was 50% and the molar ratio of methanol to oil was 25:1. It was found that the increase in space time increased the yield of methyl ester. Based on the results of this study, it can be concluded that both batch and continuous systems have high potential for non-catalytic biodiesel transesterification in supercritical methanol.

Department……Chemical Engineering……Student's Signature..ณรุพล จอมทิบ.......
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CHAPTER I

INTRODUCTION

1.1 Motivation

As the demand of diesel fuel is increasing while fossil fuel is becoming limited, research is underway to search for alternative source of energy. Vegetable oil is an interesting renewable resource for this purpose and there have been a number of reports concerning the production of triglyceride based diesel. Studies have also shown that these oils cause fewer environmental concerns compared with petroleum diesel which is believed to intensify local air pollution and magnify the global warming problems (Shay, 1993). There had been attempts to use vegetable oils directly in diesel engine, however due to high viscosity of vegetable oil, low cetane number, oil deterioration, and incomplete combustion (Peterson et al., 1983), direct use is proven to be impractical. Modification of oil properties by physical or chemical means could be performed to obtain more favorable triglyceride based fuel. Dilution of vegetable oil with petroleum diesel or organic solvent is one approach but severe coking and sticking of injection valves have been a major problem with these modified oils. Microemulsion of vegetable oil with use of solvent such as methanol, ethanol and 1-butanol is another approach for physical modification. Although the technique resulted in oil with more favorable properties, these oils are not recommended for long term use due to fuels formulated as microemulsions have low cetane numbers and low heating values as compared to No. 2 diesel fuel (Bagby, 1987). Attempts have been made to chemically modify vegetable oil by means of pyrolysis. This is a thermal decomposition of oil in air free environment. Schwab et al. (1988) characterized the predominant thermal decomposition products of soybean and high oleic safflower oil and evaluated their potential usage as alternative diesel fuels. Their results showed that 75 % of the products obtained were alkanes, alkenes, aromatics, and carboxylic acids with carbon number ranging from 4 to more than 20. The pyrolsates had lower viscosities and higher cetane number than vegetable oils. This process requires high temperature and the decomposition of vegetable oils was found to increase with increasing temperature.

Alternatively, biodiesel could be produced successfully by transesterification, a reaction that convert vegetable oil into alcohol esters of fatty acids (biodiesel) and glycerol by product. Freedman et al. (1984) studied the variables that affect yield and purity of alcohol ester product from crude and refined vegetable oil via a process called transesterification. These are such as molar ratio of methanol and oil, type of catalyst, and temperature. Their results showed that alkaline catalyzed reaction of fully refined oil at 60 ^{o}C or higher, with the molar ratio of 6:1 could be complete within 1 hr, whereas at 32 ^{o}C, 99% transesterification of vegetable oil was obtained in 4 hr. The reason for low reaction rate at low temperature was that the miscibility of methanol and oil was low. This could be improved by the addition of a co-solvent such as toluene or benzene (Krisnangkura and Simamaharnnop, 1992). Although the reaction time could be rather short at appropriate reaction conditions, or with use of organic solvent, the alkali catalyst can react with free fatty acid in vegetable to form soap which makes it difficult to separate glycerol from methyl ester. For the vegetable oil with high free fatty acid, the use of acid catalyst is more suitable. However, the transesterification with acid catalysis was much slower than that with alkali catalysis (Srivastava and Prasad, 2000, Canakci and Van Gerpen, 1999). In addition to high temperature and long reaction time required with acid catalyzed transesterification, water present in the reaction mixture, particularly in used oil whose water content is high, could be problematic because acid tends to bind with water causing deactivation of acid catalyst. Furthermore, like alkali catalyzed process, washing and neutralizing the reaction products with large amount of water is required. This leads to generation of large volume of wastewater. Enzyme catalyzed process could be used, however the cost of enzyme makes the process less practical in industrial scale.

Alternatively, transesterification of triglycerides in subcritical and supercritical alcohol has been investigated, and has been shown to be a fast and environmentally friendly method for production of biodiesel. Soybean oil (Weiliang et al., 2005), rapeseed oil (Saka et al. 2001 a), and sunflower oil (Madras et al., 2004) have been reported as the starting materials for this reaction. Moreover, the kinetic of such catalyst-free transesterification of rapeseed oil (Saka et al. 2001 b) and soybean oil (Diasakou et al., 1998) in subcritical and supercritical methanol has been investigated. This non-catalytic process is known to require shorter reaction time and simpler purification procedure. Saka and Kusdiana, (2001 a) studied the transesterification reaction of rapeseed oil in supercritical methanol in the bath-type reaction vessel. At 350^{o}C with a molar ratio of 1:42 of the rapeseed oil to methanol without using any catalyst gave 95% conversion to methyl esters after 240 s. In addition, unlike alkali or acid catalyzed reactions, the presence of free fatty acid and water does not affect transesterification in supercritical methanol (Saka et al., 2004 b). The finding demonstrated that, by this approach, crude vegetable oil as well as its wastes oil could be readily used for biodiesel fuel production in a simple preparation. Nevertheless, this process requires high temperature and pressure to reach the supercritical state. To solve this problem, Zhang et al., (2004) investigated the transesterification reaction of soy bean oil in supercritical condition with use of propane as a co-solvent. They reported that the reaction rate constant for transesterification increased markedly due to the presence of propane which may cause a single phase in the reaction system and found that reduction in operating temperature, pressure and molar ratio of alcohol to vegetable oil were achieved. The optimal temperatures, molar ratio of methanol to oil and of propane to methanol were reported to be 280 ^{o}C, 24:1, and 0.05, respectively. In addition to propane, supercritical carbon dioxide was also tested as a potential co-solvent (Weiliang et al., 2005). The results showed that the optimal reaction condition was at 280^{o}C, methanol to oil ratio of 24:1, and CO_2 to methanol ratio of 0.1:1. At this condition, a 98% yield of methyl esters was observed in 10 min at reaction pressure of 14.3 MPa.

Due to huge supply of palm trees in Thailand, we aim to investigate transesterification of palm oil with supercritical alcohol. Preliminary study was also conducted in our laboratory for transesterification of palm oil with supercritical methanol in a batch type reactor. A results show that the reaction rate was lower than that reported in the study by Saka et al. (2001 a,b) for esterificatin of rapeseed oil in supercritical methanol. The type and thickness of the reactor and heat transfer, (mixing of reaction mixture) could have significant effects on thee results. Furthermore, the different composition of fatty acid profile in different oils (Anjana Srivastava et al., 2000) could be another reason attributed to the difference in the reaction rate. Saka et al. (2004 a) investigated the effect of transesterification of triglycerides and esterification of different major fatty acids present in rapeseed oil at reaction temperature 300^{o}C in types of alcohol as the reactant such as methanol, ethanol, 1-propanol, 1-butanol or 1-octanol. The result turned out that transesterification of triglycerides (rapeseed oil) was slower than alkyl esterification of fatty acids for any of the alcohols employed. Furthermore, saturated fatty acids such as palmitic and stearic acids had slightly lower reactivity than that of the unsaturated fatty acids; oleic, linoleic and linolenic. Also, Kusdiana and Saka (2001 c) studied methyl esterification reaction of fatty acids in rapeseed oil in supercritical methanol and showed that complete conversion for saturated fatty acid to methyl ester at temperature above 400 ^{o}C whereas for unsaturated fatty acids, low temperature of 350 ^{o}C is appropriate and high temperature resulted in a degradation for the products. From these results, it can be concluded that unsaturated fatty acids could be converted to esters at lower temperatures than the saturated fatty acids.

Unlike rapeseed or soybean oil, palm oil is contains high amount of palmitic acid which is saturated acid, thus the reaction temperature required for transesterification would be higher. Nevertheless it also has a considerable amount of oleic acid which is unsaturated acid, which converts to esters at lower temperature and may even degrade at high temperature. Thus the production of the methyl esters from palm oil requires an optimal temperature. In this study, we propose to determine the kinetics of transesterification of palm oil in supercritical methanol at various temperatures in a batch type reactor. In addition, we attempt to investigate the possibility to bring down the reaction temperature of palm oil transesterification by use of various co-solvents, in which the effect of type and concentration of co-solvent will be determined. Furthermore, transesterification will be carried out in a tubular flow reactor to investigate the effect of residence time on the yield of biodiesel produced in supercritical conditions for further design of the continuous process.

1.2 Objectives

1. To investigate the kinetics of transesterification reaction of palm oil in supercritical methanol in a batch reactor.
2. To determine the effect of co-solvents on the production of biodiesel from palm oil via transesterification in supercritical methanol in a batch reactor.
3. To determine, under selected conditions, the effect of residence time on the yield of biodiesel produced from palm oil in a tubular flow reactor.

1.3 Working Scope

1. Determine the effect of reaction temperatures (250-300 ^{o}C) and molar ratio of methanol to palm oil (6:1-45:1) for the production of biodiesel from palm oil in supercritical methanol in a batch type reactor and propose a kinetic model for this reaction.
2. Determine the effect of type (toluene, benzene and hexane) and concentration (0-50 % v/v) of co-solvents on the yield of biodiesel produced in supercritical methanol.
3. Determine the effect of residence time (5-25 min) on the production yield of biodiesel in a plug flow reactor under selected conditions.

1.4 Expected benefits

1. This investigation provides the suitable condition for production of biodiesel in supercritical methanol from palm oil produced domestically.
2. This investigation provides useful information such as kinetics model and effect of residence time on production yield, which is useful for scale-up of biodiesel production process.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Petroleum based diesel fuel

Diesel fuel, like gasoline is a complex mixture of normal, branched, and cyclic alkanes aromatic compounds, and small amounts of alkenes obtained from the middle-distillate, gas-oil fraction during petroleum separation. There are two grade of diesel fuel used: 1-D and 2-D. Number 1 diesel is more volatile, and therefore is more suitable for use in automobiles, while number 2 diesel fuel has a lower volatility and is blended for higher loads and steady speeds, thus works best in large trucks. Nowadays, the source of fossil oil for production of petroleum oil is limited making the price of crude oil and petroleum oil increase. Diesel fuels also cause a great deal of environmental problem due to emissions of gaseous toxic chemicals, thus an alternative renewable energy is being considered. Triglyceride based fuel is an example of this.

2.2 Triglyceride based diesel fuel

Although triglyceride from vegetable oils is becoming important for the development of renewable resource, the properties of vegetable oils are quite different from diesel fuel as shown in Table 2.1. Thus, the direct use of vegetable oil as diesel fuel in diesel engine is uncommon and would cause a great deal of engine problems.

Table 2.1 The properties of vegetable oils

Vegetable oil	Kinematic viscosity at 38 ^oC (mm^2/s)	Heating value MJ/kg	Density (kg/l)	Flash point (^oC)	Cloud point (^oC)	Pour point (^oC)	Cetane No. (^oC)
[1]Soybean	32.6	39.6	0.9138	254	-3.9	-12.2	37.9
[1]Palm	39.6	-	0.9180	267	31.0	-	42.0
[1]Cottonseed	33.5	39.5	0.9148	234	1.7	-15.0	41.8
[1]Rapeseed	37.0	39.7	0.9115	246	-3.9	-31.7	37.6
[1]Safflower	31.3	39.5	0.9144	260	18.3	-6.7	41.3

Vegetable oil	Kinematic viscosity at 38 ^{o}C (mm^2/s)	Heating value MJ/kg	Density (kg/l)	Flash point (^{o}C)	Cloud point (^{o}C)	Pour point (^{o}C)	Cetane No. (^{o}C)
[1]Sunflower	33.9	39.6	0.9161	274	7.2	-15.0	37.1
[1]Sesame	35.5	39.3	0.9133	260	-3.9	-9.4	40.2
[2]Diesel	3.06	43.8	0.855	76	-	-16	50

Source: [1]Srivastava et al., 2000, [2]Barnwal et al., 2005

The high viscosity of vegetable oils interferes with the injection process and resulted in poor fuel atomization. Furthermore, mixing of vegetable oil with air contributes to incomplete combustion. The high flash point means the lower volatility characteristics, which leads to deposit formation, carbonization of injector tips, ring sticking and lubricating oil dilution and degradation. Oxidative and thermal polymerization of vegetable oils causes a deposition on the injectors forming a film that will continue to trap fuel and interfere with combustion. Therefore, vegetable oils need to be modified to obtain the properties and performance that are closer to those of the diesel fuels. This can be done by physical or chemical means. The physical means includes dilution and microemulstion of vegetable oil, while chemical means include pyrolysis and transesterification of vegetable oil.

2.2.1 Dilution

To improve the properties of vegetable oils, they can be blended with petroleum diesel in any proportion. The dilution of vegetable oils, such as sunflower oil with diesel fuel (1/3 v/v), provided a fuel with a viscosity of 4.47 mPa s at 40°C (Bagby, 1987). Although this viscosity value was greater than the maximum ASTM specification of 3.66 mPa s, it was markedly less than that of neat sunflower oil (31 mPa s). However, Ziejewski et al. (1984) concluded that the blend could not be recommended for long term use in the direct injection diesel engine because of severe injector nozzle coking and sticking. A comparable blend with high-oleic safflower oil replacing the sunflower oil passed the 200-h Engine Manufacturers Association (EMA) test (Ziejewski et al., 1984). A 1:1 blend of soybean oil and stoddard solvent (48% paraffins and 52% naphthenes) also passed the 200-h EMA test in their study. However, this fuel produced heavy carbon deposits on the tulips of the intake valves and showed considerable top-ring wear (Goering, 1984).

2.2.2 Microemulsification

The formation of microemulsions from vegetable oils is one of the solutions to solve the problem with high viscosity. Microemulsions are defined as transparent, thermodynamically stable colloidal dispersions in which the diameter of the dispersed-phase particles ranges from 1-150 nm. Microemulsion-based fuels can be made of vegetable oils and dispersant (solvent) such as methanol, ethanol and 1-butanol, or of vegetable oils, an alcohol and a surfactant, with or without diesel fuels and are classified as non-ionic or ionic, depending on the surfactant present.

Ziejewski et al. (1984) prepared an emulsion of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) 190-proof ethanol and 33.4% (vol) 1-butanol. This nonionic emulsion had a viscosity of 6.31 cSt at 40°C, a cetane number of 25 and an ash content of less than 0.01%. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol. However, fuels formulated as microemulsions have low cetane numbers and low heating values as compared to No. 2 diesel fuel (Bagby, 1987).

2.2.3 Pyrolysis

Pyrolysis (or thermal cracking) can be used to make triglyceride based biodiesel. Pyrolysis is the thermal degradation of vegetable oils by heat in the absence of oxygen, which results in the production of alkanes, alkenes, alkadienes, carboxylic acids, aromatics and small amounts of gaseous products (Schwab et al. 1988). The starting material can be vegetable oils, animal fats, fatty acids and methyl esters of fatty acids. The mechanism of pyrolysis of triglycerides for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids is show in Figure 2.1. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism. The formation of homologous series of alkanes and alkenes is described as the generation of the RCOO radical from triglyceride cleavage and subsequent loss of carbon dioxide. The formation of aromatics is supported by the Diels-Alder reaction which is an organic chemical reaction (specifically, is cycloaddition) between a conjugate diene and substituted alkene, commonly termed the dienophile to form a substituted cyclohexane system. Soybean oil could be thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus (Niehaus et al., 1986; Schwab et al., 1988). Schwab et al. (1988) used safflower oil as a high oleic oil control. The total identified hydrocarbons obtained from the distillation of soybean and high oleic safflower oils were 73-77 and 80-88% respectively.

Copra oil and palm oil stearin had also been cracked over a standard petroleum catalyst $SiO_2/Al2O_3$ at 450 °C to produce gases, liquids and solids with lower molecular weight (Pioch et al., 1993). The condensed organic phase was fractionated to produce biogasoline and biodiesel fuels. The chemical compositions (heavy hydrocarbons) of the diesel fractions were similar to fossil fuels. This process use very high temperature consequently, when the temperature increases as the decomposition levels of the vegetable oil increases. Although the pyrolysed vegetable oils possess acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values, however they give unacceptable ash, carbon residue amounts and pour point. Engine testing on pyrolysed oil has been limited to short-term tests.

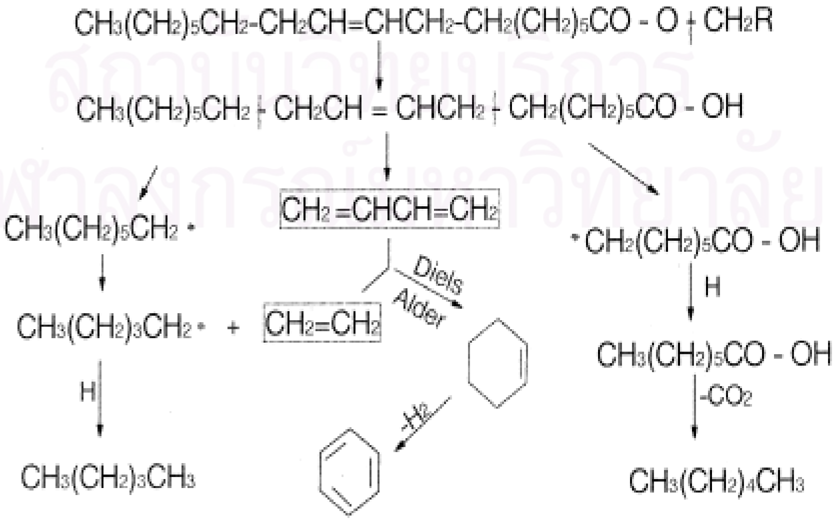


Figure 2.1 The mechanism of pyrolysis of triglycerides (Schwab et al., 1988).

2.2.4 Transesterification

Transesterification (also called alcoholysis) is a reaction of vegetable oils such as soybean oil, sunflower oil, coconut oil, rapeseed oil, palm oil, or animal fat (or known as triglycerides) to produce fatty acid esters biodiesel, and glycerol as a co-product. This reaction takes a long time to complete, and thus generally requires some base or acid catalyst to improve reaction rate and yield. Examples of these catalysts are sodium or potassium hydroxide, or sulfuric acid. General equation of this reaction is shown in Figure 2.2 R_1, R_2, and R_3 of the oil molecules are long chain of hydrocarbon constituting fatty acids which may be the same or different.

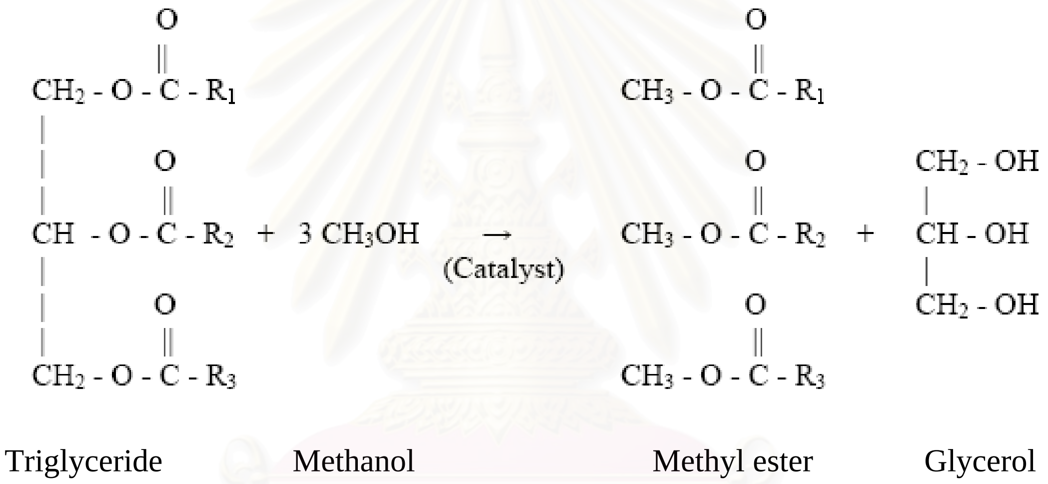


Figure 2.2 Chemical reaction of transesterification

The stoichiometry requires three moles of alcohol and one mole of triglyceride to produce three moles of fatty esters and one mol of glycerol. However, this reaction is reversible, and therefore excess alcohol is used in reaction to shift the equilibrium to the right side (products). Typically, the variables affecting reaction rate and yield include: type and amount of catalyst, type of alcohol, reaction temperature, reaction time, molar ratio of vegetable oil and alcohol, glycerol separation and quality of vegetable oil such as fatty acid composition.

The transesterification reaction shown in Figure 2.2 is indeed the overall reaction for three stepwise reactions with intermediate formation of diglyceride and monoglyceride (Figure 2.3). In the first reaction, triglyceride (TG) react with alcohol to produce diglyceride (DG), then in the second reaction, diglyceride (MG) react with alcohol to form monoglyceride (MG). Finally, in the third reaction, monoglyceride (MG) react with alcohol to give glycerol.

Stepwise Reaction:

1. Triglyceride (TG) + R'OH $\underset{k_4}{\overset{k_1}{\rightleftarrows}}$ Diglyceride (DG) + R'COOR$_1$

2. Diglyceride (DG) + R'OH $\underset{k_5}{\overset{k_2}{\rightleftarrows}}$ Monoglyceride (MG) + R'COOR$_2$

3. Monoglyceride (MG) + R'OH $\underset{k_6}{\overset{k_3}{\rightleftarrows}}$ Glycerol (GL) + R'COOR$_3$

Figure 2.3 The transesterification reactions of vegetable oil with alcohol to esters and glycerol (Freedman et al., 1986).

2.2.4.1 Transesterification reaction with catalyst process

Alkali catalyzed process

All commercial biodiesel production today employs an alkali-catalyzed transesterification process. This process is accomplished by mixing methanol (alcohol) with sodium hydroxide or potassium hydroxide to make sodium methoxide. Then the sodium methoxide is added to vegetable oil in a reactor at molar ratio of oil and alcohol 6:1. The mixture was stirred and heat at 60-63 ^{o}C. After complete reaction mixture is allowed to cool to room temperature, and the ester and glycerol in were separated. Glycerol is left on the bottom and methyl esters, or biodiesel, is left on top. The ratio of 6:1 was found to be the best condition because methanol/oil molar ratio less than 6:1 the reaction resulted in incomplete reaction, and that above 6:1 methanol/oil molar ratio makes the separation of glycerol difficult, since the excess methanol hindered the decantation by gravity so that the apparent yield of esters decreased because part of the glycerol remained in the biodiesel phase (Freedman et al., 1984).

The mechanisms of alkaline catalyzed transesterification are depicted in Figure 2.4. The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride (Fangrui Ma et al., 1999)

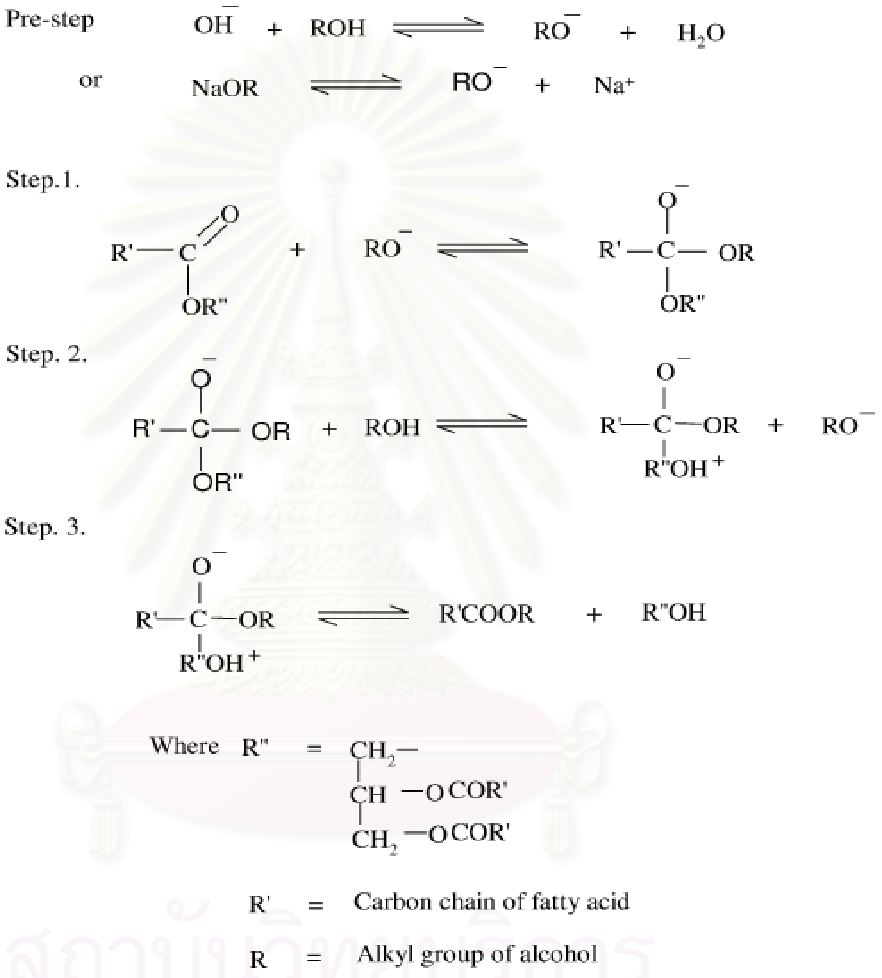
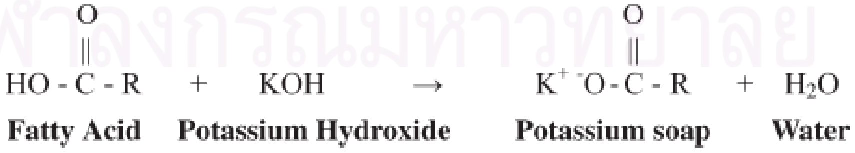


Figure 2.4 Mechanism of base catalyzed transesterification (Meher, 2004).



$$HO-\overset{\overset{O}{\|}}{C}-R + KOH \rightarrow K^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-R + H_2O$$

Figure 2.5 Reaction of fatty acid reacts with base catalyst

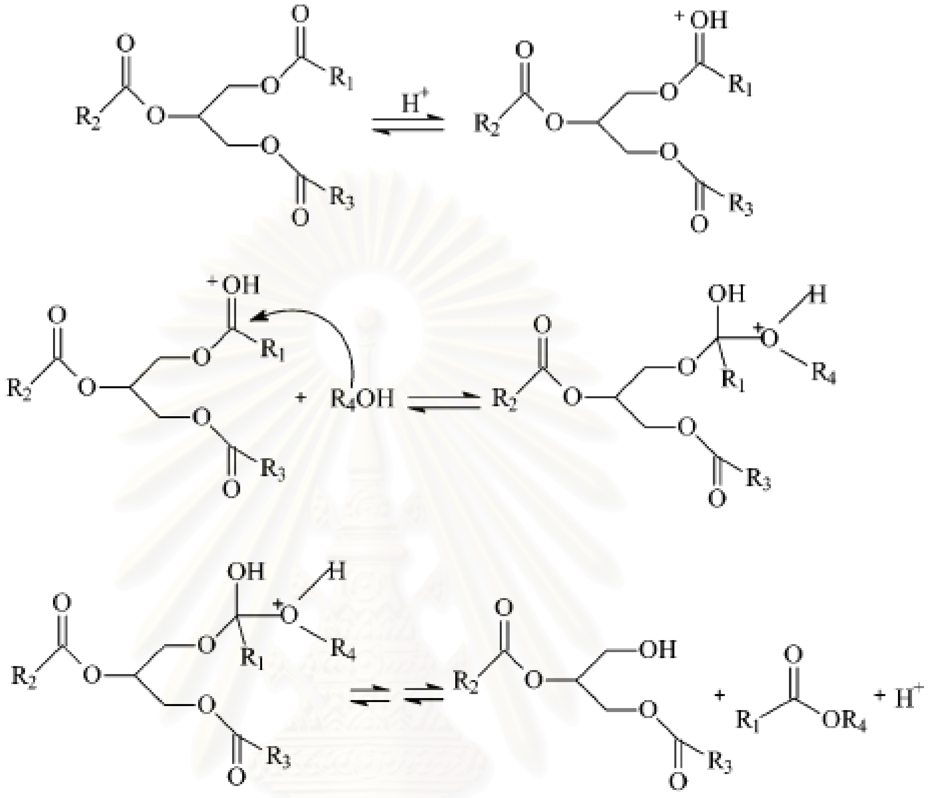
When the vegetable oil contain high free fatty acid (about 5%), alkali-catalyst ineffective because reaction want more alkali-catalyst for neutralization and the excess catalyze can react with free fatty acid to form soap (Figure 2.5). The soap increases the viscosity or formation of gel or emulsion and interfered with separation of ester and glycerol (Freedman et al., 1984). Although the alkali catalyzed process has short reaction time and high conversion, the process has several problems such as difficult recovery of glycerol due to the soap production from free fatty acid and the catalyst. In addition, the alkaline catalyst has to be removed from the product by washing with water, thus alkaline waste water is generated. Thus, for oil with high content of free fatty acids, an acid catalyst, such as sulfuric acid, can be used to esterify the free fatty acids to methyl esters.

Acid catalyzed process

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, if there are large amounts free fatty acids in the starting oil such as in waste oils and fats, this large amount of free fatty acids cannot be effectively converted to biodiesel using alkaline catalyst. Consequently, acid catalyst can be used for transesterification. Thus acid catalyzed process can reduce biodiesel production cost as low cost feedstock (waste frying oil) with high free fatty acid can be used as a raw material.

The mechanism of acid catalysed transesterification of vegetable oil (for a monoglyceride) is shown in Figure 2.6. However, it can be extended to di- and tri-glycerides. The protonation of carbonyl group of the ester leads to the carbonation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst (Lotero et al., 2005).

Although this process can be used with vegetable oils and fats that have more free fatty acids, it requires long reaction time, high temperature (above 100 ^{o}C) and the acid catalyst has to be removed from product. In addition, the presence of water in the vegetable oil has negative effect on the yield methyl ester. With the acid catalyzed process, water has more negative effect on methyl ester formation than the alkali catalyzed process. Because the presence of polar compounds during acid catalyzed transesterification significantly reduce reaction rates. Considering the strong affinity acid has for water, it is likely that the acid will interact more strongly with water molecules than alcohol molecules. Thus, if water is present in the reactant or during the reaction, the acid catalyst will bind to the water, leading to a reversible type of catalyst deactivation.



R$_1$, R2, R3: carbon chain of the fatty acids

R$_4$: alkyl group of the alcohol

Figure 2.6 Mechanism of acid catalyzed transesterification (Lotero et al., 2005).

For base or acid catalyzed processes, the most commonly used primary alcohol used in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. Furthermore, in these processes, neutralizers are generally used to remove the base or acid catalysts from the product biodiesel and glycerol. If a base catalyst is used, the neutralizer is typically an acid which can be added to the wash water. For example hydrochloric acid is a common choice to neutralize base catalysts. As many processes such as neutralization, washing and drying process are required in the acid or alkali processes, production is complicated and requires a long time, thus an alternative process such as enzymatic transesterification is considered.

Enzymatic transesterification

Enzymatic transesterification of triglycerides has been suggested as a realistic alternative to the conventional physiochemical methods. Lipase is an effective enzyme for the transesterification of triglyceride. It is generally effective biocatalyst due to its substrate specificity, functional group specificity and stereo specificity in aqueous media. Lipases enzyme, present in living organisms, hydrolyse triacylglycerols. This ability has been used until now for the synthesis of many compounds in very mild conditions. Through the use of these enzymes in water media, esterification and transesterification reactions can also be carried out. The major problem with this process however is the enzyme stability and recovery. Therefore, immobilization is the most widely used method for achieving favorable stability of lipases and to make them more attractive for reaction (Cowan, 1996; Clark, 1994). Moreover immobilization provides enzyme reuse and eliminates the costly processes of enzyme recovery and enzymes recycle. The reaction generally requires the following conditions: 30% enzyme based on oil weight; oil/alcohol molar ratio of 1:4; the temperature of 50 ^{o}C; and the reaction time of 7 h (Oznur Kose et al., 2002). In transesterification of rapeseed oil with 2-ethyl-1-hexanol and using *Candida rugosa* lipase powder gave 97 % conversions of ester (Linko et al., 1998). The addition of methanol into the reaction to avoid lipase inactivation converted 98.4% of the oil to methyl esters at 30 ^{o}C after 48 h (Shimada et al., 1999). In this method, the recovery of glycerol is easy without any complex process and free fatty acid contain in waste oil or fat can be completely converted to methyl ester. On the other hand, the production of biodiesel fuel by enzymatic method has not often been used in industry because of the high cost of enzyme catalyst. An alternative process such as non-catalyzed transesterification is considered.

2.2.4.2 Biodiesel production in supercritical (Non-Catalysted Systems)

When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. Firstly, there no longer is a distinct liquid and vapor phase, but a single, fluid phase present. Secondly, solvents containing a hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids. For this reason, transesterification in supercritical alcohol can be achieved without use of catalyst for production of biodiesel. With this process, used oil with high amount of free fatty acids can be used as no alkali is used. The only reactions products are the ester or biodiesel (the upper phase) and lower phase is glycerol. No soap is produced, thus the separation process is simple. In addition, alcohol used in biodiesel production such as methyl or ethyl alcohol are polar solvents and have hydrogen bonding between OH oxygen and OH hydrogen to which normally form clusters of these molecules, separating them from other non-polar compounds such as glyceride. However, because the degree of hydrogen bonding decreases with increasing temperature, the polarity of the alcohol would decrease in supercritical state, thus supercritical alcohol has a hydrophobic nature with the lower dielectric constant. As a result, non-polar triglycerides can dissolve in the supercritical alcohol to form a single phase of vegetable oil/methanol mixture (Kusdiana and Saka, 2001). The reaction mechanism of vegetable oil in supercritical methanol is shown in Figure 2.7.

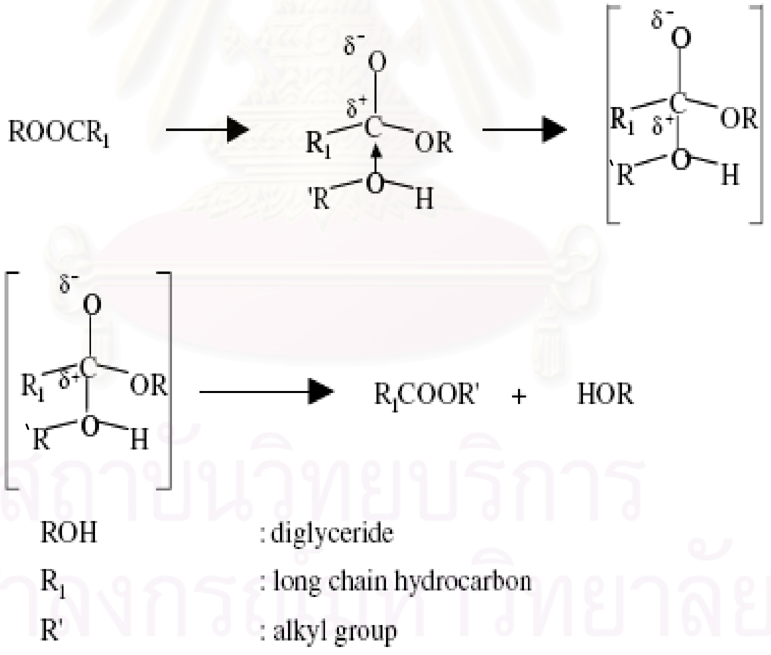


Figure 2.7 A reaction mechanism of transesterification of vegetable oil/triglycerides in supercritical methanol.

The alcohol molecule attacks the carbonyl atom of the triglyceride because of the high pressure. In the supercritical state, depending on pressure and temperature, hydrogen bonding would be significantly decreased, which would allow methanol to be a free monomer. Transesterification is completed via a methoxide transfer, whereby the fatty acid methyl ester and diglyceride are formed.

Saka et al. (2001) studied the transesterification reaction of rapeseed oil in supercritical methanol which was carried out in the bath-type reaction vessel preheated at 350°C and 400°C at a pressure of 45-65 MPa, and with a molar ratio of 1:42 of the rapeseed oil to methanol without using any catalyst. The reaction was found to complete in about 4 minutes and as a higher molar ratio of methanol was applied, the methyl esterified compounds were increased with a decrease in the intermediate compounds. This was due perhaps to the increased contact area between methanol and triglycerides.

2.3 Kinetics of transesterification reaction and Arrhenius energy of activation

There have been a few attempts to develop kinetic models for transesterification of triglycerides in alcohol with and without catalysts (Freedman et al., 1986; Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000); Diasakou et al., 1998); Mohanprasad et al., 2003; and Saka and Kusdiana, 2001 b). In these studies, only forward reaction was considered because excess amount of alcohol was used to drive the reaction forward. In a few studies, kinetics of each of the three steps of transesterification were determined, while in others, simpler mathematical models for the overall reaction was proposed by ignoring the intermediate reactions of diglycerides and monoglycerides. This was found to reasonably describe experimental data investigated by Saka and Kusdiana (2001 b).

$$\text{A} \longrightarrow \text{products} \qquad (1)$$

the first-order rate equation has the following form,

$$-r_A = -\frac{dC_A}{dt} = kC_A \qquad (2)$$

where C_A is the content of triglyceride. Separating and integrating this equation obtains

$$-\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt \qquad (3)$$

or

$$-\ln\frac{C_A}{C_{AO}} = kt \tag{4}$$

In terms of conversion (X_A), the rate equation, Eq. (2), becomes

$$\frac{dX_A}{dt} = k(1-X_A)$$

which on rearranging and integrating give

$$\int_0^{X_A}\frac{dX_A}{1-X_A} = k\int_0^t dt$$

or

$$-\ln(1-X_A) = kt \tag{5}$$

A plot of ln (1-X_A) or ln (C_A/C_{AO}) vs. t, as show in Figure 2.8, gives a straight line through the origin for this form of rate of equation. If the experimental data seem to be fitted by a curve than by straight line, the first-order reaction does not satisfactorily fit the data, another rate law should be attempted.

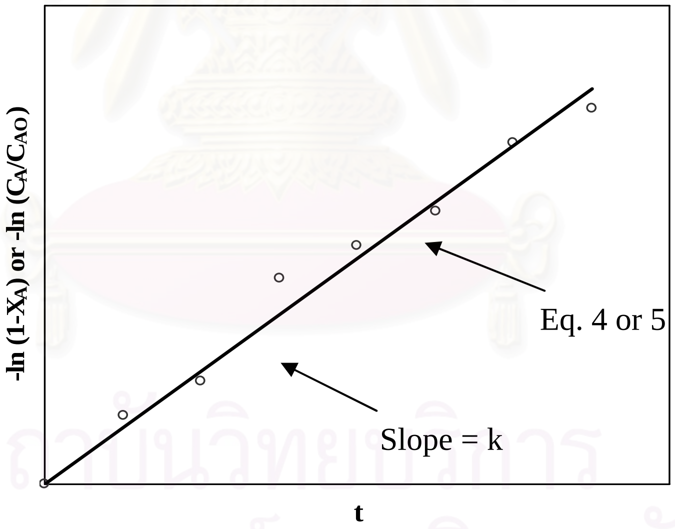


Figure 2.8 Test for the first-order rate equation, Eq. 2.

In addition, the effect of temperature with reaction rate constant can be described by Arrhenius equation.

Arrhenius energy of activation

For many reaction the rate expression can be written as a product of temperature dependent term and a composition dependent term, or

$r_i = f_1(\text{temperature}).f_2(\text{composition})$
$= k.f_2(\text{composition})$

For such reactions the temperature dependent term, the reaction rate constant has been found in practically all cases to be well represent by Arrhenius' law indicates that

$$k = k_o e^{-E_a / RT} \qquad (6)$$

Rearrange the Arrhenius equation

$$\ln k = \ln k_o - \frac{E_a}{RT} \qquad (7)$$

or

$$\log_{10} k = (-E_a / 2.303R)T + C \qquad (8)$$

where k_o is called the frequency or pre-exponential factor (L/(mol-s)), E_a is called the activation energy of the reaction (KJ), R is called Gas constant (kJ/(mol-K)) and T is absolute temperature (K). This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency. From equation (7), a plot of ln k vs. 1/T give a straight line, with a slope equal to E_a. Reactions with high activation energies are very temperature sensitive; reactions with low activation energies are relatively temperature insensitive.

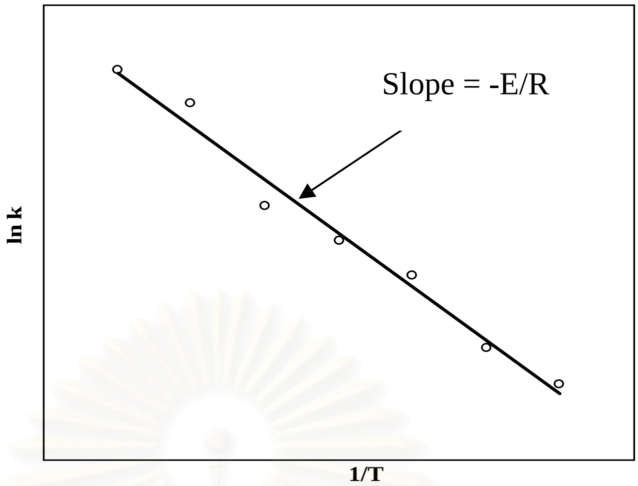


Figure 2.9 Plot of Arrhenius equation

2.4 Literature review

A number of studies on preparation of biodiesel from vegetable oils have been reported using a variety of oils, alcohols, different catalysts, and reaction conditions. Review of previous work on the preparation of biodiesel is summarized in Table 2 and 3. Schwab et al. (1988) characterized the predominant thermal decomposition products of soybean and high oleic safflower oil and evaluated their potential usage as alternative diesel fuels. Their results showed that 75 % of the products obtained were alkanes, alkenes, aromatics, and carboxylic acids with carbon number ranging from 4 to more than 20. The pyrolsates had lower viscosities and higher cetane number than vegetable oils. This process requires high temperature and the decomposition of vegetable oils increases with increasing temperature.

Freedman et al., (1984) studied the variables that affect yield and purity of alcohol ester product from crude and refined vegetable oil. These are such as molar ratio of methanol and oil, type of catalyst, and temperature. Their results showed that alkaline catalyzed reaction of fully refined oil at 60 ^{o}C or higher, with the molar ratio of 6:1 could be complete and the conversion to esters resulted in 1 hr. At 32 ^{o}C, vegetable oil 99% transesterification was obtained in 4 hr with alkali catalyst. The reason for low reaction rate at low temperature was that the miscibility of methanol and oil was low. This could be improved by addition of a solvent. Krisnangkura and Simamaharnnop (1992) studied a continuous transmethylation at 70 ^{o}C in the presence of toluene, a mutual solvent for methanol and palm oil, with sodium methoxide as a catalyst. The optimum ratio of toluene to palm oil was 1:1 (v/v). At molar ratio of methanol to oil of 13:1, transmethylation was 96 % complete within 60 seconds and at the molar ratio of 17:1, transmethylation was 99 % complete in 15 seconds. Beside toluene, benzene was also good solvent for transmethylation, but the yield was slightly lower than toluene. Although the reaction time could be rather short at appropriate reaction conditions, or with use of organic solvent, the alkali catalyst can react with free fatty acid in vegetable oil to form soap which makes it difficult to separate glycerol from methyl ester. For the vegetable oil with high free fatty acid, the use of acid catalyst is more suitable. However, transesterification with acid catalysis was much slower than that with alkali catalysis (Srivastava and Prasad, 2000). Canakci and Van Gerpen (1999) studied the molar ratio of methanol to oil affected reaction rates and product yield in the transmethylation of soybean oil by sulfuric acid. Five different molar ratios, from 3.3:1 to 30:1, were studied. Their results indicated that ester formation increased with increasing molar ratio, reaching its highest value, 98.4%, at the highest molar ratio of used, 30:1 used. Beside oil and methanol molar ratio, the effect of temperatures were determined in the study by Freedman et al. (1986), in which five different temperatures from 77 to 117 °C were examined. At 117 °C, the reaction rate of triglyceride complete required only 3 h, while comparable conversions at 77 °C required 20 h (Freedman et al., 1986). At higher temperatures, the extent of phase separation decreases and rate constants increase, due to increased reaction kinetics as well as improved miscibility, leading to substantially shorter reaction time. In addition, with acid catalyzed transesterification, water present in the oil, particularly in used oil whose water content is high, could be problematic because the alcohol tends to bind with water rather than react with triglycerides. Furthermore, like alkali catalyzed process, washing and neutralizing the reaction products with large amount of water is required. This leads to generation of large volume of wastewater.

Alternatively, non-catalytic transesterification was investigated. Studies in these areas had been related to using rapeseed and soybean oils as starting materials. Saka and Kusdiana, (2001 a) studied the transesterification reaction of rapeseed oil in supercritical methanol in the bath-type reaction vessel. At 350 ^{o}C and a molar ratio of 1:42 of the rapeseed oil to methanol, a non-catalytic transesterification gave a 95%

conversion after 240 s. And unlike alkali or acid catalyzed reactions, the presence of free fatty acid or water does not affect transesterfication in supercritical methanol. The finding demonstrated that, by a supercritical methanol approach, crude vegetable oil as well as its wastes oil could be readily used for biodiesel fuel production in a simple preparation. However, this reaction requires high temperature and pressure to reach the supercritical state. To solve this problem, Weiliang Cao et al. (2005) investigated the transesterification reaction of soy bean oil in supercritical condition with use of propane as a co-solvent. They reported that the reaction rate constant for transesterification increased markedly due to the presence of propane which may cause a single phase in the reaction system. Consequently, reducing in operating temperature, pressure and molar ratio of alcohol to vegetable oil were achieved. The optimal temperatures, molar ratio of methanol to oil and of propane to methanol were reported to be 280 ^{o}C, 24:1, and 0.05, respectively. Moreover, supercritical carbon dioxide was also tested as a potential co-solvent (Hengwen Han et al., 2005). The results showed that for an optimal reaction condition, the temperature of 280 ^{o}C, methanol to oil ratio of 24:1 and CO_2 to methanol ratio of 0.1:1, 98% yield of methyl esters (biodiesel) was observed in 10 min at a reaction pressure of 14.3 MPa.

For design the reactor used to produce biodiesel, study of reaction kinetics is important. A number of studies had been conducted to determine the kinetics of transesterification with and without catalysts. Some studies expressed the evolution of each species in the reaction by kinetic models of three individual steps, while others expressed the overall reaction kinetics. Freedman et al. (1986) investigated the kinetics of the transesterification of soybean oil in butanol with acid and alkali catalysts. They found that when butanol was in excess with the molar ratio of 30:1 butanol:soybean oil, the forward and reverse reactions followed a pseudo-first and second-order kinetics, respectively, for both acidic or alkali catalysts. On the other hand, the kinetics of the reaction of butanol and soybean oil at a 6:1 molar ratio were second order for the forward and reverse reactions. Noureddini and Zhu (1997) investigated the kinetics of the transesterification of soybean oil with methanol using sodium hydroxide as a catalyst. They studied the effect of mixing intensity and temperature on the reaction rates for a 6:1 methanol:soybean oil molar ratio. A reaction mechanism was proposed, consisting of an initial mass transfer-controlled region followed by a second-order kinetically controlled region. On the other hand, the kinetics of the transesterification of palm oil catalyzed by potassium hydroxide has also been reported (Darnoko and Cheryan, 2000). They suggested a pseudo-second-order model for the initial stages of the reaction, followed by first order or zero order.

A number of studies have been conducted on the kinetics of transesterification without catalyst. Diasakou et al. (1998) investigated the kinetics of the non-catalytic thermal transesterification of soybean oil with methanol at 220-235 ^{o}C. They suggested the evolution of concentration of each component in ester phase followed the first order kinetic model derived from the proposed consecutive reaction mechanism. Furthermore, triglyceride and diglyceride conversion rate were much higher than the conversion rate of monoglyceride to glycerol. Mohanprasad et al. (2003) determined the kinetics of noncatalytic transesterification of soybean oil and three different alcohols: methanol, ethanol, and isopropanol (1:6 oil:alcohol molar ratio), for the reaction temperature between 120 and 180 ^{o}C in a glass capillary tube. They suggested that this two phase reaction could be controlled either by diffusion or kinetics. In their work, however, because of the observed relatively slow reaction rate, the reactions were most likely controlled by kinetics, and thus the solubility of methanol in oil, rather than by diffusion. The reaction rate was also found to increase as the reaction proceeded because the ester product helped increase the solubility of methanol in the reaction mixture. Moreover, they found that the reactions followed the first order kinetics and the reactivity was found to be higher in methanol, and then followed by ethanol, and isopropanol. For the kinetic of transesterification reaction of rapeseed oil in supercritical methanol at the temperature between 200^{o}C and 500^{o}C studied by Saka and Kusdiana (2001 b), the first order overall reaction based on triglyceride concentration was found to reasonably their experimental data.

Table 2.2 Review studies production of biodiesel in commercial method.

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (^oC)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
Pedro Felizardo et al.(2005)	waste frying oil , MeOH, NaOH	Conventional (base catalyst)	65	-	3.6 to 5.4	1 hr	-	GC	To describes the optimum conditions for biodiesel production using waste frying oils as raw material in the transesterification process.
Choo Yuen May (2004)	palm oil (crude or refined), MeOH, NaOH, H_2SO_4, Na_2SO_4	Conventional (base and acid catalyst)	30 to 60	-	3:1 to 1:15.6	-	500	GC	To investigate the reaction variables affecting the transesterification such as type of catalyst, oil/alcohol ratio, temperature, stirring speed and FFA content
Cheng Sit Foon et al. (2004)	crude palm oil, MeOH, NaOMe, Na_2SO_4	Conventional (base catalyst)	50 to 70	-	6:1 to 10:1	1 to 25 min	-	GC	1. To optimize the conditions to produce palm oil methyl ester by transesterification of crude palm oil. 2. To study the kinetics of the formation of palm oil methyl ester.

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (^oC)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
Darnoko and Munir Cheryan (2000)	refined, bleached and deodorized palm oil, MeOH, KOH	Conventional (base catalyst)	50 to 65	-	6:1	90 min	1000	GC	To study the kinetics of transesterification of palm oil.
Darnoko and Munir Cheryan (2000)	refined, bleached and deodorized palm oil, MeOH, KOH	Conventional (base catalyst)	60	-	6:1	40 to 70 min	1000	GC	1.To develop a process for the continuous trans-esterification of palm oil. 2. To determine the optimal residence time for maximum production of methyl ester from palm oil.
Freedman et al. (1986)	Refined soybean oil, MeOH, BuOH, $NaOCH_3$, sulfuric acid	Conventional (base and acid catalyst)	20 to 117	-	6:1 and 30:1	60 min	400	TLC and GC	To study the kinetics of transesterification reaction from soybean oil.

Reference	**Material**	**Method**	**Condition**					**Analysis**	**Objective**
			Temp. (^{o}C)	**Pressure**	**Molar ratio (MeOH:Oil)**	**Time**	**Volume reactor (ml)**		
Edward Crabbe et al. (2001)	crude palm oil (CPO), Methanol, hexane, petroleum ether and sulphuric acid	Conventional (acid catalyst)	70, 80, 95	-	40:1	3, 6, 9, 12, 24 hr	250	GC	1. To optimize the parameters that affect transesterification of CPO to its corresponding methyl ester (CPOE). 2. To evaluate its solvent extraction and fuel properties.
Jon Van Gerpen (2004)	soybean oil, used cooking oil, methanol	Conventional	60	-	-	1 hr	-	-	To describe the processing and production of biodiesel.
Ayhan Demirbas (2002)	cottonseed oil, hazelnut kernel oil, poppy seed oil, rapeseed oil,safflower seed oil, sunflower oil	Conventional	67	-	-	2 hr	100	GC	To investigate the variables affecting the methyl ester yield during the transesterification reaction.
		SC-MeOH	177-250		1:1, 3:1, 9:1, 20:1 and 41:1	300 s	100	GC	

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (^{o}C)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
Freedman B. et al. (1984)	Refined vegetable oil (edible grade) and crude oils, NaOH, H_2SO_4, MeOH, EtOH, BuOH	Conventional (base and acid catalyst)	60-63	-	3:1 and 6:1	0.1 to 4 hr	100	TLC	1. To develop basic formation the transesterification reaction of crude and refined oils. 2. To delineate optimum reaction conditions for maximum conversion to fatty ester with alkali and acid catalyst.
B.K. Barnwal et al. (2005)	vegetable oil	-	-	-	-	-	-	-	To review the possibilities of using neat vegetable oils and biodiesel, the processes available, fuel characteristics, performance analysis and economic analysis of biodiesel production.

Table 2.3 Review studies production of biodiesel in supercritical alcohol method.

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (°C)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
Yuichiro Warabi et al. (2004)	rapeseed oil MeOH, EtOH, 1-propanol, 1-butanol or 1-octanol	SC-alcohol	300	-	42:1	4-45 min	5	HPLC	To study the reactivity of transesterification of triglycerides and alkyl esterification of fatty acids in the supercritical alcohol process.
S. Saka and D. Kusdiana (2001 a)	rapeseed oil MeOH	SC-MeOH	400	-	42:1	10-240 s	5	HPLC	1. To study transesterification of rapeseed oils in supercritical methanol. 2. To investigate the possibility of converting the triglycerides of the rapeseed oil to methyl esters as biodiesel fuels.
Saka et al. (2001 b)	rapeseed oil MeOH	SC-MeOH	200°C to 500°C	-	42:1	10-7200 s	5	HPLC	To study kinetics of transesterification of rapeseed oil to biodiesel fuel as treated in supercritical

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (^{o}C)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
									methanol without using any catalyst.
Saka et al. (2004 a)	rapeseed oil, methanol, ethanol, 1-propanol, 1-butanol,1-octanol	SC-MeOH	300	-	42:1	4-45 min	5	HPLC	To study the effect of transesterification of triglycerides and esterification of fatty acids in rapeseed oil by varying types of alcohol as the reactant.
Saka et al. (2004 b)	rapeseed oil, methanol	Subcritical and SC-MeOH	220-250	-	42:1	60-240 s	5	HPLC	To investigate the effect of water on the yield of methyl esters in transesterification of triglycerides and methyl esterification of fatty acids as treated by supercritical methanol

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (°C)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
Giridhar Madras et al. (2004)	sunflower oil, CO_2 , MeOH , EtOH, toluene	Supercritical fluid	200-400	200 bar	40:1	10-40 min	8	GPC, GC	1. To study kinetics of transesterification of sunflower oil to biodiesel fuel in supercritical methanol and ethanol without using any catalyst. 2. To study conversion of enzymatically synthesized biodiesel in supercritical carbon dioxide.
Weiliang Cao et al. (2005)	soybean oil, Methanol	SC-MeOH	200-310	-	-	13-15 min	-	-	To study the transesterification of soybean oil in methanol under supercritical conditions in the presence of propane as co-solvent.

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (^oC)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
Diasakou M. et al. (1998)	soybean oil, MeOH	Subcritical methanol	220 and 235	55 and 62 bar	6:1 to 27:1	-	-	TLC	To investigate the non-catalytic thermal transesterification of soybean oil with methanol, present a kinetic study.
Yuichiro Warabi et al. (2004)	rapeseed oil, methanol, ethanol, 1-propanol, 1-butanol, 1-octanol,	SC-alcohol	300	-	42:1	45 min	5	HPLC	To study the reactivity of transesterification of triglycerides and alkyl esterification of fatty acids in the supercritical alcohol process.
Mohanprasad A. et al (2003)	refined soybean oil, MeOH, EtOH, isopropanol	subcritical alcohol	120 to 180		3:1 to 12:1	4 to 32 hr	0.2	GC and GC-MS	To investigated reaction rate of methanol and reactivity of higher alcohol.

CHAPTER III

MATERIALS AND METHODS

3.1 Chemicals

Palm oil samples used in this study was manufactured by Chumporn Palm Oil Industry Public Company Limited. Methyl ester standard (methyl palmitate, methyl stearate and methyl oleate, and eicosane internal standard) were obtained from Wako Chemicals, USA. Methanol and hexane analytical grade was from Fisher scientific, UK

3.2 Supercritical methanol transesterification reaction

3.2.1 Experiment in batch reactor

A batch type reactor was used for conversion of palm oil and supercritical methanol into biodiesel. A schematic diagram of the reactor and the reaction system employed is shown in Figure 3.1. The 8.8 ml stainless steel reactor (AKICO, Japan) was charged with calculated amounts of liquid methanol and oil with a molar ratio of ranging between 45:1 and 15:1. The reaction vessel was heated with a heater to the desired reaction temperature (200 ^{o}C or 300 ^{o}C), after which the reaction continued for a set time period (from 10 – 60 min). After each reaction, the vessel was removed from the heater and placed into a water bath to stop the reaction. The reaction products were discharged from the reactor and were allowed to settle and separated into three phases. The top phase was unreacted methanol which was removed by evaporation. The remaining phases consisting of the upper phase and the lower phase were methyl ester (biodiesel) and glycerol, respectively. In addition to the investigation of reaction conditions on the palm oil biodiesel production in supercritical methanol, the effect of co-solvents was determined for hexane, toluene, and benzene at different oil to solvent and methanol to oil ratios. The range of percentage of co-solvents added studied were between 10-50 %v/v solvent to oil. The sample calculation for the amount of raw materials charged in the reactor is shown in Appendix B-2.

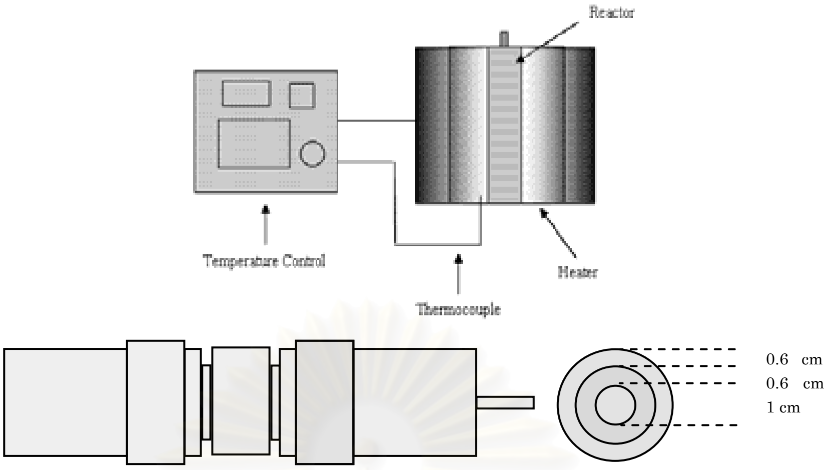


Figure 3.1 Schematic diagram of apparatus for biodiesel production in supercritical methanol.

3.2.2 Experiment in plug flow reactor

The transesterification reaction experiment was conducted in the continuous system shown in Figure 11. This system consists of two HPLC pumps (PU 2080, JASCO, Japan), stainless steel capillary tubing (1/16 inch inside diameter), a tubular flow reactor (3/8 inch inside diameter, 1 mm tube wall thickness, and 65 cm. of length), a back-pressure regulator (AKICO, Japan), heating ban, temperature controller, temperature monitor and a collecting flask. The first pump was used for deliver palm oil and the second pump was used for deliver methanol. Oil and methanol were pumped to the preheating coil before being mixed at a three way connector. The mixture entered the tubular reactor (65 cm of length and 3/8 inch outside diameter) where the reaction took place. The cooling coil at the outlet of the tubular flow reactor was used to cool down the product and stop the reaction. The temperature of reactor and preheat was adjusted by a temperature controller. The pressure of the system was adjusted to the desired condition by using a back-pressure regulator at the outlet pump solvent and cooling coil. Reactions were carried out to determine the effect of residence time on the product yield. The range residence times considered are between 5-25 min. After pressure and temperature were constant, approximately 10 ml of liquid product was collected, the liquid product was checked for percent of methyl esters by gas chromatography to ensure that the system reached steady state, which was indicated by a constant value, and then methanol was removed by evaporation. The sample was collected after the system reached steady state and was then analyzed for the amount of methyl esters produced by a gas chromatography.

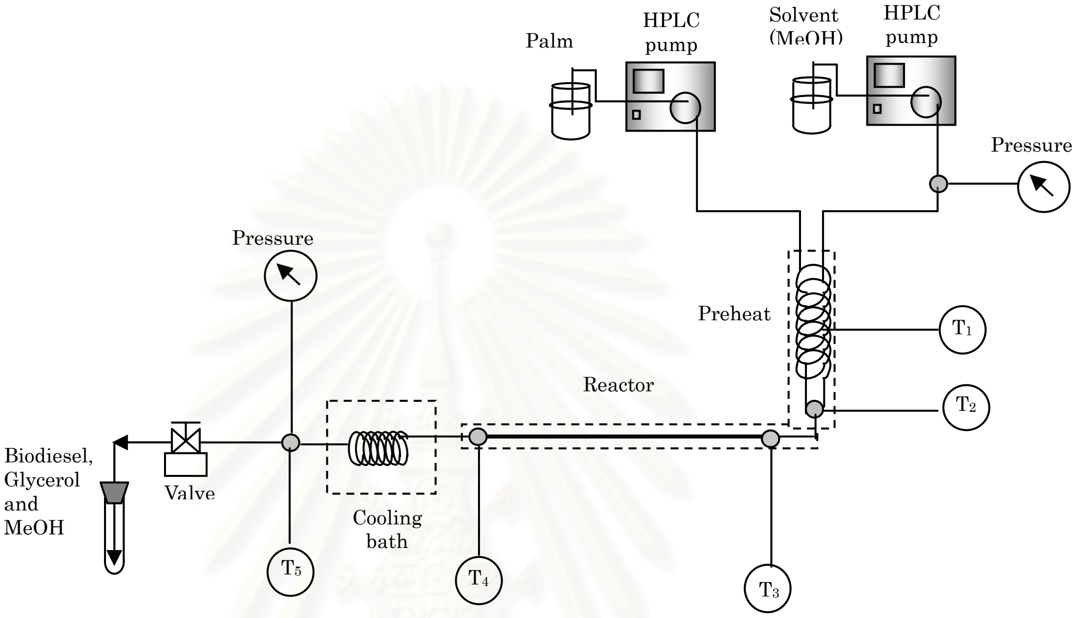


Figure 3.2 Continuous process system for production of biodiesel in SC-MeOH

3.3 Methyl ester analysis

Analysis of methyl ester in products was carried out using gas chromatography (GC) (Shimadzu 14B) which consists of a column (Rtx 5, 30m, 0.25 mm ID, 0.25 μm) and flame ionisation detector (FID). The parameters for the oven temperature program consisted of: start at 150 ^{o}C (2 min), ramp at 5 ^{o}C/min to 250 ^{o}C (5 min). Sample were prepared by adding 0.1 ml of oil to 4.9 ml of n-hexane and eicosane was used an internal standard. The injection volume of sample used for the analysis was two microliters.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter presents the results for the study of transesterification of palm oil in supercritical methanol in absence of catalyst with and without co-solvents. Firstly, the effects of different operating conditions such as temperature (between 250 and 300 ^{o}C), and molar ratio of methanol to palm oil (between 6:1 and 45:1) and reaction time (10-230 min) on the percent methyl esters conversion was determined in a batch type reactor. Then the use of co-solvent to enhance the efficiency of methyl ester production was evaluated. The co-solvents investigated were toluene, benzene, and hexane, in the composition varies between 10 and 50 % v/v of co-solvent/oil. Lastly, continuous transesterification of palm oil in supercritical methanol in a tubular flow reactor was investigated and the results were presented for the effect of space time on the percent methyl ester produced.

4.1 Supercritical transesterification in batch reactor without co-solvent

4.1.1 Effect of molar ratio of methanol to palm oil

In this work, experiments were carried out at the temperature of 250 and 300 ^{o}C for 50 min to determine the effect of molar ratio of methanol to palm oil in range of 6:1 to 45:1 on the methyl esters conversion. The results are shown in Figure 4.1 which showed the increase in the percent of methyl ester produced with the increase in the molar ratio of methanol to palm oil both at 250 and 300 ^{o}C. At 300 ^{o}C, the biodiesel yield was much higher than that at 250 ^{o}C. The results for the effect of reaction temperature will be discussed in more detail in the following section. From the result in Figure 4.1, it is clear that excess methanol was required to shift the equilibrium of the reversible transesterification reaction to the right. Moreover, the high molar ratio of methanol allows the better opportunity for methanol molecules to attack triglyceride molecules, thus increases the contact area between methanol and palm oil during the reaction. For the transesterification reaction with alkali catalyst, Freedman et al. (1984) reported the methanol to oil ratio of 6:1 to be optimal. For the transesterification under supercritical conditions, the result from this study was in accordance with those in the literatures that higher ratio of methanol (42:1 to 45:1) is generally required (Saka et al., 2001 a, b, Diasakou et al., 1998). This could be explained more clearly considering the critical temperature of the mixtures of methanol and oil.

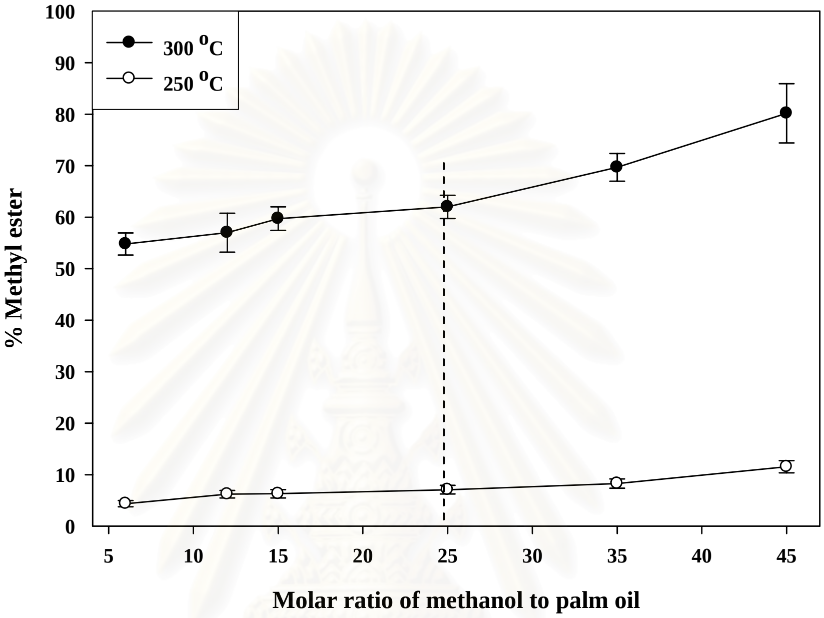


Figure 4.1 Effect of the molar ratios of methanol to palm oil on the yield of methyl esters at 250 and 300^{o}C, reaction time of 50 min.

Table 4.1 The critical properties of palm oil and methanol mixture at various compositions.

Molar ratio	T_c (K)	T_c (^{o}C)	P_c (MPa)	V_c (L/mol)	Z_c
45:1	554.24	281.24	6.77	0.15	0.22
35:1	563.38	290.38	6.46	0.16	0.22
25:1	577.77	304.77	5.98	0.18	0.22
15:1	604.18	331.18	5.11	0.22	0.23
12:1	617.24	344.24	4.69	0.25	0.23
6:1	662.22	389.22	3.37	0.37	0.23

The critical temperatures for the mixture of methanol and palm oil at the different molar ratios are shown in Table 4.1. The critical properties of the methanol and oil mixtures at various molar ratios of methanol to oils were calculated by first assuming oil is a single pseudo-triacylglyceride according to Espinosa S. et al. (2002), which allows the calculation of critical properties of the interested oil to be calculated using Lydersen's method of group contributions. Then, the critical point of methanol and palm oil mixture can be calculated by Lorentz-Berthelot-type mixing rules (Bunyakiat et al., 2006). The sample calculation is shown in Appendix C.

From Table 4.1, at the highest methanol ratio used in this study, the minimum corresponding critical temperature was estimated to be 280 ^{o}C. Thus, when the reaction was carried out at the temperature of 250 ^{o}C, the temperature was too low to achieve supercritical state. The resulting conversion is therefore low at this condition for all molar ratios. At this temperature, the conversion was limited by the temperature of the reaction and the effect of the methanol molar ratio was not significant. At the reaction temperature of 300 ^{o}C however, the critical state could almost be achieved when the ratio of methanol to oil was approximately 45:1 and the supercritical state was achieved at higher methanol to oil molar ratios. This change from subcritical to critical and supercritical state as a result of increasing methanol to oil ratio allows the noticeable increase in the percent biodiesel conversion.

4.1.2 Effect of temperature on methyl esters production

To determine the effect of temperature on methyl esters formation, transesterification reactions of palm oil were carried out at a fixed molar ratio of 25 and 45 in methanol, at the temperature ranges between 250 and 300 ^{o}C and for the reaction of between 10 and 230 min. As expected, the results in Figure 4.2 show that the percent of methyl ester increased when temperatures increased for both methanol to oil ratio of 45:1 and 25:1. For the methanol to oil molar ration of 45:1, after 80 min of reaction, percent of methyl ester increase from of 30 to 78, and to 85 % for the reactions at 250, 280, 300 ^{o}C, respectively. The trend in the results for molar ratio of methanol to palm oil of 25:1 was similar to those at 45:1, however the yield of methyl ester was lower at all the reaction temperatures. When the reaction temperature increases, the degree of hydrogen bonding decreases, thus the polarity of the alcohol decreases, and has increased hydrophobic nature with the lower dielectric constant. As a result, non-polar triglycerides can dissolve in the supercritical alcohol more readily to form a single phase of triglyceride and methanol mixture. When the temperature of the reaction exceeds the critical temperature of the reaction mixture, methanol and oil form a single supercritical fluid phase. At this condition, the rate of reaction was increased considerably and therefore the complete conversion could almost be achieved. The reaction time required to achieve 80% biodiesel conversion in this study was about 50 min for the reaction temperature of 300 ^{o}C. This was higher than that required for the same conversion of sunflower oil which was 20 min (Madras et al., 2004). For the rapeseed oil, Saka et al. (2001 a and b) reported much shorter time was required for a 95% conversion. The types of fatty acids profile could be attributed to the reaction temperature required and the resulting reaction rate. Oils with large amount of unsaturated fatty acids were found to require lower reaction temperature than those containing high amount of saturated fatty acids (Saka et al., 2001 c). Compare to sunflower and rapeseed oils, which contain mostly unsaturated fatty acids, palm oil contains approximately equal amount of saturated and unsaturated fatty acids. Therefore, palm oil transesterification requires higher operating temperature than the reaction of the other two oils above mentioned.

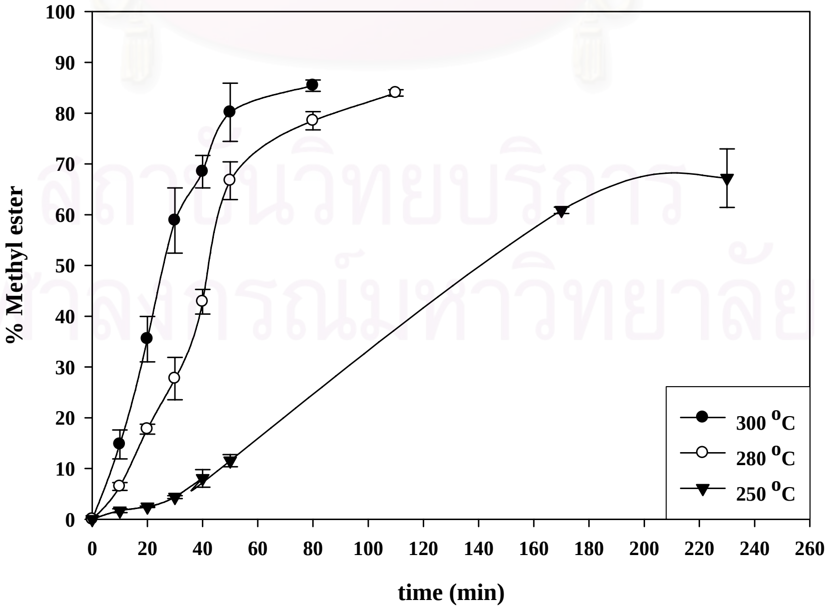


Figure 4.2 Effect the reaction temperature on the methyl esters formation. At molar ratio of methanol to palm oil of 45.

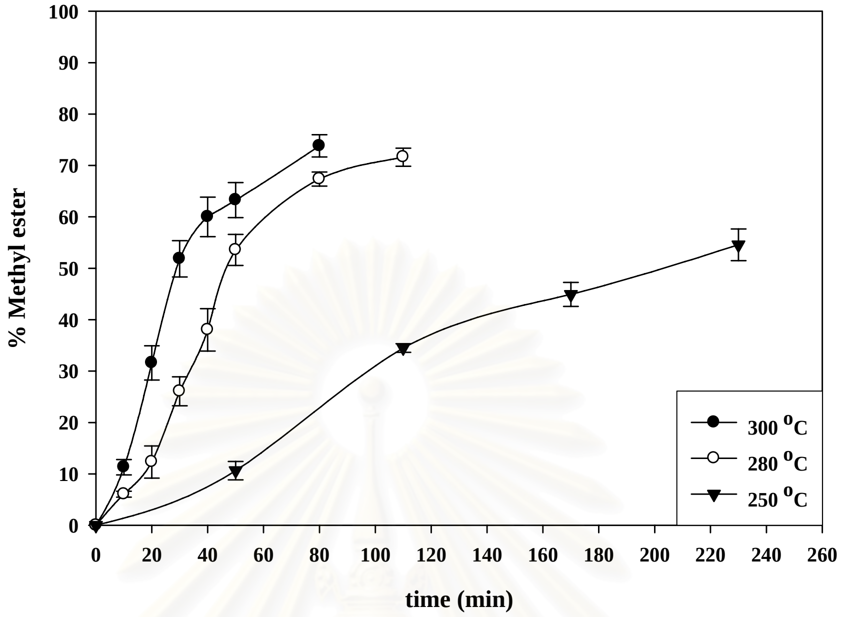


Figure 4.3 Effect the reaction temperature on the methyl esters formation. At molar ratio of methanol to palm oil of 25.

4.1.3 Kinetic of transesterification reaction

A study of the kinetics of transesterification will provide parameters that can be used to predict the extent of the reaction at any time under particular conditions and can be used for the design of the reactor. In this study, the model of kinetic reaction will be based on overall reaction and transesterification reaction is assumed to proceed in the nth order reaction as a function of the concentration of triglyceride, methanol, and reaction time, as shown below.

$$-r_A = -\frac{dC_A}{dt} = kC_{TG}^{n}C_{MeOH}^{m}$$

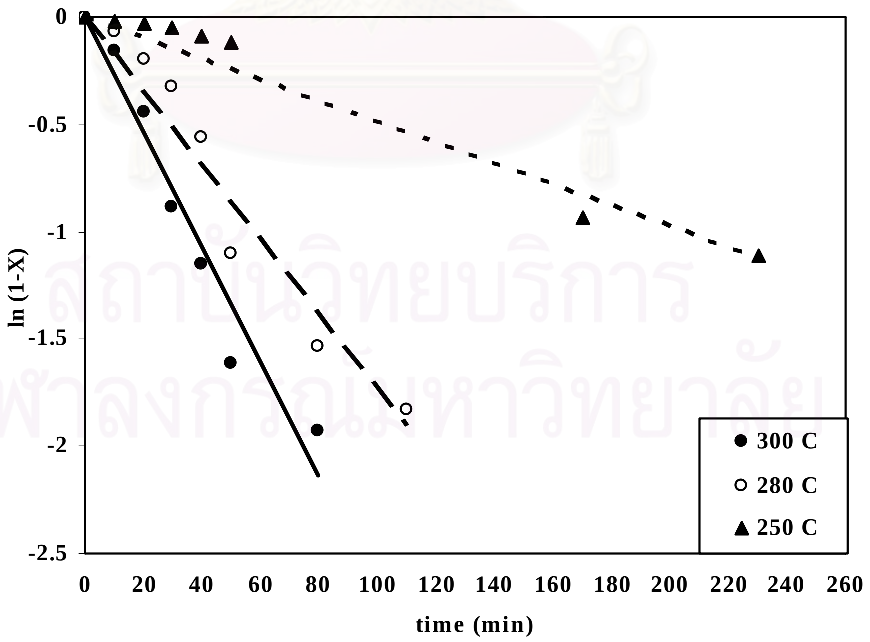
Since the reaction was carried out in excess methanol, the rate equation could be simplified as:

$$-r_A = -\frac{dC_A}{dt} = kC_{TG}^{n}$$

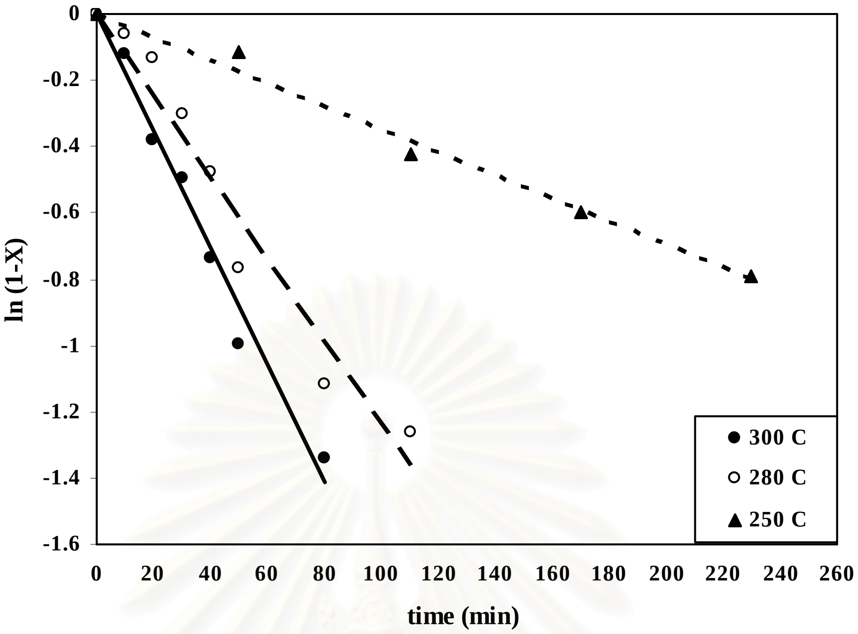
The first order kinetics was found to best describe the experimental results as shown from a straight line plot of ln (1-X) versus time in Figure 4.4. Plots for zero and second order did not give good agreements and these plots can be seen in Appendix A. For the first order kinetics, the rate constant for each temperature could be evaluated from the slope of each line in Figure 4.4, and the results (k) are tabulated in Table 4.2.

Table 4.2 The rate constant of transesterification at different molar ratios of methanol to palm oil.

Temperature (^{o}C)	**k (min^{-1})**	
	45:1	**25:1**
300	0.0267	0.0189
280	0.0173	0.0124
250	0.0049	0.0035



a



b

Figure 4.4 First order kinetic plot (molar ratio of methanol to palm oil (a) 45:1 and (b) 25:1).

Arrhenius type relationship of the form $k = k_O e^{-E/RT}$ could describe the relationship between the kinetic constant and the temperature and the activation energy of the reaction (E) was determined from the slope of the of ln k and 1/T as shown in Figure 4.5.

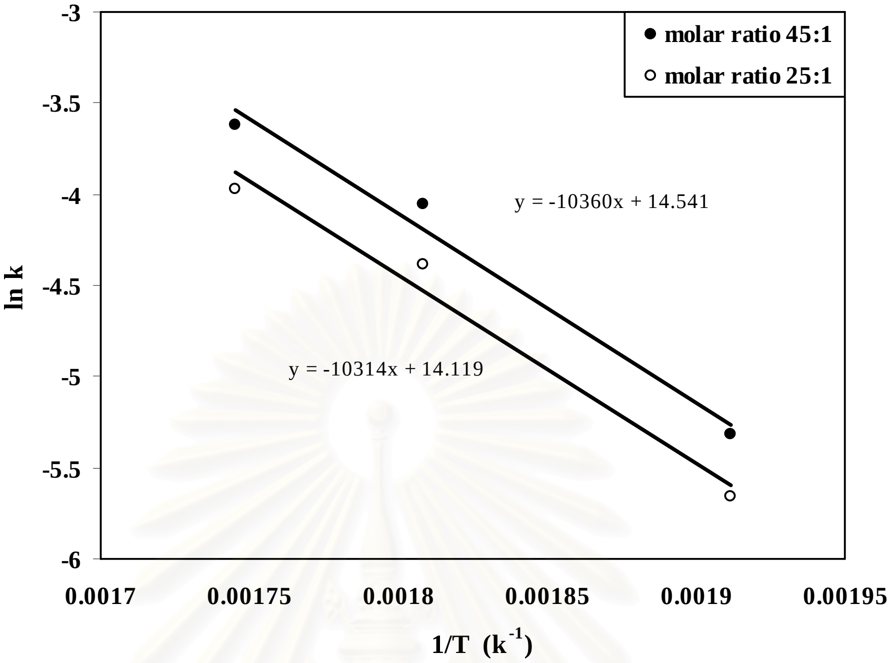


Figure 4.5 First order reaction rate constant in Arrhenius plot of palm oil in methanol during transesterification reaction.

The apparent activation energy of transesterification of palm oil in supercritical methanol condition was therefore estimated to be approximately 86 kJ/mol. Compare with This was higher than the activation energy found in previous work for methyl transesterification of rapeseed oil (Saka et al., 2001 b), which was found to be 69 kJ/mol. The difference was possibly due to the different type of vegetable oils and system used in the studies.

4.2 Transesterification of biodiesel from palm oil in supercritical methanol and co-solvent in batch reactor

To enhance the efficiency of transesterification of palm oil in supercritical methanol, the effect of addition of co-solvents was evaluated. In previous work, propane and CO_2 were added to the reaction system (Weiliang C. et al., 2005 a and b). The use of these co-solvents resulted in the reduction of the required reaction temperature to be about 280 ^oC. This was due to the fact that the addition of propane (T_c =96.67 ^oC and P_c=4.20 MPa) and CO_2 (T_c=31.0 ^oC and P_c=7.28 MPa) reduces the critical temperature of oil and methanol mixture to about 260 ^oC. In this study, hexane, benzene and toluene were used as co-solvents and the effect of the concentrations of the co-solvents to oil was determined on the formation of methyl ester in range 10 to 50%v/v. In these experiments, transesterification of palm oil were carried out at a fix molar ratio of methanol to oil at 45:1 and at 300 ^oC for 50 min. The results in Figure 4.6 show that the higher yield of methyl esters of about 82 and 85 % could be achieved for the reaction with the addition of benzene or toluene at 10 %v/v solvent to oil, a slight increase from the 80% methyl esters produced without addition of these solvents. However, comparison of means by Duncan’s new multiple range test at 95 % confidence interval indicated no significant difference among these results. Therefore, it can be concluded that at this condition (molar ratio of methanol to oil of 45:1, 300 ^oC, 50 min), toluene and benzene had no effect on biodiesel production. The small effect observed could be due to the fact that at this condition, the mixture of methanol and oil is in supercritical state and the two reactants were already completely mixed even without co-solvent. These results are on the other hand different when hexane was added in the 10-30% v/v range. In this case, significantly lower yield was obtained ($p<0.05$). In general, hexane is soluble in oil but has low solubility in methanol. It acts therefore as an antisolvent, and thus reduced the biodiesel production yield. When the amount of hexane was increased to 40-50 %v/v however, no significant difference was found for the production yield with and without the addition of hexane ($p>0.05$). At high percentage, hexane mixes well with palm oil and help reduces the viscosity of the oil. The decrease in viscosity could give better mixing of methanol and oil, which possibly cancel out the negative anti-solvent effects. These results found are in accordance with Mohanprasad et al. (2003) where low percentage and high percentage of hexane produced opposite effects on the biodiesel production in subcritical conditions.

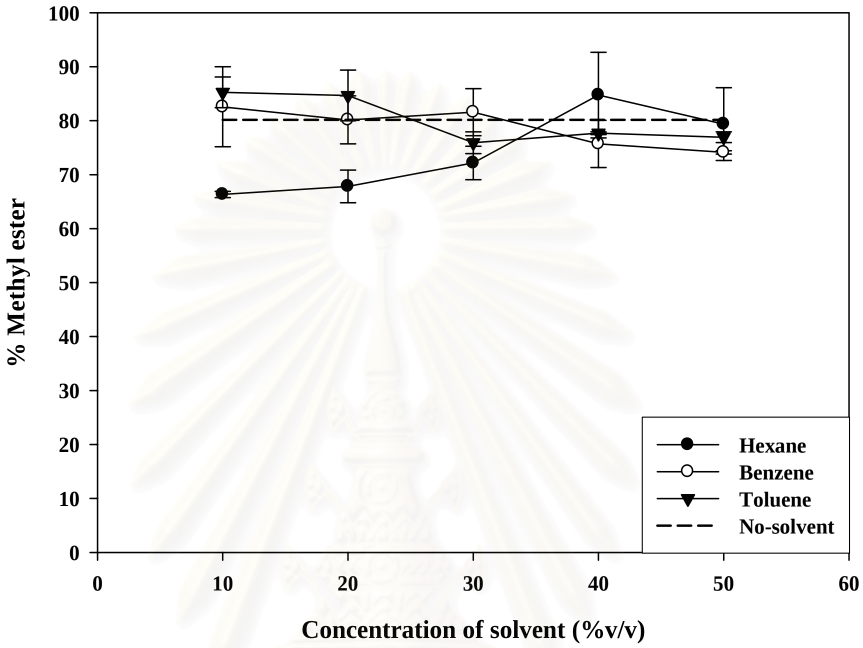


Figure 4.6 Effect of vary concentration of co-solvent to palm oil, at methanol:oil molar ratio of 45:1 and 300 ^{o}C and reaction time 50 min.

The effect of varying molar ratio of methanol to palm oil on the yield of methyl ester was investigated at the solvent concentration of 10 %v/v in oil for benzene and toluene, and at 40 %v/v for hexane. The reaction temperature and the reaction time for these experiments were 300 ^{o}C and 50 min. The results are shown in Figure 4.7 for molar ratio of methanol to oil in the range of 6:1 to 45:1. Compared with no solvent control, the significantly higher methyl ester yield was obtained when any one of the co-solvents were used at any of the molar ratios of methanol to oil except for the ratio 45:1. Furthermore, benzene and toluene were generally found to give similar results, and both are more favorable than hexane. At the molar ratio of 45:1, use of co-solvent did not significantly increase the biodiesel yield. As mentioned earlier, this was possibly because at this ratio, the system was already at supercritical state and the reaction was not limited by mass transfer between methanol and oil. In addition to the above observations, it is also demonstrated by the result here that for methanol to oil molar ratios of 45:1, 35:1 and 25:1, there was no significant difference in the yield of biodiesel when either benzene or toluene at 10%v/v was added. Therefore use of these solvents could reduce the amount of methanol required for the reaction to 25:1 from 45:1 (when no co-solvent was added).

When consider the critical temperature of the mixture of oil, methanol, and solvents at different composition employed in the experiment, the critical temperature was not significantly changed as a result of solvent addition (Table 4.3-4.5). The critical temperature and pressures of mixtures of methanol, palm oil and solvent were calculated by Lee-Kesler method which was reported to be the most accurate general method available for nonpolar substances and mixture. From these tables, it can be seen that the addition of solvents did not give a reduced critical temperature of the reaction mixture, thus this was not the key reason for the enhanced production. The enhancement in biodiesel product as a result of the addition of benzene and toluene was possibly due to the fact that benzene and toluene are good solvents for vegetable oil and both are miscible with methanol. These solvents are therefore expected to help mix methanol and oil in reactor (Krisnangkura et al., 1992). When hexane was added to the reaction system, the antisolvent capabilities of hexane were noticeable at the lower percentage, while at the higher percentages, this antisolvent property was less pronounced compared to the effect of reduction in viscosity.

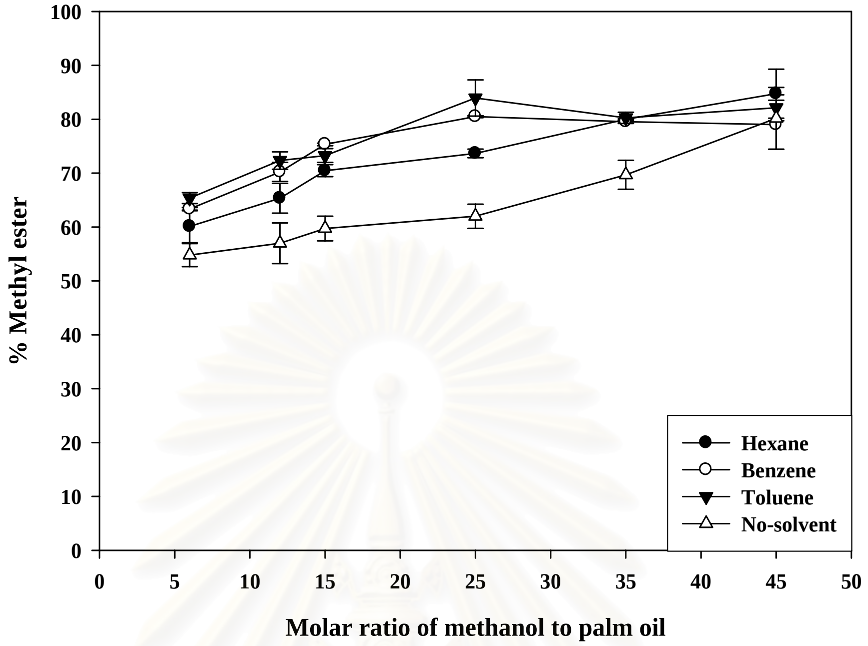


Figure 4.7 Effects of varying the molar ratio of methanol to oil on the formation of methyl esters, at temperature 300 ^{o}C and reaction time 50 min.

From the proper ratios of methanol to oil determined (25:1 for benzene and toluene and 45:1 for hexane), the effect of solvent addition at various reaction temperatures was investigated in the range 250–300 ^{o}C on the formation of methyl esters. For benzene and toluene, the reactions were carried out at a fixed methanol and palm oil molar ratio of 25:1 and the concentration of solvent and palm oil of 10 %v/v. For transesterification with hexane addition, the reaction was carried out at a fixed molar ratio of methanol to palm oil of 45:1 and the concentration of hexane to palm oil of 40 %v/v. The results are shown in Figure 4.8 and 4.9. In both cases, experiments were carried out for 50 min.

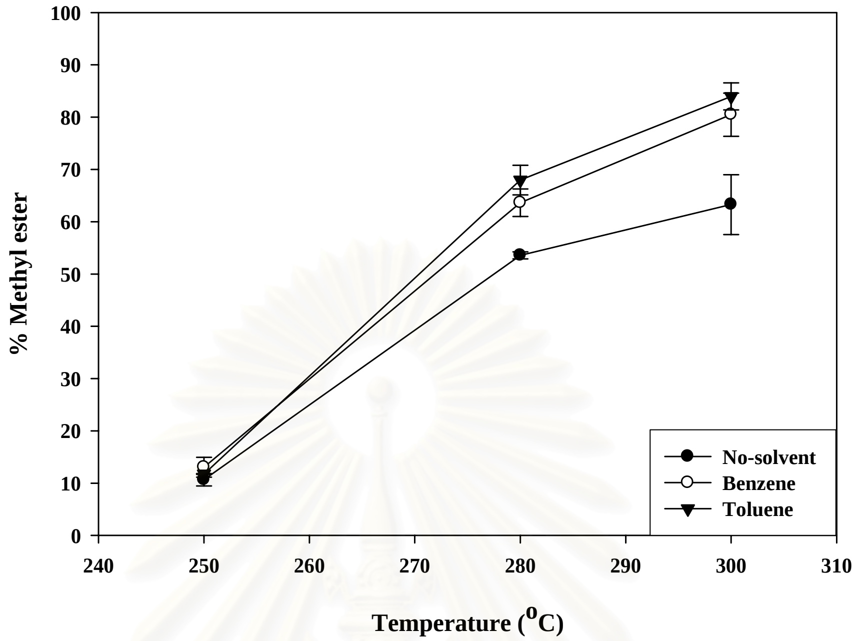


Figure 4.8 Effect of temperature on yield of biodiesel at molar methanol to oil ratio of 25:1, 10 %v/v solvent to palm oil, and reaction time of 50 min.

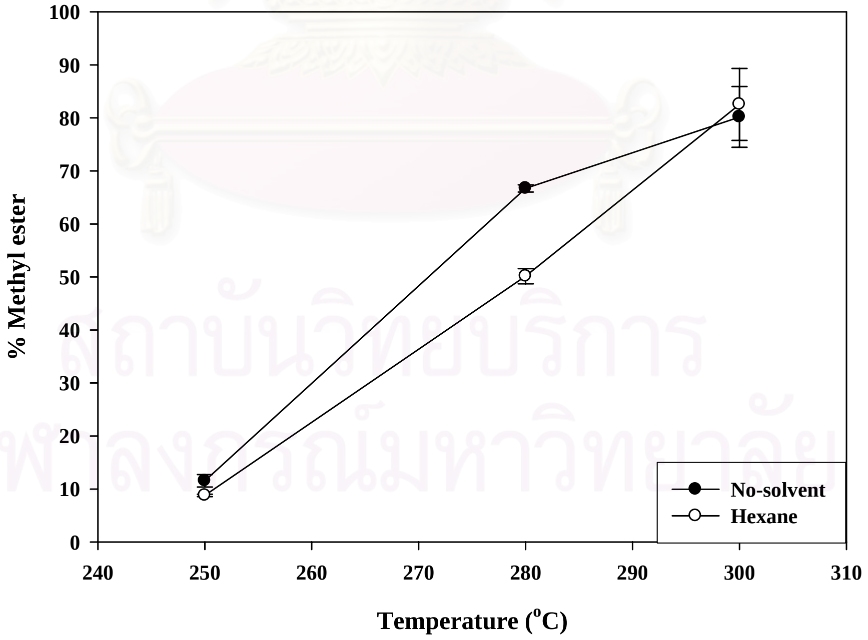


Figure 4.9 Effect of temperature on the yield of biodiesel at methanol to oil molar ratio of 45:1, 40 %v/v solvent to palm oil, and reaction time of 50 min.

Figure 4.8 and 4.9 shows the percentages of methyl esters resulted from transesterification with addition of different co-solvents. Figure 4.8 show that the percentages of methyl ester produced were generally higher in the reactions with toluene and benzene co-solvents than those without co-solvents. Comparison of means by Duncan’s new multiple range tests at 95 % confidence interval on the results in Figure 4.9 indicated on the other hand that when hexane was added as co-solvent at 280 C, the conversion was lower than that without hexane addition. At 250 ^{o}C and 300 ^{o}C on the other hand, the effect was minimal.

From the study of the effect of co-solvents, it can be concluded from these results that hexane is generally not a proper co-solvent for the production of biodiesel. Furthermore, the enhanced production was found across all the temperatures when toluene and benzene were used. The suitable percentage was 10%v/v and the molar ratio of methanol to oil was 25:1.

Table 4.3 The critical temperature and pressure of palm oil, methanol and hexane mixture at various compositions (T_C hexane= 234 ^{o}C).

Molar ratio	**% volume solvent /palm oil**	**Critical point**	
		T (^{o}C)	**P (MPa)**
45:1	10	281.21	7.32
	20	281.14	7.32
	30	281.11	7.32
	40	281.22	7.32
	50	281.09	7.28
25:1	10	304.67	6.46
	20	304.57	6.46
	30	303.37	6.44
	40	304.37	6.46
	50	304.73	6.46

Table 4.4 The critical temperature and pressure of palm oil, methanol and benzene mixture at various compositions (T_C benzene= 289 ^{o}C).

Molar ratio	**% volume solvent /palm oil**	**Critical point**	
		T (^{o}C)	**P (MPa)**
45:1	10	281.19	7.32
	20	281.13	7.32
	30	281.08	7.32
	40	281.00	7.32
	50	280.95	7.32
25:1	10	304.65	6.46
	20	304.53	6.46
	30	303.06	6.44
	40	303.06	6.44
	50	304.29	6.46

Table 4.5 The critical temperature and pressure of palm oil, methanol and toluene mixture at various compositions (T_C toluene= 319 ^{o}C).

Molar ratio	**% volume solvent /palm oil**	**Critical point**	
		T (^{o}C)	**P (MPa)**
45:1	10	281.18	7.32
	20	281.15	7.32
	30	281.09	7.32
	40	281.03	7.32
	50	280.97	7.32
25:1	10	304.68	6.46
	20	304.55	6.46
	30	304.46	6.46
	40	304.32	6.46
	50	303.17	6.44

4.3 Transesterification of biodiesel from palm oil in supercritical methanol and co-solvent in a tubular flow reactor

Under selected conditions, the transesterification in continuous tubular flow reactor to determine the effect of residence time on the yield of biodiesel produced from palm oil. In this experiment, the reactor was constructed from a 65 cm length of 3/8 inch outside diameter with 1/16 inch preheating and connecting coils. The transesterification reaction was carried out at the reaction temperature of 300 ^{o}C, the molar ratio of methanol to palm of 25:1 oil and concentration of solvent to palm oil at and with benzene or toluene added as a co-solvent. Because palm oil is highly viscous and the small diameter of the preheating and connecting lines, 50 %v/v solvent to oil is required to allow it to flow through the reactor system. To ensure the supercritical state, the pressure of system was fixed at 19 MPa as recommended in the literature review (Saka et al., 2001 b and Bunyakiat et al., 2006). The reaction at below19 MPa was reported to resulted in the instability of the supercritical state of mixture, thus the complete reaction. The residence time of reaction for this experiment was varied by changing the flow rate of methanol and palm oil (between 2 to 10 ml/min in the liquid state). In supercritical state, the properties of methanol and solvent change, thus affect the flow rate of methanol within system. Specifically, the volume flow rate of methanol and solvent in supercritical state increased from liquid to supercritical state. The calculation of the volumetric flow rate and space time (τ) of the supercritical fluids in the reaction system is shown in Appendix B. For the calculation of the flow rate of supercritical fluids, real gas law was used with the compressibility factor, Z, determined using the Pitzer method. The space time was then calculated from the palm oil and methanol and solvent real gas volumetric flow rate. Although the flow rate of methanol and solvent in supercritical state increases, compared with the flow rate of methanol and solvent at liquid state, the mass flow rate of methanol and solvent did not change, therefore the molar ratio of methanol to oil not change for solvent to oil, specified for the reaction did not change. The results for the biodiesel production at various space times are shown in Figure 4.10, which indicate that when space time increases, the percent of methyl ester also increases. At the space time 182 and 230 sec, the percent of methyl ester conversion was found to be 50 and 52 %, for reaction with addition of benzene and toluene, respectively. Due to the limitation of the reactor system that limit the maximum space time at 230 sec, higher biodiesel yield could not be achieved in this experiment. For the future experiment, changing in the sizes of preheating and connecting coils is recommended to reduce the pressure drop within the system, to allow the oil reaction mixture to flow at slower flow rate. In addition, the size and length of the tubular reactor could be increase to allow higher space time. Despite such limitation, the results in this study was comparable to that obtained in Boonyakieat et al. (2006) in which about 50% methyl esters are produced by palm kernel oil transesterification at 300 ^{o}C with the space time of about 190 sec.

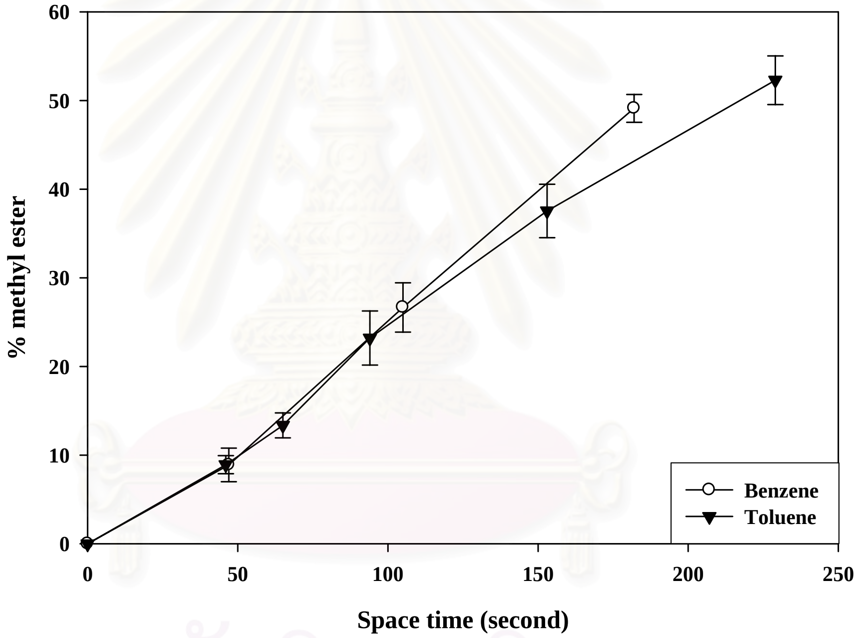


Figure 4.10 The percent of methyl ester conversion from palm oil in supercritical methanol in benzene and toluene at 300 ^{o}C, molar ratio of methanol to palm oil 25:1, volume ratio of solvent to palm oil 50 %v/v.

It should be noted here that to achieve the conversion of 50%, it requires only 180 sec, or 3 min. This is significantly shorter than the time required to achieve the same conversion in the batch reactor. This result suggested that continuous systems employed could be more effective than the batch system used in this study. The possible reason was due to the preheating line which allows the reactants to be heated to the desired temperature before entering the reactor. Furthermore, it was able to adjust the pressure in the continuous system to be about 19 MPa, the condition in which supercritical state was ensured. Further investigations are recommended for the improvements of the production both in batch and continuous flow system.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Biodiesel can produced by non-catalytic transesterification of palm oil supercritical methanol. The product of reaction contain only methyl ester and glycerol. Since no soap was produced, the separation process became much simpler compared with the usual alkali catalyzed process.

5.1.2 The most suitable condition for transesterification reaction by supercritical methanol were 45:1 at 300 °C and 80 min in which 85 % methyl ester was produced.

5.1.3 The rate reaction of transesterification reaction could be expressed by the first order kinetics having the following form of equation:

$$r_{ME} = kC_{TG}$$

or

Rate = (rate constant) (concentration of triglyceride)

5.1.4 The rate constant at 300 °C of this reaction were found 0.0267 and 0.0189 min^{-1} for molar ratio 45:1 and 25:1, respectively and activation energy were found 86 kJ/mol.

5.1.5 Use of benzene and toluene could enhance the biodiesel production when compared with the production from transesterification without a co-solvent at the same reaction condition, however the addition of hexane mostly gave a negative effect on the production.

5.1.6 Continuous transesterification seemed to be a feasible process for biodiesel production. The methyl ester yields were found to increase with increasing space time.

5.2 Recommendations

5.2.1 In present work, there was an equipment limit on the reaction. Maximum temperature of 300 °C was possible for the reaction in the 316 stainless steel. Other materials such as Inconel alloy could be used to allow higher reaction temperature. Further experiment should be improved reactor and heater useful for higher temperature.

5.2.2 For the batch reaction, the direct measurement of temperature and pressure inside the reactor is recommended.

5.2.3 The kinetics of transesterification in supercritical methanol in tubular flow reactor should be investigated.

5.2.4 Glycerol by-product of the reaction can be purified or transformed into higher value products for uses as raw materials in chemical industry.

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APPENDICES

APPENDIX A

EXPERIMENTAL AND DATA ANALYSIS

A-1 Typical fatty acid composition of palm oil (Kincs, 1985)

Table A-1 Fatty acid composition in palm oil sample

Fatty acid	**% wt**
Lauric	0.10
Myristic	1.00
Palmitic	42.80
Stearic	4.50
Oleic	40.50
Linoleic	10.10
Linolenic	0.20

A-2 Standard calibration curve of methyl ester

Table A-2.1 Standard calibration curve data of methyl palmitate

Concentration of methyl palmitate (g/ml)	Peak area ratio of standard to internal standard		
	Exp. 1	Exp. 2	Average
0.00000	0.00	0.00	0.00
0.00046	0.44	0.50	0.47
0.00093	1.13	1.20	1.17
0.00186	2.15	2.00	2.07
0.00279	3.48	3.60	3.54
0.00371	4.22	4.10	4.16

Table A-2.2 Standard calibration curve data of methyl stearate

Concentration of methyl stearate (g/ml)	Peak area ratio of standard to internal standard		
	Exp. 1	Exp. 2	Average
0.00000	0.00	0.00	0.00
0.00026	0.26	0.25	0.26
0.00051	0.54	0.53	0.54
0.00077	0.85	0.86	0.85
0.00153	1.66	1.66	1.66

Table A-2.3 Standard calibration curve data of methyl oleate

Concentration of methyl oleate (g/ml)	Peak area ratio of standard to internal standard		
	Exp. 1	Exp. 2	Average
0.00000	0.00	0.00	0.00
0.00025	0.31	0.30	0.30
0.00076	0.89	0.90	0.89
0.00101	1.10	1.20	1.15
0.00152	1.66	1.67	1.66

Table A-2.4 Standard calibration curve data of methyl linoleate

Concentration of methyl linoleate (g/ml)	Peak area ratio of standard to internal standard		
	Exp. 1	Exp. 2	Average
0.00000	0.00	0.00	0.00
0.00028	0.27	0.26	0.26
0.00083	0.86	0.87	0.87
0.00111	1.13	1.12	1.13
0.00166	1.79	1.80	1.79

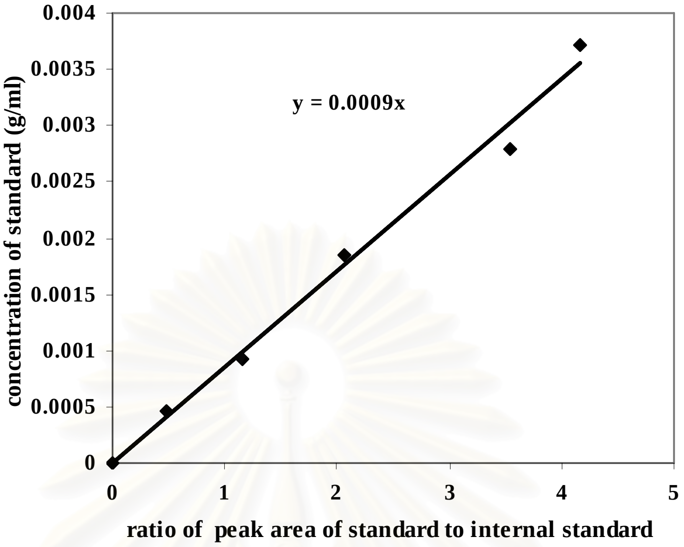


Figure A-2.1 Standard calibration curve of Methyl palmitate

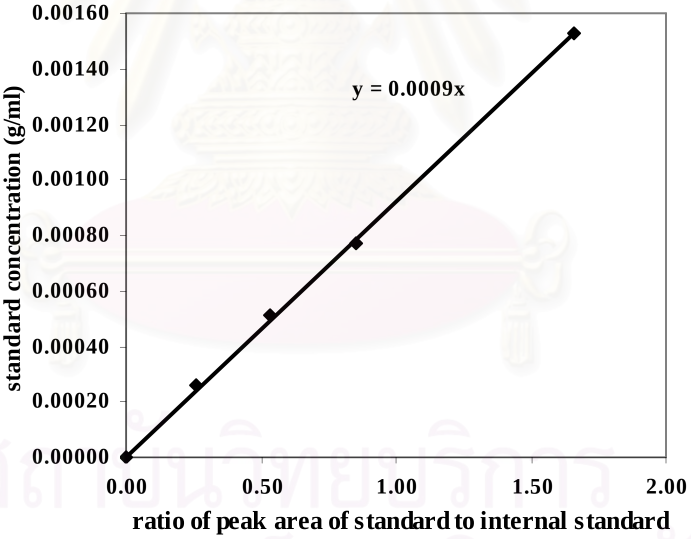


Figure A-2.2 Standard calibration curve of Methyl stearate

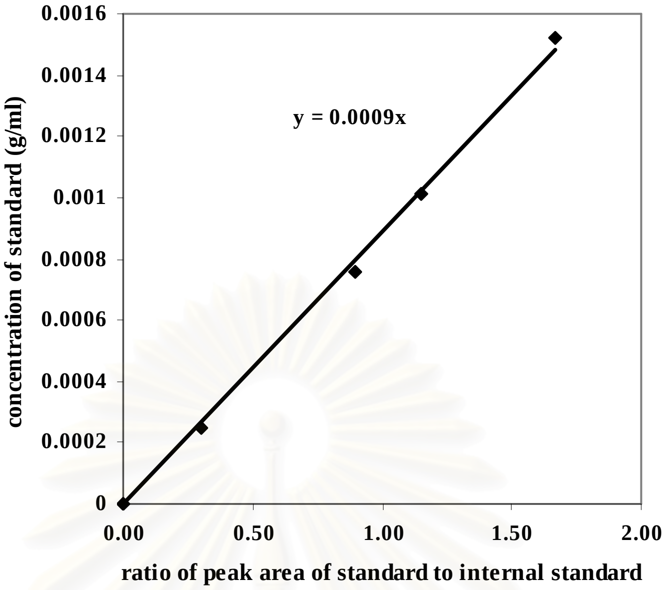


Figure A-2.3 Standard calibration curve of methyl oleate

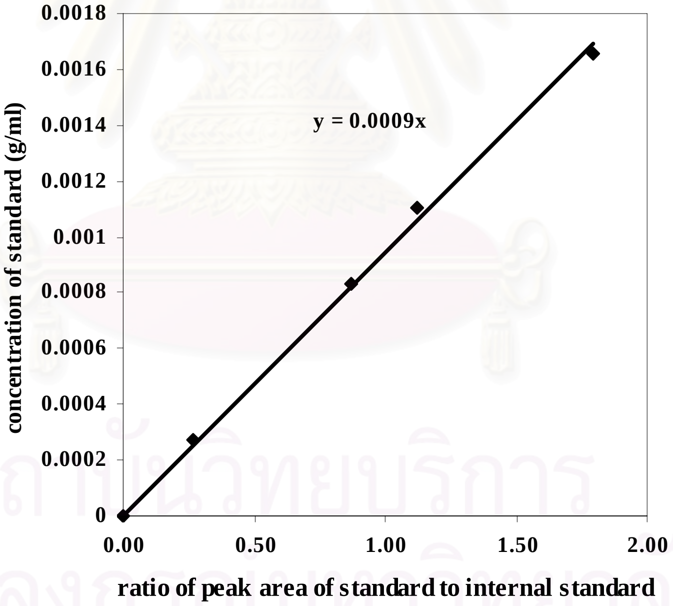


Figure A-2.4 Standard calibration curve of methyl linoleate

A-3 Experimental data of transesterification reaction in batch reactor with out solvent

Table A-3.1 The percent of methyl ester at 300 ^{o}C, molar ratio of methanol to palm oil 6:1 to 45:1 and 50 min

Molar ratio	% Methyl ester (1)	% Methyl ester (2)	Average
45	76.11	84.21	80.16
35	67.77	71.57	69.67
25	60.38	63.57	61.98
15	58.08	61.30	59.69
12	54.32	59.65	56.99
6	53.28	56.29	54.79

Table A-3.2 The percent of methyl ester at 250 ^{o}C, molar ratio of methanol to palm oil 6:1 to 45:1 and 50

Molar ratio	% Methyl ester (1)	% Methyl ester (2)	Average
45	45	10.70	12.37
35	35	7.63	8.93
25	25	6.48	7.67
15	15	6.86	5.72
12	12	5.69	6.71
6	6	3.93	4.81

Table A-3.3 The percent of methyl ester at 300, 280 and 250 °C, molar ratio of methanol to palm oil 45:1

Time (min)	% Methyl ester*		
	300 °C	280 °C	250 °C
0	0	0	0
10	14.75	6.45	1.68
20	35.49	17.75	2.45
30	58.84	27.70	4.36
40	68.48	42.84	8.06
50	80.16	66.69	11.54
80	85.41	78.50	-
110	-	83.97	-
170	-	-	60.86
230	-	-	67.19

***** Average data

Table A-3.4 The percent of methyl ester at 300, 280 and 250 °C, molar ratio of methanol to palm oil 25:1

Time (min)	% Methyl ester*		
	300 °C	280 °C	250 °C
0	0	0	0
10	11.29	6.04	-
20	31.60	12.32	1.88
30	51.83	26.07	-
40	59.98	38.01	-
50	63.27	53.55	10.63
80	73.80	67.35	-
110	-	71.605	34.49
170	-	-	44.91
230	-	-	54.565

***** Average data

A-4 Experimental data of transesterification reaction in solvent in batch reactor

Table A-4.1 The percent of methyl ester at 300^{o}C, molar ratio of methanol to palm oil 45:1 and reaction time 50 min

Concentration of solvent (%v/v)	% Methyl ester *		
	Hexane	Benzene	Toluene
10	66.32	82.56	85.25
20	67.82	80.14	84.65
30	72.15	81.56	75.91
40	84.73	75.69	77.68
50	79.36	74.12	76.93

***** Average data

Table A-4.2 The percent of methyl ester at 300^{o}C, concentration of hexane 40 %v/v, concentration of benzene and toluene 10 %v/v and reaction time 50 min

Molar ratio of methanol to palm oil	% Methyl ester *		
	Hexane	Benzene	Toluene
6:1	60.1	63.32	65.36
12:1	65.32	70.21	72.32
15:1	70.45	75.32	73.25
25:1	73.65	80.46	83.94
35:1	79.98	79.53	80.24
45:1	84.73	78.98	82.12

***** Average data

Table A-4.3 The percent of methyl ester when vary temperature and fix concentration of hexane at 40 %v/v, and reaction time 50 min

Temperature (^oC)	% Methyl ester*
300	79.94
280	40.21
250	6.65

***** Average data

Table A-4.4 The percent of methyl ester when vary temperature and fix concentration of benzene and toluene at 10 %v/v, and reaction time 50 min

Temperature (^oC)	% Methyl ester*	
	Benzene	Toluene
300	80.46	83.94
280	63.62	67.96
250	13.03	11.74

***** Average data

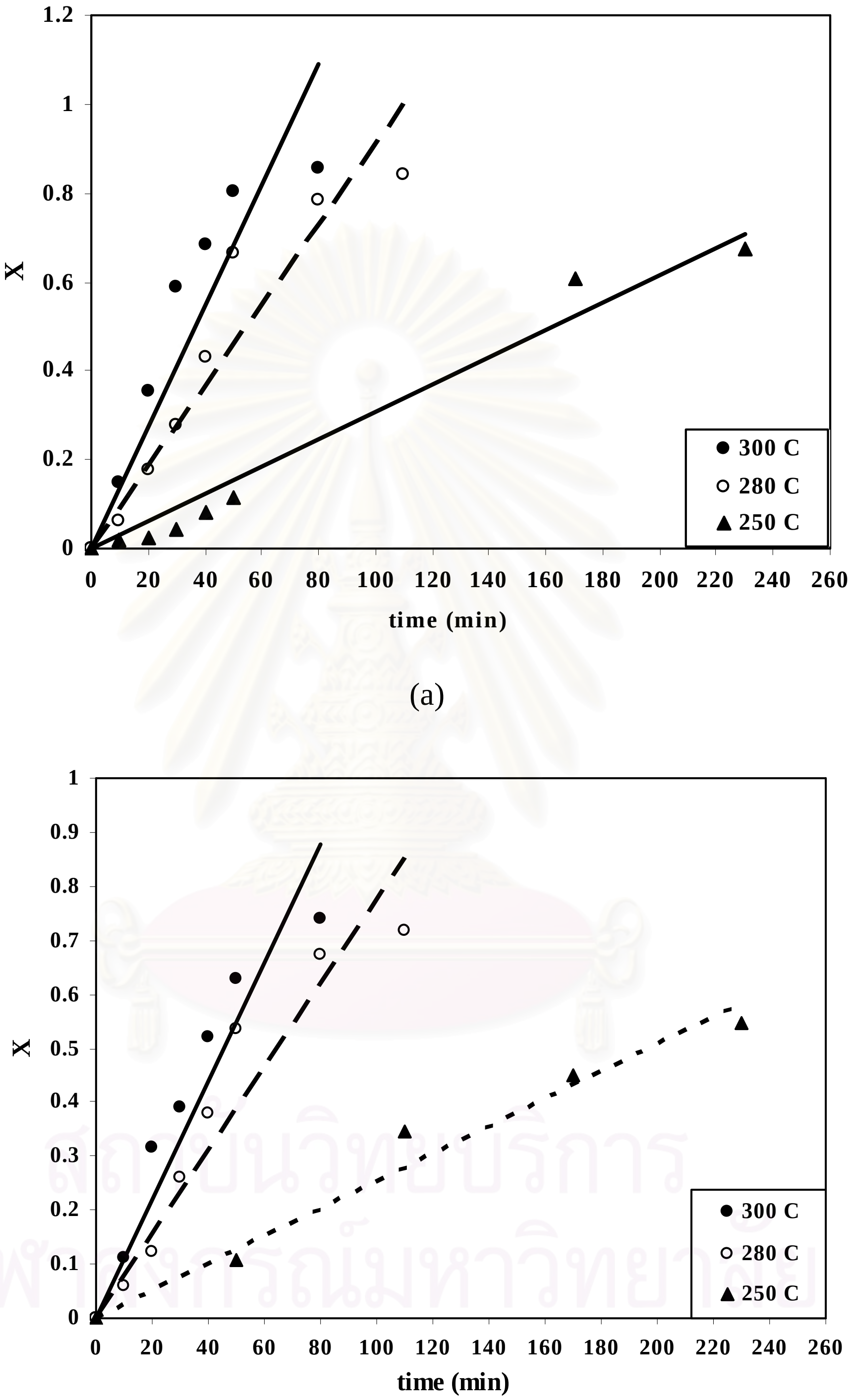
A-5 Experimental data of transesterification reaction in solvent in tubular flow reactor

Table A-5.1 The percent of methyl ester when varying space time and fix concentration of benzene and toluene at 10 %v/v, concentration of hexane 40 % v/v and reaction temperature 300 ^{o}C

Type of solvent	Space time (sec)	% Methyl ester*
Hexane	0	0
	48	8.01
	96	37.975
	120	46.75
Benzene	0	0
	47	8.895
	105	26.66
	182	49.12
Toluene	0	0
	46	8.93
	65	13.36
	94	23.21
	153	37.55
	229	52.30

* Average data

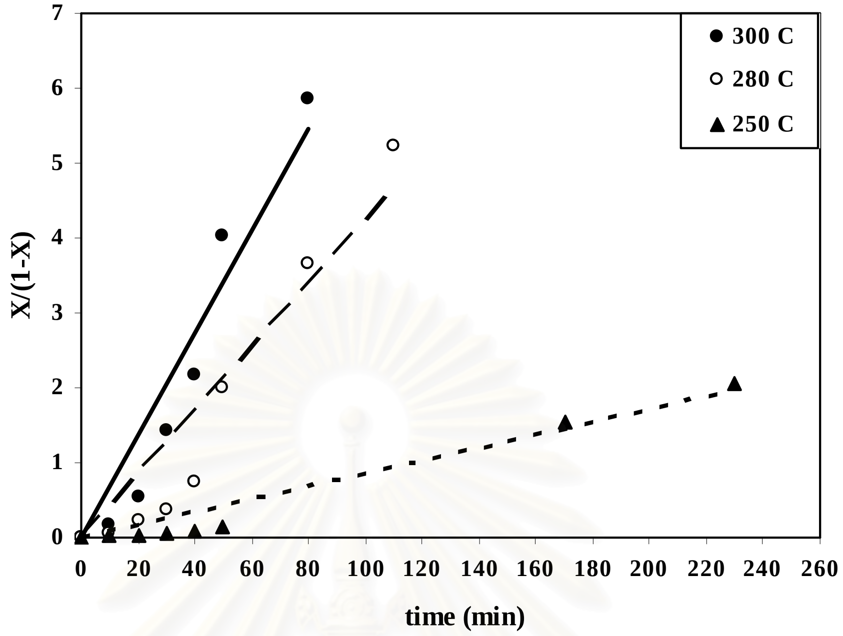
A-6 prove kinetic model



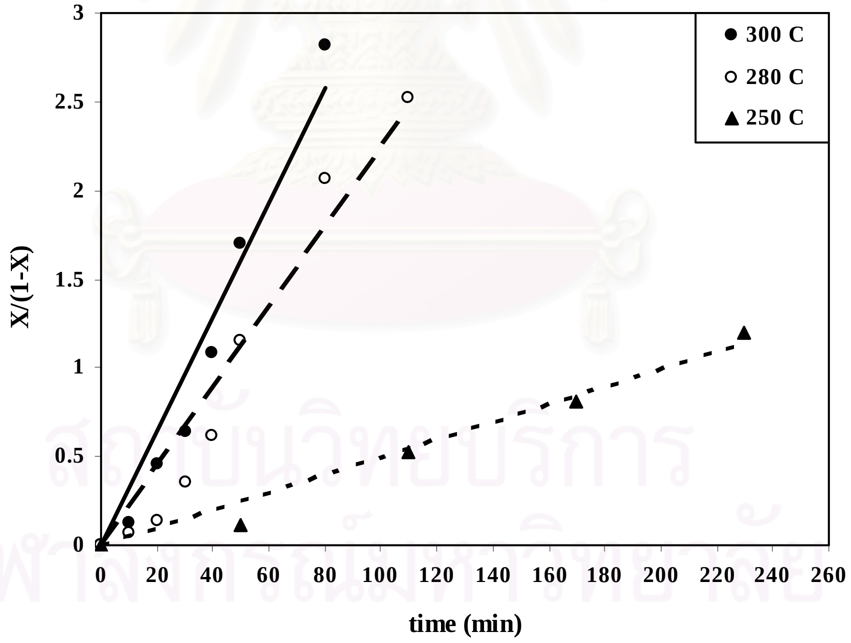
(a)

(b)

Figure A-5.1 Zero order kinetic plot (molar ratio of methanol to palm oil (a) 45:1 and (b) 25:1).



(a)



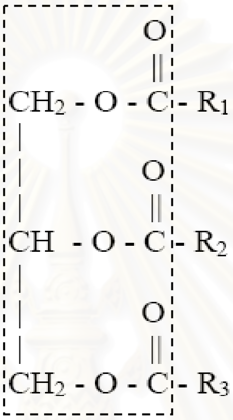
(b)

Figure A-5.2 Second order kinetic plot (molar ratio of methanol to palm oil (a) 45:1 and (b) 25:1).

APEENDIX B

CALCULATION OF PERCENT OF METHYL ESTER

B-1 Calculation molecular weight of palm oil



Triglyceride

R_1, R2, R3: carbon chain of the fatty acids

Molecular weight of triglyceride

$$Mw_{TG} = 3R_{aver} + 173$$

$$R_{aver} = \sum \left(\frac{\%Fa_n}{100} \ x \ Mw_n \right)$$

Where

Mw_{TG} = molecular weight of triglyceride

R_{aver} = average molecular weight of fatty acid

% Fa_n = percent of fatty acid in vegetable oil

Mw_n = molecular weight of fatty acid

Example Find molecular weight of palm oil

$$R_{aver} = \left(\frac{0.1}{100}\times 200\right)+\left(\frac{1}{100}\times 228\right)+\left(\frac{42.8}{100}\times 256\right)+\left(\frac{4.5}{100}\times 284\right)$$

$$+\left(\frac{40.5}{100}\times 282\right)+\left(\frac{10.1}{100}\times 280\right)+\left(\frac{0.2}{100}\times 278\right)$$

$$= 267.08$$

$$3R_{aver} = 3\times 267.08 = 801.23$$

$$Mw_{TG} = 801.23 + 173$$

$$= 974.23$$

B-2 Calculation of reactants

B-2.1 Calculation of reactants in batch reactor

Molar ratio of methanol to palm oil $\frac{N_{MeOH}}{N_{palmoil}} = N$

Volume of palm oil $\frac{Mw_{palmoil}N_{palmoil}}{\rho_{palmoil}} + \frac{Mw_{MeOH}N_{MeOH}}{\rho_{MeOH}} = V_{reaction}$

Volume of methanol $V_{reactor} - V_{MeOH} = V_{palmoil}$

B-2.2 Calculation of reactants in tubular flow reactor (flow rate)

In tubular reactor, molar ratio of methanol to palm oil in system can be calculated base on flow rate of methanol and palm oil.

Molar ratio of methanol to palm oil	$\frac{N_{MeOH}}{N_{palmoil}}$
Volume of methanol at N mol	V_{MeOH}
Volume of palm oil at N mol	$V_{palmoil}$
Total flow rate of methanol and palm oil	F_T

Flow rate of methanol (F_{MeOH}) $$\frac{V_{MeOH}\, x F_T}{V_{MeOH} + V_{palmoil}}$$

Flow rate of palm oil ($F_{palm\ oil}$) $$\frac{V_{palmoil}\, x F_T}{V_{MeOH} + V_{palmoil}}$$

Example Base on molecular weight of palm oil and methanol is 974.23 and 32.04, respectively. The density of palm oil and methanol is 0.92 and 0.79, respectively. The volume of reactor used for all preparation was 5 ml.

Molar ratio of methanol to palm oil $$\frac{N_{MeOH}}{N_{palmoil}} = \frac{45}{1}$$

$$N_{MeOH} = 45 N_{palmoil}$$

Volume of palm oil $$\frac{974.23 \times N_{palmoil}}{0.92} + \frac{32.04 \times 45 N_{palmoil}}{0.79} = 5$$

$$N_{palmoil} = 0.001734$$

$$V_{palmoil} = \frac{974.23 \times 0.001734}{0.92}$$

$$V_{palmoil} = 1.84 \quad ml$$

Methanol volume $5 - 1.84 = 3.16 \quad ml$

B-3 Calculation of space time

Space time was calculated from the methanol, palm oil and solvent flow rates at liquid state to obtain the real gas volumes employing the compressibility factor, *Z*, obtained by the Pitzer method**.**

From theory of real gas:

$$PV^{*} = Zn^{*}RT$$

$$V_{MeOH}^{*} = \frac{ZF_{MeOH}\rho_{MeOH}RT}{Mw_{MeOH}P}$$

$$V_{solvent}^{*} = \frac{ZF_{solvent}\rho_{solvent}RT}{Mw_{solvent}P}$$

$$\tau = \frac{V}{V_{MeOH}^{*} + V_{solvent}^{*} + F_{palmoil}}$$

The compressibility factor Z can be calculated by Pitzer method:

$$Z = Z(P_r, T_r, \omega)$$

$$Z = Z^{0}(P_r, T_r) + \omega Z^{1}(P_r, T_r)$$

where

τ = space time

$$T_r = \frac{T}{T_c}$$

$$P_r = \frac{P}{P_c}$$

T_c = absolute critical temperature

P_c = absolute critical pressure

ω = acentric factor

V = volume of reactor (ml)

V* = flow rate at supercritical sate (ml/min)

F = flow rate at liquid state (ml/min)

ρ = density (g/cm^3)

T = absolute temperature

P = absolute pressure

R = gas constant

B-4 Analysis of methyl ester

Analysis of methyl ester in product by gas chromatography (GC). The retention time of each methyl ester is different. Therefore, for find the type of methyl ester by compare retention time of each methyl ester with methyl ester standard.

B-4.1 GC chromatogram of methyl ester from experiment

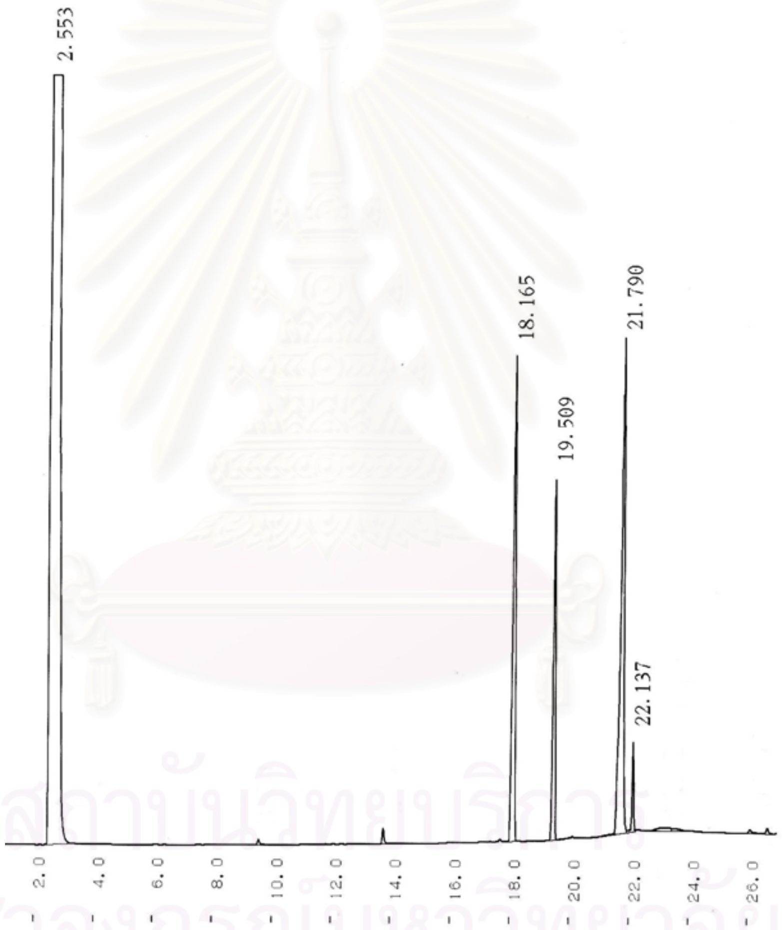


Figure B-4.1 GC chromatogram of methyl ester

Table B-4.1 Retention time of methyl ester in GC chromatogram

Number of peak	Retention time (min)	Peak of sample
1	2.553	Hexane
2	18.165	Methyl palmitate
3	19.509	Eicosane
4	21.790	Methyl oleate + Methyl linoleate
5	22.137	Methyl stearate

B-4.2 Calculation weight of each methyl ester

$$W_{ME} = \left(\frac{C \times V_{TD}}{V_S} \right) \times V_P$$

Where

W_{ME} = weight of methyl ester (g)

C = concentration of each methyl ester from calibration curve (g/ml)

V_{TD} = total volume dilute (ml)

V_S = volume product dilute (ml)

V_P = total volume of product (ml)

B-4.3 Calculation weight of each fatty acid in triglyceride

B-4.3.1 Batch reactor

$$W_{Fa} = W_O \times \%\ fatty\ \ acid$$

Where

W_{Fa} = weight of fatty acid (g)

W_O = weight of vegetable oil (g)

% fatty acid = percent of each fatty acid in vegetable oil

B-4.3.2 Tubular reactor

$$W_{Fa} = W_O \times \%\ fatty\ \ acid$$

Where

$$W_o = F_{palmoil} \times t \times \rho$$

When $F_{\text{palm oil}}$ = flow rate of palm oil (ml/min)

t = colleting time (min)

ρ = density of palm oil (g/cm^3)

B-4.4 Calculation of percent methyl ester

In this study, methyl ester formation base on palmitic acid, stearic acid, oleic acid and linoleic acid.

$$\%\ \ Methyl\ \ ester = \frac{W_{ME}}{W_{Fa} \times (x_i)} \times 100$$

Where

W_{ME} = weight of methyl ester (g)

W_{Fa} = weight of fatty acid (g)

x_i = weight fraction of fatty acid

<u>Example</u> Find % methyl ester at molar ratio of methanol to palm oil 25:1, temperature 300 ^{o}C, 90 min. The volume of product 2.8 ml and 0.1 of product add to 4.9 ml of hexane and 1 ml of eicosane. The percent weight of palmitate, stearate, oleate and linoleate were 42.8, 4.5, 40.5 and 10.1, respectively.

<u>Weight of each methyl ester</u>

Weight of methyl palitate = $\frac{0.003507 \times 6}{0.1} \times 2.8 = 0.5892\ \ g$

Weight of methyl stearate = $\frac{0.000556 \times 6}{0.1} \times 2.8 = 0.0934\ \ \ g$

Weight of methyl oleate and linoleate $= \dfrac{0.005536 \times 6}{0.1} \times 2.8 = 0.9300 \quad g$

<u>Weight of each fatty acid in triglyceride</u>

Weight of Lauric acid $2.50 \times 0.001 = 0.0024 \quad g$

Weight of myristic acid $2.50 \times 0.01 = 0.0236 \quad g$

Weight of palmitic acid $2.50 \times 0.428 = 1.0082 \quad g$

Weight of stearic acid $2.50 \times 0.045 = 0.1060 \quad g$

Weight of oleic acid $2.50 \times 0.405 = 0.9540 \quad g$

Weight of linoleic acid $2.50 \times 0.101 = 0.2379 \quad g$

Weight of linolenic acid $2.50 \times 0.002 = 0.0047 \quad g$

% Methyl ester

$$= \frac{0.5892 + 0.0934 + 0.9300}{(0.0024 + 0.0236 + 1.0082 + 0.1060 + 0.9540 + 0.2379 + 0.0047) \times 0.979} \times 100$$

$= 70.49 \ \%$

APPENDIX C

CRITICAL POINT OF PALM OIL AND MIXTURE

C-1 Pseudo-triacylglyceride (Espinosa S. et al., 2002)

One of the problems of fatty acid oil mixtures is the representation of the oil chemical structure. Fatty oils are essentially mixtures of saturated and unsaturated mixed triacylglycerides. It is not possible to know the exact distribution of the different fatty acid chains in the mixed triacylglyceride molecules. One possible solution to the problem is to represent the oil as a mixture of simple triacylglyceride, in accordance with the fatty acid composition of the natural oil. Another alternative, and in this work, is represent the oil by a single pseudo-component. First, the critical property of a vegetable oil that is a mixture of various triglycerides is represented by a single pseudo-triacylglyceride with the following molecular structure:

$$[(CH_2COO)_2CHCOO](CH{=}CH)_m(CH_2)_n(CH_3)_3$$

Where

m = degree of unsaturation of the natural oil

n = molecular weight

The values of n and m in the pseudo-triacylglyceride are calculated as follows:

$$n = \sum_{i=1}^{N} n_i x_i$$

$$m = \sum_{i=1}^{N} m_i x_i$$

Where

N = the number of fatty acids present in the natural oil.

x_i = weight fraction of fatty acid composition

Then the critical temperature and pressure were then calculated using Lydersen’s method of group contributions.

Example Pseudo-triaclyglyceride of palm oil

Fatty acid	**% wt**	**x_i**	**n_i**	**m_i**	**x_in_i**	**x_im_i**
Lauric	0.1	0	30	0	0.03	0
Myristic	1	0.01	36	0	0.36	0
Palmitic	42.8	0.43	42	0	18.12	0
Stearic	4.5	0.05	48	0	2.18	0
Oleic	40.5	0.41	42	3	17.15	1.22
Linoleic	10.1	0.1	36	6	3.67	0.61
Linolenic	0.2	0	30	9	0.06	0.02
Total	**99.2**	**1**			**41.56**	**1.85**

The application of equations above and to the fatty acid composition shown in the previous table gives:

$$n = 41.56$$

$$m = 1.85$$

After rounding these values to the nearest integer number, the pseudo-triaclyglyceride molecule used to represent palm oil is:

$$[(CH_2COO)_2CHCOO](CH{=}CH)_2(CH_2)_{42}(CH_3)_3$$

C-2 Critical point of triglyceride

The critical temperature and pressure of triglyceride were calculated using Lydersen's method of group contributions.

The formulas are

$$T_b = \theta T_c = \left[0.567 + \sum(N)(\Delta T) + \sum(N)(\Delta T) - \left(\sum(N)(\Delta T)\right)^2\right] T_c$$

$$T_c = \frac{e^{\beta}}{R}$$

$$\beta = \frac{\left[(1-\theta)^{2/7} - 0.048\right]\ln(V_c) + \left[(1-\theta)^{2/7}\ln P_c + 1.255\right]}{(1-\theta)^{2/7}}$$

$$P_c = Mw\left[0.34 + (N)(\Delta P)\right]^{-2}$$

$$V_c = 40 + (N)(\Delta V)$$

$$Z_c = \frac{P_c V_c}{R T_c}$$

Where

T_c = critical temperature (K)

P_c = critical pressure (atm)

V_c = critical volume (cm^3/(g.mol))

Z_c = critical compressibility factor

The value of ΔT, ΔP and ΔV of group contribution are show in table C-1.

Example

1. Obtain molecular structure and molecular weight

Palm oil structure is $[(CH_2COO)_2CHCOO](CH{=}CH)_2(CH_2)_{42}(CH_3)_3$ and molecular weight is 974.23.

2. Sum up structural contributions of the individual property increments from table C-1

The calculations can be set out in the following arrays, in which *N* stands for the number of groups.

Group type	**N**	**ΔT**	**ΔP**	**ΔV**	**(N)(ΔT)**	**(N)(ΔP)**	**(N)(ΔV)**
COO (ester)	3	0.047	0.47	80.00	0.14	1.41	240.00
CH_3 (nonring)	3	0.020	0.23	55.00	0.06	0.68	165.00
CH_2 (nonring)	44	0.020	0.23	55.00	0.88	9.99	2420.00
CH (nonring)	1	0.012	0.21	51.00	0.01	0.21	51.00
	2	0.018	0.20	45.00	0.04	0.40	90.00
Total					**1.13**	**12.69**	**2966.00**

From the formulas show in above

$$V_c = 40 + 2966 = 3006 \ \ cm^3/(g.mol)$$

$$P_c = 974.23[0.34 + 12.69]^{-2} = 5.74 \ \ atm$$

$$\theta = 0.567 + 1.13 - (1.13)^2 = 0.42$$

$$\beta = \frac{\left[(1-0.42)^{2/7} - 0.048\right] \ \ln(3006) + \left[(1-0.42)^{2/7} \ \ \ln(5.74) + 1.255\right]}{(1-0.42)^{2/7}}$$

$$= 11.17$$

$$T_c = \frac{e^{11.17}}{82.06} = 863.09 \ \ K, \quad R = 82.06 \ \ cm^3.atm/g.mol.K$$

$$Z_c = \frac{(5.74)(3006)}{(82.06)(863.09)} = 0.24$$

So, the critical properties of palm oil from calculation are:

$$T_c = 863.09 \ \ K$$
$$P_c = 5.74 \ \ atm$$
$$V_c = 3006 \ \ cm^3/g.mol$$
$$Z_c = 0.24$$

Table C-1 Critical Property Increment Lydersen’s Structural Contribution

Symbols	ΔT	ΔP	ΔV
Nonring increments			
$-CH_3$	0.020	0.227	55
$-\overset{\vert}{C}H_2$	0.020	0.227	55
$-\overset{\vert}{\underset{\vert}{C}}H$	0.012	0.210	51
$-\overset{\vert}{\underset{\vert}{C}}-$	0.00	0.210	41
$=CH_2$	0.018	0.198	45
$=\overset{\vert}{C}H$	0.018	0.198	45
$=\overset{\vert}{C}-$	0.0	0.198	36
$=C=$	0.0	0.198	36
$\equiv CH$	0.005	0.153	(36)
$\equiv C-$	0.005	0.153	(36)
Ring increments			
$-CH_2-$	0.013	0.184	44.5
$-\overset{\vert}{\underset{\vert}{C}}H$	0.012	0.192	46
$-\overset{\vert}{\underset{\vert}{C}}-$	(−0.007)	(0.154)	(31)
$=\overset{\vert}{C}H$	0.011	0.154	37
$=\overset{\vert}{C}-$	0.011	0.154	36
$=C=$	0.011	0.154	36
Halogen increments			
$-F$	0.018	0.221	18
$-Cl$	0.017	0.320	49
$-Br$	0.010	(0.50)	(70)
$-I$	0.012	(0.83)	(95)
Oxygen increments			
$-OH$ (alcohols)	0.082	0.06	(18)
$-OH$ (phenols)	0.031	(−0.02)	(3)
$-O-$ (nonring)	0.021	0.16	20
$-O-$ (ring)	(0.014)	(0.12)	(8)
$-\overset{\vert}{C}=O$ (nonring)	0.040	0.29	60

Symbols	ΔT	ΔP	ΔV
Oxygen increments (cont)			
$-\overset{\vert}{C}=O$ (ring)	(0.033)	(0.2)	(50)
$H\overset{\vert}{C}=O$ (aldehyde)	0.048	0.33	73
$-COOH$ (acid)	0.085	(0.4)	80
$-COO-$ (ester)	0.047	0.47	80
$=O$ (except for combinations above)	(0.02)	(0.12)	(11)
Nitrogen increments			
$-NH_2$	0.031	0.095	28
$-\overset{\vert}{N}H$ (nonring)	0.031	0.135	(37)
$-\overset{\vert}{N}H$ (ring)	(0.024)	(0.09)	(27)
$-\overset{\vert}{N}-$ (nonring)	0.014	0.17	(42)
$-\overset{\vert}{N}-$ (ring)	(0.007)	(0.13)	(32)
$-CN$	(0.060)	(0.36)	(80)
$-NO_2$	(0.055)	(0.42)	(78)
Sulfur increments			
$-SH$	0.015	0.27	55
$-S-$ (nonring)	0.015	0.27	55
$-S-$ (ring)	(0.008)	(0.24)	(45)
$=S$	(0.003)	(0.24)	(47)
Miscellaneous			
$-\underset{\vert}{\overset{\vert}{Si}}-$	0.03	(0.54)	
$-\underset{\vert}{B}-$	(0.03)		

C-3 Pseudocritical properties

There is no reason to suppose that the principle of corresponding states can not be applied to mixtures as well as to pure substances and it has been found applicable with some restrictions. Although reduced equations of state prove not to valid when base on the true critical properties of mixture, it has been found possible to devise satisfactory pseudocritical properties in terms of compositions and critical properties of the pure constituents. These pseudocritical properties usually differ quite markedly from the true value. In fact, the true critical properties of mixture often can be evaluated with equation of state base on pseudocritical properties.

The critical points of mixture were calculated by Lorentz-Berthelot-type rules and the Lee-Kesler method. Many other combining rules for pseudocritical properties and equation parameters have been proposed, often superior to the rules already mentioned but usually more complicated.

Lorentz-Berthelot-type rules for binary mixture

$$T_{cm}V_{cm} = \sum_i \sum_j x_i x_j T_{ij} V_{ij} = x_i^2 T_{ci} V_{ci} + 2 x_i x_j T_{cij} V_{cij} + x_j^2 T_{cj} V_{cj}$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} = x_i^2 V_{ci} + 2 x_i x_j V_{cij} + x_j^2 V_j$$

$$Z_{cm} = \sum_i \sum_j x_i x_j Z_{cij} = x_i^2 Z_{ci} + 2 x_i x_j Z_{cij} + x_j^2 Z_{cj}$$

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}}$$

The terms of T_{cij}, V_{cij} and Z_{cij} were calculated by the combining rule as the following equations:

$$T_{cij} = \sqrt{T_{ci}T_{cj}}$$

$$P_{cij} = \frac{1}{V_{cij}}\sqrt{P_{ci}P_{cj}V_{ci}V_{cj}}$$

$$Z_{cij} = 0.5\left(Z_{ci} + Z_{cj}\right)$$

$$V_{cij}^{1/3} = \frac{1}{2}\left(V_{ci}^{1/3} + V_{cj}^{1/3}\right)$$

Where

i and j = subscripts for vegetable and methanol

T_c = critical temperature of vegetable oil or methanol

V_c = molar volume of vegetable oil or methanol

Z_c = compressibility factor of vegetable oil or methanol

x = mole fraction of vegetable oil or methanol

T_{cm} = critical temperature of mixture

V_{cm} = critical volume of mixture

P_{cm} = critical pressure of mixture

Z_{cm} = critical compressibility factor of mixture

Pseudocritical properties for used with the Lee-Kesler method

$$Z_{ci} = 0.2905 - 0.085\omega_i$$

$$\omega = \sum x_i\omega_i$$

$$Z_{cm} = 0.2905 - 0.085\sum x_i\omega_i$$

$$V_{cm} = \frac{1}{8}\sum_i\sum_j x_i x_j \left(V_{ci}^{1/3} + V_{cj}^{1/3}\right)^3$$

$$V_{cm} = x_1^2V_{c1} + x_2^2V_{c2} + x_3^2V_{c3} + 0.25\left[x_1x_2\left(V_{c1}^{1/3} + V_{c2}^{1/3}\right)^3 + x_1x_3\left(V_{c1}^{1/3} + V_{c2}^{1/3}\right)^3 + x_2x_3\left(V_{c2}^{1/3} + V_{c3}^{1/3}\right)^3\right]$$

$$V_{cm}T_{cm} = x_1^2V_{c1}T_{c1} + x_2^2V_{c2}T_{c2} + x_{c3}^2V_{c3}T_{c3} + 0.25\left[x_1x_2\left(T_{c1}T_{c2}\right)^{0.5}\left(V_{c1}^{1/3} + V_{c2}^{1/3}\right)^3 + x_1x_3\left(T_{c1}T_{c3}\right)^{0.5}\left(V_{c1}^{1/3} + V_{c3}^{1/3}\right)^3\right.$$

$$+ x_2 x_3 \left(T_{c2} T_{c3}\right)^{0.5} \left(V_{c2}^{1/3} + V_{c3}^{1/3}\right)^3 \Big]$$

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}}$$

Where

1, 2 and 3 = subscripts for vegetable, methanol and solvent

Example: Binary system Calculation of the critical point of methanol and palm oil mixtures (binary mixture) by Lorentz-Berthelot-type rules when the molar ratio of methanol to palm oil 45:1.

The critical properties of methanol and palm oil set out in following array.

Component	**Mole fraction**	**T_c (^oC)**	**P_c (atm)**	**V_c (L/mol)**	**Z_c**
MeOH	0.98	512.60	79.90	0.118	0.224
Palm oil	0.02	863.09	5.74	3.006	0.240

From the combining rules:

$$T_{cij} = \sqrt{(512.60)(863.09)} = 665.15 \;\; K$$

$$V_{cij}^{1/3} = \frac{1}{2}\left[(0.118)^{1/3} + (3.006)^{1/3}\right] = 0.97 \;\; (L/mol)^{1/3}$$

$$V_{cij} = 0.90 \;\; (L/mol)$$

$$P_{cij} = \frac{1}{0.90}\sqrt{(79.90)(5.74)(0.118)(3.006)} = 14.11 \;\; atm$$

$$Z_c = 0.5(0.224 + 0.240) = 0.23$$

So, the critical properties of methanol and palm oil mixture calculate by Lorentz-Berthelot-type rules.

$$V_{cm} = (0.98)^2(0.118) + 2(0.98)(0.02)(0.90) + (0.02)^2(3.006) = 0.15 \ \ (L/mol)$$

$$T_{cm}V_{cm} = (0.98)^2(512.60)(0.118) + 2(0.98)(0.02)(665.15)(0.90) + (0.02)^2(863.09)(3.006)$$

$$= 84.68 \ \ (K.L/mol)$$

$$T_{cm} = \frac{84.68}{0.15} = 554.24 \ \ K = 281.24^{o}C$$

$$Z_{cm} = (0.98)^2(0.224) + 2(0.98)(0.02)(0.23) + (0.02)^2(0.24) = 0.22$$

$$P_{cm} = \frac{(0.22)(0.0821)(554.24)}{(0.15)} = 66.82 \ \ atm \ \ = 6.77 \ \ MPa, \qquad R = 0.0821 \ \ L.atm/mol.K$$

So that, the critical properties of methanol and palm oil mixtures at molar ratio 45:1 are:

$$T_{cm} = 281.24^{o}C$$
$$P_{cm} = 6.77 \ \ MPa$$
$$V_{cm} = 0.15 \ \ L/mol$$
$$Z_{cm} = 0.22$$

Example: Ternary system Calculation of the critical point of methanol, palm oil and hexane mixtures (ternary mixture) by the Lee-Kesler method at molar ratio of methanol to palm oil 45:1 and hexane 50 % v/v.

The critical properties of methanol and palm oil set out in following array

Component	**Mole fraction**	**T_c (K)**	**P_c (atm)**	**V_c (cm^3/mol)**	**Z_c**	**ω**
MeOH	0.9781	512.60	79.86	118	0.224	0.556
Palm oil	0.0217	863.09	5.74	3006	0.240	0.590
Hexane	0.0002	507.50	29.71	370	0.264	0.299

From the Lee-Kesler method:

$$\omega = (0.9781)(0.556) + (0.0217)(0.590) + (0.0002)(0.299) = 0.5611$$

$$Z_{cm} = 0.2905 - 0.085(0.5611) = 0.24$$

$$\begin{aligned} V_{cm} &= (0.9781)^2(118) + (0.0217)^2(3006) + (0.0002)^2(370) \\ &\quad + 0.25\Big[(0.9781)(0.0217)\left((118)^{1/3} + (3006)^{1/3}\right)^3 \\ &\quad + (0.9781)(0.0002)\left((118)^{1/3} + (370)^{1/3}\right)^3 \\ &\quad + (0.0217)(0.0002)\left((3006)^{1/3} + (370)^{1/3}\right)^3\Big] \\ &= 153.59\ cm^3/mol \end{aligned}$$

$$\begin{aligned} V_{cm}T_{cm} &= (0.9781)^2(118)(512.60) + (0.0217)^2(3006)(863.09) + (0.0002)^2(370)(507.50) \\ &\quad + 0.25\Big[(0.9781)(0.0217)((512.60)(863.09))^{0.5}\left((118)^{1/3} + (3006)^{1/3}\right)^3 \\ &\quad + (0.9781)(0.0002)((512.60)(507.50))^{0.5}\left((118)^{1/3} + (370)^{1/3}\right)^3 \\ &\quad + (0.0217)(0.0002)((863.09)(507.50))^{0.5}\left((3006)^{1/3} + (370)^{1/3}\right)^3\Big] \\ &= 85102.09\ K.cm^3/mol \end{aligned}$$

$$T_{cm} = \frac{85102.09}{153.59} = 554.09\ K = 281.09\ ^oC$$

$$P_{cm} = \frac{(0.24)(82.06)(554.09)}{153.59} = 71.87\ atm = 7.28\ MPa\ , \qquad R = 82.06\ cm^3.atm/g.mol.K$$

So that, the critical properties of methanol, palm oil and hexane mixtures at molar ratio methanol to palm oil 45:1 and hexane 50 %v/v are:

$$T_{cm} = 281.09\ ^oC$$

$$P_{cm} = 7.28\ MPa$$

$$V_{cm} = 0.15\ L/mol$$

$$Z_{cm} = 0.24$$

VITA

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