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CONTINUOUS PRODUCTION OF BIOFUEL FROM PALM OIL IN SUPERCRITICAL ETHYL ACETATE

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Petrochemistry
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Thesis Title	CONTINUOUS PRODUCTION OF BIOFUEL FROM PALM OIL IN SUPERCRITICAL ETHYL ACETATE
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วัตถุประสงค์ของการวิจัยนี้คือผลิตเชื้อเพลิงชีวภาพจากน้ำมันปาล์มในเอทิลแอซีเทตภาวะเหนือวิกฤตด้วยระบบต่อเนื่องและศึกษาปัจจัยที่มีผลต่อการเกิดปฏิกิริยา ปฏิกิริยาอินเทอร์เอสเทอริฟิเคชันโดยไม่ใช้ตัวเร่งปฏิกิริยาของสารผสมในระบบต่อเนื่องนี้มีความซับซ้อนในการเข้าใจสมบัติทางเทอร์โมไดนามิกส์โดยเฉพาะความหนาแน่นของสารผสมในเครื่องปฏิกรณ์ โดยขั้นแรกเป็นการทดลองหาความสัมพันธ์ของอุณหภูมิ ความดันและความหนาแน่นของสารผสมน้ำมันปาล์มและเอทิลแอซีเทตโดยใช้เทคนิคไอโซคลอริกด้วยเครื่องปฏิกรณ์ปริมาตรคงที่ เพื่อสร้างกราฟ PVT โดยความไม่ต่อเนื่องของความชันของเส้นไอโซคลอริกแสดงขอบเขตระหว่างสารผสมสถานะของเหลว-ไอและของผสมรวมเป็นเนื้อเดียว ซึ่งจุดเปลี่ยนสถานะนี้นำมาใช้ประมาณจุดวิกฤตของสารผสมของน้ำมันปาล์มและเอทิลแอซีเทตที่องค์ประกอบต่างๆ โดยข้อมูลที่ได้นี้นำมาใช้ทดลองการผลิตเชื้อเพลิงชีวภาพจากน้ำมันปาล์มในเอทิลแอซีเทตภาวะเหนือวิกฤตด้วยเครื่องปฏิกรณ์แบบต่อเนื่อง โดยความหนาแน่นของสารผสมในการทดลองนี้ ประมาณโดยใช้การจำลองกระบวนการด้วยสมการสถานะของเปง-โรบินสัน (PR EOS) จากนั้นนำค่าที่ได้ไปคำนวณเวลาในการเกิดปฏิกิริยา โดยภาวะที่เหมาะสมในการผลิตเชื้อเพลิงชีวภาพจากน้ำมันปาล์มในเอทิลแอซีเทตเป็นร้อยละ 90.9 โดยน้ำหนัก คือ อุณหภูมิ 653 เคลวิน ความดัน 16 เมกะพาสคัลและอัตราการไหลของสารผสมเป็น 1.5 กรัม/นาที โดยมีค่าพลังงานก่อกัมมันต์เป็น 50.06 กิโลจูล/โมล ในช่วงอุณหภูมิ 593-653 เคลวิน นอกจากนี้ยังทดลองการเติมน้ำลงในสารผสมที่ภาวะเหนือวิกฤตด้วยสำหรับนำน้ำมันพืชใช้แล้วมาเป็นวัตถุดิบเพื่อเป็นแนวทางในการลดต้นทุนของกระบวนการผลิต

สาขาวิชา ปิโตรเคมี	ลายมือชื่อนิสิต ....
ปีการศึกษา 2557	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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KEYWORDS: PALM OIL / ETHYL ACETATE / ISOCHORIC METHOD / BIOFUEL / CONTINUOUS SYSTEM / VALUE ADDED BY-PRODUCT

CHOLADA KOMINTARACHAT: CONTINUOUS PRODUCTION OF BIOFUEL FROM PALM OIL IN SUPERCRITICAL ETHYL ACETATE. ADVISOR: ASSOC. PROF. SOMKIAT NGAMPRASERTSITH, Dr. de l'INPT, CO-ADVISOR: RUENGWIT SAWANGKAEW, Ph.D., 89 pp.

The objective of this study is to produce biofuel from palm oil in supercritical ethyl acetate (ETA) in continuous system and study the effects of reaction parameters. The non-catalytic interesterification of the reactants in continuous system to produce biofuel is complex to understand thermodynamic properties during extreme condition, particularly density of the mixture in the reactor. In the first part, the relation of temperature, pressure and global density of palm oil and ETA by isochoric technique with constant volume reactor were investigated to generate PVT diagrams. The discontinuity of slope of the isochoric line indicates the boundaries between the vapor-liquid phase and homogeneous regions for the reacting systems. These phase transition points can be estimated critical point of palm oil and ETA mixture at different compositions. The subsequent information is utilized for investigating biofuel production from palm oil in supercritical ETA using continuous tubular reactor. The density of the mixtures in this second part was estimated using the Peng–Robinson equation of state (PR EOS) process simulator, and the residence time was calculated. The optimum conditions required to obtain 90.9 wt% of total biofuel production of palm oil in supercritical ETA were 653 K and 16 MPa at the optimum mixture mass flow rate of 1.5 g/min with the activation energy by 50.06 kJ/mol in 593–653 K range. Furthermore, water addition to the supercritical mixture was also investigated to reuse a raw material of waste cooking oil for economic feasibility.

Field of Study: Petrochemistry

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Student's Signature ....

Advisor's Signature ....

Co-Advisor's Signature ....

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CONTENTS

Page

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 The problems statement

Excessive dependence on petroleum fuel for daily activities has raised a concern due to the unpredictability of oil prices and issues surrounding energy security. Moreover, the incomplete combustion of petro-diesel in engines continuously increases greenhouse gases, which adversely affects ecosystems worldwide and causes climate change [1, 2]. Thus, the potential of bioenergy, with alternative biofuels produced from biomass [3] such as fatty acid methyl ester (FAMEs) and fatty acid ethyl ester (FAEEs), as a partial substitute for petroleum diesel fuel has attractively increased [4]. Conventional biodiesel, FAMEs or FAEEs, is produced via a transesterification reaction of vegetable oil and short-chain alcohol in the presence of either a basic [5] or an acidic [6] catalyst as illustrated in Figure 1.1. After the completion of the reaction, the catalyst and glycerol by-products have to be removed from mixture products and the resultant FAEEs was pretreated before utilization [7-9]. This step limits biodiesel production that uses the catalytic transesterification processes. Thus, many researchers are exploring and developing non-catalytic procedures for biodiesel production [10].

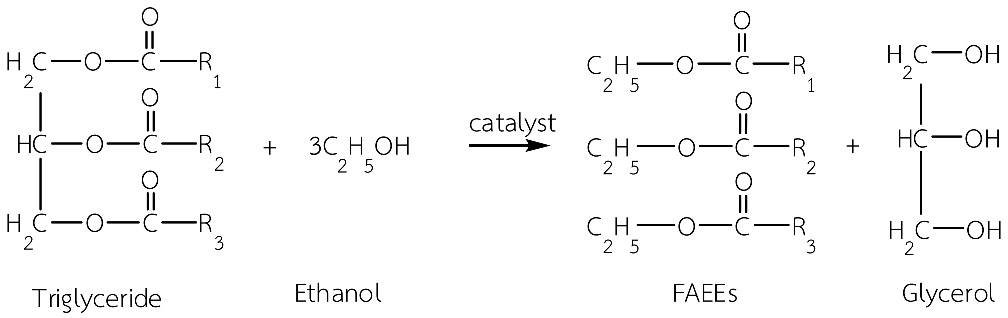


Figure 1.1 The transesterification reactions of palm oil (triglycerides) with ethanol.

The non-catalytic transesterification of vegetable oil and alcohol in supercritical conditions has been widely investigated [11] with studies suggesting that it may be an alternative method for clean biodiesel production [12]. As the reaction operates under high-temperature and high-pressure conditions, it enhances the phase solubility, mitigates mass transfer limitations, provides higher reaction rates, and facilitates the separation and purification steps of the products [13]. Moreover, research has shown that the supercritical method is more resistant to contamination by water and free fatty acids (FFAs) than the conventional alkali-catalyzed technique. However, the catalyst-free production of biodiesel in supercritical alcohols does not prevent the formation of glycerol by-products, which have to be removed [14], and the glycerol has to be purified.

In the supercritical reactor for biofuel production, phase characteristics during the homogeneous reaction depends on the reactants and reaction conditions [10]; many solvents can be chosen to operate the system in a single fluid phase. A systematic procedure to find solvents to achieve homogeneous conditions has been developed to produce biodiesel [15-17]. One among other solvents, ethyl acetate (ETA) is a carboxylate ester that can be used as supercritical solvent instead of alcohols in interesterification reaction [18], to obtain FAEEs and triacetin (TA) as by-product following the reaction shown in Figure 1.2. TA is a fuel additive, completely soluble in biofuel and can improve cold flow properties [19]. The combination of biodiesel and TA will be identified as biofuel [20].

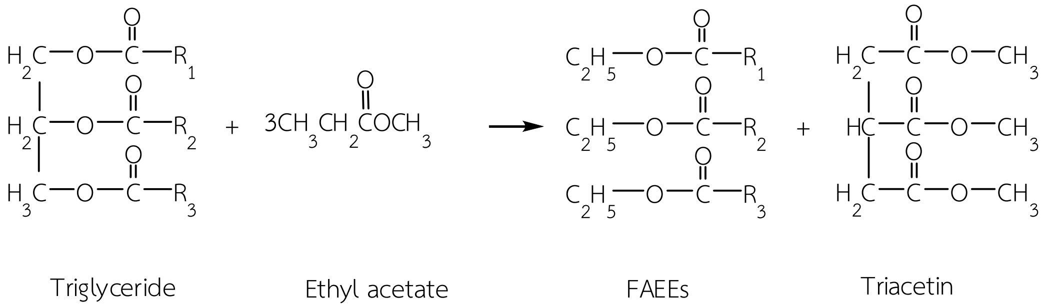


Figure 1.2 The interesterification reaction of palm oil (triglycerides) with ethyl acetate.

Due to the complex theory of fluid mixtures, the studies of Economou [21] and You et al. [22] experimentally explored an understanding of the thermodynamic behavior of pure fluids, leading to the development of quantitative prediction methods [23]. Among thermodynamic properties describing variable state of condition such as pressure (p), temperature (T) and density (ρ), the accurate measurement of fluid mixture density is the most difficult to measurement. Recently, Isochoric method [24, 25] was used to measure the density of reacting mixtures of oil and alcohol in supercritical condition for produce biodiesel. This technique is an attractive procedure for obtaining accurate densities and phase transitions using a batch reactor with temperature and pressure monitoring.

To understand the relationship of temperature and pressure at a given global density, the indirect isochoric method has been proposed for this research. This is due to the fact that, at this condition, the combination of two substances in homogeneity is difficult to directly observe. Additionally, the temperature and pressure determination at constant global density by isochoric method is readily and convenient for mixture at supercritical conditions. The relationship of temperature, pressure and global density will be investigated and it can generate a diagram of temperature-pressure-global density of individual reaction. It is thus possible to locate the boundaries between the vapor-liquid phase and homogeneous regions for the reacting systems. The information obtained from isochoric method for phase boundary determination will be used in continuous production of biofuel from palm oil in supercritical ethyl acetate.

1.2 Objective of research

To produce biofuel from palm oil in supercritical ethyl acetate through continuous system and study effects of operating parameters on the biofuel production.

1.3 Scope of research

1. To study the preparation of materials and chemical reagents that involves in the experiments part I and II.

Part I: Density determination of palm oil and ETA under supercritical condition

Part II: Continuous production of palm oil in supercritical ethyl acetate

2. To investigate the relationship of temperature, pressure and global density of mixtures under supercritical conditions using isochoric method.

3. To investigate biofuel production from palm oil in supercritical ethyl acetate using a continuous tubular reactor and to study the parameters affected on products as follows;

- Effects of reaction pressure
- Effects of the reactants compositions
- Effects of mass flow rate
- Effects of reaction temperature

4. To evaluate the apparent rate coefficient and activation energy of reaction of interesterification of palm oil in supercritical ethyl acetate.

5. To determine the fuel properties of biofuel from palm oil under supercritical ethyl acetate.

6. To study the presence of water in the interesterification of palm oil in supercritical ethyl acetate.

CHAPTER II
LITERATURE REVIEWS

This chapter provides an overview of previous research on knowledge of supercritical process for biofuel production and focuses on the transesterification and interesterification reactions for clean biofuel production without glycerol formation. The literature review begins with information on current enzymatic catalytic and non-catalytic production processes. The key aspects of enzymatic transesterification and complication are reviewed. The review of catalyst-free biofuel production both via transesterification and alternative interesterification reactions are illustrated in the field and categorized for additional research.

2.1 Enzymatic transesterification

The enzyme “lipases” is considered to be one of effective biocatalysts for esterification and transesterification reactions in producing biofuel. It can break fats and oils with successive release of FFAs and glycerol [26] in non-aqueous media and organic solvents [27]. To avoid the glycerol formation, the organic solvent free method is used in the enzymatic transesterification and carboxylate esters as acyl acceptors.

Modi et al. [28] studied the preparation of biofuel from *Jatropha curcas* oil by enzymatic transesterification. The experiments were carried out in a test tube by adding Novozym-435 to a mixture of oil and ETA. The achieved products consist of FAEEs and TA instead of glycerol, which deactivates the Novozym-435 activity. At 323 K and 12 h, they obtained 91.3 wt% of FAEEs in the product at 1:11 molar ratio of oil to ETA, by using lipase 10% base on oil weight. This study suggested a reduction in the cost of operation by repetition the lipase utilization for 12 cycles and, afterwards, the results did not significantly differ, indicating that ETA had no negative effect on enzyme activity.

In addition, Su et al. [29] investigated FAEEs production using lipase in ETA by combining the extraction and transesterification into a two-step-one-pot as in situ reactive extraction system. The experimental investigation was carried out in a shaker flask at 323 K, 180 rpm and 12 h. This method delivered yields by 76.4 % FAEEs, higher than achieving from the conventional two-step hexane extraction and EtOH/KOH transesterification (62.5 % FAEEs in comparison).

Besides, Du et al. [30] investigated reaction of soybean oil in methyl acetate (MTA) catalyzed by lipase Novozym 435, carried out in a shaking flask at 313 K for FAMEs production. The reaction yielded 92% FAMEs and TA as by-product in 14 h with a molar ratio of oil to MTA of 1:12 and 30% of lipase base on oil weight.

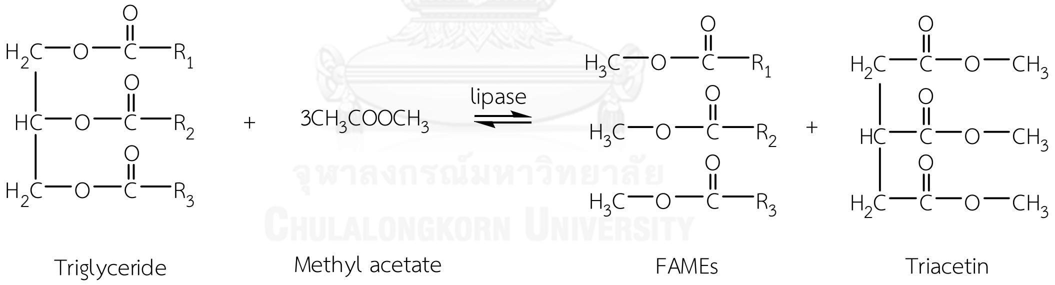


Figure 2.1 Biofuel production from enzymatic interesterification of vegetable oil and MTA.

Zhang et al. [31] investigated transesterification of palm oil using dimethyl carbonate (DMC) as acyl acceptor and immobilized-lipase Novozym 435 in solvent-free system. The obtained yields were up to 90.5 wt% of FAMEs and glycerol dicarbonate (GDC) as by-product at 328 K for 24 h with the molar ratio of oil to DMC of 1:10 and the catalyst amount of 20% Novozym 435 based on the oil weight. In addition, it was found that the Novozym 435 can be reused to catalyze the reaction for 8 cycles without loss of activity.

Although the enzymatic system can eliminate glycerol by-product, it has some restrictions as follows;

(a) An enzyme is suitable for conversion only short chain of fatty acids (FAs) [32, 33].

(b) Some chemical reagents such as methanol (MeOH), ethanol (EtOH) and glycerol in the process are toxic to enzyme [34].

(c) Enzymes are more expensive than conventional catalysts that could be affecting operation cost [35].

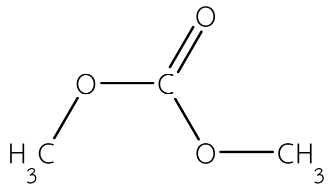
(d) A long reaction time is required especially for step-wise method.

Even though the enzyme can be reused without lost activity [36], the rate of reaction is much slower than that of conventional and heterogeneous catalysts. On the other hand, the non-catalytic supercritical technologies adapted those alternative solvents to produce the lipid-based biofuel without generating glycerol as by-product.

2.2 Non-catalytic supercritical technologies

An enzyme-catalyzed system is more tolerant of impurities and has simple post reaction separations, but it is very expensive to operation. The limitations of this process have led to exploration and development of non-catalytic processes. The non-catalytic supercritical technologies adapted those alternative solvents such as DMC, MTA, ETA and methyl *tert* butyl ether (MTBE) to conventional alcohols to produce the lipid-based biofuel without generating glycerol as by-product.

2.2.1 Dimethyl carbonate (DMC)



Dimethyl carbonate (T_c= 548 K, P_c = 4.63 MPa) [37]

DMC is interested as acyl acceptor for biofuel synthesis in the enzymatic transesterification. DMC is a multipurpose alkylating agent with nontoxic and biodegradable due to green process preparation [38]. DMC contains high oxygen content and can be blended with diesel for improved delivery and spray of diesel fuel engine [39].

Ilham and Saka [37] selected DMC as a supercritical reactant for one-step transesterification of rapeseed oil to biofuel in a batch system. The results of 94 wt% FAMEs in 12 min were obtained in this study that separated from by-products of glycerol carbonate (GC), glyoxal and citramalic acid in the lower portion which are much higher in value than glycerol. The schematic diagram of the experiment is shown in Figure 2.2.

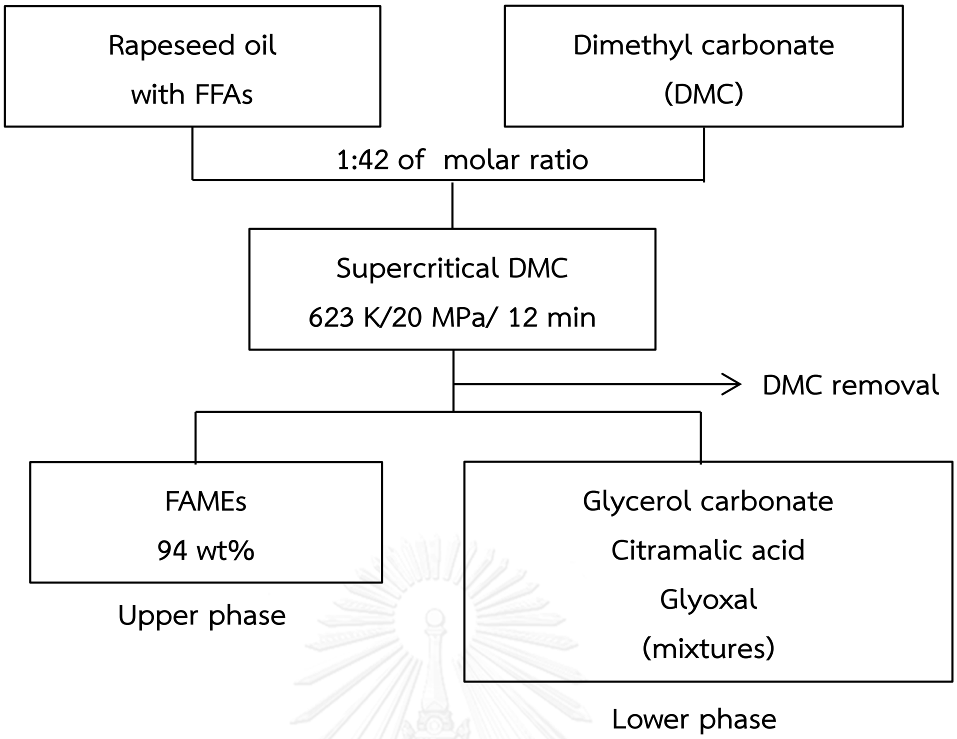
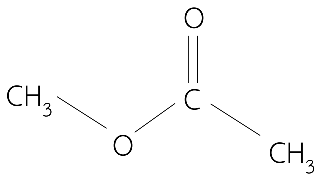


Figure 2.2 The schematic diagram of biofuel production by supercritical dimethyl carbonate treatment.

The effects of other important parameters for esters and value-added GC production from supercritical DMC condition in a batch type system were studied by Tan et al. [40]. The parameters include reaction temperature, molar ratio of DMC to oil and reaction time while they were optimized using response surface methodology (RSM) analysis. The main findings of this work are that the developed mathematical model is statistically adequate to predict the maximum yield of esters.

The supercritical DMC in transesterification process improves biofuel production and generates valuable by-products, i.e. glycerol carbonate, glyoxal, citramalic acid instead of glycerol. However, there are polar substances which are eventually separate from the ester compounds. Additionally, they have to be purified prior to further utilization in a similar manner to the case of glycerol.

2.2.2 Methyl acetate (MTA)



Methyl acetate (T_c = 507 K, P_c = 4.69 MPa) [18]

MTA is intensively interesting as this reactant converts triglycerides into FAMEs and TA as a by-product, instead of glycerol as previously mentioned in the enzymatic system. TA is a fuel additive, completely soluble in biofuel and can improve cold flow properties [19]. MTA is produced from esterification of acetic acid and MeOH over acidic catalyst [41]. It is a flammable liquid with a characteristically pleasant smell and less toxic. It can be used as a solvent with weakly polar and classified as lipophilic compounds dissolved in fats, oils, lipids, and non-polar solvents. MTA solubility is 25 wt% in water at room temperature [42].

The application of the MTA as supercritical reactant has been proposed by Saka and Isiyama [43] for non-catalytic method to transform triglycerides into FAMEs and TA, the schematic diagram of flow system is shown in Figure 2.4. Later, some researchers have been interested to use MTA as supercritical reactant in biofuel production for both batch and continuous systems [44-47].

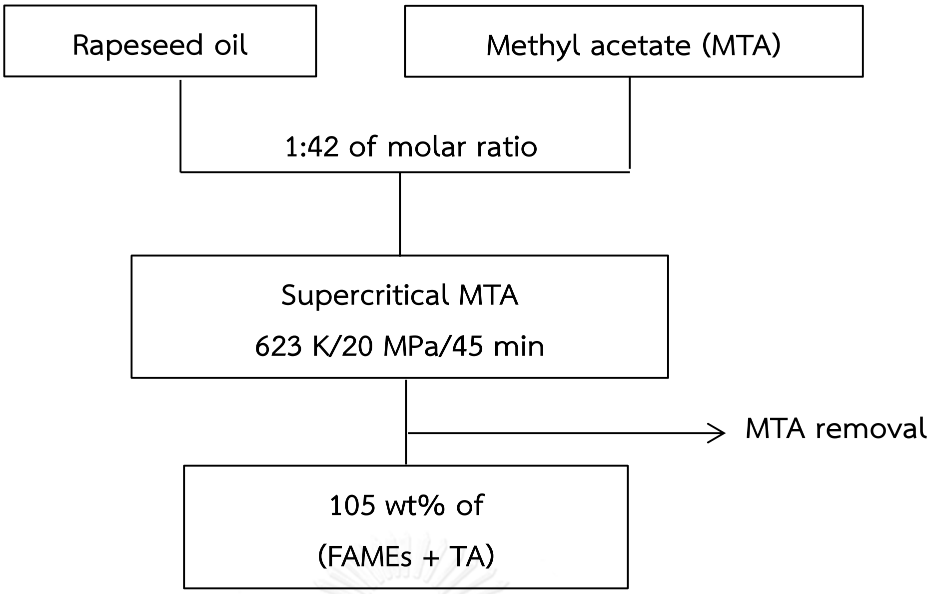
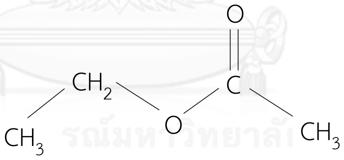


Figure 2.3 The schematic diagram of the process for biofuel production from rapeseed oil and supercritical methyl acetate [43].

2.2.3 Ethyl acetate (ETA)

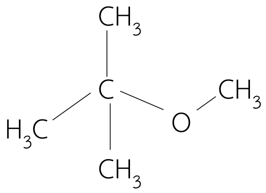


Ethyl acetate (T_c = 523 K, P_c = 3.9 MPa) [18].

The non-catalytic transesterification of vegetable oil and carboxylate esters in supercritical condition intensely depends on alkyl groups and acyl moieties of carboxylate esters. ETA is an organic solvent with fruity smell, low toxic and widely used in various industries [48]. It can be produced from an esterification reaction of EtOH and acetic acid by several processes [49, 50]; these two reactants can be manufactured from low cost agricultural waste materials [51]. In term of biofuel production, ETA has been considered as an oxygenated fuel additive in gasoline for improving octane number and exhaust gas emissions in comparison to EtOH and

MTBE [52]. ETA has been successfully used as supercritical reactant in interesterification reaction to produce FAEEs and TA in batch type reactor [18].

2.2.4 Methyl tert-butyl ether (MTBE)



Methyl *tert*-butyl ether (T_c = 497 K, P_c = 3.5 MPa) [53]

Oxygenated additives such as EtOH, diethyl ether, ethyl *tert*-butyl ether (ETBE) or MTBE are usually employed as octane enhancer for gasoline [54]. Different from diesel or biodiesel, these oxygenated compounds are additives for improving exhaust gas emissions and some properties of the fuel. Recently, Farobie et al. [53] were interested in *tert*-butyl group in MTBE to produce biofuel under supercritical conditions. They investigated biofuel from canola oil in supercritical MTBE using a flow reactor system. The canola oil was reacted with MTBE to generate FAMEs and glycerol tert-butyl ether (GTBE) without glycerol by-product. The effect of parameters such as temperature, pressure and reaction time on product yield were investigated. The optimization condition was attained at 673 K/10 MPa in 12 min with a molar ratio of oil to MTBE of 1:40 to achieve 95.36 wt% of total FAMEs and GTBE. The by-product GTBE is an advantage oxygenate additive for diesel and biodiesel [55].

2.2.5 The value added by-products from non-catalytic transesterification and applications

The value added by-products from each supercritical reactant can be used in different applications such as improve fuel properties or used as a raw material in pharmaceutical and agrochemical industries [56]. In general, these by-products can be directly produced from glycerol separated from biofuel or oleochemical manufacturing [57]. The crude glycerol has been increasing with expansion of biodiesel production. Therefore, it gains interested in using glycerol as building block for business of high added value chemical products [58]. The schematic reaction of selected glycerol derivative for different compounds through several chemistry routes was shown in Figure 2.4 [57].

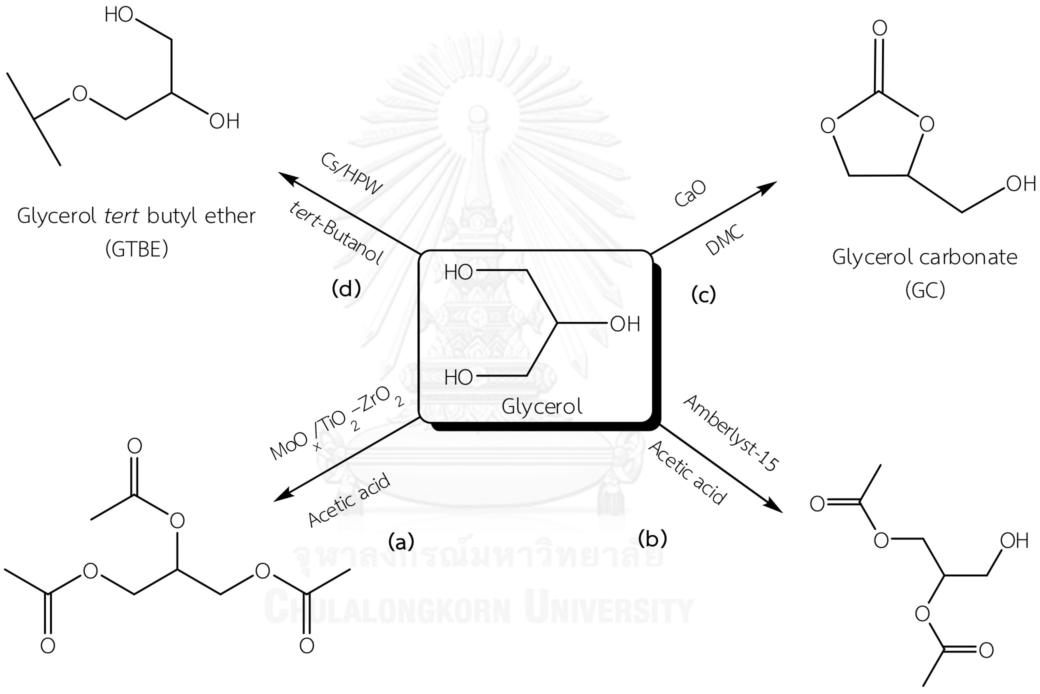


Figure 2.4 The catalytic reaction of glycerol to produce various oxygenated additives.
(a) acetylation/esterification [59] **(b)** acetylation/esterification [60]
(c) transesterification [61] **(d)** etherification [62]

The value added by-products in Figure 2.4 were catalytically synthesized via chemical reactions utilizing glycerol molecule as raw material and catalyzed by specific catalyst and conditions. The objective of separating GC after complete reaction is for polymer synthesis [61] while TA, DA and GTBE are classified as oxygenated additives for fuels. These oxygenated additives are added to biodiesel or diesel for a cleaner burning, ignition improvement, higher efficiency combustion, more stable fuel mixtures, more ability to protect the motor from abrasion and wax deposition. In addition, it increases more capability to reduce pollutants of greenhouse gases emissions through complete combustion [57, 63].

2.2.6 Parameters affecting supercritical transesterification

2.2.6.1 The reaction temperature and pressure

The supercritical fluid has unique properties, similar to both gases and liquids. At temperature and pressure above their critical points, these substances exist in either gaseous or liquid phase. Similar to high density liquids, gas-like diffusivity overcomes the restriction of mass transfer between heterogeneous phases. The chemical reactions of supercritical conditions allow opportunities to control the reaction condition to eliminate interphase transport limitations [64, 65].

Tan et al. [40] investigated for optimization study of supercritical DMC technology for biodiesel and value-added GC production in batch reactor and found that FAMEs and GC increased with high DMC concentration when the temperature was 603 K. However, reaction rate at low temperature is usually slow due to poor solubility between oil and DMC which forms a two-phase mixture. The optimum reaction conditions in this study are 643 K at the molar ratio of oil to DMC of 1:50 for 30 min.

Ilham and Saka [66] studied the transesterification of rapeseed oil in supercritical DMC using tubular flow type reactor. It was found that the esters yield decreased when operated the reaction for 30 min at temperature above 543 K, the DMC tended to decompose at 5 MPa and 10 MPa to CO_2 and MeOH. The stability system can be observed at higher pressures of 20 MPa and 573 K.

Niza et al. [67] studied on thermal stability of FAMEs and TA from *Jatropha curcas* oil in supercritical MTA process. The experiments were carried out in a batch-type reactor at reaction temperature ranging from 603-693 K and 20–60 min. The results revealed that the appropriate temperature for producing biofuel (1:30 of *Jatropha curcas* oil to MTA molar ratio) without thermal degradation of the products was lower than 633 K in 30 min of reaction and pressure above 4.7 MPa.

Table 2.1 The single step biofuel production under supercritical conditions

System	Molar ratio (Oil:Reactant)	Conditions (K/MPa/min)	Esters (wt%)	By-product (wt%)	Process
Palm oil-MeOH [68]	1:42	623/19/6.7	96.0	Glycerol	Continuous
Rapeseed oil-DMC [37]	1:40	623/20/12	94.0	GC	Batch
Soybean oil-MTA [46]	1:42	618/20/50	100	TA (4.0)	Batch
Rapeseed oil-MTA [45]	1:42	623/20/45	96.7	TA (8.8)	Continuous
Canola oil-MTBE [53]	1:40	673/8/12	94.0	GTBE (1.36)	Continuous

From Table 2.1 for supercritical DMC, MTA and MTBE system, the reaction temperatures for obtaining satisfied yield of total products (esters and synthetic oxygenates additive) were higher than 618 K. In supercritical condition, increasing reaction temperature enhances reaction rate to obtain higher yields and decreases hydrogen bonding, resulting in a stronger nucleophilic attacks the carbonyl compound [53, 69]. The molecular structure of MTBE is steric bulkier compared with others, therefore, this system requires a higher temperature to enable the transesterification reaction to proceed completely.

The reaction pressures for all system of up to 15 MPa excepted for the reaction pressure in supercritical MTBE [53] system were lower than MTA. This is due to that, in the experiment, yield of FAMEs increased with increasing pressure from 6 to 8 MPa and the yield was relatively constant for the pressures higher than 8 MPa; the results are illustrated in Figure 2.5.

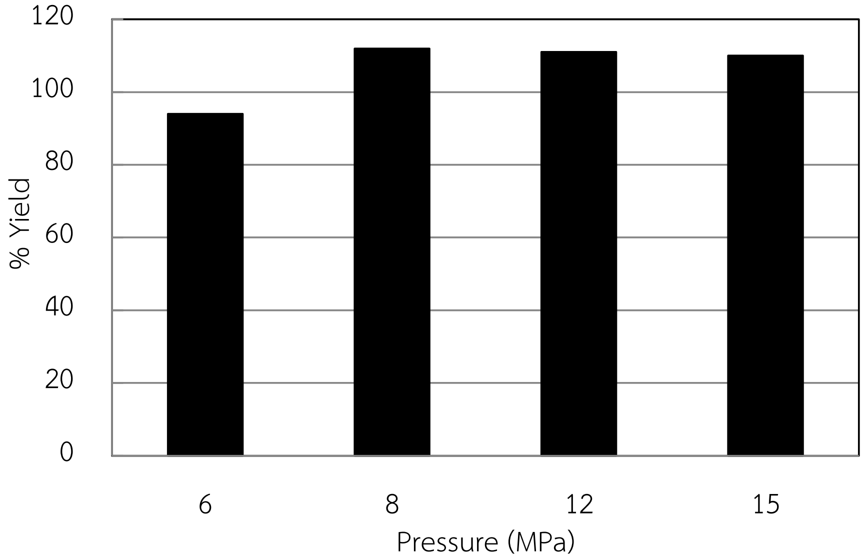


Figure 2.5 Effect of pressure on FAMEs yield (623 K, molar ratio of oil to MTBE of 1:40 and 5 min) [53].

2.2.6.2 The composition of the reactants

The composition of the reactants is one of the important parameters for assessment of quantity of product and system cost, in terms of raw materials. The stoichiometric molar ratio of TGs to co-reactant such as MTA and MTBE is 1:3 [18, 53] but this ratio cannot accomplish the complete reaction. In practice, excess amount of co-reactant was required by the reaction to drive the reversible transesterification to forward side to produce more esters in supercritical condition [11].

From Table 2.1, the molar ratios of oil to reactant employed in supercritical condition were at high amount for avoiding the reversible reactions. It can be observed that lower composition of oil to reactant provides lower yields for all systems. The alternative supercritical reactant of DMC, MTA and MTBE systems shows the value added by-products simultaneously formed during the reaction. These synthetic compounds were oxygenated and usually are used with diesel and biodiesel for improving engine combustion and emission characteristics.

2.2.6.3 The water addition to supercritical fluids reaction

In catalytic transesterification of vegetable oils and alcohols to ester compounds, the oil utilized as raw material have to be water-free as the entrained water can reduce catalyst efficiency and increase FFAs from TGs hydrolysis which causes saponified-products. However, supercritical technology for biofuel production does not use catalyst circumvents a complication of water addition or contamination in the oil.

In the supercritical transesterification, the condition requires high temperature and pressure to drive the reaction forward to products according to the study of Kusdiana and Saka [70] in the effects of water on biodiesel production from supercritical MeOH treatment in a batch type system. The results reflect that the water in vegetable oil enhances methyl ester content from three reactions of transesterification and hydrolysis of triglycerides as well as methyl esterification of FAs. In addition, this method has a feature of easier product separation as glycerol by-product of transesterification is more soluble in water than in MeOH.

Doná et al. [44] studied biofuel production from vegetable oils with different FFA and water content using supercritical MTA as reactant in a tubular packed bed reactor. The results have revealed that the highest yield of 83 wt% was obtained from macauba oil at 598 K/20 MPa/45 min and molar ratio of MTA to oil was 50 with 17 wt% decomposition. It was also found that water content in oil feedstocks played an important role in the process as TGs in the oil was hydrolyzed to acetic acid which can improve the yields due to its catalyst effect and reduce the thermal degradation of TA.

2.2.6.4 Phase behavior and density of supercritical reactants

The phase behavior of two reactants mixture in the process is an important consideration in biofuel production. The first generation of supercritical transesterification of vegetable oil and short chain alcohols for liquid fuel production has been concerned as this reaction perform faster in a single phase than in a multiphase system [71].

The supercritical reactants were assessed as alternative reactant which can replace conventional alcohols. Their structures and polarity characteristics can solvate vegetable oil at room temperature and can significantly fast drive the reaction without limitation of phase separation. This advantage can encourage the reaction at condition above their critical points and accomplish to obtain products in a short time. However, the phase behavior of mutual solubility of two reactants can be observed at room condition but this does not mean that chemical reaction appears to occur. Therefore, the critical properties of pure fluid and binary mixtures are necessary to determine the phase behavior of the reacting mixtures at supercritical conditions [72].

The values of critical pressure and temperature as well as other key properties of the pure substances used for data calculation from the Peng-Robinson equation of state (PR EOS) for predicting the vapor pressure and phase behavior near the critical temperature of single-component system was achieved [73] in Eqs. 2.1-2.6.

$$P = \frac{RT}{V-b} - \frac{a}{V(b+V)+b(V-b)} \qquad 2.1$$

where

$$a = \frac{0.45724\alpha(T)R^2T_c^2}{P_c} \qquad 2.2$$

$$b = \frac{(0.077796RT_c)}{P_c} \qquad 2.3$$

$$\alpha = (m(1-\sqrt{T_R}) + 1)^2 \qquad 2.4$$

$$m = 0.3463+1.54226\omega-0.26992\omega^2 \qquad 2.5$$

$$T_R = \frac{T}{T_c} \qquad 2.6$$

Where P is the pressure (MPa), R is the universal gas constant (8.314 cm^3MPa $K^{-1}mol^{-1}$), T is the temperature (K), and V is the molar volume (cm^3). The parameters *a* and *b* are EOS parameters, respectively. The ω is acentric factor (Ω) and subscript c presents critical properties of pure compounds.

The phase behavior of the mixtures associated with phase boundary and pressure-volume-temperature (PVT) [74] for phase transition in supercritical regions have been concerned. To observe the phase change from liquid-vapor (LV) to a single-phase of supercritical fluid phase, it could be monitored and confirmed by conducting experiments at a high temperature and pressure view-cell [75]. However, this technique is complicated as the visual observation at the boundary between interphase during liquid begins to condense may be difficult to distinguish in these phenomena.

An isochoric technique has been applied for observation and correction the phase transition points [76]. The isochoric method can dignify the relationship of conditions at phase boundaries for mixtures proved by thermodynamic identities for density and for entropy as a function of temperature, pressure, and composition [77]. The densities of mixtures at supercritical conditions are important data for chemical process design in continuous system [78]. The reacting mixture at specific volume at the operating conditions plays an important role in volumetric flow rate of a compressible fluid mixture and relates to residence time calculation [79, 80].

Velez et al. [24, 25] used isochoric method to determine the phase transitions points and relationship of temperature and pressure at a specific global density with known compositions of oil/alcohol mixtures in a constant volume reactor. At the specific global density, during temperature raised, both pressures and temperatures were stabilized and recorded then generated PVT diagram. The phase transition point from LV region to homogeneous region of supercritical phase obtained from discontinuity of slope of the isochoric line.

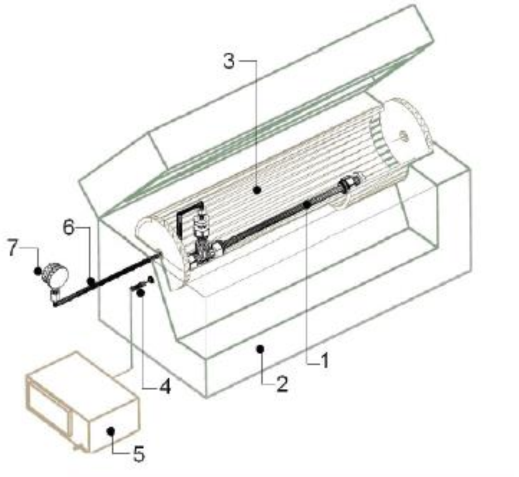


Figure 2.6 Schematic diagram of isochoric apparatus: (1) constant-volume reactor, (2) electric oven, (3) aluminum foil, (4) temperature sensor, (5) process control equipment, (6) silicone line, (7) pressure gauge [24].

These authors [79] also used isochoric method to predict density of mixture in continuous system at specified experimental condition for produce FAEEs in the operation conditions of oil:EtOH molar ratio of 1:40, temperature and pressure range of 573– 618 K and 16.5–20.0 MPa and mass flow rates of mixture varying from 3 to 16 g/min. The correlation for binary interaction parameters of the PR EOS with the classic quadratic mixing rule were used to estimate volumetric properties and residence time. In the range of operating conditions, it attained up to 90 wt% of FAEEs.

2.2.6.5 Kinetics of non-catalytic transesterification

The volumetric properties have a direct influence in the calculation of residence time and reaction kinetics [79]. The kinetics of alcohol transesterification are controlled by the mass transfer rate in the two phase system [81]. The supercritical reactants, MTA and ETA, are miscible with oil at room condition and, therefore this limitation is overcome and can decrease temperature and pressure of supercritical systems to obtain products. However, there have been a few researches to model the kinetics of non-catalytic transesterification. The kinetics model with the first order reaction from transesterification in supercritical condition as Diasakou et al. [82] investigated non-catalytic thermal transesterification of soybean oil with MeOH at 493 and 508 K in batch system.

There were some studies for kinetics of non-catalytic transesterification in different high temperature to determine a rate constant with temperature dependency, consequently to the improved rate of reaction. The activation energy (E_a) of transesterification without catalyst was calculated by Arrhenius equation.

Campanelli et al. [46] evaluated the apparent rate coefficients (k) and activation energies (E_a) for synthesized biodiesel from vegetable oil in supercritical MTA transesterification in a batch reactor. The system employed high amount of MTA and, therefore, the reversible reaction can be ignored. They used a pseudo-first order reaction with respect to TGs concentration (C^{oil}) where k is the apparent rate coefficient. The following equation for a batch reactor is obtained in Eq 2.7 and integrated to Eq 2.8:

$$-dC_t/dt = kC^{oil} \qquad 2.7$$

$$\ln (C^{oil}/C_0^{oil}) = \ln k \qquad 2.8$$

The various k with temperature were plotted and fitted with the Arrhenius first order. The E_a was calculated in Eq. 2.9.

$$\ln k = \ln A - E_a/RT \qquad 2.9$$

2.3 The major properties of biodiesel

2.3.1 Density

Density is a key fuel property, which directly affects the engine performance [83]. As fuel injection pump meters fuel by volume, not by mass, a greater or lesser mass of fuel is injected depending upon its density. Thus, the air–fuel ratio and energy content within the combustion chamber are influenced by fuel density. In general, density of biodiesel is slightly higher than that of petroleum diesel.

2.3.2 Kinematic viscosity

Viscosity is a critical property because it affects the behavior of fuel injection. In general, higher viscosity leads to poorer fuel atomization [84]. High viscosity can cause larger droplet sizes, poorer vaporization, narrower injection spray angle, and greater in-cylinder penetration of the fuel spray. This can lead to overall poorer combustion, higher emissions, and increased oil dilution. The viscosity of biodiesel is typically higher than that of petroleum diesel.

2.3.3 Iodine value

The iodine value as one of those quality parameters measures the degree of unsaturation present in a biodiesel composition [85]. The unsaturated fatty acids (existence of double bonds) are susceptible to the oxidation reactions that can lead to the formation of polymeric compounds by heating. Moreover, these polymeric compounds can produce gum and induce water, which is detrimental to the vehicle engine due to its corrosive actions. For determining the iodine value in biodiesel, the standardized procedures use volumetric titration with starch as an indicator as the main technique for iodine value measurement.

2.3.4 Cold flow properties

One of the major problems associated with the use of biodiesel is poor cold flow properties indicated by relatively high cloud points (CP), the temperature at visible indication of paraffin wax in fuels. Solids and crystals rapidly grow and agglomerate, clogging fuel lines and filters and causing major operability problems.

CHAPTER III
EXPERIMENTAL

The objective for continuous production of palm biofuel in supercritical ethyl acetate is to study the effect of parameters such as density of mixture at experimental conditions, reaction temperature and pressure, reactant composition, mixture flow rate and kinetics parameters on the ester yield. Among that, the density of mixture at supercritical conditions significantly affects reaction condition for the designed experiment in continuous system. Therefore, the experiments in this section were separated in two parts as follow; the density determination of palm oil and ETA in supercritical condition and the biofuel production from palm oil in supercritical ETA using continuous tubular reactor.

3.1 Density determination of ethyl acetate-palm oil mixture under supercritical condition

3.1.1 Materials

The compounds used in this experiment were ETA (99.97% from Fisher Scientific) and palm oil (with a major fatty acid composition w/w of 37% palmitic acid, 46% oleic acid and 11% linoleic acid). The palm oil was obtained from Morakot Industries Co., Ltd.

3.1.2 Apparatus and experimental procedures

The measurement cell configuration is shown in Figure 3.1 [24]. The global density of ETA and palm oil mixture was calculated from the known mixture weight divided by the cell volume. The dimension of the measurement cell made from SUS316 stainless steel are 0.95 cm outside diameter and 50 cm length with a working volume of 23 cm^3 by water substitution at room temperature. A tubular furnace from Lenton, model 2416CG, was used as a heating source. This cell was insulated with ceramic fiber and aluminum foil to stabilize the inside temperature during the measurement. The pressure in the cell was measured by a high-temperature, tube and socket pressure gauge, model EN 837-1 (Fantinelli Srl, Italy) with a 10 cm panel diameter.

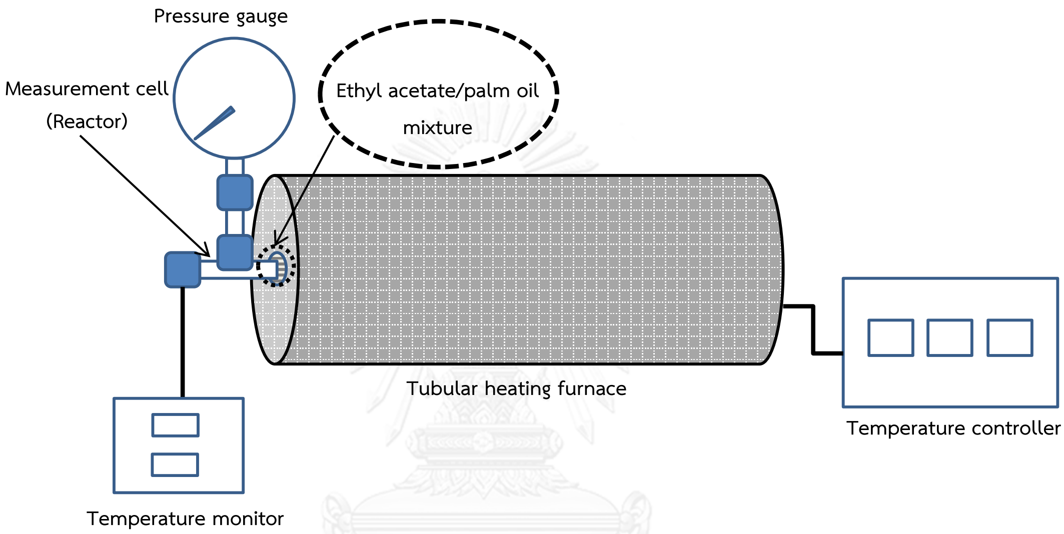


Figure 3.1 Schematic diagram of density determination of palm oil-ethyl acetate mixture in supercritical condition.

At the beginning, the predetermined masses of ETA and palm oil were added to the cell. The temperature was increased slowly at the rate of 5 K/min from room temperature to 673 K. During the temperature increment, both pressure and temperature were stabilized and recorded. In this way, the pressure variations with temperature of mixtures of a given mass charged into the cell were measured; the global density (mass charged divided by cell volume) was known for each run.

This information provided the variation of one value of density with temperature and pressure over the range of 303 K to 673 K and 3.0 MPa to 15.0 MPa By repeating this procedure for different densities and reacting mixture compositions, the values of density over the range of conditions required were subsequently attained. To obtain precise transition points, all conditions were repeated for three times; repeatability and reproducibility can be achieved. In each condition, the results shown in later sections represent average values with error bars at 95% confidence.

In order to accurately correlate the pressure measurement of the palm oil-ETA system, the experimental measurement values were compared with the data calculation from the PR EOS [73] for predicting the vapor pressure and phase behavior near the critical temperature of single-component system. The values of critical pressure and temperature as well as other key properties of the pure substances (palm oil and ETA) used in this study are listed in Table 3.1 [86, 87].

Table 3.1 Characteristics of pure compounds

Substance	T_c (K)	P_c (MPa)	Mw (g/mol)	ω
Palm oil [86]	954	0.36	850.0	1.800
Ethyl acetate [87]	523	3.88	88.11	0.362

3.2 Continuous production of palm oil under supercritical ethyl acetate

3.2.1 Materials

The refined palm oil used in this experiment was from Morakot Industries Co., Ltd. The fatty acid compositions of the palm oil are given in Table 1 [88]. The ETA (99.97% purity) used for the reaction and the analysis was obtained from Fisher Scientific (UK), and FAEEs, TA, and DA were purchased from Sigma-Aldrich (Germany). The TGs was represented as triolein. The pure FAEEs, triolein, and TA were used to generate an external calibration curve.

Table 3.2 The fatty acid composition of palm oil

Fatty acid	Composition (wt%)
C12:0	0.4
C14:0	0.8
C16:0	37.4
C16:1	0.2
C18:0	3.6
C18:1	45.8
C18:2	11.1
C18:3	0.3
C20:0	0.3
C20:1	0.1

3.2.2 Apparatus and experimental procedure

The experimental setup of the continuous biofuel production system is schematically shown in Figure 3.2. Supercritical interesterification was conducted using a tubular reactor with a volume of 189 cm^3 made of stainless steel tubing (550-cm long with an internal diameter of 0.635 cm). The reactor was placed in a fluidized sand bath, electrically heated, and controlled by a temperature controller (Sigma Model SF48, USA). The reactor was monitored by two K-type thermocouples directly connected at the inlet and outlet of the reactor inside the bath. The reactor also comprised a back-pressure regulator (Swagelok, UK) and external cooling water for cooling down the obtained product.

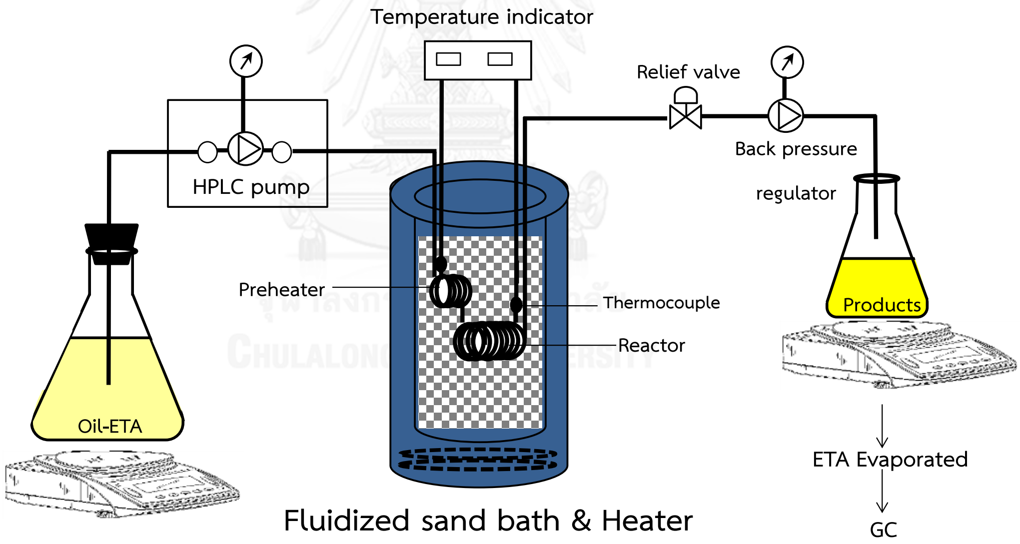


Figure 3.2 Schematic of continuous interesterification of palm oil in supercritical ethyl acetate.

When the operating condition reached a steady state [79], the mixture of palm oil and ETA stored in a beaker was fed into the reaction system by a high-pressure liquid pump (Model P-50, Thar Technology, USA). The reactant mixture was heated and pressurized under a desired condition. After the residence time (the expected time needed from entering at the input of the flow system to exiting at the output [89]) had passed for three times, approximately 50 cm^3 of the liquid product was collected in a glass flask and placed at the reactor outlet. The product was weighed and put in a rotary evaporator to remove excess ETA. The FAEEs and by-products were then quantitatively analyzed by gas chromatography (GC). To investigate the effects of water on the production of FAEEs and TA products, a predetermined amount of water was initially measured and added to the reaction mixture. The resultant mixture was then examined for FAEEs and TA using GC using the aforementioned procedure.

3.2.3 Analysis of reaction products

Excess ETA in the sample product was first removed by a rotary evaporator (Heidolph, Germany). The product was then weighed, and ~ 0.1 g was sampling and dissolved in n-heptane. Subsequently, 1 μl of the prepared sample was injected into a GC. External calibration curves were generated using 0.02–0.10 g of standard ethyl palmitate, ethyl oleate, and ethyl stearate dissolved in n-heptane. Calibration curves were then generated by curve fitting as a straight line, with $R^2 \geq 0.999$.

The intermediate compounds (a mixture of monoacetin and DA) [18] and the by-product TA produced by supercritical interesterification of the palm oil and ETA were quantitatively analyzed. As the boiling point of DA (532 K) and TA (531 K) is very close, their separation is difficult [90]. Therefore, the known composition of commercial TA was used as a reference standard for the calibration of the combination of DA and TA (hereafter, referred to as TAs).

The qualitative and quantitative analyses of the biofuel components were performed using a gas chromatograph (Agilent Technology Model 7890A), equipped with a capillary column (MTX-65TG, 30 m long and an outside diameter of 0.25 mm) and a FID (flame ionization detector). The temperatures of the injector and detector were set to 603 K and 653 K, respectively. The column temperature program was set to 313 K for 3 min and then increased to 643 K at a rate of 5 K/min. The total analysis time was 60 min. Helium was used as the carrier gas at a flow rate of 1 mL/min, with a split ratio of 1:30.

3.2.4 Residence time estimation

In the continuous system, the experiments were conducted at various mass flow rates (different global densities) of mixture feeds corresponding to different average residence times in the reactor. Temperatures from 593 to 673 K were used. Moreover, in addition to pressures of 14–20 MPa, molar ratios of palm oil to ETA from 1:10 to 1:35, and molar ratios of palm oil to water from 1:5 to 1:10 were utilized. The residence time (τ) in the tubular reactor was calculated using Eqs. 3.1 and 3.2 as follows [91]:

$$\tau = V/v_0 \qquad 3.1$$

with

$$v_0 = W_{feed}/\rho_{mixture\ at\ reaction\ condition} \qquad 3.2$$

where V is the volume in the reactor (about 189 cm^3), v_0 is the volumetric flow rate of the fed mixture under the system conditions (cm^3/min), W_{feed} is the flow rate of the palm oil and ETA mixture, and ρ is the global density of the fed mixture at the reaction temperature and pressure obtained from a HYSYS 3.2 process simulator (Aspen Technology, USA) and the PR EOS model.

3.3 Determination of biofuel properties

The biofuel sample obtained from the optimum condition was verified according to the international specification of the American Society for Testing and Materials (ASTM) and European Standard (EN) as follows in Table 3.3.

Table 3.3 List of fuel properties tested methods.

Properties	Unit	Test Method
Density	g/cm^3	ASTM D4052
Kinematic viscosity	mm^2/s	ASTM D445
Iodine value	g Iodine/100 g	EN14111
Cloud Point	K	ASTM D5771
Cold Filter Plugging Point (CFPP)	K	ASTM D6371

CHAPTER IV

DENSITY DETERMINATION OF PALM OIL-ETHYL ACETATE MIXTURE UNDER SUPERCRITICAL CONDITION

4.1 The PVT relationship of ethyl acetate

The pressures corresponding to the temperature of ETA obtained by experiment and calculation by the PR EOS in comparison are shown in Figure 4.1 at the constant molar volume of 9.86×10^{-4} m^3/mol. It has apparently shown that the measured data are in good agreement with those from the PR EOS, indicating that there is a potential for the further experimental results being acceptable.

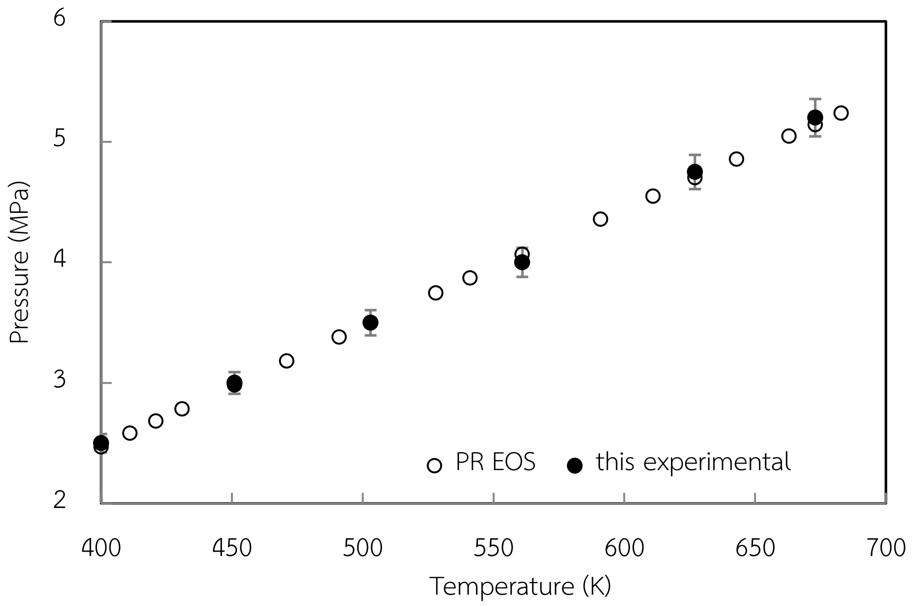


Figure 4.1 Comparison of experimental data for the ethyl acetate with predictions using the Peng-Robinson equation of state and experimental.

4.2 The PVT relationship of ethyl acetate-palm oil system

In the constant volume reactor, the relationship of pressure and temperature at constant global density or molar volume was investigated. The information during the process generates P-T diagram as shown in Fig 4.2. The discontinuity of slope of the isochoric line indicates phase transition point [92].

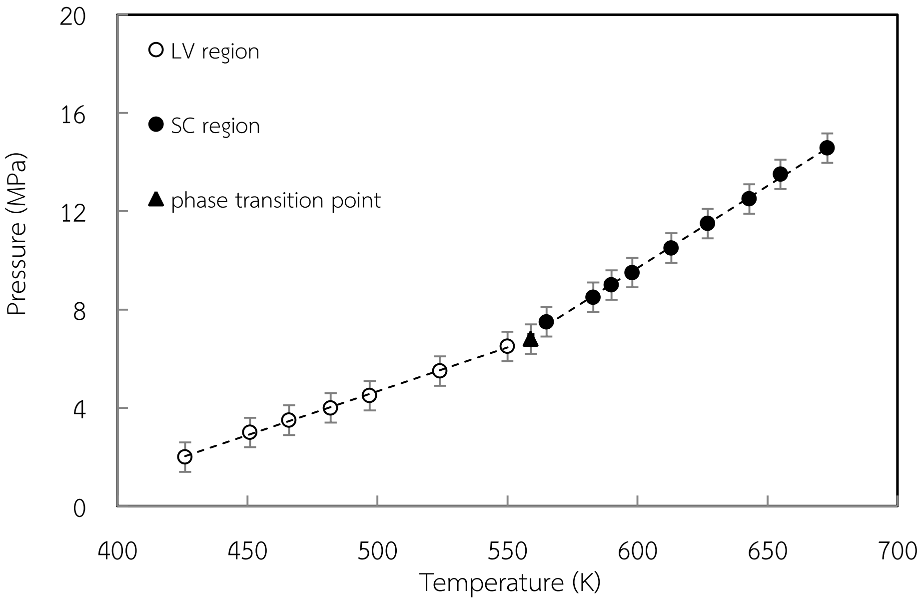


Figure 4.2 Pressure vs. temperature for the reactive mixture of palm oil:ethyl acetate molar ratio of 1:20, global density = 0.44 g/cm^3.

The palm oil is completely miscible in ETA at ambient condition. After temperature increased the vapor-liquid (LV) region of ETA-palm oil mixture changes to supercritical (SC) fluid. The pressure-temperature curve consists of two sections with separated linear isochoric lines. The lower pressure-temperature line corresponds to the LV region of the mixture. In this range, the liquid phase of ETA-palm oil mixture forms mutual solubility system while the vapor phase is ETA rich phase. It is to note that the isochoric line of the mixture has a lower slope comparing to the vapor pressure line of pure ethyl acetate (Figure 4.1) due to the low volatility of palm oil [93].

In Figure 4.2, when the phase transition point was reached, the LV phase was transformed into vapor and the system performs as a single-phase supercritical fluid. It could be deduced that the mixture in the single phase region was a monophasic dense gas; the appearance of the phase boundaries must be, however, confirmed by conducting experiments in a high temperature and pressure view-cell [75] but this technique has both strength and limitation. Visual observation at the boundary between phases may sometimes be obscured or may be poor or absent [94]. In Figure 4.2, phase transition point of the mixture was observed at 553 K and 6.6 MPa where it is above the critical point of pure ETA (0.308 g/cm^3). The phase transition points of palm oil-ETA systems at different compositions and global densities were tabulated in Table 4.1.

Table 4.1 Phase transition points of ethyl acetate-palm oil systems at various conditions

Oil:Ethyl acetate Molar ratio	Global density (g/cm^3)	Phase transition point Temperature (K)	Phase transition point Pressure (MPa)
1:10	0.26	–	–
	0.35	572	7.4
	0.44	570	7.2
	0.53	559	6.7
1:20	0.26	–	–
	0.35	558	6.8
	0.44	553	6.6
	0.53	549	6.1
1:30	0.26	–	–
	0.35	541	6.1
	0.44	537	5.9
	0.53	533	5.7

(T_c and P_c of palm oil = 954 K/0.36 MPa and ETA = 523 K/3.88 MPa, respectively)

The phase transition points in Table 4.1 were assumingly observed as critical points of the mixture at different compositions. The mixtures have lower critical temperature than that of palm oil and slightly higher than that of ethyl acetate. As the mixtures contain ETA in greater proportion than palm oil, the critical temperature of mixture is close to that of ETA rather than palm oil.

4.3 The effect of global densities and molar ratio of ETA to palm oil

The P-T diagram of molar ratio of ETA: palm oil and global densities varied from 0.26 to 0.53 g/cm^3 in this study are shown in Figure 4.3-4.5. The slope of P-T diagram slightly changes at the individual phase transition point corresponding to its global density, except at the global density of 0.26 g/cm^3. In lower pressure (3-7 MPa) and temperature (400-560 K) region, the mixture with a higher density generated a higher pressure. Within the SC region, the mixture that has higher global density simultaneously shifts the transition point to the lowered temperatures and pressures. The obtained results are in agreement with Hegel et al. [95] who reported that the phase transitions in a dense liquid phase depend mainly on the reactant concentration and global density.

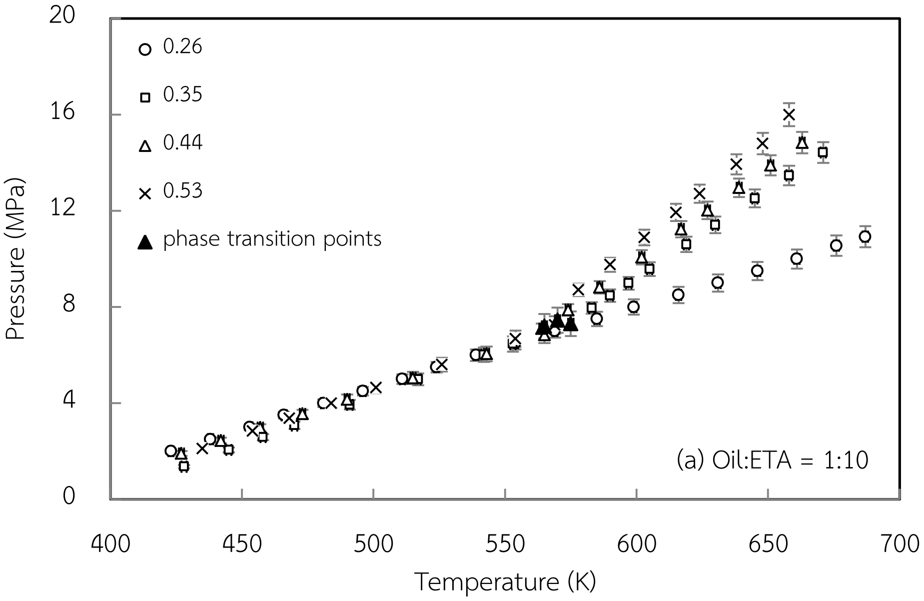


Figure 4.3 Pressure vs. temperature of ethyl acetate and palm oil mixtures in molar ratio of 1:10 in different global densities.

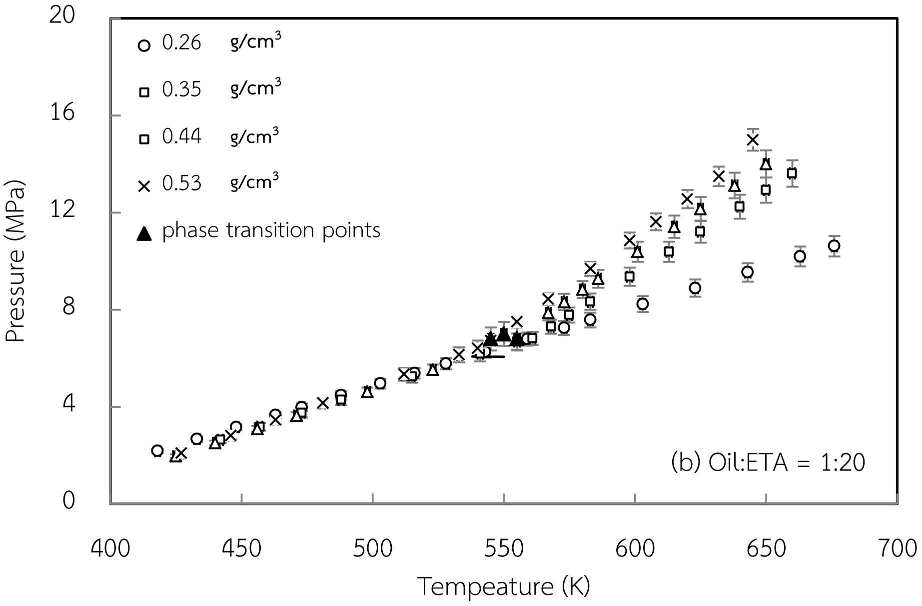


Figure 4.4 Pressure vs. temperature of ethyl acetate and palm oil mixtures in molar ratio of 1:20 in different global densities.

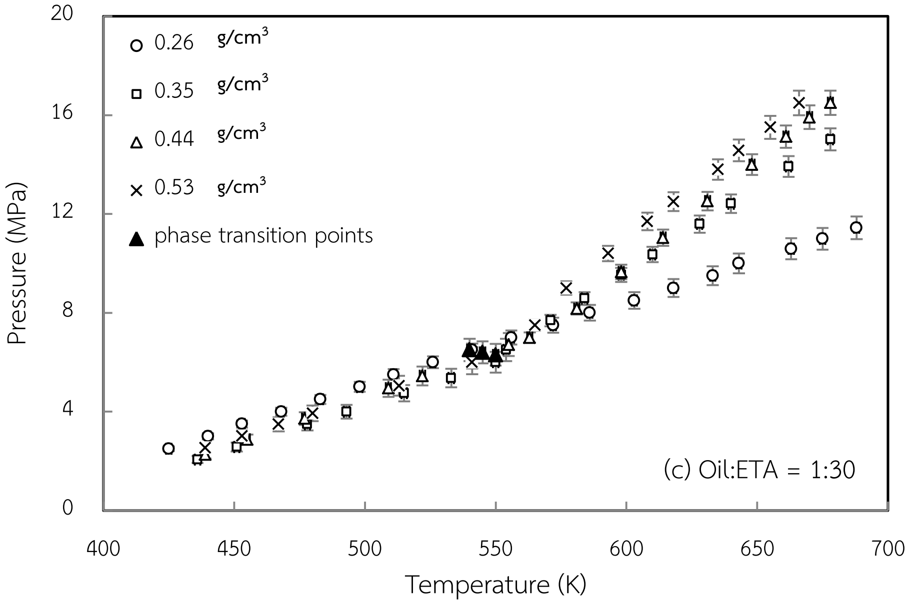


Figure 4.5 Pressure vs. temperature of ethyl acetate and palm oil mixtures in molar ratio of 1:30 in different global densities.

In the LV region in Figure 4.3– 4.5 (left hand side of the phase transition point), the pressure-temperature slopes for all densities are nearly identical. Konynenburg and Scott [96] described the phase behavior of a binary mixture that the critical point of the mixture was located at where the density and composition of the two phases are assembling. Therefore, the critical points of ETA-palm oil mixture at different molar ratios in this study were predicted as phase transition points. It can also be seen in Figure 4.3–4.5 that at the density of 0.26 g/cm^3 of all the molar ratios of ethyl acetate to palm oil, there is no transition point, due to the density of the mixtures lower than the critical density of ETA.

Table 4.2 Pressure and temperature at phase transition of a reacting system in supercritical reactor

System	Molar ratio	global density (g/cm^3)	Phase transition point Temperature (K)	 Pressure (MPa)
Sunflower oil/EtOH [25]	1:40	0.44	588	11
Palm oil/ethyl acetate (this work)	1:30	0.44	553	6.6

Velez et al. [25] determined the phase transition of sunflower oil and EtOH mixture in supercritical condition using isochoric method. Comparing to the palm oil/ethyl acetate mixture, the phase transition points of the two systems at constant global density of 0.44 g/cm^3 are shown in Table 4.2. The phase transition point of the sunflower oil/EtOH mixture was significantly higher for temperature and pressure than this work. It can be presumed that the sunflower oil/ EtOH mixture requires high temperature and pressure to transform heterogeneity towards homogeneity. It is to note that the higher molar ratio of EtOH to sunflower oil generates a rich vapor phase of EtOH, increasing the system temperature and pressure. In addition, the polarity of vegetable oil and reactant at room temperature affects the solubility of mixture and phase transition points in supercritical condition [97].

4.4 Summary

The non-catalytic interesterification of palm oil in supercritical ethyl acetate in continuous system to produce biofuel is complex to understand thermodynamic properties during extreme condition, particularly density of two reactants. In this chapter, an indirect procedure for density measurement of palm oil and ETA mixture in a batch system at high temperature and pressure was experimentally investigated using isochoric method. Its apparatus comprise a constant volume reactor which was individually loaded with a mixture of palm oil and ETA in different molar ratios (10:1 to 30:1) and global densities (0.26 to 0.53 g/cm^3). During temperature increment, the changing of pressure was recorded in real-time to obtain the pressure-temperature relationship. After measuring the change of pressure at various global densities, the pressure-temperature related specific global density diagram was successfully constructed. At high global densities and high molar ratios of palm oil to ETA, the transition point took place closing to the estimated phase boundaries separating the region of vapor-liquid and homogenous phase of the mixture. The results will be further employed as database for accurate residence time calculation in continuous reactor, especially for biofuel production from palm oil in supercritical ETA.

CHAPTER V

CONTINUOUS PRODUCTION OF PALM BIOFUEL UNDER SUPERCRITICAL ETHYL ACETATE

5.1 Interesterification of palm oil in supercritical ethyl acetate

ETA is a volatile organic compound, which is produced by the reaction of EtOH and acetic acid and yields water as a co-product. ETA is relatively nontoxic and environment friendly. Under ambient conditions, TGs in palm oil and ETA dissolve due to their non-polar properties. The mixture of palm oil and ETA was subjected to high temperature and pressure to produce FAEEs and TA. The stoichiometric ratio for the interesterification reaction requires 3 moles of ETA and 1 mole of TG to yield 3 moles of FAEE and 1 mole of TA. The fuel yield of interesterification ((FAEEs and TA mixture) was 123% based on input triglyceride weight [18]. The interesterification of palm oil and ETA is depicted in Figure 5.1.

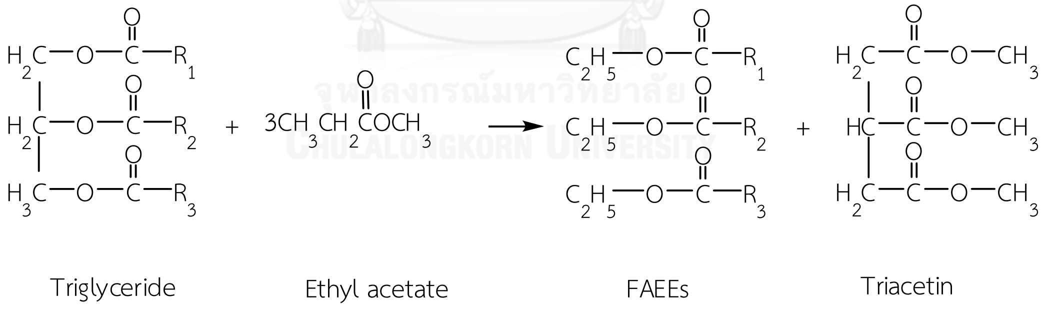


Figure 5.1 Interesterification reaction of triglycerides and ethyl acetate to produce FAEEs and triacetin.

5.2 Effect of reaction pressure

The pressure and temperature exert important effects on supercritical fluid. The effects of the pressure on the interesterification of the palm oil in the supercritical ETA were investigated in a tubular flow reactor with a back-pressure regulator. The pressure range evaluated was based on previous studies of vegetable oil in supercritical carboxylate esters [18]. The temperature and molar ratio of the palm oil to ETA were kept constant at 623 K and 1:30, respectively. The palm oil and ETA mixture was fed into the reactor at a flow rate of 2.3 g/min and various pressures of 14, 16, 18, and 20 MPa. Table 5.1 shows the effect of the different reaction pressures on the global densities of the mixture and the residence time. When feeding the mixture at a constant mass flow rate, the density of the mixture changed with alternate pressure. In this study, the subsequent residence times were 32–38 min.

Table 5.1 The effects of pressure on FAEEs and TAs yield from palm oil in supercritical ETA in molar ratio of palm oil to ETA of 1:30 at 623 K of reaction temperature

P (MPa)	$\rho^*_{mixture}$ (g/cm^3)	W_{feed} (g/min)	v_0 (cm^3/min)	τ (min)
14	0.4005	2.3	5.743	32.91
16	0.4219	2.3	5.452	34.67
18	0.4401	2.3	5.226	36.16
20	0.4558	2.3	5.046	37.45

* = density at reaction condition calculated from PR EOS by AspenTech software.

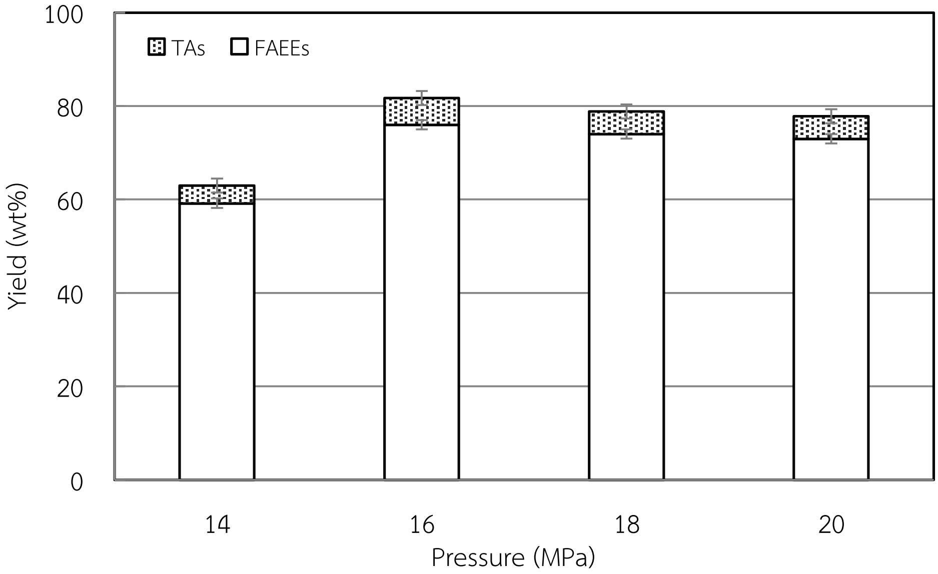


Figure 5.2 Effects of pressure on the FAEEs and TAs yield in the interesterification of palm oil and ethyl acetate under supercritical condition at 623 K, 1:30 molar ratio of palm oil to ethyl acetate, and 2.3 g/min mixture flow rate.

Figure 5.2 shows the effects of the pressure on the ester products in the experiment. At 14 MPa, the FAEEs yields were relatively low compared to the yields at higher pressures. Similar results were obtained for the TAs content at all the reacting pressures. It appears that the reaction pressure was insufficient for the mixture to reach a supercritical state, and the pressure was inadequate for the formation of a large quantity of TAs. At the higher reaction pressure of 16 MPa, the ester yields increased. The increase in the pressure improved the density and solubility [98, 99]; therefore, the collision frequency between the reactants increased [100]. The pressure-dependent density is a unique property of this supercritical fluid [101].

However, when the reaction pressures increased to 18 and 20 MPa, the ester products decreased from 76.9 wt% to 74.8 and 74.1 wt%, respectively. The results indicate that increasing the pressure does not always significantly improve the ester products, as reported by He et al. [102] and Bunyakiat et al. [103]. Furthermore, other flow rates (1.5 and 3.3 g/min) at constant temperature of 623 K and molar ratio of palm oil to ethyl acetate of 1:30 and different pressures were also studied. The results showed a similar trend to a flow rate of 2.3 g/min, that is, the maximum yield was obtained at a reaction pressure of 16 MPa.

5.3 Effect of the composition of the reactants

The molar ratio of palm oil to ETA is one of the most important variables affecting the yield of FAEEs in supercritical interesterification. In non-catalytic reactions, increasing the reactant to oil molar ratio encourages the reaction of interesterification [104]. In a continuous biofuel production system, the reaction requires a large amount of ETA to drive the reaction and requires the complete conversion of TGs. Excess ETA has to be removed from the product following the completion of interesterification. The recovery of unreacted ETA increases recovery costs. To evaluate the optimum molar ratio of palm oil to ETA under a supercritical condition, the stoichiometric molar ratio of TGs in the interesterification of the palm oil to ETA was 1:3. However, these ratios cannot accomplish the interesterification reaction. Therefore, a 1:10 to 1:35 higher molar ratio of palm oil to ETA is needed to stimulate the reaction.

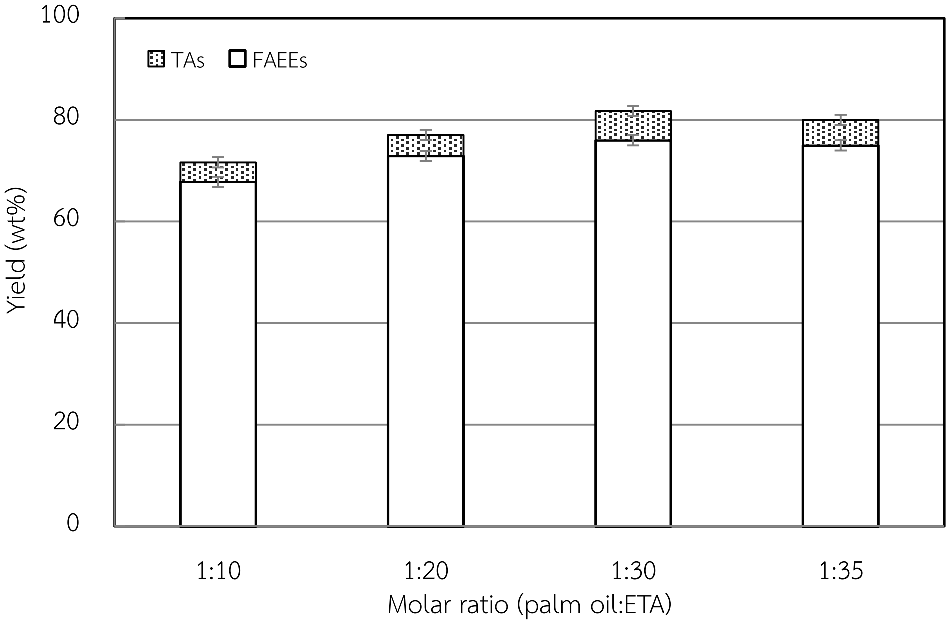


Figure 5.3 Effects of molar ratio of palm oil to ethyl acetate on FAEEs and TAs yield under supercritical condition at 623 K, 16 MPa, and 2.3 g/min mixture flow rate.

Figure 5.3 depicts the effects of the molar ratio of palm oil to ETA in the range of 1:10 to 1:35 at 623 K, 16 MPa, and a 2.3 g/min mixture flow rate on the production of FAEEs and TAs. The maximum yield of FAEEs and TAs (82.1 wt%) was achieved at a 1:30 molar ratio of palm oil to ETA. As interesterification is a reversible reaction [105], an excess of ETA causes an equilibrium shift backward and causes a decrease in FAEEs and TAs. Thus, a 1:30 molar ratio of palm oil to ETA is optimal to obtain maximum yields of FAEEs and TAs. The portion of TAs increased in accordance with an increase in the palm oil to ETA ratio. This is in-line with the interesterification reaction.

The results were compared with previous research of the continuous production of FAEEs from sunflower oil in supercritical EtOH [79] in a 1:40 molar ratio of oil to EtOH. In that study, 90 wt% FAEEs was achieved at higher pressure and temperature

(19 MPa, 618 K) and a greater amount of EtOH was required to produce FAEEs. In addition, post-treatment was required for glycerol separation.

5.4 Effect of mass flow rate and reaction temperature

The effects of the mass flow rate and the reaction temperature on the production of FAEEs and TAs were investigated. All the experiments were performed in a range of 1.5–3.3 g/min under different temperatures, at a constant reaction pressure of 16 MPa. The mass flow rate of the mixture, corresponding to the different estimated residence times in the continuous reactor [91] are shown in Table 5.2 and Figure 5.4, respectively. The residence times decreased when the mass flow rate of the mixture was increased at a constant temperature and pressure. The calculated residence time was also dependent on the temperature, thus, an increase in the temperature resulted in a decrease in the residence time.

Table 5.2 The experimental data of palm oil in supercritical ethyl acetate at 1:30 molar ratio, 16 MPa reaction pressure at different temperatures and mixture flow rates

Experiment no.	Temperature (K)	W_{feed} (g/min)	v_0 (cm^3/g)	τ (min)
1	593	1.5	3.3	57.3
2		2.3	5.1	37.3
3		3.3	7.3	26.0
4	623	1.5	3.6	53.2
5		2.3	5.5	34.7
6		3.3	7.8	24.2
7	653	1.5	3.8	49.3
8		2.3	5.9	32.1
9		3.3	8.4	22.4
10	673	1.5	4.0	46.6
11		2.3	6.2	30.4
12		3.3	8.9	21.2

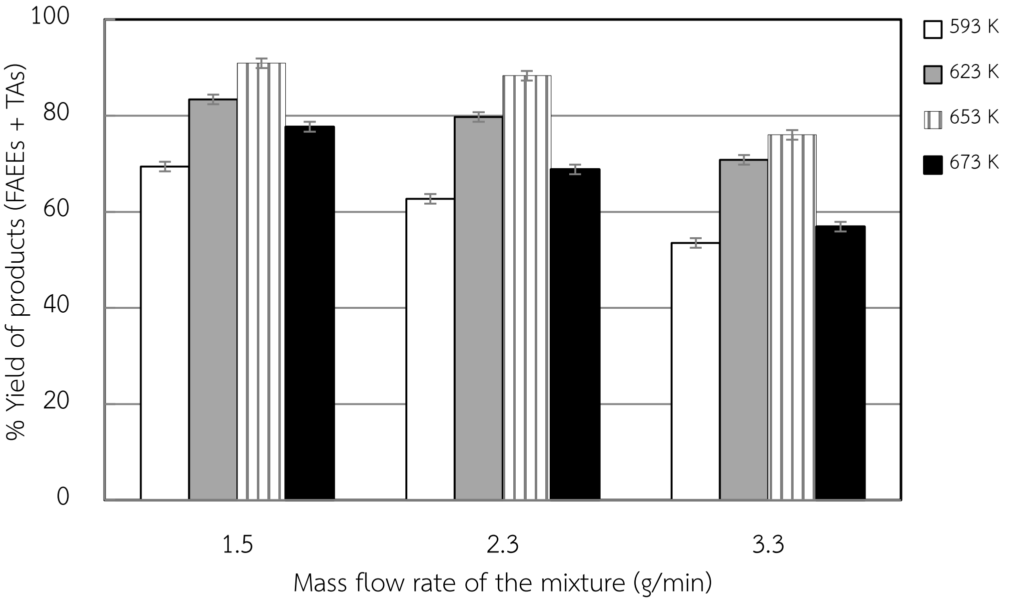


Figure 5.4 Effects of mass flow rate of palm oil in supercritical ethyl acetate on production of FAEEs and TAs over the estimated residence times at 593-673 K, 16 MPa, and 1:30 molar ratio of palm oil to ethyl acetate.

As shown in Figure 5.4, the yield of the products increased with temperature, with the maximum yield obtained at a flow rate of 1.5 g/min and a 1:30 molar ratio of palm oil to ETA. The maximum total FAEEs and TA yield of 90.9 wt% was obtained when the system was operated at a temperature of 653 K and the mass flow rate of the mixture was 1.5 g/min. In contrast, when the flow rates were increased to 2.3 and 3.3 g/min, the total yields were diminished by 6.6 wt% and 13.9 wt%, respectively. According to Vieitez et al. [106], a reduction in the flow rate is associated with a rise in the residence time, leading to an increase in the FAEEs content up to a critical point of the mixture. The results from this study demonstrate that the specific volume ($\mathbf{v}_0$) of the reacting mixture under the operating conditions and the composition of the mixture are significant in supercritical reactions. Therefore, the residence time in a continuous flow reactor is more dependent on the mass flow rate of the mixture than the reactor volume.

Note that, the product yields decreased when the temperature of the system exceeded 653 K and a mass flow rate of 1.5 g/min, corresponding to a prolonged residence time over 46 min. The thermal decomposition of unsaturated ester products was responsible for the yield reduction in FAEEs and TAs, because the palm oil used in this study contained 45.8 wt% of oleic acid. The thermal decomposition of the FAEEs occurred at a higher reaction temperature than the critical temperature of the supercritical co-reactants (T_c of ETA = 523 K). The isomerization of cis-type oleic acid (C=C) into trans-type, unstable fatty acid led to a lower yield of FAEEs [107, 108]. Therefore, the optimum theoretical yield of 123 wt% of biofuel over fed triglyceride seems unachievable. It can be concluded that the flow rate of the mixture, operation temperature, and fatty acid composition of the oil feedstock affect the FAEEs yield in a continuous system.

5.5 Evaluation of the apparent rate coefficients and activation energies of the interesterification

The experimental data reported in Table 5.3, attained under a temperature of 593–653 K, a fixed pressure of 16 MPa, and a 1:30 molar ratio of palm oil to ETA can be used to calculate the apparent rate coefficient and activation energies of the overall interesterification reaction in this study. The process requires a high amount of ETA (molar ratio of palm oil to ETA = 1:30). The reversible reaction and unsaturated ester decomposition can be ignored. A simplified first-order kinetic model was proposed to calculate the kinetics of the supercritical conditions of vegetable oils in both batch and continuous systems [79, 80] in Eq. 5.1 as follows;

$$\ln (C_t/C_0) = \ln k \qquad 5.1$$

where C_0 and C_t respectively refer to the content of TGs used in this study at initial and actual time determination.

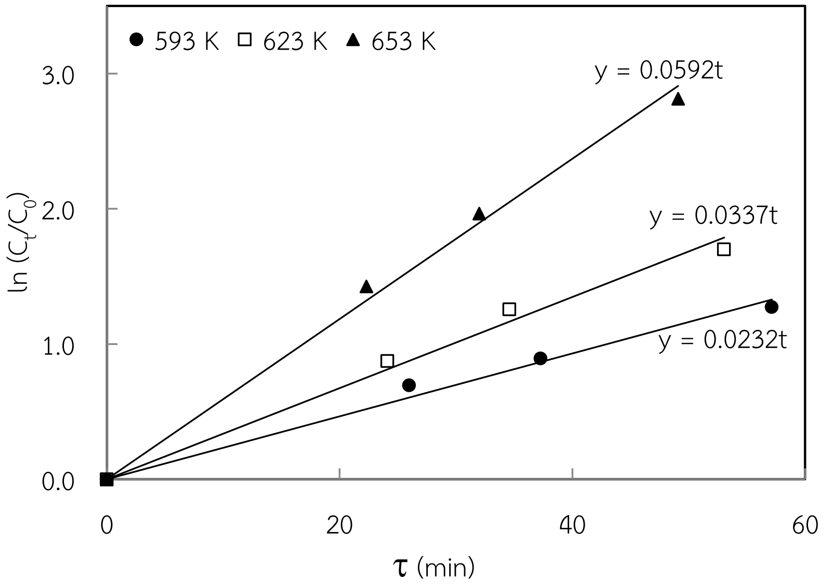


Figure 5.5 Semi-logarithmic plot of the ratio of actual and the initial oil concentration against the reaction time at different temperatures.

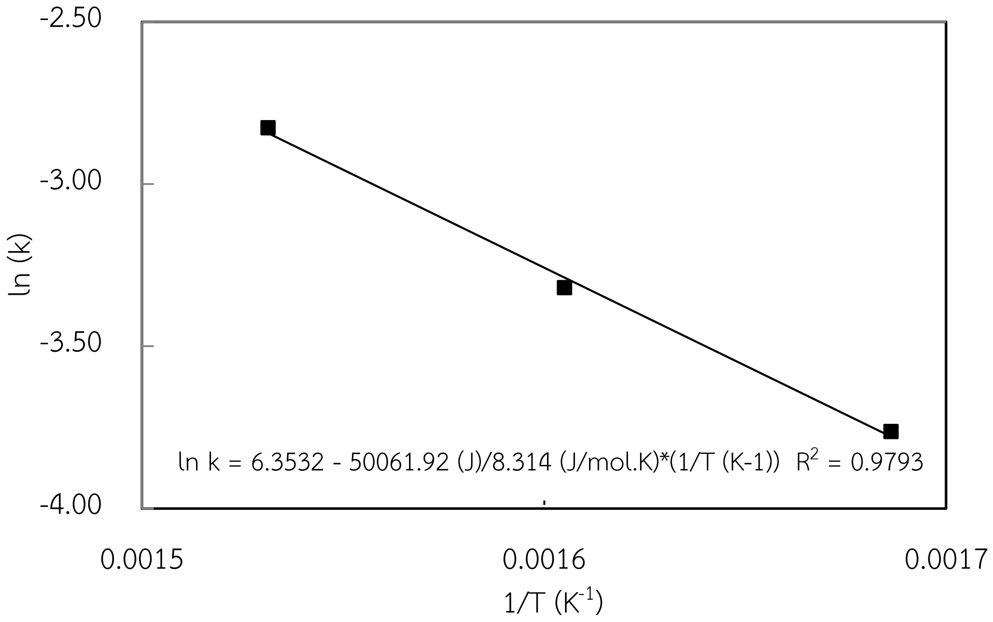


Figure 5.6 Arrhenius plot for the supercritical interesterification of palm oil.

Figures 5.5 and 5.6 demonstrate the relationship between the concentration of unesterified compounds and the reaction times at different temperatures. The gradient of the linear regression of ln C_t/C_0 curve with respect to the residence time is regarded as the apparent rate coefficient (*k*) at different temperatures. The *k* value increased with an increase in the reaction temperatures [69] and the apparent activation energy (E_a) was calculated from Arrhenius equation [109]. Arrhenius equation fitted to the experimental reaction data supports the first-order kinetic model used in this study. The apparent activation energy (E_a) was 50.06 kJ/mol. The reaction rate constants (*k*) are shown in Table 5.3.

Table 5.3 The rate constant and activation energy of interesterification reaction of palm oil in supercritical ethyl acetate molar ratio = 1:30 at 16 MPa

Reaction temperature (K)	*k* (min^{-1})	R^2
593	0.0232	0.9893
623	0.0337	0.9895
653	0.0592	0.9953
Apparent activation energy (kJ/mol)	50.06	

The reaction rate constant (*k*) for palm oil interesterification in supercritical ETA was compared with that from literature. Transesterification of vegetable oils in supercritical EtOH using a continuous system to produce FAEEs with the E_a value of 67.6 kJ/mol was investigated by Velez et al. [79] This value of E_a is higher than the value found in this work (50.06 kJ/mol). An important finding of this work is that to produce biofuel supercritical interesterification requires less activation energy than supercritical transesterification.

5.6 The properties of biofuel from palm oil in supercritical ethyl acetate

The biofuel with the optimized conditions discussed above was subsequently carried out for fuel properties. The PTT Research and Technology Institute, where is the institute for the quality assessment of petroleum products and alternative fuels, carried out all measurements of lipid-based biofuels properties derived from vegetable oils in Thailand. The basic test results and methods are summarized in Table 5.4.

Table 5.4 The properties of biofuel from palm oil in supercritical ethyl acetate

Properties	Unit	Test results (this work)	Test results (other reports)
Density at 288 K	g/cm^3	0.92	0.87**
Kinematic viscosity at 313 K	mm^2/s	6.12	5**
Iodine value	g Iodine/100 g	39.67	55**
Oxidation stability at 383 K	h	0.19	0.18 [110]
Cloud Point	K	292	289 [111]
Cold Filter Plugging Point (CFPP)	K	293	281 [110]

**Refer to PTT RTI

The major fuel properties such as density, kinematic viscosity, iodine value and cold flow properties of pure biofuel were compared with those from other reports for FAEEs from palm oil in Table 5.4. It was observed that the density and viscosity of the biofuel were slightly higher than those from other reports, indicating that the obtained fuel may have a drawback in lubrication. In addition, iodine value, a measure of total unsaturation, for the obtained biofuel is lower than others reported elsewhere. This can be pointed out that the resultant fuel is comparatively stable to oxidation as seen by the oxidation stability numerated in Table 5.4. The lowest of temperature at which the oil become solid can be observed at 292-293 K whereas un-saturated fatty acid rich oils have less oxidation stability. This property correlated with the iodine value of the biofuel, lower than the EN 1411 value significantly. As the palm oil contains oleic acid (C18:1) 45.8% and linoleic acid (C18:2) 11.1%, the un-saturated compounds affect the cold flow properties. This result agreed with Ilham and Saka work [112], they pointed out that the poly-unsaturated fatty acids in plant oils tends to be exposed to thermal degradation in a reaction condition higher than 573 K. The thermal degradation is a term describing the isomerization of from cis-type to trans-type and a difference between cis-type and trans-type alkyl esters is reflected in the cold flow properties.

The cold flow properties of cloud point and CFPP of the biofuel show higher temperature than ASTM standard significantly. However, the cold flow property has no effect on usability in Thailand, which located in the tropics near the equator; the climate has a tropical or generally hot all year round.

Furthermore, the biofuel production from palm oil in supercritical ETAavoid glycerol generation and in the liquid product increment without affected in utilization in tropical country. On behalf of economical purposed, the water addition to the operating system was investigated for alternatively used wasted cooking oil as raw material.

5.7 Interesterification of palm oil with supercritical ethyl acetate in the presence of water

The effects of the addition of water to the reaction mixture of palm oil in supercritical ETA were compared with the results achieved with pure ETA in the continuous system. The water was added to the reaction mixture in a 1:30:5, 1:30:10, and 1:30:15 molar ratio of palm oil to ETA to water (3, 7, and 10 wt%, respectively, based on the weight of the ETA) at 653 K, 16 MPa, and a mixture flow rate of 1.5 g/min. At the initiation of the reaction, the water did not dissolve in the palm oil and ETA mixture. Therefore, the magnetic stirring bar was used to vigorously stir the mixture while the reactants were continuously fed into the reactor. Rahimi et al. [113] also reported non-efficient mixing of two miscible liquids at a low flow rate in a continuous reactor. However, in the present study, at the supercritical condition above 647 K, the density of the water decreased. As a result, it behaved as a non-aqueous fluid [114, 115], dissolving non-polar compounds. Water was completely miscible in the palm oil and ETA mixture under supercritical conditions. Note that, the addition of water reduced the density of the mixture. Consequently, the estimated residence times were reduced, as shown in Table 5.5.

Table 5.5 The effects of water addition on FAEEs and TAs productions at 653 K and 16 MPa

Experimental no.	Molar ratio of Oil:ETA:Water	ρ (g/cm^3)	v_0 (cm^3/min)	τ (min)
1	1:30	0.3897	3.849	49.3
2	1:30:5	0.3605	4.161	45.5
3	1:30:10	0.3361	4.463	42.4
4	1:30:15	0.3153	4.757	39.8

The addition of the water in this study was intended to prevent the thermal decomposition of FAEEs and TAs in the interesterification reaction. The results are shown in Figure 5.7. It can be seen that the addition of water to the mixture had a positive effect on the production of FAEEs and TAs due to the hydrolysis of ETA to acetic acid and EtOH at a high temperature (573 K) [116]. These results were in agreement to the study of Tan et al. [117] the presence of water in supercritical methyl acetate increased the yield, and all reactions occurred simultaneously during product formation, as shown in Figure 5.8. The generated EtOH from ETA hydrolysis reacted with the TG in the palm oil via transesterification reaction into FAEEs and glycerol, which subsequently combined with acetic acid in esterification reaction to form TA under supercritical conditions.

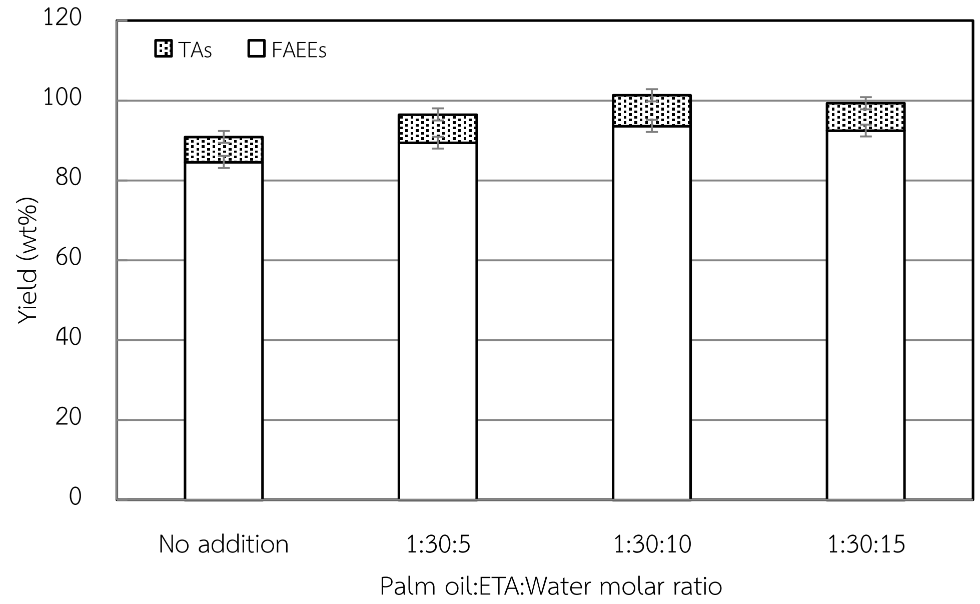
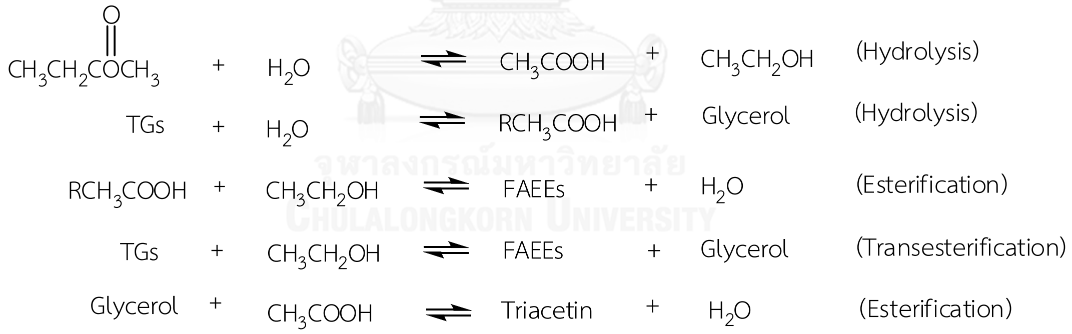


Figure 5.7 The effects of water addition base on molar ratio of palm oil to ethyl acetate on FAEEs and TAs productions at 653 K, 16 MPa, and mixture flow rate 1.5 g/min.



$$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3CH_2OH \quad \text{(Hydrolysis)}$$

$$\text{TGs} + H_2O \rightleftharpoons RCH_3COOH + \text{Glycerol} \quad \text{(Hydrolysis)}$$

$$RCH_3COOH + CH_3CH_2OH \rightleftharpoons \text{FAEEs} + H_2O \quad \text{(Esterification)}$$

$$\text{TGs} + CH_3CH_2OH \rightleftharpoons \text{FAEEs} + \text{Glycerol} \quad \text{(Transesterification)}$$

$$\text{Glycerol} + CH_3COOH \rightleftharpoons \text{Triacetin} + H_2O \quad \text{(Esterification)}$$

Figure 5.8 The proposed reactions during water addition to palm oil in supercritical ethyl acetate [117].

The addition of the water to the reaction mixture enhanced the production yields as compared to the cases where no water was added. The highest yield of 101.5 wt% was obtained when the water was added at a 1:30:10 molar ratio of palm oil to ETA to water at 653 K, 16 MPa, and a reactant flow rate of 1.5 g/min. The addition of the water increased the ester content more than the TA content due to the hydrolysis of ETA and the transesterification reaction. In addition, the transesterification reaction proceeded faster than glycerol esterification. TA is also relatively unstable, especially at temperatures above 633 K. At these temperatures, thermal degradation of ETA is significant [118]. The results of this study were compared with those of earlier studies, which used EtOH as a supercritical reactant and water addition of 10 wt% [106] and the flow rate was 1.5 g/min, as shown in Table 5.6.

Table 5.6 Comparison of the yields of ethyl esters in supercritical condition in the presence of water

System	Molar ratio (mol:mol)	Temperature/Pressure (K/MPa)	Water (wt%)	Flow rate (g/min)	FAEEs (wt%)
Soybean oil/EtOH [106]	1:40	623/20	10	1.5	77.5
Palm oil/ETA (this work)	1:30	653/16	10	1.5	89.5

From Table 5.6, it can be seen that the presence of water in the reaction mixture under supercritical conditions had a positive effect on the FAEEs yield in this study. The significantly higher yield obtained in the present study is due to the lower temperature required to convert TG to FAEEs and TAs and the lower proportion of reactant. In addition, the polarity of ETA was lower than that of EtOH. Therefore, the oil was more soluble in ETA at room condition than EtOH. The results of the present study illustrate the process by which the mass transfer of TG and ETA can be circumvented in a biphasic system.

5.8 Summary

The interesterification of palm oil in supercritical ETA to produce fatty acid ethyl ester (FAEEs) or biofuel was conducted in a continuous tubular reactor. The density of the mixtures in the system was estimated using the PR EOS using a process simulator, and the residence time was calculated. The effects of the reaction conditions, including the molar ratios of palm oil to ETA, the temperature, and the pressure, were investigated under various mass flow rates of the mixtures and optimized. The results showed that reaction temperatures above 653 K and long residence times affected the content of FAEEs and TA, a valuable by-product. The addition of water to the mixture in a 1:30:10 molar ratio of palm oil to ethyl acetate to water at 653 K, 16 MPa, and a mixture mass flow rate of 1.5 g/min increased the total production of FAEEs and TA from 90.9 to 101.5 wt% in 42.4 min. The main finding of the present study is that triglyceride associated with ETA hydrolysis used to form acetic acid protected the products from decomposition at high temperatures and long residence times. The results will aid the selection of an efficient and economical process for alternative biofuel production from palm oil in supercritical ETA.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATION

6.1 Conclusions

6.1.1 Density determination of ethyl acetate-palm oil mixture in supercritical condition

The relationship of ethyl acetate and palm oil system in supercritical condition has been accomplished by indirect isochoric method. The molar ratio and global density of the mixture affected the LV region transformation to single phase of the mixture. The phase transition point from the LV region to SC region was also approximately located. The transition points were lowered by increasing global density and oil:ethyl acetate molar ratio. The subsequent data can be applied to find conditions of temperature and pressure that a homogeneous mixture of palm oil and ETA and is optimized for producing biofuel in supercritical conditions.

6.1.2 Continuous production of palm oil in supercritical ethyl acetate

The production of FAEEs from palm oil in supercritical ETA was evaluated in a continuous tubular reactor. The effects of the temperature, pressure, palm oil to ETA molar ratio, and flow rate of the mixture on FAEEs and TAs yields were investigated and optimized. The optimum conditions required to obtain 90.9 wt% of total biofuel production (FAEEs and TAs) of palm oil in supercritical ETA were 653 K and 16 MPa. The optimum mass flow rate of the mixture was 1.5 g/min. The activation energy for interesterification of palm oil in supercritical ETA in the range of 593–653 K was 50.06 kJ/mol. Furthermore, the addition of water (1:30:10 molar ratio of palm oil to ETA to water) under the same conditions favored the production of FAEEs and TAs due to the acetic acid generated from TGs and the hydrolysis of ETA. It also prevented the thermal decomposition of the products. These results suggest that oil feedstock, such as waste frying oil and water can be used to produce biofuel in supercritical ETA.

6.2 Recommendation

Supercritical fluid technology is an essential alternative to produce biofuel with quality as one of the cleaner fuels. This work is for supercritical reactants with oxygen component in their structures, which can be reacted with vegetable oils transition to ester compounds and other by-products instead of glycerol. The purified glycerol can produce an additive with specific chemical reaction and catalyst for future biodiesel blending to improve fuel properties. However, several methods such as enzymatic transesterification, non-catalytic transesterification, two-step method of sub- and supercritical fluids, avoid glycerol formation but take time for several stages and purification compared with the one-step method. The parameters affecting the one-step supercritical fluids transesterification to achieve clean biofuel have been addressed by not only glycerol by-products but also other additives, simultaneously obtained with esters. The supercritical condition parameters such as temperature and pressure, reactants compositions, density of mixture at the condition, and residence time were found to have an influence on the obtaining yield and the latter two parameters were significantly influenced by continuous operation system.

According to the study in this thesis, there are many further important studies that need to be investigated. This section would recommence some issues for the future directions in the field.

- In the isochoric methodology of phase transition determination study, the relationship of temperature pressure and specific global density of palm oil and ethyl acetate mixtures from PVT diagram at room temperature to supercritical condition can indicate the phase boundaries between LV phase and single phase of supercritical fluids. The points of this phase transition can be estimated critical points of the binary mixtures. In the presence of other reactants such as co-solvent or water, the multi-component should be investigated to determine phase transitions for attaining their critical points.

- For continuous system of this study for biofuel production from palm oil in ethyl acetate, the reduction of total yields were from high reaction temperature and long residence time. Thermal stability of products during reaction should be studied. According to FAEEs and TA by-product can be decomposed at temperature higher than 573 K. The acetic acid content can be generated by high reaction temperature from ETA decomposed to EtOH and acetic acid. The acid can be acted as acid catalyst to increase rate of reaction but if excess and unremoved from the final products it can be disadvantage in the fuel properties. The water addition in good proportion is a method to resolve the acidity. The co-solvent such as EtOH is recommended for the future work in biofuel production from vegetable oil in ethyl acetate.

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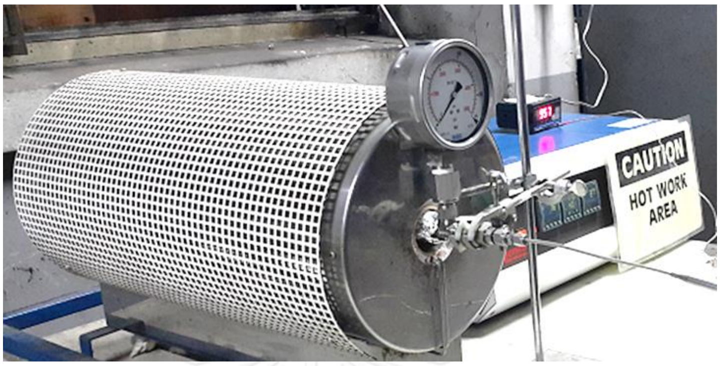
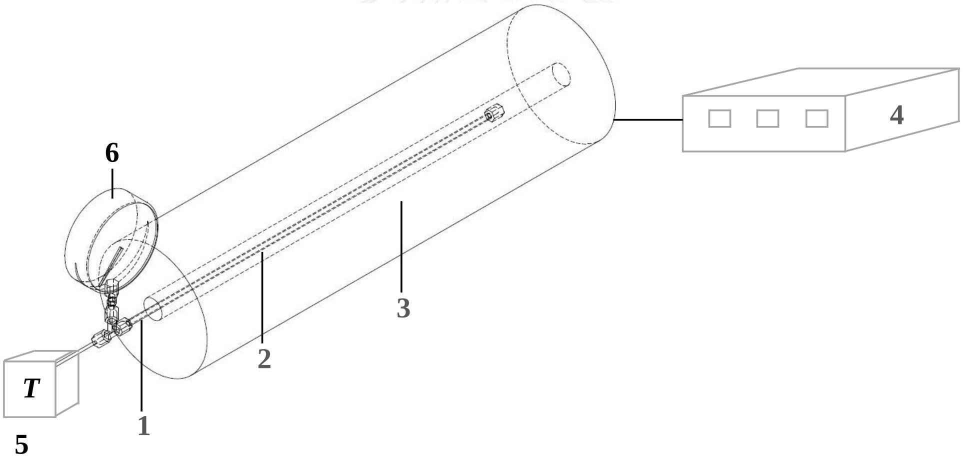
APPENDIX

Appendix A

Determination of ethyl acetate-palm oil mixture in supercritical condition





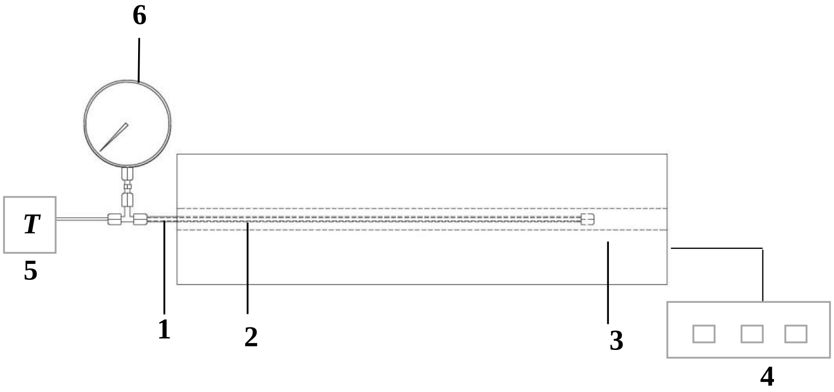


Figure A1 Overview of schematic diagram for density determination using isochoric method. (1) Measurement cell, (2) Aluminum foil (3) Tubular furnace, (4) Temperature controller, (5) Temperature monitor and (6) Pressure gauge.

Table A1 The experimental average data for temperature and pressure at molar ratio of palm oil to ethyl acetate of 1:10 and various global densities.

Density of palm oil-ethyl acetate (g/cm^3) (10:1)							
0.26		0.35		0.44		0.53	
T	P	T	P	T	P	T	P
(K)	(Mpa)	(K)	(Mpa)	(K)	(Mpa)	(K)	(Mpa)
423	2.00	445	2.06	427	2.0	435	2.1
438	2.50	458	2.59	442	2.4	454	2.8
453	3.00	470	3.08	457	3.0	468	3.4
466	3.50	491	3.93	473	3.6	484	4.0
481	4.00	517	4.99	490	4.2	501	4.6
496	4.50	542	6.01	515	5.1	526	5.6
511	5.00	553	6.46	543	6.1	554	6.7
524	5.50	565	6.95	565	6.8	569	7.3
539	6.00	583	7.96	564	7.1	578	8.7
554	6.50	590	8.47	574	7.9	590	9.8
569	7.00	597	8.99	586	8.8	603	10.9
585	7.50	605	9.58	602	10.1	615	11.9
599	8.00	619	10.61	617	11.2	624	12.7
616	8.50	630	11.41	627	12.0	638	13.9
631	9.00	645	12.52	639	13.0	648	14.8
646	9.50	658	13.47	651	13.9	658	15.7
661	10.00	671	14.43	663	14.8	658	16.0

Table A2 The experimental average data for temperature and pressure at molar ratio of palm oil to ethyl acetate of 1:20 and various global densities.

Density of palm oil-ethyl acetate (g/cm^3)							
0.26		0.35		0.44		0.53	
T	P	T	P	T	P	T	P
(K)	(Mpa)	(K)	(Mpa)	(K)	(Mpa)	(K)	(Mpa)
418	2.2	442	2.64	425	1.97	427	2.09
433	2.7	457	3.18	440	2.51	446	2.81
448	3.2	473	3.75	456	3.09	463	3.46
463	3.7	488	4.29	471	3.64	481	4.15
473	4.0	515	5.25	498	4.62	512	5.34
488	4.5	541	6.19	523	5.53	533	6.14
503	5.0	555	6.69	538	6.07	540	6.41
516	5.4	561	6.82	567	7.87	545	6.73
528	5.8	568	7.30	573	8.32	555	7.51
543	6.3	575	7.78	580	8.83	567	8.44
559	6.8	583	8.33	586	9.28	583	9.69
573	7.2	598	9.36	601	10.38	598	10.85
583	7.6	613	10.39	615	11.42	608	11.63
603	8.2	625	11.21	625	12.16	620	12.56
623	8.9	640	12.24	638	13.12	632	13.49
643	9.5	650	12.93	650	14.00	645	15.00

Table A3 The experimental average data for temperature and pressure at molar ratio of palm oil to ethyl acetate of 1:30 and various global densities.

Density of palm oil-ethyl acetate (g/cm^3)							
0.26		0.35		0.44		0.53	
T	P	T	P	T	P	T	P
(K)	(Mpa)	(K)	(Mpa)	(K)	(Mpa)	(K)	(Mpa)
410	2.0	436	2.1	439	2.26	423	2.00
425	2.5	451	2.6	455	2.88	439	2.54
440	3.0	478	3.5	477	3.72	453	3.01
453	3.5	493	4.0	509	4.95	467	3.49
468	4.0	515	4.7	522	5.45	480	3.93
483	4.5	533	5.4	541	6.18	513	5.05
498	5.0	550	6.0	555	6.72	541	6.00
511	5.5	565	7.5	563	7.00	565	7.50
526	6.0	577	9.0	581	8.17	577	9.00
541	6.5	593	10.4	598	9.65	593	10.40
556	7.0	608	11.7	614	11.04	608	11.70
572	7.5	618	12.5	631	12.52	618	12.50
586	8.0	635	13.8	648	14.00	635	13.80
603	8.5	643	14.6	661	15.13	643	14.57
618	9.0	655	15.5	670	15.91	655	15.51
633	9.5	666	16.5	678	16.50	666	16.49

Appendix B

Peng-Robinson Equation of State process model simulator

The following tables summarize the experimental data of global densities of palm oil-ethyl acetate mixture at different conditions for biofuel production calculated by HYSYS 3.2 process simulator (Aspen Technology, USA).

Table B1 Global densities of 1:10 of molar ratio of palm oil to ethyl acetate

X_{oil}	X_{ETA}	T	P	Global density
mol	mol	(K)	(MPa)	(g/cm^3)
0.092413	0.907587	573	10	0.4381
0.092413	0.907587	573	12	0.4521
0.092413	0.907587	593	16	0.4607
0.092413	0.907587	623	14	0.4273
0.092413	0.907587	623	16	0.4404
0.092413	0.907587	623	18	0.4518
0.092413	0.907587	623	20	0.4617
0.092413	0.907587	653	14	0.4051
0.092413	0.907587	653	16	0.4201
0.092413	0.907587	673	16	0.4067

Table B2 Global densities of 1:20 of molar ratio of palm oil to ethyl acetate

X_{oil}	X_{ETA}	T	P	Global density
mol	mol	(K)	(MPa)	(g/cm^3)
0.048445	0.951555	573	10	0.4227
0.048445	0.951555	573	12	0.4433
0.048445	0.951555	593	16	0.4555
0.048445	0.951555	623	14	0.4092
0.048445	0.951555	623	16	0.4276
0.048445	0.951555	623	18	0.4432
0.048445	0.951555	623	20	0.4569
0.048445	0.951555	653	14	0.3797
0.048445	0.951555	653	16	0.4003
0.048445	0.951555	673	16	0.3829

Table B3 Global densities of 1:30 of molar ratio of palm oil to ethyl acetate

X_{oil}	X_{ETA}	T	P	Global density
mol	mol	(K)	(MPa)	(g/cm^3)
0.032827	0.967173	573	10	0.4155
0.032827	0.967173	573	12	0.4401
0.032827	0.967173	593	16	0.4544
0.032827	0.967173	623	14	0.4005
0.032827	0.967173	623	16	0.4219
0.032827	0.967173	623	18	0.4401
0.032827	0.967173	623	20	0.4558
0.032827	0.967173	653	14	0.3671
0.032827	0.967173	653	16	0.3909
0.032827	0.967173	673	16	0.3714

Table B4 Global densities of palm oil to ethyl acetate in the presence of water at different compositions at 653 K, 16 MPa and 1.5 g/min of mixture flow rate.

Molar ratio of Oil:ETA:H_2O	X_{oil} mol	X_{ETA} mol	X_{H2O} mol	Global density (g/cm^3)
1:30:5	0.0278	0.8333	0.1389	0.3605
1:30:10	0.0244	0.7317	0.2439	0.3361
1:30:15	0.0217	0.6522	0.3261	0.3153

Appendix C

Continuous production of biofuel from palm oil in supercritical ethyl acetate

Table C1 The effects of pressure on FAEEs and TAs yield of 1:30 molar ratio of palm oil to ethyl acetate, 623 K of reaction temperature and 2.3 g/min of mixture flow rate.

P (MPa)	FAEEs (wt%)	TAs (wt%)
14	59.2	3.8
16	76.0	5.7
18	74.8	4.8
20	74.1	4.8

Table C2 The effects of molar ratio of palm oil to ethyl acetate on FAEEs and TAs yield under supercritical condition at 623 K, 16 MPa and 2.3 g/min mixture flow rate.

Molar ratio of Oil:ETA	FAEEs (wt%)	TAs (wt%)
1:10	67.8	3.8
1:20	72.9	4.1
1:30	76.0	5.7
1:35	75.1	5.0

Table C3 The effects of mass flow rate of palm oil in supercritical ethyl acetate at 1:30 molar ratio, 16 MPa reaction pressure at different temperatures and mixture flow rates.

Experiment no.	Temperature (K)	W_{feed} (g/min)	FAEEs (wt%)	TAs (wt%)
1	593	1.5	64.6	4.79
2		2.3	58.4	4.34
3		3.3	49.4	4.11
4	623	1.5	78.7	4.68
5		2.3	74.0	5.74
6		3.3	65.6	5.18
7	653	1.5	84.6	6.29
8		2.3	82.4	5.91
9		3.3	70.9	5.09
10	673	1.5	70.0	5.08
11		2.3	64.2	4.65
12		3.3	52.8	4.15

Table C4 The effects of water addition on FAEEs and TAs productions at 653 K, 16 MPa and 1.5 g/min mixture flow rate.

Molar ratio of Oil:ETA:water	FAEEs (wt%)	TAs (wt%)
1:30	84.6	6.3
1:30:5	89.4	7.1
1:30:10	93.7	7.7
1:30:15	92.5	6.9

VITA

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