Study of Multicomponent Systems and Saponification Reaction in Biodiesel Production Observed by LCD Digital Microscope

Issara Chanakaewsomboon

A Thesis Submitted in Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Chemical Engineering
Prince of Songkla University
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Author	Mr. Issara Chanakaewsomboon
Major Program	Chemical Engineering

Major Advisor	**Examining Committee:**
....	....Chairperson
(Assoc. Prof. Dr.Chakrit Tongurai)	(Assoc. Prof. Dr.Penjit Srinophakun)
	....Committee
Co-Advisor	(Assoc. Prof. Dr.Chakrit Tongurai)
....	....Committee
(Asst. Prof. Dr.Suratsawadee Kungsanant)	(Asst. Prof. Dr.Suratsawadee Kungsanant)
	....Committee
	(Assoc. Prof. Dr.Kulchanat Prasertsit)

The Graduate School, Prince of Songkla University, has approved this thesis as fulfillment of the requirements for the Doctor of Philosophy Degree in Chemical Engineering.

....

(Prof. Dr.Damrongsak Faroongsarng)

Dean of Graduate School

This is to certify that the work here submitted is the result of the candidate's own investigations. Due acknowledgment has been made of any assistance received.

…………...…...…...…..............Signature
(Assoc. Prof. Dr.Chakrit Tongurai)
Major Advisor

…………...…...…...…..............Signature
(Asst. Prof. Dr.Suratsawadee Kungsanant)
Co-Advisor

………...………….……......……..Signature
(Mr. Issara Chanakaewsomboon)
Candidate

I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

…………....…………..…….Signature
(Mr. Issara Chanakaewsomboon)
Candidate

ชื่อวิทยานิพนธ์	การศึกษาระบบสารผสมหลายองค์ประกอบและปฏิกิริยาสะปอนนิฟิเคชันในการผลิตไบโอดีเซลโดยกล้องจุลทัศน์แบบดิจิตอล
ผู้เขียน	นายอิสระ ชนะแก้วสมบูรณ์
สาขาวิชา	วิศวกรรมเคมี
ปีการศึกษา	2561

บทคัดย่อ

งานวิจัยนี้ศึกษาการผสมของสารผสมหลายองค์ประกอบในกระบวนการผลิตไบโอดีเซล ตัวอย่างเช่น ไตรกลีเซอไรด์ เมทิลเอสเตอร์ของกรดไขมัน เมทานอล เตตระไฮโดรฟูแรน กล้องจุลทัศน์แบบดิจิตอลถูกประยุกต์ใช้สำหรับการศึกษาด้วยการมองเห็นของอันตรกิริยาระหว่างตัวทำปฏิกิริยาและบริเวณของการทำปฏิกิริยาในการผลิตไบโอดีเซล ศึกษาปัจจัยที่มีผลสำคัญต่อการเกิดปฏิกิริยาทรานส์เอสเตอริฟิเคชัน เช่น ปริมาณกรดไขมันอิสระ ปริมาณน้ำ ปริมาณตัวเร่งปฏิกิริยา จากการศึกษาพบว่าสภาพความเป็นขั้วของสารประกอบมีบทบาทสำคัญต่อการเกิดปฏิกิริยา โดยส่งผลต่อการผสมเข้ากันได้ของสารตั้งต้น และความสามารถของการเกิดปฏิกิริยา จากการศึกษาพฤติกรรมสภาพการละลายของสารผสมในระบบปฏิกิริยาทรานส์เอสเตอริฟิเคชันทำให้ทราบว่าเป็นปฏิกิริยาของเหลว-ของเหลว การแพร่ของเฟสแอลกอฮอล์และตัวเร่งปฏิกิริยาไปยังเฟสของสารตั้งต้นจัดเป็นตัวแปรสำคัญของขั้นที่ช้าที่สุดของปฏิกิริยา ตัวทำละลายร่วมเช่น เตตระไฮโดรฟูแรน หรือ เมทิลเอสเตอร์ของกรดไขมัน ช่วยเพิ่มความสามารถการละลายของเมทานอลที่มีสภาพความเป็นขั้วในไตรกลีเซอไรด์ที่ไม่มีสภาพความเป็นขั้ว แต่อย่างไรก็ตาม กลีเซอรอลและสบู่จะไปขัดขวางความสามารถในการละลายในระบบดังกล่าว ตัวทำละลายร่วมไม่สามารถช่วยให้สภาพการละลายในระบบสารผสมหลายองค์ประกอบของการผลิตไบโอดีเซลเป็นเนื้อเดียวกัน การแพร่ของแอลกอฮอล์และตัวเร่งปฏิกิริยาจะมีบทบาทต่ออัตราเร็วการเกิดปฏิกิริยา การศึกษาการเกิดสบู่ในปฏิกิริยาทรานส์เอสเตอริฟิเคชัน พบว่าสบู่เป็นปัจจัยสำคัญที่ทำให้สูญเสียปริมาณตัวเร่งปฏิกิริยาและทำให้เกิดสูญเสียผลิตภัณฑ์ การเกิดสบู่ทำให้เกิดชั้นขัดขวางการแพร่ระหว่างเฟสแอลกอฮอล์และเฟสไตรกลีเซอไรด์ ทำให้ยับยั้งอัตราการแพร่ของแอลกอฮอล์และตัวเร่งปฏิกิริยา ส่งผลให้ลดอัตราการเกิดปฏิกิริยา น้ำมันวัตถุดิบที่มีปริมาณกรดไขมันอิสระและปริมาณน้ำสูงจะทำให้เกิดสูญเสียผลิตภัณฑ์อย่างมีนัยสำคัญในขั้นตอนการล้าง เนื่องจากปริมาณสบู่ในเฟสไบโอดีเซลดิบ ซึ่งควรมีค่าน้อยกว่า 3,000 ppm

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Major Program Chemical Engineering
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ABSTRACT

This work studied the mixing of multiple components (triglyceride, FAME, methanol, and THF) in the biodiesel production process. An LCD digital microscope is applied as visual observations in this work to clarify the interactions of key substances and the reaction zone in biodiesel production. This work aimed to find out the effects of FFA, water and amount of alkaline catalyst on biodiesel production from refined palm oil. The polarity of the components in transesterification reaction plays a crucial role in the reaction, affecting the miscibility of compounds in the reaction mixture, and influencing efficiency and extent of conversion. The observed behaviors of multicomponent mixture indicate that the reaction is a liquid-liquid reaction. The diffusivity of alcohol reactant together with the catalyst to another reactant phase plays a key role as rate limiting step. The co-solvent THF or FAME improved solubility of polar methanol in the non-polar triglyceride, but the strongly polar products, such as glycerol and soap emulsifier, could interrupt this effect. The co-solvent THF or FAME cannot enhance solubility of the multicomponent systems in biodiesel production to provide a homogeneous mixture. Diffusivity of alcohol and catalyst plays a key role in the reaction rate. In transesterification via alkaline catalysis, soap formation is a major factor causing catalyst depletion and yield loss by saponification reaction and via losses on purification. Soap formation establishes a barrier between an alcohol droplet and surrounding triglyceride, and restrains the diffusion rate of alcohol and catalyst, thus lessens the transesterification rate. A low-quality feedstock with high FFA and water contents gives significant yield losses in washing step. The soap content in crude biodiesel is a key parameter affecting washing losses, and our suggestion is it should be below 3,000 ppm.

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ISSARA CHANAKAEWSOMBOON

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LIST OF ABBREVIATION

		Definition in this thesis
RPO	Refined palm oil………………………………	A refined oil was received from oil palm refining process
TG	Triglyceride……………………………………	An ester derived from glycerol and three fatty acid
FAME	Fatty Acid Methyl Ester……………………	The finished product from biodiesel production
FFA	Free Fatty Acid………………………………	A fatty acid is carboxylic acid
$NaOCH_3$	Sodium methoxide………………………...	A basic catalyst was used in transesterification
NaOH	Sodium hydroxide…………………………	A basic catalyst was used in transesterification
$KOCH_3$	Potassium methoxide……………………..	A basic catalyst was used in transesterification
KOH	Potassium hydroxide………………….…...	A basic catalyst was used in transesterification
H_2SO_4	Sulfuric acid………………………………..	An acid catalyst was used in esterification
MeOH	Methanol…………………………………….	An alcohol was used in biodiesel production
THF	Tetrahydrofuran……………………………	A co-solvent was used in biodiesel production

CHAPTER 1

INTRODUCTION

1.1 Rational/Problem Statement

Biodiesel is developed as an alternative fuel to supplement or replace petroleum-diesel according to its numerous advantages such as renewability, biodegradability and lower gaseous emission (sulfur, aromatic hydrocarbons, metals or crude oil residues). Thus, it can lower the net greenhouse gas emissions from the transportation sector and reduce the mass and carcinogenicity of particulate matter emissions [1]–[3]. Biodiesel is defined as a mixture of alkyl esters obtained from vegetable oils, animal fats, or waste oils, by using short-chained alcohol (typically methanol or ethanol) in the presence of a suitable catalyst [4]–[7].

Transesterification reaction is the major step in current industrial biodiesel plants and there are two types of catalysts: heterogeneous and homogeneous. The former, such as solid acid catalyst or solid base catalyst, is more effective in reducing soap formation, but gives slower reaction rate, needs more alcohol, and requires rather sophisticated equipment [8]–[11]. The latter in contrast, such as alkaline hydroxide alkaline methoxide used in commercial biodiesel plants, consumes less time and alcohol in a relatively simple process; but involves more saponification and requires more water in the washing process [12]–[15].

The mixing of the two phases can be improved by increasing the reaction temperature or by increasing the stirring intensity, but then the operating costs are increased by high energy consumption. Adding co-solvents in the reaction mixture is one suggested method to improve the mixing of oil and alcohol and increase the reaction rate. The co-solvent needs both polar and non-polar parts in its molecules in order to reduce interfacial tension between alcohol and triglyceride and enhance their interactions [16].

Using a co-solvent has been reported to facilitate mixing during transesterification under mild conditions and short reaction time. Additionally, tetrahydrofuran (THF) is among the most effective co-solvents for transesterification, because it has a low boiling point (67 °C) similar to that of methanol (65 °C) [17] making temperature control easy.

The reaction mechanism consisting of an initial mass transfer controlled region followed by a kinetically controlled region [18]. Mass transfer limitation between the polar methanol-glycerol phase and the non-polar oil phase causes slow reaction rates at the initial and final stages of base-catalyzed transesterification [19]. The kinetics models are based on the liquid-liquid reaction and the stability of phase continuity in the liquid-liquid reaction, where a large excess phase tends to be continuous and the minority phase is disperse [20], [21]. When the phase volumes are fairly similar, either phase may be continuous. In a small droplet of the liquid-liquid system, internal circulation is minimal if the mass transfer coefficient of the internal film is lowest. Thus, mass transfer can be enhanced by droplet coalescence and redispersion. A model based on the immiscibility of oil and methanol, with methanol as droplets in a viscous oil phase and, through reaction, are changed to rigid glycerol droplets. The reaction only occurs at the interface of the methanol and triglyceride film [21].

In biodiesel production, the key parameters affecting the yield of biodiesel are FFA and moisture contents. According to industrial biodiesel companies such as Lurgi GmbH [22] and Crown Iron Works [23], they had specified feedstock properties as maximum acidity 0.1% or 0.5% and maximum moisture and volatiles as 0.1% or 0.05%. These impurities are significant to soap formation in the transesterification process. It is undesirable because it consumes the catalyst, decreases the yield of biodiesel, and complicates the subsequent purification steps [24]. Among the other reaction parameters, the molar ratio of alcohol to oil, catalyst type and its concentration, reaction temperature, and reaction time play key roles in biodiesel yield, which is related to soap formation.

Soap is produced by neutralization of FFA in the oil and by saponification of triglyceride and ester. In neutralization, the FFA reacts with an alkaline catalyst (NaOH or $NaOCH_3$) and turns to soap, water, or alcohol. However, the water in the oil and alcohol phases plays a very important role in soap formation. If a high amount of water is present, it can hydrolyze the ester and cause reversed esterification, yielding FFA and alcohol again. In saponification reaction, triglyceride or fatty acid methyl ester (FAME) reacts with a base catalyst to form soap, glycerol, and methanol.

Soap could act as a barrier compound at the outer surface of the disperse alcohol-glycerol phase due to being a natural emulsifier. The intermediate products on transesterification of triglycerides, such as diglyceride and monoglyceride, as emulsifiers also play the same role as soap, especially if lacking the alcohol catalyst, gradually affecting all three reaction steps. Thus, water and free fatty acid are critical impurities inducing soap formation. So, the kinetics of transesterification are altered by barrier substances forming an outer shell around alcohol droplets. If glycerol, a product of transesterification reaction, goes back to the alcohol droplets according to Slinn's model, the barrier should be thicker. A new paradigm with merging of glycerol, alcohol, and catalyst to form a new glycerol droplet is also possible.

As mentioned above, understanding the solubility and mixing of multiple components in the biodiesel production process is fundamentally important. An LCD digital microscope is applied in this work to clarify the interactions of key substances in biodiesel production. The behaviors of triglyceride, FAME, methanol, and THF were examined by visual observation using LCD microscope. Refined palm oil (RPO) and FAME in the mixture were observed for their roles as reaction intermediates. The effects of alkaline and acid catalysts on transesterification reaction mixture were the main interest in this study. The addition THF as a co-solvent to transesterification was studied to clarify the single- or two-phase reaction aspects mentioned by several reviews. The self-transesterification of FAME and methanol with an alkaline catalyst. Soap formation during the reaction and effects of THF were also examined. Finally, preliminary observations of the reaction zone were conducted to provide an obvious clarification.

The effects of soap formation on transesterification reaction need to clarify. Visual observations of methanolysis on a concave glass slide micro-reactor at room temperature were performed. The microscope pictures of the reaction zone may reveal mechanisms and events. Soap formation from fatty acid methyl ester with alkaline in methanol solution is a benchmark for comparisons.

1.2 Theoretical Background

1.2.1 Biodiesel

Biodiesel, a renewable fuel, which is composed mainly of fatty acid alkyl esters supplied from vegetables oil/or fats which primarily contains triglycerides (TG) and free fatty acids (FFA). Biodiesel can be called fatty acid ethyl ester (FAEE, from ethanol), or fatty acid methyl ester (FAME, from methanol). The fuel properties are similar to mineral diesel. Hence, it can be used direct as B100 or blend with mineral diesel in diesel engines. Biodiesel is superior to diesel in several ways such as higher flash point, higher lubricity, lower sulphur content, and lower particulate emissions [16]. Biodiesel is usually produced through several techniques such as direct use/blending [17], micro-emulsion [18], pyrolysis [19], esterification [20], and transesterification [21].

The renewable raw materials used to produce biodiesel are edible and non-edible vegetable oils since they can be cultivated on a large area in many parts around the world. Selection criteria of vegetable oils are: availability, cost, oil quality (composition) and product shelf-life. Unlike fossil reserves, different regions of the world have their own vegetable oil resources that could be exploited for biodiesel production [22]. In Thailand, palm oil is mainly raw material for biodiesel commercial production [23].

1.2.2 Alcohol

Alcohol is one of the most important raw materials for the production of biodiesel. The most widely used alcohols are methanol ethanol due to their acyl acceptors [25]. Other alcohols utilized in biodiesel are the short-chain alcohols such as propanol, butanol and isopropanol, however, these alcohols are costly [26]. Regarding the choice between methanol and ethanol, the former is lower cost and better physical and chemical advantages. However, ethanol is less toxic and renewable source [27]. Verma and Sharma (2016) recommended that ethanol is an acyl acceptor and a completely renewable biodiesel but yield obtained is lesser and more reaction time requirement [28]. The properties of methanol and ethanol are shown in Table 1.1.

Table 1.1 Properties of methanol and ethanol [1], [26]

Property	Unit	Methanol	Ethanol
Molecular formula	-	CH_3OH	C_2H_5OH
Molecular weight	g/mol	32.04	46
Density at 15 °C	kg/m^3	791.3	789.4
Viscosity	cSt s at 40 °C	0.58	1.13
Boiling temperature	°C	65	78
Flash point	°C	11.11	12.78
Auto ignition temperature	°C	463-465	420-425

1.2.3 Catalyst

Basically, there are two types of catalysts used for transesterification process such as homogeneous and heterogeneous catalysts. The heterogeneous catalysts are selected for biodiesel synthesis includes solid acid catalyst [29] and solid base catalyst [10], [30]. These solid catalysts are more effective in reducing soap formation, but are relatively more time-consuming in the reaction process, needs more alcohol, and requires rather sophisticated equipment [10], [30]. The homogeneous catalysts, alkaline hydroxide [13] and alkaline methoxide [13], are often used in commercial biodiesel plants due to less reaction time and less alcohol usage under mild reaction conditions.

The most frequently used in the biodiesel industry are sodium and potassium hydroxides and alkoxides (NaOH, KOH, $NaOCH_3$, and $KOCH_3$). For small biodiesel producers, the alkoxides, sodium hydroxide (NaOH) and potassium hydroxide (KOH) flakes, are mostly preferred due to lower cost, easier transportation and storage. In biodiesel commercial production, sodium methoxide ($NaOCH_3$) and potassium methoxide ($KOCH_3$), are prior selected because it released the lower amount of water during transesterification reaction than that the hydroxides. But, they present some drawbacks such expensive and more difficult to handle [24].

1.2.4 Transesterification reaction

Transesterification (also called alcoholysis) is the reaction of vegetable oils or animal fats with an alcohol in the presence of a suitable catalyst to form alkyl esters and glycerol [31]. A catalyst is usually used to improve the reaction rate and yield. Generally, homogeneous base catalysts, sodium and potassium hydroxides and alkoxides, are often used for alcoholysis according to their excellence catalytic activity under mild reaction conditions [29]. According to reversible transesterification reaction, an excess alcohol is used to shift the equilibrium to the product side [26]. The general equation of transesterification reaction is presented in Fig. 2-1.

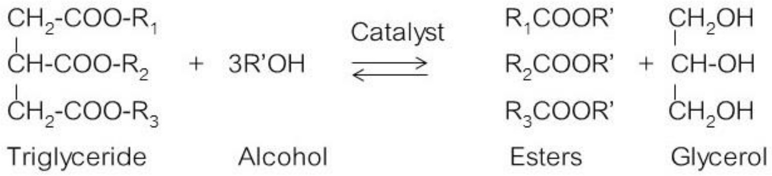


Fig. 1.1 Transesterification reaction

Where: R_1, R_2 and R_3 are long-chain hydrocarbons. R´ is alkyl group of alcohol

Generally, transesterification reaction (**Fig. 1.1**) is a reversible reaction which a triglyceride is converted stepwise to diglyceride (DG), monoglyceride (MG) and finally glycerol (GL), as follows:

$$\begin{aligned}
&\text{Triglyceride (TG)} + \text{ROH} \longleftrightarrow \text{Diglyceride (DG)} + \text{R'COOR} \\
&\text{Diglyceride (DG)} + \text{ROH} \longleftrightarrow \text{Monoglyceride (MG)} + \text{R''COOR} \\
&\text{Monoglyceride (MG)} + \text{ROH} \longleftrightarrow \text{Glycerol} + \text{R'''COOR}
\end{aligned}$$

The reaction mechanism of alkaline-catalyzed transesterification has been proposed by several literatures [27], [32]. The actual catalytic species, the methoxide ion, is formed in the alkoxide-methanol solution. The methoxide ion directly acts as a strong nucleophile. In the first step, transesterification is initiated by nucleophilic attack of alkoxide ion on the carbonyl carbon atom of the triglyceride molecule, after that the tetrahedral intermediate is formed. In the second step, this intermediate is changed into the methyl ester and the anion of the glyceride. The latter reacts with methanol to form a glyceride molecule. After that it will be converted into the monoglyceride and glycerol, and a methoxide ion, which can catalyze another catalytic cycle.

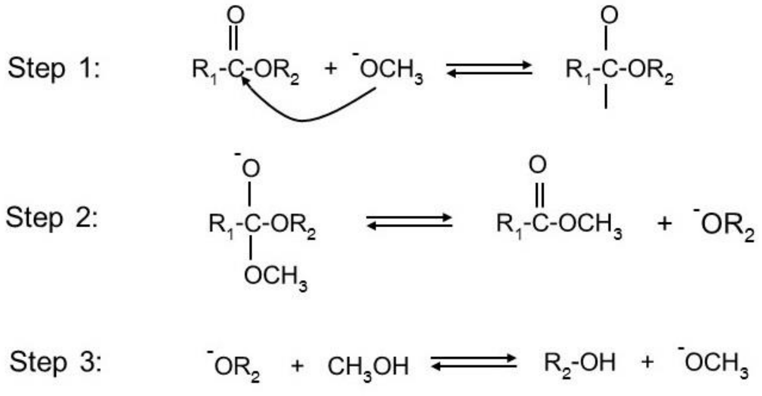


Fig. 1.2 Reaction mechanism of transesterification reaction [33]

1.2.5 Soap formation in biodiesel production

In biodiesel production, FFA and moisture contents are the key parameters affecting the yield of biodiesel according to Lurgi GmbH [34] and Crown Iron Works [23], they had specified feedstock properties as maximum acidity 0.1% or 0.5% and maximum moisture and volatiles as 0.1% or 0.05%. These impurities are significant to soap formation in the transesterification process. Soap can be produced by neutralization of the free fatty acid (FFA) in the oil and by saponification of triglyceride and ester.

Saponification reaction is a reaction leads to the formation of soap, triglycerides in fat/oil react with aqueous sodium hydroxide (NaOH) or potassium hydroxide (KOH), and they are converted into soap and glycerol (called alkaline hydrolysis of ester) as present in alkaline catalysts, for the neutralization reaction of fatty acid/ester, alkaline catalysts are hydroxides and methoxides. Basic catalysts present the disadvantages of soap formation such as it consumes catalyst, decrease biodiesel yield, and enhance emulsifier of the mixture of glycerol and ester.

In neutralization [14], the FFA reacts with an alkaline catalyst (NaOH or $NaOCH_3$) and turns to soap, water, or alcohol as shown in Eq. (1.1) and Eq. (1.2):

$$\text{FFA} + \text{NaOH} \longrightarrow \text{Soap} + \text{Water} \qquad \text{Eq. (1.1)}$$

$$\text{FFA} + \text{NaOCH}_3 \longrightarrow \text{Soap} + \text{Alcohol} \qquad \text{Eq. (1.2)}$$

However, the water in the oil and alcohol phases plays a very important role in soap formation. If a high amount of water is present it can hydrolyze the ester and cause reversed esterification, yielding FFA and alcohol again. Hydrolysis reaction is a nucleophile substitution reaction where the nucleophile (water or hydroxide ion) attacks an electrophilic carbon and displaces a leaving group.

Hydrolysis of fats/oils produces fatty acids and glycerol as shown in Eq. (1.3) [35]. The stoichiometry hydrolysis of triglycerides can be produced one mole of glycerol and three moles of fatty acids.

$$\text{TG} + 3\text{Water} \longleftrightarrow 3\text{FFA} + \text{Glycerol} \qquad \text{Eq. (1.3)}$$

For hydrolysis of ester [36], there are reactions between ester and water to forms free fatty acid (FFA) and alcohol, the mechanism of hydrolysis reaction is described in Eq. (1.4). This reaction is reversible reaction, can be catalyzed by acid or base catalysts.

$$\text{Ester} + \text{Water} \longleftrightarrow \text{FFA} + \text{Alcohol} \qquad \text{Eq. (1.4)}$$

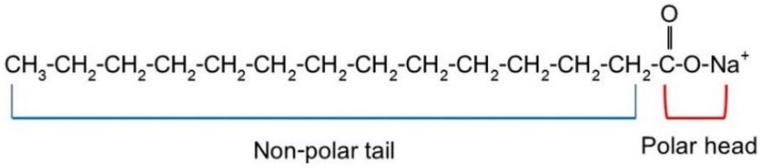
In saponification reaction [14], triglyceride or fatty acid methyl ester (FAME) reacts with a base catalyst to form soap, glycerol, and methanol as in Eq. (1.5) and Eq. (1.6). The ester is transferred into potassium or sodium salt of a long-chain carboxylic acid (soap) and alcohol. It is difficult to recover ester from gel and to separate ester from the emulsion. Therefore, saponification is a significant key parameter of the biodiesel yield loss.

$$TG + 3NaOH \longrightarrow 3Soap + Glycerol \qquad \text{Eq. (1.5)}$$

$$FAME + NaOH \longrightarrow Soap + Methanol \qquad \text{Eq. (1.6)}$$

In transesterification using alkaline-catalyst, the main product glycerol is highly polar whereas the side-product soap is an amphiphile and considered an emulsifier. These may disturb the mixing and interactions of the components in the system. In acid-catalyzed transesterification there is no soap formation and the interactions between phases may be different from those with an alkaline catalyst.

In soap molecule (**Fig. 1.3**), it has two parts: a polar group (-COO-Na+) which called the polar head, and a non-polar group (R-hydrocarbon part) which called the non-polar tail. The polar head is hydrophilic in nature (water loving) and the non-polar tail is hydrophobic (water repelling) in nature [37]. According to emulsifying property of soap, it could enhance the dissolution of oil and alcohol, so, the effect soap on transesterification process should be further examined.



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-Na^+$$

Fig. 1.3 General representation of soap molecule [38]

The self-transesterification of FAME and methanol with a catalyst is shown in Eq. (1.7) [39].

$$RCOOR'' + R'OH \longleftrightarrow RCOOR' + R''OH \qquad \text{Eq. (1.7)}$$

where R’ and R” are some given alkyl groups.

1.3 Literature Reviews

The reaction variables such as FFA content, water content, catalyst concentration are key roles in biodiesel yield as shown in **Table 1.2**, which is related to soap formation affecting the yield of biodiesel. Moreover, the solubility behavior of alcohol and oil is important issue due to the mass transfer effect of transesterification reaction.

The effect of FFA on biodiesel production is a significant reaction parameter according to industrial biodiesel companies such as Lurgi GmbH [34] and Crown Iron Works [23] had specified feedstock properties as maximum acidity 0.1% or 0.5% and maximum moisture and volatiles as 0.1% or 0.05%. The low-quality feedstocks with high FFA content can be generated high soap formation due to the neutralization reaction. Therefore, the addition of an excess amount of alkaline catalyst is a one of the solution choice. But, it renders the high soap formation.

For the effect water content in feedstock, oil and ester (biodiesel) will be hydrolyzed to FFA [35], [40], [41]. So, FFA can be reacted with the alkaline to form soap. Soap is produced by neutralization of the free fatty acid (FFA) in the oil and by saponification of triglyceride and ester. In neutralization, the FFA reacts with an alkaline catalyst (NaOH or $NaOCH_3$) and turns to soap, water, or alcohol. Kwiecien et al (2009) demonstrated that yield of methyl ester (biodiesel) is significantly reduced by a higher acid number, as well as enhanced soap formation [42].

However, the water in the oil and alcohol phases plays a very important role in soap formation. If a high amount of water is presented, it can hydrolyze the ester [43] and cause reversed esterification [40], [44], yielding FFA and alcohol again.

Table 1.2 The effect of soap formation in transesterification reaction on the remaining catalyst, soap, yield and ester content, as reported by various researchers

Feedstock	Transesterification condition: initial catalyst content, alcohol/oil, time (min), temp (°C)	Soap formation (wt%)	Yield (wt%)	Ester content (wt%)	Reference
Refined sunflower oil with acid value (AV) < 0.1 wt%	KOH, NaOH, $NaOCH_3$, and $KOCH_3$, catalyst content (0.172 to 0.257 mol/L), MeOH (25 v/v%) and ETOH (25 to 40 v/v%), 60 to 180 min, and 20 to 70 °C.	100% (KOH and NaOH), 25% ($NaOCH_3$) and 28% ($KOCH_{3)}$	N.D.	N.D.	[13]
Crude soybean oil with different acid value (AV) of 0.01, 0.41 and 1.13 wt%	$NaOCH_{3,}$ $KOCH_3$, NaOH, KOH, catalyst content (7.8 to 13.2 mol%), MeOH (25 vol%), 90 min, and 60°C.	18, 70, and 75% for acid value of 0.01, 0.41 and 1.13 wt% respectively.	N.D.	>96.5 (for $NaOCH_{3,}$ $KOCH_3$, and NaOH) and 95 (for KOH)	[14]
Canola oil	$NaOCH_{3,}$ $KOCH_3$, NaOH, KOH, catalyst content (0.1 to 0.3 mol/mol), MeOH/oil molar ratio (3:1 to 6:1), 90 min, 10 min and 40 to 60°C.	Soap 7.56 mmol/mol (0.75 wt%)	N.D.	95.8 (for $KOCH_3$ 0.2 mol/mol)	[45]

Haas et al (2005) indicated that water inhibits transesterification reactions according to the required ester transfer reaction into ester hydrolysis, leading to formation of FFAs [46].

However, triglyceride or fatty acid methyl ester (FAME) can be reacted with a base catalyst to form soap, glycerol, and methanol by saponification reaction [47].

Eze et al (2015) showed that FAME saponification rate in ethanol–alkaline hydroxide was 3.5 times higher than that in methanol–alkaline hydroxide due to the presence of high water content in ethanol [48].

Kwiecien et al (2009) revealed that the rate of soap formation increased with increasing of acid value of crude soybean oil from 0.01 to 1.13 wt% [42].

In the effect of catalyst concentration on transesterification, catalysts used for the alkaline-catalytic transesterification of triglyceride is such as sodium hydroxide, sodium methoxide, potassium hydroxide and potassium methoxide.

Mendow et al (2011) [13] studied the performance of different homogeneous alkali catalysts during transesterification of refined sun flower oil using NaOH, KOH, $NaOCH_3$ and $KOCH_3$ as catalyst. The reaction is carried out in a single reaction step. The amounts of catalyst varied from 0.45-1.5g/100 mL oil. The results found that the best conversion when using either sodium methoxide or potassium methoxide [13].

So, these impurities (such as FFA, water) in feedstocks are significant to soap formation in the transesterification process because of the catalyst consumption, biodiesel yield reduction and of and purification problem [14].

In the effect solubility behavior on kinetic studies of transesterification reaction, it has mostly been on a homogeneous system, and many studies have observed that the initial mass transfer of the reacting components is probably negatively impacted by the poor mixing of the components. Visibly the nonpolar phase (triglyceride) and polar phase (alcohol) are initially immiscible and create two different phases. Thus, the immiscibility of alcohol and triglyceride leads to a mass-transfer resistance in transesterification [19]. Hence, the mass transfer between these phases could limit the reaction rate. Noureddini and Zhu (1997) proposed a reaction mechanism consisting of an initial mass transfer controlled region followed by a kinetically controlled region [18]. Mass transfer limitation between the polar methanol-glycerol phase and the non-polar oil phase causes slow reaction rates at the initial and final stages of base-catalyzed transesterification.

Some studies of kinetics models [18], [21] are based on the liquid-liquid reaction and the stability of phase continuity in the liquid-liquid reaction, where a large excess phase tends to be continuous and the minority phase is disperse. When the phase volumes are fairly similar, either phase may be continuous. In a liquid-liquid reaction, mass transfer with a chemical reaction is well described by Levenspiel (1999) [49] and the standard theory used to explain mass transfer is the two-film theory by Whitman (1923) [50]. In a small droplet of the liquid-liquid system, internal circulation is minimal if the mass transfer coefficient of the internal film is lowest. Thus, mass transfer can be enhanced by droplet coalescence and redispersion. Tubino, M. et al. (2014) proposes that methanolysis with alkaline catalysts should be assumed to be heterogeneous [51].

A mass transfer limited model was proposed by Slinn, M. (2008) [21] in **Fig. 1.4.** This model based on the immiscibility of oil and methanol, with methanol as droplets in a viscous oil phase and, through reaction, are changed to rigid glycerol droplets. Hence, the reaction only occurs at the interface of the methanol and triglyceride film.

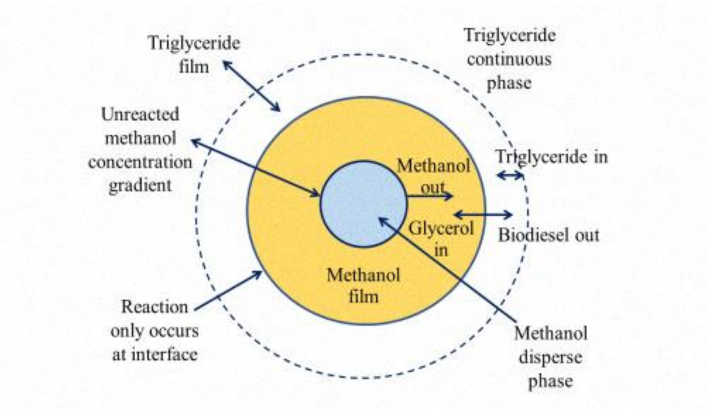


Fig. 1.4 Mass transfer limited model [21]

The mixing of the two phases can be improved by increasing the reaction temperature or by stirring. However, there are high production costs. Adding co-solvents in the reaction mixture is one suggested method to improve the mixing of oil and alcohol and increase the reaction rate [52], [53]. The co-solvent needs both polar and non-polar parts in its molecules in order to reduce interfacial tension between alcohol and triglyceride and enhance their interactions [52], [53]. Using a co-solvent has been reported to facilitate mixing during transesterification under mild conditions and short reaction time. Additionally, tetrahydrofuran (THF) is among the most effective co-solvents for transesterification (**Table 1.3**), because it has a low boiling point (67 °C) similar to that of methanol (65 °C) making temperature control easy [54].

Table 1.3 The effects of a co-solvent on transesterification reaction

Feedstock	Transesterification conditions					Ester content (wt%)	Reference
	Catalyst (wt%)	MeOH/oil molar ratio	Time (min)	temp. (°C)	Oil/THF weight ratio (g/g)		
Soybean oil and coconut oil	NaOH (1.0)	27:1	7	23	approx. 0.97:1	99.4	[55]
Soybean oil	$NaOCH_3$ (1.0-3.0),	27:1	1-480	23-50	approx. 0.98:1	N.D.	[56]
Soybean oil	NaOH (1.0),	6:1,	240,	23,	approx. 0.41:1,	97.5,	[57]
	KOH (1.4),	6:1,	240,	23,	approx. 0.41:1,	98.2,	[57]
	$NaOCH_3$ (1.35)	6:1	240	23	approx. 0.41:1	99.1	[57]

As mentioned above, understanding the solubility and mixing of multiple components in the biodiesel production process is fundamentally important. The addition THF as a co-solvent to transesterification was studied to clarify the single- or two-phase reaction aspects mentioned by several reviews (**Table 1.4**).

Table 1.4 The scope of our solubility studies in the context of transesterification and saponification reactions

No	Initial Substances in the System				Expected Reaction	Solubility according to literature	References
1	MeOH	RPO	-	-	None	Partially Miscible	[20]
2	MeOH	RPO	THF	-	None	Homogeneous	[58]
3	MeOH	FAME	-	-	None	Homogeneous	[59]
4	MeOH	-	THF	-	None	-	this study
2	MeOH	RPO	-	Alkaline	Transesterification /saponification	Suspension	[14], [45], [60]
3	MeOH	RPO	THF	Alkaline	Transesterification /saponification	Homogeneous	[57], [61]–[63]
6	MeOH	FAME	-	Alkaline	Transesterification /saponification	Homogeneous	[36], [48]
7	MeOH	FAME	THF	Alkaline	Transesterification /saponification	-	this study
8	MeOH	RPO	-	Acid	Transesterification	Suspension	[64]–[66]
9	MeOH	RPO	THF	Acid	Transesterification	Homogeneous	[67], [68]
10	MeOH	FAME	-	Acid	Transesterification	-	this study
11	MeOH	FAME	THF	Acid	Transesterification	-	this study

1.4 Research objective

This study aims to understand the mixing of multicomponent (triglyceride, FAME, methanol, and THF) in the biodiesel production process, to clarify the effect of FFA, water, and catalyst amount on the reaction zone of saponification, and to examine the source of losses (physical loss and chemical loss) in transesterification process.

1.5 Scopes of research work

1) To study the solubility and mixing of multiple components in the biodiesel production process.
2) To study the effect of FFA, water and catalyst amounts on the saponification and transesterification reactions.

1.6 Expected Outputs

1) The study of the effect of the solubility of multicomponent systems on biodiesel production can explain the solubility behaviors of alcohol and raw materials in the production system.
2) The study of the effect of FFA, water and catalyst amounts on saponification and transesterification can explain the interaction of the reaction zone in saponification reaction and the source of losses (physical loss and chemical loss) in biodiesel production process.

CHAPTER 2

RESEARCH METHODOLOGY

2.1 Materials

2.1.1 Raw materials

Refined palm oil (RPO) containing approximately 0.1wt% of FFA and with 0.2wt% moisture content, palm fatty acid distillate (PFAD) containing approximately 92wt% of FFA, and a commercial grade fatty acid methyl ester (FAME, about 97.3wt% purity) were all received from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University, Thailand.

All the raw materials, RPO, PFAD, and FAME were dewatered by heating at 105 °C for 3 h, and then analyzed for remaining moisture (<0.05wt%).

2.1.2 Chemicals

1) Methanol (CH_3OH, MeOH) 99.8wt% purity commercial grade was purchased from P-General Co. Ltd.

2) Tetrahydrofuran (C_4H_8O, THF) 99.9wt% purity HPLC grade was bought from RCI Labscan Limited.

3) Sulfuric acid (H_2SO_4) 98.0wt% purity commercial grade was purchased from AGC Chemicals (Thailand) Co., Ltd.

4) Solid sodium methoxide ($NaOCH_3$) 99.5wt% purity commercial grade was purchased from Dezhou Longteng Chemical Co. Ltd, People's Republic of China.

2.2 Equipment and instrument

1) An apparatus set-up for visual observations (**Fig. 2.1**) was used for study of multicomponent systems in biodiesel production process.

2) An apparatus set-up for reaction zone study (**Fig. 2.2**) was used for study of reaction zone of transesterification and saponification reactions.

3) A 1.0 L glass three-neck flat bottom flask equipped with a magnetic stirrer, a thermometer, a reflux condenser and one spout for sampling and/or chemical addition (**Fig. 2.3**) was used for transesterification process.

2.3 Methodology

The mixing of multiple components (triglyceride, FAME, methanol, and THF) in the biodiesel production process was studied in an apparatus set-up for visual observations and an LCD digital microscope for the visual observations in this work to clarify single-phase (homogeneous system) or two-phase (suspension system) of mixtures.

The study of effect of FFA, water, and catalyst amount on the reaction zone of transesterification and saponification reaction was studied in order to determine the interactions of key substances in reaction zone.

The effect of important reaction variables such as FFA, water and catalyst amount on the transesterification reaction were preliminary investigated in order to explain the source of losses (physical loss and chemical loss) in biodiesel production process.

2.3.1 Solubility of methanol in refined palm oil (RPO), fatty acid methyl ester (FAME), tetrahydrofuran (THF) and their mixture

The experiment used a 1-L glass three-neck round bottom flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser. The flask contains one port for product sampling and adding chemicals.

The apparatus set up is shown in **Fig. 2.1** For operation, 100 grams of oil mixture containing FAME, RPO, and THF was added in the flask at room temperature. Then methanol was gradually added. During the reaction, approximately 1 mL of the mixture was sampled and immediately analyzed with an LCD digital microscope (Novel NLCD-307) at 100X magnification. The solubility of methanol in RPO was monitored from the start until the transesterification reaction was completed.

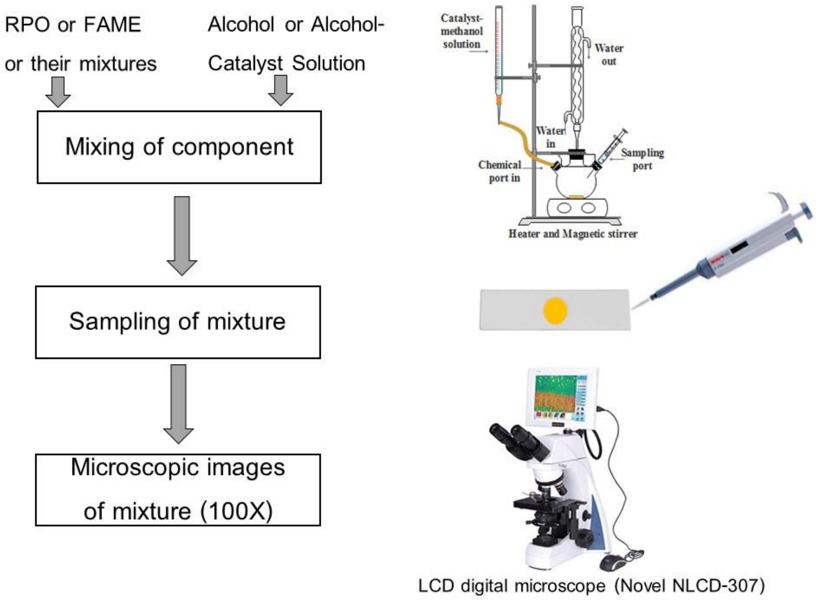


Fig. 2.1 Schematic of the microscopic visualization experiments to clarify single-phase (homogeneous system) or two-phase (suspension system) of multicomponent in biodiesel production system

2.3.2 Formation of soap-methanol droplets or sulfuric-methanol droplets in fatty acid methyl ester (FAME) as continuous phase

The experiment was similarly performed in section 2.3.1, except that methanol was premixed with soap or catalyst. The methanol was mixed with FAME at the molar ratio of 2:1 (22.64 g of methanol and 100 g of FAME). In the case of soap-methanol solution, soap containing 1wt% of FAME was premixed with methanol. The concentrations of $NaOCH_3$ and H_2SO_4 in methanol were 5.30wt% and 22.10wt%, respectively. Phenolphthalein indicator was used to stain the alkaline-methanol solution. Methyl orange indicator was used to stain the acid-methanol solution.

2.3.3 Solubility of methanol in transesterification system having alkaline catalyst

The procedures were similar to those in section 2.3.1, but without adding catalyst, and with methanol premixed with $NaOCH_3$. The concentration of $NaOCH_3$ in methanol was 5.34wt%. Phenolphthalein indicator was used to stain the alkaline-methanol solution.

2.3.4 Solubility of methanol in transesterification reaction added with tetrahydrofuran (THF), alkaline, and acid catalysts

These procedures were similarly as in section 2.3.1, but with catalyst, except that the oil was premixed with THF at the ratio of 1 to 0.4 (100 g of oil and 40.67 g of THF). In addition, two types of catalyst were applied separately, namely $NaOCH_3$ and H_2SO_4. The concentrations of $NaOCH_3$ and H_2SO_4 in methanol were 5.34wt% and 13.80wt%, respectively. In the case of acid catalyst, methyl orange indicator was used to stain the acid-methanol solution.

2.3.5 Soap formation and self-transesterification of fatty acid methyl ester (FAME)

Soap formation was observed in biodiesel (FAME) production. The experiment was similarly to that in section 2.3.1, except that methanol was now premixed with the catalyst. The methanol was mixed with FAME at the molar ratio of 6:1 (67.61 g of methanol and 100 g of FAME). When co-solvent was used, 123.13 g of THF was premixed with 100 g of FAME to obtain the THF/FAME weight ratio 1.2:1. The concentrations of $NaOCH_3$ and H_2SO_4 in methanol were 1.80wt% and 4.60wt%, respectively.

2.3.6 Reaction zone study

2.3.6.1 Reaction zone of transesterification using alkaline and acid catalysts

This work is aimed to clarify the reaction zone during the transesterification reaction of RPO and FAME using alkaline ($NaOCH_3$, 8.20wt% of MeOH) or acid catalyst (H_2SO_4, 11.03wt% of MeOH). The experiment was performed on a concave glass slide used as a micro-reactor. A drop of RPO (about 10 µL) was placed at the center of the concave glass slide at room temperature. The slide was moved for centered view on the NLCD-307 microscope (40X magnification). Then, a small amount of methanol-alkaline-phenolphthalein solution (about 1µL) was placed on the drop of RPO. A photo was then taken every 5 seconds. Reversed experiments were then done by putting a drop of methanol-alkaline-phenolphthalein solution at the center of the concave slide, and then a small amount of RPO was placed on it, and immediately imaged every 5 seconds. These trials were repeated several times. For the acid catalyzed cases, methyl orange indicator was used to stain the acid-methanol solution. For FAME, the same staining was applied.

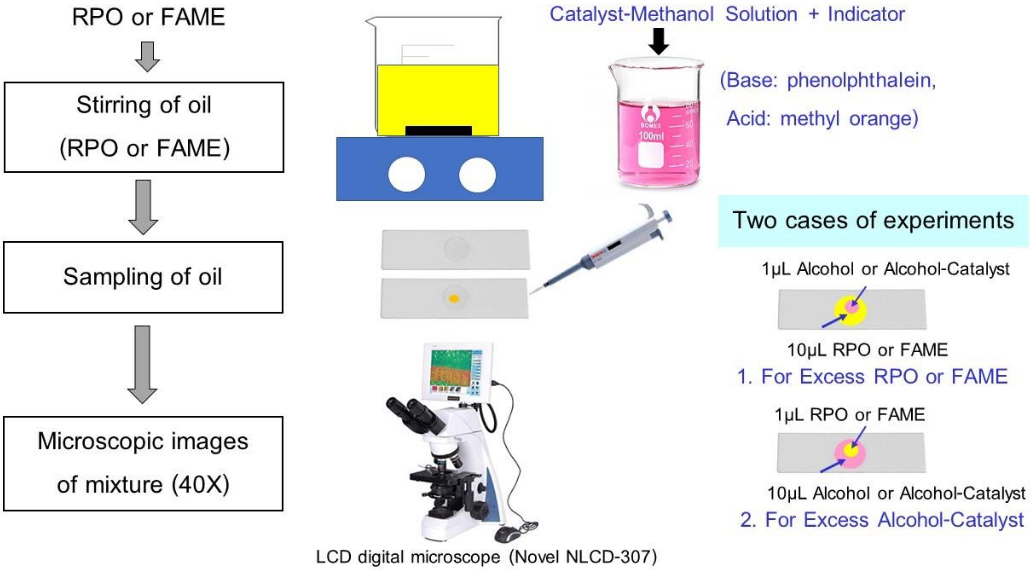


Fig. 2.2 Schematic of the reaction zone of transesterification and saponification reactions

2.3.6.2 Effect of FFA on the reaction zone of the saponification reaction

This work aimed to clarify the effects of FFA in the raw materials (RPO or FAME) on the reaction zone of saponification reaction. The experiments were performed on a concave glass slide serving as a micro-reactor. A small pool of raw material (10 μL approximately) at room temperature was placed on the concave glass and was arranged to central location in the view of the NLCD 307 microscope. Phenolphthalein indicator was added early to the sodium methoxide-methanol solution in order to identify the alkaline catalyst. A very fine drop of methanol-alkoxide-phenolphthalein solution (1 μL approximately) was spotted on the pool of raw material. A photo was taken every 5 seconds. A reversed trial was done by putting a fine drop of the raw material (RPO or FAME,1 μL approximately) on the center of the concave slide and adding a small amount of methanol-alkoxide-phenolphthalein solution (10 μL approximately) over it, with photo taken every 5 seconds. These trials were repeated several times.

2.3.6.3 Effects of FFA content in fatty acid methyl ester (FAME) on the reaction zone of the saponification reaction

In saponification of FAME with sodium methoxide-methanol solution, there is only soap and alcohol formation but no glycerol formation. Thus, effects of glycerol on the reaction zone will be negligible. This section aims to examine the reaction zone of real soap formation during saponification of FAME. High quality FAME with 100% purity and 0.03wt% moisture content was used. The FFA content in FAME was varied from 0.1 to 2 wt% by adding PFAD in FAME. The sodium methoxide concentration was 4.42wt% in methanol (1wt% of oil mass, if using 1:6 molar ratio of methanol to oil). The same procedures were done as described in the previous section.

2.3.6.4 Effects of FFA content in refined palm oil (RPO) on the reaction zone of the saponification reaction

In saponification of RPO with the alkaline catalyst-methanol solution, glycerol and soap may be produced. Thus, the reaction zone of this case may different from the previous one. The various FFA contents in RPO from 0.1 to 2wt% were prepared by adding PFAD in RPO. The sodium methoxide concentration was 4.42wt% in methanol (1wt% of oil mass if using 1:6 molar ratio of methanol to oil). The experiments were similar to those explained earlier.

2.3.6.5 Effects of water content in refined palm oil (RPO) on the reaction zone of the saponification reaction

The effects of water on the reaction zone of saponification of RPO were investigated. The various water contents in RPO from 0.1 to 1wt% oil were prepared by adding water to RPO. In this section, the FFA content of RPO was kept at 0.1wt% of oil since this can avoid the neutralization of FFA. The sodium methoxide concentration was

4.42wt% in methanol (1wt% of oil mass if using 1:6 molar ratio of methanol to oil). The procedures were as before.

2.3.6.6 Effects of alkaline concentration on the reaction zone of saponification reaction of refined palm oil (RPO)

These experiments assess the effects of alkaline concentration on the reaction zone of RPO saponification reaction. The sodium methoxide concentration was varied between 2.21 and 8.83wt% in methanol (0.5-2.0wt% in oil if using 1:6 molar ratio of methanol to oil). RPO with FFA and water contents (0.1 and 0.1wt%, respectively) was used to examine the low soap formation phenomena. For high soap formation RPO with FFA and water contents of 1 and 0.5wt%, respectively, was used. The procedures were as before.

2.3.7 Variables (FFA, water, and catalyst concentration) affecting the $NaOCH_3$-catalyzed transesterification of refined palm oil (RPO) with methanol

The transesterification of RPO was carried out in a 1-L glass three-neck flat bottom flask equipped with a magnetic stirrer, a thermometer, a reflux condenser and one spout for sampling and/or chemical addition. All experiments were performed at 50 °C, the initial methanol-to-oil molar ratio was 6:1, and stirring was at 500 rpm for 30 min. The experiment began as follows. Two hundred grams of refined palm oil was poured into the reactor and heated up to the desired reaction temperature. A sodium methoxide-methanol solution was earlier prepared from solid $NaOCH_3$ by dissolving in methanol, and this was added into the reactor. The mixture was then stirred for the next 30 min. The reaction mixture was transferred to a separation funnel and let stand for 3 hours. The glycerol rich phase (lower phase) was separated from the ester rich phase. The remaining catalyst and soap contents were determined in each phase by titration (modified AOCS Official Method Cc 17-79). The ester rich phase was washed to remove impurities including methanol, remaining catalyst, soap, and glycerol. The washed ester was heated to remove the residual water. Finally, the ester content was analyzed by using Thailand Petty Patent 5060. Photographs (100X magnification) of the interface between biodiesel and water phases in the washing step were taken by an LCD digital microscope (Novel NLCD-307).

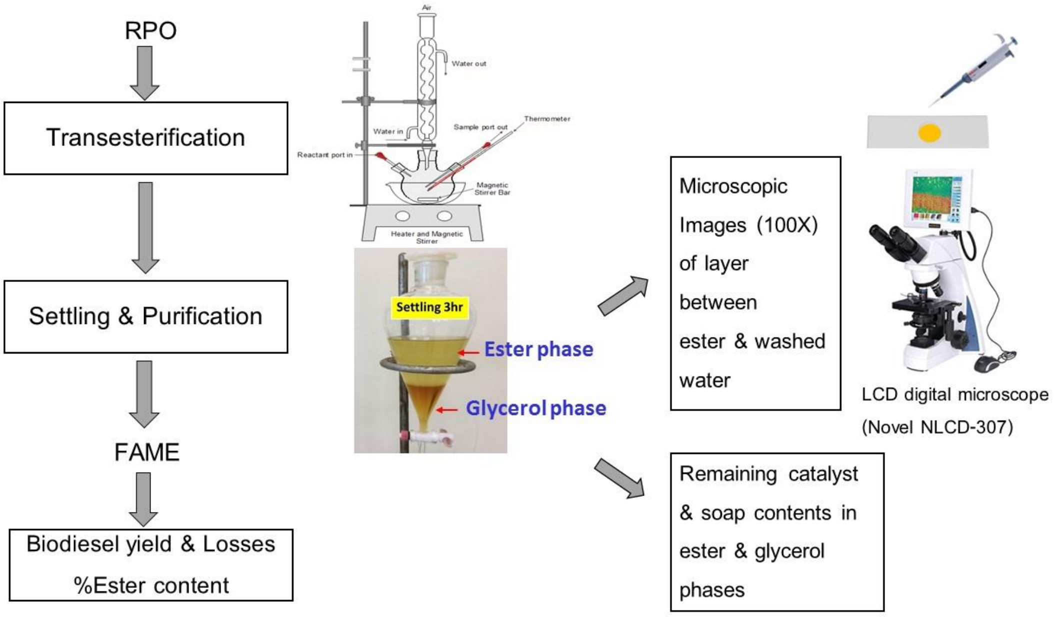


Fig. 2.3 Schematic of the effect of FFA, water and catalyst amount on $NaOCH_3$-catalyzed transesterification of refined palm oil and methanol

2.3.7.1 Effects of FFA content on the $NaOCH_3$-catalyzed transesterification of refined palm oil (RPO) with methanol

A set of experiments was carried out to determine the effects of FFA content. The FFA content was varied between 0.12 and 1wt% referred to oil mass. The $NaOCH_3$ concentration used was 0.98wt% referred to oil mass. The water content was fixed at 0.18wt% referred to oil mass.

2.3.7.2 Effects of water content on the $NaOCH_3$-catalyzed transesterification of refined palm oil (RPO) with methanol

A set of experiments was performed to demonstrate the effects of the water content. The water content was varied between 0.05 and 0.8wt% referred to oil mass, while the FFA content was fixed at 0.18wt% referred to oil mass. The $NaOCH_3$ concentration used was 0.98wt% referred to oil mass.

2.3.7.3 Effects of catalyst concentration on the $NaOCH_3$-catalyzed transesterification of refined palm oil (RPO) with methanol

A set of experiments was done to evaluate the effects of catalyst concentration. The $NaOCH_3$ concentration was varied between 0.49 and 1.11wt% referred to oil mass, while the FFA and water contents were fixed at 0.17 and 0.18wt% referred to oil mass, respectively.

2.4 Analytical methods

The water contents in refined palm oil and methanol were measured by Karl Fischer method (ISO 12937). FFA content was tested by titration (Method AOAC 940.28). Catalyst and soap contents were measured by titration (modified AOCS Official Method Cc 17-79) [60].

CHAPTER 3

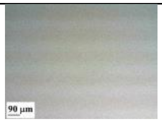
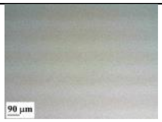
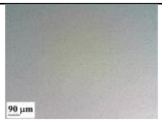
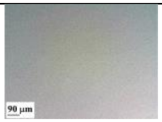
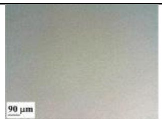
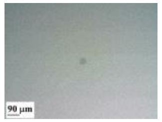
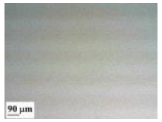
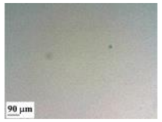
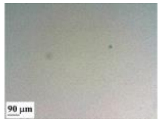
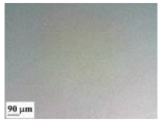
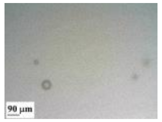
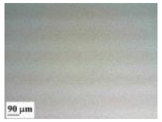
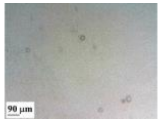
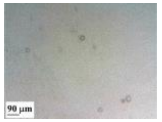
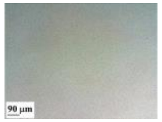
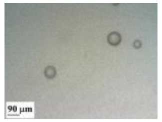
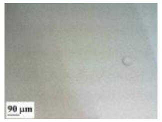
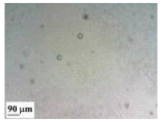
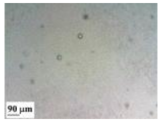
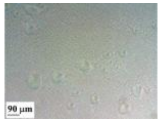
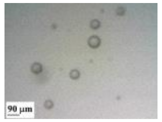
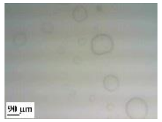
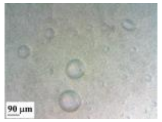
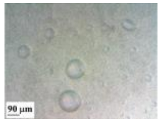
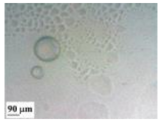
RESULT and DISCUSSION

3.1 Solubility of methanol in refined palm oil (RPO), fatty acid methyl ester (FAME), tetrahydrofuran (THF) and their mixture

The images of methanol solubility in RPO, FAME, THF and their mixture are listed in **Tables 3.1** and **3.2**. Regarding solubility of methanol in RPO, the microscope images show fine droplets of methanol present at 7.9wt% of the RPO. This concentration is similar to those reported earlier (8 to 10wt%), though the prior experiment was performed at different condition [20]. It should be noted that the more methanol was added in RPO, the greater drop formation was observed. Besides, the mixture of RPO/THF (at a weight ratio of 1:0.4) provides better methanol solubility. Fine droplets appeared as the amount of methanol was 13.6wt% in 100 g of RPO. Interestingly, FAME and methanol mixture shows perfect miscibility.

The results are similar to those with added THF. Increasing the FAME proportion could reduce methanol drop formation in the solution, as could be seen in the reduction of methanol drop formation at 7.9wt% of methanol in mixture A (15% FAME), compared with 11.3wt% methanol in mixture B (50% FAME), and at 13.6wt% of methanol in mixture C (85% FAME), respectively. FAME has lower polarity than THF and possibly acted as a co-solvent for RPO. Moreover, the difference between the non-polar triglyceride and the polar methanol is very significant, so that even the co-solvent THF could only induce partial miscibility. With a large proportion of methanol, the methanol might separate and be suspended in the RPO/THF system. Thus, from this study, FAME could facilitate mixing and interactions of MeOH and RPO.

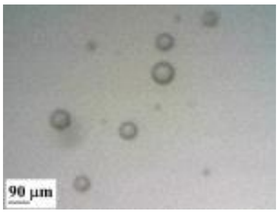
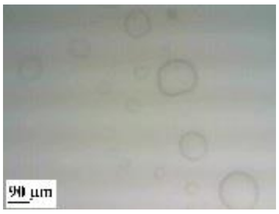
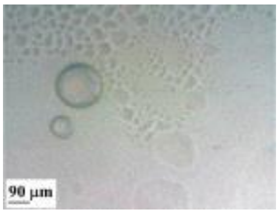
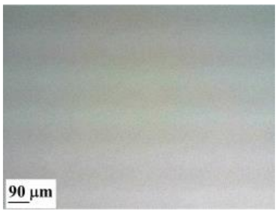
Table 3.1 Photographs of methanol solubility in refined palm oil (RPO), fatty acid methyl ester (FAME), tetrahydrofuran (THF) and their mixture at 32 °C (Photographs taken with 100X magnification)

MeOH wt%	RPO	RPO/THF	RPO/FAME A (85: 15wt%)	RPO/FAME B (50: 50wt%)	RPO/FAME C (15: 85wt%)	FAME
0.2						
7.9						
11.3						
13.6						
22.6						

Note: A is the RPO/FAME weight ratio of 85:15, B is the RPO/FAME weight ratio of 50:50, C is the RPO/FAME weight ratio of 15:85.

Experimental conditions: Raw material (100 g, RPO, or FAME, or RPO/FAME); THF (40.67 g); THF/RPO weight ratio (0.4:1); MeOH (22.64 g).

Table 3.2 Expected solubility and expected reaction of methanol solubility in refined palm oil (RPO), fatty acid methyl ester (FAME), tetrahydrofuran (THF) and their mixture at 32 °C

Images of MeOH adding 22.6wt%	Components	Expected solubility	Expected reaction
	RPO+MeOH	Partial miscibilty	-
	RPO/THF+MeOH	MeOH was not completed soluble in RPO (Suspension)	-
	RPO/FAME (18:85)+MeOH	MeOH was not completed soluble in RPO (Suspension)	-
	FAME+ MeOH	Perfect miscibility (Homogeneous)	-

From **Table 3.2**, methanol shows partial miscible in refined palm oil (RPO), however, it shows perfect miscible in fatty acid methyl ester (FAME). In case of methanol addition into the mixture of RPO/FAME, an increase of mass ratio of biodiesel to RPO (15:85) renders the methanol soluble in RPO, but the partial miscibility is still observed. For tetrahydrofuran (THF) addition in RPO, this indicates that the same phenomena as suspension system. So, THF cannot enhance the homogeneous mixture in these systems.

3.2 Formation of soap-methanol droplets in FAME as continuous phase

In analysis of the images, we use FAME as the benchmark substance to study methanol solubility in our system. In **Table 3.3**, Figure (a) is a perfect miscible solution of MeOH and FAME. When we add some soap (around 1wt% of FAME) into this mixture, small droplets emerge, probably emulsified methanol-soap as in Figure (b). The mixture of FAME and alkaline-methanol solutions is seen in Figure (c). The pink color indicates alkaline-phenolphthalein-methanol drops separated from the miscible methanol-FAME solution, forming a two-phase system. The possible reaction is saponification of FAME.

$$\mathrm{FAME} + \mathrm{NaOH} \longrightarrow \mathrm{Soap} + \mathrm{Methanol} \qquad \text{Eq. (1.6)}$$

This is caused by soap formation and we confirmed this by soap measurement in this mixture. Therefore, a small amount of soap acts as an emulsifier that suspends methanol droplets in the methanol-FAME continuous solution phase.

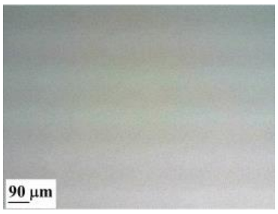
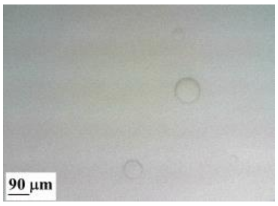
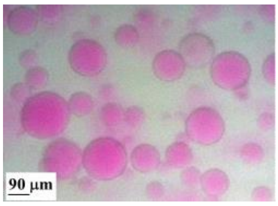
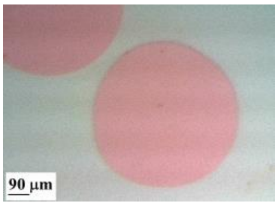
The mixture of FAME and acid-methanol is shown in Figure (d). Methyl orange indicator stains the dispersed acid-methanol solution. As “like dissolves like” there were strong polar attractive forces between sulfuric acid and methanol. The possible reaction is a self-transesterification (Eq. 1.7) with an acid catalyst. This is a slow reaction.

$$\mathrm{RCOOR''} + \mathrm{R'OH} \xleftrightarrow{\text{Catalyst}} \mathrm{RCOOR'} + \mathrm{R''OH} \qquad \text{Eq. (1.7)}$$

Where R’ and R” are some given alkyl groups

The results indicate that esterification is a liquid-liquid reaction because even though FAME is more polar than triglyceride, it still is insoluble in acid solutions of methanol.

Table 3.3 Formation of soap-methanol droplets or sulfuric-methanol droplets in FAME as continuous phase (Photographs taken with 100X magnification)

Components	Images (100X)	Expected solubility	Expected reaction
FAME+MeOH		Perfect miscibilty	-
FAME+MeOH+Soap		Partial miscibility	-
FAME+MeOH+Alkaline (Saponification)		Suspension	Saponification
FAME+ MeOH+Sulfuric acid		Suspension	Self-transesterification

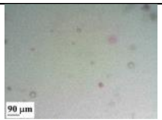
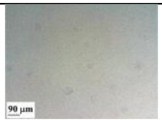
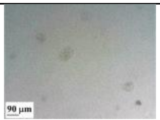
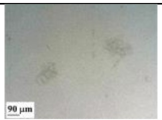
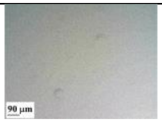
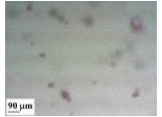
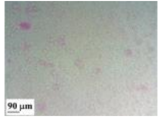
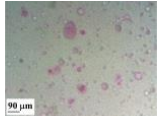
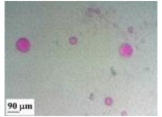
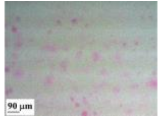
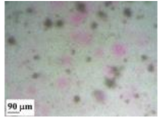
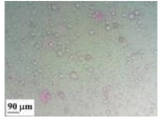
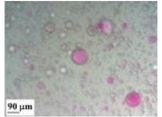
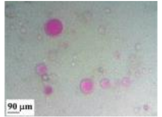
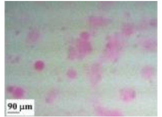
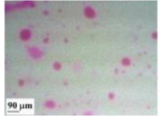
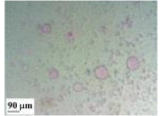
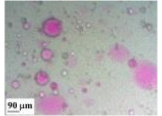
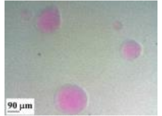
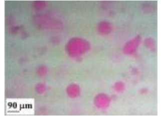
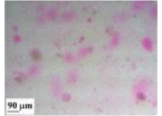
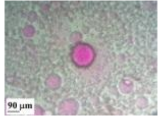
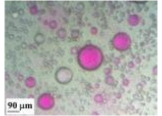
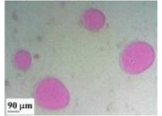
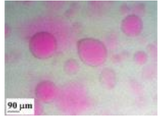
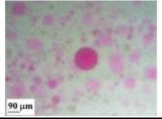
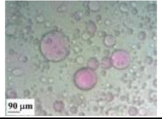
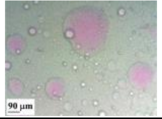
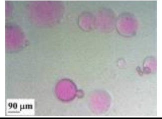
3.3 Solubility of methanol in transesterification system having an alkaline catalyst

The images of our studies are listed in **Tables 3.4**. As the methanol contains some alkaline sodium methoxide, the images show solubility. The methanol droplet suspended on the RPO gave only 0.2wt% of methanol solution in the system. In contrast, a clear solution was obtained without an alkaline catalyst. The 0.2wt% of methanol equals 1:16 molar ratio of methanol to triglyceride. The stability of methanol suspension was possibly due to the fast transesterification with an alkaline catalyst. This slightly alters the solubility of generated glycerol in the methanol-RPO environment. The glycerol possibly merged with methanol, due to their similar polarities, and created very fine droplets. In addition, the generated glycerol tended to attach to the nearby methanol droplet and coagulate together with it. Therefore, suspended droplets of methanol-glycerol were observed at all tested RPO/FAME mixing ratios. This clearly demonstrates a liquid-liquid reaction system. The reaction between the alkaline methanol solutions and FAME is saponification according to Eq. (1.6).

The generated soap acts as an emulsifier and forms a layer surrounding the methanol droplet, and isolates it from the continuous FAME phase. At a low content of RPO in the RPO/FAME mixture, we notice that the number of fine droplets was reduced while the large ones tended to increase. This is possibly caused by the coagulation of fine droplets to form larger drops.

When the added methanol solution is 7.9wt%, the molar ratio of methanol to oil is around 2.1:1 for pure RPO, 2.48:1 for A, 4.2:1 for B, and 14:1 for C (as shown in **Table 3.4**), respectively. The labels A, B, and C are here used to indicate these compositions of the mixture. The molar ratio of methanol to oil at 14:1 for the C mixture is quite a lot higher than that conventionally used in the industry (6:1). The transesterification reaction is expected to reach 96.5wt% ester content required by standard biodiesel specifications. In the C mixture, the ester phase is less viscous and promotes round drops of methanol-glycerol phase. The high 14:1 methanol to oil molar ratio should give a high conversion to ester.

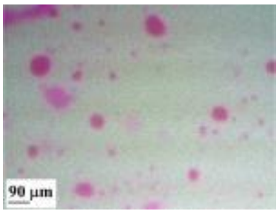
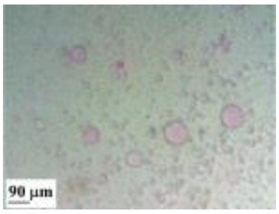
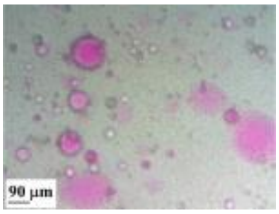
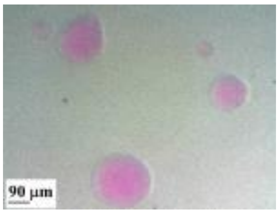
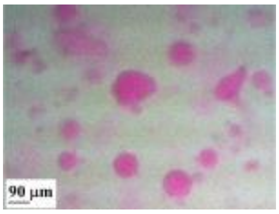
Table 3.4 The solubility of methanol in the transesterification reaction with alkaline catalyst (Photographs taken with 100X magnification)

MeOH +catalyst (wt%)	RPO	RPO/FAME A (85: 15wt%)	RPO/FAME B (50: 50wt%)	RPO/FAME C (15: 85wt%)	FAME+MeOH +Alkaline (Soap Formation)
0.2					
7.9					
11.3					
13.6					
17.9					
22.6					

Note: A is the RPO/FAME weight ratio of 85: 15, B is the RPO/FAME weight ratio of 50: 50, C is the RPO/FAME weight ratio of 15: 85.

Experimental conditions: Raw material (100 g, RPO, or FAME, or RPO/FAME); MeOH (22.64 g); $NaOCH_3$ in methanol (5.34wt%)

Table 3.5 Expected solubility and expected reaction of the solubility of ethanol in the transesterification reaction with alkaline catalyst (Photographs taken with 100X magnification)

Images of methanol and catalyst adding 13.6wt%	Components	Expected solubility	Expected reaction
	RPO+MeOH +$NaOCH_3$	Suspension	Transesterification /Saponification
	RPO/FAME (85:15)+MeOH+ $NaOCH_3$	Suspension	Transesterification /Saponification
	RPO/FAME (50:50)+MeOH+ $NaOCH_3$	Suspension	Transesterification /Saponification
	RPO/FAME (15:85)+MeOH+ $NaOCH_3$	Suspension	Transesterification /Saponification
	FAME+MeOH+ $NaOCH_3$	Suspension	Saponification

When 11.3wt% of methanol and catalyst solution was added to pure RPO, A mixture, or B mixture, the molar ratio of methanol to oil was 3:1, 3.54:1 or 6:1, respectively. The B mixture has more excess methanol and shows larger round drops of methanol-glycerol phase than in a blend of A mixture and pure RPO. Adding methanol at 17.8wt% (22.6wt%) gives 6:1 molar ratio of methanol to oil with A mixture (pure RPO). We can clearly see the appearance of large round droplets of methanol-glycerol phase.

Zhou et al. (2006) demonstrated that when FAME content is increased to 70 %, the oil - methanol - FAME mixture becomes homogeneous; so the reaction rate depends strongly on the solubility of oil in the methanol phase [59]. Our work (**Table 3.5**) shows that even at the low 15: 85 weight ratio oil: FAME, partial solubility of methanol is still observed.

From **Table 3.5**, the reaction between RPO and alkaline-methanol solution is transesterification (Fig. 1.1) and saponification (Eq. 1.5). However, FAME reacts with alkaline to form soap by saponification (Eq. 1.6). All components in these systems are liquid-liquid reaction. In addition, all of components indicate the suspension systems.

3.4 Solubility of methanol in transesterification reaction added with THF, alkaline, and acid catalysts

The effects of adding co-solvent THF on solubility of methanol in transesterification reaction was studied with alkaline and acid catalysts individually. The results are listed in **Table 3.6.** It can be seen that even a small amount of excess methanol (0.2wt%) the mixture of RPO/THF shows a suspended phase in the system. On using alkaline catalyst, THF seems to enhance the solubility of methanol in the RPO/THF phase. The fast transesterification converts the triglyceride to an ester and drastically reduces the viscosity of solution as well as increases solubility of methanol in the ester phase. In acid-catalyzed transesterification, the THF plays a different role than with alkaline catalyst. Sulfuric acid is strongly polar and is well compatible with methanol. The mixture of methanol and sulfuric acid is also polar. Then, the methanol and sulfuric acid mix forms dispersed droplets in the continuous triglyceride phase.

The relative polarities of THF and methanol are reported as 0.207 and 0.762, respectively [69]. Thus, THF prefers to merge with the methanol. Additionally, the slow transesterification with acid catalyst provides a small amount of ester, indicated by a slight change in triglyceride phase viscosity.

Besides, the small amount of generated glycerol also tends to merge with methanol no outer layer was observed on the methanol droplets to isolate them. Consequently, the THF can easily diffuse through the methanol drop surface and cause the droplet to grow.

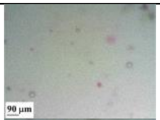
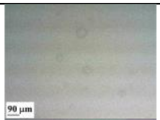
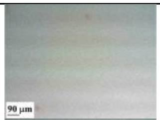
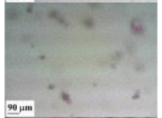
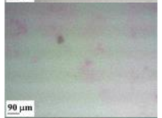
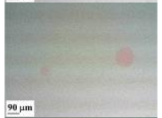
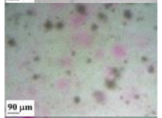
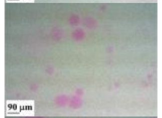
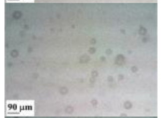
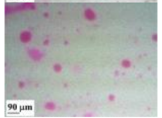
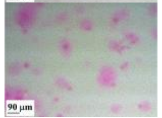
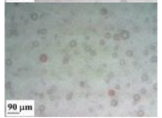
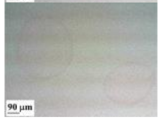
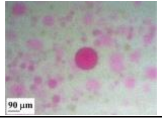
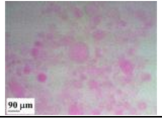
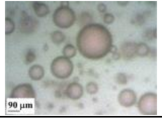
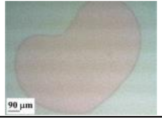
Thus, adding THF may have both advantages and disadvantages regarding alcohol solubility in the acid-catalyzed transesterification system. The effects of co-solvent on acid-catalyzed transesterification are of interest for future studies.

From **Table 3.7**, the solubility of methanol-alkaline in RPO or RPO/THF mixture indicate that the expected reactions are transesterification and saponification while, solubility of methanol-acid in RPO or RPO/THF mixture indicate that the expected reaction is acid-catalyzed transesterification.

The co-solvent THF improved solubility of polar methanol in the non-polar triglyceride, but the strongly polar products, such as glycerol and soap emulsifier, could interrupt this effect.

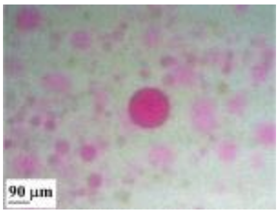
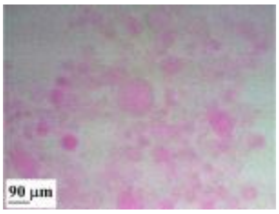
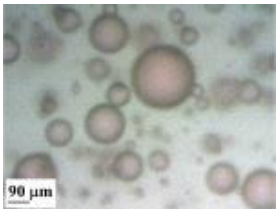
The polar similarity of THF and methanol provides them mutual miscibility, while methanol is less compatible with ester or triglyceride. The co-solvent THF cannot enhance solubility of the multicomponent systems in biodiesel production to provide a homogeneous mixture as mentioned in several literatures [53], [54], [70]. So, all components in these systems are liquid-liquid reaction.

Table 3.6 The solubility of methanol in transesterification with THF and alkaline or acid catalyst (Photographs taken with 100X magnification)

MeOH + Catalyst wt%	RPO + MeOH + Alkaline	RPO/THF + MeOH + Alkaline	RPO + MeOH + Acid	RPO/THF + MeOH + Acid
0.2				
0.5				
5.8				
17.9				
22.6				

Experimental conditions: Raw material (100 g, RPO); THF (40.67 g); THF/RPO weight ratio (0.4:1); MeOH (22.64 g); $NaOCH_3$ in methanol (5.3wt%); H_2SO_4 in methanol (13.8wt%).

Table 3.7 Expected solubility and expected reaction of the solubility of methanol in transesterification with THF and alkaline or acid catalyst at 32 °C

Images of methanol and catalyst addition 22.6wt%	Components	Expected solubility	Expected reaction
	RPO+MeOH +$NaOCH_3$	Suspension	Transesterification /Saponification
	RPO/THF +MeOH+$NaOCH_3$	Suspension	Transesterification /Saponification
	RPO+MeOH +H_2SO_4	Suspension	Acid-catalyzed Transesterification
	RPO/THF+MeOH +H_2SO_4	Suspension	Acid-catalyzed Transesterification

3.5 Soap formation and transesterification of FAME

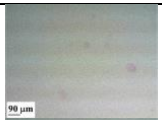
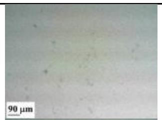
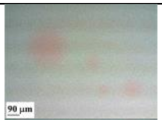
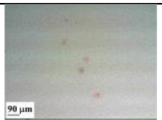
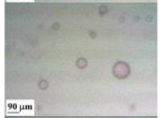
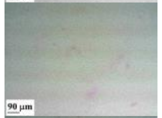
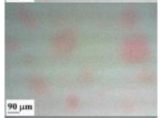
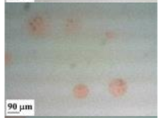
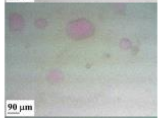
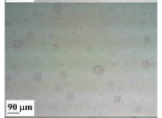
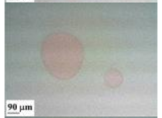
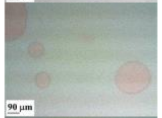
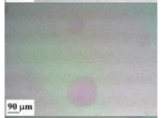
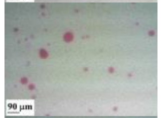
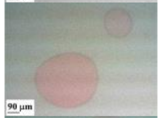
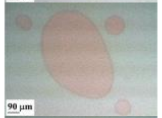
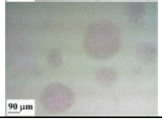
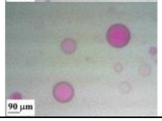
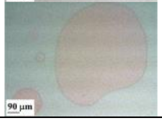
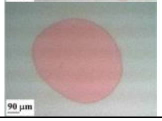
In transesterification, FAME and methanol were reacted with either alkaline or acid catalyst, and the results are reported in **Table 3.8**. The reaction of FAME with alkaline catalyst in methanol solution is saponification. The reaction between FAME and methanol with acid catalyst is normally self-transesterification, but in this case R' and R" are the same methyl group (CH_3^+). So, we cannot notice any change in the products, because this is a self-transesterification as mentioned in Eq. (1.7). We did observe the reaction between FAME and ethanol, which produced ethyl ester. If the system contains some water, the reaction instead is reverse esterification.

$$RCOOR'' + R'OH \overset{\text{Catalyst}}{\longleftrightarrow} RCOOR' + R''OH \qquad \text{Eq. (1.7)}$$

Where R' and R" are some given alkyl groups

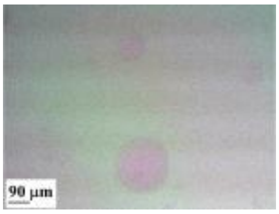
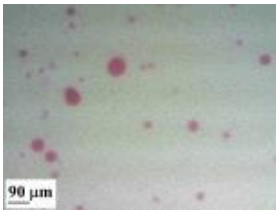
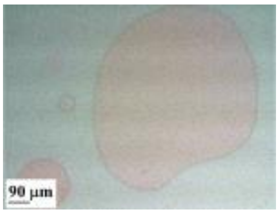
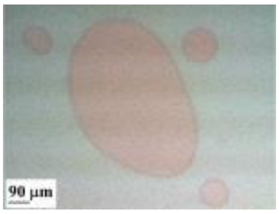
From **Table 3.1**, FAME and methanol are perfectly miscible, but the addition of the third compound like alkaline turns the system to a dispersion. This is possibly caused by soap formation (saponification). The generated soap generally has amphiphilic structures with hydrophilic and hydrophobic parts. In FAME and methanol mixture, the amount of FAME is much higher than that of methanol, thus the bulk solution is dominantly nonpolar. As soap concentration increases in the solution, it tends to aggregate and cluster forming reversed micelles where the hydrophilic parts orient towards the center while the hydrophobic parts orient towards the nonpolar FAME and methanol mixture. This creates a polar region inside the reversed micelle. Thus, the methanol solubilized in FAME tends to migrate and accumulated to centers of the reversed micelles. This might be the reason why we observed small drops of methanol randomly dispersed in the mixture, and incomplete esterification due to inactivity of the methanol encapsulated in the micelles.

Table 3.8 Transesterification reaction and soap formation of FAME (Photographs taken with 100X magnification)

Methanol +catalyst	Soap formation		Transesterification reaction	
wt%	FAME+MeOH+ Alkaline	FAME/THF+ MeOH +Alkaline	FAME+MeOH+ Acid	FAME/THF+ MeOH +Acid
2.7				
10.7				
23.3				
40.0				
67.6				

Experimental conditions: Raw material (100 g, FAME); THF (123.13 g); THF/FAME weight ratio (1.2:1); MeOH (67.61 g); $NaOCH_3$ in methanol (1.8wt%); H_2SO_4 in methanol (4.6wt%).

Table 3.9 Expected solubility and expected reaction transesterification reaction and soap formation of FAME

Images of methanol and catalyst addition 40.0wt%	Components	Expected solubility	Expected reaction
	FAME+MeOH +$NaOCH_3$	Suspension	Saponification
	FAME/THF +MeOH+$NaOCH_3$	Suspension	Saponification
	FAME+MeOH +H_2SO_4	Suspension	Self-Transesterification
	FAME/THF+MeOH +H_2SO_4	Suspension	Self-Transesterification

The experiment (**Table 3.9**) performed using FAME, methanol, and sulfuric acid also provided a suspension. This was caused by the mixture of methanol and sulfuric acid separating from the FAME phase. The greater number of methanol-sulfuric acid droplets made the suspension cloudy as the amount of methanol was increased. The polarity of sulfuric acid (**Table 3.10**) enables the formation of methanol-sulfuric acid droplets and the phase separation of FAME and methanol.

However, addition of co-solvent (THF) in the mixture of FAME and catalyst-methanol solution cannot create the single-phase mixture as mentioned in previous literature reports [54], [70], [71].

The results confirm that all components (FAME+methanol+catalyst or FAME/THF+methanol+catalyst) should be a liquid-liquid reaction.

From polarity index of substances in **Table 3.10**, the polarity of the components in transesterification reaction plays a crucial role in the reaction, affecting the miscibility of compounds in the reaction mixture, and influencing efficiency and extent of conversion. A highly polar compound like glycerol could enable clear separation of methanol from the less polar substances, such as FAME (ester) and RPO (triglyceride). A sulfuric acid mixed with methanol is highly polar, giving a dispersion of methanol droplets in continuous triglyceride phase. The formation of soap could emulsify and suspend methanol drops in otherwise compatible methanol-FAME solution.

Table 3.10 Polarity index of substances

Substance	Polarity index (dielectric constant, 25°C)	Reference
Sulfuric acid	100	[72]
Water	80	[72]
Glycerol	46	[72]
Methanol	33	[72]
Tetrahydrofuran (THF)	7.52	[73]
Fatty acid methyl ester (FAME)	2.2	[74]
Refined palm oil (RPO)	2.0	[72]
Sodium methoxide	1.5	[72]
Soap (powder)	1.2-1.7	[75]

3.6 Reaction zone study

3.6.1 Reaction zone of transesterification using alkaline and acid catalysts

The results from the previous experiment (3.1) indicate that a liquid-liquid phase system is preferable for having a homogeneous transesterification reaction. RPO and FAME are the starting material and final product of transesterification, respectively. They have many differing physical properties, such as polarity, viscosity, density, and surface tension. Similarly, pure methanol, sodium methoxide-methanol solutions, and sulfuric acid-methanol solutions, have mutually differing properties. This diversity could affect the diffusion of reacting substances and generated products, and thereby the overall reaction rate of transesterification. For example, some of reaction products might retard the mass transfer of free reactants or act as a barrier isolating the reaction zone. Thus, this part aimed to clarify the diffusion behaviors of those substances, as well as their roles in kinetics of the reaction between the alcohol phase and triglyceride phase, by imaging with an LCD digital microscope. A substrate droplet on a concave glass slide is assumed to be ellipsoidal. This matches a comparison of calculated drop volume with the diameter on the glass slide. The semi-minor axis is about 1/10 of the semi-major axis. An added spot of about 1/10 of the droplet volume is also assumed to take ellipsoidal shape.

The experiment was divided into 4 cases. Case I is the mixing behavior of FAME, methanol, and an alkaline catalyst. Case II is the mixing behavior of RPO, methanol, and an alkaline catalyst. Case III is the mixing behavior of FAME, methanol, and an acid catalyst. Finally, in case IV the mixing behavior of RPO, methanol, and acid catalyst was examined.

For case I, the results are shown in **Table 3.11.** The methanol-alkaline solution is identified by phenolphthalein staining. The reactions and solubility behaviors in this system are expected to be the easiest or simplest to understand.

As can be seen images in **Table 3.11**, a spot of methanol on a drop of FAME (**Case A**) or a spot of FAME on a drop of methanol (**Case C**) shows perfect miscibility of methanol and FAME. According to **Fig. 3.1**, a spot of alkaline-methanol forms a round drop in the FAME phase (**Case B**), and the pink color of alkaline-phenolphthalein gradually turned pale due to the diffusion of methanol and alkaline catalyst out of the drop. The boundary between alkaline-methanol solution and FAME is quite stable and assumed to have a soap film. This is due to the saponification of alkaline and FAME (ester). The reaction between alkaline-methanol solution and FAME (**Table 3.12**) is saponification (Eq.1.6). So, only soap alters the solubility in the system. This seems to be a comparatively fast reaction.

However, a spot of FAME on alkaline-methanol solutions (**Case D**) behaved differently (**Table 3.11**). The boundary of a spot of FAME on a drop of alkaline-methanol solution shrunk after three minutes and then maintained the same size for 7 minutes. According to **Fig. 3.1**, this indicates that the FAME diffused into the alkaline-methanol solution. A small amount of soap formation is the reason why FAME did not totally dissolve in the methanol solution. Maximal soap formation depends on the number of moles of FAME.

A spot of alkaline-methanol solution contains much more alkaline reactant (in moles) than FAME of similar volume. The large amount of soap formed in the case of alkaline-methanol solution on FAME inhibits the diffusion of methanol and alkaline into the FAME phase, so it is hard to notice any changes in the drop size, which reflects the slow reaction rate. Thus, soap acts as a barrier limiting the rate of reaction.

Regarding the liquid-liquid phase reaction, which phase is diffusing is an interesting issue. Methanol and FAME form a miscible solution. The diffusion between the two liquids should be of counter diffusion type. When there is a boundary layer like soap, then pressure differential is assumed to dominate as determinant of the mass transfer rate. The diffusion from a droplet into an expansive pool is easier than the reversed diffusion from a large volume into the droplet.

Table 3.11 Photographs of the reaction zone for FAME with initial excess alcohol/alkaline or alcohol/alkaline with excess FAME, imaged for up to 600 seconds (Photographs taken with 40X magnification)

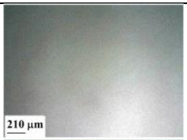
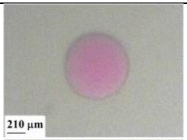
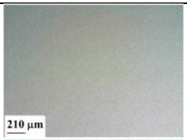
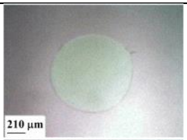
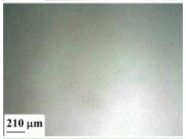
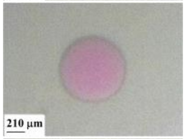
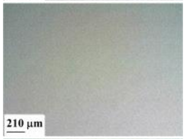
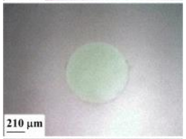
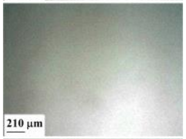
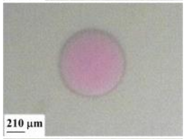
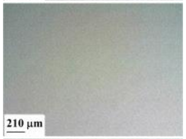
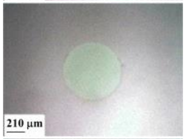
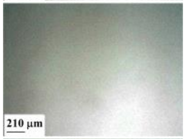
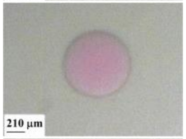
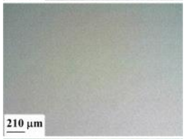
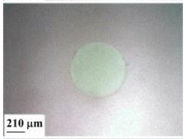
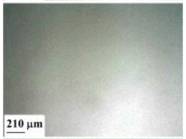
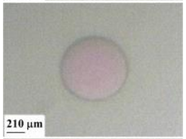
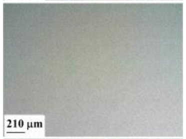
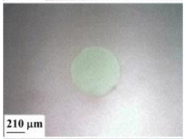
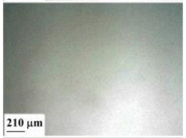
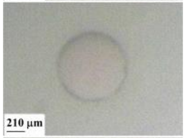
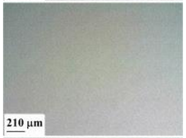
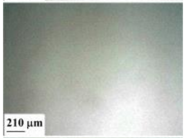
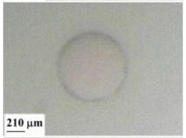
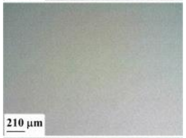
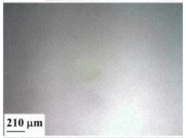
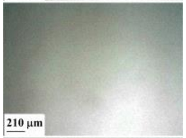
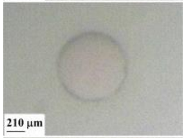
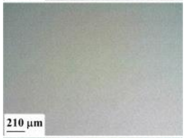
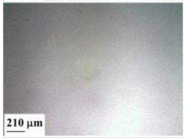
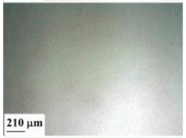
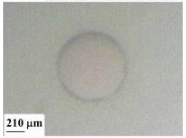
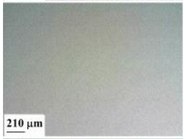
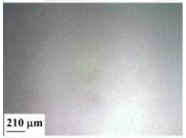
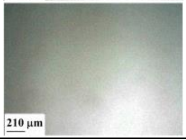
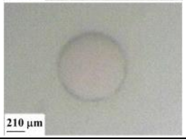
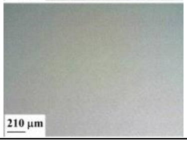
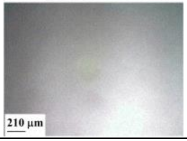
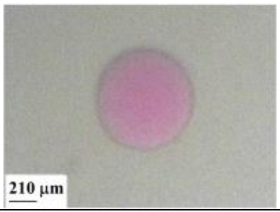
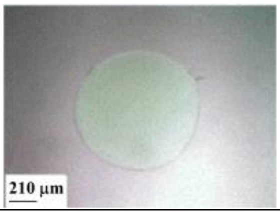
Time (s)	Case A	Case B	Case C	Case D
	A spot of methanol on a drop of FAME	A spot of alkaline-methanol solution on a drop of FAME	A spot of FAME on a drop of methanol solution	A spot of FAME on a drop of alkaline-methanol solution
5				
10				
30				
60				
90				
120				
180				
240				
480				
600				

Table 3.12 Expected solubility and expected reaction of the reaction zone for FAME with initial excess alcohol/alkaline or alcohol/alkaline with excess FAME

Images at 5 seconds	Component	Expected solubility	Expected reaction
1. Excess FAME (Case B) 	FAME+MeOH+$NaOCH_3$	Suspension	Saponification
2. Excess Alkaline-Alcohol (Case D) 	FAME+MeOH+$NaOCH_3$	Suspension	Saponification

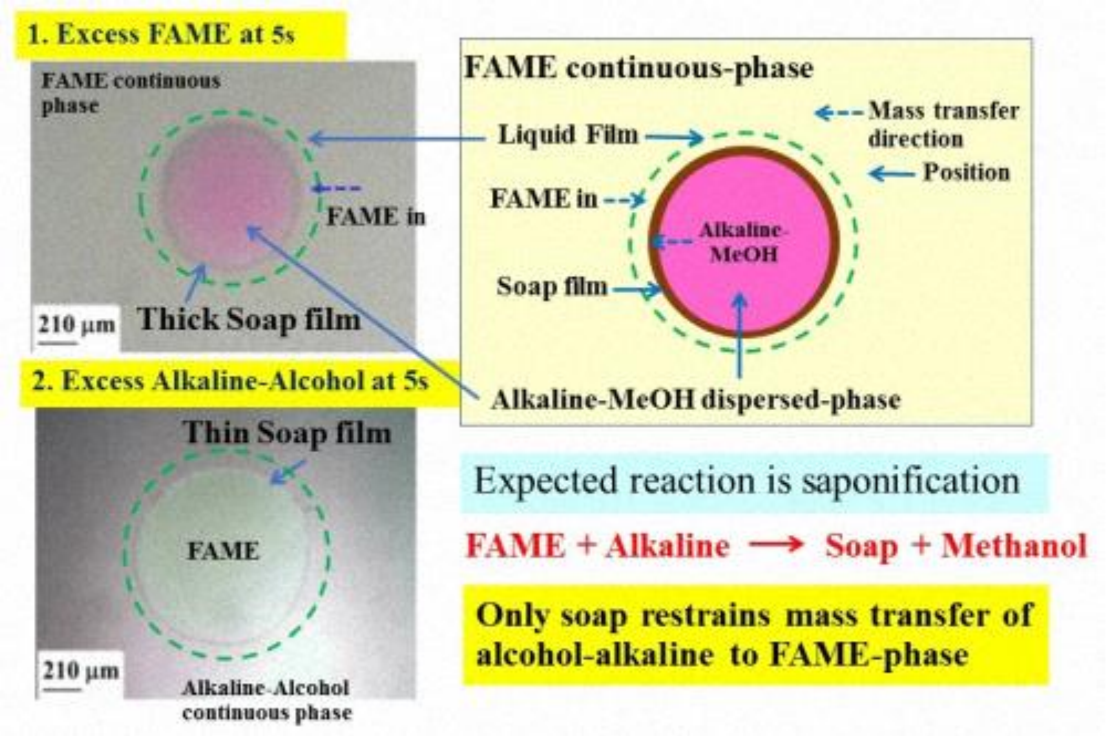


Fig. 3.1 The possible model of reaction zone for FAME with initial excess alcohol/alkaline

The results of case II are shown in **Table 3.13**. From **Table 3.14**, the possible reactions of alkaline-methanol solution and RPO are transesterification and saponification. Transesterification of triglyceride with methanol yields esters and glycerol. In this context, the relation of glycerol behavior and reactions was examined. Thus, extra glycerol was added in case II. A spot of methanol on a drop of RPO (**Case A**) looks like a round drop and it is hard to notice any changes in drop size due to the low solubility of methanol in triglyceride. However, we can notice slight growth of the spot of RPO on a methanol pool (**Case C**). This is consistent with prior literature indicating that methanol is soluble in triglyceride better than triglyceride in methanol [20], [59]. The pink droplet of alkaline-methanol solution rapidly turned pale in RPO (**Case B**), more so than that observed on FAME, and shrinkage of the drop was also observed. From **Fig. 3.3**, this indicates faster diffusion of methanol, $NaOCH_3$, and phenolphthalein into RPO. Diffusion rate is usually proportional to the concentration gradient, so we assume a high rate of methanol consumption in the RPO. Transesterification of triglyceride is a faster reaction than saponification [76].

The final products of transesterification are ester and glycerol. According to polarity index of components (**Table 3.10**), glycerol is a polar substance and ester is nonpolar, so we assume glycerol prefers to attach to the alkaline methanol droplet, while ester stays in the RPO and counter diffuses with triglyceride. From **Table 3.13**, when a drop of RPO is in the center of alkaline-methanol solution (**Case D**), we see a pink layer diffusing into the droplet, and within 120 seconds the whole drop turns pink. The good methanol solubility in triglyceride enables this mass transfer. Triglyceride has the higher molecular weight so in equal volumes its number of moles is less than that of methanol. The amounts of glycerol and soap produced from RPO are small in this experiment. Glycerol dissolves in a large amount of methanol due to these having similar polarities. However, we could assume very little formation of soap, since soap is an emulsifier but no emulsion was observed. The produced FAME is more polar than triglyceride and is well soluble into the alkaline methanol, so we cannot see any interfacial layer in this trial.

Table 3.13 Photographs of the reaction zone for RPO on excess alcohol/alkaline, and for alcohol/alkaline on excess RPO, observed for up to 600 seconds (Photographs taken with 40X magnification)

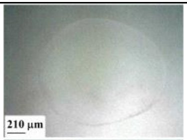
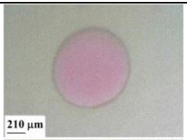
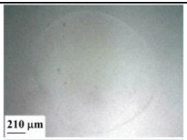
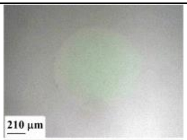
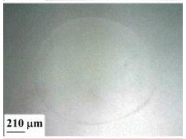
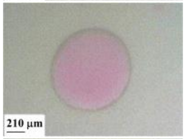
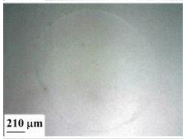
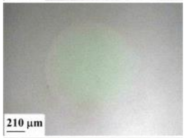
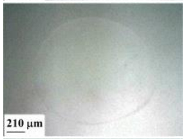
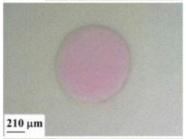
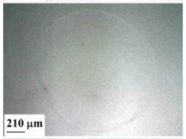
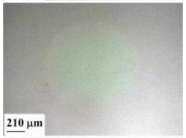
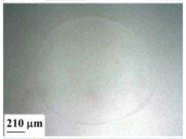
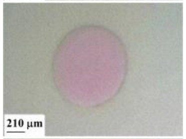
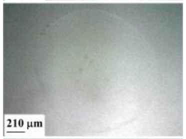
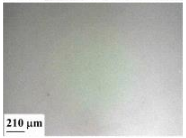
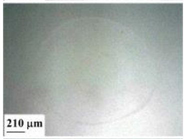
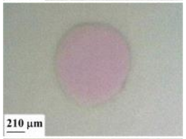
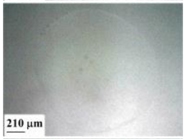
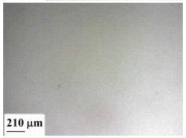
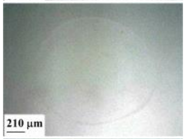
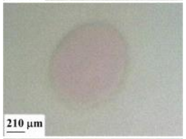
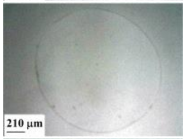
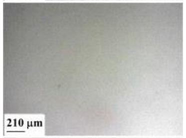
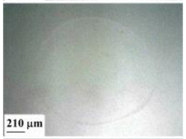
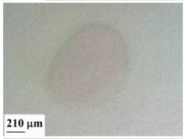
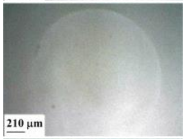
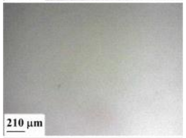
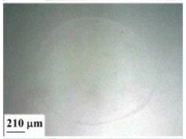
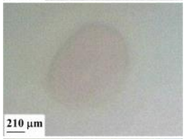
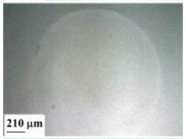
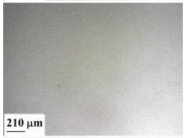
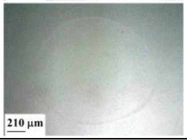
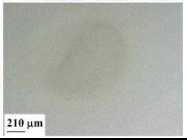
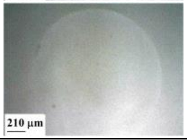
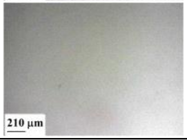
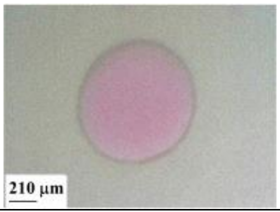
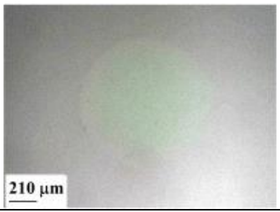
Time (s)	Case A	Case B	Case C	Case D
	A spot of methanol on a drop of RPO	A spot of alkaline solution of methanol on a drop of RPO	A spot of RPO on a drop of methanol	A spot of RPO on a drop of alkaline solution of methanol
5				
10				
30				
60				
90				
120				
180				
240				
600				

Table 3.14 Expected solubility and expected reaction of the reaction zone for RPO with initial excess alcohol/alkaline or alcohol/alkaline with excess RPO

Images at 5 seconds	Component	Expected solubility	Expected reaction
1. Excess RPO (Case B) 	RPO+MeOH+$NaOCH_3$	Suspension	Transesterification /Saponification
2. Excess Alkaline-Alcohol (Case D) 	RPO+MeOH+$NaOCH_3$	Suspension	Transesterification /Saponification

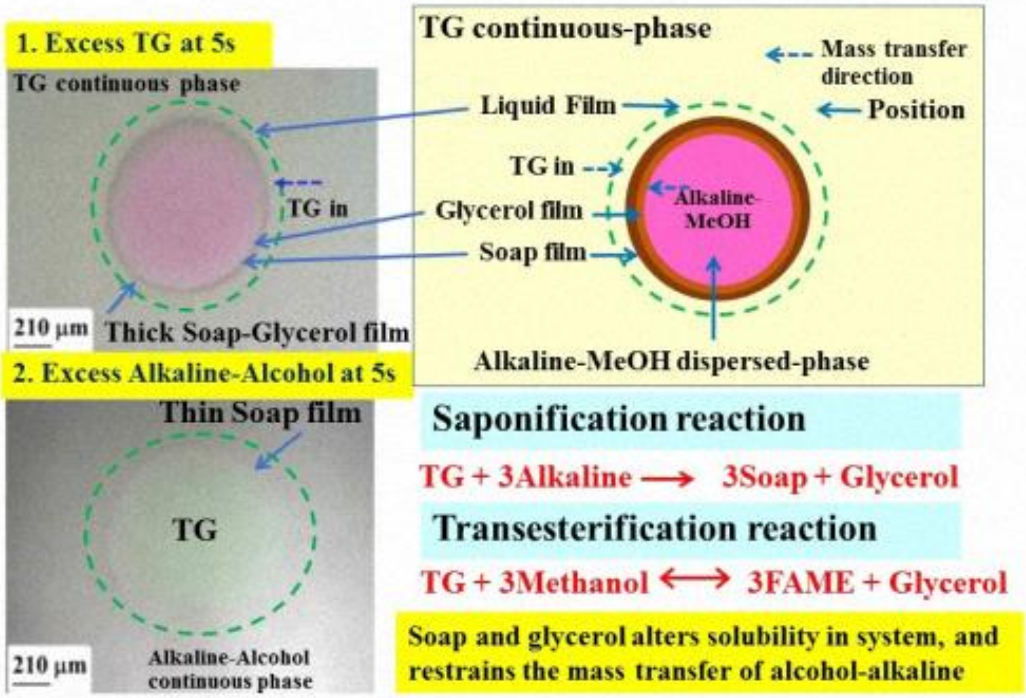


Fig. 3.2 The possible model of reaction zone for RPO with initial excess alcohol/alkaline

Therefore, based on the observations, we assume that transesterification reaction (**Fig. 3.2**) starts by the diffusion of alcohol and catalyst into the triglyceride film. The complicated mass transfer related factors, such as polarity, viscosity, and diffusivity, play important roles as determinants of the kinetics of transesterification reaction. For example, a layer of glycerol and soap restrains diffusion of alcohol and catalyst, and the counter-diffusion of ester and triglyceride disturbs the reaction zone, and inhibits the transfer of triglyceride. The change in viscosity of ester and triglyceride mixture favors alcohol and catalyst diffusion, etc.

For comparison of soap formation between FAME and triglyceride in **Fig. 3.3**, the reaction of alkaline-methanol solution and triglyceride creates thicker film due to glycerol and soap produced from transesterification and saponification. Hence, glycerol and soap restrains the diffusion of alkaline-alcohol from a droplet into a triglyceride continuous phase. However, the reaction of alkaline-methanol solution and FAME creates thinner film due to only soap formation. So, only soap alters the diffusion of alkaline-alcohol from a droplet into a FAME continuous phase.

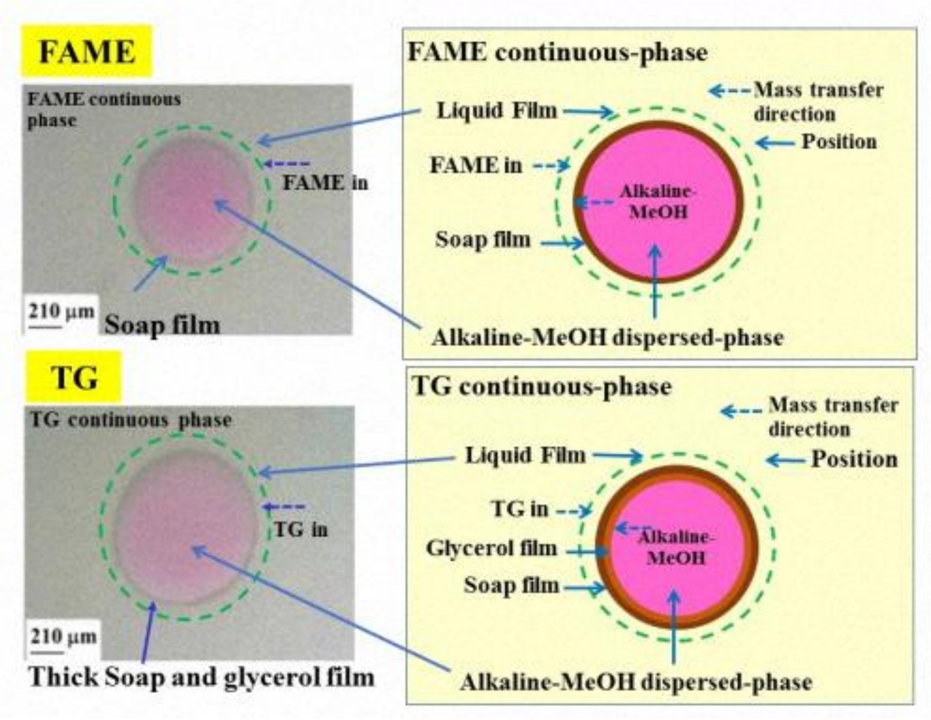


Fig. 3.3 The possible model of reaction zone of soap formation between FAME and TG

Regarding case III (**Tables 3.15**), we do not expect any chemical reaction but only observe the solubility behavior of reacting substances. Though self-transesterification (Eq. 1.7) is the only possible reaction, with an acid catalyst this is a slow reaction.

$$\mathrm{RCOOR'' + R'OH} \xleftrightarrow{\text{Catalyst}} \mathrm{RCOOR' + R''OH} \qquad \text{Eq. (1.7)}$$

Where R’ and R” are some given alkyl groups

Putting a spot of acid solution of methanol on a drop of FAME is not possible due slipping of the spot, possibly caused by lower density of methanol and stronger polarity than that of FAME, and the high interfacial tension between methanol and FAME. However, in **Case B**, adding 0.0125wt% of sulfuric acid in methanol can provide a small spot on the FAME droplet, and this spot disappeared within 10 seconds due to the dissolution of methanol in FAME.

This observation (**Table 3.16**) demonstrates good mutual solubility of methanol and FAME (both **Case A** and **C**). In contrast, this does not occur with methanol-sulfuric acid solution. For **Case D**, FAME is not completely dissolved in methanol-sulfuric acid (3wt%) and forms a stable droplet. This is possibly caused by the higher polarity of the methanol-sulfuric acid solution relative to pure methanol, causing poor solubility of FAME.

Table 3.15 Photographs of the reaction zone when FAME is added on top of excess sulfuric-methanol (0.0125 or 3wt% of MeOH), and when sulfuric-methanol (0.0125 or 3wt% of MeOH) is added on top of FAME, observed for up to 600 seconds (Photographs taken with 40X magnification)

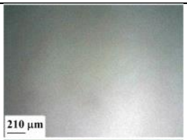
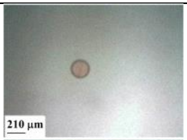
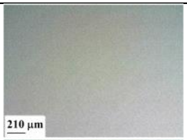
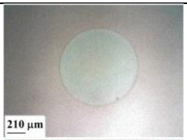
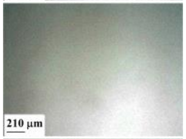
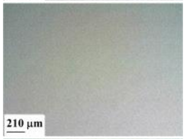
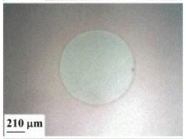
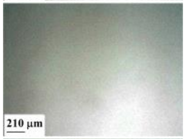
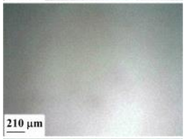
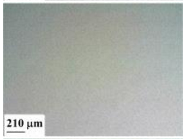
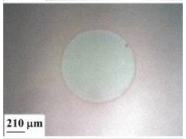
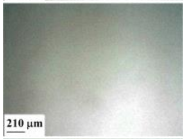
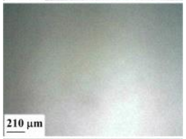
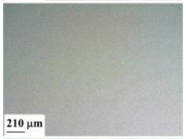
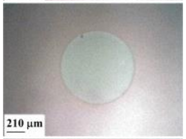
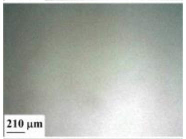
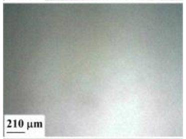
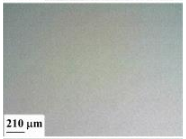
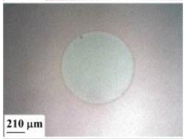
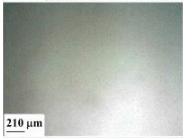
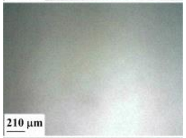
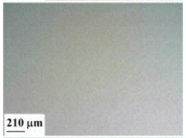
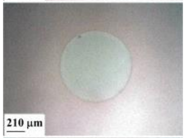
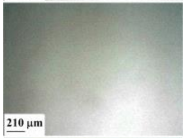
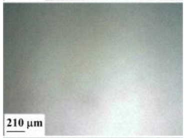
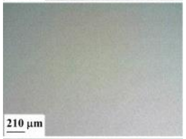
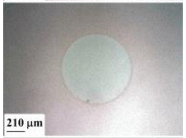
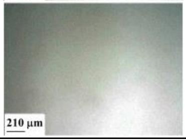
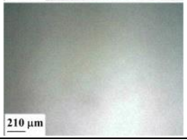
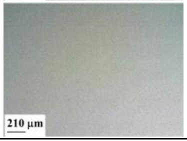
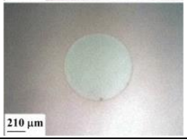
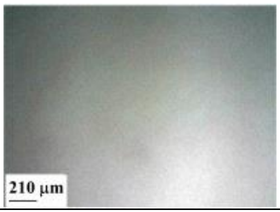
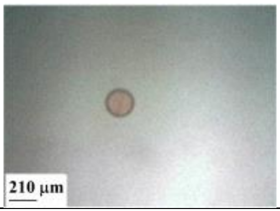
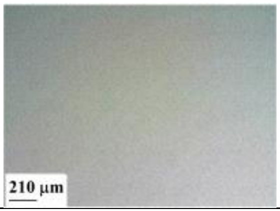
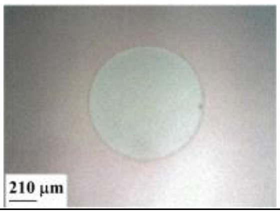
Time (s)	Case A	Case B	Case C	Case D
	A spot of methanol on a drop of FAME	A spot of sulfuric-methanol solution (0.0125wt%) on a drop of FAME	A spot of FAME on a drop of methanol	A spot of FAME on a drop of sulfuric-methanol solution(3wt%)
5				
10				
30				
60				
120				
180				
360				
600				

Table 3.16 Expected solubility and expected reaction of the reaction zone when FAME is added on top of excess methanol/sulfuric (0.0125 or 3.0wt% of MeOH), and when methanol/sulfuric (0.0125 or 3.0wt% of MeOH) is added on top of FAME

Images at 10 seconds	Components	Expected solubility	Expected reaction
Case A 	FAME+MeOH (Excess FAME)	Perfect miscibilty	-
Case B 	FAME+MeOH +H_2SO_4 (0.0125wt%) (Excess FAME)	Suspension	After 10 seconds disappeared due to dissolution in MeOH
Case C 	FAME+MeOH (Excess MeOH)	Perfect miscibilty	-
Case D 	FAME+MeOH +H_2SO_4 (3wt%) (Excess MeOH/Catalyst)	Suspension	Self-Transesterification

Finally, for case IV, the results on the mixing behavior of RPO, methanol, and acid catalyst are reported in **Tables 3.17.** The expected reaction is acid catalyzed transesterification and the main products are ester and glycerol. Methyl orange indicator was used to stain acid-methanol solution and distinguish it from triglyceride. As the methanol-sulfuric acid solution was spotted on RPO, within 10 minutes there was neither change of the color nor of the drop size, and the same happened when the phases were reversed. Strong polarity of sulfuric acid is a dominant cause of this behavior.

From **Table 3.18**, spot of methanol in a pool of RPO shows partial miscibilty due to methanol can soluble in oil 8-10wt% [20], [59]. In contrast, spot of RPO into a pool of methanol shows partial miscible due to methanol can soluble in methanol < 1wt% [20]. Spot of sulfuric acid (11.03wt%)-methanol solution caused a suspension due to high polar of sulfuric acid.

The liquid-liquid acid catalyzed transesterification is easy to see. This reaction needs the diffusion of acid into the triglyceride phase for the acid-catalyzed carbonyl reaction. Is a low concentration of sulfuric acid in the methanol-sulfuric acid mixture preferable over a high concentration of acid? Does low viscosity of triglyceride-FAME mixture enhance the diffusivity of alcohol and sulfuric acid? These questions should be pursued in future studies.

Table 3. 17 Photographs of the methanolysis of RPO with excess oil and excess alcohol/acid (sulfuric 11.03wt% of MeOH) for up to 600 seconds (Photographs taken with 40X magnification)

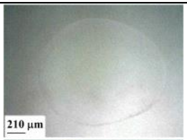
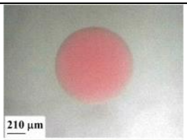
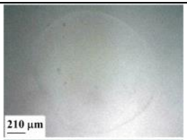
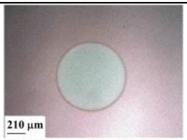
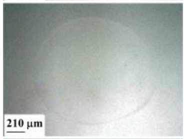
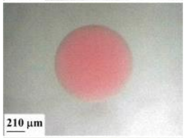
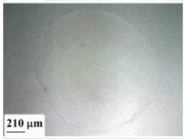
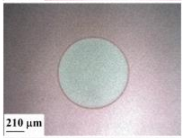
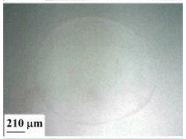
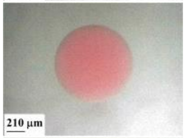
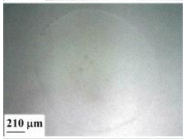
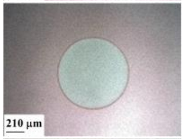
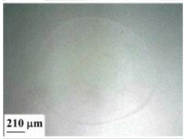
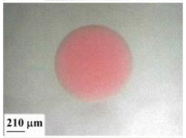
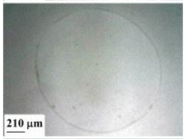
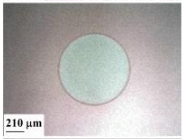
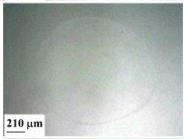
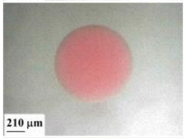
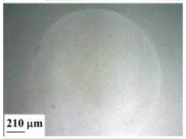
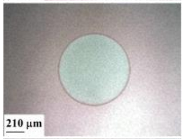
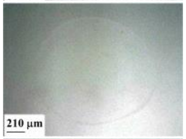
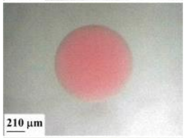
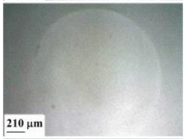
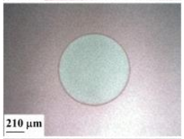
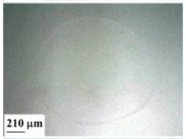
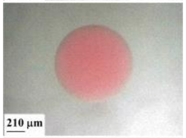
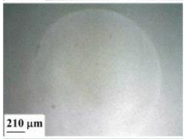
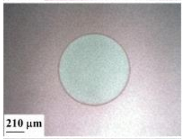
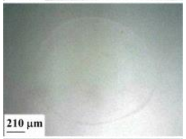
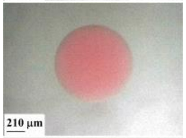
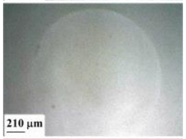
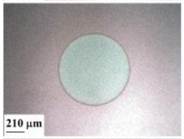
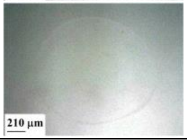
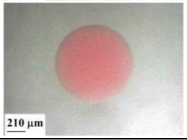
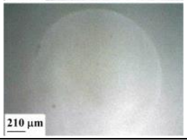
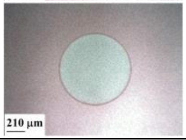
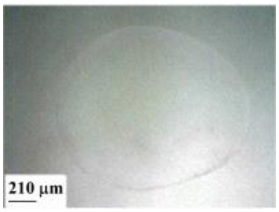
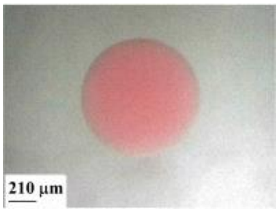
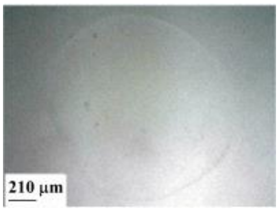
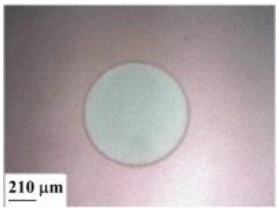
Time (s)	Case A	Case B	Case C	Case D
	A spot of methanol on a drop of RPO	A spot of methanol-acid on a drop of RPO	A spot of RPO on a drop of methanol	A spot of RPO on a drop of acid-methanol
5				
30				
60				
120				
180				
240				
360				
480				
600				

Table 3. 18 Expected solubility and expected reaction of the reaction zone the methanolysis of RPO with excess oil and excess alcohol/acid (sulfuric 11.03wt% of MeOH)

Images at 5 seconds	Components	Expected solubility	Expected reaction
	RPO+MeOH (Excess FAME)	Partial miscibilty due to MeOH soluble in oil 8-10wt%	-
	RPO+MeOH +H_2SO_4 (11.03wt%) (Excess FAME)	Suspension due to high polar of sulfuric acid	Acid-catalyzed Transesterification
	RPO+MeOH (Excess MeOH)	Partial miscibilty due to oil soluble in MeOH <1wt%	-
	RPO+MeOH +H_2SO_4 (11.03wt%) (Excess MeOH/Catalyst)	Suspension due to high polar of sulfuric acid	Acid-catalyzed Transesterification

3.6.2 Effects of FFA on saponification reaction

3.6.2.1 Effect of FFA on saponification of FAME

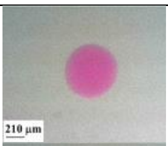
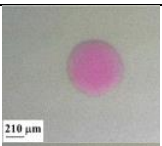
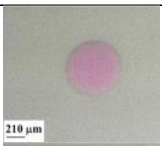
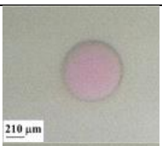
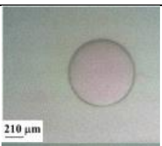
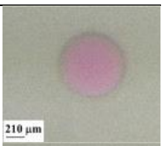
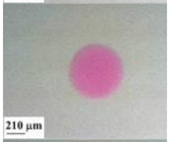
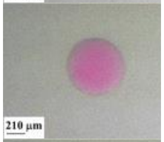
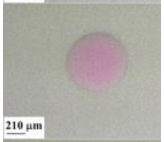
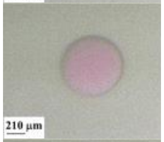
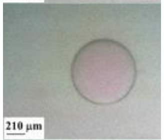
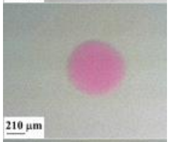
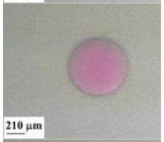
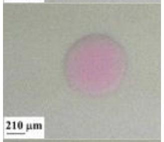
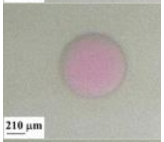
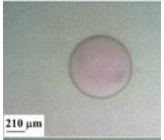
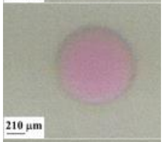
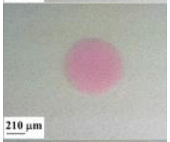
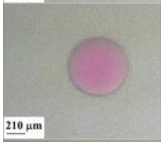
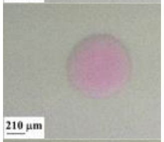
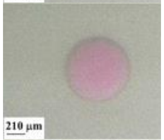
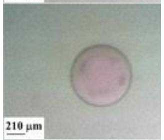
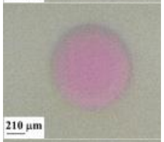
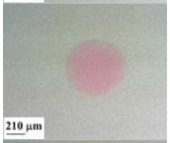
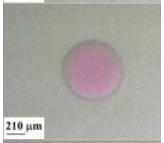
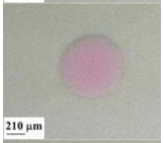
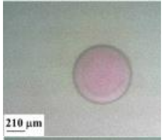
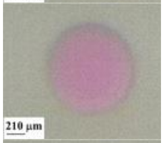
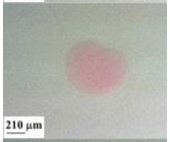
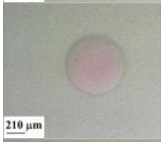
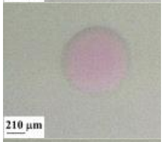
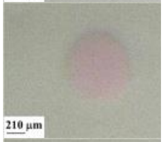
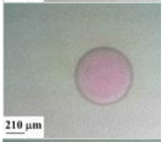
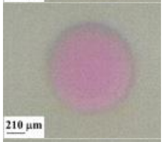
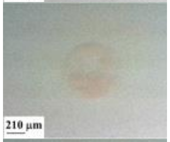
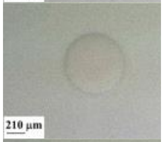
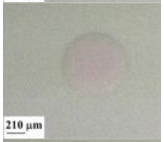
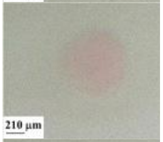
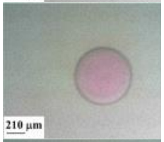
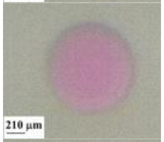
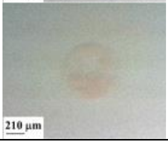
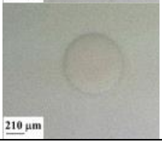
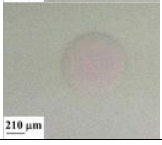
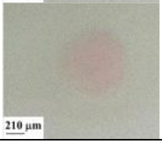
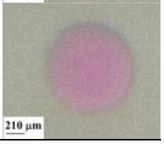
To lessen the soap formation in biodiesel production, we chose FAME as the organics ester. Soap formation by FAME containing FFA when reacted with an alkaline substance is expected from two major reactions, neutralization and saponification of FAME. The saponification of triglyceride and transesterification of oil are excluded and also the effects of water on saponification reaction are limited.

From **Table 3. 19**, a drop of sodium methoxide- methanol solution containing phenolphthalein on a pool of FAME indicates some interesting facts of the kinetics of the reaction. Also, a drop of FAME on the pool of alkaline- methanol solution confirms the same facts (**Table 3.21**). Methanol and alkaline diffuse to the FAME phase within a few seconds when FFA content in FAME is quite low.

From **Table 3.20**, the proposed explanation is the difference in the amount of soap from neutralization (Eq. 1.2) and saponification (Eq. 1.4). High FFA content in FAME creates a lot of soap that restrains the diffusion of alcohol and catalyst. Without FFA in FAME, methanol and alkaline diffuse faster.

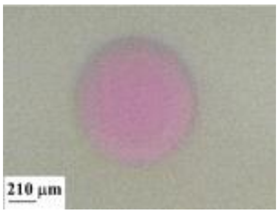
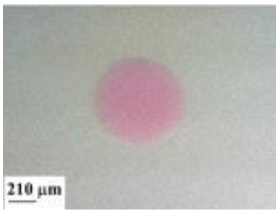
From **Fig. 3.4**, The trials indicate that high FFA content (2wt%) in FAME creates a lot of soap as thick film that restrains the diffusion of alcohol and catalyst. These soap barriers could possible form a thick film as mentioned above. So, in this system, only soap barrier restrains the diffusion of alcohol-alkaline to FAME-phase.

Table 3.19 Photographs of the reaction zone of the effect of FFA on FAME saponification with initial excess FAME, for up to 60 seconds (Photographs taken with 40X magnification)

Time	FFA content of FAME					
(s)	0.02wt%	0.1wt%	0.25wt%	0.5wt%	1.0wt%	2.0wt%
5						
10						
20						
30						
40						
45						
50						
60						

Note: an approx. 10 µL of FAME with varied FFA content (0.02, 0.1, 0.25, 0.5, 1.0 and 2.0wt%) and moisture content 0.03wt%; an approx. 1 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH).

Table 3.20 Expected solubility and expected reaction of the effect of FFA on FAME saponification with initial excess FAME

Images at 30 seconds	Component	Expected solubility	Expected reaction
1.High FFA (2wt%) 	FAME+MeOH+$NaOCH_3$	Suspension	Neutralization /Saponification
2.Low FFA (0.02wt%) 	FAME+MeOH+$NaOCH_3$	Suspension	Neutralization /Saponification

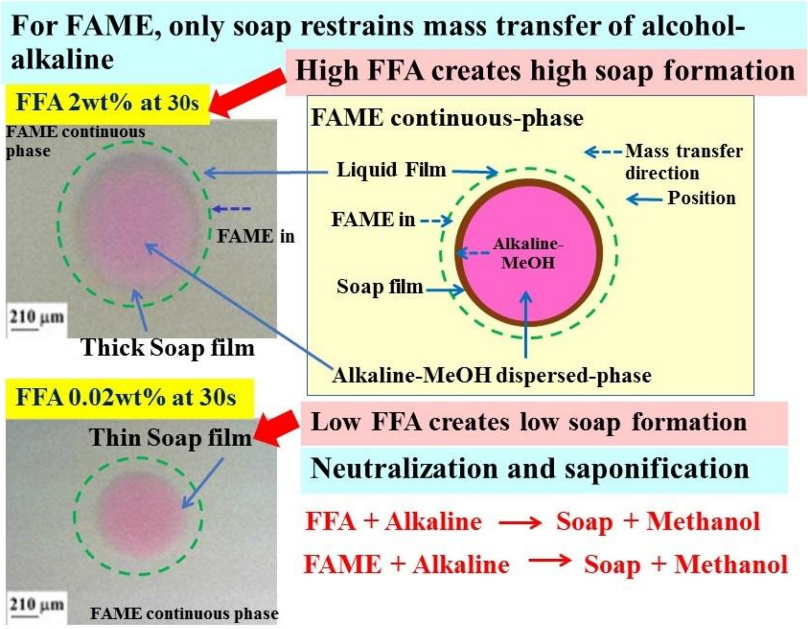


Fig. 3.4 The possible model of reaction zone for the effect of FFA on FAME saponification with initial excess FAME

In the reversed trials in **Table 3.21**, the boundary of a spot of FAME on a drop of alkaline-methanol solution shrunk for 60 minutes after spotting, and then maintained the same size up to 240 minutes for all FFA contents from 0.1 to 2wt%.

The possible reactions are neutralization of FFA (Eq. 1.2) and saponification of FAME (Eq. 1.4). This observation indicates diffusion of FAME into the alkaline-methanol solution.

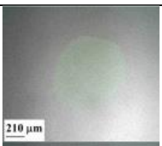
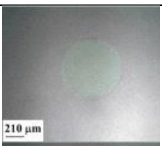
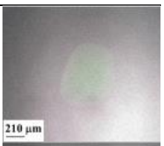
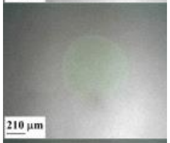
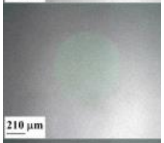
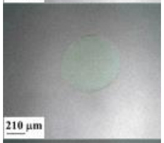
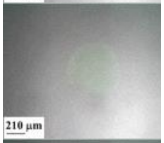
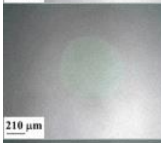
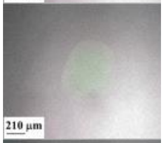
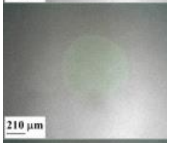
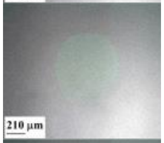
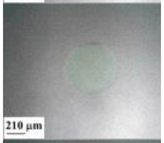
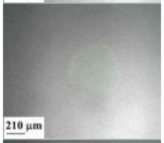
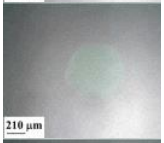
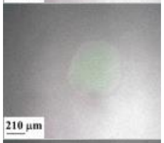
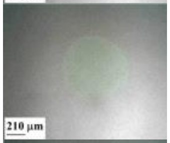
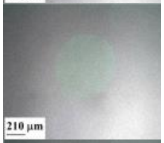
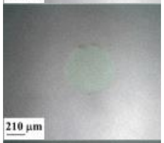
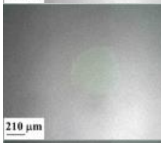
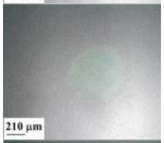
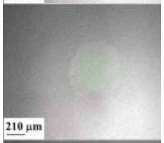
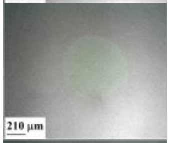
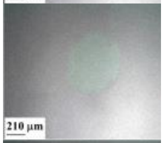
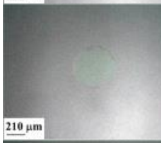
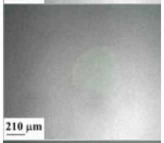
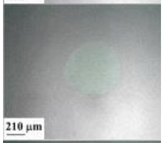
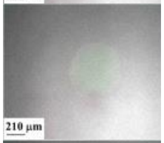
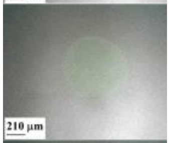
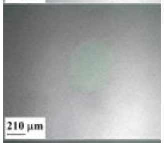
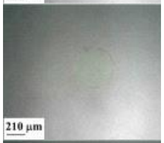
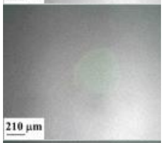
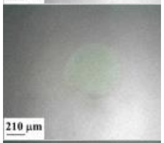
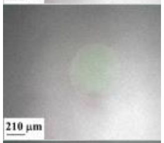
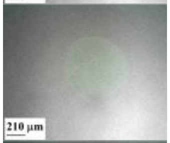
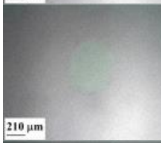
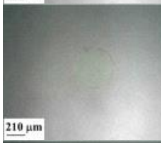
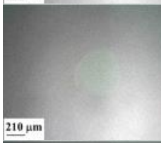
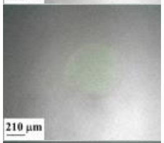
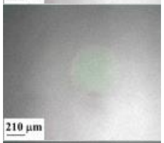
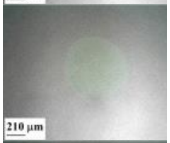
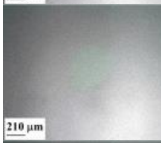
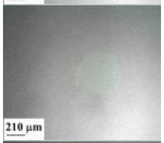
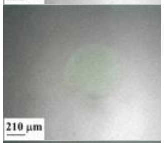
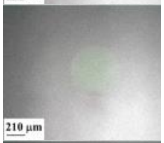
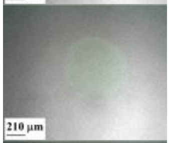
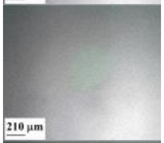
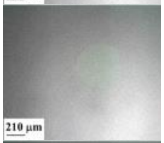
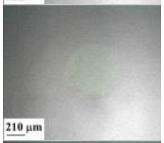
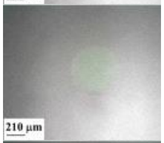
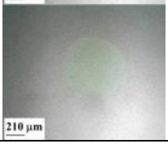
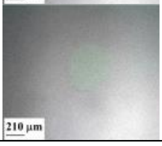
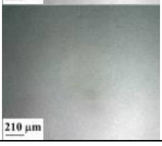
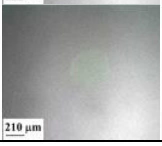
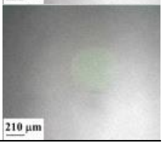
The drop of alkaline-methanol solution on a drop of FAME (0.02wt% FFA) was quite stable in its apparent size. This is possibly due to the soap barrier.

It can be seen that a spot of alkaline-methanol solution on FAME and a spot of FAME on alkaline-methanol solution showed different phenomena. A spot of alkaline-methanol solution contains much more alkaline reactant moles than the same volume of FAME.

High soap formation in the case of alkaline-methanol solution on FAME inhibits the diffusion of methanol and alkaline into FAME phase, so it is hard to notice any changes of the drop size, reflecting a slow reaction rate. Thus, soap acts as a reaction barrier.

The trial with a drop of FAME on a pool of alcohol solution gave similar results (**Table 3.21**), the diffusion of methanol and alkaline was fast. The boundary of FAME disappeared in a short time (50 seconds). This indicates the expected reactions are neutralization and saponification

Table 3.21 Photographs of the reaction zone when FFA on FAME is saponified with initially excess alkaline-alcohol solution, for up to 300 seconds (Photographs taken with 40X magnification)

Time	FFA content of FAME					
(s)	0.02wt%	0.1wt%	0.25wt%	0.5wt%	1.0wt%	2.0wt%
5						
10						
30						
60						
90						
120						
150						
180						
240						
300						

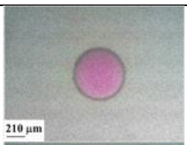
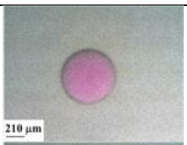
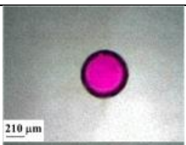
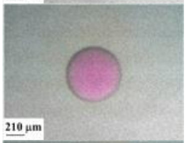
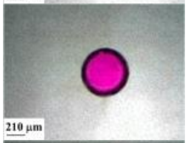
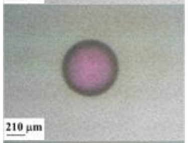
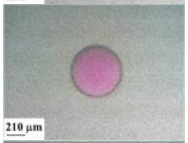
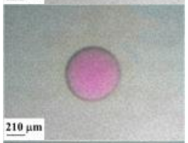
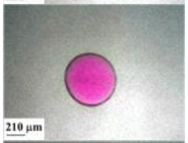
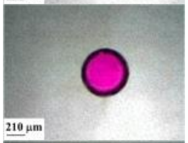
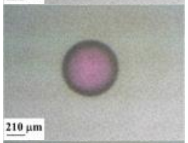
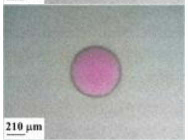
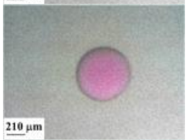
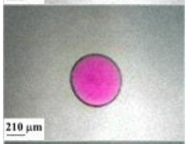
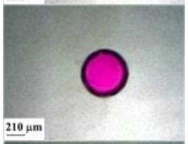
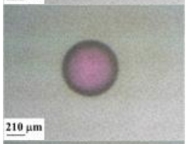
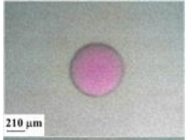
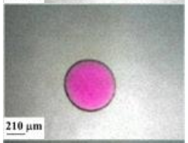
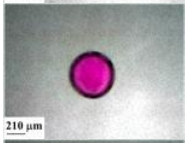
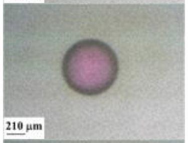
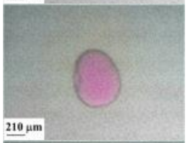
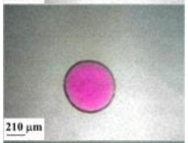
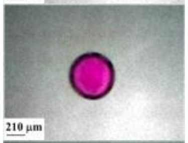
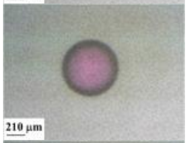
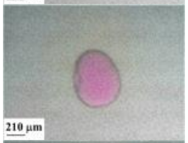
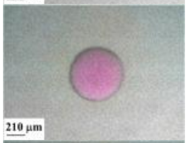
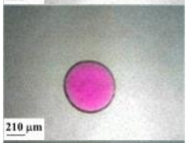
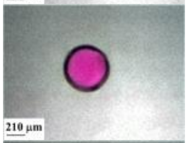
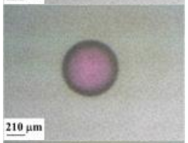
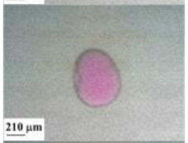
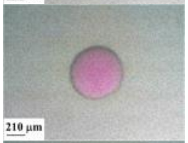
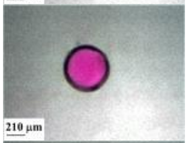
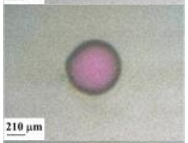
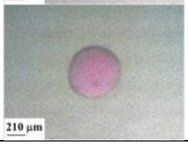
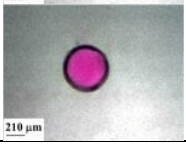
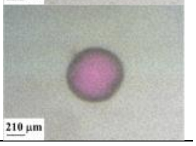
Note: an approx. 1 µL of FAME (0.03wt% water) with varying FFA contents (0.02, 0.1, 0.25, 0.5, 1.0 and 2.0wt%); an approx. 10 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH).

3.6.2.2 Effects of FFA on saponification of RPO

Saponification of alkaline solution on RPO is expected to behave differently from FAME due to the transesterification reaction. Transesterification of triglyceride gives ester and by-product glycerol. Glycerol is a strongly polar compound unlike other esters. Glycerol should prefer to stay with methanol, and if the reaction takes place near the interface of alcohol and triglyceride, the glycerol should leave the ester and move to the methanol phase. The exploration (**Table 3.22**) of a drop of alcohol-alkaline solution on a pool of RPO showed, first, a pale pink color with a low content of FFA in RPO for up to 300 seconds. Second, a small distortion of the alcohol drop appears with 0.1wt% FFA content in RPO, and the weak boundary layer of glycerol and soap may be the cause of this. Third, a strong round boundary was observed with higher contents of FFA in RPO.

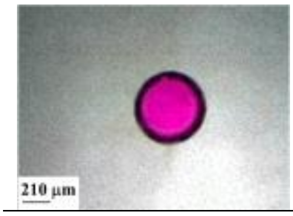
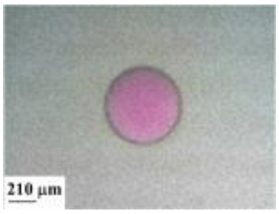
The proposed reaction zone is the film volume of triglyceride, and the expansion of the RPO drop in **Fig. 3.5** supports this concept. The possible mechanism of reaction (**Table 3.23**) should be that methanol accompanies alkaline to the reaction zone and two major reactions take place, neutralization, and transesterification. The neutralization product is soap, an emulsifier, and its polar heads prefer to stay with methanol and so it forms a boundary layer. The FFA neutralization is spontaneous even though FFA is a weak acid. Transesterification is supposed to be a fast reaction but is slower than a spontaneous reaction. So, soap is formed first and it moves to the alcohol interface and creates a thin boundary layer. From **Fig. 3.5**, high FFA (1wt%) oil crates high soap formation as thick black layer while low FFA oil (0.1wt%) creates lower soap formation as thin layer. High FFA content in RPO creates a lot of soap that restrains the diffusion of alcohol and catalyst. The thick boundary layer of soap and glycerol does not allow the diffusion of alcohol and catalyst to the reaction zone, and slows down transesterification.So, oils with 0.1 and 0.5wt% acidity (or 0.05 and 0.25wt% FFA) are at the maximum allowed of feedstocks for Lurgi GmbH [22] and Crown Iron Works [23], respectively.

Table 3.22 Photographs of the reaction zone of the effect of FFA on RPO saponification with initial excess RPO, for up to 300 seconds (Photographs taken with 40X magnification)

Time	FFA content of RPO				
(s)	0.1wt%	0.25wt%	0.5wt%	1.0wt%	2.0wt%
5					
10					
30					
60					
90					
120					
150					
240					
300					

Note: an approx. 10 µL of RPO with varied FFA (0.1, 0.25, 0.5, 1.0 and 2.0wt%); an approx. 1 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH).

Table 3.23 Expected solubility and expected reaction of the effect of FFA on RPO saponification with initial excess RPO

Images at 30 seconds	Component	Expected solubility	Expected reaction
1.High FFA (1wt%) 	RPO+MeOH+$NaOCH_3$	Suspension	Neutralization /Saponification /Transesterification
2.Low FFA (0.1wt%) 	RPO+MeOH+$NaOCH_3$	Suspension	Neutralization /Saponification /Transesterification

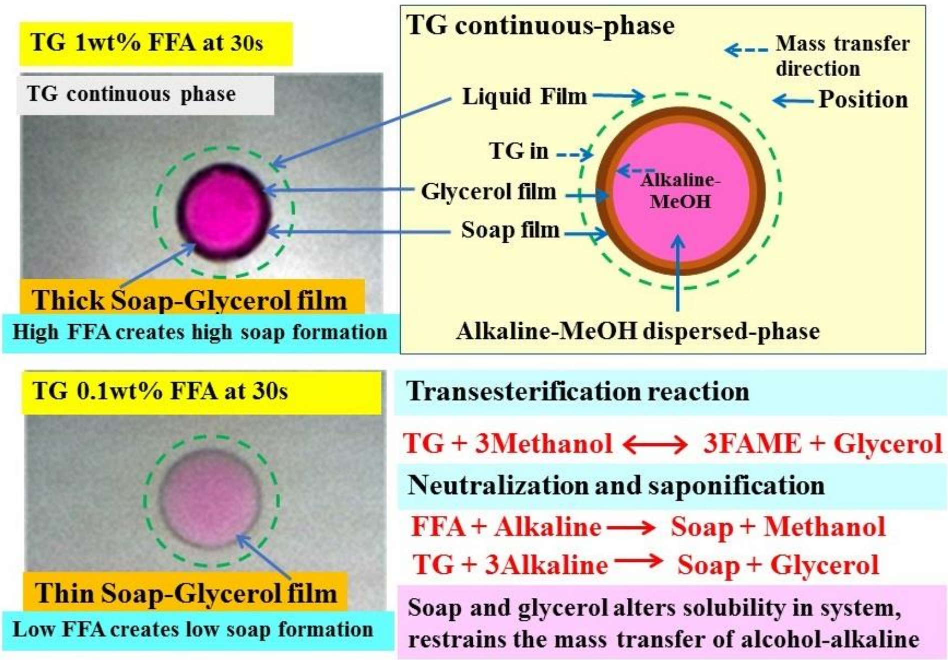
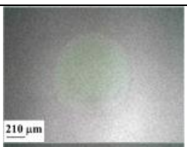
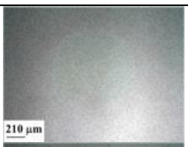
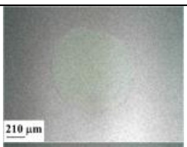
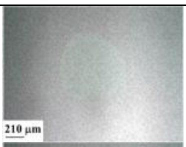
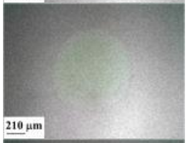
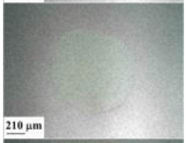
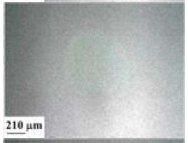
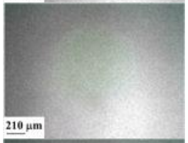
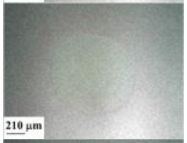
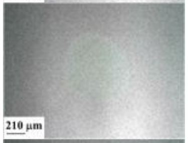
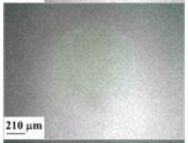
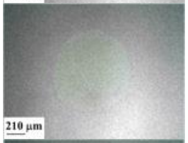
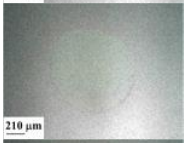
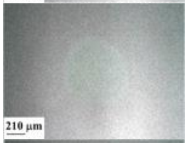
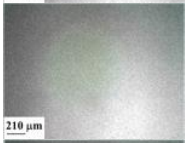
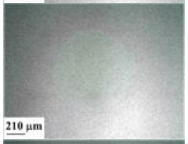
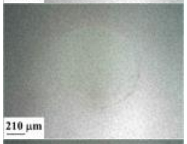
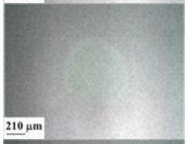
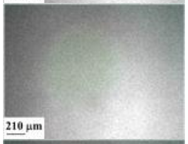
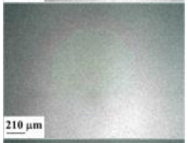
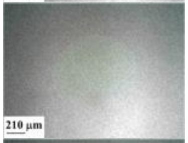
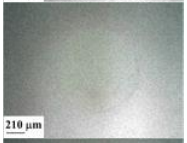
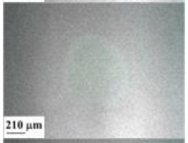
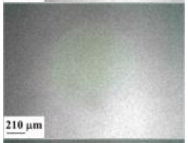
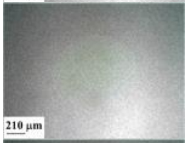
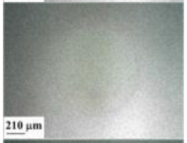
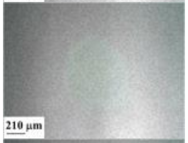
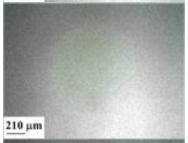
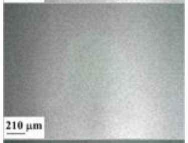
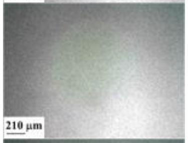
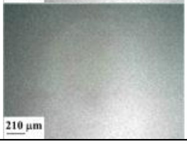
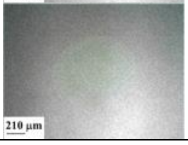
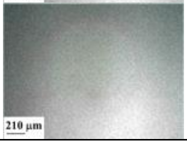
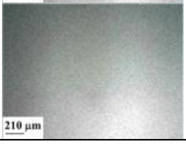


Fig. 3.5 The possible model of reaction zone for the effect of FFA on RPO saponification with initial excess RPO

Table 3.24 Photographs of the reaction zone show the effect of FFA on RPO saponification with initial excess alkaline-alcohol solution, for up to 300 seconds (Photographs taken with 40X magnification)

Time	FFA content of RPO				
(s)	0.1wt%	0.25wt%	0.5wt%	1.0wt%	2.0wt%
5					
10					
30					
60					
90					
120					
180					
240					
300					

Note: an approx. 1 µL of RPO with varied FFA (0.1, 0.25, 0.5, 1.0, and 2.0wt%); an approx. 10 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH)

From **Fig. 3.5**, the possible reactions are neutralization, saponification and transesterification. So, soap and glycerol acted as film resistance of mass transfer of alcohol-alkaline to oil-phase.

The pictures of a drop of RPO on a pool of alkaline-methanol solution support these hypotheses (**Table 3.24**). The possible reactions are neutralization, saponification and transesterification. A drop of RPO carries a limited amount of FFA, and soap formation depends on the FFA content. The soap layer spreads out to the alcohol pool as more alcohol and alkaline diffuse into the oil. The transesterification reaction continues and transforms triglyceride to ester and glycerol. The boundary layer may come from the diffusion of glycerol that is moving to alcohol phase and brings back the alcohol and alkaline molecules.

3.6.3 Effect of water on saponification reaction of RPO

Effect of water on saponification (**Tables 3.25**) was investigated on RPO containing 0.1wt% FFA to reduce the effect of soap from acid neutralization. A real feedstock for biodiesel production will have some FFA, so we chose a realistic but low content. The drop of alkaline solution of methanol in the pool of RPO having different water contents illustrates some interesting variations. At a low water content of 0.1wt%, the pink color in alcohol drop becomes pale within 30 seconds. This indicates fast diffusion of methanol and alkaline into the RPO. At a medium 0.5wt% water content level, the pink color disappeared within 180 seconds, and at the high 1wt% of water in RPO, a pale pink color persisted.

The proposed reaction zone is the film volume of triglyceride, and the expansion of the RPO drop in **Fig. 3.6.** Boundary layer thickness is clearly seen at a high content of water in RPO (1wt%), due to the soap formation. In contrast, at low content of water in RPO, thin layer is observed. One weight percent of water in RPO is approximately 0.48: 1 molar ratio of water to oil.

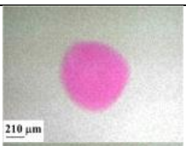
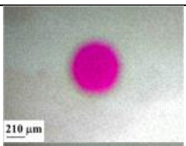
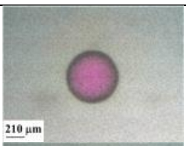
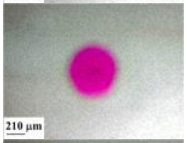
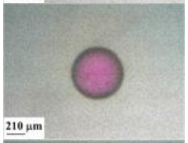
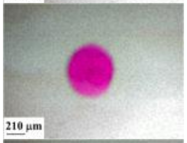
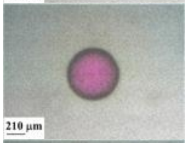
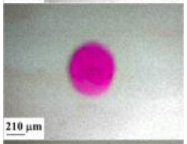
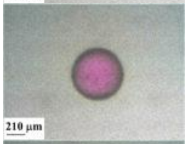
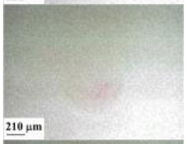
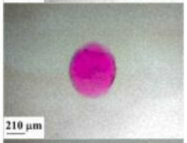
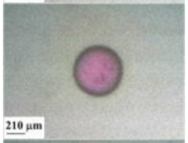
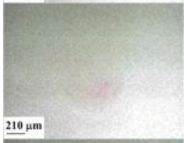
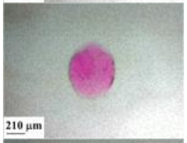
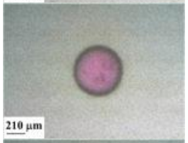
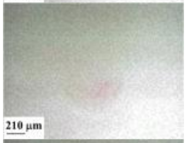
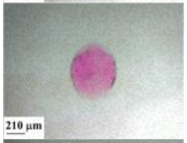
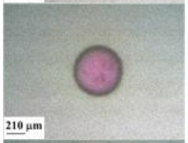
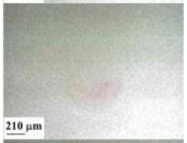
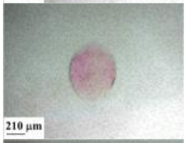
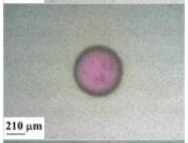
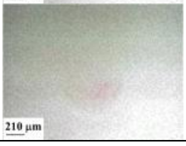
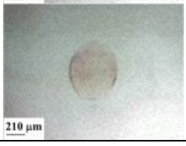
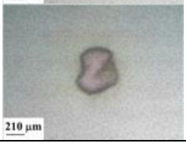
The possible reactions (**Table 3.26**) are hydrolysis, neutralization, saponification and transesterification. However, the reverse esterification of water and triglyceride to FFA may be slow after the preparation step and it is accelerated by alkaline catalyst [35].

The possible reaction model in **Fig. 3.6** indicates that high water content (1wt%) in RPO creates a thick layer (glycerol and soap) restraining the diffusion of alcohol and catalyst. Thick boundary layer of glycerol and soap does not allow the diffusion of alcohol and catalyst to the reaction zone, and slows down transesterification. So, oils with 0.1 and 0.05wt% water are the maximum allowed of feedstocks for Lurgi GmbH [22] and Crown Iron Works [23], respectively.

In the reversed trial of a drop of RPO on the pool of alkaline solution (**Table 3.27**), methanol and alkaline try to diffuse in an oil drop. The high-water content in RPO tends to have a thicker film. Thick film should be glycerol and soap which possibly reduces the diffusion rate of alkaline-methanol solution to the oil drop. The brown shell became thick within a few seconds and disappeared after 240 seconds. This indicates the diffusion of methanol-alkoxide solution into the drop.

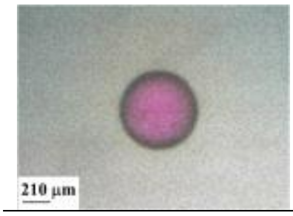
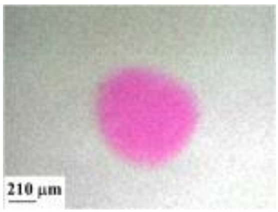
We assume that the glycerol shell was dissolved in methanol-alkoxide solution. High level of water contamination in feedstocks causes hydrolysis of triglyceride and spontaneous soap formation [13], [42], [77]. From the results, it can be seen that high-water content in oil induces a barrier of soap that possibly reduces the rate of mass transfer. So, the maximum moisture and volatiles contents of 0.1 (Lurgi GmbH) [22] and 0.05wt% (Crown Iron Works) [23] are suitable to oil feedstocks for biodiesel production and respectively.

Table 3.25 Photographs of the reaction zone of the effect of water on RPO saponification with initial excess RPO, for up to 300 seconds (Photographs taken with 40X magnification)

Time	Water content of RPO		
(s)	0.1wt%	0.5wt%	1.0wt%
5			
10			
20			
30			
60			
120			
180			
240			
300			

Note: an approx. 10 µL of RPO (0.1wt% FFA) and varied moisture content (0.1, 0.5 and 1.0wt%); an approx. 1 µL of NaOCH3 -methanol solution (4.42wt% in MeOH)

Table 3.26 Expected solubility and expected reaction of the effect of water on RPO saponification with initial excess RPO

Images at 10 seconds	Component	Expected solubility	Expected reaction
1.High Water (1wt%)  	RPO+MeOH+$NaOCH_3$	Suspension	Hydrolysis /Neutralization /Saponification /Transesterification
2.Low Water (0.1wt%)  	RPO+MeOH+$NaOCH_3$	Suspension	Hydrolysis /Neutralization /Saponification /Transesterification

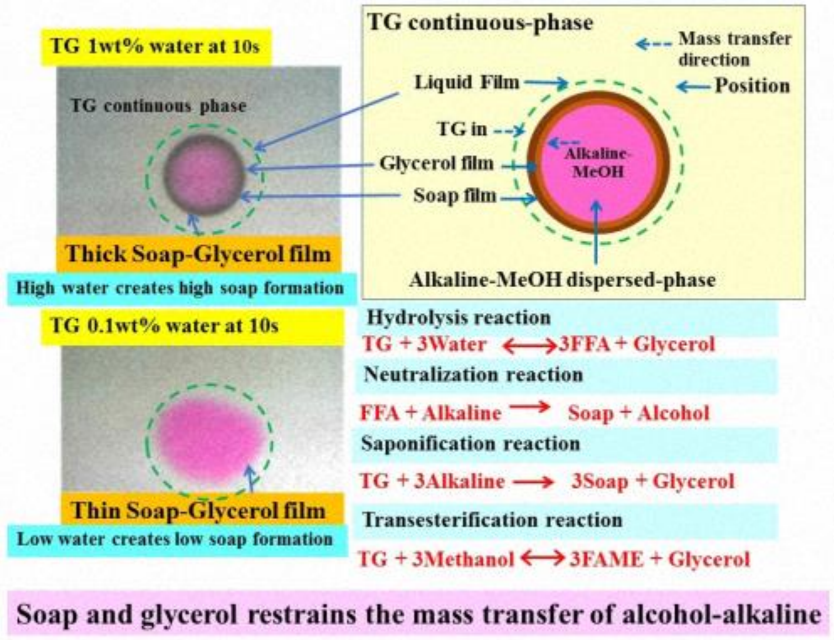
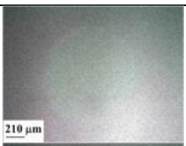
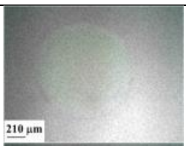
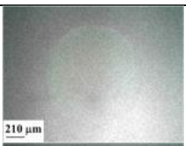
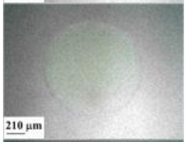
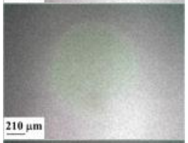
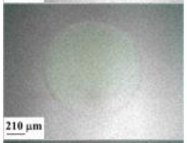
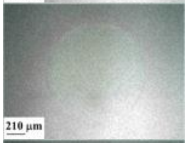
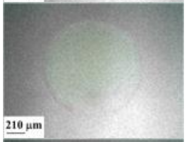
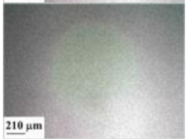
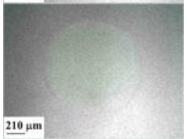
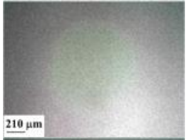
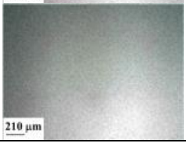
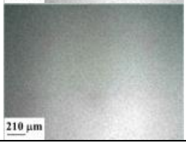
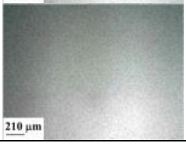


Fig. 3.6 The possible model of reaction zone for the effect of water on RPO saponification with initial excess RPO

Table 3. 27 Photographs of the reaction zone show the effect of water on RPO saponification for RPO with initial excess alkaline-alcohol solution, for up to 300 seconds (Photographs taken with 40X magnification)

Time	Water content of RPO		
(s)	0.1wt%	0.5wt%	1.0wt%
5			
10			
30			
60			
90			
120			
180			
240			
300			

Note: an approx. 1 µL of RPO (0.1wt% FFA) with varied water content (0.1, 0.5 and 1.0wt%); an approx. 10 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH)

3.6.4 Effects of alkaline concentration on saponification reaction of RPO

In this study in **Tables 3.28**, the effects of catalyst concentration (2.21, 4.42 and 8.83wt% in MeOH) on the reaction zone of transesterification of RPO with different FFA oil (low FFA and high FFA) was investigated.

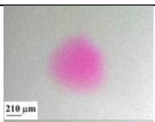
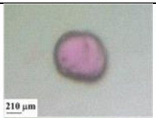
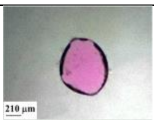
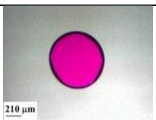
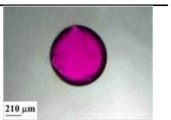
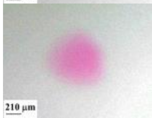
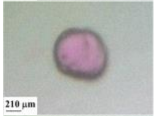
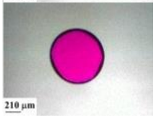
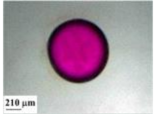
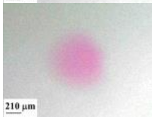
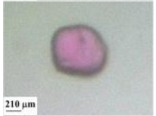
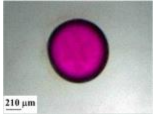
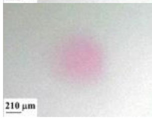
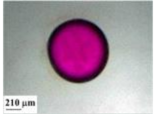
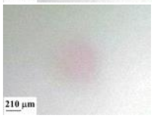
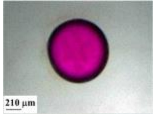
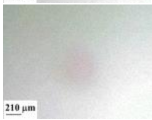
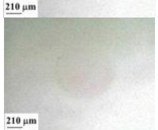
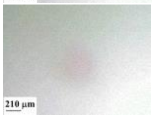
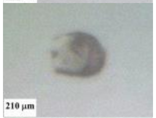
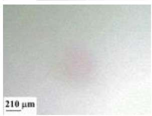
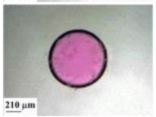
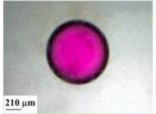
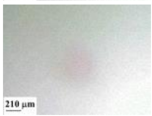
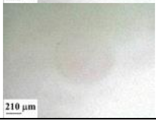
The proposed reaction zone is the film volume of triglyceride in **Fig. 3.7.** When a drop of alkaline-methanol solution is on a pool of RPO, the possible reactions are transesterification and saponification. Both transesterification and saponification have high rates as a high content of catalyst produces a high amount of glycerol and soap, which makes thick shell barriers that retain the catalyst and alcohol in the droplets.

From **Table 3.28**, in the case of low FFA oil (0.1wt%), thinner barriers were generated at lower reaction rates. High FFA oil (1wt%) tends to give thicker barriers with an increased catalyst concentration. The high FFA contents cause neutralization reactions [6], [42]. These thick shells possibly hinder mass transfer of alcohol and catalyst to the reaction zone.

From **Table 3.29** and **Fig. 3.7**, at high FFA oil (1wt%), the high catalyst concentration (8.83wt% in methanol) creates thicker barrier that possible due to higher glycerol generation at higher reaction rates. These thick shells possibly hinder mass transfer of alcohol and catalyst to the reaction zone. However, the lower catalyst concentration (4.43wt% in methanol) creates thinner barrier that possible due to lower glycerol formation.

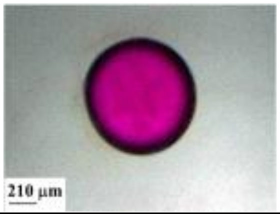
Regarding the reversed trials in **Table 3.30**, when a drop of RPO is on a pool of alkaline- methanol solution, the possible reactions are transesterification and saponification. For high FFA oil, we see a pink layer diffuse into the droplet, and within 300 seconds the whole drop is pink. These same phenomena were found in all cases tested. The results suggest that the initially loaded catalyst will be partly consumed by neutralization with free fatty acids forming soap (emulsifier) that acts as mass transfer barriers.

Table 3.28 Photographs of the reaction zone of the effects of $NaOCH_3$ concentration on RPO (high FFA vs. low FFA) saponification with initial excess RPO, for up to 180 seconds (Photographs taken with 40X magnification)

Time (s)	Catalyst concentration (wt% in MeOH)					
	2.21wt%		4.42wt%		8.83wt%	
	Low FFA	High FFA	Low FFA	High FFA	Low FFA	High FFA
5						
10						
20						
30						
40						
60						
80						
100						
180						

Note: an approx. 10 µL of RPO (0.1wt% FFA for low FFA vs. 1wt% FFA for high FFA); an approx. 1 µL of $NaOCH_3$ -methanol solution (vary catalyst concentration 2.21 to 8.83wt% in methanol

Table 3. 29 Expected solubility and expected reaction of the effects of $NaOCH_3$ concentration on RPO (high FFA vs. low FFA) saponification with initial excess RPO

Images at 20 seconds	Component	Expected solubility	Expected reaction
1.High FFA+Catalyst (8.83wt%)  	RPO+MeOH+$NaOCH_3$	Suspension	Neutralization /Saponification /Transesterification
2.High FFA+Catalyst (4.42wt%)  	RPO+MeOH+$NaOCH_3$	Suspension	Neutralization /Saponification /Transesterification

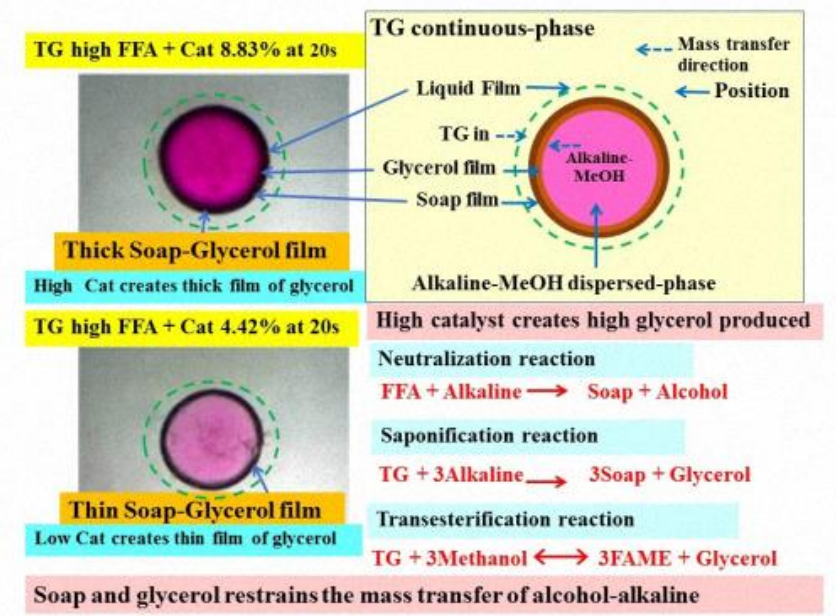
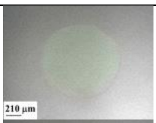
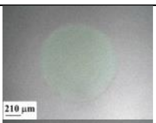
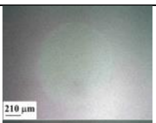
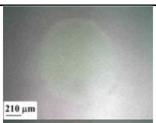
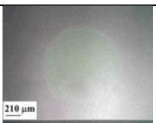
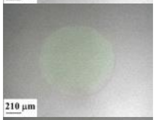
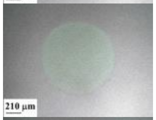
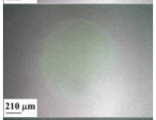
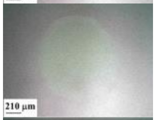
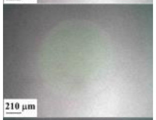
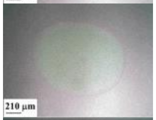
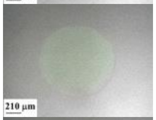
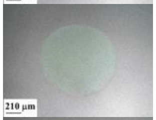
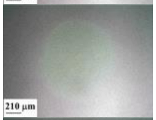
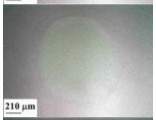
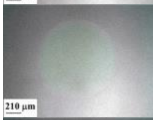
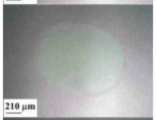
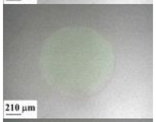
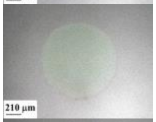
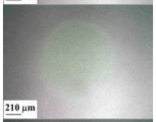
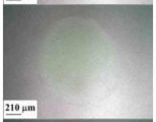
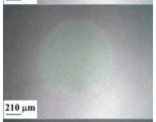
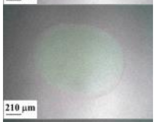
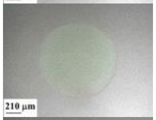
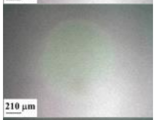
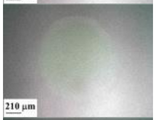
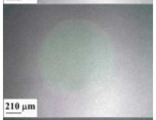
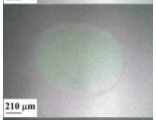
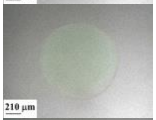
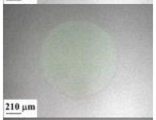
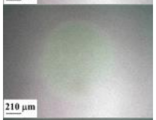
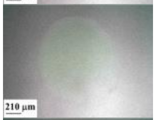
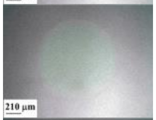
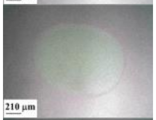
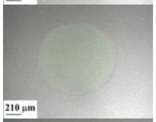
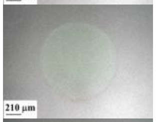
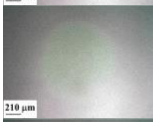
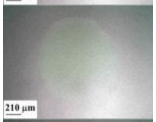
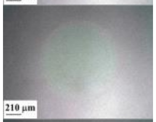
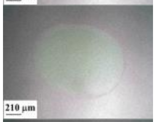
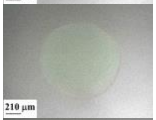
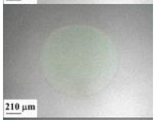
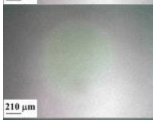
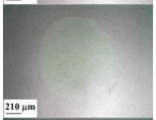
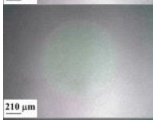
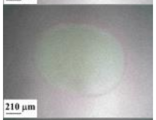
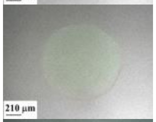
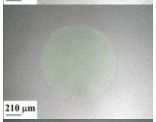
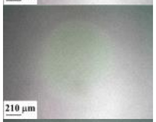
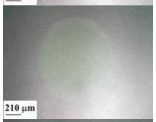
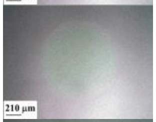
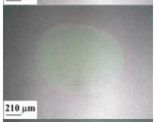
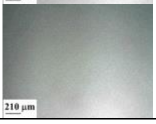


Fig. 3.7 The possible model of reaction zone for the effects of $NaOCH_3$ concentration on RPO (high FFA vs. low FFA) saponification with initial excess RPO

Table 3. 30 Photographs of the reaction zone to examine the effects of $NaOCH_3$ concentration on RPO (high FFA vs. low FFA) saponification with initial excess alkaline-alcohol solution, for up to 300 seconds (Photographs taken with 40X magnification)

Time (s)	Catalyst concentration (wt% in MeOH)					
	2.21wt%		4.42wt%		8.83wt%	
	Low FFA	High FFA	Low FFA	High FFA	Low FFA	High FFA
5						
10						
30						
60						
90						
120						
150						
180						
240						
300						

Note: an approx. 1 µL of RPO (0.1wt% FFA for low FFA vs. 1wt% FFA for high FFA); an approx. 10 µL of $NaOCH_3$ -methanol solution (vary catalyst concentration 2.21 to 8.83wt% in methanol)

3.7 Variables (FFA, water, and catalyst concentration) affecting the $NaOCH_3$-catalyzed transesterification of refined palm oil with methanol

The reaction variables such as FFA content, water content, and catalyst concentration are significant parameters in the conventional transesterification process. In order to evaluate biodiesel yield and purity, the ester content (wt% referred to biodiesel mass) in the final biodiesel phase was determined. Consequently, we need to determine the experimental biodiesel yield after the reaction and separation stages in order to evaluate all of the biodiesel losses (separation, washing, and soap losses). In this work, the theoretical biodiesel yield is 100.47, based on the molecular weight of RPO 848, which can produce 3 moles of FAME (MW 284).

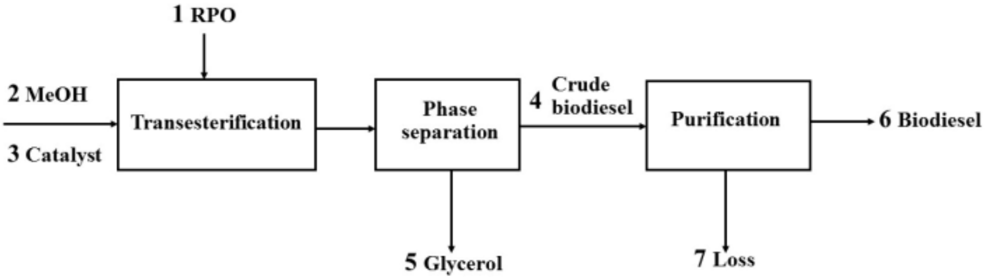


Fig. 3.8 Flow chart of a conventional transesterification process

From our transesterification experiments (Fig. 3.8), the yield loss of biodiesel came from loss in glycerol phase (5), washing loss (7) and chemical loss by saponification [6]. We combined glycerol phase loss and washing loss as a physical loss, which may be a function of the soap content in ester phase. Soap content was measured for both phases of crude biodiesel and crude glycerol, and with the weight ratio of both phases we can calculate the total soap content.

A preliminary study of FFA, water and catalyst amounts on the soap formation is summarized in **Table 3.31**. The effects of FFA content in RPO in the range 0.12-1.0 wt%, while water content and the amount of $NaOCH_3$ were held constant, are seen in Runs #1-5. The results show that increasing FFA gives more soap. The nearly 1wt% of $NaOCH_3$ and the molar ratio of methanol to oil at 6: 1 within 30 minutes of reaction give the ester content in final biodiesel $\geq$ 96.5 wt%, satisfying worldwide biodiesel specifications. But the physical yield losses are very high with 0.25wt% of FFA.

The soap content in the ester phase of Run#2 (**Table 3.32**) is about 3,016 ppm based on MW=292 of sodium soap. The specified feedstock properties of maximal acidity 0.1% or 0.5% by Lurgi GmbH [22] and Crown Iron Works [23] correspond to 0.05 or 0.25 wt% of FFA, and may be more motivated by yield losses than by chemical reactivity.

The remaining catalyst was also measured for both phases. The remaining catalysts and soap contents in each phase and their distribution are shown in **Table 3.32**. Most of the remaining catalyst was found in the glycerol phase. We assume that the barrier layer of mass transfer at the outer surface of methanol droplet is composed of glycerol, soap, diglyceride, and monoglyceride. At a critical thickness of this barrier only very small amounts of alcohol and catalyst can diffuse through this film. But the remaining alcohol and catalyst outside the droplets could proceed to react, both by transesterification and saponification. This resulted in glycerol and soap, which created very fine droplets and suspended in the ester phase. So, a very small amount of remaining catalyst was found in the ester phase. The soap was mostly found in the glycerol phase, but at higher amount in the ester phase than the remaining catalyst. We assume the suspension of very small glycerol droplets can explain this fact. We believe that if the separation of glycerol phase from the ester phase were done with a centrifuge, most of the soap would be in the glycerol phase [78].

Table 3.31 Preliminary results of FFA, water and catalyst amount effects on soap formation and yield losses

	1	RPO properties						2	3	4	5	6	Yield	Ester content	7	Biodiesel losses	
		FFA content			Water content												
RUN #	RPO							MeOH	NaOCH$_3$	Crude biodiesel	Crude glycerol	Biodiesel			Total	Chemical	Physical
	g	wt%	g	mol	wt%	g	mol	G	g	g	g	g	%	wt%	%	%	%
1	200	0.12	0.246	0.0009	0.18	0.3558	0.0198	45.28	1.96	198.75	47.67	192.15	96.08	98.13	4.40	2.90	1.50
2	200	0.25	0.500	0.0019	0.18	0.3558	0.0198	45.28	1.96	198.51	48.27	188.22	94.11	98.13	6.37	3.20	3.17
3	200	0.57	1.140	0.0042	0.18	0.3558	0.0198	45.28	1.96	198.65	48.37	184.55	92.28	98.13	8.20	3.63	4.57
4	200	0.75	1.500	0.0056	0.18	0.3558	0.0198	45.28	1.96	195.57	50.79	173.20	86.60	97.31	13.88	4.08	9.80
5	200	1.00	2.000	0.0074	0.18	0.3558	0.0198	45.28	1.96	195.37	50.85	168.28	84.14	97.31	16.34	4.38	11.96
6	200	0.18	0.364	0.0013	0.05	0.1000	0.0056	45.28	1.96	198.09	48.70	193.46	96.73	98.95	3.75	1.96	1.79
7	200	0.18	0.364	0.0013	0.15	0.3000	0.0167	45.28	1.96	198.32	47.76	192.41	96.21	98.95	4.27	2.19	2.08
8	200	0.18	0.364	0.0013	0.25	0.5000	0.0278	45.28	1.96	199.24	47.53	187.68	93.84	98.13	6.63	3.51	3.12
9	200	0.18	0.364	0.0013	0.40	0.8000	0.0444	45.28	1.96	197.53	48.43	180.40	90.20	97.72	10.28	3.84	6.44
10	200	0.18	0.364	0.0013	0.80	1.6000	0.0889	45.28	1.96	197.49	48.30	170.91	85.46	97.31	15.02	4.76	10.26
11	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	2.23	198.76	48.25	192.78	96.39	98.68	4.09	2.62	1.47
12	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.96	198.37	48.39	193.39	96.70	98.68	3.78	2.22	1.56
13	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.59	198.50	48.35	191.29	95.64	97.86	4.83	1.99	2.85
14	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.40	198.74	47.51	181.05	90.53	95.40	9.95	1.84	8.11
15	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.21	198.24	48.30	171.19	85.59	94.58	14.88	1.70	13.18
16	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	0.98	197.29	48.47	162.22	81.11	92.40	19.36	1.60	17.76

Note: RUNS #1-5 for FFA concentration effect; RUNS #6-10 for water concentration effect; RUNS #11-16 for catalyst concentration effect.

Table 3.32 Remaining catalyst and soap in ester and glycerol phases

Run #	Ester-phase		Glycerol-phase		Total		Remaining catalyst distribution		Soap distribution	
	Remaining catalyst	Soap	Remaining catalyst	Soap	Remaining catalyst	Soap	Ester-phase	Glycerol-phase	Ester-phase	Glycerol-phase
	mol	mol	mol	mol	mol	mol	%	%	%	%
1	0.000024	0.000987	0.016375	0.018900	0.016399	0.019887	0.14	99.86	4.96	95.04
2	0.000025	0.002053	0.014376	0.019891	0.014401	0.021944	0.17	99.83	9.36	90.64
3	0.000052	0.002808	0.011386	0.022059	0.011438	0.024867	0.45	99.55	11.29	88.71
4	0.000050	0.004365	0.007819	0.023604	0.007869	0.027969	0.64	99.36	15.61	84.39
5	0.000080	0.004732	0.006443	0.025253	0.006523	0.029985	1.23	98.77	15.78	84.22
6	0.0000157	0.0009149	0.0228462	0.0125130	0.0228619	0.0134279	0.07	99.93	6.81	93.19
7	0.0000153	0.0009736	0.0211952	0.0140201	0.0212105	0.0149937	0.07	99.93	6.49	93.51
8	0.0000155	0.0022428	0.0119083	0.0221824	0.0119238	0.0244252	0.13	99.87	9.18	90.82
9	0.0000155	0.0033975	0.0101915	0.0228459	0.010207	0.0262434	0.15	99.85	12.95	87.05
10	0.0000156	0.0045867	0.0031871	0.0280382	0.0032027	0.0326249	0.49	99.51	14.06	85.94
11	0.000048	0.001320	0.022919	0.016628	0.022967	0.017948	0.21	99.79	7.35	92.65
12	0.000015	0.001285	0.021071	0.013936	0.021086	0.015221	0.07	99.93	8.44	91.56
13	0.000016	0.001301	0.015990	0.012307	0.016006	0.013608	0.10	99.90	9.56	90.44
14	0.000016	0.001477	0.012749	0.011126	0.012765	0.012603	0.13	99.87	11.72	88.28
15	0.000016	0.001795	0.010884	0.009836	0.010900	0.011631	0.15	99.85	15.43	84.57
16	0.000016	0.002035	0.007082	0.008931	0.007098	0.010966	0.23	99.77	18.56	81.44

Note: RUNS #1-5 for FFA concentration effect; RUNS #6-10 for water concentration effect; RUNS #11-16 for catalyst concentration effect.

The effects of water content in RPO from 0.05 to 0.8wt%, while the FFA content was kept fixed, were tested in Runs #6-10. Please be reminded that the MW of water is 18 while the average MW of FFA in RPO is 270, so the number of moles of 0.05wt% of water is equivalent that of 0.75wt% FFA. The hydrolysis of water with TG (Eq. 1.3) or FAME (Eq. 1.4) to FFA was confirmed by soap content increasing with water content in

RPO. But that increase is not linear with the number of moles of water, because of limitation by the number of moles of $NaOCH_3$.

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$$\text{TG} + 3\text{Water} \longleftrightarrow 3\text{FFA} + \text{Glycerol} \qquad \text{Eq. (1.3)}$$

$$\text{Ester} + \text{Water} \longleftrightarrow \text{FFA} + \text{Alcohol} \qquad \text{Eq. (1.4)}$$

The effects of catalyst concentration were investigated in Runs #11-16 (**Tables 3.31** and **3.32**). Using a low content of NaOCH3 below 0.70wt% of RPO (Runs #14-16) resulted in off quality biodiesel with too low ester content (96.5wt%). The soap content in these runs was below 3,000 ppm, but the physical losses were very high. The loss in separation step of these runs does not differ from all other runs in the same trial series. Anyway, we noticed difficulty of washing, and found that the middle layer between the upper layer ester phase and the lower layer water phase had varying thicknesses. This interface layer was photographed as shown in **Table 3.33**. The emulsions with low ester conversion are denser than with high conversion, but the soap contents in this trial series are below 3,000 ppm. We assume that the large emulsification was caused by the by-products mono- and diglyceride from incomplete conversion of triglyceride to ester. Freedman et al., 1984 [79] demonstrated low levels of monoglyceride and diglyceride in the case of high ester content (approx. 98 wt%), while high levels of monoglyceride and diglycerides were still observed at low ester contents (approx. 82wt%). From this reference, at 95% ester conversion, di- and monoglyceride are present at the high 2-3wt% level of total biodiesel.

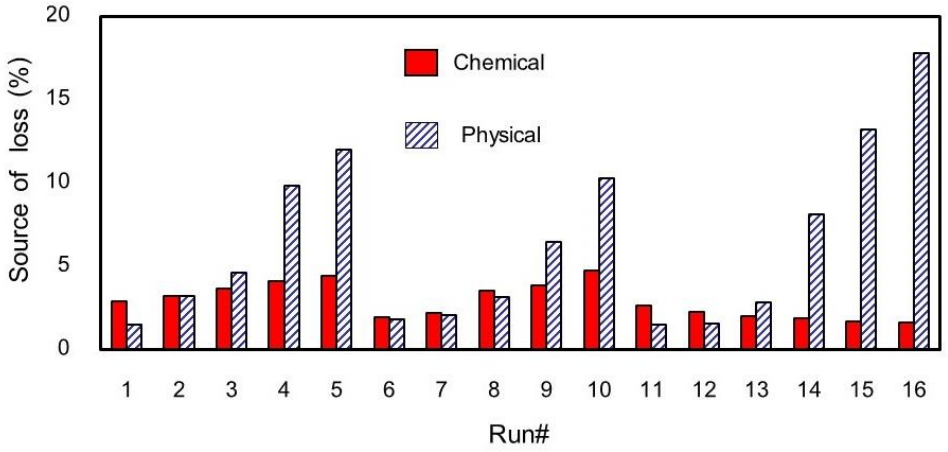
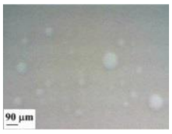
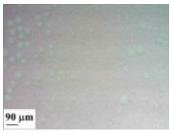
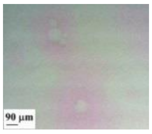
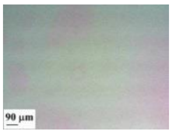
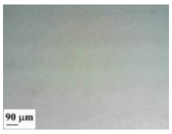
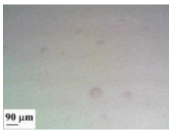


Fig. 3.9 Sources of biodiesel yield loss

Table 3.33 Protographs of the interface layer between biodiesel and water phases in the washing step

Catalyst concentration					
0.49wt%	0.6wt%	0.7wt%	0.8wt%	0.98wt%	1.1wt%
					

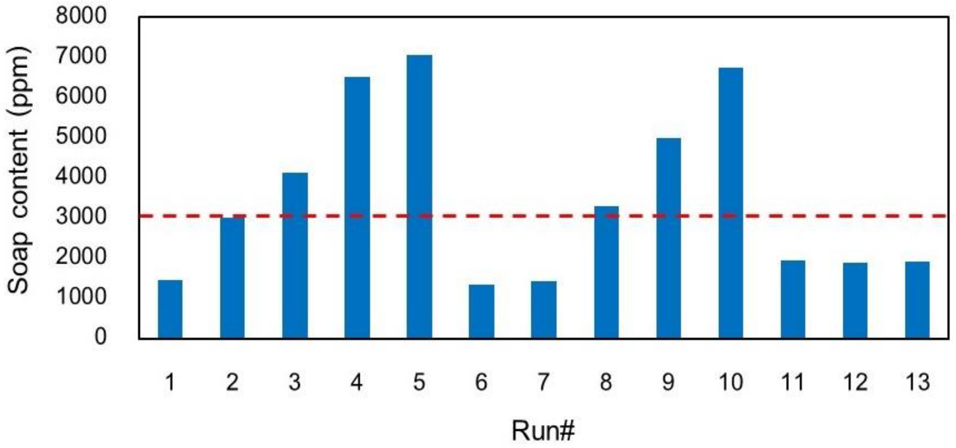


Fig. 3.10 The soap content in ester-phase

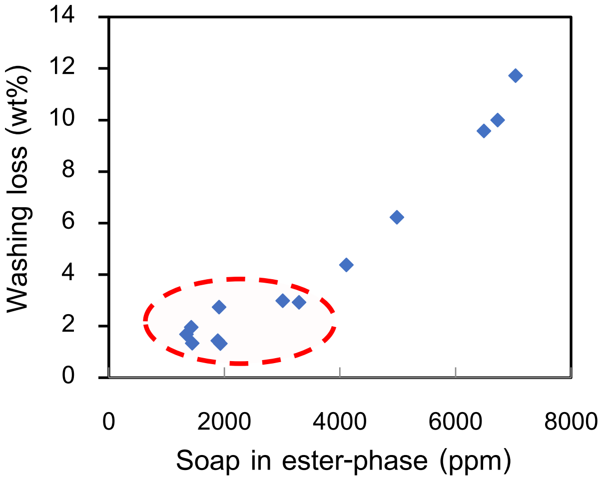


Fig. 3.11 The relationship between soap content in ester-phase and washing loss

The effects of soap content in crude biodiesel on washing losses are shown in **Fig. 3.11.** The data from Runs #14-16 were excluded from this Figure, due to the high content of di- and monoglyceride. We propose that the soap content in crude biodiesel should be below 3,000 ppm for wash step losses below 3%. Our results suggest as maximum soap content in crude biodiesel about 3000 ppm. Washing the crude biodiesel with a dilute water solution of an acid, such as citric acid, may reduce the losses in washing, but as a drawback the soap is converted to FFA, which is not desirable due to biodiesel specifications.

CHAPTER 4

CONCLUSIONS and SUGGESTIONS

This study aims to understand the mixing of multicomponent (triglyceride, FAME, methanol, and THF) in the biodiesel production process. An LCD digital microscope is applied as visual observations in this work to clarify the interactions of key substances and the reaction zone in biodiesel production. This study aims to clarify the effect of FFA, water, and catalyst amount on the reaction zone in transesterification process. Finally, the effect of important reaction variables such as FFA, water and catalyst amount on the transesterification reaction are preliminary investigated.

4.1 Solubility of multicomponent in biodiesel production

The polarity of the components in transesterification reaction plays a crucial role in the reaction, affecting the miscibility of compounds in the reaction mix, and influencing efficiency and extent of conversion. A highly polar compound like glycerol could enable clear separation of methanol from the less polar substances, such as ester and triglyceride. A sulfuric acid mix with methanol is highly polar, giving a dispersion of methanol droplets in continuous triglyceride phase. The formation of soap could emulsify and suspend methanol drops in otherwise compatible methanol-FAME solution. The observed behaviors of multi-compound solubility in a transesterification system indicate that the reaction is a liquid-liquid reaction. The diffusivity of alcohol reactant together with the catalyst to another reactant phase plays a key role as rate limiting step. The smaller alcohol molecules might enhance diffusion through obstructing triglyceride or long chained fatty acid ester. The co-solvent THF or FAME improved solubility of polar methanol in the non-polar triglyceride, but the strongly polar products, such as glycerol and soap emulsifier, could interrupt this effect. The polar similarity of THF and methanol provides them mutual miscibility, while methanol is less compatible with ester or triglyceride. The co-solvent THF or FAME cannot enhance solubility of the multicomponent systems in biodiesel production to provide a homogeneous mix. Imaging at room temperature helped elucidate the behavior in the multicomponent transesterification system. The conceptual mechanisms in esterification and transesterification should be properly revised.

The kinetics of transesterification should depend on the rate of mass transfer, especially of the catalyst. The catalytic compound interacts at carbonyl groups of the ester in the first step. However, if it is accompanied by alcohol, then the alcohol diffusivity plays a key role in the reaction rate. Diffusivity in a multicomponent system depends on several factors, including viscosity, polarity, molecular size, concentration gradients, etc. We need to understand these factors clearly before proposing the possible reaction mechanisms, and eventually models of transesterification kinetics.

4.2 Reaction zone study

The reaction zone of soap formation is in the oil (TG and FAME) film near the interface of the methoxide-methanol solution. Soap is an emulsifier that prefers to stay at the interface of polar and nonpolar substances. The soap layer is a barrier resisting the transfer of alcohol and catalyst solution. The glycerol from transesterification reaction is a polar substance, and while the reaction zone is at the interface or in the oil film area, the glycerol diffuses back to the more polar methoxide-methanol solution. We assume that soap prefers to stay at the outer layer from the glycerol because the lipophilic part of soap likes to be near the nonpolar oil. The produced glycerol creates a thicker barrier than soap, because the number of moles of soap is limited dependent on availability of the alkaline catalyst. The water content in triglyceride feedstock enhances soap formation via hydrolysis with triglyceride or FAME to FFA, and these further react with an alkaline catalyst to form soap.

4.3 Variables (FFA, water, and catalyst concentration) affecting the $NaOCH_3$-catalyzed transesterification of refined palm oil with methanol

The amount of alkaline catalyst plays an important role in biodiesel production. The catalyst concentration controls the intermediate step of transesterification between the alkoxide ion ($-OCH_3$) and the carboxyl group of fatty acids.

A high concentration of alkaline catalyst gives a high rate of ester and glycerol production, making thicker glycerol layer that entraps the methanol and alkaline catalyst within methoxide-methanol solution droplets. But the remaining alkaline outside the droplet is high enough to keep the transesterification going on. The remaining catalyst after 30 minutes of reaction is not the reactive catalyst in the reaction; we believe that the acting catalyst for transesterification must have a higher concentration. The saponification of alkaline to FAME and triglyceride consume the catalyst. We found that the number of moles of soap is higher than the number of moles of FFA plus water, but never greater than the number of moles of alkaline catalyst.

The physical yield losses depend on the soap content in crude biodiesel. We suggest 3,000 ppm as maximum limit of soap in crude biodiesel. The soap formation by transesterification is very complicated. Anyway, the soap formation from FFA is the fastest reaction. The soap formation via hydrolysis of FAME or triglyceride and water to FFA proceeds slower further to soap. The soap formation from the saponification of alkaline and FAME or triglyceride was found in our trials, which suggests not using too high amounts of alkaline catalyst in the production process.

The glycerol product contributes to saponification by the shell barriers that restrain the diffusion of alcohol and alkaline catalyst into the triglyceride body. The rate of shell formation also plays an important role in the overall chemical reaction rate.

4.4 Suggestions for future work

1) Rate of saponification should be further investigated due to complications in the liquid-liquid reaction system.

2) Effect of glycerol on biodiesel production should be studied to examine the inhibitory effect in the saponification reaction.

3) Effect of category of alcohol types (i.e. ethanol, propanol) on the solubility of oil should be studied to evaluate the solubility behavior.

4) The ethanolysis reaction of refined palm oil should be evaluated to compare with methanolysis reaction of refined palm oil.

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APPENDIX

APPENDIX A

DETERMINATION METHOD

A.1 Analysis of free fatty acids (FFA) content using AOCS Ca 5a-40 method

The free fatty acids (FFAs) in palm oil in this study is determined by acid-base titration method (AOCS Ca 5a-40). Each sample (between 1-10 g) was dissolved in 50 mL of ethanol, and titrated with standard 0.1 M NaOH solution, using Phenolphthalein as an indicator to determine the FFAs content. For palm oil, the free fatty acids are normally calculated as oleic acid.

FFA content as palmitic, wt.%, was calculated as the following equation:

$$\%\mathrm{FFA} = \frac{\text{alkaline volume (mL) x C x 28.2}}{\text{Sample weight (g)}} \qquad \text{(Eq. A-1)}$$

Where C is the concentration of NaOH solution.

A.2 Proximately method for ester content determination (Petty Patent 5060)

According to the Thailand petty patent 5060, total glycerides in biodiesel was determined by transesterification in Centrifuge Tube (Koehler, Long-Style for ASTM D1796) using microwave irradiation. The residue glycerides in biodiesel is reacted with methanol in the presence of alkali catalyst to produce methyl ester and glycerol. The glycerol content can be approximately referred to glycerides content by use the correlation curve. The total glycerides content (wt%) can be proximately converted into ester content by minus with 100 wt%.

A.3 Analysis of catalyst and soap analysis

Catalyst and soap contents in sample were determined by an acid-base titration method (AOCS Cc17-79). The samples of the reacting mixture were taken at interval time. Each sample was dissolved in 50 mL of ethanol, and titrated with 0.1 M HCl solution. For catalyst content, Phenolphthalein was used as an indicator to determine the catalyst concentration. For soap content, Bromophenol blue was used to determine the soap concentration.

For catalyst content in sample (g/g sample), it was calculated using the following equation:

$$\text{Catalyst content (g / g sample)} = \frac{\text{mL of HCl} \times C \times MW_1}{\text{g of Sample} \times 1000} \qquad \textbf{(Eq A-2)}$$

where C is the concentration of HCl solution and MW_1 is molecular weight of catalyst such as NaOH = 40.0, KOH = 56.1, $NaOCH_3$ = 54.0, and $KOCH_3$ = 70.1.

For soap content in sample (g/g sample), it was calculated using the following equation:

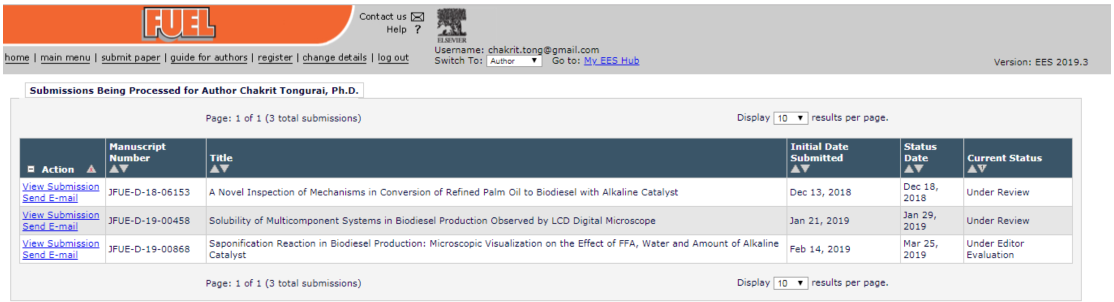
$$\text{Soap content (g / g sample)} = \frac{\text{mL of HCl} \times C \times MW_2}{\text{g of Sample} \times 1000} \qquad \textbf{(Eq A-3)}$$

where C is the concentration of HCl solution and MW_2 is molecular weight of soap such as potassium oleate = 320.56 and sodium oleate = 304.4.

APPENDIX B

FIRST MANUSCRIPT

I. Chanakaewsomboon, C. Tongurai, S. Photaworn, S. Kungsanant. *Solubility of Multicomponent Systems in Biodiesel Production Observed by LCD Digital Microscope*. This article is under peer reviewing for Publication on Fuel (ISI, Q1, IF = 4.908) Initial Date Submitted: 21/01/2019, Under Review Status Date: 29/01/2019.



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View Submission Send E-mail	JFUE-D-18-06153	A Novel Inspection of Mechanisms in Conversion of Refined Palm Oil to Biodiesel with Alkaline Catalyst	Dec 13, 2018	Dec 18, 2018	Under Review
View Submission Send E-mail	JFUE-D-19-00458	Solubility of Multicomponent Systems in Biodiesel Production Observed by LCD Digital Microscope	Jan 21, 2019	Jan 29, 2019	Under Review
View Submission Send E-mail	JFUE-D-19-00868	Saponification Reaction in Biodiesel Production: Microscopic Visualization on the Effect of FFA, Water and Amount of Alkaline Catalyst	Feb 14, 2019	Mar 25, 2019	Under Editor Evaluation

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Solubility of Multicomponent Systems in Biodiesel Production Observed by LCD Digital Microscope

I. Chanakaewsomboon, C. Tongurai*, S. Photaworn, S. Kungsanant

Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Songkhla 90112, Thailand

*Corresponding author: chakrit.tong@gmail.com

Abstract

The mutual solubilities of multiple components in the transesterification reaction are among the key factors affecting biodiesel production. Our trials aimed to clarify their behaviors during the reaction by visual observation using an LCD digital microscope. In the experiments, refined palm oil and fatty acid methyl ester were the main raw materials, and methanol was used as alcohol reactant. Sodium methoxide and sulfuric acid were used as alkaline and acid catalysts, respectively. The co-solvent, tetrahydrofuran (THF), was used for solubility enhancement and its effects on the transesterification reaction were also observed. The experiments were carried out at room temperature in order to eliminate methanol loss. The imaging observations show that the reactions were of liquid-liquid phase type. The by-products glycerol and soap play significant roles as reaction barrier and suspension component in the system. The THF enhanced solubility of methanol in the triglyceride phase and did not create any separation phases. Additionally, a concave slide glass was employed as a micro-reactor and to observe the reaction zone, for examining the diffusion of methanol to triglyceride phase. Observations of transesterification reaction at an elevated temperature are expected to confirm this study. The kinetics of transesterification and esterification reactions possibly depend on the diffusivity of

the catalyst in alcohol. The different polarities of alkaline and acid catalysts can affect diffusivities, which should be studied further.

Keywords: LCD digital microscope, Biodiesel, Liquid-liquid reaction, Transesterification, Saponification

1. Introduction

Biodiesel is a mixture of alkyl esters obtained from vegetable oils, animal fats, or waste oils containing triglyceride (TG) as the main component reacted with a short chained alcohol (typically methanol or ethanol) in the presence of a suitable catalyst [1], [30], [80]. The reaction is called transesterification and is shown in Eq. (1).

$$\mathrm{TG} + 3\,\mathrm{Alcohol} \xleftrightarrow{\mathrm{Catalyst}} 3\,\mathrm{Ester} + \mathrm{Glycerol} \qquad \text{Eq. (1)}$$

For this type of reaction, there are two alternative types of catalysts, namely heterogeneous (solid) or homogeneous (liquid). A solid catalyst, either acid or base, has an advantage in low soap formation, but gives relatively time-consuming reactions, requiring also a large amount of alcohol and subsequent separations [1], [30], [80]. In contrast, a liquid catalyst, such as alkaline hydroxide or alkaline methoxide, is widely used in commercial biodiesel plants. It provides faster reactions with low alcohol consumption, and is easy to mix in with the reactants. However, it can allow saponification reactions and requires a high amount of water in a later washing process [3], [13], [14], [81]–[83].

Kinetic studies of transesterification reaction have mostly been on a homogeneous system, and many studies have observed that the initial mass transfer of the reacting components is probably negatively impacted by the poor mixing of the components. Visibly the nonpolar phase (triglyceride) and polar phase (alcohol) are initially immiscible and create two different phases. Thus, the mass transfer between these phases could limit the reaction rate. The mixing of the two phases can be improved by increasing the reaction temperature or by increasing the stirring intensity, but then the operating costs are increased by high energy consumption. Adding co-solvents in the reaction mixture is one suggested method to improve the mixing of oil and alcohol and increase the reaction rate. The co-solvent needs both polar and non-polar parts in its molecules in order to reduce interfacial tension between alcohol and triglyceride and enhance their interactions [16]. Using a co-solvent has been reported to facilitate mixing during transesterification under mild conditions and short reaction time, as listed in Table 1 [55]–[57]. Additionally, tetrahydrofuran (THF) is among the most effective co-solvents for transesterification, because it has a low boiling point (67 °C) similar to that of methanol (65 °C) [17] making temperature control easy.

Furthermore, another obstacle to transesterification is the soap formation. It is undesirable because it consumes the catalyst, decreases the yield of biodiesel, and complicates the subsequent purification steps [24]. Soap is produced by neutralization of the free fatty acid (FFA) in the oil and by saponification of triglyceride and ester.

In neutralization, the FFA reacts with an alkaline catalyst (NaOH or $NaOCH_3$) and turns to soap, water, or alcohol as shown in Eq. (2) and Eq. (3):

$$\text{FFA} + \text{NaOH} \longrightarrow \text{Soap} + \text{Water} \qquad \text{Eq. (2)}$$

$$\text{FFA} + \text{NaOCH}_3 \longrightarrow \text{Soap} + \text{Alcohol} \qquad \text{Eq. (3)}$$

However, the water in the oil and alcohol phases plays a very important role in soap formation. If a high amount of water is present it can hydrolyze the ester and cause reversed esterification, yielding FFA and alcohol again. This is shown in Eq. (4):

$$\text{Ester} + \text{Water} \longleftrightarrow \text{FFA} + \text{Alcohol} \qquad \text{Eq. (4)}$$

In saponification reaction triglyceride or fatty acid methyl ester (FAME) reacts with a base catalyst to form soap, glycerol, and methanol as in Eq. (5) and Eq. (6):

$$\text{TG} + 3\text{NaOH} \longrightarrow 3\text{Soap} + \text{Glycerol} \qquad \text{Eq. (5)}$$

$$\text{FAME} + \text{NaOH} \longrightarrow \text{Soap} + \text{CH}_3\text{OH} \qquad \text{Eq. (6)}$$

In transesterification using alkaline-catalyst, the main product glycerol is highly polar whereas the side-product soap is an amphiphile and considered an emulsifier. These may disturb the mixing and interactions of the components in the system. In acid-catalyzed transesterification there is no soap formation and the interactions between phases may be different from those with an alkaline catalyst.

As mentioned above, understanding the solubility and mixing of multiple components in the biodiesel production process is fundamentally important. An LCD digital microscope is applied in this work to clarify the interactions of key substances in biodiesel production. The scope of our studies is summarized in Table 2. The behaviors of triglyceride, FAME, methanol, and THF were examined by visual observation using LCD microscope. Refined palm oil (RPO) and FAME in the mixture were observed for their roles as reaction intermediates. The effects of alkaline and acid catalysts on transesterification reaction mixture were the main interest in this study. The addition THF as a co-solvent to transesterification was studied to clarify the single- or two-phase reaction aspects mentioned by several reviews. The self-transesterification of FAME and methanol with an alkaline catalyst is shown in Eq. (7). Soap formation during the reaction and effects of THF were also examined. Finally, preliminary observations of the reaction zone were conducted to provide an obvious clarification.

$$\text{RCOOR''} + \text{R'OH} \xrightarrow{\text{Catalyst}} \text{RCOOR'} + \text{R''OH} \qquad \text{Eq. (7)}$$

where R’ and R” are some given alkyl groups.

Table 1

The effects of a co-solvent on transesterification reaction

Feedstock	Transesterification conditions					Ester content	Reference
	Catalyst (wt%)	MeOH/oil molar ratio	Time (min)	temp. (°C)	Oil/THF weight ratio (g/g)	(wt%)	
Soybean oil and coconut oil	NaOH (1.0)	27:1	7	23	approx. 0.97:1	99.4	[55]
Soybean oil	$NaOCH_3$ (1.0-3.0),	27:1	1-480	23-50	approx. 0.98:1	N.D.	[56]
Soybean oil	NaOH (1.0),	6:1,	240,	23,	approx. 0.41:1,	97.5,	[57]
	KOH (1.4),	6:1,	240,	23,	approx. 0.41:1,	98.2,	[57]
	$NaOCH_3$ (1.35)	6:1	240	23	approx. 0.41:1	99.1	[57]

Table 2

The scope of our solubility studies in the context of transesterification and saponification reactions.

No	Initial Substances in the System				Expected Reaction	Solubility according to literature	References
1	MeOH	RPO	-	-	None	Partially Miscible	[20]
2	MeOH	RPO	THF	-	None	Homogeneous	[58]
3	MeOH	FAME	-	-	None	Homogeneous	[59]
4	MeOH	-	THF	-	None	-	this study
2	MeOH	RPO	-	Alkaline	Transesterification /saponification	Suspension	[14], [45], [60]
3	MeOH	RPO	THF	Alkaline	Transesterification /saponification	Homogeneous	[57], [61]–[63]
6	MeOH	FAME	-	Alkaline	Transesterification /saponification	Homogeneous	[36], [48]
7	MeOH	FAME	THF	Alkaline	Transesterification /saponification	-	this study
8	MeOH	RPO	-	Acid	Transesterification	Suspension	[64]–[66]
9	MeOH	RPO	THF	Acid	Transesterification	Homogeneous	[67], [68]
10	MeOH	FAME	-	Acid	Transesterification	-	this study
11	MeOH	FAME	THF	Acid	Transesterification	-	this study

2. Materials and methods

2.1 Chemicals and materials

RPO containing approximately 0.1wt% of FFA and with 0.2wt% moisture content, and a commercial grade FAME (about 97.3wt% purity) were received from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University, Thailand. Commercial grade methanol (MeOH, 99.8wt% purity) was purchased from P-General Co. Ltd. HPLCgrade THF (99.9wt% purity) was bought from RCI Labscan Limited. Commercial grade sulfuric acid (H_2SO_4, 98.0wt% purity) was purchased from AGC Chemicals (Thailand) Co., Ltd. Commercial grade solid sodium methoxide ($NaOCH_3$, 99.5wt% purity) was purchased from Dezhou Longteng Chemical Co. Ltd, People's Republic of China. All the raw materials, RPO and FAME were dewatered by heating at 105 °C for 3 h, and then analyzed for remaining moisture (<0.05wt%).

2.2 Experimental methods

2.2.1 Visualization of methanol solubility in RPO, FAME, THF, and their mixtures

The experiment used a 1-L glass three-neck round bottom flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser. The flask contains one port for product sampling and adding chemicals. The apparatus set up is shown in Fig. 1. For operation, 100 grams of oil mixture containing FAME, RPO, and THF was added in the flask at room temperature. Then methanol was gradually added. During the reaction, approximately 1 mL of the mixture was sampled and immediately analyzed with an LCD digital microscope (Novel NLCD-307) at 100X magnification. The solubility of methanol in RPO was monitored from the start until the transesterification reaction was completed.

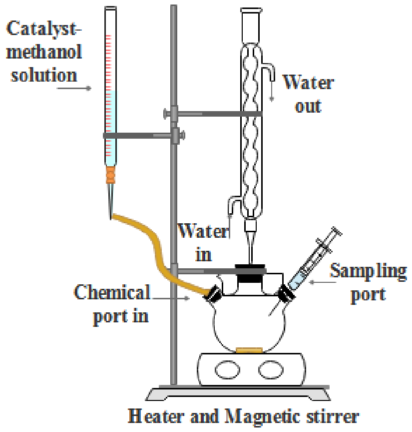


Fig. 1. The apparatus set-up for visual observations (in = inlet chemical port)

2.2.2 Visualization of methanol solubility in transesterification system using alkaline catalyst

The procedures were similar to those in section 2.2.1, but without adding catalyst, and with methanol premixed with $NaOCH_3$. The concentration of $NaOCH_3$ in methanol was 5.34wt%. Phenolphthalein indicator was used to stain the alkaline-methanol solution.

2.2.3 Influence of co-solvent on the solubility of methanol in the transesterification reaction

These procedures were similarly as in section 2.2.1, but with catalyst, except that the oil was premixed with THF at the ratio of 1 to 0.4 (100 g of oil and 40.67 g of THF). In addition, two types of catalyst were applied separately, namely $NaOCH_3$ and H_2SO_4. The concentrations of $NaOCH_3$ and H_2SO_4 in methanol were 5.34wt% and 13.80wt%, respectively. In the case of acid catalyst, methyl orange indicator was used to stain the acid-methanol solution.

2.2.4 Soap formation and self-transesterification of FAME

Soap formation was observed in biodiesel (FAME) production. The experiment was similarly to that in section 2.2.1, except that methanol was now premixed with the catalyst. The methanol was mixed with FAME at the molar ratio of 6:1 (67.61 g of methanol and 100 g of FAME). When co-solvent was used, 123.13 g of THF was premixed with 100 g of FAME to obtain the THF/FAME weight ratio 1.2:1. The concentrations of $NaOCH_3$ and H_2SO_4 in methanol were 1.80wt% and 4.60wt%, respectively.

2.2.5 Formation of soap-methanol droplets in FAME as continuous phase

The experiment was similarly performed in section 2.2.1, except that methanol was premixed with soap or catalyst. The methanol was mixed with FAME at the molar ratio of 2:1 (22.64 g of methanol and 100 g of FAME). In the case of soap-methanol solution, soap containing 1wt% of FAME was premixed with methanol. The concentrations of $NaOCH_3$ and H_2SO_4 in methanol were 5.30wt% and 22.10wt%, respectively. Phenolphthalein indicator was used to stain the alkaline-methanol solution. Methyl orange indicator was used to stain the acid-methanol solution.

2.2.6 Reaction zone study

This work is aimed to clarify the reaction zone during the transesterification reaction of RPO and FAME using alkaline ($NaOCH_3$, 8.20wt% of MeOH) or acid catalyst (H_2SO_4, 11.03wt% of MeOH). The experiment was performed on a concave glass slide used as a micro-reactor. A drop of RPO (about 10 µL) was placed at the center of the concave glass slide at room temperature. The slide was moved for centered view on the NLCD-307 microscope (40X magnification). Then, a small amount of methanol-alkaline-phenolphthalein solution (about 1µL) was placed on the drop of RPO. A photo was then taken every 5 seconds. Reversed experiments were then done by putting a drop of methanol-alkaline-phenolphthalein solution at the center of the concave slide, and then a small amount of RPO was placed on it, and immediately imaged every 5 seconds. These trials were repeated several times. For the acid catalyzed cases, methyl orange indicator was used to stain the acid-methanol solution. For FAME, the same staining was applied.

2.3 Analytical methods

The water content of raw materials and methanol was measured by Karl Fischer method (ISO 12937). The FFA content was tested by titration method (Official Method AOAC 940.28).

3. Results and discussion

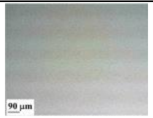
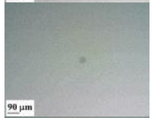
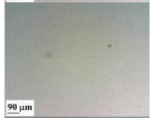
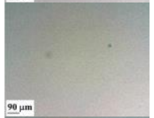
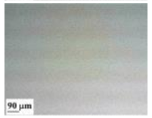
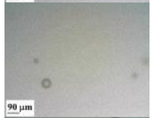
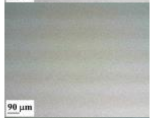
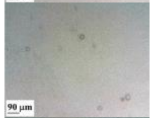
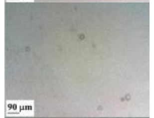
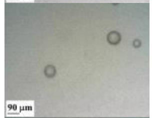
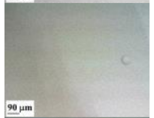
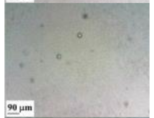
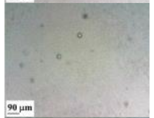
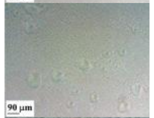
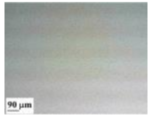
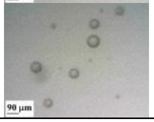
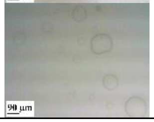
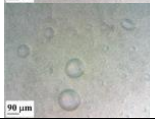
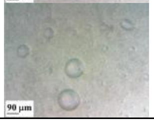
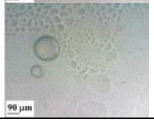
3.1 Solubility of methanol in RPO, FAME, THF and their mixture

The images of methanol solubility in RPO, FAME, THF and their mixture are listed in Table 3. Regarding solubility of methanol in RPO, the microscope images show fine droplets of methanol present at 7.9wt% of the RPO. This concentration is similar to those reported earlier (8 to 10wt%), though the prior experiment was performed at different condition [25]. It should be noted that the more methanol was added in RPO, the greater drop formation was observed. Besides, the mixture of RPO/THF (at a weight ratio of 1:0.4) provides better methanol solubility. Fine droplets appeared as the amount of methanol was 13.6wt% in 100 g of RPO. Interestingly, FAME and methanol mixture shows perfect miscibility. The results are similar to those with added THF. Increasing the FAME proportion could reduce methanol drop formation in the solution, as could be seen in the reduction of methanol drop formation at 7.9wt% of methanol in mixture A (15% FAME), compared with 11.3wt% methanol in mixture B (50% FAME), and at 13.6wt% of methanol in mixture C (85% FAME), respectively. FAME has lower polarity than THF and possibly acted as a co-solvent for RPO. Moreover, the difference of between the non-polar triglyceride and the polar methanol is very significant, so that even the co-solvent THF could only induce partial miscibility. With a large proportion of methanol, the methanol might separate and be suspended in the RPO/THF system. Thus, from this study, FAME could facilitate mixing and interactions of MeOH and RPO.

Table 3

Photographs of methanol solubility in RPO, FAME, THF and their mixture at 32 °C.

(Photographs taken with 100X magnification)

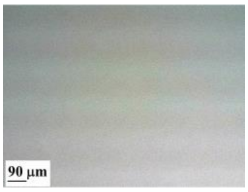
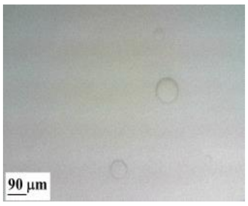
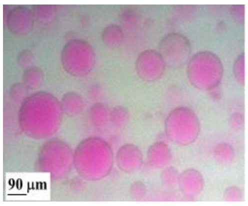
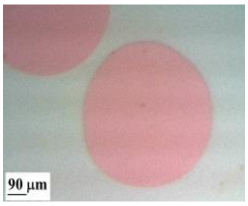
MeOH wt%	**RPO**	**solubility**	**RPO/THF**	**solubility**	**RPO/FAME A (85: 15wt%)**	**solubility**	**RPO/FAME B (50: 50wt%)**	**solubility**	**RPO/FAME C (15: 85wt%)**	**solubility**	**FAME**	**solubility**
0.2		Sol.		Sol.		Sol.		Sol.		Sol.		Sol.
7.9		Susp.		Sol.		Susp.		Sol.		Sol.		Sol.
11.3		Susp.		Sol.		Susp.		Susp.		Sol.		Sol.
13.6		Susp.		Susp.		Susp.		Susp.		Susp.		Sol.
22.6		Susp.		Susp.		Susp.		Susp.		Susp.		Sol.

Note: Sol = Solution; Susp = Suspension
A is the RPO/FAME weight ratio of 85:15, B is the RPO/FAME weight ratio of 50:50, C is the RPO/FAME weight ratio of 15:85.
Experimental conditions: Raw material (100 g, RPO, or FAME, or RPO/FAME); THF (40.67 g); THF/RPO weight ratio (0.4:1); MeOH (22.64 g).

In analysis of the images, we use FAME as the benchmark substance to study methanol solubility in our system. In Table 4, Figure (a) is a miscible solution of MeOH and FAME. When we add some soap (around 1wt% of FAME) into this mixture, small droplets emerge, probably emulsified methanol-soap as in Figure (b). The mixture of FAME and alkaline-methanol solutions is seen in Figure (c). The pink color indicates alkaline-phenolphthalein-methanol drops separated from the miscible methanol-FAME solution, forming a two-phase system. This is caused by soap formation and we confirmed this by soap measurement in this mixture. Therefore, a small amount of soap acts as an emulsifier that suspends methanol droplets in the methanol-FAME continuous solution phase. The mixture of FAME and acid-methanol is shown in Figure (d). Methyl orange indicator stains the dispersed acid-methanol solution. As "like dissolves like" there were strong polar attractive forces between sulfuric acid and methanol. The results indicate that esterification is a liquid-liquid reaction because even though FAME is more polar than triglyceride, it still is insoluble in acid solutions of methanol.

Table4

Formation of soap-methanol droplets or sulfuric-methanol droplets in FAME as continuous phase. (Photographs taken with 100X magnification).

FAME+MeOH	**FAME+MeOH+Soap**	**FAME+MeOH+Alkaline (Saponification)**	**FAME+ MeOH+Sulfuric acid**
			
(a) Sol.	**(b) Susp.**	**(c) Susp.**	**(d) Susp.**

Note: Sol = Solution; Susp = Suspension

3.2 Reaction zone of transesterification using alkaline and acid catalysts

The results from the previous experiment (3.1) indicate that a liquid-liquid phase system is preferable for having a homogeneous transesterification reaction. RPO and FAME are the starting material and final product of transesterification, respectively. They have many differing physical properties, such as polarity, viscosity, density, and surface tension. Similarly, pure methanol, sodium methoxide-methanol solutions, and sulfuric acid-methanol solutions, have mutually differing properties. This diversity could affect the diffusion of reacting substances and generated products, and thereby the overall reaction rate of transesterification. For example, some of reaction products might retard the mass transfer of free reactants or act as a barrier isolating the reaction zone. Thus, this part aimed to clarify the diffusion behaviors of those substances, as well as their roles in kinetics of the reaction between the alcohol phase and triglyceride phase, by imaging with an LCD digital microscope. A substrate droplet on a concave glass slide is assumed to be ellipsoidal. This matches a comparison of calculated drop volume with the diameter on the glass slide. The semi-minor axis is about 1/10 of the semi-major axis. An added spot of about 1/10 of the droplet volume is also assumed to take ellipsoidal shape.

The experiment was divided into 4 cases. Case I is the mixing behavior of FAME, methanol, and an alkaline catalyst. Case II is the mixing behavior of RPO, methanol, and an alkaline catalyst. Case III is the mixing behavior of FAME, methanol, and an acid catalyst. Finally, in case IV the mixing behavior of RPO, methanol, and acid catalyst was examined.

For case I, the results are shown in Table 5. The methanol-alkaline solution is identified by phenolphthalein staining. The reactions and solubility behaviors in this system are expected to be the easiest or simplest to understand. The reaction between alkaline-methanol solution and FAME is saponification (Eq.6) and self-transesterification (Eq.7). So, only soap alters the solubility in the system.

A spot of methanol on a drop of FAME or a spot of FAME on a drop of methanol shows perfect miscibility of methanol and FAME. However, a spot of alkaline-methanol solution on FAME or a spot of FAME on alkaline-methanol solutions behaved differently. A spot of alkaline-methanol forms a round drop in the FAME phase, and the pink color of alkaline-phenolphthalein gradually turned pale due to the diffusion of methanol and alkaline catalyst out of the drop.

The boundary between alkaline-methanol solution and FAME is quite stable and assumed to have a soap film. This is due to the saponification of alkaline and ester. This seems to be a comparatively fast reaction. In contrast, the boundary of a spot of FAME on a drop of alkaline-methanol solution shrunk after three minutes and then maintained the same size for 7 minutes. This indicates that the FAME diffused into the alkaline- methanol solution. A small amount of soap formation is the reason why FAME did not totally dissolve in the methanol solution. Maximal soap formation depends on the number of moles of FAME. A spot of alkaline-methanol solution contains much more alkaline reactant (in moles) than FAME of similar volume.

The large amount of soap formed in the case of alkaline-methanol solution on FAME inhibits the diffusion of methanol and alkaline into the FAME phase, so it is hard to notice any changes in the drop size, which reflects the slow reaction rate. Thus, soap acts as a barrier limiting the rate of reaction.

Regarding the liquid-liquid phase reaction, which phase is diffusing is an interesting issue. Methanol and FAME form a miscible solution. The diffusion between the two liquids should be of counter diffusion type. When there is a boundary layer like soap, then pressure differential is assumed to dominate as determinant of the mass transfer rate. The diffusion from a droplet into an expansive pool is easier than the reversed diffusion from a large volume into the droplet.

The results of case II are shown in Table 6. The possible reactions of alkaline-methanol solution and RPO are transesterification and saponification. Transesterification of triglyceride with methanol yields esters and glycerol. In this context, the relation of glycerol behavior and reactions was examined. Thus, extra glycerol was added in case II.

A spot of methanol on a drop of RPO looks like a round drop and it is hard to notice any changes in drop size due to the low solubility of methanol in triglyceride. However, we can notice slight growth of the spot of RPO on a methanol pool.

This is consistent with prior literature indicating that methanol is soluble in triglyceride better than triglyceride in methanol [20], [59]. The pink droplet of alkaline-methanol solution rapidly turned pale in RPO, more so than that observed on FAME, and shrinkage of the drop was also observed.

This indicates faster diffusion of methanol, $NaOCH_3$, and phenolphthalein into RPO. Diffusion rate is usually proportional to the concentration gradient, so we assume a high rate of methanol consumption in the RPO. Transesterification of triglyceride is a faster reaction than saponification [76].

The final products of transesterification are ester and glycerol. Glycerol is a polar substance and ester is nonpolar, so we assume glycerol prefers to attach to the alkaline methanol droplet, while ester stays in the RPO and counter diffuses with triglyceride. When a drop of RPO is in the center of alkaline-methanol solution, we see a pink layer diffusing into the droplet, and within 120 seconds the whole drop turns pink. The good methanol solubility in triglyceride enables this mass transfer. Triglyceride has the higher molecular weight so in equal volumes its number of moles is less than that of methanol.

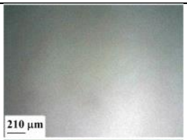
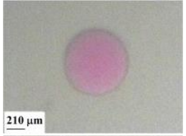
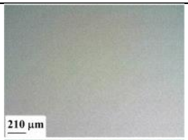
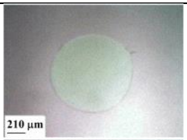
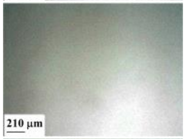
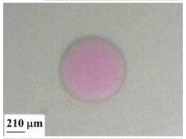
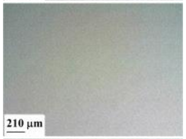
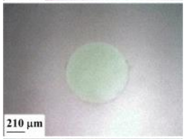
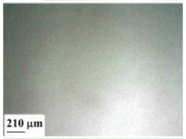
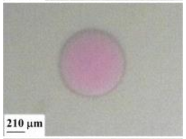
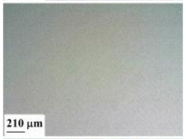
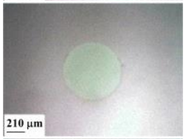
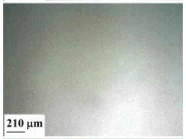
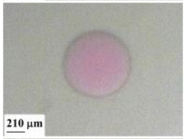
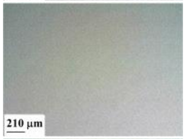
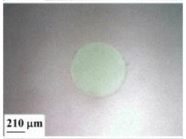
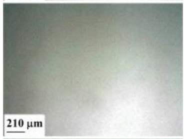
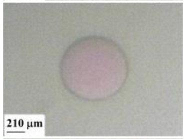
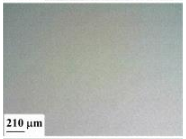
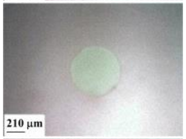
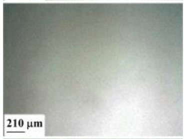
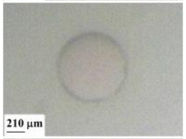
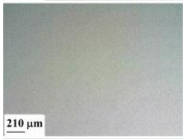
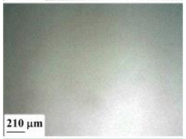
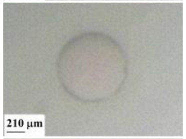
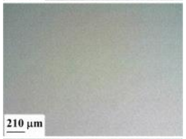
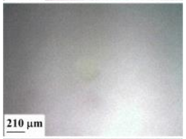
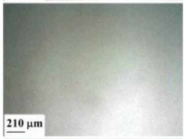
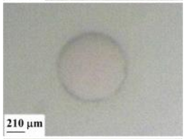
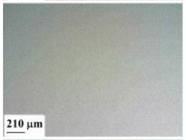
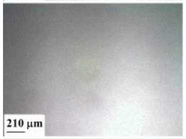
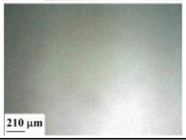
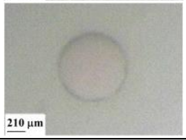
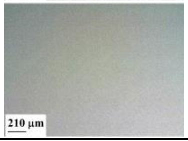
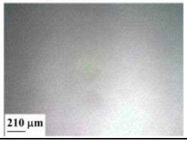
The amounts of glycerol and soap produced from RPO are small in this experiment. Glycerol dissolves in a large amount of methanol due to these having similar polarities. However, we could assume very little formation of soap, since soap is an emulsifier but no emulsion was observed. The produced FAME is more polar than triglyceride and is well soluble into the alkaline methanol, so we cannot see any interfacial layer in this trial.

Therefore, based on the observations, we assume that transesterification reaction starts by the diffusion of alcohol and catalyst into the triglyceride film. The complicated mass transfer related factors, such as polarity, viscosity, and diffusivity, play important roles as determinants of the kinetics of transesterification reaction. For example, a layer of glycerol and soap restrains diffusion of alcohol and catalyst, and the counter-diffusion of ester and triglyceride disturbs the reaction zone, and inhibits the transfer of triglyceride. The change in viscosity of ester and triglyceride mixture favors alcohol and catalyst diffusion, etc.

Table 5

Photographs of the reaction zone for FAME with initial excess alcohol/alkaline or alcohol/alkaline with excess FAME, imaged for up to 600 seconds.

(Photographs taken with 40X magnification).

Time (s)	A spot of methanol on a drop of FAME	A spot of alkaline-methanol solution on a drop of FAME	A spot of FAME on a drop of methanol solution	A spot of FAME on a drop of alkaline-methanol solution
5				
10				
30				
60				
90				
120				
240				
480				
600				

Regarding case III (Table 7), we do not expect any chemical reaction but only observe the solubility behavior of reacting substances. Though self-transesterification is the only possible reaction, with an acid catalyst this is a slow reaction. Putting a spot of acid solution of methanol on a drop of FAME is not possible due slipping of the spot, possibly caused by lower density of methanol and stronger polarity than that of FAME, and the high interfacial tension between methanol and FAME.

However, adding 0.0125wt% of sulfuric acid in methanol can provide a small spot on the FAME droplet, and this spot disappeared within 10 seconds due to the dissolution of methanol in FAME. This observation demonstrates good mutual solubility of methanol and FAME. In contrast, this does not occur with methanol-sulfuric acid solution. FAME is not completely dissolved in methanol-sulfuric acid and forms a stable droplet. This is possibly caused by the higher polarity of the methanol-sulfuric acid solution relative to pure methanol,

Finally, for case IV, the results on the mixing behavior of RPO, methanol, and acid catalyst are reported in Table 8. The expected reaction is acid catalyzed transesterification and the main products are ester and glycerol. Methyl orange indicator was used to stain acid-methanol solution and distinguish it from triglyceride.

As the methanol-sulfuric acid solution was spotted on RPO, within 10 minutes there was neither change of the color nor of the drop size, and the same happened when the phases were reversed. Strong polarity of sulfuric acid is a dominant cause of this behavior. The liquid-liquid acid catalyzed transesterification is easy to see causing poor solubility of FAME.

Table 6

Photographs of the reaction zone for RPO on excess alcohol/alkaline, and for alcohol/alkaline on excess RPO, observed for up to 600 seconds.

(Photographs taken with 40X magnification)

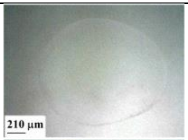
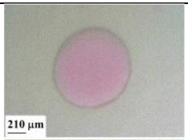
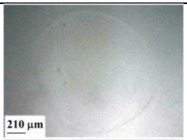
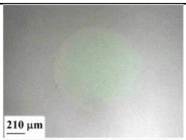
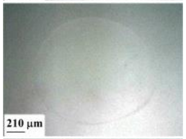
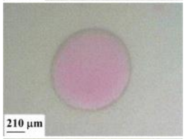
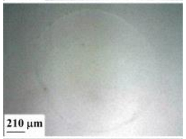
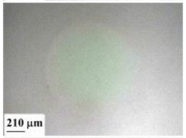
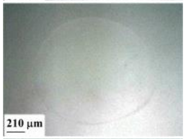
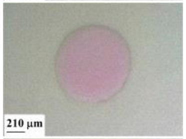
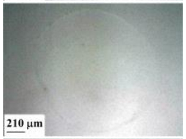
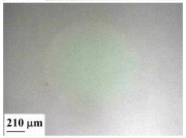
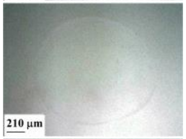
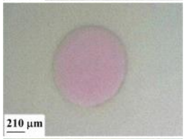
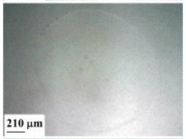
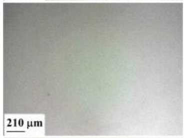
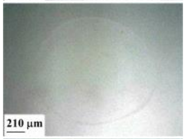
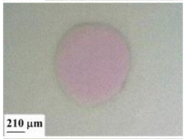
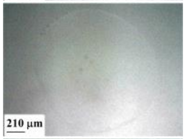
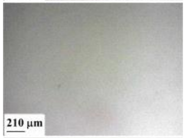
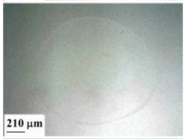
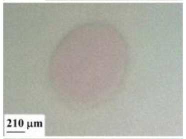
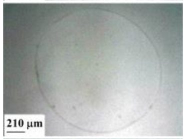
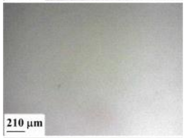
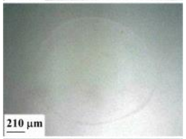
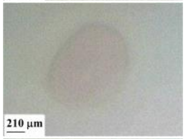
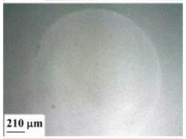
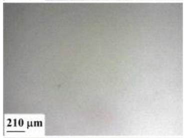
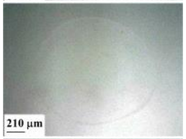
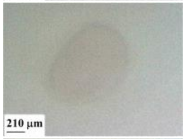
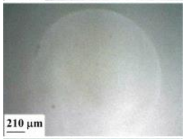
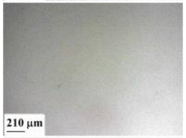
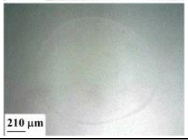
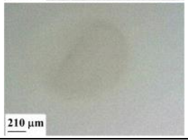
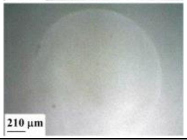
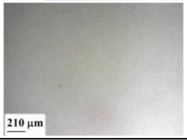
Time (s)	A spot of methanol on a drop of RPO	A spot of alkaline solution of methanol on a drop of RPO	A spot of RPO on a drop of methanol	A spot of RPO on a drop of alkaline solution of methanol
5				
10				
30				
60				
90				
120				
180				
480				
600				

Table 7

Photographs of the reaction zone when FAME is added on top of excess methanol/sulfuric (0.0125, 3wt% of MeOH), and when methanol/sulfuric (0.0125, 3wt% of MeOH) is added on top of FAME, observed for up to 600 seconds.

(Photographs taken with 40X magnification)

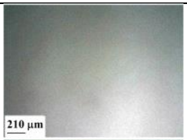
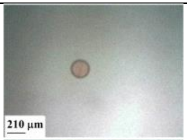
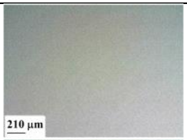
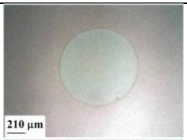
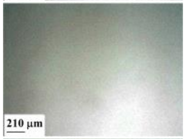
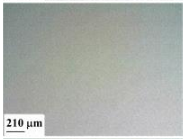
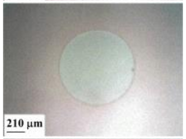
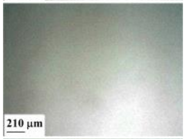
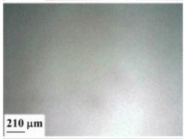
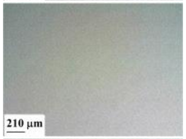
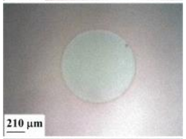
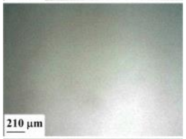
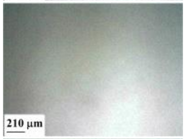
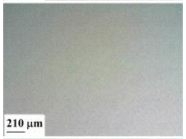
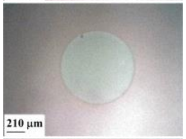
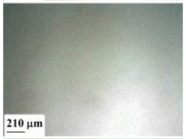
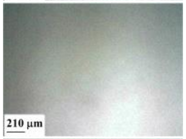
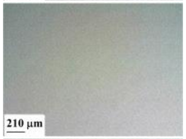
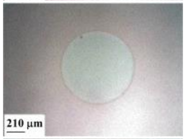
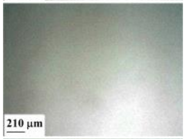
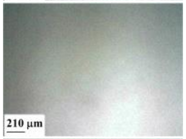
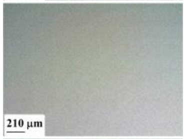
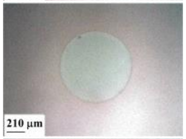
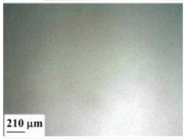
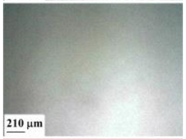
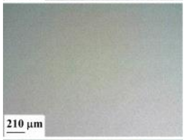
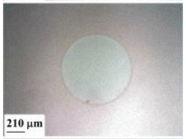
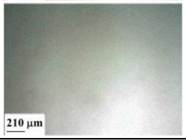
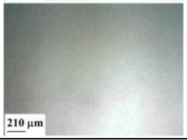
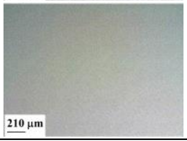
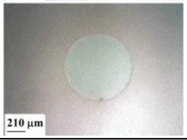
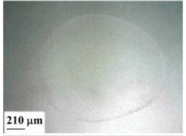
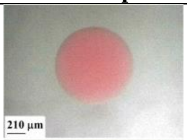
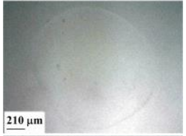
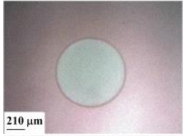
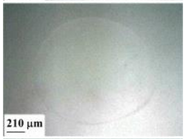
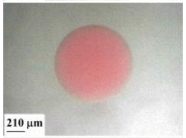
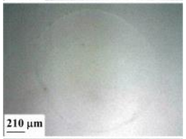
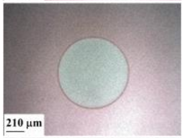
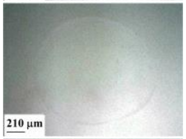
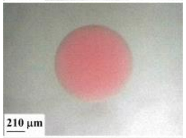
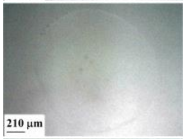
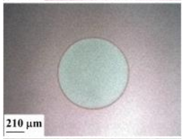
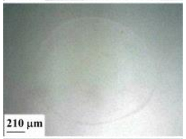
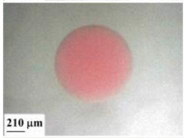
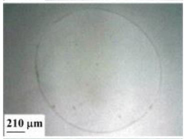
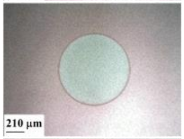
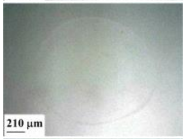
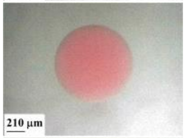
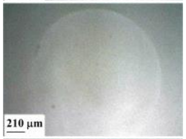
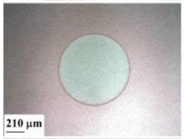
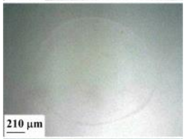
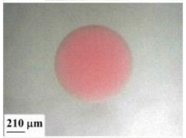
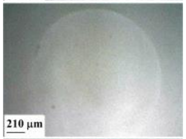
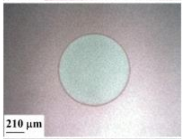
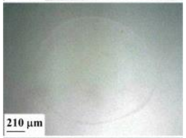
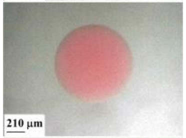
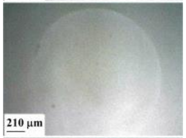
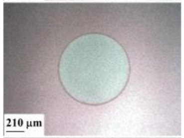
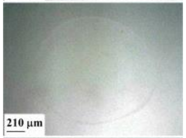
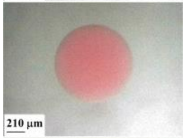
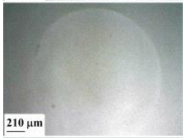
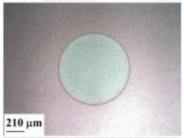
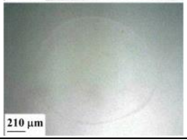
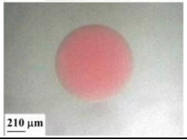
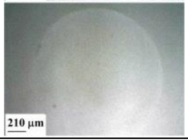
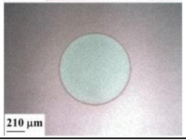
Time (s)	A spot of methanol on a drop of FAME	A spot of sulfuric-methanol solution (0.0125wt%) on a drop of FAME	A spot of FAME on a drop of methanol	A spot of FAME on a drop of sulfuric-methanol solution(3wt%)
5				
10				
30				
60				
120				
180				
360				
600				

Table 8

Photographs of the methanolysis of RPO with excess oil and excess alcohol/acid (sulfuric 11.03wt% of MeOH) for up to 600 seconds.

(Photographs taken with 40X magnification)

Time (s)	A spot of methanol on a drop of RPO	A spot of methanol-acid on a drop of RPO	A spot of RPO on a drop of methanol	A spot of RPO on a drop of acid-methanol
5				
30				
60				
120				
180				
240				
360				
480				
600				

This reaction needs the diffusion of acid into the triglyceride phase for the acid-catalyzed carbonyl reaction. Is a low concentration of sulfuric acid in the methanol-sulfuric acid mix preferable over a high concentration of acid? Does low viscosity of triglyceride-FAME mixture enhance the diffusivity of alcohol and sulfuric acid? These questions should be pursued in future studies.

3.3 Solubility of methanol in transesterification system having an alkaline catalyst

The images of our studies are listed in Table 9. As the methanol contains some alkaline sodium methoxide, the images show solubility. The methanol droplet suspended on the RPO gave only 0.2wt% of methanol solution in the system. In contrast, a clear solution was obtained without an alkaline catalyst. The 0.2wt% of methanol equals 1:16 molar ratio of methanol to triglyceride. The stability of methanol suspension was possibly due to the fast transesterification with an alkaline catalyst. This slightly alters the solubility of generated glycerol in the methanol-RPO environment.

The glycerol possibly merged with methanol, due to their similar polarities, and created very fine droplets. In addition, the generated glycerol tended to attach to the nearby methanol droplet and coagulate together with it. Therefore, suspended droplets of methanol-glycerol were observed at all tested RPO/FAME mixing ratios. This clearly demonstrates a liquid-liquid reaction system. The reaction between the alkaline methanol solutions and FAME is saponification according to Eq.(6).

The generated soap acts as an emulsifier and forms a layer surrounding the methanol droplet, and isolates it from the continuous FAME phase. At a low content of RPO in the RPO/FAME mixture, we notice that the number of fine droplets was reduced while the large ones tended to increase. This is possibly caused by the coagulation of fine droplets to form larger drops.

When the added methanol solution is 7.9wt%, the molar ratio of methanol to oil is around 2.1:1 for pure RPO, 2.48:1 for A, 4.2:1 for B, and 14:1 for C (as shown in Table 9), respectively. The labels A, B, and C are here used to indicate these compositions of the mixture. The molar ratio of methanol to oil at 14:1 for the C mixture is quite a lot higher than that conventionally used in the industry (6:1).

The transesterification reaction is expected to reach 96.5wt% ester content required by standard biodiesel specifications. In the C mixture, the ester phase is less viscous and promotes round drops of methanol-glycerol phase. The high 14:1 methanol to oil molar ratio should give a high conversion to ester.

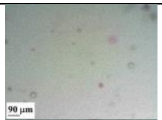
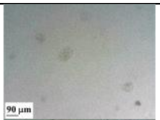
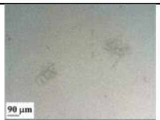
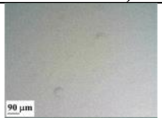
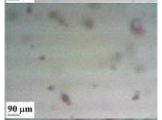
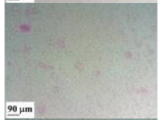
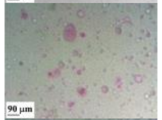
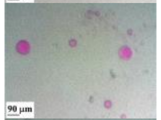
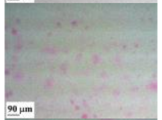
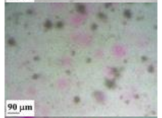
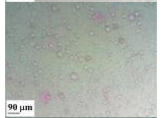
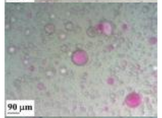
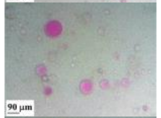
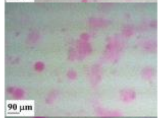
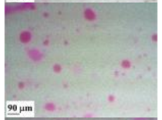
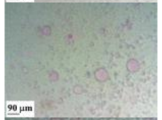
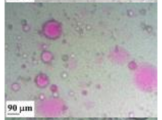
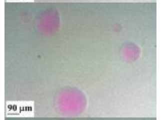
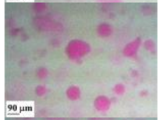
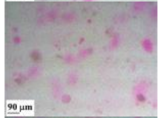
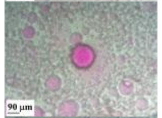
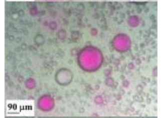
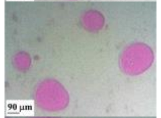
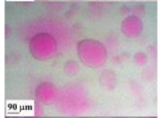
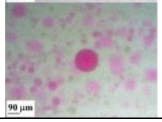
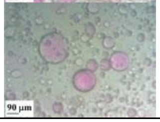
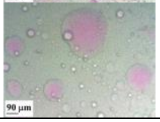
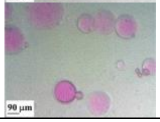
When 11.3wt% of methanol and catalyst solution was added to pure RPO, A mixture, or B mixture, the molar ratio of methanol to oil was 3:1, 3.54:1 or 6:1, respectively. The B mixture has more excess methanol and shows larger round drops of methanol-glycerol phase than in a blend of A mixture and pure RPO. Adding methanol at 17.8wt% (22.6wt%) gives 6:1 molar ratio of methanol to oil with A mixture (pure RPO).

We can clearly see the appearance of large round droplets of methanol-glycerol phase. Zhou et al. (2006) demonstrated that when FAME content is increased to 70 %, the oil - methanol - FAME mixture becomes homogeneous; so the reaction rate depends strongly on the solubility of oil in the methanol phase [59]. Our work shows that even at the low 15: 85 weight ratio oil: FAME, partial solubility of methanol is still observed.

Table 9

The solubility of methanol in the transesterification reaction with alkaline catalyst

(Photographs taken with 100X magnification)

MeOH +catalyst (wt%)	RPO	Expected Reaction and solubility	RPO/FAME A (85: 15wt%)	Expected Reaction and solubility	RPO/FAME B (50: 50wt%)	Expected Reaction and solubility	RPO/FAME C (15: 85wt%)	Expected Reaction and solubility	FAME+MeOH +Alkaline (Soap Formation)	Expected Reaction and solubility
0.2		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.
7.9		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.
11.3		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.
13.6		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.
17.9		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.
22.6		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /SAP/Susp.

Note: TRANS = Transesterification; SAP = Saponification; Susp = Suspension.
A is the RPO/FAME weight ratio of 85: 15, B is the RPO/FAME weight ratio of 50: 50, C is the RPO/FAME weight ratio of 15: 85.
Experimental conditions: Raw material (100 g, RPO, or FAME, or RPO/FAME); MeOH (22.64 g); $NaOCH_3$ in methanol (5.3wt%); H_2SO_4 in methanol (13.8wt%)

3.4 Solubility of methanol in transesterification reaction added with THF, alkaline, and acid catalysts

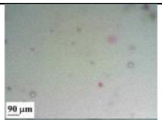
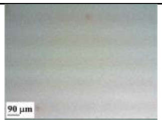
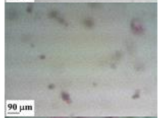
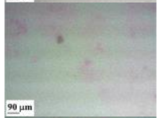
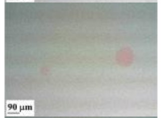
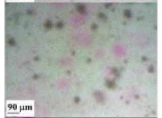
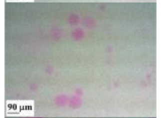
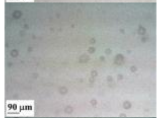
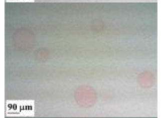
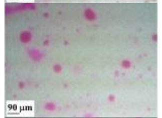
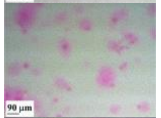
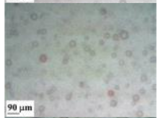
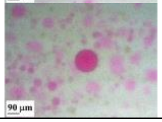
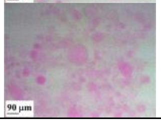
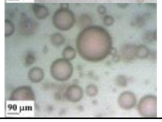
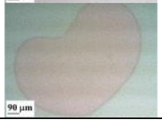
The effects of adding co-solvent THF on solubility of methanol in transesterification reaction was studied with alkaline and acid catalysts individually. The results are listed in Table 10. It can be seen that even a small amount of excess methanol (0.2wt%) the mixture of RPO/THF shows a suspended phase in the system. On using alkaline catalyst, THF seems to enhance the solubility of methanol in the RPO/THF phase. The fast transesterification converts the triglyceride to an ester and drastically reduces the viscosity of solution as well as increases solubility of methanol in the ester phase. In acid-catalyzed transesterification, the THF plays a different role than with alkaline catalyst. Sulfuric acid is strongly polar and is well compatible with methanol.

The mixture of methanol and sulfuric acid is also polar. Then, the methanol and sulfuric acid mix forms dispersed droplets in the continuous triglyceride phase. The relative polarities of THF and methanol are reported as 0.207 and 0.762, respectively [69]. Thus, THF prefers to merge with the methanol. Additionally, the slow transesterification with acid catalyst provides a small amount of ester, indicated by a slight change in triglyceride phase viscosity. Besides, the small amount of generated glycerol also tends to merge with methanol no outer layer was observed on the methanol droplets to isolate them. Consequently, the THF can easily diffuse through the methanol drop surface and cause the droplet to grow. Thus, adding THF may have both advantages and disadvantages regarding alcohol solubility in the acid-catalyzed transesterification system. The effects of co-solvent on acid-catalyzed transesterification are of interest for future studies.

Table 10

The solubility of methanol in transesterification with THF and alkaline or acid catalyst.

(Photographs taken with 100X magnification)

MeOH +catalyst wt%	RPO+MeOH+ Alkaline	Expected reaction/ solubility	RPO/THF + MeOH +Alkaline	Expected reaction/ solubility	RPO+MeOH +Acid	Expected reaction/ solubility	RPO/THF+ MeOH +Acid	Expected reaction/ solubility
0.2		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /Susp.		TRANS /Susp.
0.5		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /Susp.		TRANS /Susp.
5.8		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /Susp.		TRANS /Susp.
17.9		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /Susp.		TRANS /Susp.
22.6		TRANS /SAP/Susp.		TRANS /SAP/Susp.		TRANS /Susp.		TRANS /Susp.

Note: TRANS = Transesterification; SAP = Saponification; Susp = Suspension.
Experimental conditions: Raw material (100 g, RPO); THF (40.67 g); THF/RPO weight ratio (0.4:1); MeOH (22.64 g); $NaOCH_3$ in methanol (5.3wt%); H_2SO_4 in methanol (13.8wt%).

3.5 Soap formation and transesterification of FAME

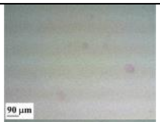
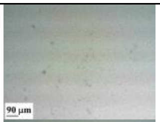
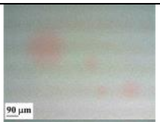
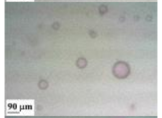
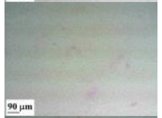
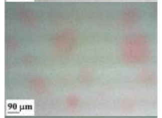
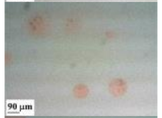
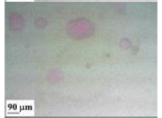
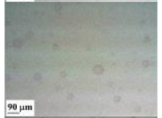
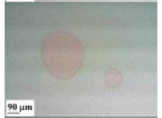
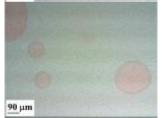
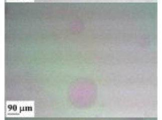
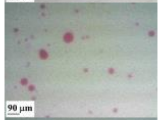
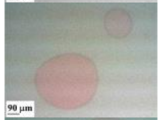
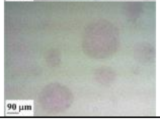
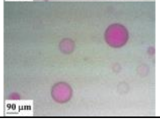
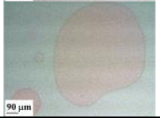
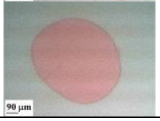
For complete transesterification, FAME and methanol were reacted with either alkaline or acid catalyst, and the results are reported in Table 11. The reaction of FAME with alkaline catalyst in methanol solution is saponification. The reaction between FAME and methanol with acid catalyst is normally transesterification, but in this case R’ and R” are the same methyl group (CH_3^+). So, we cannot notice any change in the products, because this is a self-transesterification as mentioned in Eq. (7). We did observe the reaction between FAME and ethanol, which produced ethyl ester. If the system contains some water, the reaction instead is reverse esterification.

From Table 3, FAME and methanol are perfectly miscible, but the addition of the third compound like alkaline turns the system to a dispersion. This is possibly caused by soap formation. The generated soap generally has amphiphilic structures with hydrophilic and hydrophobic parts. In FAME and methanol mixture, the amount of FAME is much higher than that of methanol, thus the bulk solution is dominantly nonpolar. As soap concentration increases in the solution, it tends to aggregate and cluster forming reversed micelles where the hydrophilic parts orient towards the center while the hydrophobic parts orient towards the nonpolar FAME and methanol mix. This creates a polar region inside the reversed micelle. Thus, the methanol solubilized in FAME tends to migrate and accumulated to centers of the reversed micelles. This might be the reason why we observed small drops of methanol randomly dispersed in the mixture, and incomplete esterification due to inactivity of the methanol encapsulated in the micelles.

Table 11

Transesterification reaction and soap formation.

(Photographs taken with 100X magnification)

MeOH +catalyst	**Soap formation**				**Transesterification reaction**			
wt%	**FAME+MeOH+ Alkaline**	**Expected reaction/ solubility**	**FAME/THF+ MeOH +Alkaline**	**Expected reaction/ solubility**	**FAME+MeOH+ Acid**	**Expected reaction/ solubility**	**FAME/THF+ MeOH +Acid**	**Expected reaction/ solubility**
2.7		SAP /Susp.		SAP /Susp.		TRANS/Susp.		TRANS/Susp.
10.7		SAP /Susp.		SAP /Susp.		TRANS/Susp.		TRANS/Susp.
23.3		SAP /Susp.		SAP /Susp.		TRANS/Susp.		TRANS/Susp.
40.0		SAP /Susp.		SAP /Susp.		TRANS/Susp.		TRANS/Susp.
67.6		SAP /Susp.		SAP /Susp.		TRANS/Susp.		TRANS/Susp.

Note: TRANS = Transesterification; SAP = Saponification; Susp = Suspension.
Experimental conditions: Raw material (100 g, FAME); THF (123.13 g); THF/FAME weight ratio (1.2:1); MeOH (67.61 g); $NaOCH_3$ in methanol (1.8wt%); H_2SO_4 in methanol (4.6wt%).

The experiment performed using FAME, methanol, and sulfuric acid also provided a suspension. This was caused by the mix of methanol and sulfuric acid separating from the FAME phase. The greater number of methanol-sulfuric acid droplets made the suspension cloudy as the amount of methanol was increased. The polarity of sulfuric acid enables the formation of methanol-sulfuric acid droplets and the phase separation of FAME and methanol. The results confirm that esterification of a fatty acid with an acid catalyst should absolutely be a liquid-liquid reaction.

4. Conclusions

The polarity of the components in transesterification reaction plays a crucial role in the reaction, affecting the miscibility of compounds in the reaction mix, and influencing efficiency and extent of conversion. A highly polar compound like glycerol could enable clear separation of methanol from the less polar substances, such as ester and triglyceride. A sulfuric acid mix with methanol is highly polar, giving a dispersion of methanol droplets in continuous triglyceride phase. The formation of soap could emulsify and suspend methanol drops in otherwise compatible methanol-FAME solution. The observed behaviors of multi-compound solubility in a transesterification system indicate that the reaction is a liquid-liquid reaction. The diffusivity of alcohol reactant together with the catalyst to another reactant phase plays a key role as rate limiting step. The smaller alcohol molecules might enhance diffusion through obstructing triglyceride or long chained fatty acid ester. The co-solvent THF or FAME improved solubility of polar methanol in the non-polar triglyceride, but the strongly polar products, such as glycerol and soap emulsifier, could interrupt this effect. The polar similarity of THF and methanol provides them mutual miscibility, while methanol is less compatible with ester or triglyceride.

The co-solvent THF or FAME cannot enhance solubility of the multicomponent systems in biodiesel production to provide a homogeneous mix, as previously mentioned [13, 21–23]. Imaging at room temperature helped elucidate the behavior in the multicomponent transesterification system. The conceptual mechanisms in esterification and transesterification should be properly revised.

The kinetics of transesterification should depend on the rate of mass transfer, especially of the catalyst. The catalytic compound interacts at carbonyl groups of the ester in the first step. However, if it is accompanied by alcohol, then the alcohol diffusivity plays a key role in the reaction rate. Diffusivity in a multicomponent system depends on several factors, including viscosity, polarity, molecular size, concentration gradients, etc. We need to understand these factors clearly before proposing the possible reaction mechanisms, and eventually models of transesterification kinetics.

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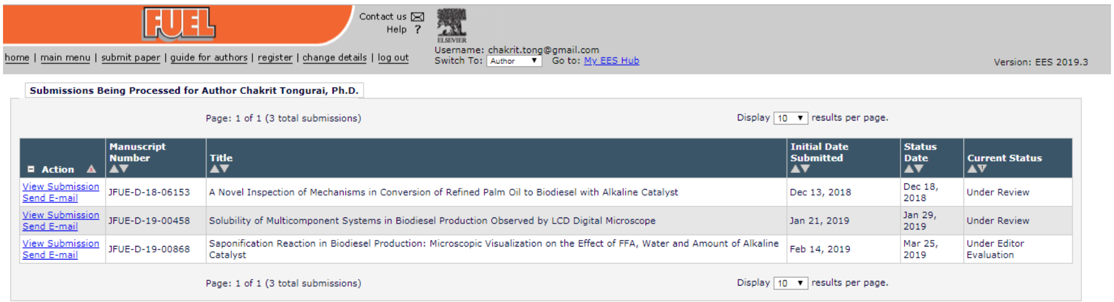
APPENDIX C

SECOND MANUSCRIPT

I. Chanakaewsomboon, C. Tongurai, S. Photaworn, S. Kungsanant, R. Nikhom. *Saponification Reaction in Biodiesel Production: Microscopic Visualization on the Effect of FFA, Water and Amount of Alkaline Catalyst.* This article is under peer reviewing for Publication on Fuel (ISI, Q1, IF = 4.908) Initial Date Submitted: 14/02/2019, Under Editor Evaluation Status Date: 25/03/2019.



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View Submission Send E-mail	JFUE-D-18-06153	A Novel Inspection of Mechanisms in Conversion of Refined Palm Oil to Biodiesel with Alkaline Catalyst	Dec 13, 2018	Dec 18, 2018	Under Review
View Submission Send E-mail	JFUE-D-19-00458	Solubility of Multicomponent Systems in Biodiesel Production Observed by LCD Digital Microscope	Jan 21, 2019	Jan 29, 2019	Under Review
View Submission Send E-mail	JFUE-D-19-00868	Saponification Reaction in Biodiesel Production: Microscopic Visualization on the Effect of FFA, Water and Amount of Alkaline Catalyst	Feb 14, 2019	Mar 25, 2019	Under Editor Evaluation

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Saponification Reaction in Biodiesel Production: Microscopic Visualization on the Effect of FFA, Water and Amount of Alkaline Catalyst

I. Chanakaewsomboon [1], C. Tongurai *,[1], S. Photaworn [1], S. Kungsanant [1], R. Nikhom [2]

[1] Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Songkhla 90112, Thailand

[2] Faculty of Engineering, Thaksin University, Phatthalung Campus, Phatthalung, 93110 Thailand

*Corresponding author: chakrit.tong@gmail.com

Abstract

In transesterification via alkaline catalysis, soap formation is a major factor causing catalyst depletion and yield loss by saponification reaction and via losses on purification. The rate of saponification reaction has complicated dependence on many factors, such as free fatty acid (FFA) content, water content, alkaline category, reaction temperature, amount of methanol, amount of glycerol, and many others factors. This work aimed to find out the effects of FFA, water and amount of alkaline catalyst on biodiesel production from refined palm oil. Microscopic visualization of transesterification on a concave glass slide at room temperature showed saponification interactions. Soap formation establishes a barrier between an alcohol droplet and surrounding triglyceride, and restrains the diffusion rate of alcohol and catalyst, thus lessens the transesterification rate. This study also preliminarily investigated the various significant factors influencing transesterification of refined palm oil, including FFA content, water content and catalyst amount. The soap content in crude biodiesel is a key parameter affecting washing losses, and our suggestion is it should be below 3,000 ppm. A low-quality feedstock with high FFA and water contents gives significant yield losses.

Keywords: LCD digital microscope, Reaction zone study, Liquid-liquid reaction, Transesterification, Saponification.

1. Introduction

Biodiesel is defined as a mixture of alkyl esters obtained from vegetable oils, animal fats, or waste oils, by using short-chained alcohol (typically methanol or ethanol) in the presence of a suitable catalyst [4]–[7]. Transesterification reaction (Eq. 1) is the major step in current industrial biodiesel plants and there are two types of catalysts: heterogeneous and homogeneous. The former, such as solid acid catalyst or solid base catalyst, is more effective in reducing soap formation, but gives slower reaction rate, needs more alcohol, and requires rather sophisticated equipment [8]–[11]. The latter in contrast, such as alkaline hydroxide alkaline methoxide used in commercial biodiesel plants, consumes less time and alcohol in a relatively simple process; but involves more saponification and requires more water in the washing process [12]–[15].

$$\mathrm{TG} + 3\,\mathrm{Alcohol} \xleftrightarrow{\mathrm{Catalyst}} 3\,\mathrm{Ester} + \mathrm{Glycerol} \qquad \text{Eq. (1)}$$

In biodiesel production, the key parameters affecting the yield of biodiesel are FFA and moisture contents. According to industrial biodiesel companies such as Lurgi GmbH [22] and Crown Iron Works [23], they had specified feedstock properties as maximum acidity 0.1% or 0.5% and maximum moisture and volatiles as 0.1% or 0.05%. These impurities are significant to soap formation in the transesterification process. Among the other reaction parameters, the molar ratio of alcohol to oil, catalyst type and its concentration, reaction temperature, and reaction time play key roles in biodiesel yield, which is related to soap formation as presented in Table 1.

Basically, homogeneous catalysts such as alkaline hydroxides (NaOH and KOH) and alkaline methoxides ($NaOCH_3$ and $KOCH_3$) all induce soap formation. Soap could be generated not only from FFA and alkaline (neutralization reaction in Eq. 2), but in the presence of triglyceride (TG) and biodiesel (FAME) (by saponification in Eqs. 3 and 4).

$$\text{FFA} + \text{NaOH} \longrightarrow \text{Soap} + \text{Water} \qquad \text{Eq. (2)}$$

$$\text{TG} + 3\text{NaOH} \longrightarrow 3\text{Soap} + \text{Glycerol} \qquad \text{Eq. (3)}$$

$$\text{FAME} + \text{NaOH} \longrightarrow \text{Soap} + \text{Methanol} \qquad \text{Eq. (4)}$$

In saponification, FAME and TG (TG is an ester) are reacted with basic species (HO^- or CH_3O^-) to form the potassium or sodium salt of a long-chained carboxylic acid (soap). This is highly undesirable due to catalyst consumption, phase separation problems, and emulsion formation, which reduce biodiesel yield [13], [14], [85].

Table 1

The effect of soap formation in transesterification reaction on the remaining catalyst, soap, yield and ester content, as reported by various researchers.

Feedstock	Transesterification condition: initial catalyst content, alcohol/oil, time (min), temp (°C)	Soap formation (wt%)	Yield (wt%)	Ester content (wt%)	Reference
Refined sunflower oil with acid value (AV) < 0.1 wt%	KOH, NaOH, $NaOCH_3$, and $KOCH_3$, catalyst content (0.172 to 0.257 mol/L), MeOH (25 v/v%) and ETOH (25 to 40 v/v%), 60 to 180 min, and 20 to 70 °C.	100% (KOH and NaOH), 25% ($NaOCH_3$) and 28% ($KOCH_3$)	N.D.	N.D.	[13]
Crude soybean oil with different acid value (AV) of 0.01, 0.41 and 1.13 wt%	$NaOCH_3$, $KOCH_3$, NaOH, KOH, catalyst content (7.8 to 13.2 mol%), MeOH (25 vol%), 90 min, and 60°C.	18, 70, and 75% for acid value of 0.01, 0.41 and 1.13 wt% respectively.	N.D.	>96.5 (for $NaOCH_3$, $KOCH_3$, and NaOH) and 95 (for KOH)	[14]
Canola oil	$NaOCH_3$, $KOCH_3$, NaOH, KOH, catalyst content (0.1 to 0.3 mol/mol), MeOH/oil molar ratio (3:1 to 6:1), 90 min, 10 min and 40 to 60°C.	Soap 7.56 mmol/mol (0.75 wt%)	N.D.	95.8 (for $KOCH_3$ 0.2 mol/mol)	[45]
Palm oil	$KOCH_3$, catalyst content (1.2 wt%), MeOH/oil molar ratio (5.5:1), 90 min, 30 min, and 60°C.	Soap approx. 12 g/Kg sample	98.0	93.1	[86]

The presence of large amounts of moisture, especially in low-quality raw materials such as waste cooking oils and animal fats, give a high hydrolysis rate of TG (Eq. 5) [35] and FAME (Eq. 6) [40], [87], to form FFA and alcohol. Then, more soap will be formed [77], [88].

$$\text{TG} + 3\text{Water} \longleftrightarrow 3\text{FFA} + \text{Glycerol} \qquad \text{Eq. (5)}$$

$$\text{Ester} + \text{Water} \longleftrightarrow \text{FFA} + \text{Alcohol} \qquad \text{Eq. (6)}$$

The reaction kinetics are important to biodiesel production. The immiscibility of alcohol and triglyceride leads to a mass-transfer resistance in transesterification [89]. Noureddini and Zhu (1997) proposed a reaction mechanism consisting of an initial mass transfer controlled region followed by a kinetically controlled region [18]. Mass transfer limitation between the polar methanol-glycerol phase and the non-polar oil phase causes slow reaction rates at the initial and final stages of base-catalyzed transesterification [19]. Some studies of kinetics models [20], [21] are based on the liquid-liquid reaction and the stability of phase continuity in the liquid-liquid reaction, where a large excess phase tends to be continuous and the minority phase is disperse. When the phase volumes are fairly similar, either phase may be continuous.

In a liquid-liquid reaction, mass transfer with a chemical reaction is well described by Levenspiel (1999) [49] and the standard theory used to explain mass transfer is the two-film theory by Whitman (1923) [50]. In a small droplet of the liquid-liquid system, internal circulation is minimal if the mass transfer coefficient of the internal film is lowest. Thus, mass transfer can be enhanced by droplet coalescence and redispersion.

Slinn, M. (2008) [21] proposed a mass transfer limited model adapted from Levenspiel (1999) shown in Fig. 1. A model based on the immiscibility of oil and methanol, with methanol as droplets in a viscous oil phase and, through reaction, are changed to rigid glycerol droplets.

The reaction only occurs at the interface of the methanol and triglyceride film. Tubino, M. et al. (2014) [51] proposes that methanolysis with alkaline catalysts should be assumed to be heterogeneous.

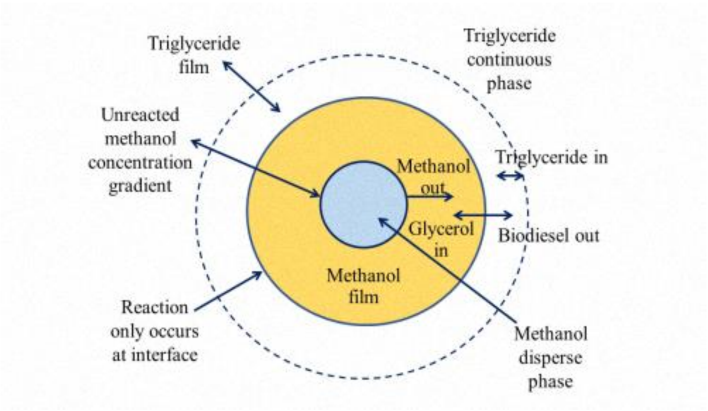


Fig. 1. Mass transfer limited model [21].

Soap acts as a barrier compound at the outer surface of the disperse alcohol-glycerol phase due to being a natural emulsifier. The intermediate products on transesterification of triglycerides, such as diglyceride and monoglyceride, as emulsifiers also play the same role as soap, especially if lacking the alcohol catalyst, gradually affecting all three reaction steps. Thus, water and free fatty acid are critical impurities inducing soap formation. So, the kinetics of transesterification are altered by barrier substances forming an outer shell around alcohol droplets. If glycerol, a product of transesterification reaction, goes back to the alcohol droplets according to Slinn’s model, the barrier should be thicker. A new paradigm with merging of glycerol, alcohol, and catalyst to form a new glycerol droplet is also possible.

This research aimed to clarify the effects of soap formation on transesterification reaction. Visual observations of methanolysis on a concave glass slide micro-reactor at room temperature were performed. The microscope pictures of the reaction zone may reveal mechanisms and events. Soap formation from fatty acid methyl ester with alkaline in methanol solution is a benchmark for comparisons.

2. Materials and methods

2.1 Chemicals and materials

Refined palm oil (RPO), having approx. 0.1 to 2wt% FFA and 0.2wt% moisture content, commercial grade fatty acid methyl ester (FAME, approx. 97.3wt% purity), and palm fatty acid distillate (PFAD) were received from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University, Thailand. Commercial grade methanol (MeOH, 99.8wt% purity) was acquired from P-General Co. Ltd. Commercial grade solid sodium methoxide ($NaOCH_3$, 99.5wt% purity) was purchased from Dezhou Longteng Chemical Co. Ltd, People’s Republic of China.

2.2 Effect of FFA on the reaction zone of the saponification reaction

This work aimed to clarify the effects of FFA in the raw materials (RPO or FAME) on the reaction zone of saponification reaction. The experiments were performed on a concave glass slide serving as a micro-reactor. A small pool of raw material (10 µL approximately) at room temperature was placed on the concave glass and was arranged to central location in the view of the NLCD 307 microscope. Phenolphthalein indicator was added early to the sodium methoxide-methanol solution in order to identify the alkaline catalyst. A very fine drop of methanol-alkoxide-phenolphthalein solution (1 µL approximately) was spotted on the pool of raw material. A photo was taken every 5 seconds. A reversed trial was done by putting a fine drop of the raw material (1 µL approximately) on the center of the concave slide and adding a small amount of methanol-alkoxide-phenolphthalein solution (10 µL approximately) over it, with photo taken every 5 seconds. These trials were repeated several times.

2.2.1 Effects of FFA content in FAME on the reaction zone of the saponification reaction

In saponification of FAME with sodium methoxide-methanol solution, there is only soap and alcohol formation but no glycerol formation. Thus, effects of glycerol on the reaction zone will be negligible. This section aims to examine the reaction zone of real soap formation during saponification of FAME. High quality FAME with 100% purity and 0.03wt% moisture content was used. The FFA content in FAME was varied from 0.1 to 2 wt% by adding PFAD in FAME. The sodium methoxide concentration was 4.42wt% in methanol (1wt% of oil mass, if using 1:6 molar ratio of methanol to oil). The same procedures were done as described in the previous section.

2.2.2 Effects of FFA content in RPO on the reaction zone of the saponification reaction

In saponification of RPO with the alkaline catalyst-methanol solution, glycerol and soap may be produced. Thus, the reaction zone of this case may different from the previous one. The various FFA contents in RPO from 0.1 to 2wt% were prepared by adding PFAD in RPO. The sodium methoxide concentration was 4.42wt% in methanol (1wt% of oil mass if using 1:6 molar ratio of methanol to oil). The experiments were similar to those explained earlier.

2.3 Effects of water content in RPO on the reaction zone of the saponification reaction

The effects of water on the reaction zone of saponification of RPO were investigated. The various water contents in RPO from 0.1 to 1wt% oil were prepared by adding water to RPO. In this section, the FFA content of RPO was kept at 0.1wt% of oil since this can avoid the neutralization of FFA. The sodium methoxide concentration was 4.42wt% in methanol (1wt% of oil mass if using 1:6 molar ratio of methanol to oil). The procedures were as before.

2.4 Effects of alkaline concentration on the reaction zone of RPO saponification reaction

These experiments assess the effects of alkaline concentration on the reaction zone of RPO saponification reaction. The sodium methoxide concentration was varied between 2.21 and 8.83wt% in methanol (0.5-2.0wt% in oil if using 1:6 molar ratio of methanol to oil). RPO with FFA and water contents (0.1 and 0.1wt%, respectively) was used to examine the low soap formation phenomena. For high soap formation RPO with FFA and water contents of 1 and 0.5wt%, respectively, was used. The procedures were as before.

2.5 Variables (FFA, water, and catalyst concentration) affecting the $NaOCH_3$-catalyzed transesterification of refined palm oil with methanol

The transesterification of RPO was carried out in a 1-L glass three-neck flat bottom flask equipped with a magnetic stirrer, a thermometer, a reflux condenser and one spout for sampling and/or chemical addition. All experiments were performed at 50 ˚C, the initial methanol-to-oil molar ratio was 6:1, and stirring was at 500 rpm for 30 min. The experiment began as follows. Two hundred grams of refined palm oil was poured into the reactor and heated up to the desired reaction temperature. A sodium methoxide-methanol solution was earlier prepared from solid $NaOCH_3$ by dissolving in methanol, and this was added into the reactor. The mixture was then stirred for the next 30 min. The reaction mixture was transferred to a separation funnel and let stand for 3 hours. The glycerol rich phase (lower phase) was separated from the ester rich phase. The remaining catalyst and soap contents were determined in each phase by titration (modified AOCS Official Method Cc 17-79). The ester rich phase was washed to remove impurities including methanol, remaining catalyst, soap, and glycerol. The washed ester was heated to remove the residual water. Finally, the ester content was analyzed by using Thailand Petty Patent 5060. Photographs (100X magnification) of the interface between biodiesel and water phases in the washing step were taken by an LCD digital microscope (Novel NLCD-307).

2.5.1 Effects of FFA content

A set of experiments was carried out to determine the effects of FFA content. The FFA content was varied between 0.12 and 1wt% referred to oil mass. The $NaOCH_3$ concentration used was 0.98wt% referred to oil mass. The water content was fixed at 0.18wt% referred to oil mass.

2.5.2 Effects of water content

A set of experiments was performed to demonstrate the effects of the water content. The water content was varied between 0.05 and 0.8wt% referred to oil mass, while the FFA content was fixed at 0.18wt% referred to oil mass. The $NaOCH_3$ concentration used was 0.98wt% referred to oil mass.

2.5.3 Effects of catalyst concentration

A set of experiments was done to evaluate the effects of catalyst concentration. The $NaOCH_3$ concentration was varied between 0.49 and 1.11wt% referred to oil mass, while the FFA and water contents were fixed at 0.17 and 0.18wt% referred to oil mass, respectively.

2.6 Analytical methods

The water contents in refined palm oil and methanol were measured by Karl Fischer method (ISO 12937). FFA content was tested by titration (Method AOAC 940.28). Catalyst and soap contents were measured by titration (modified AOCS Official Method Cc 17-79) [60]. The photographs were taken using an LCD digital microscope (Novel NLCD-307).

3. Results and discussion

3.1 Effects of FFA on saponification reaction

3.1.1 Effect of FFA on saponification of FAME

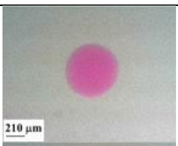
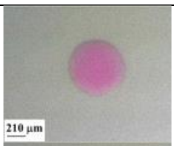
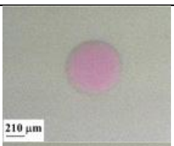
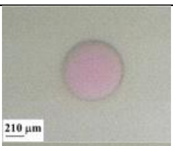
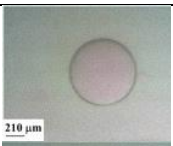
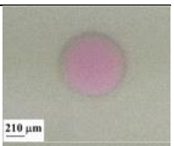
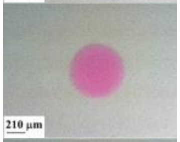
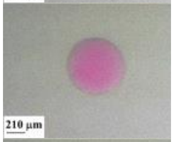
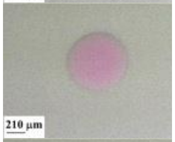
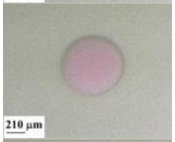
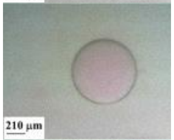
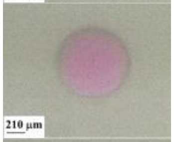
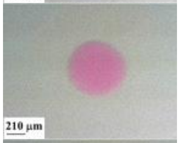
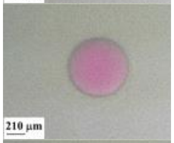
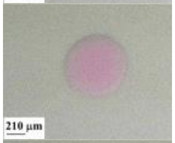
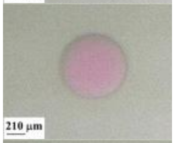
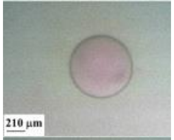
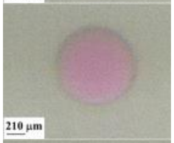
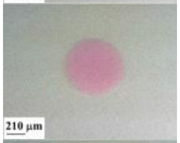
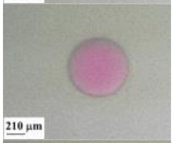
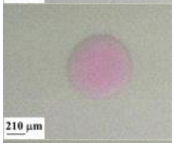
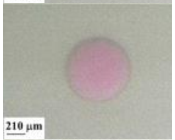
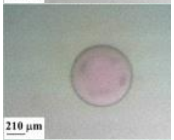
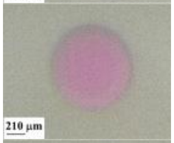
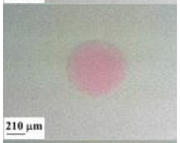
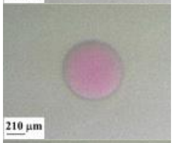
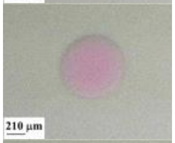
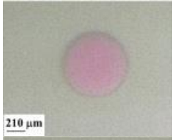
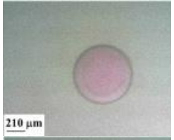
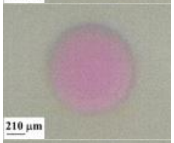
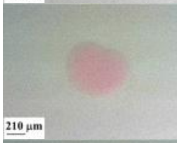
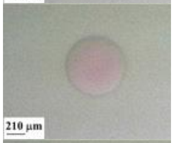
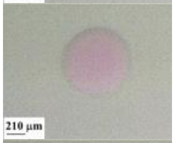
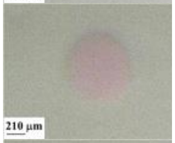
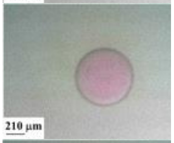
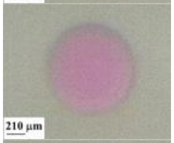
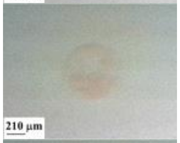
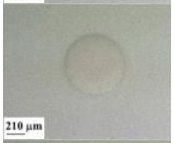
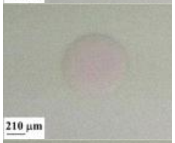
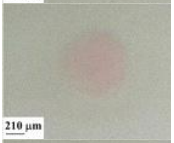
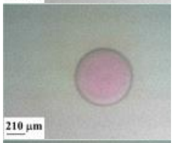
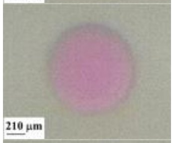
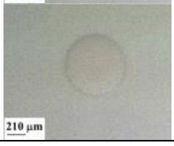
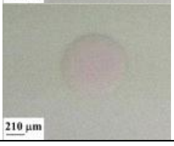
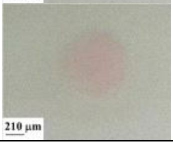
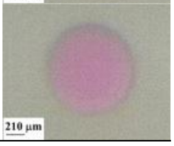
To lessen the soap formation in biodiesel production, we chose FAME as the organics ester. Soap formation by FAME containing FFA when reacted with an alkaline substance is expected from two major reactions, neutralization and saponification of FAME. The saponification of triglyceride and transesterification of oil are excluded and also the effects of water on saponification reaction are limited. From Table 2, a drop of sodium methoxide-methanol solution containing phenolphthalein on a pool of FAME indicates some interesting facts of the kinetics of the reaction. Also, a drop of FAME on the pool of alkaline-methanol solution confirms the same facts. Methanol and alkaline diffuse to the FAME phase within a few seconds when FFA content in FAME is quite low.

The proposed explanation is the difference in the amount of soap from neutralization (Eq. 2). High FFA content in FAME creates a lot of soap that restrains the diffusion of alcohol and catalyst. Without FFA in FAME, methanol and alkaline diffuse faster. The trial with a drop of FAME on a pool of alcohol solution gave similar results, the diffusion of methanol and alkaline was fast. The boundary of FAME disappeared in a short time (50 seconds).

Table 2

Photographs of the reaction zone of the effect of FFA on FAME saponification with initial excess FAME, for up to 60 seconds

(Photographs taken with 40X magnification)

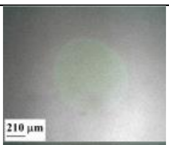
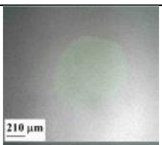
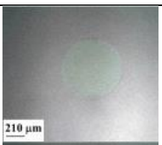
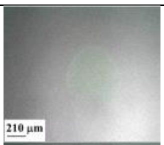
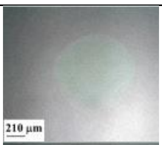
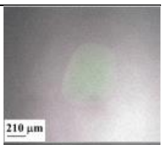
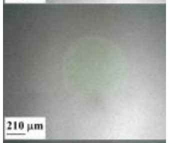
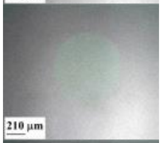
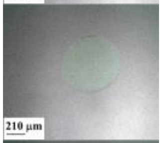
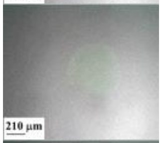
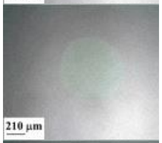
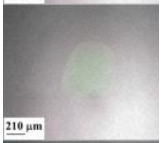
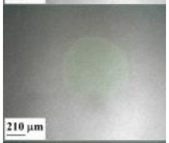
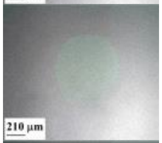
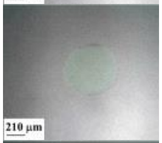
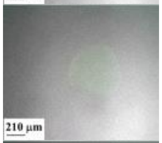
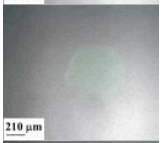
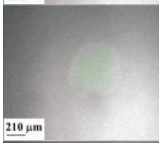
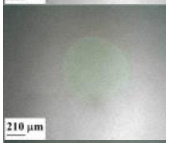
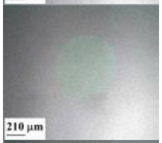
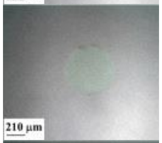
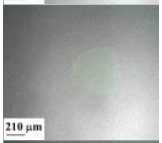
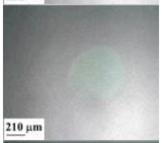
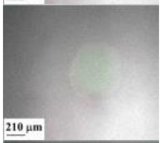
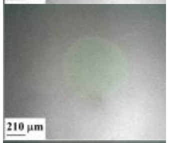
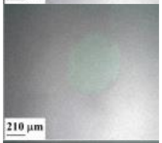
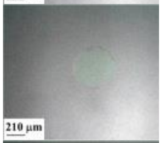
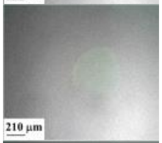
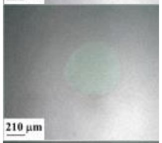
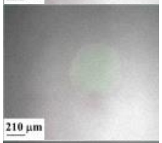
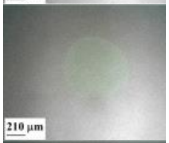
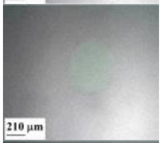
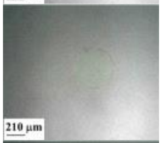
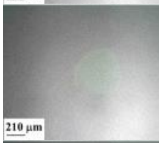
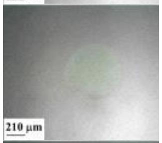
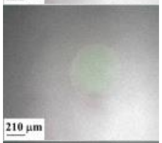
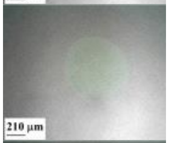
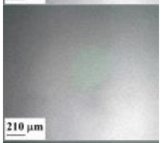
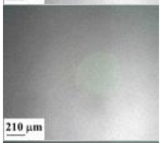
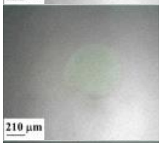
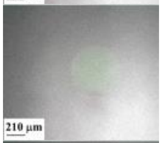
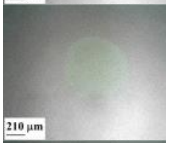
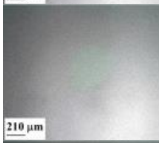
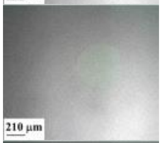
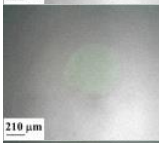
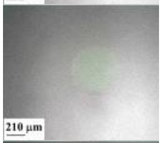
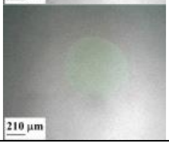
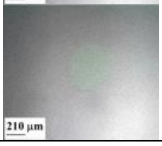
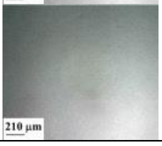
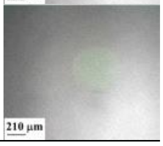
Time	**FFA content of FAME**					
(s)	**0.02wt%**	**0.1wt%**	**0.25wt%**	**0.5wt%**	**1.0wt%**	**2.0wt%**
5						
10						
20						
30						
40						
45						
50						
60						

Note: an approx. 10 µL of FAME with varied FFA content (0.02, 0.1, 0.25, 0.5, 1.0 and 2.0wt%) and moisture content 0.03wt%; an approx. 1 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH).

Table 3

Photographs of the reaction zone when FFA on FAME is saponified with initially excess alkaline-alcohol solution, for up to 300 seconds

(Photographs taken with 40X magnification)

Time	FFA content of FAME					
(s)	0.02wt%	0.1wt%	0.25wt%	0.5wt%	1.0wt%	2.0wt%
5						
10						
30						
60						
90						
120						
180						
240						
300						

Note: an approx. 1 µL of FAME (0.03wt% water) with varied FFA contents (0.02, 0.1, 0.25, 0.5, 1.0 and 2.0wt%); an approx. 10 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH).

The trials indicate that high FFA content in FAME creates a lot of soap that restrains the diffusion of alcohol and catalyst. These soap barriers could possible form a thick film as mentioned above.

In the reversed trials in Table 3, the boundary of a spot of FAME on a drop of alkaline-methanol solution shrunk for 60 minutes after spotting, and then maintained the same size up to 240 minutes for all FFA contents from 0.1 to 2wt%. This observation indicates diffusion of FAME into the alkaline-methanol solution. The drop of alkaline-methanol solution on a drop of FAME (0.02wt% FFA) was quite stable in its apparent size. This is possibly due to the soap barrier.

It can be seen that a spot of alkaline-methanol solution on FAME and a spot of FAME on alkaline-methanol solution showed different phenomena. A spot of alkaline-methanol solution contains much more alkaline reactant moles than the same volume of FAME. High soap formation in the case of alkaline-methanol solution on FAME inhibits the diffusion of methanol and alkaline into FAME phase, so it is hard to notice any changes of the drop size, reflecting a slow reaction rate. Thus, soap acts as a reaction barrier.

3.1.2 Effects of FFA on saponification of RPO

Saponification of alkaline solution on RPO is expected to behave differently from FAME due to the transesterification reaction. Transesterification of triglyceride gives ester and by-product glycerol. Glycerol is a strongly polar compound unlike other esters. Glycerol should prefer to stay with methanol, and if the reaction takes place near the interface of alcohol and triglyceride, the glycerol should leave the ester and move to the methanol phase.

The exploration of a drop of alcohol-alkaline solution on a pool of RPO showed, first, a pale pink color with a low content of FFA in RPO for up to 300 seconds. Second, a small distortion of the alcohol drop appears with 0.1wt% FFA content in RPO, and the weak boundary layer of glycerol and soap may be the cause of this. Third, a strong round boundary was observed with higher contents of FFA in RPO.

The proposed reaction zone is the film volume of triglyceride, and the expansion of the RPO drop in Table 4 supports this concept. The mechanism of reaction should be that methanol accompanies alkaline to the reaction zone and two major reactions take place, neutralization, and transesterification.

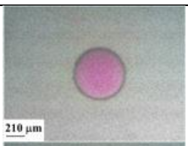
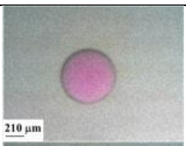
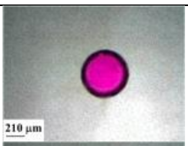
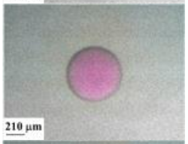
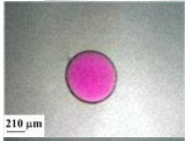
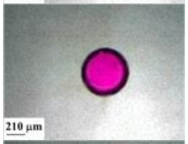
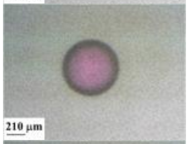
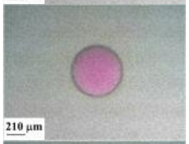
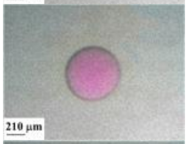
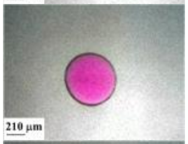
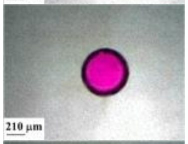
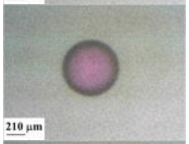
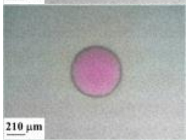
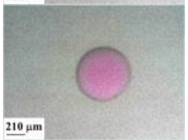
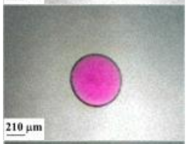
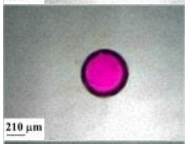
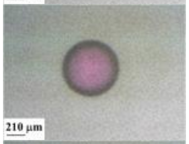
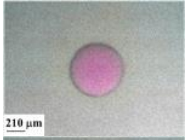
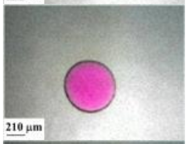
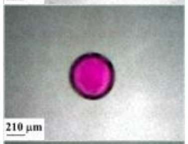
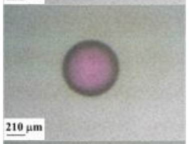
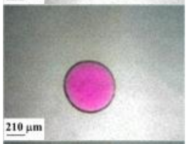
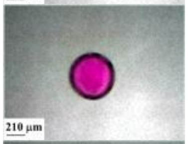
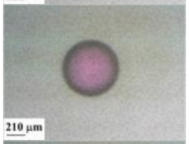
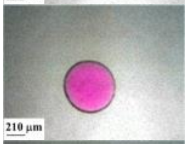
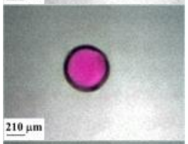
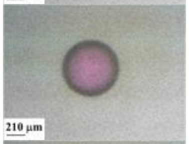
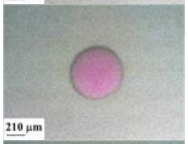
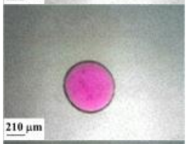
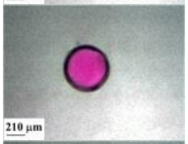
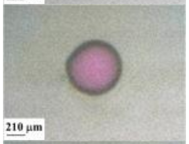
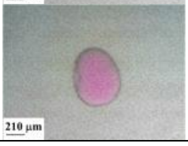
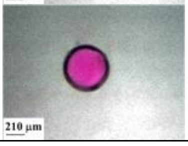
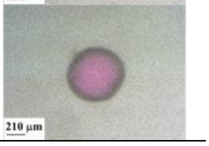
The neutralization product is soap, an emulsifier, and its polar heads prefer to stay with methanol and so it forms a boundary layer. The FFA neutralization is spontaneous even though FFA is a weak acid. Transesterification is supposed to be a fast reaction but is slower than a spontaneous reaction. So, soap is formed first and it moves to the alcohol interface and creates a thin boundary layer. High FFA content in RPO creates a lot of soap that restrains the diffusion of alcohol and catalyst.

So, oils with 0.1 and 0.5wt% acidity (or 0.05 and 0.25wt% FFA) are at the maximum allowed of feedstocks for Lurgi GmbH [22] and Crown Iron Works [23], respectively. The thick boundary layer of soap does not allow the diffusion of alcohol and catalyst to the reaction zone, and slows down transesterification.

Table 4

Photographs of the reaction zone show the effect of FFA on RPO saponification with initial excess RPO, for up to 300 seconds

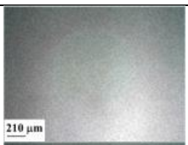
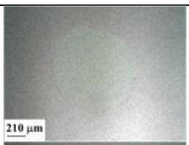
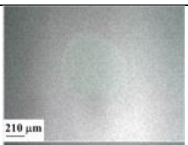
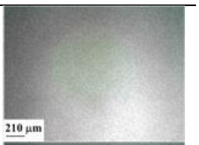
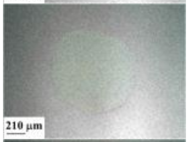
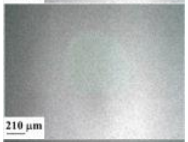
(Photographs taken with 40X magnification)

Time (s)	FFA content of RPO				
	0.1wt%	**0.25wt%**	**0.5wt%**	**1.0wt%**	**2.0wt%**
5					
10					
30					
60					
90					
120					
150					
240					
300					

Note: an approx. 10 µL of RPO with varied FFA (0.1, 0.25, 0.5, 1.0 and 2.0wt%); an approx. 1 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH).

Table 5

Photographs of the reaction zone show the effect of FFA on RPO saponification with initial excess alkaline-alcohol solution, for up to 300 seconds. (Photographs taken with 40X magnification)

Time	**FFA content of RPO**				
(s)	**0.1wt%**	**0.25wt%**	**0.5wt%**	**1.0wt%**	**2.0wt%**
5					
10					
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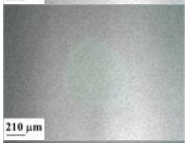
180					
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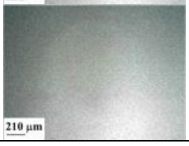
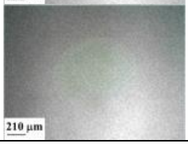
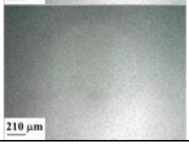
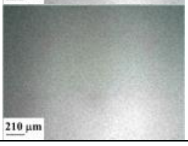
300					

Note: an approx. 1 µL of RPO with varied FFA (0.1, 0.25, 0.5, 1.0, and 2.0wt%); an approx. 10 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH)

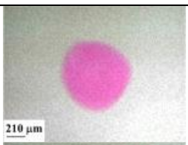
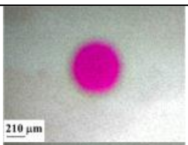
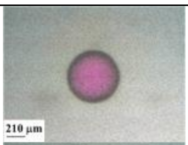
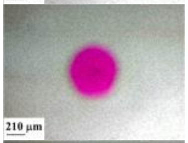
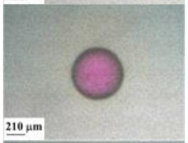
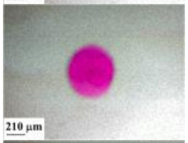
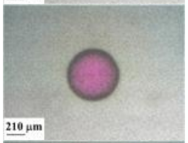
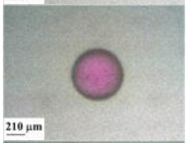
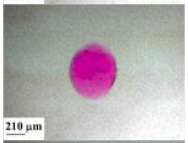
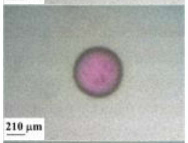
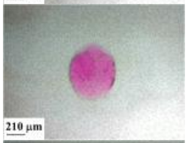
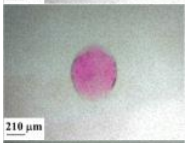
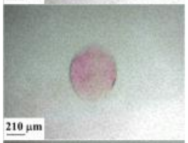
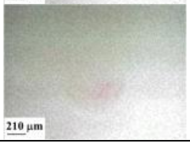
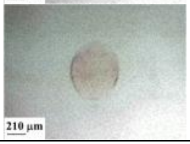
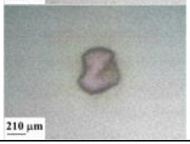
The pictures of a drop of RPO on a pool of alkaline-methanol solution support these hypotheses (Table 5). A drop of RPO carries a limited amount of FFA, and soap formation depends on the FFA content. The soap layer spreads out to the alcohol pool as more alcohol and alkaline diffuse into the oil. The transesterification reaction continues and transforms triglyceride to ester and glycerol. The boundary layer may come from the diffusion of glycerol that is moving to alcohol phase and brings back the alcohol and alkaline molecules.

3.2 Effect of water on saponification reaction of RPO

Effect of water on saponification (Tables 6 and 7) was investigated on RPO containing 0.1wt% FFA to reduce the effect of soap from acid neutralization. A real feedstock for biodiesel production will have some FFA, so we chose a realistic but low content. The drop of alkaline solution of methanol in the pool of RPO having different water contents illustrates some interesting variations. At a low water content of 0.1wt%, the pink color in alcohol drop becomes pale within 30 seconds. This indicates fast diffusion of methanol and alkaline into the RPO. At a medium 0.5wt% water content level, the pink color disappeared within 180 seconds, and at the high 1wt% of water in RPO, a pale pink color persisted. Boundary layer thickness is clearly seen at a high content of water in RPO, due to the soap formation. One weight percent of water in RPO is approximately 0.48: 1 molar ratio of water to oil. The reverse esterification of water and triglyceride to FFA may be slow after the preparation step and it is accelerated by alkaline catalyst [35].

Table 6

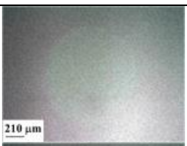
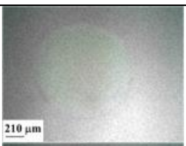
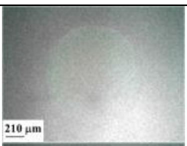
Photographs of the reaction zone show the effect of water on RPO saponification with initial excess RPO, for up to 300 seconds (Photographs taken with 40X magnification)

Time (s)	Water content of RPO		
	0.1wt%	**0.5wt%**	**1.0wt%**
5			
10			
20			
30			
60			
90			
180			
240			
300			

Note: an approx. 10 µL of RPO (0.1wt% FFA) and varied moisture content (0.1, 0.5 and 1.0wt%); an approx. 1 µL of $NaOCH_3$ -methanol solution (4.42wt% in MeOH)

Table 7

Photographs of the reaction zone show the effect of water on RPO saponification for RPO with initial excess alkaline-alcohol solution, for up to 300 seconds (Photographs taken with 40X magnification)

Time (s)	**Water content of RPO**		
	0.1wt%	**0.5wt%**	**1.0wt%**
5			
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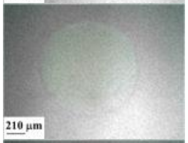
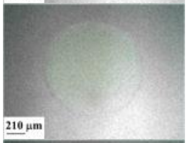
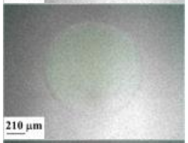
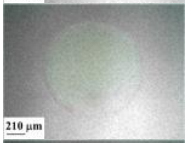
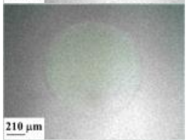
30			
60			
90			
120			
150			
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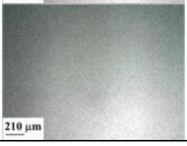
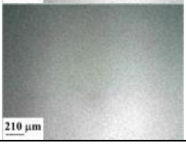
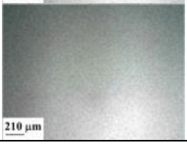
300			

Note: an approx. 1 µL of RPO (0.1wt% FFA) with varied water content (0.1, 0.5 and 1.0wt%); an approx. 10 µL of $NaOCH_3$-methanol solution (4.42wt% in MeOH)

In the reversed trial of a drop of RPO on the pool of alkaline solution, methanol and alkaline try to diffuse in an oil drop. The high-water content in RPO tends to have a thicker film, which possibly reduces the diffusion rate of alkaline-methanol solution to the oil drop. The brown shell became thick within a few seconds and disappeared after 240 seconds.

This indicates the diffusion of methanol-alkoxide solution into the drop. We assume that the glycerol shell was dissolved in methanol-alkoxide solution. High level of water contamination in feedstocks causes hydrolysis of triglyceride and spontaneous soap formation [13], [90]–[92]

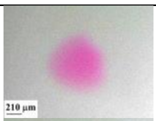
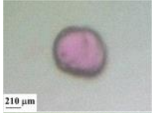
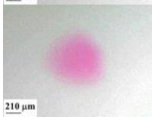
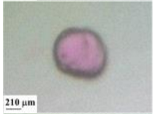
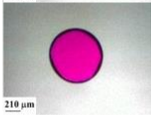
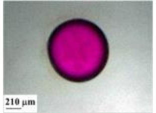
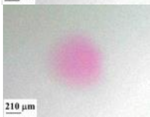
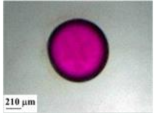
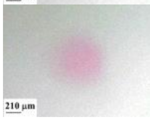
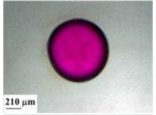
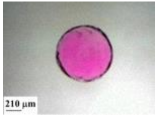
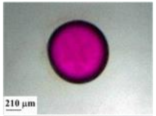
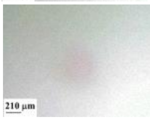
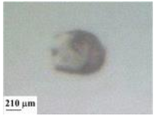
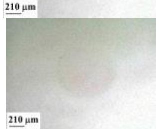
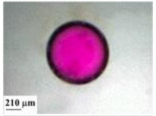
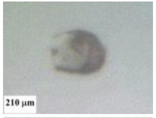
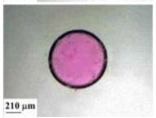
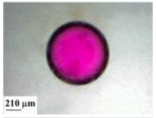
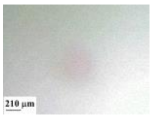
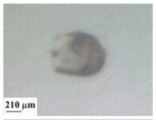
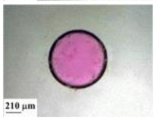
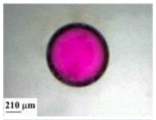
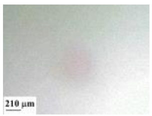
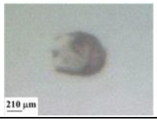
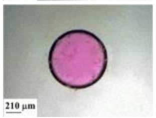
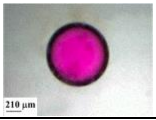
From the results, it can be seen that high-water content in oil induces a barrier of soap that possibly reduces the rate of mass transfer. So, the maximum moisture and volatiles contents of 0.1 (Lurgi GmbH) [22] and 0.05wt% (Crown Iron Works) [23] are suitable to oil feedstocks for biodiesel production.

3.3 Effects of alkaline concentration on saponification reaction of RPO

In this study in Table 8 and 9, the effects of catalyst concentration (2.21, 4.42 and 8.83wt% in MeOH) on the reaction zone of transesterification of RPO with different FFA oil (low FFA and high FFA) was investigated. When a drop of alkaline-methanol solution is on a pool of RPO, the possible reactions are transesterification and saponification. Both transesterification and saponification have high rates as a high content of catalyst produces a high amount of glycerol and soap, which makes thick shell barriers that retain the catalyst and alcohol in the droplets.

Table 8

Photographs of the reaction zone to examine the effects of $NaOCH_3$ concentration on RPO (high FFA vs. low FFA) saponification with initial excess RPO, for up to 180 seconds (Photographs taken with 40X magnification)

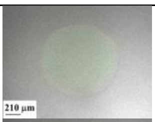
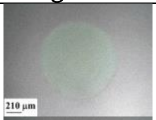
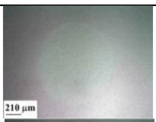
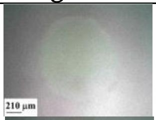
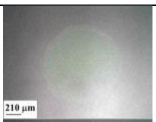
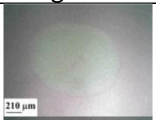
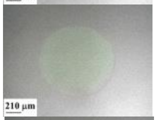
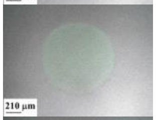
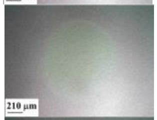
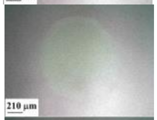
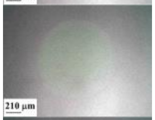
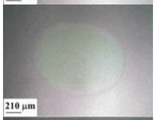
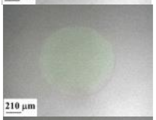
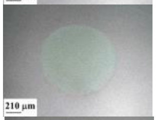
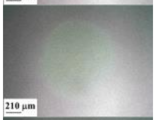
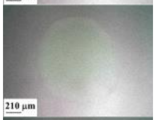
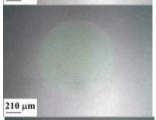
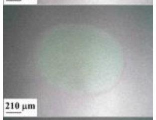
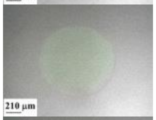
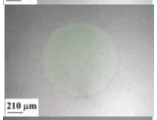
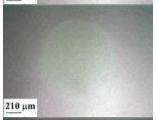
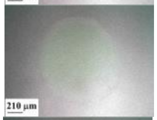
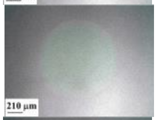
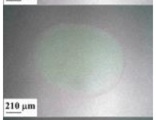
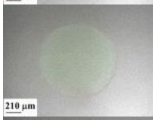
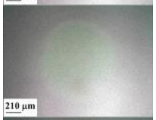
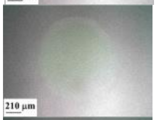
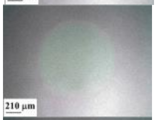
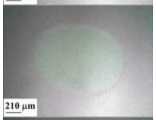
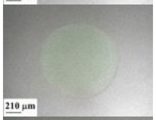
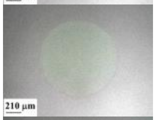
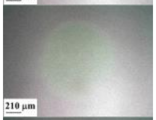
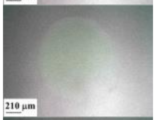
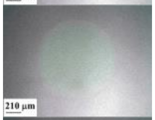
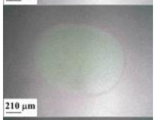
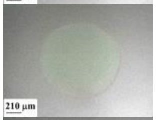
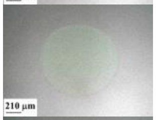
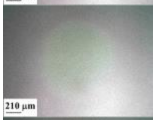
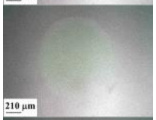
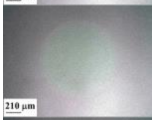
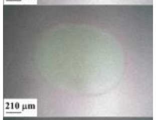
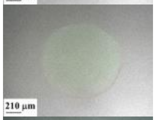
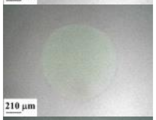
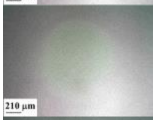
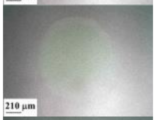
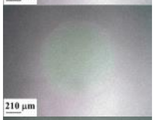
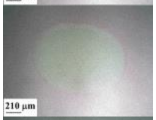
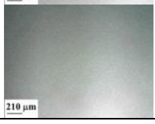
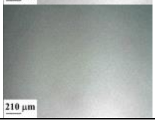
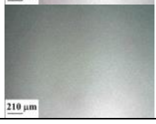
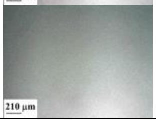
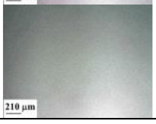
Time (s)	**Catalyst concentration (wt% in MeOH)**					
	2.21wt%		**4.42wt%**		**8.83wt%**	
	Low FFA	**High FFA**	**Low FFA**	**High FFA**	**Low FFA**	**High FFA**
5						
10						
20						
30						
40						
60						
80						
100						
180						

Note: an approx. 10 µL of RPO (0.1wt% FFA for low FFA vs. 1wt% FFA for high FFA); an approx. 1 µL of $NaOCH_3$ -methanol solution (vary catalyst concentration 2.21 to 8.83wt% in methanol

Table 9

Photographs of the reaction zone to examine the effects of $NaOCH_3$ concentration on RPO (high FFA vs. low FFA) saponification with initial excess alkaline-alcohol solution, for up to 300 seconds

(Photographs taken with 40X magnification)

Time (s)	**Catalyst concentration (wt% in MeOH)**					
	2.21wt%		**4.42wt%**		**8.83wt%**	
	Low FFA	**High FFA**	**Low FFA**	**High FFA**	**Low FFA**	**High FFA**
5						
10						
30						
60						
90						
120						
180						
240						
300						

Note: an approx. 1 µL of RPO (0.1wt% FFA for low FFA vs. 1wt% FFA for high FFA); an approx. 10 µL of $NaOCH_3$ -methanol solution (vary catalyst concentration 2.21 to 8.83wt% in methanol)

From Table 8, in the case of low FFA oil (0.1wt%), thinner barriers were generated at lower reaction rates. High FFA oil (1wt%) tends to give thicker barriers with an increased catalyst concentration. The high FFA contents cause neutralization reactions [42], [77]. These thick shells possibly hinder mass transfer of alcohol and catalyst to the reaction zone.

Regarding the reversed trials in Table 9, when a drop of RPO is on a pool of alkaline-methanol solution, the possible reactions are transesterification and saponification. For high FFA oil, we see a pink layer diffuse into the droplet, and within 300 seconds the whole drop is pink. These same phenomena were found in all cases tested.

The results suggest that the initially loaded catalyst will be partly consumed by neutralization with free fatty acids forming soap (emulsifier) that acts as mass transfer barriers.

3.4 Variables (FFA, water, and catalyst concentration) affecting the $NaOCH_3$-catalyzed transesterification of refined palm oil with methanol

The reaction variables such as FFA content, water content, and catalyst concentration are significant parameters in the conventional transesterification process. In order to evaluate biodiesel yield and purity, the ester content (wt% referred to biodiesel mass) in the final biodiesel phase was determined. Consequently, we need to determine the experimental biodiesel yield after the reaction and separation stages in order to evalute all of the biodiesel losses (separation, washing, and soap losses). In this work, the the theoritical biodiesel yield is 100.47, based on the molecular weight of RPO 848, which can produce 3 moles of FAME (MW 284).

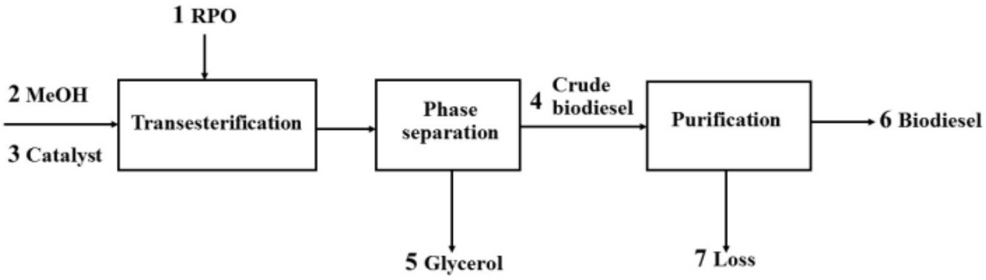


Fig. 2. Flow chart of a conventional transesterification process.

From our transesterification experiments (Fig. 2), the yield loss of biodiesel came from loss in glycerol phase (5), washing loss (7) and chemical loss by saponification [3]. We combined glycerol phase loss and washing loss as a physical loss, which may be a function of the soap content in ester phase. Soap content was measured for both phases of crude biodiesel and crude glycerol, and with the weight ratio of both phases we can calculate the total soap content. The remaining catalyst was also measured for both phases. The remaining catalysts and soap contents in each phase and their dritribution are shown in Table 10. Most of the remaining catalyst was found in the glycerol phase. We assume that the barrier layer of mass transfer at the outer surface of methanol droplet is composed of glycerol, soap, diglyceride, and monoglyceride. At a critical thickness of this barrier only very small amounts of alcohol and catalyst can diffuse through this film. But the remaining alcohol and catalyst outside the droplets could proceed to react, both by transesterification and saponification. This resulted in glycerol and soap, which created very fine droplets and suspended in the ester phase. So, a very small amount of remaining catalyst was found in the ester phase. The soap was mostly found in the glycerol phase, but at higher amount in the ester phase than the remaining catalyst.

Table 10

Remaining catalyst and soap in ester and glycerol phases.

Run #	Ester-phase		Glycerol-phase		Total		Remaining catalyst distribution		Soap distribution	
	Remaining catalyst	Soap	Remaining catalyst	Soap	Remaining $NaOCH_3$	Soap	Ester-phase	Glycerol-phase	Ester-phase	Glycerol-phase
	mol	mol	mol	mol	mol	mol	%	%	%	%
1	0.000024	0.000987	0.016375	0.018900	0.016399	0.019887	0.14	99.86	4.96	95.04
2	0.000025	0.002053	0.014376	0.019891	0.014401	0.021944	0.17	99.83	9.36	90.64
3	0.000052	0.002808	0.011386	0.022059	0.011438	0.024867	0.45	99.55	11.29	88.71
4	0.000050	0.004365	0.007819	0.023604	0.007869	0.027969	0.64	99.36	15.61	84.39
5	0.000080	0.004732	0.006443	0.025253	0.006523	0.029985	1.23	98.77	15.78	84.22
6	0.0000157	0.0009149	0.0228462	0.0125130	0.0228619	0.0134279	0.07	99.93	6.81	93.19
7	0.0000153	0.0009736	0.0211952	0.0140201	0.0212105	0.0149937	0.07	99.93	6.49	93.51
8	0.0000155	0.0022428	0.0119083	0.0221824	0.0119238	0.0244252	0.13	99.87	9.18	90.82
9	0.0000155	0.0033975	0.0101915	0.0228459	0.010207	0.0262434	0.15	99.85	12.95	87.05
10	0.0000156	0.0045867	0.0031871	0.0280382	0.0032027	0.0326249	0.49	99.51	14.06	85.94
11	0.000048	0.001320	0.022919	0.016628	0.022967	0.017948	0.21	99.79	7.35	92.65
12	0.000015	0.001285	0.021071	0.013936	0.021086	0.015221	0.07	99.93	8.44	91.56
13	0.000016	0.001301	0.015990	0.012307	0.016006	0.013608	0.10	99.90	9.56	90.44
14	0.000016	0.001477	0.012749	0.011126	0.012765	0.012603	0.13	99.87	11.72	88.28
15	0.000016	0.001795	0.010884	0.009836	0.010900	0.011631	0.15	99.85	15.43	84.57
16	0.000016	0.002035	0.007082	0.008931	0.007098	0.010966	0.23	99.77	18.56	81.44

Note: RUNS #1-5 for FFA concentration effect; RUNS #6-10 for water concentration effect; RUNS #11-16 for catalyst concentration effect.

We assume the suspension of very small glycerol droplets can explain this fact. We believe that if the separation of glycerol phase from the ester phase were done with a centrifuge, most of the soap would be in the glycerol phase.

A preliminary study of FFA, water and catalyst amounts on the soap formation is summarized in Table 11. The effects of FFA content in RPO in the range 0.12-1.0 wt%, while water content and the amount of $NaOCH_3$ were held constant, are seen in Runs #1-5. The results show that increasing FFA gives more soap. The nearly 1wt% of $NaOCH_3$ and the molar ratio of methanol to oil at 6: 1 within 30 minutes of reaction give the ester content in final biodiesel ≥ 96.5 wt%, satisfying worldwide biodiesel specifications. But the physical yield losses are very high with 0.25wt% of FFA. The soap content in the ester phase of Run#2 is about 3,016 ppm based on MW=292 of sodium soap.

The specified feedstock properties of maximal acidity 0.1% or 0.5% by Lurgi GmbH [22] and Crown Iron Works [23] correspond to 0.05 or 0.25 wt% of FFA, and may be more motivated by yield losses than by chemical reactivity.

The effects of water content in RPO from 0.05 to 0.8wt%, while the FFA content was kept fixed, were tested in Runs #6-10. Please be reminded that the MW of water is 18 while the average MW of FFA in RPO is 270, so the number of moles of 0.05wt% of water is equivalent that of 0.75wt% FFA. The hydrolysis of water with TG or FAME to FFA was confirmed by soap content increasing with water content in RPO. But that increase is not linear with the number of moles of water, because of limitation by the number of moles of $NaOCH_3$.

Table 11

Preliminary results of FFA, water and catalyst amount effects on soap formation and yield losses.

	1	RPO properties						2	3	4	5	6	Yield	Ester content	7	Biodiesel losses	
RUN #	RPO	FFA content			Water content			MeOH	$NaOCH_3$	Crude biodiesel	Crude glycerol	Biodiesel			Total	Chemical	Physical
	g	wt%	g	mol	wt%	g	mol	G	g	g	g	g	%	wt%	%	%	%
1	200	0.12	0.246	0.0009	0.18	0.3558	0.0198	45.28	1.96	198.75	47.67	192.15	96.08	98.13	4.40	2.90	1.50
2	200	0.25	0.500	0.0019	0.18	0.3558	0.0198	45.28	1.96	198.51	48.27	188.22	94.11	98.13	6.37	3.20	3.17
3	200	0.57	1.140	0.0042	0.18	0.3558	0.0198	45.28	1.96	198.65	48.37	184.55	92.28	98.13	8.20	3.63	4.57
4	200	0.75	1.500	0.0056	0.18	0.3558	0.0198	45.28	1.96	195.57	50.79	173.20	86.60	97.31	13.88	4.08	9.80
5	200	1.00	2.000	0.0074	0.18	0.3558	0.0198	45.28	1.96	195.37	50.85	168.28	84.14	97.31	16.34	4.38	11.96
6	200	0.18	0.364	0.0013	0.05	0.1000	0.0056	45.28	1.96	198.09	48.70	193.46	96.73	98.95	3.75	1.96	1.79
7	200	0.18	0.364	0.0013	0.15	0.3000	0.0167	45.28	1.96	198.32	47.76	192.41	96.21	98.95	4.27	2.19	2.08
8	200	0.18	0.364	0.0013	0.25	0.5000	0.0278	45.28	1.96	199.24	47.53	187.68	93.84	98.13	6.63	3.51	3.12
9	200	0.18	0.364	0.0013	0.40	0.8000	0.0444	45.28	1.96	197.53	48.43	180.40	90.20	97.72	10.28	3.84	6.44
10	200	0.18	0.364	0.0013	0.80	1.6000	0.0889	45.28	1.96	197.49	48.30	170.91	85.46	97.31	15.02	4.76	10.26
11	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	2.23	198.76	48.25	192.78	96.39	98.68	4.09	2.62	1.47
12	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.96	198.37	48.39	193.39	96.70	98.68	3.78	2.22	1.56
13	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.59	198.50	48.35	191.29	95.64	97.86	4.83	1.99	2.85
14	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.40	198.74	47.51	181.05	90.53	95.40	9.95	1.84	8.11
15	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	1.21	198.24	48.30	171.19	85.59	94.58	14.88	1.70	13.18
16	200	0.17	0.350	0.0013	0.18	0.3548	0.0197	45.28	0.98	197.29	48.47	162.22	81.11	92.40	19.36	1.60	17.76

Note: RUNS #1-5 for FFA concentration effect; RUNS #6-10 for water concentration effect; RUNS #11-16 for catalyst concentration effect.

The maximum water contents 0.1 [22] and 0.05wt% [23] would give maximum total losses below 4% in biodiesel production, and biodiesel yield better than 96%, which is the minimum requirement in the industry. We assume that using enough catalyst in the transesterification process is the key to obtaining high quality biodiesel, even when using low quality feedstock with high water content. But the critical effect of using low grade feedstock is the high soap content, which causes very high physical losses. Our results suggest as maximum soap content in crude biodiesel about 3000 ppm. Washing the crude biodiesel with a dilute water solution of an acid, such as citric acid, may reduce the losses in washing, but as a drawback the soap is converted to FFA, which is not desirable due to biodiesel specifications.

The effects of catalyst concentration were investigated in Runs #11-16 (Table 10-11). Using a low content of $NaOCH_3$ below 0.70wt% of RPO (Runs #14-16) resulted in off quality biodiesel with too low ester content (96.5wt%). The soap content in these runs was below 3,000 ppm, but the physical losses were very high. The loss in separation step of these runs does not differ from all other runs in the same trial series. Anyway, we noticed difficulty of washing, and found that the middle layer between the upper layer ester phase and the lower layer water phase had varying thicknesses. This interface layer was photographed as shown in Table 12. The emulsions with low ester conversion are denser than with high conversion, but the soap contents in this trial series are below 3,000 ppm. We assume that the large emulsification was caused by the by-products mono- and diglyceride from incomplete conversion of triglyceride to ester. Freedman et al., 1984 [36] demonstrated low levels of monoglyceride and diglyceride in the case of high ester content (approx. 98 wt%), while high levels of monoglyceride and diglycerides were still observed at low ester contents (approx. 82wt%). From this reference, at 95% ester conversion, di- and monoglyceride are present at the high 2-3wt% level of total biodiesel.

The effects of soap content in crude biodiesel on washing losses are shown in Fig. 3. The data from Runs #14-16 were excluded from this Figure, due to the high content of di- and monoglyceride. We propose that the soap content in crude biodiesel should be below 3,000 ppm for wash step losses below 3%.

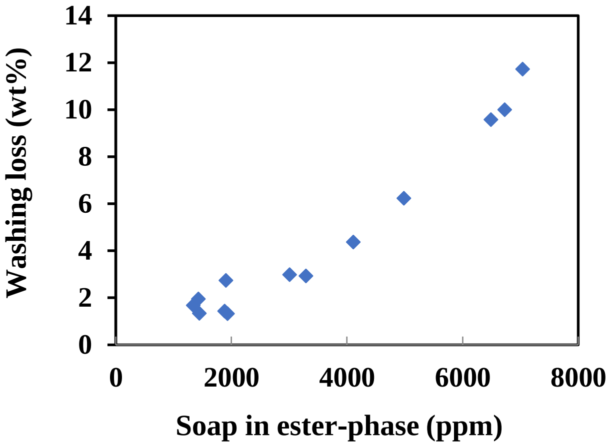
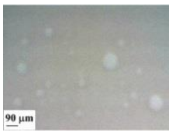
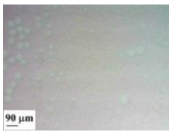
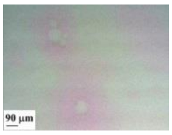
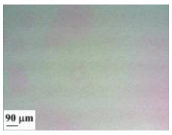
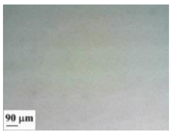
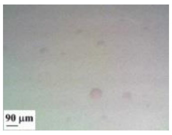


Fig. 3. The relationship between soap content in ester-phase and washing loss

Table 12

Protographs of the interface layer between biodiesel and water phases in the washing step. (Photographs taken with 100X magnification)

Catalyst concentration					
0.49wt%	**0.6wt%**	**0.7wt%**	**0.8wt%**	**0.98wt%**	**1.1wt%**
					

4. Conclusions

The reaction zone of soap formation is in the oil (TG and FAME) film near the interface of the methoxide-methanol solution. Soap is an emulsifier that prefers to stay at the interface of polar and nonpolar substances. The soap layer is a barrier resisting the transfer of alcohol and catalyst solution. The glycerol from transesterification reaction is a polar substance, and while the reaction zone is at the interface or in the oil film area, the glycerol diffuses back to the more polar methoxide-methanol solution. We assume that soap prefers to stay at the outer layer from the glycerol because the lipophilic part of soap likes to be near the nonpolar oil. The produced glycerol creates a thicker barrier than soap, because the number of moles of soap is limited dependent on availability of the alkaline catalyst. The water content in triglyceride feedstock enhances soap formation via hydrolysis with triglyceride or FAME to FFA, and these further react with an alkaline catalyst to form soap.

The amount of alkaline catalyst plays an important role in biodiesel production. The catalyst concentration controls the intermediate step of transesterification between the alkoxide ion ($^{-}OCH_3$) and the carboxyl group of fatty acids. A high concentration of alkaline catalyst gives a high rate of ester and glycerol production, making thicker glycerol layer that entraps the methanol and alkaline catalyst within methoxide-methanol solution droplets. But the remaining alkaline outside the droplet is high enough to keep the transesterification going on. The remaining catalyst after 30 minutes of reaction is not the reactive catalyst in the reaction; we believe that the acting catalyst for transesterification must have a higher concentration. The saponification of alkaline to FAME and triglyceride consume the catalyst. We found that the number of moles of soap is higher than the number of moles of FFA plus water, but never greater than the number of moles of alkaline catalyst.

The physical yield losses depend on the soap content in crude biodiesel. We suggest 3,000 ppm as maximum limit of soap in crude biodiesel. The soap formation by transesterification is very complicated. Anyway, the soap formation from FFA is the fastest reaction. The soap formation via hydrolysis of FAME or triglyceride and water to FFA proceeds slower further to soap. The soap formation from the saponification of alkaline and FAME or triglyceride was found in our trials, which suggests not using too high amounts of alkaline catalyst in the production process.

The rate of saponification should be further investigated due to complications in the liquid-liquid reaction system, that depend both on the rates of chemical reaction and on the rates of mass transfer. The glycerol product contributes to saponification by the shell barriers that restrain the diffusion of alcohol and alkaline catalyst into the triglyceride body. The rate of shell formation also plays an important role in the overall chemical reaction rate.

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VITAE

Name Mr. Issara Chanakaewsomboon

Student ID 5610130009

Educational Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Science (Industrial Chemistry)	Prince of Songkla University	2007
Master of Engineering (Chemical Engineering)	Kasetsart University	2011

Scholarship Awards during Enrollment

Faculty of Engineering Graduated Student Scholarship

Graduate School Research Support Funding for Thesis

Lists of Publication

I. Chanakaewsomboon, C. Tongurai, S. Photaworn, S. Kungsanant. Solubility of Multicomponent Systems in Biodiesel Production Observed by LCD Digital Microscope. This article is under peer reviewing for Publication on Fuel (ISI, Q1, IF = 4.908, Initial Date Submitted: 21/01/2019, Under Review Status Date: 29/01/2019).

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