Ethyl Ester from Crude Palm Oil by Two Step Process with Continuous Flow Microwave

Kittiphoom Suppalakpanya

A Thesis Submitted in Fulfillment of the Requirements for the Degree of
Doctor of Engineering in Chemical Engineering
Prince of Songkla University
2010

ชื่อวิทยานิพนธ์ เอทิลเอสเตอร์จากน้ำมันปาล์มดิบ โดยใช้กระบวนการ 2 ขั้นตอน ด้วยไมโครเวฟแบบต่อเนื่อง
ผู้เขียน นายกิตติภูมิ ศุภลักษณ์ปัญญา
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2552

บทคัดย่อ

งานวิจัยนี้ศึกษาการผลิตเอทิลเอสเตอร์จากน้ำมันปาล์มดิบซึ่งมีกรดไขมันอิสระสูงด้วยปฏิกิริยาสองขั้นตอนโดยใช้ไมโครเวฟ งานวิจัยแบ่งการศึกษาออกเป็น 2 กระบวนการ คือ กระบวนการเอสเตอริฟิเคชันแบบกะ เพื่อศึกษาปัจจัยสำคัญที่มีผลต่อการทำปฏิกิริยาเอสเตอริฟิเคชัน ได้แก่ อัตราส่วนเชิงโมลในการทำปฏิกิริยาระหว่างกรดไขมันอิสระและเอทานอล ในช่วง 1 ต่อ 4 ถึง 1 ต่อ 40 ปริมาณตัวเร่งปฏิกิริยากรดซัลฟิวริก ในช่วง 0 ถึง 16 เปอร์เซ็นต์โดยน้ำหนัก (กรดซัลฟิวริกต่อไขมันอิสระ) กำลังวัตต์ของไมโครเวฟทำการศึกษาในช่วง 70 140 และ 280 วัตต์ และเวลาในการทำปฏิกิริยาในช่วง 20 ถึง 120 นาที สภาวะที่เหมาะสมสำหรับกระบวนการเอสเตอริฟิเคชัน คือ อัตราส่วนเชิงโมลในการทำปฏิกิริยาระหว่างกรดไขมันอิสระและเอทานอล 1 ต่อ 24 ปริมาณตัวเร่งปฏิกิริยากรดซัลฟิวริก 4 เปอร์เซ็นต์โดยน้ำหนัก (กรดซัลฟิวริกต่อไขมันอิสระ) กำลังวัตต์ของไมโครเวฟ 70 วัตต์ และเวลาในการทำปฏิกิริยา 60 นาที กระบวนการทรานส์เอสเตอริฟิเคชันแบบกะได้ศึกษาปัจจัยต่างๆ ได้แก่ อัตราส่วนเชิงโมลในการทำปฏิกิริยาระหว่างน้ำมันและเอทานอล ในช่วง 1 ต่อ 4.5 ถึง 1 ต่อ 10.5 ปริมาณตัวเร่งปฏิกิริยาโปแตสเซียมไฮดรอกไซด์ ในช่วง 0 ถึง 3 เปอร์เซ็นต์โดยน้ำหนัก (โปแตสเซียมไฮดรอกไซด์ต่อน้ำมัน) และระยะเวลาในการทำปฏิกิริยาในช่วง 1 ถึง 10 นาที สภาวะที่เหมาะสมสำหรับกระบวนการทรานส์เอสเตอริฟิเคชันแบบกะ คือ อัตราส่วนเชิงโมลในการทำปฏิกิริยาระหว่างน้ำมันและเอทานอล 1 ต่อ 8.5 ปริมาณตัวเร่งปฏิกิริยาโปแตสเซียมไฮดรอกไซด์ 1.5 เปอร์เซ็นต์โดยน้ำหนัก (โปแตสเซียมไฮดรอกไซด์ต่อน้ำมัน) เวลาในการทำปฏิกิริยา 5 นาที และกำลังวัตต์ของไมโครเวฟ 70 วัตต์ กระบวนการแยกเฟสใช้กลีเซอรีนบริสุทธิ์ ในช่วง 2 ถึง 20 เปอร์เซ็นต์โดยน้ำหนัก (กลีเซอรีนบริสุทธิ์ต่อน้ำมัน) และกระบวนการทำบริสุทธิ์ด้วยดินฟอกในช่วง 0.2 ถึง 1.4 เปอร์เซ็นต์โดยน้ำหนัก (ดินฟอกต่อน้ำมัน) และเวลาในการสัมผัสในช่วง 1 ถึง 10 นาที โดยปัญหาการแยกเฟส

ของกลีเซอรีนสามารถแก้ไข โดยการเติมกลีเซอรีนบริสุทธิ์ 10 เปอร์เซ็นต์โดยน้ำหนัก ซึ่งจะเหนี่ยวนำให้กลีเซอรีนจากปฏิกิริยาแยกเฟส เอทิลเอสเตอร์ที่ได้ถูกทำความสะอาดด้วยดินฟอก 1.2 เปอร์เซ็นต์โดยน้ำหนัก เป็นเวลา 5 นาที เพื่อกำจัดกลีเซอรีน และสบู่ในเอทิลเอสเตอร์ กระบวนการผลิตแบบต่อเนื่องจึงถูกศึกษา ผลการทดลองพบสภาวะที่เหมาะสมสำหรับปฏิกิริยาเอสเตอริฟิเคชันแบบต่อเนื่อง คือ อัตราส่วนเชิงโมลระหว่างกรดไขมันอิสระและเอทานอล 1 ต่อ 24 ปริมาณตัวเร่งปฏิกิริยากรดซัลฟิวริก 5 เปอร์เซ็นต์โดยน้ำหนัก (กรดซัลฟิวริกต่อไขมันอิสระ) กำลังวัตต์ของไมโครเวฟ 78 วัตต์ และเวลาในการทำปฏิกิริยา 90 นาที ผลผลิตที่ได้เหลือกรดไขมันอิสระร้อยละ 1.7 สภาวะที่เหมาะสมสำหรับกระบวนการทรานส์เอสเตอริฟิเคชันแบบกะ คือ อัตราส่วนเชิงโมลในการทำปฏิกิริยาระหว่างน้ำมันและเอทานอล 1 ต่อ 8.5 ปริมาณตัวเร่งปฏิกิริยาโปแตสเซียมไฮดรอกไซด์ 2.5 เปอร์เซ็นต์โดยน้ำหนัก (โปแตสเซียมไฮดรอกไซด์ต่อน้ำมัน) เวลาในการทำปฏิกิริยา 7 นาที และกำลังวัตต์ของไมโครเวฟ 78 วัตต์ สภาวะที่เหมาะสมสำหรับการแยกเฟสและการทำความสะอาดแบบต่อเนื่องเหมือนกับแบบกะ จากกระบวนการร้อยละผลได้เอทิลเอสเตอร์ เท่ากับ 80 และร้อยละความบริสุทธิ์ของเอทิลเอสเตอร์ เท่ากับ 98.1 คุณสมบัติทางเชื้อเพลิงของเอทิลเอสเตอร์ที่ได้เปรียบเทียบกับมาตรฐานเมทิลเอสเตอร์ พบว่า ค่าส่วนใหญ่อยู่ในเกณฑ์ที่กำหนดของ EN 14214

Thesis Title Ethyl Ester from Crude Palm Oil by Two Step Process with Continuous Flow Microwave
Author Mr. Kittiphoom Suppalakpanya
Major Program Chemical Engineering
Academic Year 2009

ABSTRACT

Production of ethyl ester from crude palm oil (CPO) having high free fatty acids (FFA) by two step process with microwave was investigated in this work. Firstly, batch esterification process were carried out to study the influence of significant parameters; molar ratios of FFA to ethanol of 1:4 to 1:40, the amount of acid catalyst was varied in the range 0-16 %wt of H_2SO_4 to FFA, microwave power outputs of 70 140 and 280 W and reaction time of 20 to 120 minutes. The optimum condition for esterification process was 1:24 molar ratio FFA to ethanol, 4 %wt of H_2SO_4 to FFA as the catalyst, a reaction time of 1 h, and a microwave power output of 70 W. For batch transesterification process were carried out to study the influence of significant parameters; molar ratios of oil to ethanol of 1:4.5 to 1:10.5, the amount of alkaline catalyst was varied in the range 0–3 %wt of KOH/Oil and reaction time of 1 to 10 minutes. The optimum condition for transesterification process was 1:8.5 molar ratio of oil to ethanol, 1.5 %wt of KOH to oil as a catalyst, a reaction time of 5 minutes and a microwave power output of 70 W. For the separation process added 2 to 20 %wt of pure glycerin to separated glycerin from ethyl ester and purification process used bleaching earth 0.2 to 1.4 %wt of oil to purified ethyl ester and a contact time of 1 to 10 minutes. The problem of glycerin separation was solved by mixing 10 %wt of pure glycerin into the ethyl ester to induce the glycerin from the reaction to separated. The ethyl ester phase was purified with 1.2 %wt of bleaching earth and a contact time of 5 minutes, reducing the residual amounts of glycerin and soap in the ethyl ester. Then, continuous processes were studied. The optimum conditions for esterification continuous process was a 1:24 molar ratio of FFA to ethanol, 5 %wt of H_2SO_4 to FFA as the catalyst, a reaction time of 90 minutes, and a microwave power output of 78 W. The esterified crude palm oil had 1.7 %wt of FFA content. The optimum conditions for esterification continuous process was a 1:8.5 molar ratio of oil to ethanol, 1.5 %wt of KOH to oil as a catalyst, a reaction time of 5 minutes and a microwave power output of 70 W and for the continuous process was a 1:8.5 molar ratio of oil to ethanol, 2.5 %wt of KOH to oil as a catalyst, a reaction time of 7 minutes and a microwave power output of 78 W. The optimum condition for the separation process and purification process was the same as the batch process. This process gave a yield of 80 %wt of ethyl ester with ester content 98.1 %wt. The fuel properties of ethyl ester in comparison with those of methyl ester standards can be seen that most of its salient properties fall within the limits prescribed by EN 14214 standards for methyl ester.

CONTENTS

Chapter

1. INTRODUCTION

2. EXPERIMENTATION

CONTENTS (CONTINUED)

Page

3. RESULTS AND DISCUSSION

CONTENTS (CONTINUED)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

Figure **Page**

LIST OF SYMBOLS

CPO	Crude Palm Oil
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester
H_2SO_4	Sulfuric Acid
L	Liter
W	Watts
wt	Weight
XRF	X-Ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Rational / Problem Statement

Majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite and at current usage rates will be consumed shortly. Diesel fuels have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector. Economic growth is always accompanied by commensurate increase in the transport. The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental impact than the traditional one. This has stimulated recent interest in alternative sources for petroleum-based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This alternative diesel fuel can be termed as biodiesel. This fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment.

Vegetable oil such as soybean oil (US), rapeseed oil (Europe) and palm oil (South-East Asia) remains the major feedstock for biodiesel production. In Thailand has many cultivated areas of oil palm which have high the product per growing area and grow up well. Thus the palm oil has the possibility to uses in biodiesel production.

Chemically the vegetable oils and animal fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. Thus biodiesel refers to lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids.

The alkaline catalysts are the most common, since the process is faster than acid catalyst and the reaction conditions are moderated [Vicente et al., 2004]. However, their utilization in vegetable oil transesterification produces soaps by neutralizing the free fatty acid in the oil and triglyceride by saponification. Both soap formations are undesirable side-reaction, because they partially consume the catalyst, decrease the biodiesel yield and complicate the separation and purification steps. However, the free fatty acid neutralization can be avoided by using vegetable oil with low free fatty acid content (<1.0 %wt) but the most profitable raw materials (e.g. waste cooking oils and fats or low-value fats) including crude palm oil usually have high content of free fatty acid. Likewise, the soap formation can also be avoided by using an acid catalyst. In addition, the free fatty acid can produce fatty acid methyl ester from esterification by acid catalyst which increases the biodiesel yield.

Short-chain alcohols such as methanol, ethanol, and butanol are the most frequently employed. Although the use of different alcohols presents some differences with regard to the reaction kinetics, the final yield of esters remains more or less inalterable. Therefore, selection of the alcohol is based on cost and performance consideration. Ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols. Also, ethanol, as extraction solvent, is preferable to methanol because of its much higher dissolving power for oils. For this cause, ethanol is often used as an appropriate alcohol for the transesterification of vegetables oils. Therefore, producing ethyl esters rather than methyl esters is of considerable interest, because, in addition to the entirely agricultural nature of the ethanol, the extra carbon atom brought by the ethanol molecule slightly increases the heat content and the cetane number.

The general heating system for biodiesel production uses heating coils to heat the raw material but this method consumes high energy. Recently, Mazzocchoia et al., (2004) reported the use of microwave heating as a short reaction times, a short separation time and reduced energy consumption to produced biodiesel and good conversions. Using microwave for preparative chemistry, it is often possible to accelerate the rate of reactions and selectivity.

Therefore it was possible to prepare biodiesel rapidly and in good conversions by microwave heating.

Wastewater from biodiesel production constitutes soap, alcohol, glycerol and oil, so the treatment of biodiesel wastewater is necessary. However, treatment procedures for biodiesel wastewater are not described in the instruction manual because the treatment is very difficult. In refine crude vegetable oil production, is a commonly used adsorbent due to its high absorption capacity for de-colored vegetable oils, adsorb the toxins pesticide remains, remove soap in vegetable oils and remove glycerin in biodiesel. To avoid the biodiesel wastewater, bleaching earth was used in cleaning step for decrease quantity of waste water [Kheang et al., 1983].

The goal of this research is to develop the methods of biodiesel production from crude palm oil which has free fatty acid more than 2% for raw material and ethanol for the alcohol is studied. Include using the microwave in biodiesel process and apply bleaching earth in cleaning step for decrease quantity of waste water which enhance the possibility to produce biodiesel.

1.2 Theoretical Background

1.2.1 Crude palm oil (CPO)

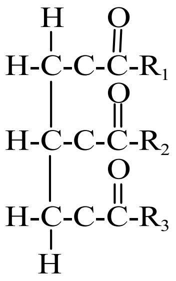
Thailand is the fourth biggest palm oil producer, with a 2.9% market share after Malaysia (43.7%), Indonesia (37.1%), and Nigeria (5%). In 2005, the total area under oil palm cultivation in Thailand was 324,160 hectares providing palm fruitlets yield of 5,003,000 tones, which is 15,434 kg/ha on average. The average yearly price per ton of oil palm fruitlets in 2007 was 4500 baht, giving a farming value of 22,513.5 million baht [Thamsiriroj, 2007].

Palm oil is extracted from the mesocarp of the fruit of the palm *Elaeis guineensis*. The mesocarp comprises about 70-80 %wt of the fruit and about 45-50 %wt of this mesocarp is oil. The rest of the fruit comprises the shell, kernel, moisture and other non fatty fiber. The extracted oil is known as CPO which until quite recently was known as the golden commodity.

CPO is deep orange red in color and is natural semi solid at room temperature with a melting point between 33 °C and 39 °C. It contains 40% oleic acid (monounsaturated fatty acid), 10% linoleic acid (polyunsaturated fatty acid), 45% palmitic acid and 5% stearic acid (saturated fatty acid). Pictures of oil palm fruitlets and crude palm oil are shown in Figure 1.1.

Figure 1.1 Oil palm fruitlets and crude palm oil

All vegetable oil and animal fats consist primarily of triglyceride molecules as shown schematically below.

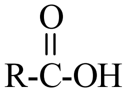


$$\begin{array}{cccccccc}
 & & H & & & & O & \\
 & & | & & & & \| & \\
H & - & C & - & C & - & C & -R_1 \\
 & & | & & & & O & \\
 & & | & & & & \| & \\
H & - & C & - & C & - & C & -R_2 \\
 & & | & & & & O & \\
 & & | & & & & \| & \\
H & - & C & - & C & - & C & -R_3 \\
 & & | & & & & & \\
 & & H & & & & &
\end{array}$$

Triglyceride

R_1, R_2, and R_3 represent the hydrocarbon chain of the fatty acid elements of the triglyceride. Note that there is a three-carbon chain called the glycerin backbone that runs along the left side of the molecule. Extending away from this backbone are the three long fatty acid chains.

In their free form, the fatty acids have the configuration shown below.



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH$$

Fatty acid

R is a hydrocarbon chain of greater than 10 carbon atoms.

Fatty acids are designated by two numbers: the first number denotes the total number of carbon atoms in the fatty acid and the second is the number of double bonds. For example, 18:1 designates oleic acid which has 18 carbon atoms and one double bond. Table 1.1 shows the structure and formula of fatty acid and table 1.2 shows the fatty acid compositions of a common vegetable oils.

Table 1.1 The structure and formula of fatty acid

Fatty acid	Systematic name	Structure	Formula	Molecular weight
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$	228
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$	256
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$	284
Oleic	Cis-9- Octadecanoic	18:1	$C_{18}H_{44}O_2$	320
Linoleic	Cis-9, cis-12-Octadecanoic	18:2	$C_{18}H_{32}O_2$	280
Linolenic	Cis-9, cis-12, cis-15 Octadecanoic	18:3	$C_{18}H_{30}O_2$	278
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$	312
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$	340
Erucic	Cis-13- Docosanoic	22:1	$C_{22}H_{42}O_2$	338
Ligoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$	368

From table 1.2 shows the compositions of fatty acid in a common vegetable oils found that the major compositions of fatty acid in palm oil were 40-48 %wt of palmitic acid and 37-46 %wt of Oleic acid. The major compositions of fatty acid in soybean oil were 52-56 %wt of linoleic acid and 20-26 %wt of oleic acid. The major compositions of fatty acid in sunflower seed oil were 67-74 %wt of linoleic acid and 17-22 %wt of oleic acid. The effect of fatty acid composition on the fuel properties are shown in table 1.3.

Table 1.2 Compositions of vegetable oils

%wt fatty acid / Oil	14:0	16:0	18:0	18:1	18:2	18:3
Corn oil	0.5-2	10-12	2-4.5	25-26	59-62	1
Cottonseed		22-28	1-2	13-15	58-59	0.5
Linseed oil		4-5	9-16	14-20	15-25	59-63
Palm oil	1-2	40-48	4-5	37-46	9-11	0.3
Peanut oil		9-11	2-3	41-49	31-32	0.5-1
Rapeseed oil		3-5	1-2	55-65	20-26	8-10
Soybean oil		11-12	3-5	23-25	52-56	6-8
Sunflower seed oil		6	3-5	17-22	67-74	

Source: Mittelbach and Remschmidt (2004)

1.2.2 Derivatives of triglycerides (vegetable oils) as diesel fuels

The alternative diesel fuels must be technically and environmentally acceptable, and economically competitive. From the viewpoint of these requirements, triglycerides (vegetable oils/animal fats) and their derivatives may be considered as viable alternatives for diesel fuels. The problems with substituting triglycerides for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character. The problems have been mitigated by developing vegetable oil derivatives that approximate the properties and performance and make them compatible with the hydrocarbon-based diesel fuels through.

Table 1.3 The fuel properties of vegetable oils

The fuel properties Oil	Kinematic Viscosity at $38^{\circ}C$ (mm^2/s)	Heating value (°C)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Corn oil	34.9	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	39.5	1.7	-15.0	234	0.9148
Linseed oil	27.2	39.3	1.7	-15.0	241	0.9236
Palm oil	39.6	-	31.0	-	267	0.9180
Peanut oil	39.6	39.8	12.8	-6.7	271	0.9026
Rapeseed oil	37.0	39.7	-3.9	-31.7	246	0.9115
Soybean oil	32.6	39.6	-3.9	-12.2	254	0.9138
Sunflower seed oil	33.9	39.6	7.2	-15.0	274	0.9161

Source: Barnwal and Sharma (2005)

1.2.2.1 Transesterification

Transesterification also called alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis. This process has been widely used to reduce the viscosity of triglycerides. Transesterification reaction is represented by the general equation (Figure 1.2)

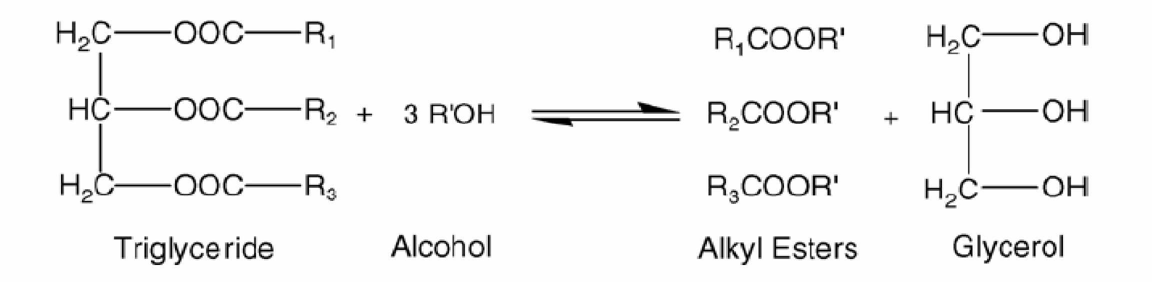


Figure 1.2 Transesterification reaction of triglyceride and alcohol

Triglycerides are readily transesterified in the presence of alkaline catalyst at atmospheric pressure and at a temperature of approximately 60°C to 70°C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower glycerin layer is drawn off while the upper methyl ester layer is washed to remove entrained glycerol and is then processed further. The excess methanol is recovered by distillation and sent to a rectifying column for purification and recycled. Transesterification works well when the starting oil is of high quality. However, quite often low quality oils are used as raw materials for biodiesel preparation. In cases where the free fatty acid content of the oil is above 1%, difficulties arise due to the formation of soap which promoted emulsification during the water washing stage and at an FFA content above 2% the process becomes unworkable. [Marchetti et al., 2007]

1) Alkali Catalyst: For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol as well as any kind of oils, refine, crude or frying. The alcohol : oil molar ratio that should be used varies from 1:1–6:1. However alcohol : oil molar ratio = 6:1 is the most used ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol. The types of alcohol are usually methanol and ethanol. The last one has fewer safety problems because it is less toxic.

The amount of catalyst that should be added to the reactor varies from 0.5% to 1 %wt. Normal amount of free fatty acid on the waste cooking oils is about 2 %wt. If the oils have an amount of free fatty acid, the oil should be a pretreatment via esterification with alcohol but with sulfuric acid. After this, we have to continue with the normal alkali process.

2) Acid catalyst: This way of production is the second conventional way of making the biodiesel. The idea is to use the triglycerides with alcohol and instead of a base to use an acid the most commonly used is sulfuric acid. This type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost always more than one day to finished. The possible operation condition is, usually, molar ratio 30:1. The type of alcohol, as well as the oils, is the same as the one that can be used in alkali catalyst reaction. The amount of catalyst supposed to be added to the reactor varies from 0.5 to 1 mol%. The temperature range varies from 55 to 80 ^{o}C. The acid transesterification is a great way to make biodiesel if the sample has relatively high free fatty acid content. In general, a 1 mol% of sulfuric acid is a good amount for a final conversion of 99% in a time around 50 h.

3) Lipase as catalyst: Lipases are enzymes used to catalyze some reaction such as hydrolysis of glycerin, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for transesterification and esterification reactions too. Biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure are the desired properties in agricultural and medical applications. The extra cellular and the intracellular lipases are also able to catalyze the transesterification of triglycerides effectively.

The advantages of using lipases

1. Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if you keep the reactive flow.
2. Use of enzymes in reactors allows use of high concentration of them and that makes for a longer activation of the lipases.
3. A bigger thermal stability of the enzyme due to the native state.
4. Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all the enzyme particles getting together.
5. Separation of product will be easier using this catalyst.

The disadvantages of using lipase.

1. You can lose some initial activity due to volume of the oil molecule.
2. Number of support enzyme is not uniform
3. Biocatalyst is more expensive that the natural enzyme.

4) Supercritical alcohols: Although this is a new topic becoming and more relevant there is an uncertainty regarding whether transesterification or alkyl esterification is a better way of production and which one has a faster reaction rate.

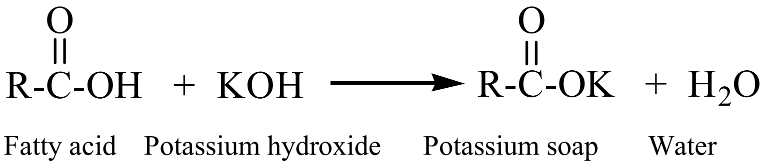
A summary of the advantages and disadvantages of each technological possibility to produce biodiesel could be found in table 1.4.

Table 1.4 Comparison of the different technologies to produce biodiesel

Variable	Alkali catalyst	Acid catalyst	Lipase Catalyst	Supercritical
Reaction temperature (^{o}C)	60-70	55-80	30-40	239-385
FFA in raw materials	Saponification	Ester	Ester	Ester
Water in raw materials	Interference with reaction	Interference with reaction	No influence	No influence
Yield of methyl ester	Normal	Normal	Higher	Good
Purification of ester	Washing	Washing	-	-
Recovery of glycerol	Difficult	Difficult	Easy	-
Production cost	Cheap	Cheap	Expensive	Medium

1.2.2.2 Esterification

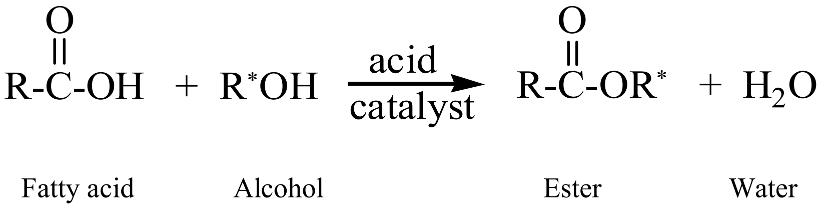
Esterification is required if the oil or fat contains more than 2 %wt of FFA. Used cooking oils typically contain 2–7 %wt of FFA and animal fats contain 5–30 %wt of FFA. Some very low-quality feedstocks, such as trap grease, can approach 100 %wt of FFA. When an alkali catalyst is added to these feedstocks, the FFA react with the catalyst to form soap and water as shown in figure 1.3.



$$\mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH} + \mathrm{KOH} \longrightarrow \mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OK} + \mathrm{H_2O}$$

Figure 1.3 Saponification reaction of fatty acid and potassium hydroxide

Up to ~2 %wt of FFA, the reaction can still be catalyzed with an alkali catalyst, but additional catalyst must be added to compensate for that lost to soap. The soap created during the reaction is either removed with the glycerin or washed out during the water wash. When the FFA level is >2 %wt, the soap inhibits separation of the glycerin from the esters and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterified the FFA to esters as shown in figure 1.4.



$$\mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH} + \mathrm{R^{*}OH} \xrightarrow[\text{catalyst}]{\text{acid}} \mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR^{*}} + \mathrm{H_2O}$$

Figure 1.4 Esterification reaction of fatty acid and alcohol

This reaction can be used as a pretreatment to convert the FFA to esters, there by reducing the FFA level. Then, the low-FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to esters.

The factors which effect on transesterification and esterification reaction

1) Moisture and FFA: The vegetable oils and fats used as a feedstock for the biodiesel production should be water-free because the presence of water has negative effects on the transesterification and esterification reaction [Kusdiana and Saka, 2004]. The presence of water has more negative effect than that of FFA. It consumes a catalyst and reduces its efficiency, so the raw material should consist of water content below 0.06% [Ma et al., 1998].

Kusdiana and Saka (2004) studied effects of water on biodiesel fuel production. It was found that the conversion for the alkaline-catalyzed transesterification was slightly reduced when more water was added. However, in the acid-catalyzed esterification, the conversion was significantly reduced to 6% when only 5% water was added. Moreover, both acid- and alkaline-catalyzed methods resulted in a lower conversion when the FFA content increased in the reaction. The alkaline-catalyzed method with 20% FFA provided only 35% of methyl ester, as the conversion of the acid-catalyzed method reduced to about a half.

The high content of FFA in vegetable oil deactivates alkaline catalyst and the addition of an excessive amount of alkaline as compensation gives rise to the formation of emulsion. Thus leading to the problems associated with glycerin separation and the loss in the yield of methyl ester.

2) Molar ratio of alcohol to oil: The conversion efficiency and biodiesel production cost depend on significant factors. One of the significant factors is the molar ratio of alcohol to oil. Commonly used short chain alcohols are methanol, ethanol, propanol and butanol. However, the methanol is used commercially because of its low price. Molar ratio is the number of moles of alcohol to number of moles of glycerides in the oil. Theoretically, transesterification reaction requires three moles of alcohol for each mole of oil. But in practice greater ester product can be obtained when a higher molar ratio is employed to drive the reaction towards completion [Ramadhas et al., 2005].

Ghadge and Raheman (2005) studied the effect of methanol quantity on the reduction of FFA content of mahua oil. It was found that the optimum molar ratio of methanol to oil was 7.68:1 for reducing the acid level to less than 1% as using sulfuric acid catalyst. After the pretreatment of mahua oil, transesterification reaction was carried out with 6:1, the optimum molar ratio of methanol to oil as using potassium hydroxide catalyst.

3) Reaction temperature: Transesterification and esterification could occur at different temperatures, depending on the oil used. The transesterification of refined soybean oil with methanol using 1 %wt of NaOH, 6:1 molar ratio of methanol to oil was studied by [Ma and Hanna, 1999]. It obtained 94, 87 and 64 %wt of ester yield at 60, 45 and 32°C, respectively, after 0.1 h. Biodiesel production from high FFA rubber seed oil obtained the maximum ester yield at the temperature of 45±5°C. When the reaction temperature went above 50°C, the yield decreased. However, using refined linseed oil and brassica carinata oil achieved better results at temperatures above 50°C and up to 70°C [Agarwal and Das, 2001 and Pilar et al., 2004]. In the case of rubber seed oil, temperatures greater than 60°C should be avoided because they tend to accelerate saponification of the glycerides by the alkaline catalyst before completion of the alcoholysis [Ramadhas et al., 2005].

4) Reaction time: The rate of reaction was influenced by time. The ester yield increased with the increase in reaction time. Biodiesel production from high FFA rubber seed oil was obtained after 30 minutes of a sufficient reaction time for the completion of the esterification [Ramadhas et al., 2005].

The high FFA level of mahua oil was reduced to less than 1% by a two-step pretreatment process. With each step it was found that the reaction progressed rapidly during the first 1 h with 0.30-0.35% v/v methanol to oil and 1% v/v sulfuric acid catalyst at 60°C. The reduction in acid value was over 50% at low-methanol and over 80% for high-methanol ratios. There was no significant reduction in the acid value after 1 h. This might be because the effect of water produced during the esterification of FFA, which prevented further reaction [Ghadge and Raheman, 2005].

5) Catalysts: A commercial biodiesel production used an alkali-catalyzed process for the transesterification process. Other approaches had been proposed including acid catalysis [Canakci. and Gerpan, 1999] and enzymes [Nelson et al., 1996]. The acid catalysts were useful for pretreatment high FFA feedstocks but the rate of reaction for converting triglycerides to ester were very slow. Enzymes had shown good tolerance for the FFA level of the feedstock, but the enzymes were expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification.

Homogeneous catalysts were taxing on equipment and at a raised temperature severely affected any metallic components. Although, acid-catalyzed reactions were slower than basic ones, they had potential if they could be immobilized. Problems with saponification were not present when esterification occurred and acid catalysts were not affected by FFA's [Khan, 2002]. Catalytic activities were related to the Lewis acid strength of the metal, which must have an optimum intermediate value, and to the molecular structure of the anion. The best catalyst was lead acetate, $Pb(Ac_2)$, for experiments which were made with the addition of water and FFA to soybean oil (7.4 %wt of FFA to oil). It obtained 96 %wt of methyl ester yields and less than 1% final FFA concentration, at 210-220°C in 200 minutes reaction time by using 0.0004:1 of a weight ratio of catalyst to oil [Di Serio, 2005]. However, the best commercial acid catalyst for promoting both esterification and transesterification processes was sulfuric acid. It had the advantages of using a lower molar methanol to oil ratio and did not necessitate a heavy neutralization process of the acid catalyst [Zhang et al., 2003].

Heterogeneous catalysts were important to the developments of biodiesel production, combined with their application in a continuous process and easy separation. They could decrease the production costs. Problems with water had not been fully addressed [Khan, 2002]. Tungstated zirconia-alumina (WZA) was a promising solid acid catalyst for the biodiesel production from soybean oil. Catalysts should be active enough for the esterification of FFA, a source of soap. The acid strength of WZA was suitable for both esterification and transesterification. It obtained over 90% conversions for both of the reactions of soybean oil with methanol at 175-200°C in 20 h [Furuta, et al., 2004].

In conclusion, the parameters affecting the methyl ester formation are water content, FFA content, molar ratio, reaction temperature and time. It was observed that increasing the reaction temperature had a favorable influence on the yield of ester conversion. The yield of alkyl ester increased with increasing the molar ratio of oil to alcohol. Water content is an important factor in the conventional catalytic transesterification of vegetable oil. In the conventional transesterification of fats and vegetables for biodiesel production, FFA and water always produce negative effects since the presence of FFA and water causes soap formation, consumes catalyst and reduces catalyst effectiveness. The presence of water has negative effects on the yield of methyl ester [Demirbas, 2006].

1.2.3 Alcohol

Short-chain alcohols such as methanol and ethanol are the most frequently employed. Although the use of different alcohols presents some differences with regard to the reaction kinetics, the final yield of esters remains more or less inalterable. Therefore, selection of the alcohol is based on cost and performance consideration.

1.2.3.1 Methanol

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical compound with chemical formula CH_3OH. It is the simplest alcohol, and is a light, volatile, colorless, flammable, poisonous liquid with a distinctive odor that is somewhat milder and sweeter than ethanol (ethyl alcohol). It is used as an antifreeze, solvent, fuel, and as a denaturant for ethyl alcohol Because of its poisonous properties, methanol is frequently used as a denaturant additive for ethanol manufactured for industrial uses this addition of a poison economically exempts industrial ethanol from the rather significant 'liquor' taxes that would otherwise be levied as it is the essence of all potable alcoholic beverages.

1.2.3.2 Ethanol

Ethanol, also known as ethyl alcohol, drinking alcohol or grain alcohol, is a flammable, colorless, slightly toxic chemical compound with a distinctive perfume-like odor, and is best known as the alcohol found in alcoholic beverages. In common usage, it is often referred to simply as alcohol. Its molecular formula is variously represented as EtOH, CH_3CH_2OH, C_2H_5OH or as its empirical formula C_2H_6O. Ethanol's hydroxyl group is able to participate in hydrogen bonding. At the molecular level, liquid ethanol consists of hydrogen-bonded pairs of ethanol molecules; this phenomenon renders ethanol more viscous and less volatile than less polar organic compounds of similar molecular weight. Ethanol, like most short-chain alcohols, is flammable, colorless, has a strong odor, and is volatile. Furthermore, ethanol is used as a solvent in dissolving medicines, food flavorings and colorings that do not dissolve easily in water. Once the non-polar material is dissolved in the ethanol, water can be added to prepare a solution that is mostly water. The ethanol molecule has a hydrophilic -OH group that helps it dissolve polar molecules and ionic substances. The short, hydrophobic hydrocarbon chain can attract non-polar molecules. Thus ethanol can dissolve both polar and non-polar substances.

Table 1.5 Properties of alcohol in biodiesel production

Properties	Methanol	Ethanol
Molecular formula	CH_3OH	C_2H_5OH
Molecular weight (g/mol)	32.04	46.06
Density (g/cm^3)	0.7918	0.789
Melting point (°C)	-97	-114.3
Boiling point (°C)	64.7	78.4
Acidity (pK_a) (H^+ from OH group)	15.5	15.9
Viscosity (mPa·s at 20 °C)	0.59	1.20
Flash point (°C)	11	13

Methyl and ethyl esters of fatty acids are the most popular esters used as biodiesel. The methods of preparation of methyl and ethyl esters have their own advantages and disadvantages. In the case of methanolysis the solubility of oil in methanol is less and reaction is mass transfer limited. On the other hand, methanol makes higher equilibrium conversion due to higher reactive intermediate methoxide. Unlike methanol, ethanol has better solvent properties and can be obtained from renewable resources. But the formation of emulsion after the transesterification of oil with ethanol makes the separation of ester very difficult. [Issariyakul et al., 2007]

Meher et al., (2006) studied effect of molar ratio of alcohol and type of alcohol to produce biodiesel. One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerin. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters. The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters. The emulsions are caused in part by formation of the intermediates monoglycerides and diglycerides, which have both polar hydroxyl groups and non-polar hydrocarbon chains. These intermediates are strong surface active agents. In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide is dissolved in polar alcohol phase, in which triglycerides must transfer in order to react. The reaction is initially mass-transfer controlled and does not conform to expected homogeneous kinetics. When the concentrations of these intermediates reach a critical level, emulsions form. The larger non-polar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, the concentration of mono glycerides and diglycerides are very low, then the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of monoglycerides and diglycerides.

Issariyakul et al., (2007) studied transesterification of waste fryer grease which contain 5–6 %wt of FFA with methanol, ethanol, and mixtures of methanol/ethanol maintaining the oil to alcohol molar ratio of 1:6 and KOH as a catalyst. Found that Mixtures of methanol and ethanol were used for transesterification in order to use the better solvent property of ethanol and rapid equilibrium using methanol. Two-stage (acid and alkali catalyzed) method was used in biodiesel synthesis for solve formation of soap problem which instigated difficulty in the separation of glycerin from biodiesel. More than 90% ester was obtained when two-stage method was used compared to 50% ester in single stage alkaline catalyst.

1.2.4 Microwave irradiation

Microwave irradiation is electromagnetic irradiation in the frequency range 0.3 to 300 GHz, corresponding to wavelengths of 1 mm to 1 m. The microwave region of the electromagnetic spectrum (Figure 1.5) therefore lies between infrared and radio frequencies. The major use of microwaves is either for transmission of information (telecommunication) or for transmission of energy. Wavelengths between 1 and 25 cm are extensively used for radar transmissions and the remaining wavelength range is used for telecommunications. All domestic kitchen microwave ovens and all dedicated microwave reactors for chemical synthesis that are commercially available today operate at a frequency of 2.45 GHz (corresponding to a wavelength of 12.25 cm) in order to avoid interference with telecommunication, wireless networks and cellular phone frequencies. There are other frequency allocations for microwave heating applications, but these are not generally employed in dedicated reactors for synthetic chemistry.

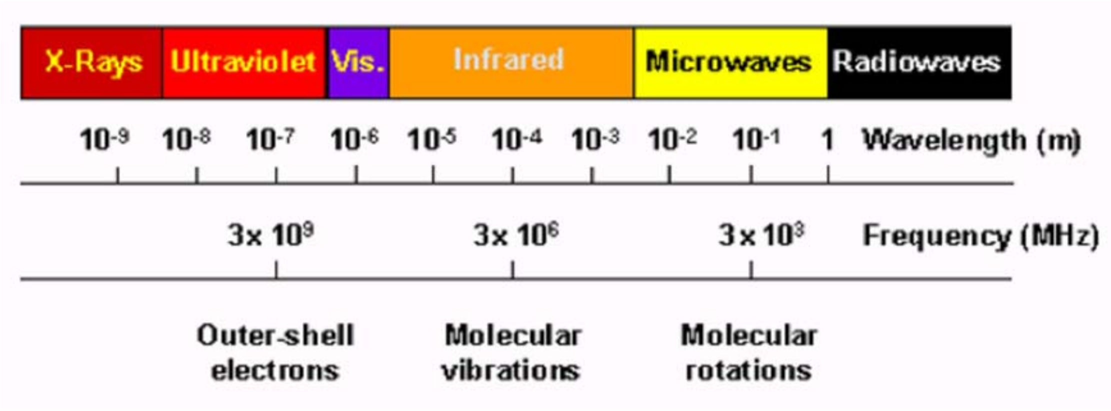


Figure 1.5 The electromagnetic spectrum and the microwave range. The most commonly used frequency is 2.45GHz with a wavelength of 12.2 cm

1.2.4.1 Microwave Dielectric Heating

Microwave chemistry is based on the efficient heating of materials by microwave dielectric heating effects. Microwave dielectric heating is dependent on the ability of a specific material (e.g. a solvent or reagent) to absorb microwave energy and convert it into heat. Microwaves are electromagnetic waves which consist of an electric and a magnetic field component (Figure 1.6). For most practical purposes related to microwave synthesis it is the electric component of the electromagnetic field that is of importance for wave material interactions, although in some instances magnetic field interactions (e.g. with transition metal oxides) can also be of relevance.

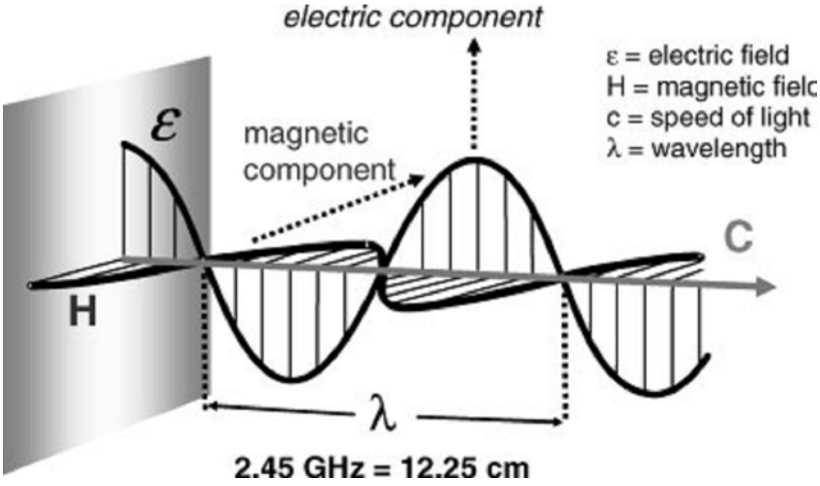


Figure 1.6 Electric and magnetic field components in microwaves

The electric component of an electromagnetic field causes heating by two main mechanisms: dipolar polarization and ionic conduction. The interaction of the electric field component with the matrix is called the dipolar polarization mechanism (Figure 1.7a) [Baghurst et al., 1991 and Gabriel et al., 1998]. For a substance to be able to generate heat when irradiated with microwaves it must possess a dipole moment. When exposed to microwave frequencies, the dipoles of the sample align in the applied electric field. As the field oscillates, the dipole field attempts to realign itself with the alternating electric field and, in the process, energy in the form of heat is lost through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself with the frequency of the applied field. If the dipole does not have enough time to realign (high frequency irradiation) or reorients too quickly (low frequency irradiation) with the applied field, no heating occurs. The allocated frequency of 2.45 GHz, used in all commercial systems, lies between these two extremes and gives the molecular dipole time to align in the field but not to follow the alternating field precisely. Therefore, as the dipole reorients to align itself with the electric field, the field is already changing and generates a phase difference between the orientation of the field and that of the dipole. This phase difference causes energy to be lost from the dipole by molecular friction and collisions, giving rise to dielectric heating. In summary, field energy is transferred to the medium and electrical energy is converted into kinetic or thermal energy, and ultimately into heat. It should be emphasized that the interaction between microwave radiation and the polar solvent, which occurs when the frequency of the radiation approximately matches the frequency of the rotational relaxation process, is not a quantum mechanical resonance phenomenon. Transitions between quantized rotational bands are not involved and the energy transfer is not a property of a specificmolecule but the result of a collective phenomenon involving the bulk [Baghurst et al., 1991 and Gabriel et al., 1998]. The heat is generated by frictional forces occurring between the polar molecules whose rotational velocity has been increased by the coupling with the microwave irradiation. It should also be noted that gases cannot be heated under microwave irradiation since the distance between the rotating molecules is too far. Similarly, ice is also (nearly) microwave transparent, since the water dipoles are constrained in a crystal lattice and cannot move as freely as in the liquid state.

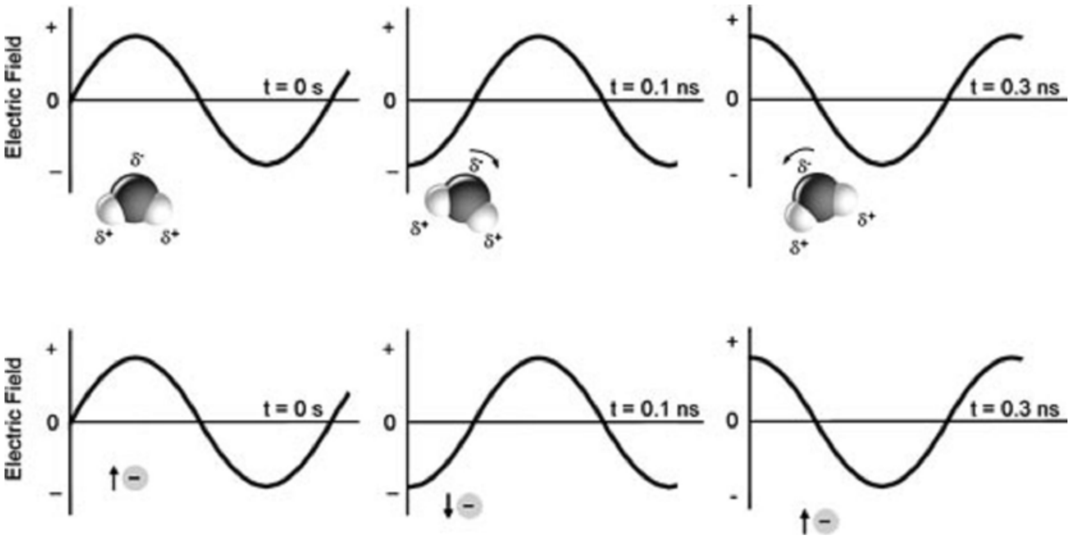


Figure 1.7 (a) Dipolar polarization mechanism. Dipolar molecules try to align with an oscillating electric field. (b) Ionic conduction mechanism. Ions in solution will move in the electric field

The second major heating mechanism is the ionic conduction mechanism (Figure 1.7b) [Baghurst et al., 1991 and Gabriel et al., 1998]. During ionic conduction, as the dissolved charged particles in a sample (usually ions) oscillate back and forth under the influence of the microwave field, they collide with their neighboring molecules or atoms. These collisions cause agitation or motion, creating heat. Thus, if two samples containing equal amounts of distilled water and tap water, respectively, are heated by microwave irradiation at a fixed radiation power, more rapid heating will occur for the tap water sample due to its ionic content. Such ionic conduction effects are particularly important when considering the heating behavior of ionic liquids in a microwave field. The conductivity principle is a much stronger effect than the dipolar rotation mechanism with regard to the heat-generating capacity. A related heating mechanism exists for strongly conducting or semiconducting materials such as metals, where microwave irradiation can induce a flow of electrons on the surface. This flow of electrons can heat the material through resistance (ohmic) heating mechanisms [Glasnov et al., 2008]. In the context of organic synthesis this becomes important for heating strongly microwave absorbing materials, such as thin metal films (Pd, Au), graphite supports or so-called passive heating elements made out of silicon carbide.

1.2.4.2 Dielectric Properties

The heating characteristics of a particular material (e.g. a solvent) under microwave irradiation conditions are dependent on the dielectric properties of the material. The ability of a specific substance to convert electromagnetic energy into heat at a given frequency and temperature is determined by the so-called loss tangent, tanδ. The loss factor is expressed as the quotient, $\tan\delta = \varepsilon'/\varepsilon''$, where ε'' is the dielectric loss, indicative of the efficiency with which electromagnetic radiation is converted into heat, and ε' is the dielectric constant describing the polarizability of molecules in the electric field. A reaction medium with a high tanδ is required for efficient absorption and, consequently, for rapid heating. Materials with a high dielectric constant, such as water (ε' at 25^{o}C = 80.4), may not necessarily also have a high tan d value. In fact, ethanol has a significantly lower dielectric constant (ε' at 25^{o}C = 24.3) but heats much more rapidly than water in a microwave field due to its higher loss tangent (tanδ: ethanol = 0.941, water = 0.123). The loss tangents for some common organic solvents are summarized in table 1.6. In general, solvents can be classified as high (tanδ >0.5), medium (tanδ 0.1–0.5), and low microwave absorbing (tanδ <0.1). Other common solvents without a permanent dipole moment, such as carbon tetrachloride, benzene and dioxane, are more or less microwave transparent. It has to be emphasized that a low tanδ value does not preclude a particular solvent from being used in a microwave-heated reaction. Since either the substrates or some of the reagents/catalysts are likely to be polar, the overall dielectric properties of the reaction medium will, in most cases, allow sufficient heating by microwaves. Furthermore, polar additives (such as alcohols or ionic liquids) or passive heating elements can be added to otherwise low-absorbing reaction mixtures in order to increase the absorbance level of the medium.

1.2.4.3 The character of microwave irradiation

1.2.4.3.1 Reflection: Microwave irradiation affects with the equipment that is the metal or participate mix of the metal, they can not through the aforementioned equipment, thus a substance that add in the equipment that is the metal.

1.2.4.3.2 Transmission: Microwave irradiation can through the equipment with glass, paper, wood and plastic because the aforementioned equipments not have the compound of the metal, then the equipments are used well in the microwave irradiation.

1.2.4.3.3 Absorption: In the food compose molecule of water, which absorb microwave and it will disintegrate suddenly then give the hot food.

To heat a substance, the material must couple to the microwave. In other words, the substance must absorb electromagnetic energy. Generally speaking, two mechanisms are available.

Table 1.6 Loss tangents (tanδ) of different solvents (2.45 GHz, 20 ^{o}C, [Amore et al., 2006])

Solvent	tanδ	Solvent	tanδ
Ethylene glycol	1.350	N,N-dimethylformamide	0.161
Ethanol	0.941	1,2-dichloroethane	0.127
Dimethylsulfoxide	0.825	Water	0.123
2-propanol	0.799	Chlorobenzene	0.101
Formic acid	0.722	Chloroform	0.091
Methanol	0.659	Acetonitrile	0.062
Nitrobenzene	0.589	Ethyl acetate	0.059
1-butanol	0.571	Acetone	0.054
2-butanol	0.447	Tetrahydrofuran	0.047
1,2-dichlorobenzene	0.280	Dichloromethane	0.042
1-methyl-2-pyrrolidone	0.275	Toluene	0.040
Acetic acid	0.174	Hexane	0.020

1.2.4.4 Heating Mechanism of microwave: Energy in the form of microwaves can be transferred to substances that are present in the beam line of the microwave radiation. Absorption of the energy occurs when dipolar molecules rotate to align themselves with the fluctuating electric field component of the irradiation or when ions move back and forth by the same phenomena.

The energy-quantum of the microwave irradiation is totally inadequate for interacting directly with atom-atom bonds or for exciting specific molecules. When molecules rotate or move back and forth in a matrix they generate heat by friction. The amount of heat generated by a given reaction mixture is a complex function of its dielectric property, volume, geometry, concentration, viscosity and temperature. Thus, two samples irradiated at the same power level for the same period of time will most likely end up with rather different final temperatures.

Chemical reactions, performed using microwave, are rapid mainly because the reactions are performed at temperatures higher than their conventional counterparts. Quantitatively the relationship between the reaction rate and its temperature is determined by the Arrhenius Equation.

Arrhenius Equation: $K = A\,e^{-Ea/RT}$

where k is the rate coefficient

A is a constant, Ea is the activation energy

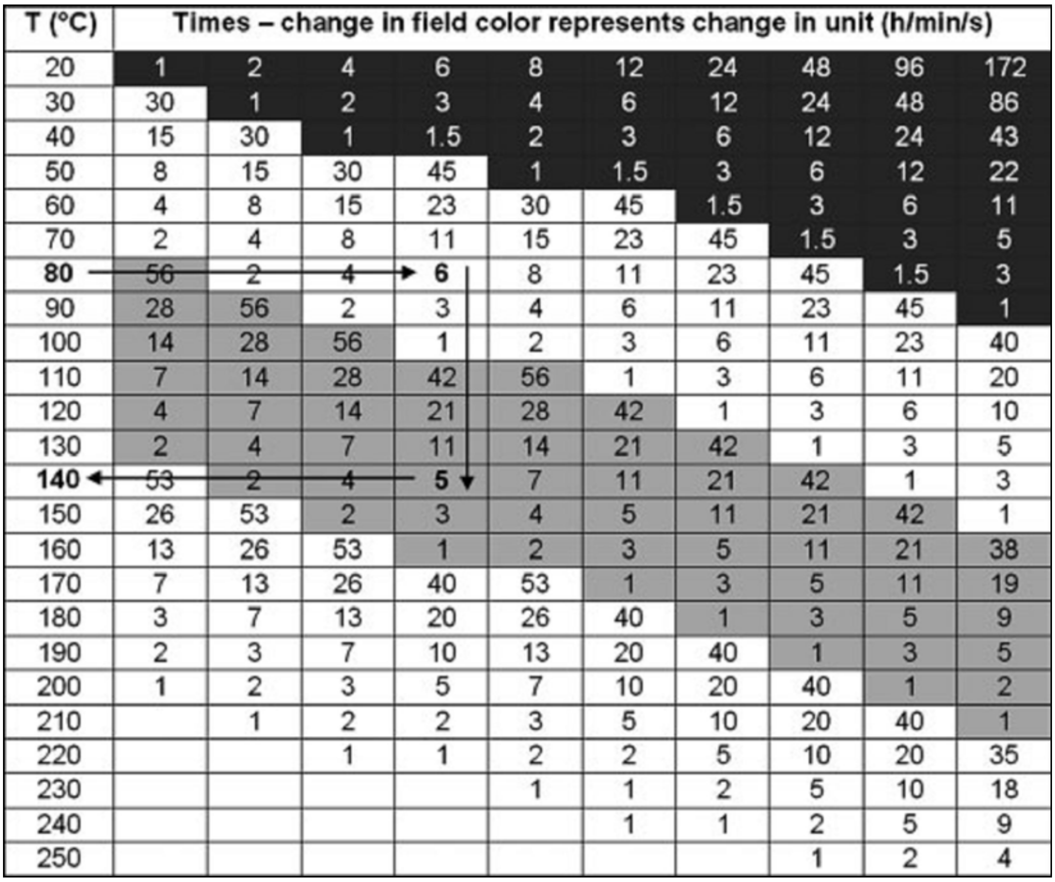
R is the universal gas constant (8.314×10^{-3} kJ $mol^{-1}K^{-1}$)

T is the temperature (in degrees Kelvin)

As a general rule of thumb, for every 10 °C that is added the reaction temperature the reaction rate doubles. At higher temperatures, the probability that two molecules will collide is higher. This higher collision rate results in a higher kinetic energy, which has an effect on the activation energy of the reaction. With this rule of thumb, many conventional protocols can be converted into effective microwave-mediated processes. The time-temperature prediction chart displayed in figure 1.8 is based on the Arrhenius equation and provides a way of estimating the time to run a reaction in different temperature regimes as reported in the literature or in databases. As an example, the time for a reaction can be reduced from 6 h to approximately 5 minutes by increasing the temperature from 80 to 140 °C (see arrows in figure 1.8).

Under some circumstances, the rapid rate of microwave heating can produce heat profiles that are not easily accessible using traditional heating techniques. In such cases experiments performed using microwave may well result in a different outcome to conventionally heated reactions, even if the final reaction temperature is the same.

Figure 1.8 Time–temperature prediction chart [www.biotagepathfinder.com]



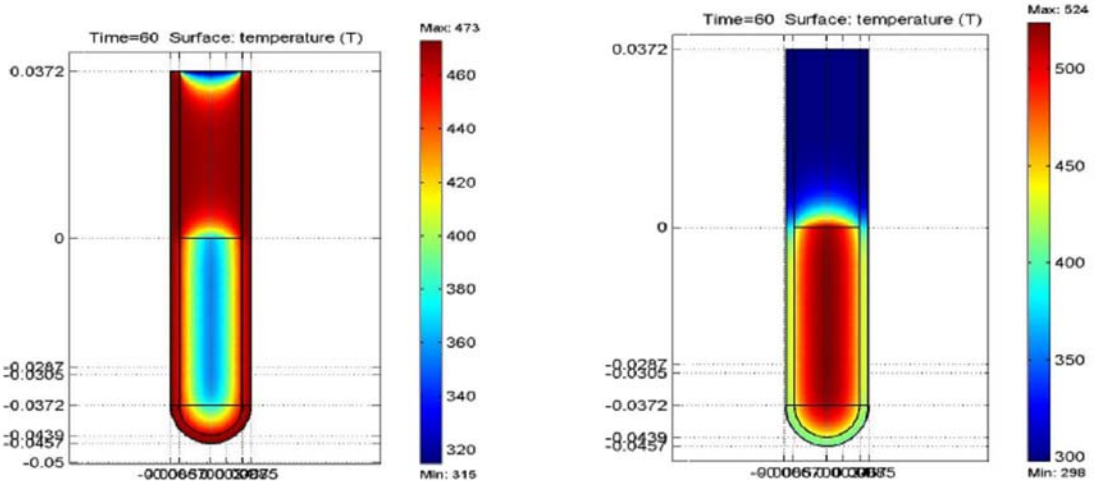
T (°C)	Times – change in field color represents change in unit (h/min/s)									
20	1	2	4	6	8	12	24	48	96	172
30	30	1	2	3	4	6	12	24	48	86
40	15	30	1	1.5	2	3	6	12	24	43
50	8	15	30	45	1	1.5	3	6	12	22
60	4	8	15	23	30	45	1.5	3	6	11
70	2	4	8	11	15	23	45	1.5	3	5
80	56	2	4	**6**	8	11	23	45	1.5	3
90	28	56	2	3	4	6	11	23	45	1
100	14	28	56	1	2	3	6	11	23	40
110	7	14	28	42	56	1	3	6	11	20
120	4	7	14	21	28	42	1	3	6	10
130	2	4	7	11	14	21	42	1	3	5
140	53	2	4	**5**	7	11	21	42	1	3
150	26	53	2	3	4	5	11	21	42	1
160	13	26	53	1	2	3	5	11	21	38
170	7	13	26	40	53	1	3	5	11	19
180	3	7	13	20	26	40	1	3	5	9
190	2	3	7	10	13	20	40	1	3	5
200	1	2	3	5	7	10	20	40	1	2
210		1	2	2	3	5	10	20	40	1
220			1	1	2	2	5	10	20	35
230					1	1	2	5	10	18
240						1	1	2	5	9
250								1	2	4

It is now well accepted that the major part of rate enhancements observed with microwave is strictly due to thermal effects even though the unique temperature profiles accessible by microwave radiation may result in novel outcomes. While the existence of a “specific microwave effect” cannot be completely ruled out, the effect appears to be a rarity and of marginal synthetic importance [www.biotage.com].

1.2.4.5. The advantages and the disadvantages of microwave irradiation

The advantages of microwave irradiation

- Traditionally, organic synthesis is carried out by conductive heating with an external heat source (e.g. an oil-bath or heating mantle). This is a comparatively slow and inefficient method for transferring energy into the system since it depends on convection currents and on the thermal conductivity of the various materials that must be penetrated, and generally results in the temperature of the reaction vessel being higher than that of the reaction mixture (Figure 1.9A). In contrast, microwave irradiation produces efficient internal heating (in core volumetric heating) by direct coupling of microwave energy with the molecules (solvents, reagents, catalysts) that are present in the reaction mixture. Microwave irradiation, therefore, raises the temperature of the whole volume simultaneously (bulk heating) whereas in the conventionally heated vessel, the reaction mixture in contact with the vessel wall is heated first (Figure 1.9B).



A B

Figure 1.9 Heating a vessel in an oil bath (A) and using microwaves (B)

- Microwaves generate higher power densities, enabling increased production speeds and decreased production costs.

- Microwave systems are more compact, requiring a smaller equipment space or footprint.

- Microwave energy is precisely controllable and can be turned on and off instantly, eliminating the need for warm-up and cool-down.

- Lack of high temperature heating surfaces reduces product fouling in cylindrical microwave heaters. This increases production run times and reduces both cleaning times and chemical costs.

- The use of industrial microwave systems avoids combustible gaseous by-products, eliminating the need for environmental permits and improving working conditions.

The disadvantages of microwave irradiation.

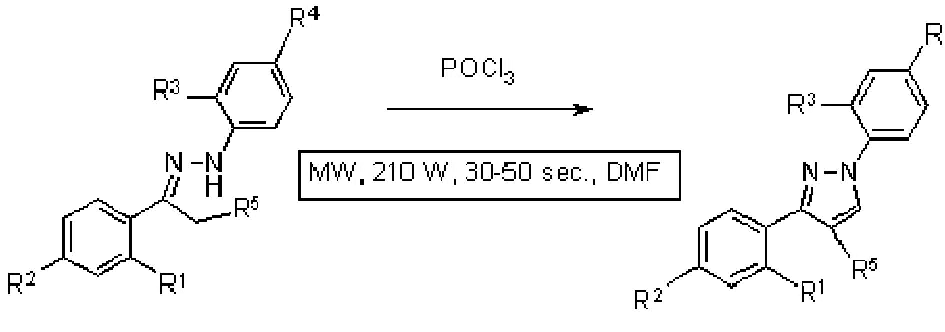
- The total cost of microwave processing equipment usually is greater than conventional equipment.

- Historically, the primary technological drawback to using microwave energy for industrial processing has been the inability to create uniform energy distribution. If uniform energy distribution is not present, wet regions of the target material are underexposed, and other regions are overexposed. This is analogous to the hot spots and cold spots generated in your microwave oven at home when heating or defrosting food likes a potato or frozen chicken. Severe overexposure of non-uniform energy distribution may provide excessive focus of heat build up resulting in burnt material or a fire hazard. The uniformity of distribution designed into IMS microwave equipment overcomes this problem.

- The depth of penetration achievable using microwave energy is a function of microwave frequency, dielectric properties of the material being heated and its temperature. As a general rule, the higher the frequency, the lower the depth of penetration.

- The uncontrolled heating of body tissue by microwaves is, once again, under intense discussion, particularly since the mobile phone revolution. Health risks occurring as a direct or indirect result of the electromagnetic radiation in this frequency range are feared. The first criterion for the evaluation of the health hazard caused by microwaves is the intensity or even radiation capacity of microwaves. Whilst microwaves with a frequency of 2.45 GHz and an intensity less than 100 mW cm^{-2} are used therapeutically for the local irradiation of body tissue, the same treatment for the entire body with the same intensity leads to a drastically increased risk of heart attack and arteriosclerosis after only a few minutes. This occurs as a result of excessive, direct heating of deeper tissues, which, as a result of their higher water content, heat up more rapidly than the upper skin layers, which have lower water content. However, the thermoreceptors are located here. These are responsible for adequate heat dissipation into the body interior. They are not sufficiently stimulated by microwaves and a delayed and inadequate temperature control results in the irradiated tissues. In Germany, a reference value of 0.2 mW cm^{-2} for exposure to microwave radiation applies to the general population. This value is exceeded by some mobile telephones with transmission capacities of 4 W cm^{-2} in some cases considerably. This is the reason why some scientists and experts describe them as health hazards. The microwave ovens available for private use however, are closed radiation sources. The metal casing with the perforated metal sheet on the door of the device, which makes it partially transparent, screens the surroundings from the microwave radiation to such a degree that the radiation is less than 5 mW cm^{-2} at a distance of 5 cm. The casing should not be modified by laymen as otherwise a radiation leak may occur. However, if you would rather convince yourself of the safety of your microwave oven, it is worth purchasing a microwave leak tester. These are usually available at low cost in electrical stores [Arnim Lühken and Hans Joachim Bader].

A Katritzky et al., (2003) studied production of heterocyclic by microwave. The heterocyclic ring formation and in other important reactions such as nucleophilic substitution, hetero-Diels Alder reactions etc. have been discussed and shown in figure 1.10-1.12. In comparison to conventional methods, microwave heating offers advantages such as reduced reaction times and temperatures, better yields, selectivity and reproducibility especially due to the advent of single-mode technology.



Microwave: 35-50 sec., 45-78%
Conventional: 4-5 h, 41-76%

R^1 = H, OH; R^2 = H, CH_3;
R^3 = H, NO_2; R^4 = NO_2;
R^5 = CH_3, C_2H_5

Figure 1.10 Preparation of pyrazoles from hydrazones

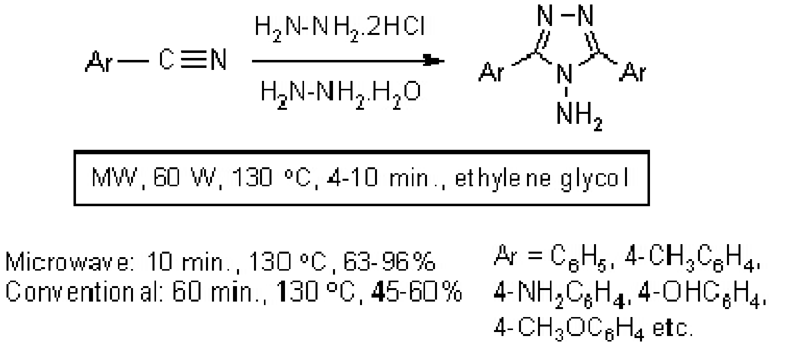


Figure 1.11 Preparation of 1,2,4–triazoles from aryl cyanides

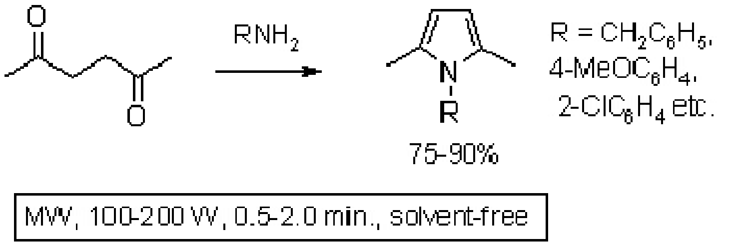


Figure 1.12 Preparation of 1 pyrroles from 4-diketones

Saifuddin et al., (2004) studied production of ethyl ester from used vegetable oil. The optimum conditions were 0.5% sodium hydroxide catalyst (dissolved in ethanol) based on weight of used vegetable oil and 100% excess of the stoichiometric amount of required anhydrous alcohol, extremely vigorous agitation with a little splashing until the reaction mixture (oil and ethanol) becomes thoroughly mixed, microwave irradiation of the mixture at 50% of its exit power of 750 W. The microwave irradiation of the reaction mixture inside a microwave oven greatly reduced the time required to achieve maximum conversion. The conventional process required 75 minutes, the microwave assisted process only required 4 minutes. During microwave irradiation, polar molecules such as alcohol align with the continuously changing magnetic field generated by microwaves. The changing electrical field that interacts with the molecular dipoles and charged ion, cause these molecules or ions to have rapid rotation and heat is generated due to friction of this motion. The increase in the reaction rate most probably is due to an elevated temperature at local reaction site: the catalytic surface. This is supposed to accelerate various chemical, biological and physical processes.

Michael et al., (2007) studied preparation of biodiesel using microwave. The method allows for the reaction to be run under atmospheric conditions and performed at flow rates of up to 7.2 L/minutes using a 4 L reaction vessel. It can be utilized with new or used vegetable oil with methanol and a 1:6 molar ratio of oil/alcohol. Energy consumption calculations suggest that the continuous-flow microwave methodology for the transesterification reaction is more energy-efficient than using a conventional heated apparatus.

Table 1.7 Energy consumption estimations for the preparation of biodiesel using conventional and microwave heating

Entry	reaction conditions	energy consumption (kJ/L) [a]
1	conventional heating [b]	94.3
2	microwave, continuous flow at 7.2 L/minutes	26.0
3	microwave, continuous flow at 2 L/minutes [c]	60.3 (92.3) [d]
4 [e]	microwave heating, 4.6 L batch reaction	90.1

a Normalized for energy consumed per liter of biodiesel prepared. *b* On the basis of values from the joint U.S. Department of Agriculture and U.S. Department of Energy 1998 study into the life cycle inventory of biodiesel and petroleum diesel for use in an urban bus. *c* Assuming a power consumption of 1700 W and a microwave input of 1045 W. *d* Assuming a power consumption of 2600 W and a microwave input of 1600 W. *e* Assuming a power consumption of 1300 W, a microwave input of 800 W, a time to reach 50 °C of 3.5 minutes, and a hold time at 50 °C of 1 minutes.

From the table 1.7 founded that microwave can be prepare biodiesel and the methodology offer fast, easy and low energy consumption. It is evident that, while the energy consumption of the batch process may be on the order of that of the conventional method, the continuous-flow processes are more energy efficient. The reaction is performed under atmospheric conditions and at flow rates up to 7.2 L/minutes using a 4 L reaction vessel. It can be utilized with new or used vegetable oil with methanol in a 1:6 molar ratio of oil/alcohol with, in our case, no observable differences in performance. Rudimentary energy consumption calculations suggest that the continuous-flow microwave methodology for the transesterification reaction is more energy-efficient than using a conventional heated apparatus.

1.2.5 Bleaching Earth

Bleaching earth or clay, sometimes called bentonite, is the adsorbent material that has been used most extensively. This substance consists primarily of hydrated aluminium silicate. In general, bleaching earth is a decolorizing agent, which will change the tint of any colored oil to a lighter shade by changing the basic color units in oil, without altering the chemical properties of the oil. Bleaching earths are normally used in the bleaching of vegetable oils and in the refining of mineral oils.

While some of these earths are naturally bleaching, some have to be treated with mineral acids. This activation results in the replacement of some of the aluminium ions by hydrogen ions from the acid. This result in the creation of net negative charges on the clay lattice structure and creates the cation adsorption properties of the acid-activated bleaching earth clays.

Acid activated bleaching earths (Figure 1.13) are in general produced from naturally occurring high-purity montmorillonite clays [Howes et al., 1991]. The structural features of the clay are modified by treatment with acid. During this process the physical structure and chemical composition are altered in a controlled way to maximize specific properties.

Figure 1.13 Bleaching Earths

Bleaching earth works based on its character of adsorption and ion exchange. The adsorption process is influenced by some factors as follow:

- Particle size
- Adsorbent polarity
- Surface area
- Pore volume
- Pore size

Bleaching earth as found in special strata and naturally active. This material is also used for bleaching. According to Rossi et al., (2003) they are excellent metal adsorbents as they are able;

1. To decrease the levels of chlorophyll and color bodies**.**
2. To remove soaps and phospholipids**.**
3. To minimizes free fatty acid increase during bleaching.

Spent bleaching earth (SBE) is an industrial waste, mainly generated from the edible oil processing. It is noted that SBE can present a fire hazard (i.e. spontaneous combustion), because it usually contains 20–40 %wt oil by weight. These oils retained and not removed by filter pressing may possess the pyrogenic nature due to the unsaturation. The waste is commonly disposed to landfill without any pretreatment. From the environmental, safe and regulatory points of view, it is urgent to restrict the landfill practice in the future. Based to the resource conservation and recovery, the utilization of this food processing waste has increased in recent years. Tsai et al., (2002) summarized some alternatives to landfill disposal. These include: (a) burning; (b) utilization in cementation furnaces; (c) utilization in brick industry; (d) soil improvement; (e) extraction for oil recovery; (f) regeneration; (g) utilization in biogas digesters; (h) utilization in water treatment plants; (i) addition to animal feed; and (j) addition to bitumen products.

Kojima et al., (2004) studied preparation methyl ester from waste bleaching earth discarded by the crude oil refining industry. The optimum condition for methyl ester production was C. Cylindracea lipase 10 %wt of waste bleaching earth, diesel as a solvent 60 %wt of waste bleaching earth, molar ratio of oil to methanol 1:4 and reaction temperature 37 $^{\circ}$C with mixing at 250 rpm. At 3 hr of reaction time was sufficient to obtain a yield of approximately 100% of oil from bleaching earth.

Ong (1983) studied recovery oil from spent bleaching earth. The method for oil recovery were blowing steam through the cake in the filter, circulating hot water through the cake in the filter, circulating hexane through the cake in the filter, hexane extraction of the cake after removal from the filter and boiling the cake in water containing soda and salt. Ong found that blowing steam and circulating hot water through the cake reduced its oil content to only 25 % and 20 %, respectively. Hexane extraction of spent bleaching earth is economically feasible for expensive and relatively stable oils only. Because of its simplicity and low cost, extraction with an aqueous solution of soda and salt is economically feasible. Extracted bleaching earth was used in cement manufacture, as a source of silicium dioxide, or mixing with sandy oils.

1.2.6 Parameters applicable to biodiesel and fossil diesel fuel [Mittelbach and Remschmidt, 2004]

1.2.6.1 Ester content

EN 14214 defines a minimum percentage of 96.5 %wt of ester for biodiesel fuels. This parameter is an important tool for proving the illegal admixture of other substances, such as fossil diesel, to the final fuel product. Low value for pure biodiesel sample originate from inappropriate reaction conditions, may in the some cases be caused by the respective standardized analytical procedure, stem from various minor components within the original fat or oil source. So a high concentration of unsaponifiable matter, residual alcohol, partial glycerides and unseparated glycerin can lead to value below the limit. The standardized procedure for the determination of ester contents in biodiesel fuel, also several other methods have been suggested, mainly serving as simple and fast means of process control. Sample directly drawn from the transesterification reaction mixture can be subjected to thin-layer chromatography or gas chromatography involving separation on packed columns. They determined the ester content by comparing the respective peak area. Various other chromatographic methods provide information not only on the content of esters, but also on the concentrations of partial glycerides, triglycerides or free glycerin.

1.2.6.2 Density

Biodiesel fuels generally display higher densities than mineral diesel, which is also reflected by the respective limits within the FAME standard (860-900 kg/m^3 at 15 $^{\mathrm{O}}$C) and EU fossil diesel norm EN 590 (820-845 kg/m^3 at 15 $^{\mathrm{O}}$C). This difference has impacts on heating value and fuel consumption, as the amount of fuel introduced into the combustion chamber is determined volumetrically. However, Tat and Van Gerpen (2000) showed that temperature-dependent changes in biodiesel densities are similar to those of fossil diesel. Values for ester samples depend on their fatty acid consumption as well as their purity. On the other hand, density increases with decreasing chain length and increasing number of double bonds. The standard analytical procedures for the determination of density in both fossil diesel and biodiesel fuels either involve the use of a standardized glass hydrometer at the prescribed temperature.

1.2.6.3 Kinematic viscosity

Fuel viscosity has impacts on injection and combustion. Higher viscosity leads to a higher drag in the injection pump and thus causes higher pressures and injection volumes, especially at low engine operating temperatures. As a direct consequence the timing for fuel injection and ignition tends to be slightly advanced for biodiesel, which might in turn lead to increased nitrogen oxide exhaust emissions due to higher maximum combustion temperatures. The standardized analytical procedure for both biodiesel and mineral diesel utilizes a calibrated glass capillary viscometer, measuring the time for a defined sample volume to flow through the device under gravity at the prescribed temperature.

1.2.6.4 Flash point

Flash point is a measure of the flammability of fuels and thus an important parameter for assessing hazards during fuel transport and storage. As reflected by the limits within the respective standards ($\geq$ 120$^{\mathrm{o}}$C for methyl ester as opposed to > 55$^{\mathrm{o}}$C for mineral diesel), flash points of diesel samples are only of about half the value of those for biodiesel. This is considered to be an important safety asset for the bio-fuel, especially for niche applications such as underground mining. The basic principle of the respective determination method is identical, different measuring devices are prescribed for biodiesel and fossil diesel fuels.

1.2.6.5 Sulfur content

Sulfur is limited to a maximum content of 10 ppm in the biodiesel standard. Fossil diesel fuel, for which now concentrations of up to 350 ppm are permissible, will have to be desulfurized to level of 50 ppm and below by 2005. Fuels with high sulfur contents have been associated with negative impacts on human health and on the environment, which is reason for the current tightening of nation limits. Vehicles operated on high-sulfur fuels produce more sulfur dioxide and particulate matter, and their emissions are ascribed a higher mutagenic potential. Moreover, these fuels may cause engine were and rescue the efficiency and life span of oxidation catalytic converters. On the other hand, many ultra low-sulfur mineral diesel fuels have turned out to be lacking in lubricity, which can lead to injection pump failure. The standardized analytical methods for both biodiesel and fossil diesel fuels either involve ultraviolet fluorescence spectrometry or wavelength dispersive X-ray fluorescence spectrometry.

1.2.6.6 Carbon residue

Carbon residue is defined as the amount of carbonaceous matter left after evaporation and pyrolysis of a fuel sample under specified conditions. Although this residue is not solely composed of carbon, the term is found in all discussed standards because it has long been commonly used. The parameter serves as a measure of the tendency of a fuel sample to produce deposits on injector tips and inside the combustion chamber. While it is only of minor relevance for fossil diesel fuel, carbon residue is considered to be one of most important biodiesel quality criteria, as it is linked with many other limited parameters. So for biodiesel fuels carbon residue correlates with the respective amounts of glycerides, free fatty acid, soaps and catalyst residues. In the standardized analytical procedure a small portion of the distillation residue is placed into a glass vial, heated under defined conditions in a nitrogen stream, and the remaining carbonaceous residue within the vial is weighed.

1.2.6.7 Cetane number

This parameter serves as a measure of the ignition quality of diesel fuels. High cetane numbers signify only short delays between fuel injection and ignition, and thus ensure good cold start behavior and a smooth run of the engine. Fuels with low cetane numbers tend to cause diesel knocking and show increased gaseous and particulate exhaust emissions due to incomplete combustion. As determination of cetane number requires equipment which is not available in every laboratory, sometimes cetane index (CI) is offered instead.

1.2.6.8 Ash content

Ash content describes the amount of inorganic contaminants, such as abrasive solids and catalyst residues, and the concentration of soluble metal soaps contained in a fuel sample. These compounds are oxidized during the combustion process to form ash, which is connected with engine deposits. The standardized analytical procedure for determination of sulfated ash in biodiesel involves the addition of sulfuric acid to the residue after combustion to transfer metallic impurities into the corresponding sulfates. This strategy is preferred to direct combustion yielding oxide ash. Because sodium and potassium sulfates produced from catalyst residues are less volatile than the corresponding oxides, so that materials loss at higher temperatures can be minimized.

1.2.6.9 Water content

Fee water promotes biological growth, so that sludge and slime formation thus induced may cause blockage of fuel filters and fuel lines. Moreover, high water contents are also associated with hydrolytic reactions, partly converting esters into free fatty acids, which are linked with filter blockages as well. Finally, also corrosion of chromium and zinc parts within the engine and injection system was reported. The analytical procedure for determination of water in biodiesel and fossil diesel fuel involve titration, using a coulometric Karl Fischer titration apparatus. The basic principle of this procedure is a reaction between I_2 and SO_2, which only occurs in the presence of water.

1.2.6.10 Total contamination

Total contamination is defined as the quota of insoluble material retained after the filtration of a heated fuel sample over a standardized 0.8 μm filter. Total contamination tends to be of minor relevance in mineral fuels, as distillation steps during their production reduce the content of insoluble. For biodiesel fuels, however, the parameter has turned out to be an important quality criterion because normally biodiesel is not distilled. Biodiesel with a high concentration of insoluble impurities tend to cause blockages of fuel filters and injection pumps. High concentrations of soaps and sediments are mainly associated with these phenomena, leading to correspondingly increased values for ash content as well.

1.2.6.11 Copper strip corrosion

The tendency of a fuel sample to cause corrosion to copper, zinc and bronze parts of the engine and the storage tank is determined in a standardized test, according to EN ISO 2160. During this test a polished copper strip is heated to 50 ^{O}C within a fuel bath and left there for three hours. Afterwards the strip is washed and compared to standards, representing different degrees of corrosion. Both discussed norms demand that corrosion must not exceed class 1. In biodiesel samples corrosion might be induced by some sulfur compounds and by acids, so that the parameter is correlated with acid number. In practice, biodiesel samples have turned out to be very unlikely to give ratings higher than class 1.

1.2.6.12 Fuel stability

Basically, stability towards several impacts is relevant to the use of biodiesel within automotive diesel engines. The influence of oxygen and ambient air is subsumed under the term oxidative stability. A minimum Rancimat induction period of six hours is defined for biodiesel samples within EN 14214. This limit corresponds to the period of time passing before biodiesel aged at 110 ^{O}C under a constant air stream, are degraded to such an extent that the formation of volatile acids can be recorded. Due to their chemical composition, biodiesel are more sensitive to oxidation degradation than fossil diesel. This is especially true for fuels with a high content of polyunsaturated ester, as the methylene groups adjacent to double bond have turned out to be particularly susceptible to radical attack as the first step of fuel oxidation. The standard analytical method for the determination of biodiesel oxidation stability is a method derived from food chemistry. In this so-called “Rancimat procedure” a fuel sample is aged at elevated temperature (110 ^{o}C) by passing air through it at a constant rate. The effluent gases are collected in a measuring cell filled with distilled water, of which the conductivity is constantly recorded. Once hydroxides as primary oxidation products are further reacted into volatile acids (mainly formic and acetic acid), conductivity values steeply increase. The period of time up to this point is called inductive period (IP) and is expressed in hours, whereby the temperature at which the measurements were conducted needs to be specified.

1.2.6.13 Acid value

Acid value is a measure of mineral acids and free fatty acids contained in a fuel sample. It is expressed in mg KOH required to neutralize 1 g of ester and is set to a maximum value of $\leq$ 0.5 mg KOH/g. Acid number of biodiesel depends on a variety of factors. On the other hand, it is influenced by the type of feedstock used for fuel production and on its respective degree of refinement. On the other hand, acidity can also be generated during the production process, for instance, by the introduction of mineral acids as catalysts or by free fatty acids resulting from acid work-up of soaps. Finally, the parameter also mirrors the degree of fuel ageing during storage, as it gradually increases due to hydrolytic cleavage of ester bonds. High fuel acidity has been linked with corrosion and the formation of deposits within the engine.

1.2.6.14 Methanol

According to EN 14214, methanol content must not exceed 0.20 %wt in biodiesel fuels. Residual methanol in the ester product is removed by distillation or by repeated aqueous washing steps. These treatments are vital for fuel quality, as high methanol contents pose safety risks in biodiesel transport and storage due to correspondingly low flash point. As a consequence, the respective flash point readings of biodiesel samples give hints at their contents of residual alcohol, with values higher than 100 ^{O}C ensuring that the limit for methanol is met.

1.2.6.15 Iodine number and linolenic acid methyl ester

Iodine number is a measure of total unsaturation within a mixture of fatty materials, regardless of the relative shares of mono-, di- and triglycerides. It is expressed in grams of iodine which react with 100 g of the respective sample. Iodine number is limited to $\leq$ 120 (g I_2/100g) in the biodiesel standard. Moreover, EN14212 regulates the maximum contents of linolenic acid methyl ester to 12.0 %wt. Engine manufactures have long argued that fuels with high iodine numbers tend to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves, when they are heated. Iodine value has been found to correlate with viscosity and cetane number, which both decrease with increasing degree of unsaturation.

1.2.6.16 Free glycerin

Within EN 14214 free glycerin is limited to a maximum amount of 0.02 %wt. The content of free glycerin in biodiesel depends on the production process and is therefore one major criterion of fuel; quality. High values may stem from insufficient washing of the ester product, which makes glycerin separate during storage, once methanol as the common solvent has evaporated. Alternatively, glycerin may also from due to the hydrolysis of remaining mono-, di- and triglycerides in stored fuel. Free glycerin separates within the fuel tank, collects at the bottom, where it attracts other polar compounds, such as water, monoglycerides and soaps and causes damage to the injection system.

1.2.6.17 Monoglycerides, Diglycerides, Triglycerides and Total glycerin

EN14214 limits the amounts of mono-, di- and triglycerids to $\leq$ 0.80, $\leq$0.20 and $\leq$ 0.20 %wt respectively, and defines a maximum amount of 0.25 %wt for total glycerin (i.e. the sum of the concentrations of free glycerin and glycerin bound in the form of mono-, di- and triglyceride) Similar to the concentration of free glycerin, also the amount of glycerides depends on the production process. Low concentration of mono-, di- and triglycerids can only be achieved by selecting optimum reaction condition and/or by distillation of the final ester product. Fuels exceeding the limits are prone to coking and may thus cause the formation of deposits on injector nozzles, pistons and valves. Indirect hints at high glyceride contents in biodiesel samples are correspondingly increased values for viscosity and carbon residue. The gas chromatographic procedure is applicable to biodiesel samples derived from the most frequently used oil and fat sources.

1.2.6.18 Alkali and alkaline-earth metals

According to EN 14214, the concentrations for the sum of alkali metals as well as the sum of alkaline-earth metals within biodiesel sample must not exceed 5 ppm. These metal ions are introduced into biodiesel fuels mainly during the production process. Whereas alkali metals stem from catalyst residues, alkaline-earth metals may originate from hard washing water. Sodium and potassium are associated with the formation of ash within the engine, whereas calcium and magnesium soaps are discussed in the context of injection pump sticking. The parameters are interrelated with several other fuel quality criteria, such as sulfated ash content and carbon residue.

1.2.6.19 Phosphorus

Phosphorus in biodiesel mainly stems from phospholipids contained in the feedstock. It was shown that the type of oil recovery strongly influences the final phosphorus content of vegetable oils. So cold-pressed plant oils usually contain less phosphorus than hot-pressed and extracted sample. Moreover, phosphorus can also be introduced during the biodiesel production process, if phosphoric acid is used as a catalyst or added for the decomposition of soaps. Phospholipids can act as emulsifiers and thus impede phase separation during the transesterification process. Therefore, their content in feedstock material is reduced by various forms of degumming prior to the reaction. The transesterification process itself has been identified as an efficient means of lowering phosphorus content as well, as reductions from 100 ppm in the original material to about 20 to 30 ppm in the ester product are feasible. Residual phosphorus can also be removed by distillation of the final product, during which phospholipids as high molecular weight compounds collect in the distillation residue. Fuels transgressing the limit of 10 ppm of phosphorus are suspected of decreasing the efficiency of oxidation catalytic converters and of causing higher particulate matter emissions.

1.2.7 Biodiesel standards

Table 1.8 Comparison of various biodiesel standards

Specification Standards	Unit	European EN 14214	USA ASTM D6751-02	Department of Energy Business (Thailand)
Ester content	%wt	≥ 96.5	-	≥ 96.5
Density 15°C	kg/m^3	860-900	-	860-900
Viscosity 40°C	mm^2/s	3.5-5.0	1.9-6.0	3.5-5.0
Flash point	°C	≥ 120	130	≥ 120
Sulfur content	%wt	≤ 0.001	≤ 0.05	≤ 0.001
Carbon residue	%wt			≤ 0.30
Cetane number	number	≥ 51	≥ 47	≥ 51
Sulfated ash content	%wt	≤ 0.02	≤ 0.02	≤ 0.02
Water content	%wt	≤ 0.05	≤ 0.05	≤ 0.05
Total contamination	%wt	≤ 0.0024	-	≤ 0.0024
Copper strip corrosion	number	1	≤ 3	≤ 1
Oxidation stability	hr			> 10
Total acid number	mg KOH/g	≤ 0.5	≤ 0.8	≤ 0.5
Iodine value	g Iodine/100g			≤ 120
Linolenic acid methyl ester	%wt			≤ 12.0
Methanol content	%wt	≤ 0.2	-	≤ 0.2
Monoglyceride	%wt	≤ 0.8	-	≤ 0.8
Diglyceride	%wt	≤ 0.2	-	≤ 0.2
Triglyceride	%wt	≤ 0.2	-	≤ 0.2
Free glycerin	%wt	≤ 0.02	≤ 0.02	≤ 0.02
Total glycerin	%wt	≤ 0.25	≤ 0.24	≤ 0.25
Group I, II metals	%wt			≤ 0.0005
Phosphorous	mg/kg	≤ 10	≤ 10	≤ 0.001

Source: www.rendermagazine.com

1.2.8 Cost-related analysis of biodiesel production

Srisan (2002) conducted a feasibility study of producing biodiesel from palm oil. The analytical tool utilized in the study was a cost-benefit analysis with a number of investment criteria including Net Present Value (NPV), Internal Rate of Return (IRR), Benefit-Cost Ratio (B/C Ratio), and a sensitivity analysis. The results of the study showed that at 12% discount rate and the price of biodiesel that was equal to that of fossil diesel at 12.6 baht/litre, the NPV, IRR and B/C Ratio were 1.092, 17.76% and 1.015 respectively. The project became financially feasible, because the NPV was positive and B/C ratio was more than unity. The sensitivity analysis was performed for various cases, providing results as presented in the table 1.9

Table 1.9 The results of sensitivity analysis

Case	**Description**	**NPV**	**IRR**	**B/C Ratio**
Case I	Price of palm oil increases by 5%	1.498	6.223%	0.980
Case II	Price of by-products increase by 50%	2.806	29.759%	1.038
Case III	Price of chemicals used in production increase by 5%	0.176	12.964%	1.002
Case IV	Price of overall public utilities used in production increase by 5%	1.004	17.917%	1.014

May et al., (2005) performed an economic analysis for a 60,000 tones/year palm biodiesel production plant based on raw material prices in August 2005. The study used the following assumptions:

1) Capital expenditure: 400 million baht including 7 acres of land for the factory, with the main process building, storage tanks, office, etc., in Malaysia

2) Operational expenditure: 180 million baht including operating expenses, e.g. labor, utilities, catalyst, etc.

3) Prices of raw materials and products :

Crude palm oil : 13,400 baht per tone

Methanol : 7600 baht per tone

Glycerin : 11,340 baht per ton

Diesel : 18.3 baht per litre

Results from the analysis showed that the project has an internal rate of return (IRR) of 31.7%, a net present value (NPV) of 962 million bath, a payback period of 2 years, and a break even price of crude palm oil of 15,485 bath per ton. The study also evaluated break even prices of palm biodiesel with prices of crude palm oil at 10,000 baht per ton, 14,000 baht per ton, and 18,000 baht per ton. The results are shown in table 1.10

Table 1.10 Break even prices of palm biodiesel

Crude palm oil Price (Baht/ton)	Palm biodiesel Price (Baht/ton)	Palm biodiesel Price (Baht/litre)
10,000	15,580	13.6
14,000	19,720	17.4
18,000	23,850	20.7

1.3 Objective

- To determine suitable condition for production ethyl ester from crude palm oil by batch and continuous - flow microwave.
- To study suitable condition for purification ethyl ester by bleaching earth.
- To study properties of ethyl ester follow by biodiesel standard.

CHAPTER 2

EXPERIMENTATION

2.1 Materials

2.1.1 Raw material

Crude palm oil (CPO) was obtained from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops (Thailand).

2.1.2 Chemicals

2.1.2.1 Ethanol (C_2H_5OH) 95% commercial grade was obtained from Union Intracco (Thailand) Co., ltd.

2.1.2.2 Sulfuric acid (H_2SO_4) 98% commercial grade was obtained from AGC Chemical (Thailand) Co., ltd.

2.1.2.3 Sodium hydroxide (NaOH) 95% commercial grade was obtained from AGC Chemical (Thailand) Co., ltd.

2.1.2.4 Potassium hydroxide (KOH) 95% commercial grade was obtained from AGC Chemical (Thailand) Co., ltd.

2.1.2.5 Glycerin 95% commercial grade was obtained from The Real Tree (Thailand) Co., ltd.

2.1.2.6 Bleaching earth was obtained from Mizusawa Industrial Chemicals (Japan)

2.2 Equipments and Instruments

2.2.1 Microwave oven (Sharp model R235 and Toshiba model ER-D33SC)

2.2.2 Condenser

2.2.3 Peritranstic pump (Pulsafeeder model LD0282-PTC1-365)

2.2.4 Motor (IKA Laboratechnik model RW 20.n)

2.2.5 Gas Chromatography (Agilent 5890 gas chromatograph with a flame ionization detector and a Stabilwax column of length 30 m, film thickness 0.25 μm, and i.d. 0.25 mm)

2.3 Methodology

Ethyl ester production from CPO was studied in batch experiments to analyze the important factors that affect the production process and to find the optimum condition for that production process.

The factors (molar ratio of FFA to ethanol, reaction time, microwave power and quantity of sulfuric acid catalyst) were investigated.

The results from preliminary studies those were the optimum molar ratio of FFA to ethanol, reaction time, microwave power and quality of sulfuric acid catalyst were modified to design the continuous process experiments. This thesis was studied in the following ways:

2.3.1 A study of suitable condition for production ethyl ester from crude palm oil with 2 steps by batch microwave

2.3.1.1 Measurement of the microwave power output

Commercial microwave oven often deviates from their specified power output. A common reason for this is that microwave ovens manufactured for household use is made with inexpensive electronic components that vary from oven to oven. Output also may be affected by decreased electrical power at the outlet due to microwave energy-absorbing surfaces such as built-in or accessory trays, residues of food and the temperature of the magnetron. The microwave power output is determined by measuring the rate of temperature increase of a known quantity of water placed in the oven. The microwave power output is calculated from the following methods.

The method requires loading 1000 ml of water in a cylindrical glass vessel in the center of the microwave. The water temperature is measured before turning on the microwave. As soon as the oven shuts off, the final water temperature is measured. The microwave power output P in watts is calculated from the following formula:

$$P = \frac{4187 \times \Delta T}{t}$$

P is the microwave power output (watts), ΔT is difference between the initial and final temperature (°C) and t is the heating time (s) [Daewoo Electronics Co., Ltd].

2.3.1.2 A study of the CPO composition used in Ethyl ester production by GC-MS

Fatty acid components of the ethyl esters were identified by gas chromatography—mass spectrometry (GC-MS) using the HP 5890 gas chromatograph coupled to an HP 5972 mass-selective detector.

2.3.1.3 A study of suitable condition for reduction FFA in crude palm oil with esterification by batch microwave

All batch microwave tests have been conducted with a Sharp, model R235 compact microwave oven working at 2.45 GHz, with a microwave power of 800 W. Reactions were performed in 250 ml boiling flask which was connected to a condenser in order to prevent ethanol loss. The schematic diagram of the microwave system for ethyl ester production is shown in figure 2.1.

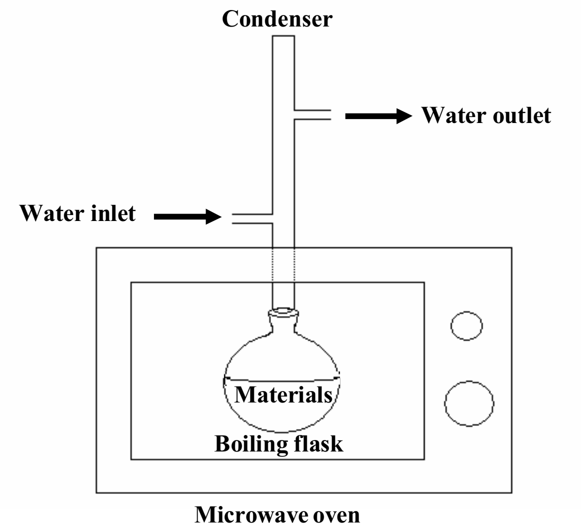


Figure 2.1 Schematic of production of ethyl ester from CPO by continuous esterification and transesterification with microwave oven

The crude palm oil was added into boiling flask. A fixed amount of fleshly prepared H_2SO_4-Ethanol solution was added into the oil. Put the boiling flask in the microwave at a desired microwave power. When the reaction reached the boiling flask was removed from the microwave and the products of reaction were allowed to settle 1 hour in separation funnel producing two distinct liquid phases: oil phase at the bottom and ethanol phase at the top. The esterified palm oil was separated from the bottom and collected to transesterification process.

The experimental factors and their values designed for optimization in the esterification reaction were as followed:

- Molar ratio of FFA to ethanol

The molar ratios of FFA to ethanol were varied in the range from 1:4 to 1:40 (1:4, 1:8, 1:12, 1:16, 1:20, 1:24, 1:28, 1:32, 1:36 and 1:40) to find the best ratio that reduced the optimum of FFA.

- Reaction time

The influence of reaction time was studied in order to get the optimum reaction. The reaction times were varied in the range of 15 – 120 minutes (15, 30, 45, 60, 90 and 120 minutes).

- Microwave power output

The effect of microwave output power on the esterifiaction reaction was studied. The microwave power outputs were varied in the range of 70 to 280 W (70, 140 and 280 W).

- Quantity of sulfuric acid catalyst

The suitable quantity of catalyst was investigated to reduce the need for acid catalysts. The quantity of sulfuric acid was varied in the range of 0 – 16 % wt of FFA (0, 1, 2, 4, 8, 12 and 16 %wt).

2.3.1.4 A study of suitable condition for production ethyl ester from esterified palm oil with transesterification by batch microwave

The esterifed palm oil was added into boiling flask. A fixed amount of fleshly prepared KOH-ethanol solution was added into the oil. Put the boiling flask in the microwave at a desired microwave power. When the reaction reached the preset time the boiling flask was removed from the microwave, glycerin was added into flask then put it back in microwave. The products were allowed to settle 3 hour in separation funnel producing two distinct liquid phases: ester phase at the top and glycerin phase at the bottom. The ethyl ester was collected to purification process.

The experimental factors and their values designed for optimization in the transesterification reaction were as followed:

- Molar ratio of oil to ethanol

Molar ratios of oil to ethanol were varied in the range from 1:4.5 to 1:10.5 (1:4.5, 1:5.5, 1:6.5, 1:7.5, 1:8.5, 1:9.5 and 1:10.5) to find the suitable ratio that produced the optimum of ethyl ester.

- Reaction time

The influence of reaction time was studied in order to get the optimum reaction. The reaction times were varied in the range of 1 – 10 minutes (1, 2, 3, 4, 5, 7 and 10 minutes).

- Quantity of potassium catalyst

The suitable quantity of catalyst was investigated to reduce the need of alkaline catalysts. The quantity of potassium hydroxide was varied in the range of 0 – 3 %wt of FFA (0, 0.5, 1, 1.5, 2, 2.5 and 3 %wt).

2.3.1.5 A study of suitable condition for separation glycerin from ethyl ester and purification by bleaching earth

At the end of transesterification process, pure glycerin (0-20 %wt of glycerin/oil) was added and heated by microwave at 70 W for 1 minute. After separation of the two layers by sedimentation in a separation funnel two layers were deserved. The access ethanol in the ethyl ester phase was evaporated by heating at 80 ^{o}C and was purified by adding bleaching earth (0-1.4 %wt of bleaching earth/oil), mixed (5 – 60 minutes) and separated by centrifuge. The residue ethyl ester in spent bleaching earth was extracted by hexane.

The ethyl ester from purification process was analyzed for its compositions. After that, the condition for the optimum reaction would be obtained. It would be an initial condition for continuous experiments.

2.3.2 Design and construction of reactors

In the design, CPO and solution of ethanol and sulfuric acid were pumped into a mixing tank I. The mixture would overflow from the reactor I and get to microwave oven for esterification process. All reactors in microwave oven made from glass. The mixture from esterification process would flow into separation tank. Here, the esterified palm oil was separated from the ethanol-water solution. The esterified palm oil phase remained at the bottom while ethanol-water phase overflowed from the top. The esterified palm oil and fresh solution of ethanol and potassium hydroxide were pumped into a mixing tank II. The mixture would overflow from the reactor II and get to microwave oven for transesterification process. The product from transesterification process would flow into mixing tank III then add glycerin. The overflow mixture from reactor III goes in microwave oven for glycerin separation process. Then the mixture would flow into separation column to separated ethyl ester and glycerin. An overview of the continuous process is shown in figure 2.2.

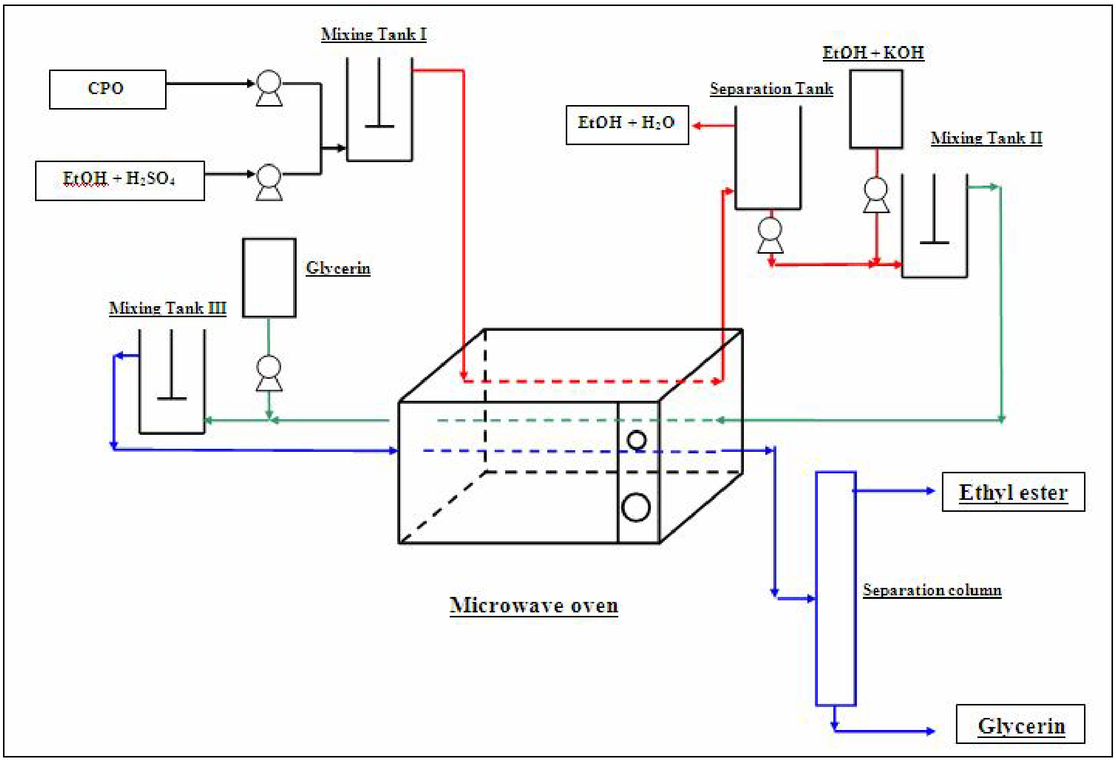


Figure 2.2 Schematic of production of ethyl ester from CPO by continuous esterification and transesterification with microwave oven

An access ethanol in the ethyl ester phase was evaporated by heating and put in separation column. The ethyl ester was pumped to bleaching earth column to purification process. The residue ethyl ester in spent bleaching earth was extracted by hexane.

2.3.3 Continuous experiments

Experiments are conducted using the optimal condition based on molar ratio and reaction temperature which obtained from the previous batch process. All continuous microwave tests have been conducted with a Toshiba, model ER-D33SC compact microwave oven working at 2.45 GHz, with a power of 1100 W. However the residence time could be adjusted by changing the flow rates of CPO, ethanol, sulfuric acid and potassium hydroxide or the size of the reactors.

2.3.3.1 A study of suitable condition for reduction FFA in crude palm oil with esterification by continuous microwave

Before the production, each pump was calibrated to find a designated flow rate. The continuous production of ethyl ester was started by the feeding of CPO and sulfuric acid in ethanol solution into the mixing tank I. The mixture would overflow into the reactor I in microwave oven for esterification process. The esterification reaction was carried out with the studied initial condition. After that it was flowed into separation tank to separation the esterified palm oil from the ethanol.

The experimental factors and their values designed for optimization in the esterification reaction were as followed:

- Molar ratio of FFA to ethanol

Molar ratios of FFA to ethanol were varied in the range from 1:4 to 1:32 (1:4, 1:8, 1:12, 1:16, 1:20, 1:24, 1:28 and 1:32) to find the best ratio that reduced the optimum of FFA.

- Reaction time

The influence of reaction time was studied in order to get the optimum reaction. The reaction times were varied in the range of 15 – 120 minutes (15, 30, 45, 60, 90 and 120 minutes).

- Quantity of sulfuric acid catalyst

The suitable quantity of catalyst was investigated to reduce the need for acid catalysts. The quantity of sulfuric acid was varied in the range of 0 – 16 % wt of FFA (0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 %wt).

2.3.3.2 A study of suitable condition for production ethyl ester from esterified palm oil with transesterification by continuous microwave

The esterification reaction products were then allowed to separation tank and to separate into 2 phases. The top phase, consisting of residual ethanol together with water formed during the reaction and the ethyl ester phase was taken off at the bottom of the separation tank while ethanol phase overflowed from the top of the separation tank. The esterified palm oil and solution of ethanol and potassium hydroxide was pumped into a mixing tank II. The mixture would overflow into the reactor II in microwave oven for transesterification process.

The experimental factors and their values designed for optimization in the transesterification reaction were as followed:

- Molar ratio of oil to ethanol

Molar ratios of oil to ethanol were varied in the range from 1:4.5 to 1:10.5 (1:4.5, 1:5.5, 1:6.5, 1:7.5, 1:8.5, 1:9.5 and 1:10.5) to find the optimum ratio that produced ethyl ester.

- Reaction time

The influence of reaction time was studied in order to get the optimum reaction. The reaction times were varied in the range of 1 – 10 minutes (1, 2, 3, 4, 5, 7 and 10 minutes).

- Quantity of potassium catalyst

The suitable quantity of catalyst was investigated to reduce the need for alkaline catalysts. The quantity of potassium hydroxide was varied in the range of 1 – 3 % wt of FFA (1, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 2.75 and 3 %wt).

2.3.3.3 A study of suitable condition for separation glycerin from ethyl ester with addition glycerin by continuous microwave

The transesterification reaction products were then allowed to mixing tank III, glycerin was pumped into a mixing tank III and the mixture would overflow from the top of the mixing tank into reactor III in microwave oven for glycerin separation process. The mixture would flow into separation column to separated ethyl ester and glycerin.

The experimental factors and their values designed for optimization in the separation process were as followed:

- Retention time

The influence of retention time was studied in order to get the optimum time to separate glycerin from ethyl ester. The retention times were varied in the range of 1 –5 minutes (1, 2, 3, 4 and 5 minutes).

- Quantity of adding glycerin

The suitable quantity of adding glycerin was investigated to reduce the need for adding glycerin. The quantity of glycerin was varied in the range of 0 – 20 % wt of oil (0, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 %wt).

2.3.4 Purification process

Ethyl ester from biodiesel production was purified by bleaching earth which is the adsorbent material. This method removes impurities, such as soap, residue glycerin, the rest catalyst and water. Purification process is shown in figure 2.3.

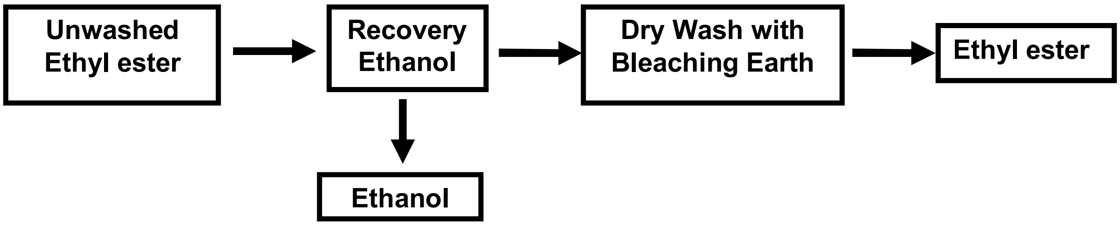


Figure 2.3 Purification ethyl ester process

2.3.4.1 A study of suitable condition for purification ethyl ester by bleaching earth

Unwashed ethyl ester from separation process was evaporated by heating at 80 ^{o}C to recover access ethanol in ethyl ester. Unwashed ethyl ester from recovery ethanol process was pumped into a bleaching earth tank and washed ethyl ester would overflow from the top of bleaching earth tank into storage tank. The influence of retention time was studied in order to get the optimum time to purified ethyl ester. The retention times were varied in the range of 10 – 120 minutes (10, 20, 30, 40, 50, 60, 80, 100 and 120 minutes).

2.3.5 The fuel properties analysis of the product

The ethyl ester product, which was obtained from the optimum reaction condition, was analyzed for fuel properties to meet the standards. The analyzed fuel properties are shown in table 2.1.

Table 2.1 The fuel properties analysis

Item	Properties, unit	Test Method	Specification
1	Ester content, %wt	EN 14103	96.5 min
2	Density at 15 ^{o}C , Kg/m^{3}.	ASTM D1298	860-900
3	Viscosity at 40 ^{o}C, cSt.	ASTM D445	3.50-5.00
4	Flash point ,^{o}C	ASTM D93	120 min
5	Carbon residue , %wt	ASTM D5452	0.0024 max
6	Sulfated ash ,%wt	ASTM D874	0.02 max
7	Water content, %wt	ASTM D2709	0.05 max
8	Total contamination, %wt	ASTM D5452	0.0024 max
9	Copper strip corrosion, number	ASTM D130	1 max
10	Total acid number, mgKOH/g	ASTM D664	0.50 max
11	Free glycerin, %wt	EN 14105	0.02 max
12	Total glycerin, %wt	EN 14105	0.25 max
13	Phosphorus, %wt	ASTM D 4951	0.001 max

2.3.6 Evaluation the cost of ethyl ester by microwave

Evaluation the cost of ethyl ester by microwave (feed stock, energy costs, etc) and compare to the commercial method.

CHAPTER 3

RESULTS and DISCUSSION

3.1 A study of suitable condition for production ethyl ester from crude palm oil with 2 steps by batch microwave

3.1.1 A study of the CPO composition

Crude palm oil (CPO) is an orange liquid at room temperature (Figure 3.1) which consists of triglycerides containing three fatty acids linked by ester linkages to a glycerol moiety. The fatty acids vary in their carbon chain lengths and in the numbers of double bonds. The fatty acid components of the CPO were determined by GC-MS and results are shown in table 3.1. It contains 47.6 %wt of palmitic acid, 41.0 %wt of oleic acid, 8.0 %wt of linoleic acid and 2.5 %wt of stearic acid. It can be seen that most of the values fall within the ranges published in the literature [Choo et al., 2005 and Wing-Keong et al., 2003]. CPO for this study contained 7.5 %wt of FFA.

Figure 3.1 The physical appearance of CPO

Table 3.1 Fatty acid composition of crude palm oil

Fatty acid	Fatty acid composition (%wt)		
	CPO [Choo et al., 2005]	CPO [Wing-Keong et al., 2003]	CPO this work
Lauric	0.3	0.2	-
Myristic	0.8	1.1	0.9
Palmitic	44.3	42.8	47.6
Palmitoleic	0.2	0.1	-
Stearic	5.0	3.8	2.5
Oleic	39.1	41.1	41.0
Linoleic	10.1	10.3	8.0
Linolenic	0.1	0.3	-
Arachidic	-	0.3	-
Other (Unknown)	-	-	2.3

3.1.2 Measurement of the microwave power output

Microwave power output in this experiment was calculated by indirectly measuring the temperature rise of water; the results were shown in table 3.2.

Table 3.2 Comparison of microwave efficiency

Microwave power input (W)	Microwave power output (W)	
	Microwave power output at 70%	Experiment
100	70	70
200	140	146
400	280	293
600	420	444
800	560	559

From table 3.2, the microwave power output estimated from these measurements was approximately 70% of the microwave power input (For example: microwave power input of 100 W and microwave power output from calculate of 70 W). The measured microwave outputs from these experiments are in good agreement with the observations of Barnard et al., (2007) who found that microwave power output is approximately 65% of the microwave power input.

3.1.3 A study of suitable condition for reduction FFA in crude palm oil with esterification by batch microwave

The objective of esterification process was to lower the FFA content of CPO from its initial level of 7.5 %wt. Important variables affecting the FFA content in the esterification process are the molar ratio of FFA to ethanol, the amount of acid catalyst, the microwave power output and the reaction time. The microwave system for ethyl ester production was shown in figure 3.2.

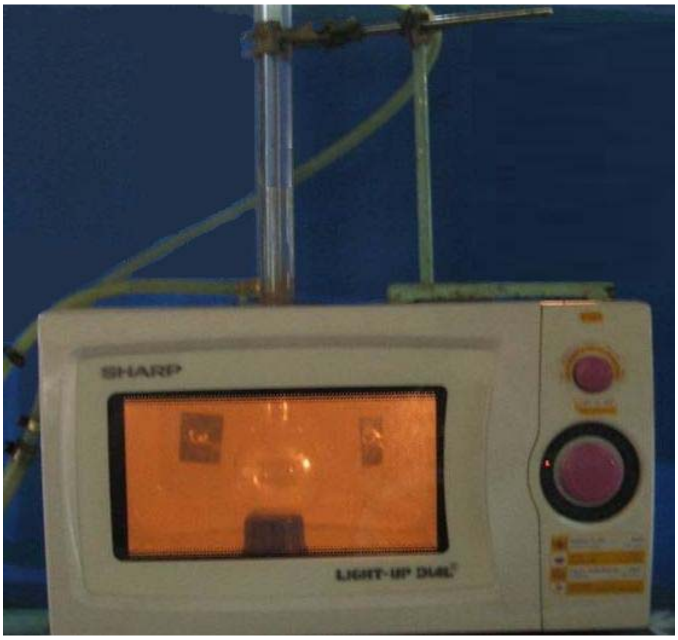


Figure 3.2 The microwave system for ethyl ester production

3.1.3.1 Effect of molar ratio of FFA to ethanol

The amount of ethanol for the esterification process was analyzed in terms of its molar ratio with respect to the FFA. Stoichiometrically, the molar ratio of FFA to ethanol is 1:1. However, in practice this is not sufficient to complete the reaction. Since, the esterification reaction is reversible, an excess of alcohol is necessary to push the reaction to completion [Ghadge and Raheman, 2005]. The effect of molar ratio on the %wt of the FFA content was shown in figure 3.3. The CPO for this reaction contained 7.5 %wt of FFA, 4 %wt of H_2SO_4 to FFA was used as the catalyst, the microwave power output was set at 70 W, and the reaction time was 1 h. The molar ratio of FFA to ethanol was varied from 1:4 to 1:40. It was found that FFA in CPO was decreased significantly when molar ratio of FFA to ethanol was increased from 1:4 to 1:24. However, further increases molar ratio of FFA to ethanol from 1:24 to 1:40 did not show any significant improvement in FFA remaining, therefore the optimum molar ratio of FFA to ethanol for esterification of CPO was determined to be 1:24 (molar ratio of oil to ethanol: 1:6). Molar ratio of oil to ethanol in this study is in good agreement with Marchetti et al., (2008) who employed a molar ratio of oil to ethanol: 1:6 for reduced FFA in refined sunflower oil by esterification process.

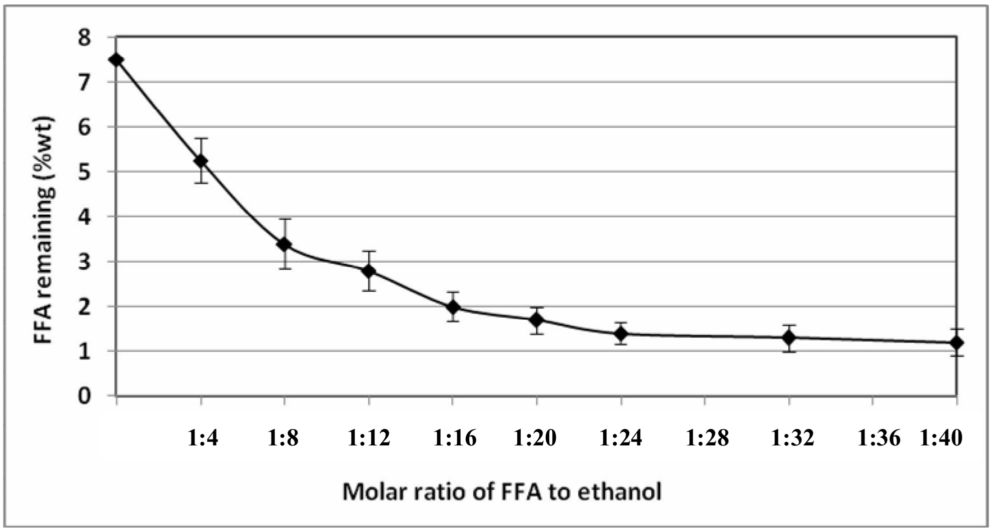


Figure 3.3 Effect of the molar ratio of FFA to ethanol on %wt of FFA remaining after 1 h of reaction time, with 4 %wt of H_2SO_4 to FFA and a microwave power output of 70 W

3.1.3.2 Effect of varying the amount of acid catalyst

The amount of acid catalyst used in the process also affects the %wt of FFA remaining. The amount of acid catalyst was varied in the range 0–16 %wt of H_2SO_4 to FFA under reaction conditions of a 1:24 molar ratio of FFA to ethanol, a reaction time of 1 h, and a microwave power output of 70 W. The effect of amount of catalyst on the %wt of FFA remaining was shown in figure 3.4. It was found that FFA in CPO was decreased significantly when the amount of catalyst was increased from 1 to 4 %wt of H_2SO_4 to FFA. However, further increases the amount of catalyst from 4 to 16 %wt of H_2SO_4 to FFA did not show any significant improvement in FFA remaining. Also, the addition of excess sulfuric acid could produce a product that was darker in color, therefore the optimum catalyst concentration for esterification of CPO was determined to be 4 %wt of H_2SO_4 to FFA (1 %wt of H_2SO_4 to Oil). This result is in good agreement with Ghadge and Raheman (2005) who employed the amount of H_2SO_4 to Oil ratio 1 %wt for reduced FFA content in Mahua oil by esterification process.

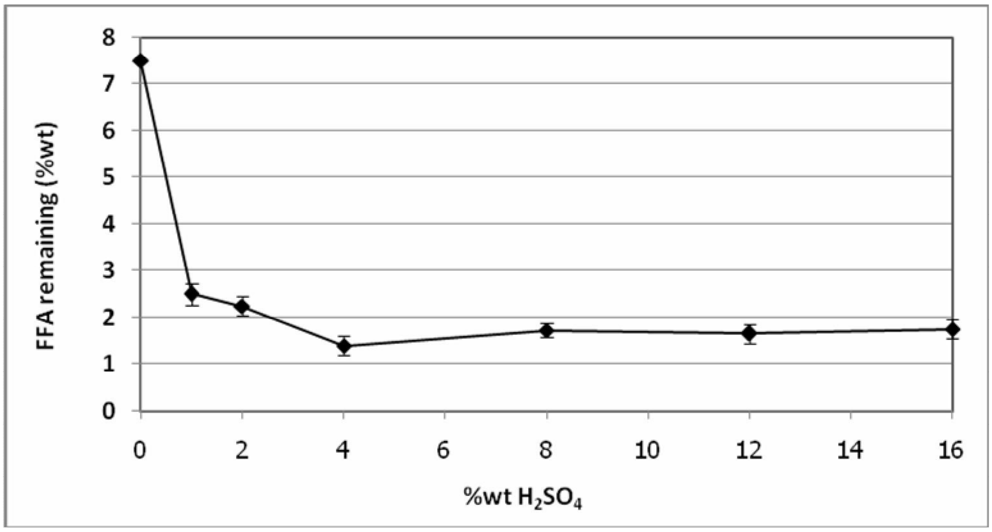


Figure 3.4 Effect of amount of acid catalyst on %wt of FFA remaining with 1:24 molar ratio of FFA to ethanol, at 1 hour and a microwave power output of 70 W

3.1.3.3 Effects of microwave power output and reaction time

Figure 3.5 shows the effect of microwave power output and reaction time on the %wt of FFA remaining compared to conventional heating at 70 °C. The microwave power outputs of this experiment were 70, 140 and 280 W and reaction times were ranging from 20 to 120 minutes, keeping the remaining reactions parameters constant (4 %wt of H_2SO_4 to FFA and 1:24 molar ratio of FFA to ethanol). From the figure shows a microwave power output of 70 W can result in the lowest FFA remaining at 60 minutes which the temperature of mixture of crude palm oil and ethanol in esterification process were approximately 70 °C. The microwave power output of 140 and 280 W were not decreased the FFA remaining lower than 2 %wt because the microwave power output of 140 and 280 W were too high and may cause damage to the organic molecules such as triglycerides which is broken to FFA [Saifuddin, 2004]. At microwave power output of 70 W; %wt of FFA remaining rapidly decreased within the first 15 minutes. After that %wt of FFA content slowly decreased until the reaction times exceeded 60 minutes. At this point, the trend of %wt FFA content increased again which may cause by triglyceride is broke to lower chained organic fractions such as FFA [Refaat and El Sheltawy, 2008]. The reaction time at 60 minutes was selected for this study while the conventional heating at 70 °C required 4 hours which is in good agreement with Wang et al., (2006) who have taken reaction time 4 hours and reaction temperature 95 °C for esterification process. Therefore the optimum microwave power output and reaction time for esterification of CPO was determined to be 70 W for 60 minutes. This study confirms that microwave assisted chemical reaction reduces the reaction time significantly and increases the product yield as it is mentioned in the literature [Saifuddin, 2004, Refaat and El Sheltawy, 2008 and Barnard et al., 2007]. Microwave treatment brings greater accessibility of the susceptible bonds and hence a much more efficient chemical reaction [Azcan and Danisman, 2008]. Consequently, microwave irradiation accelerates the chemical reaction and high product yield can be achieved within a short time.

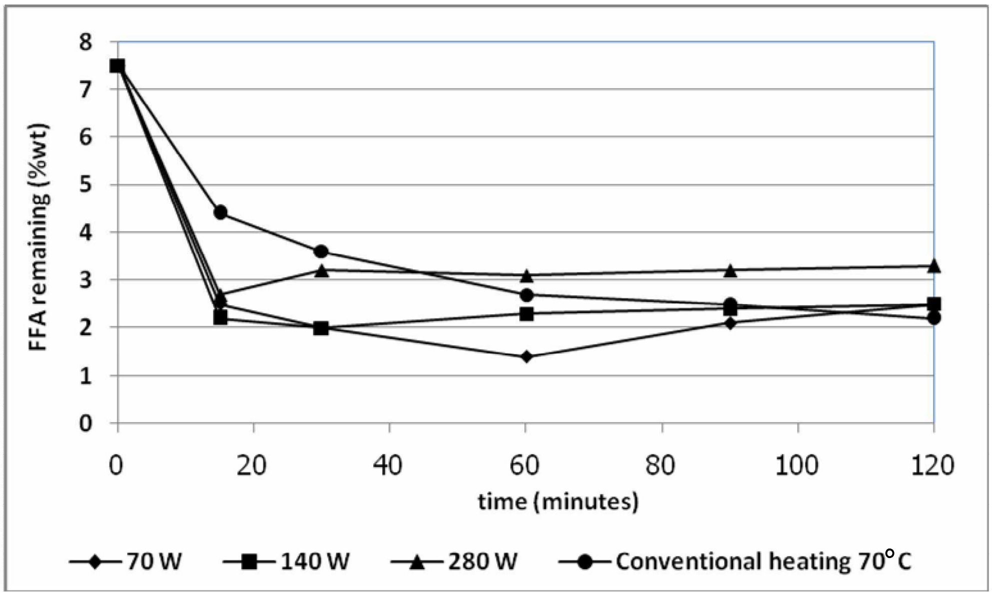


Figure 3.5 Effect of microwave power output and reaction time compare to conventional heating at 70 °C on %wt of FFA remaining with 4 %wt of H_2SO_4 to FFA and 1:24 molar ratio of FFA to ethanol

The optimum conditions for the esterification process which reduced FFA remaining lower than 2 %wt have been identified as a 1:24 molar ratio FFA to ethanol, 4 %wt H_2SO_4 to FFA as the catalyst, a reaction time of 1 h, and a microwave power output of 70 W. At the end of the esterification process, the amount of FFA remaining was reduced from 7.5 %wt to 1.7 %wt. Then, the esterified palm oil can be transesterified with an alkali catalyst to convert the triglycerides to esters in transesterification process. The esterified palm oil is shown in figure 3.6.

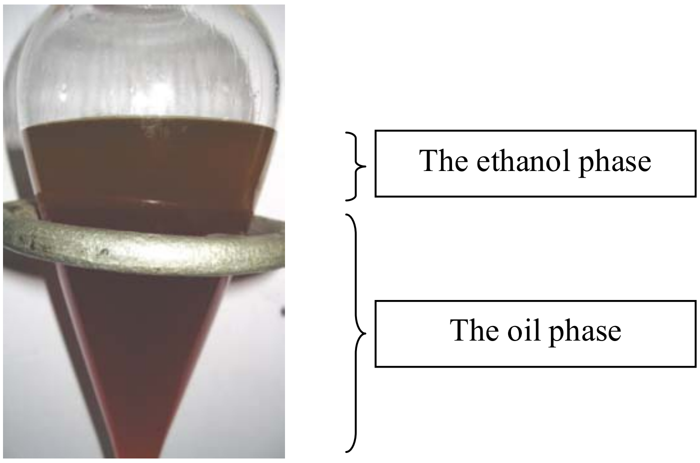


Figure 3.6 The esterified palm oil

The product from esterification process was separated into 2 phases. The upper layer was excess ethanol phase and the lower layer was esterified palm oil. The composition of the esterified palm oil was 82.4 %wt of oil content, 16.8 %wt of ethanol content, 0.5 %wt of H_2SO_4 content and 0.3 %wt of water content.

3.1.4 A study of suitable condition for production ethyl ester from esterified palm oil with transesterification by batch microwave

The objective of transesterification process is to change the triglyceride to ester. A study case of alkaline-catalyzed transesterification was run using esterified crude palm oil that had 1.7 %wt of FFA content and 1:4.5 molar ratio of oil to ethanol. Important variables affecting the ester content in the transesterification process were the oil to ethanol molar ratio, the amount of catalyst and the reaction time.

3.1.4.1 Effect of molar ratio of oil to ethanol

The amount of ethanol required for transesterification was analyzed in terms of the molar ratio with respect to the triglyceride. Stoichiometrically, the molar ratio of triglyceride to ethanol is 1:3. However, in practice this is not sufficient to complete the reaction. Higher molar ratios are required to high ester content [Demirbas, 2002]. The effect of molar ratio on the %wt of ester content is shown in figure 3.7. It has been seen that %wt of ester content increased when the molar ratio of oil to ethanol was increased from 1:4.5 to 1:8.5. However, further increases molar ratio of oil to ethanol from 1:8.5 to 1:10.5 did not show any significant improvement in ester content. Therefore the optimum molar ratio of oil to ethanol for transesterification of esterified palm oil was determined to be 1:8.5. This result is in good agreement with Encinar et al., (2007) who employed a molar ratio of oil to ethanol 1:12 for produced ethyl ester from used frying oil by transesterification process.

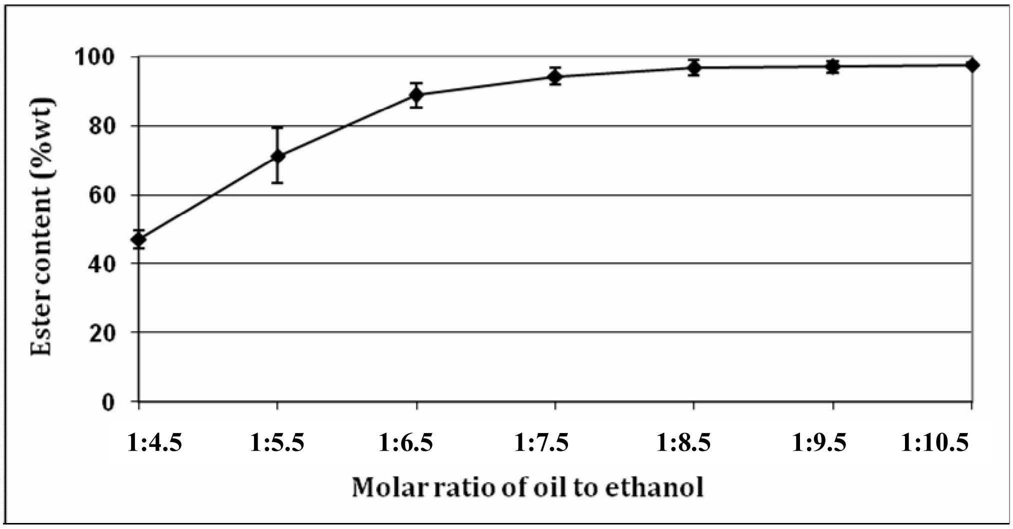


Figure 3.7 Effect of the molar ratio of oil to ethanol on %wt of ester content after 5 minutes of reaction, with 1.5 %wt KOH to oil and a microwave power output of 70 W

3.1.4.2 Effects of alkaline catalyst amounts

The amount of alkaline catalyst was varied in the range of 0–2 %wt KOH to oil under reaction conditions of a 1:8.5 molar ratio of oil to ethanol, at reaction time of 5 minutes and a microwave power output of 70 W. The effect of the amount of catalyst on the %wt of ester content is shown in figure 3.8. It was found that ester content was increased significantly when the amount of catalyst was increased from 0.5 to 1.5 %wt of KOH to oil. However, further increases the amount of catalyst from 1.5 to 3.0 %wt of KOH to oil did not show any significant improvement in ester content. Also, the addition of excess amount of catalyst, gave rise to the formation of an emulsion which led to the formation of gels and decreased %wt of ethyl ester. Therefore the optimum catalyst concentration for transesterification of esterified palm oil was determined to be 1.5 %wt of KOH to oil. This result was different from Kulkarni et al., (2007) who employed the amount of alkaline catalyst of 0.7 %wt of KOH to oil for produced ethyl ester from used canola oil by transesterification process. Because part of the difference may be attributed to the differences in the raw material used and the amount of alkaline catalyst was plus the amount needed to neutralize the acid catalyst in esterification product.

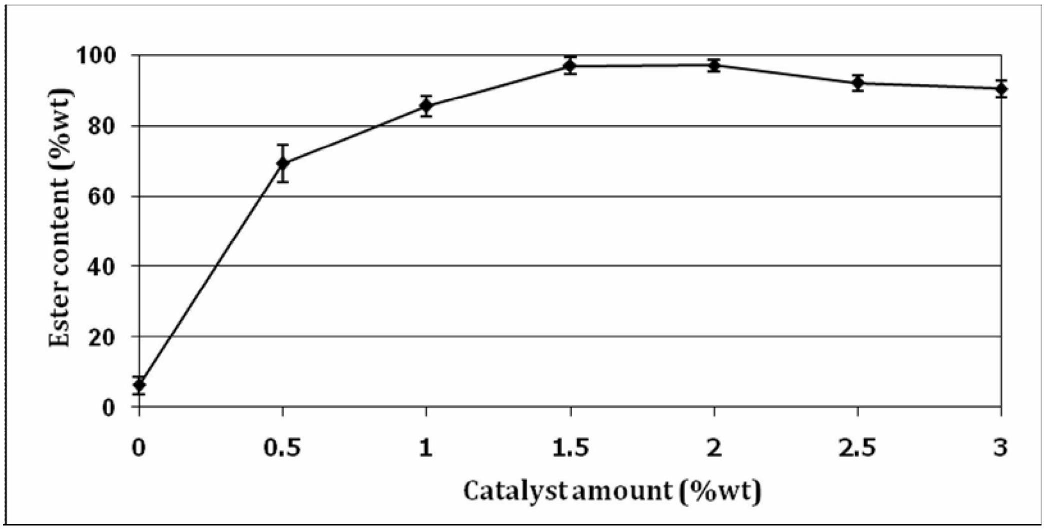


Figure 3.8 Effect of alkaline catalyst quantity on %wt of ester content with a 1:8.5 molar ratio of oil to ethanol, after a reaction time of 5 minutes at a microwave power output of 70 W

3.1.4.3 Effects of reaction time

Figure 3.9 shows the effect of reaction time on the %wt of ester content which compared between microwave heating and conventional heating process at 70 °C. The reaction times ranged from 1 to 10 minutes, keeping the other reaction parameters constant (1.5 %wt of KOH to oil, a 1:8.5 molar ratio of oil to ethanol and a microwave power output of 70 W for both heating processes). For microwave heating system, the %wt of ester content rapidly increased within the first 1 minute. Thereafter, the %wt of ester content slowly increased until the reaction times exceeded 5 minutes. Thus, the reaction time at 5 minutes was selected for this study, whereas conventional heating system at 70 °C required 1 h; the latter is in good agreement with the findings of Issariyakul et al., (2007) who employed a reaction time of 1 h and a reaction temperature of 60 °C for produced ethyl ester from waste fryer grease by transesterification process. This study has confirmed that microwave-assisted chemical reaction significantly reduces the reaction time and increases the product yield, as mentioned in the literature [Barnard et al., 2007, Saifuddin and Chua, 2004 and Refaat and El Sheltawy, 2008]. It is an expected result since the changing electrical field activates the smallest degree of variance of molecules and ions leading to molecular friction and therefore initiation of chemical reactions is possible. Microwave treatment induces greater accessibility of the pertinent bonds and hence a much more efficient chemical reaction [Azcan et al., 2008]. Consequently, microwave irradiation accelerates the chemical reaction and a high product yield can be achieved within a short time. The obtained results are in good agreement with the finding of Hernando et al., (2007) who employed a reaction time of 5 minutes and worked on microwave oven for produced biodiesel from rapeseed oil by transesterification process. In the present study, the optimum conditions for the transesterification process have been identified as a 1:8.5 molar ratio of oil to ethanol, 1.5 %wt of KOH to oil as a catalyst, a reaction time of 5 minutes and a microwave power output of 70 W which is in good agreement with the reported data.

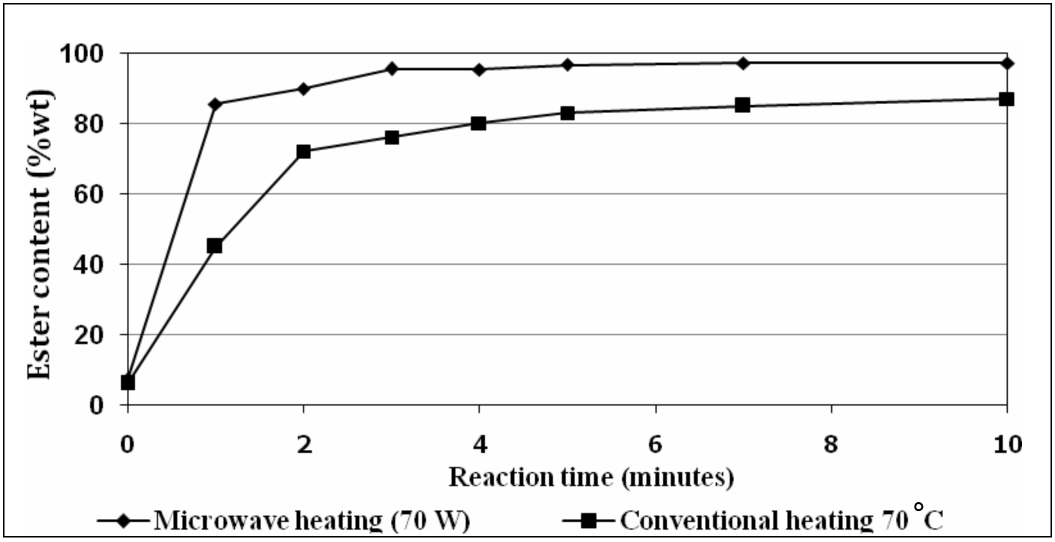
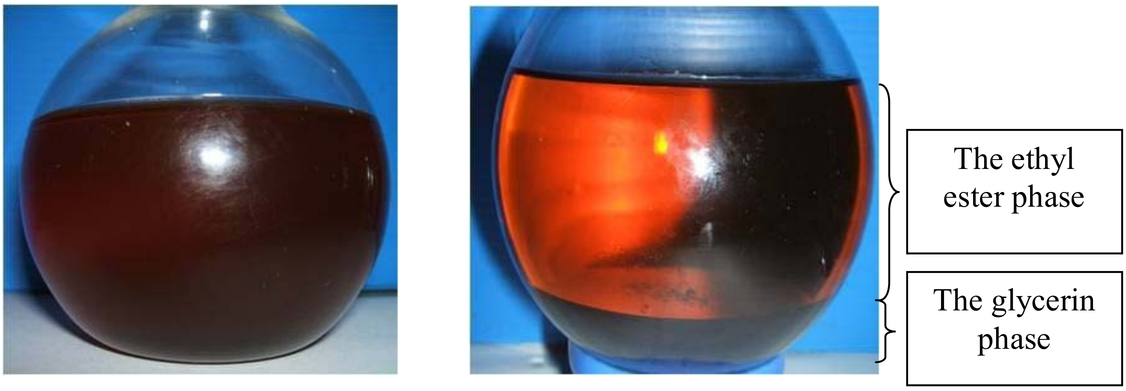


Figure 3.9 Effect of reaction time compared to conventional heating at 70 °C on %wt of ester content with 1.5 %wt of KOH to oil, 1:8.5 molar ratio of oil to ethanol and a microwave power output of 70 W

3.1.5 A study of suitable condition for separation glycerin from ethyl ester

3.1.5.1 Effect of amount of pure glycerin

At the end of transesterification process, glycerin from the reaction did not separated from ethyl ester by gravity. This problem was solved by adding pure glycerin in ethyl ester and the resulting mixture was heated in the microwave oven at 70 W for 1 minute, which resulted in the formation of an upper phase consisting of ethyl esters and a lower phase containing glycerin (Figure 3.10). Figure 3.11 shows %wt of pure glycerin which was added in ethyl ester to reduced glycerin content by separated glycerin from the ethyl ester. Addition of 2-4 %wt of pure glycerin to mixture from transesterification process, the glycerin content not decreased because all pure glycerin which was added in ethyl ester dissolved in ethyl ester so it can not induced the glycerin from the reaction to separated from ethyl ester. But addition of pure glycerin higher than 4 %wt of pure glycerin to mixture from transesterification process, the glycerin content greatly decreased because glycerin separated from ethyl ester. At 10 %wt of pure glycerin to mixture from transesterification process, the glycerin content was decreased to 1.7 %wt of glycerin content to ethyl ester. The added pure glycerin higher than 10 %wt of pure glycerin to mixture from transesterification process had no significant effect on glycerin content in ethyl ester. The optimum of pure glycerin which was added in ethyl ester was 10 %wt to mixture from transesterification process. This result was different from Encinar et al., (2007) report in which added glycerin for 25 %wt. Part of the difference may be attributed to the differences in the process used.



A B

Figure 3.10 Ethyl ester before mixing with pure glycerin (A) and ethyl ester after mixing with pure glycerin (B)

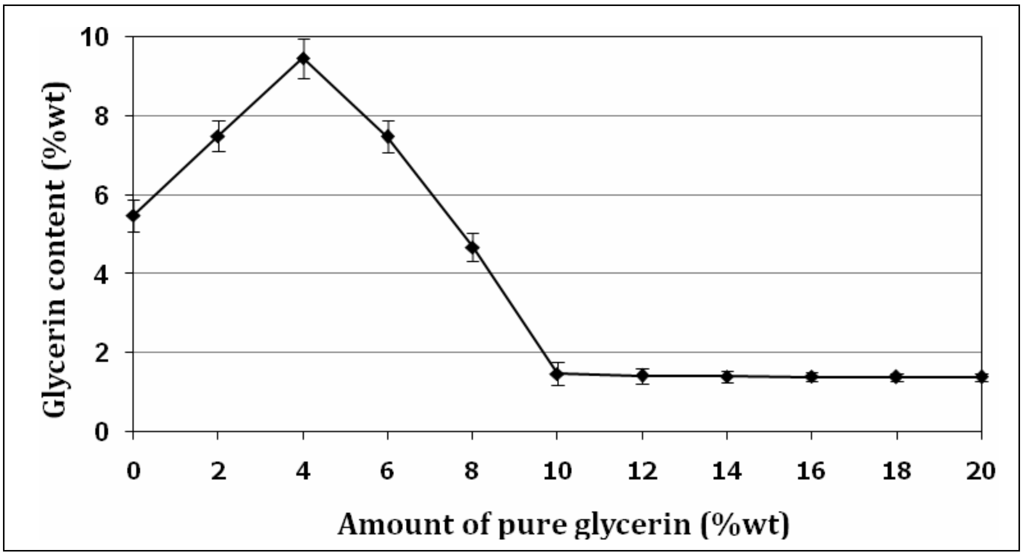


Figure 3.11 Effect of adding pure glycerin quantity on %wt of glycerin content in ethyl ester

Access ethanol in the ethyl ester phase was evaporated by heating at 80 ^{o}C and was left in a separatory funnel 30 minutes. The glycerin was separated from ethyl ester and caused to decrease the glycerin content in ethyl ester. In this work, the glycerin content in ethyl ester before added glycerin, after added glycerin and after evaporated ethanol was 5.49, 1.47 and 0.21 %wt, respectively.

3.1.6 A study of suitable condition for purification of ethyl ester by using bleaching earth

The crude ethyl ester was purified by mixing with bleaching earth and separated by centrifuge. The bleaching earth which was used in this process is a white powder from Galleon Brand (Figure 3.12). The chemical composition and physical properties of bleaching earth are shown in table 3.3 and table 3.4, respectively.

Figure 3.12 The physical appearance of bleaching earth

Table 3.3 The Chemical Composition of bleaching earth (% at 110 °C drying basis)

Substance	**%wt**
SiO_2	84.4
Al_2O_3	9.1
MgO	3.3
Fe_2O_3	2.0
CaO	0.7
Other	0.5

Table 3.4 The Physical Properties of bleaching earth

Parameters	**Results**
Moisture (%)	8.0
Fineness (%) (100 mesh)	99.2
Fineness (%) (150 mesh)	98.26
Fineness (%) (200 mesh)	93.55
Fineness (%) (325 mesh)	64.19
Residual acidity (mgKOH/g)	1.1
pH (at 25°C)	2.69
Bulk density (g/cm^3)	0.55
Specific surface area (m^2/g)	348
Average particle size (μm)	29.3

3.1.6.1 The effect of bleaching earth dosage

The bleaching earth dosage in the purification process also affects the %wt of glycerin content. The amount of bleaching earth was varied in the range of 0.2–1.4 %wt of bleaching earth dosage to ethyl ester under reaction conditions of 5 minutes of contact time, at room temperature and mixed at the rate 600 rpm. The effect of bleaching earth dosage on the %wt of glycerin content was shown in figure 3.13. It was found that %wt of glycerin content decreased when bleaching earth dosage was increase from 0.2 to 1.2 %wt of bleaching earth dosage to ethyl ester. An appropriate bleaching earth dosage was found to be 1.2 %wt of bleaching earth dosage to ethyl ester as this gave the %wt of glycerin content less than 0.02 which is the biodiesel standard. However, further bleaching earth dosage from 1.2 to 1.4 %wt of bleaching earth dosage to ethyl ester did not show any significant improvement in %wt of glycerin content but increasing in the oil losses. Therefore the optimum bleaching earth dosage for purified ethyl ester was determined to be 1.2 %wt of bleaching earth dosage to ethyl ester.

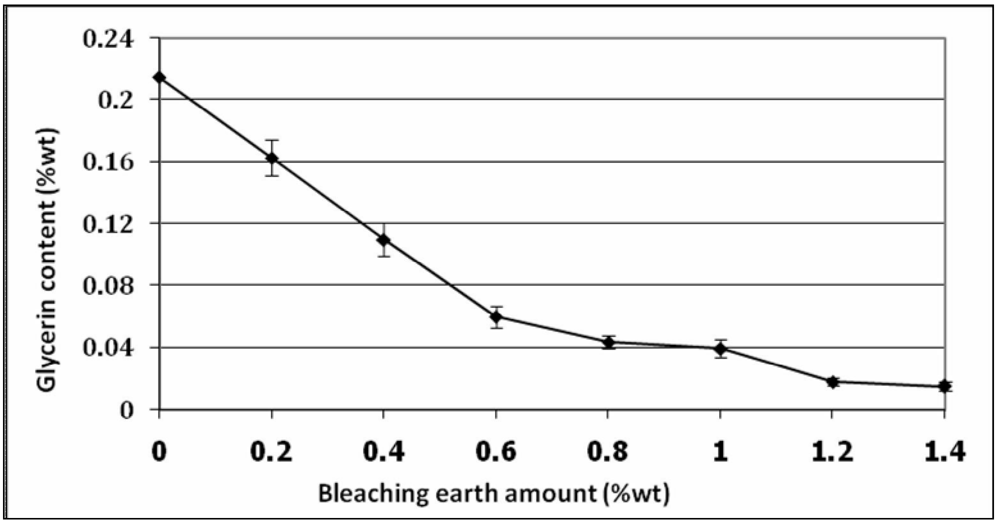


Figure 3.13 Effect of bleaching earth amount on %wt of glycerin content in ethyl ester

3.1.6.2 The effect of contact time

The contact time used in the purification process also affects the %wt of glycerin content. The contact time was varied in the range of 0-10 minutes under reaction conditions of 1.2 %wt of bleaching earth dosage to ethyl ester, at room temperature and mixed at the rate 600 rpm. The effect of contact time on the %wt of glycerin content was shown in figure 3.14. It was found that high amount of glycerin content was adsorbed in the first minutes of the experiment and the steady state is reached in about 8 minutes. In theory, adsorption should be practically instantaneous; however, in practice, this is not the case. The glycerin content decrease is very rapid during the first few minutes that the adsorbent is in contact with the oil and then decreases to a point where equilibrium is reached and no more glycerin content was removed [Rini, 1960].

An appropriate contact time was found to be 5 minutes as this gave the %wt of glycerin content less than 0.02 which is in the limit of the biodiesel standard.

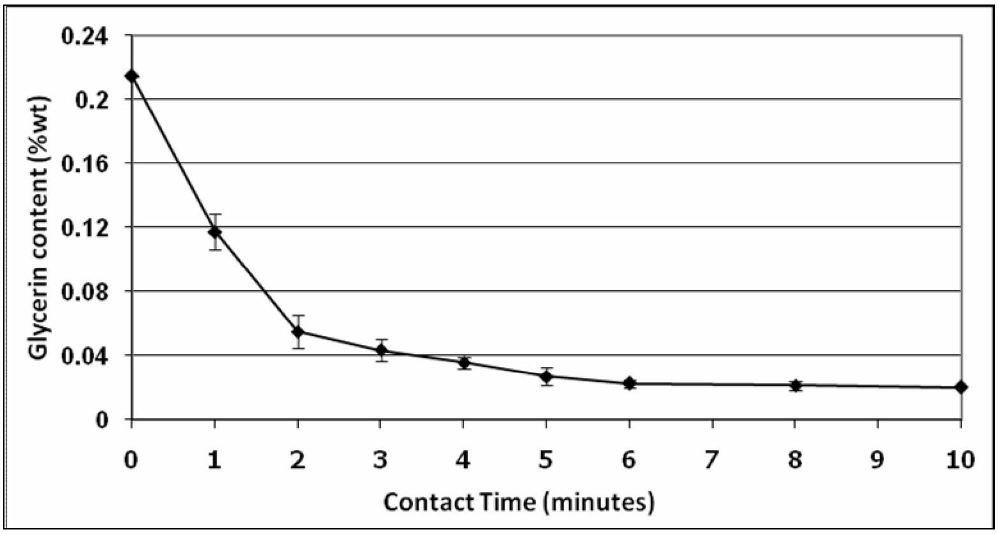


Figure 3.14 Effect of contact time on %wt of glycerin content in ethyl ester

The optimum conditions for production ethyl ester from crude palm oil by batch microwave have been identified for the esterification process as a 1:24 molar ratio FFA to ethanol, 4 %wt of H_2SO_4 to FFA as the catalyst, a reaction time of 1 h, and a microwave power output of 70 W, for the transesterification process as a 1:8.5 molar ratio of oil to ethanol, 1.5 %wt of KOH to oil as a catalyst, a reaction time of 5 minutes and a microwave of 70 W. For the separation process was a 10 %wt of pure glycerin, and purification process was 1.2 %wt of bleaching earth and a contact time of 5 minutes.

3.2 Design and construction the apparatus used in the continuous experiments

The apparatus used in the continuous experiments (Figure 3.15) made up of 2 L glass tube, 1 L separator, mixing tank and CPO + H_2SO_4 in ethanol solution pump for esterification process. The apparatus used in transesterification process were 150 mL glass tube, mixing tank, KOH in ethanol solution pump and esterified palm oil pump. The apparatus used in separation process were 25 mL glass tube, mixing tank and glycerin pump.

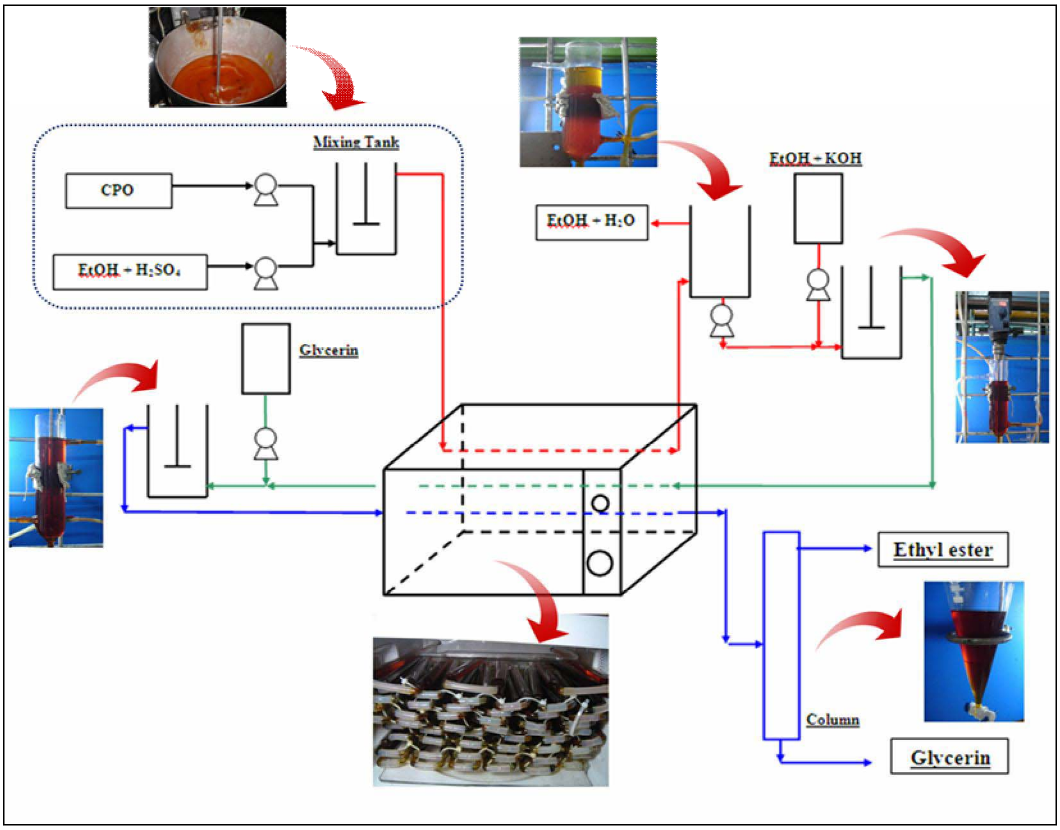


Figure 3.15 The apparatus used in the continuous experiments

3.3 A study of suitable condition for production ethyl ester from crude palm oil with 2 steps by continuous microwave

3.3.1 Measurement of the microwave power output

Microwave power output in this experiment was calculated by indirectly measuring the temperature rise of water; the results are shown in table 3.5.

Table 3.5 Comparison of microwave efficiency

Microwave power input (W)	Microwave power output (W)	
	Microwave power output at 70%	Experiment
110	77	78
330	231	240
550	385	389
770	539	554
1100	770	798

The microwave power output estimated from these measurements for continuous process. At microwave power input of 110, 231, 385, 539 and 770 W, microwave power output from calculation was 78, 240, 289, 554 and 789 W, respectively. The microwave power output was approximately 70% of the microwave power input which was similar to batch process.

3.3.2 A study of suitable condition for reduction FFA in crude palm oil with esterification by continuous microwave

The objective of esterification process is to lower the FFA content of CPO from its initial level of 7.5 %wt. Important variables affecting the FFA content in the esterification process are the molar ratio of FFA to ethanol, the amount of acid catalyst and the reaction time.

3.3.2.1 Effect of molar ratio of FFA to ethanol

The amount of ethanol for the esterification process was analyzed in terms of its molar ratio with respect to the FFA. The effect of molar ratio on the %wt of the FFA remaining was shown in figure 3.16. The CPO for this reaction contained 7.5 %wt of FFA, 4 %wt of H_2SO_4 to FFA was used as the catalyst, the microwave power output was set to 78 W and the reaction time was 1 h. The molar ratio of FFA to ethanol was varied from 1:4 to 1:32. It was found that FFA in CPO was decreased significantly when molar ratio of FFA to ethanol was increased from 1:4 to 1:24. At 1:24 molar ratio of FFA to ethanol, FFA remaining was 1.7 %wt which was suitable raw material in transesterification process. However, further increases molar ratio of FFA to ethanol from 1:24 to 1:32 did not show any significant improvement in FFA content, therefore the optimum molar ratio of FFA to ethanol for esterification of CPO was determined to be 1:24. The obtained result is in good agreement with the batch result which has the optimum molar ratio of FFA to ethanol of 1:24.

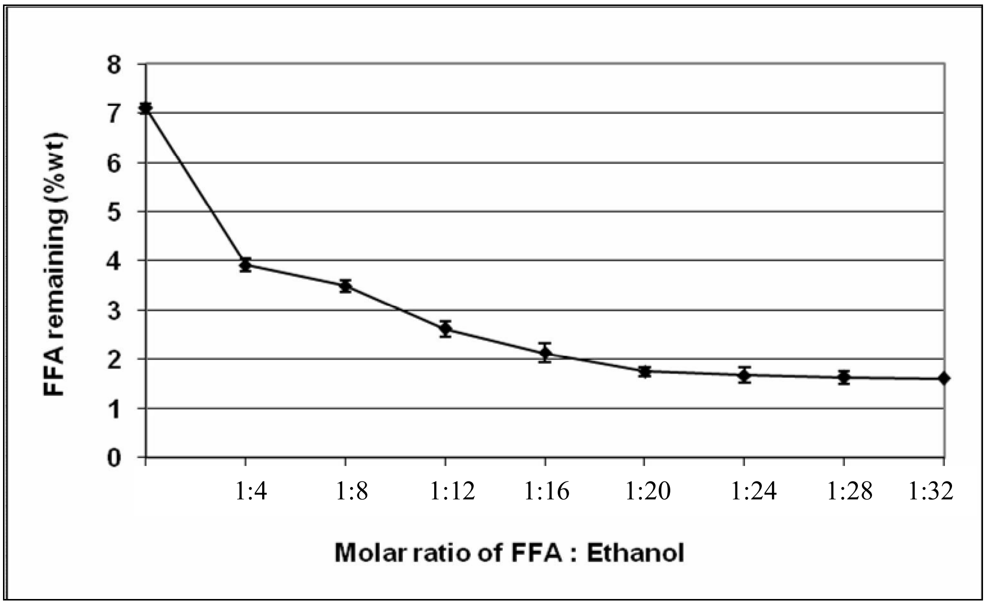


Figure 3.16 Effect of the molar ratio of FFA to ethanol on %wt of FFA remaining after 1 h of reaction, with 4 %wt H_2SO_4 to FFA and a microwave power output of 78 W

3.3.2.2 Effect of varying the amount of acid catalyst

The amount of acid catalyst used in the process also affects the %wt of FFA content. The amount of acid catalyst was varied in the range 0-7 %wt of H_2SO_4 to FFA under reaction conditions of a 1:24 molar ratio of FFA to ethanol, a reaction time of 1 h, and a microwave power output of 78 W. The effect of amount of catalyst on the %wt of FFA remaining was shown in figure 3.17. It was found that FFA in CPO was decreased significantly when the amount of catalyst was increased from 1 to 5 %wt of H_2SO_4 to FFA. However, further increases the amount of catalyst from 5 to 7 %wt of H_2SO_4 to FFA did not show any significant improvement in FFA remaining; therefore the optimum catalyst concentration for esterification of CPO was determined to be 5 %wt of H_2SO_4 to FFA. The obtained result is in good agreement with the batch result which has the optimum amount of catalyst of 4 %wt of H_2SO_4 to FFA.

.

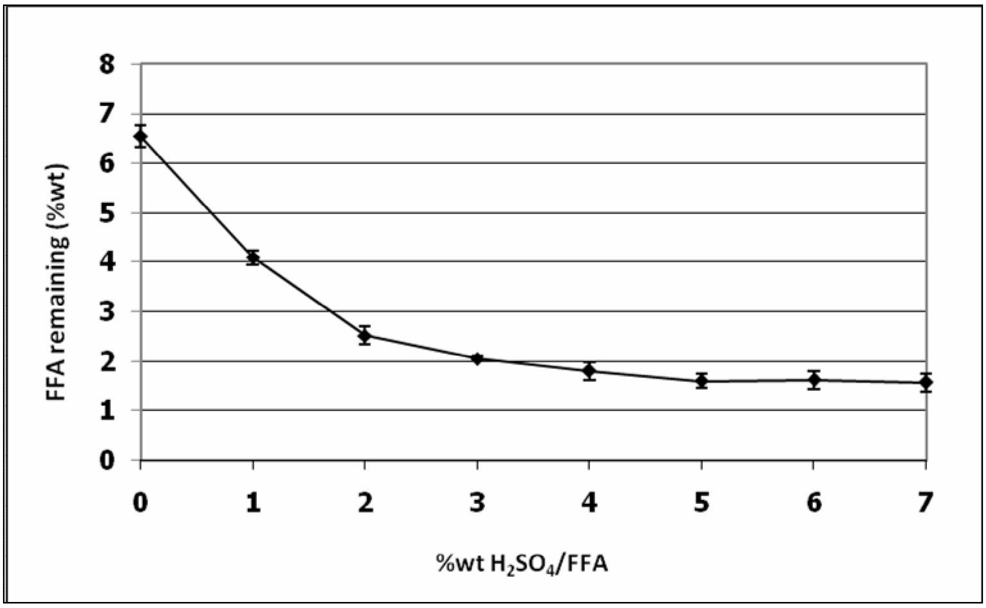


Figure 3.17 Effect of acid amount of catalyst of FFA remaining with 1:24 molar ratio of FFA to ethanol, at 1 hour and a microwave power output of 78 W

3.3.2.3 Effects of reaction time

Figure 3.18 shows the effect of reaction time on the %wt of FFA remaining. The reaction time are ranging from 15 to 120 minutes, keeping the remaining reactions parameters constant (5 %wt of H_2SO_4 to FFA, a microwave power output of 78 W and 1:24 molar ratio of

FFA to ethanol). From the figure found that FFA remaining in CPO was decreased significantly when the reaction time was increased from 15 to 90 minutes. However, further increases the reaction time from 90 to 120 minutes, the trend of %wt FFA content increased again which may cause by triglyceride is broke to lower chained organic fractions such as FFA [Refaat and El Sheltawy, 2008]. Therefore the reaction time for esterification of CPO was determined to be 90 minutes and FFA remaining was 1.4 %wt. The obtained result is in good agreement with the batch results which has the optimum amount of the reaction time of 60 minutes.

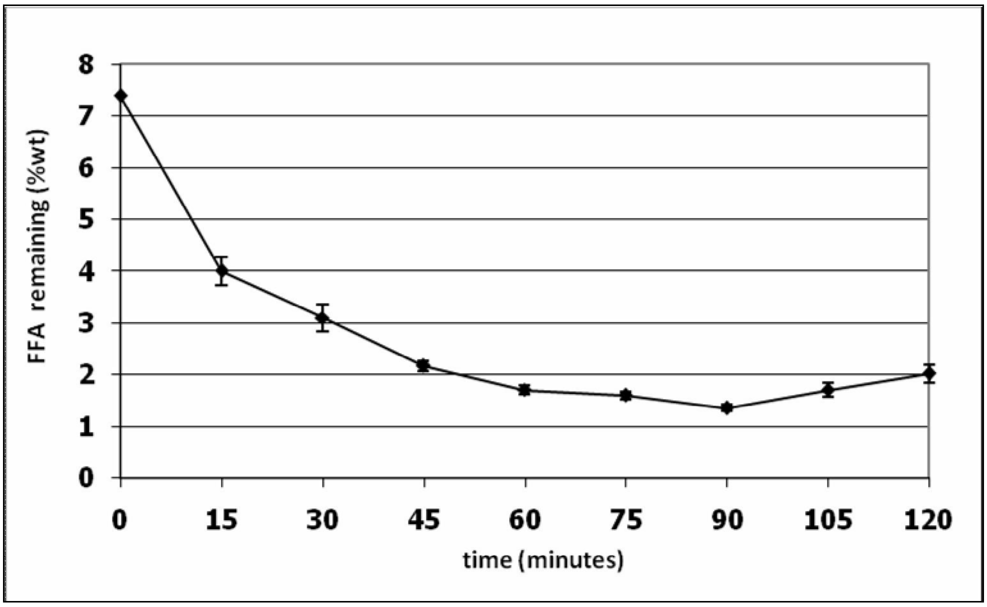


Figure 3.18 Effect of reaction time on %wt of FFA remaining with 5 %wt of H_2SO_4 to FFA and 1:24 molar ratio of FFA to ethanol and a microwave power output of 78 W

The optimum condition for the continuous esterification process which reduced FFA remaining lower than 2 %wt had been identified as a 1:24 molar ratio of FFA to ethanol, 5 %wt of H_2SO_4 to FFA as the catalyst, a reaction time of 90 minutes, and a microwave power output of 78 W. At the end of the esterification process, the amount of FFA remaining was reduced from 7.5 %wt to 1.4 %wt. Then, the esterified palm oil can be transesterified with an alkali catalyst to convert the triglycerides to esters in transesterification process.

3.3.3 A study of suitable condition for production ethyl ester from esterified palm oil with transesterification by continuous microwave

The objective of transesterification process is to change the triglyceride to ester. A study case of alkaline-catalyzed transesterification was run using esterified crude palm oil. Important variables affecting the ester content in the transesterification process were the oil to ethanol molar ratio, the amount of catalyst and the reaction time.

3.3.3.1 Effect of molar ratio of oil to ethanol

The effect of molar ratio on the %wt of ester content was shown in figure 3.19. It has been seen that %wt of ester content increased when the molar ratio of oil to ethanol was increased from 1:4.5 to 1:8.5. However, further increases molar ratio of oil to ethanol from 1:8.5 to 1:10.5 did not show any significant improvement in ester content. Therefore the optimum molar ratio of oil to ethanol for transesterification of esterified palm oil was determined to be 1:8.5. The obtained result is in good agreement with the batch result which has the optimum molar ratio of oil to ethanol of 8.5.

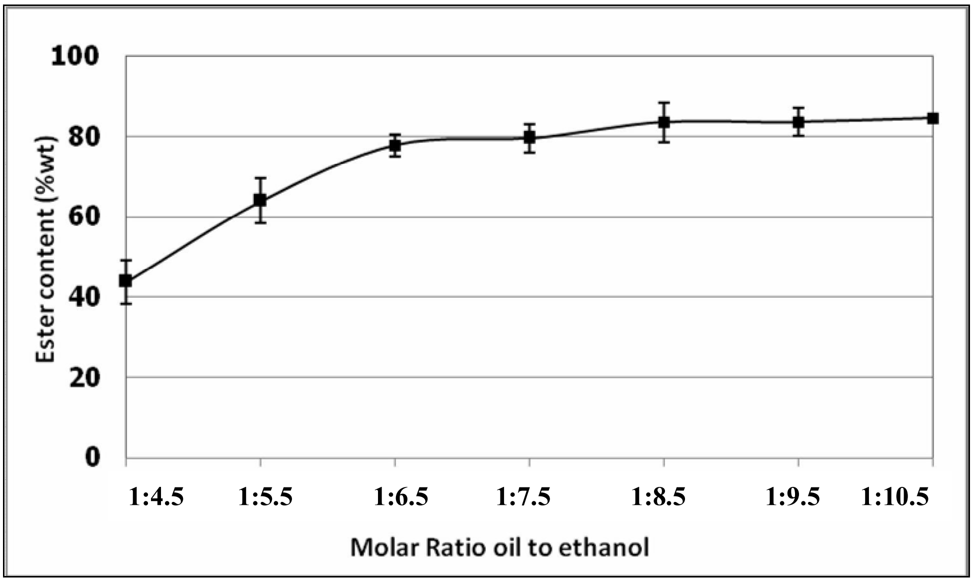


Figure 3.19 Effect of the molar ratio of oil to ethanol on %wt of ester content after 5 minutes of reaction, with 1.5 %wt of KOH to oil and a microwave power output of 78 W

3.3.3.2 Effects of alkaline catalyst amounts

The amount of alkaline catalyst was varied in the range of 1-3 %wt of KOH to oil under reaction conditions of a 1:8.5 molar ratio of oil to ethanol, at reaction time of 5 minutes and a microwave power output of 78 W. The effect of the amount of catalyst on the %wt of ester content was shown in figure 3.20. It was found that ester content was increased significantly when the amount of catalyst was increased from 0.5 to 2.5 %wt of KOH/oil. However, further increases the amount of catalyst from 2.5 to 3.0 %wt of KOH to oil did not show any significant improvement in ester content. Also, the addition of excess amount of catalyst, gave rise to the formation of an emulsion which led to the formation of gels and decreased %wt of ethyl ester. Therefore the optimum catalyst concentration for transesterification of esterified palm oil was determined to be 2.5 %wt of KOH to oil. However, the obtained result is not agreement with the batch result which has the optimum amount of catalyst of 1.5 %wt of KOH to oil. Because the amount of acid catalyst in continuous esterification process higher than in batch esterification process, so the amount of alkaline catalyst in continuous esterification process higher than in batch esterification process for neutralized the residual acid catalyst in oil.

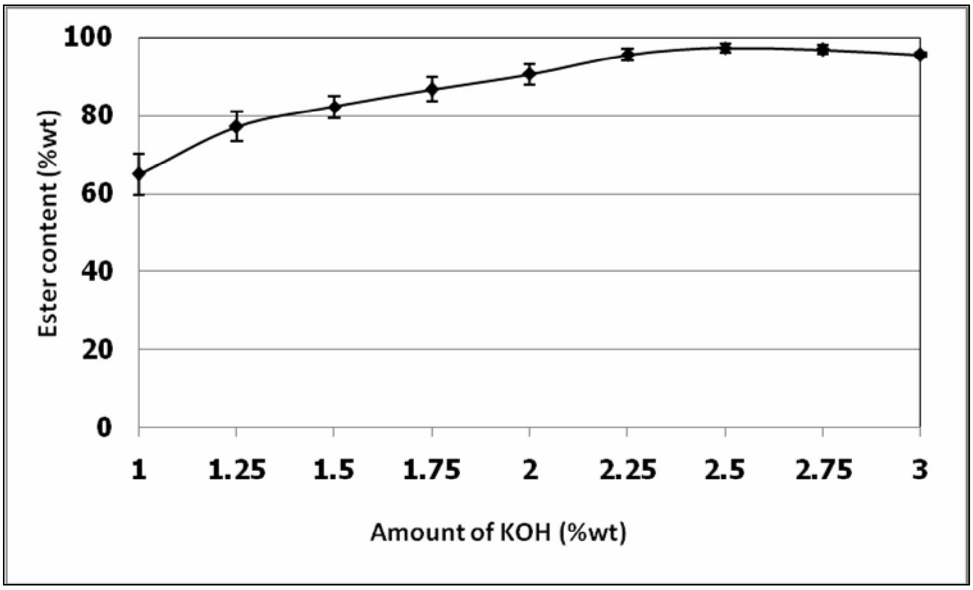


Figure 3.20 Effect of alkaline catalyst quantity on %wt of ester content with a 1:8.5 molar ratio of oil to ethanol, after a reaction time of 5 minutes at a microwave power output of 78 W

3.3.3.3 Effects of reaction time

Figure 3.21 showed the effect of reaction time on the %wt of ester content. The reaction times ranged from 1 to 10 minutes, keeping the other reaction parameters constant (2.5 %wt of KOH to oil, a 1:8.5 molar ratio of oil to ethanol and a microwave power output of 78 W). The %wt of ester content rapidly increased within the first 1 minute. Thereafter, the %wt of ester content slowly increased until the reaction times exceeded 7 minutes. Thus, the reaction time at 7 minutes was selected for this study.

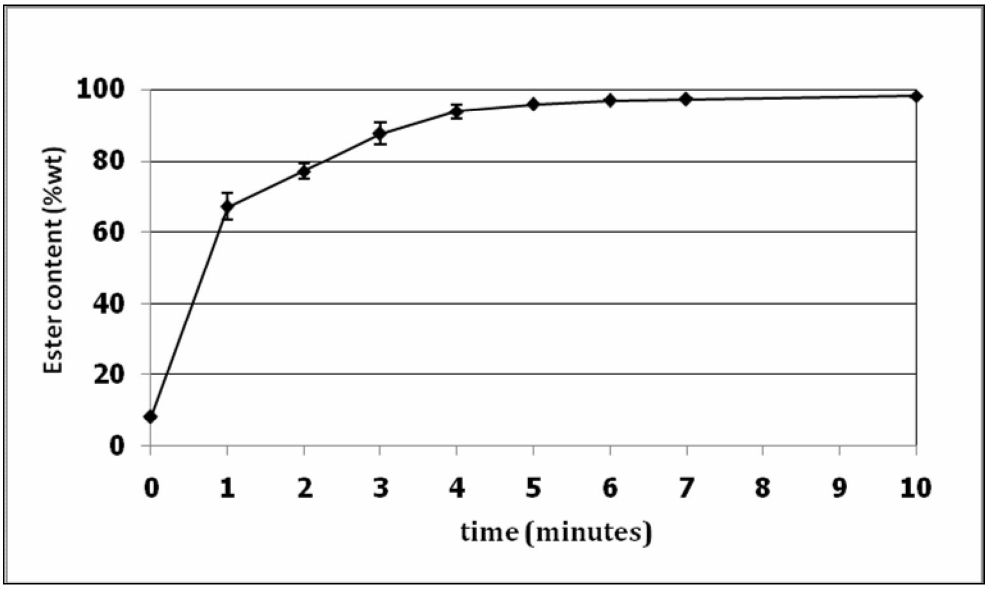


Figure 3.21 Effect of reaction time on %wt of ester content with 2.5 %wt of KOH to oil, 1:8.5 molar ratio of oil to ethanol, and a microwave power output of 78 W

At the end of transesterification process, glycerin form the reaction did not separated from ethyl ester by gravity, 10 %wt of pure glycerin was mixed and the resulting mixture was heated in the microwave oven at 78 W for 1 minute, which resulted in the formation of an upper phase consisting of ethyl esters and a lower phase containing glycerin (same in batch process). Access ethanol in the ethyl ester phase was evaporated by heating at 80 °C and was left in a separatory funnel 30 minutes. The ethyl ester was purified by bleaching earth in purification process.

3.3.4 A study of suitable condition for purification by bleaching earth

The crude ethyl ester was purified by pumping thought the column of bleaching earth and separated residue bleaching earth in ethyl ester by paper filter. The apparatus used in the purification continuous experiments (Figure 3.22) made up of 1 L bleaching earth tank and ethyl ester pump.

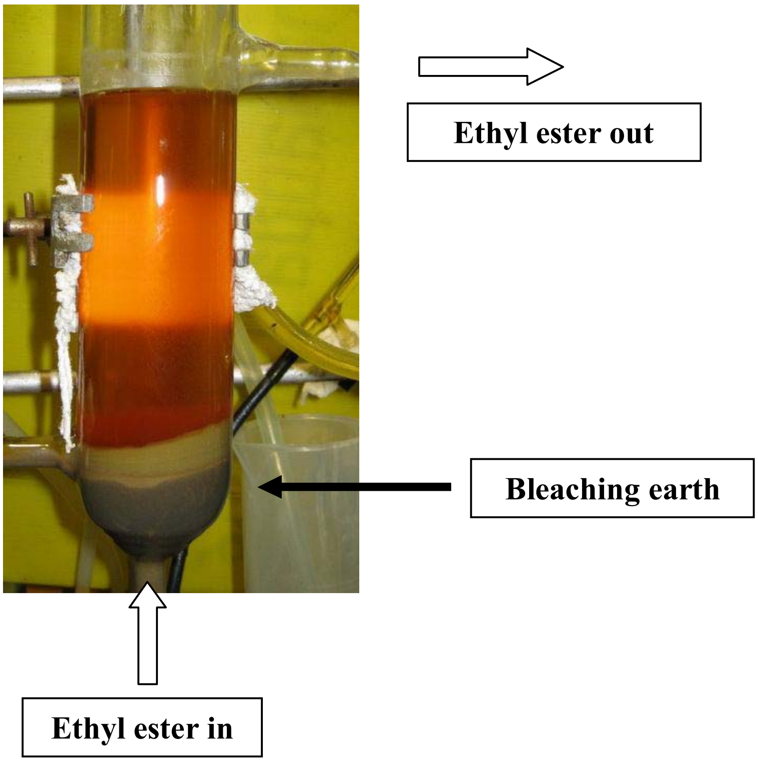


Figure 3.22 The apparatus used in the purification continuous experiments

3.3.4.1 The effect of contact time

The contact time used in the purification process also affects the %wt of glycerin content. The contact time was varied in the range of 0–10 minutes under reaction conditions of 50 g of bleaching earth and at room temperature. The effect of contact time on the %wt of glycerin content was shown in figure 3.23. It was found that high amount of glycerin content was adsorbed in the first minute of the experiment and the steady state is reached in 8 minutes. An appropriate contact time was found to be 5 minutes as this gave the %wt of glycerin content lower than 0.02 which is in the limit of the biodiesel standard. However, the capacity of ethyl ester which was purified by bleaching earth to bring the glycerin content down to an acceptable standard was 5000 mL of ethyl ester to 50 g of bleaching earth (1.2 %wt of bleaching earth to ethyl ester) was shown in figure 3.24. The obtained results are in good agreement with the batch results which has the optimum amount of bleaching earth to ethyl ester of 1.2 %wt.

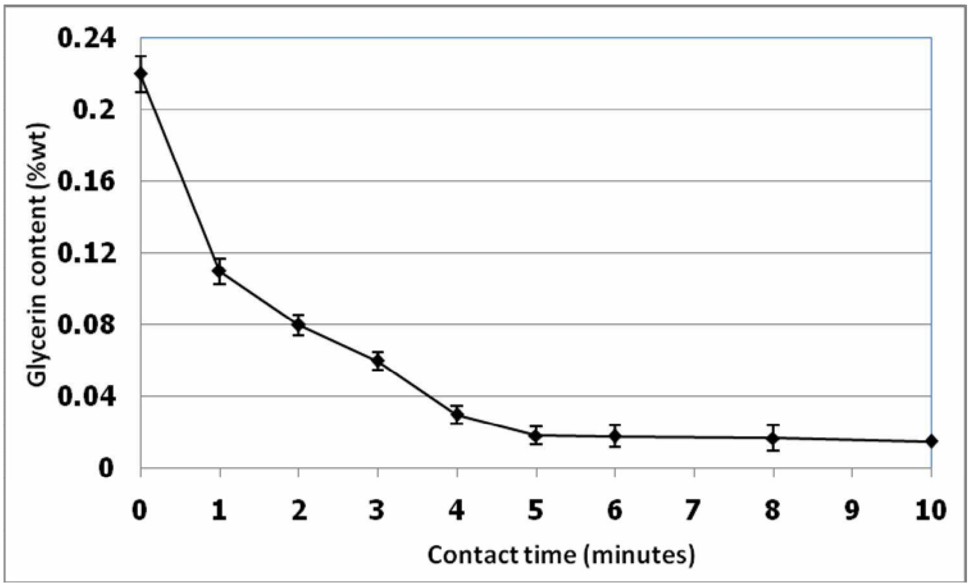


Figure 3.23 Effect of contact time on %wt of glycerin content in ethyl ester

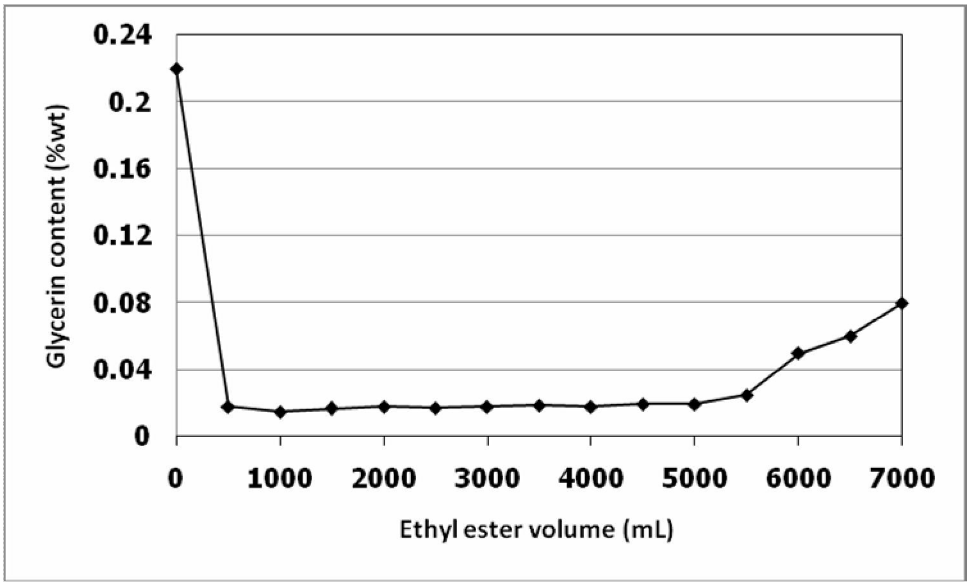


Figure 3.24 Evolution of glycerin content vs. mL ethyl ester to 50 g bleaching earth

The bleaching earth which was used in this process is a white powder (Figure 3.25A), but the spent bleaching earth turned to a light brown color (Figure 3.25B) due to adsorption of colored compounds, soap, glycerin, residual catalyst and ethyl ester. The spent bleaching earth was extracted by hexane (Figure 3.25C). Their properties were given in table 3.6. The surface area of fresh bleaching earth was 277 m^2/g while that the spent bleaching earth was 28 m^2/g and the spent bleaching earth after extract ethyl ester by hexane was 159 m^2/g. The surface area of the spent bleaching earth after extract ethyl ester by hexane was decreased more than 40% compare with fresh bleaching earth. For this case the spent bleaching earth after extract ethyl ester by hexane unsuitable to purified ethyl ester, however the spent bleaching earth was used in cement manufacture, as a source of silicium dioxide, or mixing with sandy oils [Ong, 1983 and Tsai et al., 2002]. Figure 3.26 presents scanning electron micrographs of bleaching earth which was used in purification process.

A B C

Figure 3.25 Appearance of fresh bleaching earth (A), spent bleaching earth (B) and spent bleaching earth after extract ethyl ester by hexane (C)

The SEM micrographs of the surface of fresh bleaching earth, the spent bleaching earth and the extracted bleaching earth by hexane are illustrated in figure 3.26, showing a great difference between these samples. The surface structure examination of fresh bleaching earth (A) was similarly in the extracted bleaching earth (C) which was clearly seen in the SEM photographs. Because the residual ethyl ester in spent bleaching earth (B) was extracted by hexane. Spent bleaching earth adsorbed ethyl ester approximately 90 %wt of bleaching earth. This ethyl ester was extracted by hexane and the efficiency of extracted ethyl ester from spent bleaching earth by hexane was 75 %. Extracted bleaching earth was unsuitable purification ethyl ester because the surface area of extracted bleaching earth decreased more than 45% compared with fresh bleaching earth (Surface area of fresh bleaching earth 277.1 m^2/g and extracted bleaching earth 159.2 m^2/g). The glycerin content in ethyl ester which was removed by fresh bleaching and extracted bleaching earth was 0.019 and 0.063 %wt, respectively (The initial glycerin content in ethyl ester was 0.105 %wt). The efficiency of remove glycerin content in ethyl ester of extracted bleaching earth decreased more than 40% compared with fresh bleaching earth. However, the extracted bleaching earth can be applied in cement manufacture, as a source of silicium dioxide, or mixing with sandy oils.

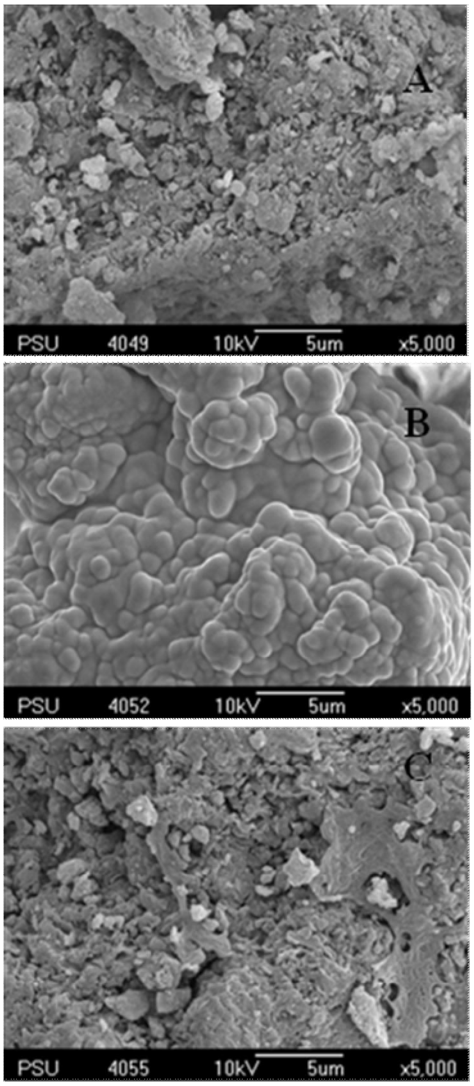


Figure 3.26 Scanning electron micrographs (X5000) of (A) fresh bleaching earth, (B) spent bleaching earth and (C) spent bleaching earth after extract ethyl ester by hexane

The optimum condition for production ethyl ester from crude palm oil by continuous microwave have been identified for the esterification process as a 1:24 molar ratio FFA to ethanol, 5 %wt of H_2SO_4 to FFA as the catalyst, a reaction time of 90 minutes, and a microwave power output of 78 W, for the transesterification process as a 1:8.5 molar ratio of oil to ethanol, 2.5%wt of KOH to oil as a catalyst, a reaction time of 7 minutes and a microwave power output of 78 W. For the separation process used 10 %wt of pure glycerin to separated glycerin from ethyl ester and purification process used bleaching earth to purified ethyl ester and a contact time of 5 minutes. This process gave a yield of 80 %wt of ethyl ester with ester content 98.1 %wt.

3.4 The fuel properties analysis of the final product

The fuel properties of ethyl ester in comparison with those of methyl ester standards are shown in table 3.6. It can be seen that most of its salient properties fall within the limits prescribed by EN14214 standards for methyl ester.

Table 3.6 Properties of ethyl ester in comparison with diesel and biodiesel standards

Item	Properties, unit	Test Method	Specification (EN14214)	This work
1	Ester content , %wt	EN 14103	96.5 min	
2	Density at 15 °C, Kg/m^3	ASTM D4052	875-900	879.8
3	Viscosity at 40 °C, cSt	ASTM D445	3.5-5.0	5.57
4	Flash point, °C	ASTM D93	120 min	160
5	Sulfur ,%wt	ASTM D5453	0.001 max	0.0002
6	Carbon residue ,%wt	ASTM D4530	0.3 max	0.12
7	Sulfated ash ,%wt	ASTM D874	0.02 max	0.0066
8	Water content ,%wt	ASTM D2709	0.05 max	0.03
9	Total acid number, mgKOH/g	ASTM D664	0.50 max	0.33
10	Iodine value, g Iodine/100g	EN 14111	120 max	47.75

Item	Properties, unit	Test Method	Specification (EN14214)	This work
11	Copper strip corrosion	ASTM D130	1 max	1
12	Oxidation stability at 110 °C	EN 14112	10.0 min	1.14
13	Group II metals (Calcium, mg/kg)	ASTM D5185	5 max	0.12
	Group II metals (Magnesium, mg/kg)		5 max	0.14
14	Phosphorus, %wt.	ASTM D 4951	0.001 max	<0.0005

3.5 The un-reacted ethanol recycling by distillation

The un-reacted ethanol consisted of about 3.3 %wt residual H_2SO_4 (pH was about 5.5) and was distillated by ASTM D86. The results show in table 3.7. It can be seen that the major product from distillation was ethanol because the distillation temperature from the product was 78°C. However, the minor product from distillation was water which was not separated from ethanol by distillation because ethanol and water are azeotrope. Ethanol boils at 78.4°C, water boils at 100°C, but the azeotrope boils at 78.1°C, which is lower than either of its constituents. However, ethanol and water was separated by other method such as azeotropic distillation, pervaporation and other membrane methods.

The distillated residue ethanol from esterification process is shown in figure 3.27. It can be seen that the distillated product (5-70 % distillation) was colorless liquid. The residue from distillation was sulfuric acid, oil and gum. The ethanol from distillation can blend with fresh ethanol and use as alcohol in esterification process.

Table 3.7 Distillation temperatures and water content of the un-reacted ethanol

%Distillation	Distillation temperature (°C)	Water content* (%wt)
First drop	78	
5	78	4.1
10	78	4.0
20	78	4.0
30	78	4.4
40	78	4.0
50	78	3.9
60	78	4.1
70	78	4.3

*The initial water content in the un-reacted ethanol (Before distillation) is 4.0 %wt.

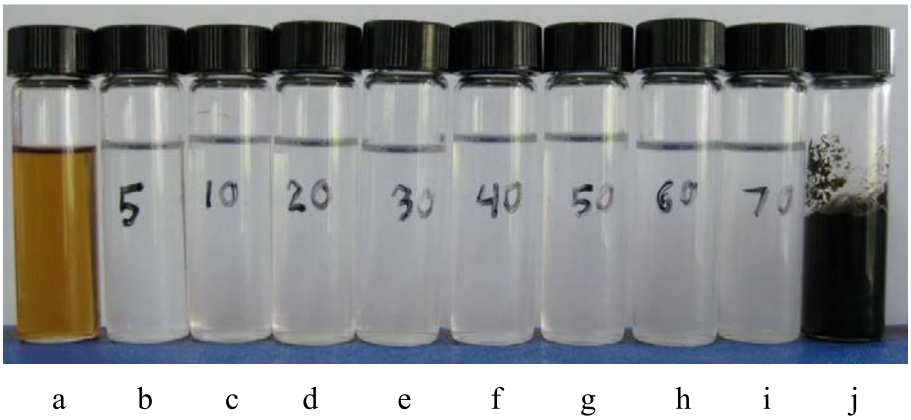


Figure 3.27 The physical appearance of distillated un-reacted ethanol

(a) un-reacted ethanol before distillation; (b) 1-5 %faction; (c) 6-10 %faction; (d) 11-20 %faction; (e) 21-30 %faction; (f) 31-40 %faction; (g) 41-50 %faction; (h) 51-60 %faction; (i) 61-70 %faction; (j) residual product from distillation

3.6 Evaluation the cost of ethyl ester by microwave

3.6.1 Energy consumption

These calculations can be extended to our original batch processes. The results are summarized in table 3.8 (Appendix A)

To probe the energy consumption during the course of the reaction, we monitored the power consumption in the 0.5 L batch reaction, 1 L/hr continuous reaction using a microwave and 1 L batch reaction by conventional heating. From the table 3.16 we found that for 0.5 L batch process, 1 L continuous flow process and conventional heating process, the total energy consumption for ethyl ester production was 780, 567 and 731 kJ/L of ethyl ester prepared, respectively. It is evident that, while the energy consumption of the batch process may be on the order of that of the conventional process, the continuous-flow processes are more energy efficient.

Table 3.8 Energy consumption estimations for the preparation of biodiesel using conventional and microwave heating

Entry	Reaction conditions	Energy consumption (kJ/L)	
		Esterification	Transesterification
1	Microwave 0.5 L batch process	720	60
2	Microwave 1 L continuous process	567	
3	Conventional heating 1 L batch process	515	216
4	Microwave heating, 4.6 L batch reaction [a]	-	90.1
5	Microwave, continuous flow at a 2 L/minutes [b]	-	60.3
6	Conventional heating [c]	-	94.3

a A microwave input of 800 W, a time to reach 50 °C of 3.5 minutes. [Michael Barnard et al., 2007]

b A microwave input of 1045 W. [Michael Barnard et al., 2007]

c On the basis of values from the joint U.S. Department of Agriculture and U.S. Department of Energy 1998. [Michael Barnard et al., 2007]

The obtained results are in good agreement with the finding of Barnard et al., (2007) who employed the microwave process to produce biodiesel. The microwave continuous process is more energy efficient than conventional process and the energy consumptions in transesterification from this study was similar valuable with Bernard et al., (2007).

3.6.2 Production cost

A production cost analysis is shown in table 3.9. The primary cost of biodiesel was the feedstock. CPO prices have jumped over 40% during year 2009, resulting in the rising price of CPO from 18 baht/kg in November 2008 to 26 baht/kg in July 2009. The secondary cost was ethanol. The price of ethanol has been increasing with increasing agriculture prices because ethanol is produced from agriculture. The costs of the other factors were less substantial. The total production cost was 40.5 baht/L. The production cost from these experiments was in good agreement with the observations of Thamsiriroj (2007) who found that the total production cost of biodiesel from CPO was 35.6 baht/L. However the biodiesel producers also have revenue from selling glycerin and recovery ethanol from ethyl ester and glycerin, thus reducing their costs.

Table 3.9 Production cost for the preparation of ethyl ester by microwave heating

Materials	Unit cost	Quantity	Production cost of biodiesel (baht)
Crude palm oil	18 baht/kg	1000 g	18
H_2SO_4	10 baht/kg	12.5 g	0.1
KOH	85 baht/kg	25 g	2.1
Ethanol	25 baht/kg	516 g	12.9
Pure glycerin	45 baht/kg	100 g	4.5
Bleaching earth	20 baht/kg	12 g	0.2
Electricity	3.5 baht/kw h	0.158 kw.h	0.5
Total			38.3 (42.5 baht/L)

The amount of biodiesel product was 0.9 L from CPO 1 kg by continuous process

CHAPTER 4

CONCLUSIONS and SUGGESTIONS

4.1 Conclusions

This study showed the potential of ethyl ester production from CPO which has high FFA. In esterification process the FFA content changed considerably with molar ratio of CPO to ethanol, reaction time and amount of acid catalyst. The FFA content decreased with the increasing of each of the three factors. Similarly, a good conversion rate was obtained from an appropriate microwave power. The high amount of 7 %wt of FFA in CPO can be reduced to less than 2 %wt by esterification processes using the optimum batch and continuous operating conditions. Those were, 1:24 molar ratio FFA to ethanol, 4 %wt of H_2SO_4 to FFA as the catalyst, a reaction time of 1 h, and a microwave power output of 70 W. The optimum condition for continuous process was a 1:24 molar ratio FFA to ethanol, 5 %wt of H_2SO_4 to FFA as the catalyst, a reaction time of 90 minutes, and a microwave power output of 78 W.

The esterified crude palm oil that had 1.7 %wt of FFA content and molar ratio of oil to ethanol : 1:4 was reacted in transesterification process for change the triglyceride to ester. The optimum condition for batch process was a 1:8.5 molar ratio of oil to ethanol, 1.5 %wt of KOH to oil as a catalyst, a reaction time of 5 minutes and a microwave power output of 70 W and for the continuous process was a 1:8.5 molar ratio of oil to ethanol, 2.5 %wt of KOH to oil as a catalyst, a reaction time of 7 minutes and a microwave power output of 78 W.

For the separation process used 10 %wt of pure glycerin to separated glycerin from ethyl ester and purification process used bleaching earth to purified ethyl ester and a contact time of 5 minutes. This process gave a yield of 80 %wt of ethyl ester with ester content 98.1 %wt.

The fuel properties of ethyl ester in comparison with those of methyl ester standards can be seen that most of its salient properties fall within the limits prescribed by EN 14214 standards for methyl ester.

Microwave irradiation accelerates the chemical reaction within a short time compare with conventional heating.

The bleaching earth can purified ethyl ester. The spent bleaching earth after extract ethyl ester by hexane unsuitable to purified ethyl ester, however the spent bleaching earth was used in cement manufacture, as a source of silicium dioxide, or mixing with sandy oils.

4.2 Suggestions

1) For this study, microwave was pierced. So, the operator should be careful the microwave irradiation which leak from experiment.

2) The reactor in microwave oven made from glass tube, it could not using metal to make the reactor in microwave oven. So, it easy to broken. The reactor may use plastic to make the reactor in microwave oven.

3) The capacity of ethyl ester production depends on the size of microwave oven. Because the reactor was in the microwave oven. So, if microwave oven was enlarged, the production rate of ethyl ester was increased too.

4) The separation process for this study used pure glycerin which was expensive. So, for decreasing the cost, the other separation process should be study. For example, adding water or adding crude glycerin.

REFERENCES

Agarwal, A.K. and Das, L.M. 2001. Biodiesel development and characterization for use as a fuel in compression ignition engines. *Trans. ASAE*. 123: 440-447.

Amore, K.M., Leadbeater, N.E., Miller, T.A. and Schmink, J.R. 2006. Fast, easy, solvent-free, microwave-promoted Michael addition of anilines to α,β-unsaturated alkenes: synthesis of N-aryl functionalized beta-amino esters and acids. *Tetrahedron Letters* 47: 8583–8586.

Azcan, N. and Danisman, A. 2008. Microwave assisted transesterification of rapeseed oil. *Fuel* 87 : 1781–1788.

Baghurst, D.R. and Mingos, D.M.P. 1991. Application of Microwave Dielectric Heating Effects to Synthetic Problems in Chemisry. *Chemical Society Reviews* 20: 1–47.

Barnard, T. M., Leadbeater, N.E., Boucher, M.B., Stencel, L.M. and Wilhite, B.A. 2007. Continuous-Flow Preparations of Biodiesel Using Microwave Heating. *Energy & Fuels* 21: 1777-1781.

Barnwal, B.K. and Sharma, M.P. 2005. Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable Energy Reviews* 9**:** 363–378.

Bender, M. 1999. Economic feasibility review for community-scale farmer cooperatives for biodiesel. *Bioresource Technology* 70: 81-87.

Canakci, M. and Gerpan, J.V. 1999. Biodiesel production via acid catalysis. *Trans. ASAE* 42: 1203-1210.

Choo, Y.M., Yung, C.L., Cheng, S.F. Ma, A.N., Chuah, C.H. and Yusof, B. 2005. Key fuel properties of palm oil alkyl ester, *Short Communication Fuel*; 84 : 1717-1720.

Daewoo Electronics Co., Ltd., Service Manual Microwave Oven.

Demirbas, A. 2006. Biodiesel production via non-catalytic SCF method and Biodiesel fuel characteristic. *Energy Conversion and Management* 47: 2271-2282.

Di Serio, M., Tesser, R. M., Dimiccoli, M., Cammarota, F., Nastasi, M. and Santacesaria, E. 2005. Synthesis of biodiesel via homogeneous Lewis acid catalyst. *Journal of Molecular Catalysis A: Chemical* 239: 111-115.

Encinar, J.M. González, J.F. and Rodríguez-Reinares A., 2007. Ethanolysis of used frying oil. Biodiesel preparation and characterization. *Fuel Processing Technology* 88: 513–522.

Furuta, S., Matsuhashi, H. and Arata, K. 2004. Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catalysis Comunications* 5: 721-723.

Gabriel, C., Gabriel, S., Grant, E.H., Halstead, B.S. and Mingos, D.M.P. 1998. Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews* 27: 213–223.

Ghadge, S.V. and Raheman, H. 2005. Biodiesel production from mahua oil having high free fatty acids. *Biomass and Bioenergy* 28: 601-605.

Glasnov, T.N., Tye, H. and Kappe, C.O. 2008. Integration of High Speed Microwave Chemistry and a Statistical "Design of Experiment" Approach for the Synthesis of the Mitotic Kinesin Eg5 Inhibitor Monastrol. *Tetrahedron* 64: 2035–2041.

Goebel, E.H. 1976. Bleaching practices in the U.S. *JAOCS* 53: 342–343.

Hernando, J., Leton, P., Matia, M.P., Novella, J.L. and Alvarez-Builla, J. 2007. Biodiesel and FAME synthesis assisted by microwaves: homogeneous batch and flow processes. *Fuel* 86: 1641–1644.

Issariyakul, T., Kulkarni, M. G., Dalai, A. K. and Bakhshi, N.N. 2007. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. *Fuel Processing Technology* 88: 429–43.

Khan, A.K. 2002. Research into biodiesel kinetics & Catalyst development. Ph.D. Brisbane, Queensland, Australia.

Kheang, L.S., Foon, C. S. May, C. Y. and Bgan, M. A. 2006. A Study of Residual Oils Recovered from Spent Bleaching Earth. *American Journal of Applied Sciences* 10: 2063-2067.

Kojima, S.D., Sato, D.M. and Park, E. Y. 2004. Efficient Production of Fatty Acid Methyl Ester from Waste Activated Bleaching Earth Using Diesel Oil as Organic Solvent. *Journal of Bioscience and Bioengineering* 98: 420–424.

Kulkarni, G.M. Dalai, A.K. and Bakhshi, N.N. 2007. Transesterification of canola oil in mixed methanol/ethanol system and use of esters as lubricity additive. *Bioresource Technology* 98: 2027–2033.

Kusdiana, D. and Saka. S. 2004. Kinetics of Transesterification in Rapeseed Oil to Biodiesel Fuels as Treated in Supercritical Methanol. *Fuel* 80: 693-698.

Lühken, A. and Bader, H. J. 2009. Energy input from microwaves and ultrasound – examples of new approaches to green chemistry. Available online at: http://www.rsc.org/education/teachers/learnnet/green/docs/microwaves.pdf [accessed: 9 September 2009]

Ma, F. and Hanna, M.A. 1999. Biodiesel production: a review. *Bioresource Technology* 70: 1-15.

Marchetti, J.M., Miguel, V.U. and Errazu, A.F. 2007. Possible Methods for Biodiesel Production. *Renewable and Sustainable Energy Reviews* 11: 1300-1311.

Marchetti, J.M. and Errazu A.F. 2008. Shot communication. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. *Biomass and Bioenergy* 32: 892-895.

May C.Y., Ngan M.A., Yoo C.K., Majid R.A., Chung A.Y.K., Nang H.L.L., Foon C.S., Liang Y.C., Wei P.C., Han N.M. and Basiron Y. 2005. Palm Diesel: Green and Renewable Fuel from Palm Oil. *Palm Oil Developments* 42: 3-7.

Mazzocchia, C., Modica, G., Kaddouri, A. and Nannicici, R. 2004. Fatty Acid Methyl Esters Synthesis from Triglycerides over Heterogeneous Catalysts in Presence of Microwaves. *C.R. Chime* 601-604.

Meher, L.C., Vidya Sagar, D. and Naik, S.N. 2006. Technical Aspects of Biodiesel Production by Transesterification. *Renewable and Sustainable Energy Reviews* 10: 248-268.

Mittelbach, M., Remschmidt, C. 2004. Biodiesel The comprehensive handbook. First edition. Boersedruck Ges.m.b.H, Vienna, Austria.

Nelson, Y.A., Foglia, T.A. and Marmer, W.N. 1996. Lipase-catalyzed production of biodiesel. *Journal American Oil of Chemical Society* 73(3): 1191-1195.

Ong, J.T.L. 1983. Oil Recovery from Spent Bleaching Earth and Disposal of the Extracted Material. *Journal American Oil of Chemical Society* 60: 314-315.

Pilar, D.M., Evaristo, B., Franscisco, J.L. and Mattin, M. 2004. Optimization of alkali-catalyzed transesterification of brassica calinata oil for biodiesel production. *Energy Fuels* 18: 77-83.

Refaat, A.A. and El Sheltawy, S.T. 2008. Time factor in microwave-enhanced biodiesel production. *WSEAS Transactions on Environment and Development* 4: 279-288.

Ramadhas, A.S., Jayaraj, S. and Muraleedharan, C. 2005. Biodiesel production from high FFA rubber seed oil. *Fuel* 84: 335-340.

Rini, S.J. 1960. Refining, bleaching, stabilization, deodorization, and plasticization of fats, oil and shortening. *Journal of the American Oil Chemists' Society* 37: 515–520.

Rossi, M., Gianazza, M., Alamprese, C. and Stanga, F. 2003. The Role of Bleaching Clays and Synthetic Silica in Palm Oil Physical Refining. *Food Chemistry* 82: 291-296.

Saifuddin, N. and Chua. K.H. 2004. Production of Ethyl Ester (Biodiesel) from used Frying Oil: Optimization of Transesterification Process using Microwave Irradiation. *Malaysian Journal of Chemistry* 6: 77-82.

Srisan, K. 2002. Feasibility Study of Producing Biodiesel from Palm Oil. M.D. Thesis, Chulalongkorn University.

Tat, M.E. and Van Gerpen, J.H. 2000. The specific gravity of biodiesel and its blends with diesel fuel. *Journal of the American Oil Chemists' Society* 77: 115-119.

Thamsiriroj, T. 2007. Optimal Biomass and Technology for Production of Biofuel as a Transport Fuel. M.D. Thesis, University College Cork, National University of Ireland.

Tsai, W.T., Chen, H.P., Hsieh, M.F., Sun. H.F. and Chien, S.F. 2002. Regeneration of spent bleaching earth by pyrolysis in a rotary furnace. *Journal of Analytical and Applied Pyrolysis* 63: 157–170.

Vicente, G., Martinez, M. and Aracil, J. 2004. Intergrated Biodiesel Production: a Comparison of Different Homogeneous Catalysts Systems. *Bioresource Technology* 92: 297-305.

Wang, Y., Ou, S., Liu, P., Xue, F. and Tang, S. 2006. Comparison of two different processes to synthesize biodiesel by waste cooking oil. *Journal of Molecular Catalysis A*: Chemical 252: 107–12.

Wing-Keong, N., Phaik-Kin, L. and Peng-Lim, B. 2003, Dietary lipid and palm oil source affects growth, fatty acid composition and muscle α-tocopherol concentration of African catfish Clarias gariepinus, *Aquaculture* 215: 229-243.

APPENDIX A

SAMPLE CALCULATION

1. Mass balance for batch process

Molecular weight

CPO = 860 g/mol Ethanol = 46 g/mol FFA = 256 g/mol

Glycerin = 92 g/mol Ethyl ester = 300 g/mol Water = 18 g/mol

1.1 Esterification

CPO 300 g (0.349 mol) FFA 7.5%wt

Condition for esterification

Molar ratio of FFA : ethanol 1:24 Ethanol = 97 g

Sulfuric acid 4%wt (H_2SO_4/FFA) Sulfuric acid = 3 g

Composition of the product from esterification

Esterified palm oil phase 341 g

FFA 1.4%wt Water 1.2g Sulfuric acid = 1.9 g Ethanol = 60.9 g

Ethanol phase 29.7 g

Water 1.4 g Sulfuric acid = 1.0 g Ethanol = 31.3 g

1.2 Transesterification

Condition for transesterification

Molar ratio of oil : ethanol 1:8 Ethanol = 145.2 g (esterification 60.9 adding 84.1 g)

Potassium hydroxide 1.5%wt Potassium hydroxide = 4.5 g

Pure glycerin 10%wt Pure glycerin = 30 g

Composition of the product from transesterification

Ethyl ester 247.6 g glycerin 114.2 g Ethanol 117.9 g

1.3 Theory

CPO 300 g FFA 7.5 %wt = Triglyceride 277.5 g FFA 22.5 g

Esterification process

FFA in esterified palm oil 1.4 %wt FFA was reacted in esterification process 6.1 %

FFA 6.1% = 18.3 g = 0.071 mol

Water from reaction = 0.071 mol = 1.3 g

Ethanol consumes = 0.071 mol = 3.3 g

Ethyl ester from reaction = 0.071 mol = 21.3 g

Transesterification process

Triglyceride 277.5 g = 0.32 mol

Ethyl ester from reaction= 0.96 mol = 288 g

Glycerin from reaction = 0.32 mol = 29.4 g

Ethanol consumes = 0.92 mol = 42.3 g

	Theory (g)	Experiments (g)
CPO 300 g FFA 7.5 %wt		
Esterification		
Amount of ethanol	3.3	92.4
Water from reaction	1.3	1.2
Transesterification		
Amount of ethanol	42.3	145.2
Ethyl ester from reaction	309.3	247.6
Glycerin from reaction	29.4	84.2

2 Energy for production ethyl ester

2.1 Energy for production ethyl ester using hot plate

CPO 1000 g Cp of CPO = 2.2 J/g^{O}C CPO 100 g give ethyl ester 100 ml

Heat loss from only hot plate

Ethanol (308 g for esterification and 410 g for transesterification)

Cp of ethanol = 2.44 J/g^{o}C

Initial temperature 28 ^{o}C and reaction temperature 68 ^{o}C $\Delta T = 68 - 28 = 40\ ^{o}C$

Surface area of heat plate = 49 in^{2}

Surface temperature of hot plate = 248.6 ^{o}F (120 ^{o}C)

From figure watt loss at 248.6 ^{o}F = 0.5 W/in^{2} Heat loss = 24.5 W

Time for pre heat = 30 minutes, time for esterification process = 240 minutes and time for transesterification process = 30 minutes

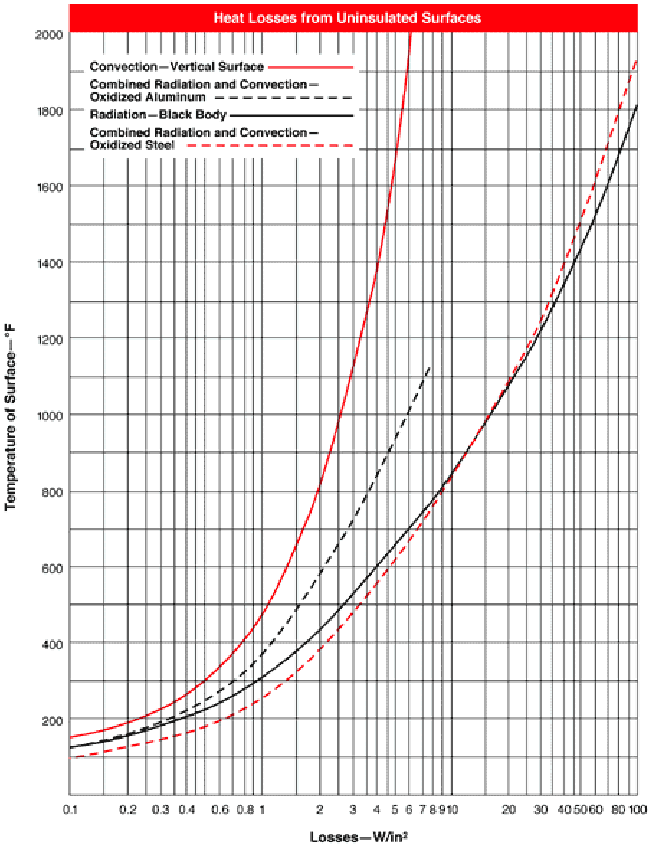


Figure A1 Heat losses from uninsulated surfaces [www.watlow.com]

Esterification process

Q = mCpΔT

CPO = 1000g X 2.2 J/g^{O}C X 40 ^{O}C = 88,000 J (49 W)

Ethanol = 308g X 2.44 J/g^{O}C X 40 ^{O}C =30,060 J (16.7 W)

Heat loss from hot plate = 24.5W X (30 min + 240 min) X 60 s/min = 396,900 J

Power for esterification process = 515 KJ (90.2 W, 143 Whr)

Transesterification process

$Q = mCp\Delta T$

CPO = 1000g X 2.2 J/g^{O}C X 40 ^{O}C = 88,000 J (49 W)

Ethanol = 410g X 2.44 J/g^{O}C X 40 ^{O}C = 40,016 J (22.2 W)

Heat loss from hot plate = 24.5 W X (30 min + 30 min) X 60 s/min = 88,200 J

Power for transesterification process = 216.2 KJ (95.7 W, 60.1 Whr)

Total power for production ethyl ester using hot plate = 515 + 216.2 = 731.2 KJ (203.1Whr)

2.2 Energy for production ethyl ester using batch microwave

CPO 500 g Ethanol (154 g for esterification and 210 g for transesterification)

Time for reaction = 65 min (time for esterification process = 60 min and time for transesterification process = 5 min) Microwave power input 100 W

Total power for production ethyl ester using batch microwave = 100 J/S X 65 min X 60 S/min = 390 KJ (108 Whr)

2.3 Energy for production ethyl ester using continuous microwave

CPO 1000 g Ethanol (308 g for esterification and 410 for transesterification)

Flow rate of CPO 1000 g/hr

Pump 3 units. Power of pump 44 W (using 20% of power) =

8.8 W (31 KJ, 8.8 Whr) / unit

Motor for mixing 3 units.

Power of motor 72 W (using 10% of power) = 7.2 W (25.9 KJ, 7.2 Whr) / unit

Microwave power input 110 W (396 KJ)

At steady state

Total power for production ethyl ester using continuous microwave /ethyl ester 1000 ml

= (31 X 3) + (25.9 X 3) + 396

= 566.7 KJ (158 Whr)

APPENDIX B

PHISICAL ANALYTICAL METHODS FOR BIODIESEL

1. Specific gravity

The specific gravity is a relative measure of the density of a substance. It is defined as the ratio of the density of the substance, ρ, to a reference density, ρref. The equation for the specific gravity (SG) is SG = ρ/ρref. The most common reference density used in the measurement of specific gravity is the density of water at 4°C, which corresponds to a reference density of 1 g/cc. The specific gravity of conventional No. 2 diesel fuel is about 0.85 while a typical density of biodiesel is 0.88, which means that biodiesel is more density than conventional diesel fuel. Figure B1 shows a hydrometer for measuring specific gravity. Other methods are also in common use.

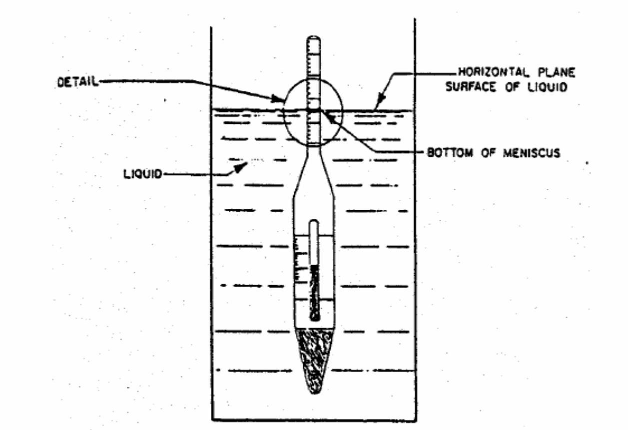


Figure B1 Hydrometer for measuring specific gravity

2. Kinematic viscosity

To define kinematic viscosity it is useful to begin with the definition of viscosity. Simply stated, viscosity, which is also called dynamic viscosity (η), is the ease with which a fluid will flow. We intuitively understand viscosity as evidenced by the fact that we know, for example, honey is more viscous than water. There is a hydrodynamic definition of viscosity as well. Technically it is the ratio of the shear stress to the shear rate for a fluid. In contrast, the kinematic viscosity (ν) is the resistance to flow of a fluid under gravity. Therefore, the kinematic viscosity of a fluid is related to the dynamic viscosity through the density (ρ), i.e., ν

= η/ρ. The standard procedure for measuring kinematic viscosity in diesel or biodiesel fuels is ASTM D 445. The summary of the test method as presented in the standard is “The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature.” The repeatability of the test is within 0.5- 1.0%, while the reproducibility is 1-2%. The test is usually conducted by measuring the time required for a volume of liquid to flow under gravity through a calibrated glass capillary tube. The kinematic viscosity is then equal to the product of this time and a calibration constant for the tube. Figure B2 shows a Cannon-Fenske style glass capillary tube that is commonly used for ASTM D 445. Biodiesel is more viscous than No. 2 diesel fuel, but only by a small amount. Depending on feedstock and the amount of oxidation, biodiesel’s viscosity will vary between 4.0 and 6.2, while No. 2 diesel fuels tend to fall in the a narrower range of 2.4 to 2.6.

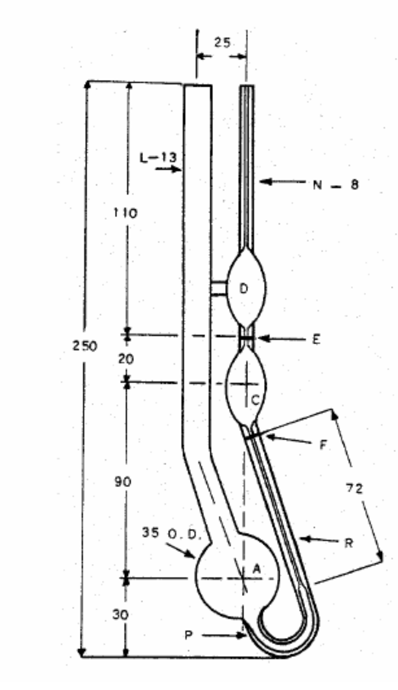


Figure B2 Cannon-Fenske capillary viscometer tube

3. Flash point

A key property determining the flammability of a fuel is the flash point. The flash point is the lowest temperature at which an applied ignition source will cause the vapors of a sample to ignite. Therefore, it is a measure of the tendency of a sample to form a flammable mixture with air. As a side note, the value of the flash point is used for the classification of flammable and combustible materials needed for safety and shipping regulations. The standard procedure for measuring the flash point for diesel and biodiesel fuels is ASTM D 93. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed. The flash need not correspond to a sustained flame. The "fire point" is sometimes used to designate the fuel temperature that will produce sufficient vapor to maintain a continuous flame. The equipment was shown in figure B3. The cup is filled with fuel and heated with an external heater. The agitator ensures that the fuel temperature is uniform. A small open flame is maintained from an external supply of natural gas. Periodically, the stirrer is stopped and the flame is pivoted down to an opening in the top of the cup to see if the fuel vapors will ignite. When the flash point has been reached, there will be a small flash that is sometimes accompanied by an audible popping sound. Occasionally, the flash may actually extinguish the flame on the ignition source. Figure 8 shows the test cup with its heat source and a heat shield that ensures uniform heating. The repeatability of the test is within 2°C and the reproducibility is 5°C.

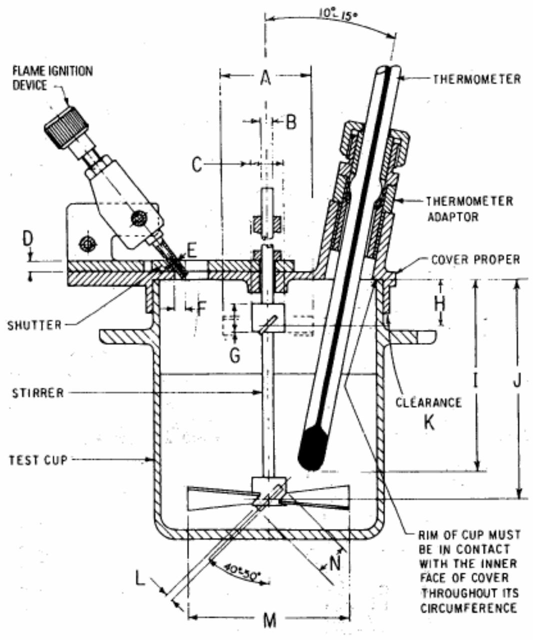


Figure B3 Test cup for ASTM D 93 flashpoint test

4. Distillation temperature

A property related to the flash point is the boiling point, which is the temperature at which a liquid transitions to a gas. For a pure substance the boiling point is a single temperature value. However, for a mixture of hydrocarbons as exists in diesel fuel there is a range of boiling points for the different constituent chemical species. The distillation test is used to determine the boiling range characteristics of a hydrocarbon sample. As one would expect, the distillation characteristics, i.e., the boiling point range, have an important effect on the performance, storage, and safety of fuels. Distillation limits are commonly included in petroleum product specifications due to the number of chemicals species that can be present. The standard procedure for measuring the boiling point range for diesel fuels is the distillation test, which is ASTM D 86. The simple distillation apparatus used for this test is shown in figure B4. To run the test, a simple batch distillation process is conducted on a sample of the fuel and boiling point data are collected. These data include the initial boiling point, the final boiling point, and the boiling temperature corresponding to increments of the volume of fuel distilled (5%, 10%, 20%, etc.). Unfortunately, the boiling temperatures of the compounds in biodiesel are so high at atmospheric pressure that the compounds may decompose (crack) during the distillation test. When this happens, the distillation information no longer corresponds to the original fuel. Distillation tests following ASTM D 86 are not appropriate for biodiesel. The ASTM standard D 6751 specifies a distillation test although it recommends ASTM D 1160, which is conducted under vacuum. The equipment used for the vacuum distillation test is shown in Figure 10. While this test will allow the biodiesel to be distilled without decomposing, the procedure specified in the technique for converting the distillation curve back to atmospheric pressure is only valid for petroleum products and should be used with caution for biodiesel.

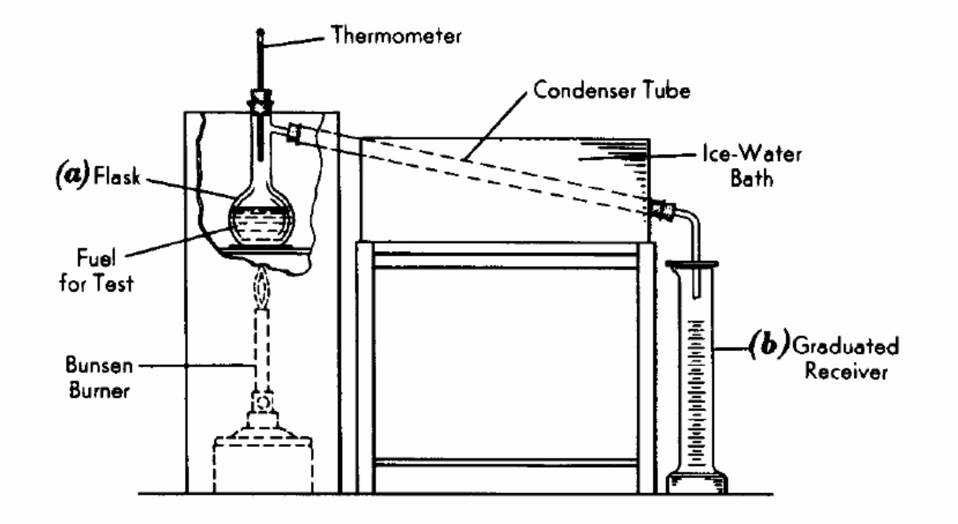


Figure B4 Distillation apparatus for ASTM D 86

5. Cloud point

A fuel property that is particularly important for the low temperature operability of diesel fuel is the cloud point. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid upon cooling. Therefore, it is an index of the lowest temperature of the fuel's utility under certain applications. Operating at temperatures below the cloud point for a diesel fuel can result in fuel filter clogging due to the wax crystals. As described in ASTM D 2500, the cloud point is determined by visually inspecting for a haze in the normally clear fuel, while the fuel is cooled under carefully controlled conditions. The apparatus used for this test is shown in figure B5. The cloud point is an important property for biodiesel since biodiesel fuels typically have higher cloud points, i.e., crystals begin to form at higher temperature, than standard diesel fuel. This feature has implications on the use of biodiesel in cold weather applications. An alternative procedure for measuring the cloud point of diesel/biodiesel fuels is ASTM D 5773. A summary of the procedure steps is 1) the sample is cooled in a Peltier device at a constant rate, 2) the sample is continuously monitored by optical detectors, and 3) the temperature is recorded that corresponds to the first formation of a cloud in the fuel. The repeatability of the cloud point test is <0.5°C and the reproducibility is <2.6°C.

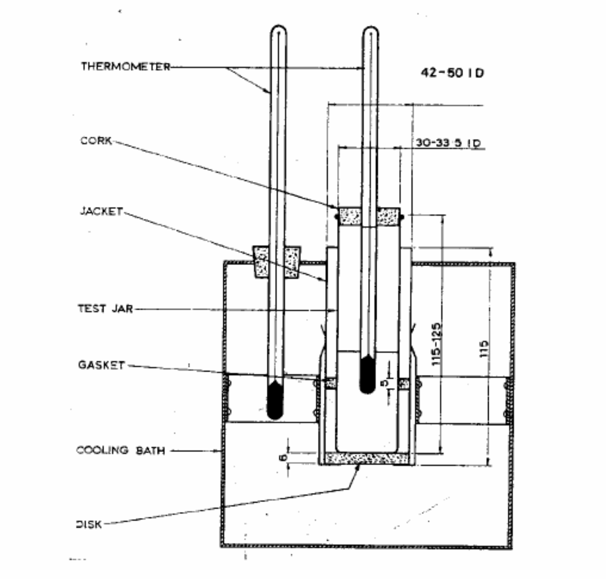


Figure B5 Cloud Point Apparatus

6. Pour point

A second measure of the low temperature performance of diesel/biodiesel fuels is the pour point. The pour point is the lowest temperature at which a fuel sample will flow. Therefore, the pour point provides an index of the lowest temperature of the fuel’s utility for certain applications. The pour point also has implications for the handling of fuels during cold temperatures. The standard procedure for measuring the pour point of fuels is ASTM D 97. A summary of the procedure steps is 1) the sample is cooled at a specified rate, 2) the sample is examined at 3°C intervals for flow, and 3) the lowest temperature at which sample movement is observed is noted. The repeatability of the pour point test is < 3°C and the reproducibility is < 6°C.

7. Copper strip corrosion

Many of the compounds in diesel fuel can be corrosive. The corrosiveness of a fuel is measured using the copper strip corrosion test, which is ASTM D 130. Copper and copper compounds tend to be particularly susceptible to chemical attack. The corrosivity of a fuel has implications on storage and use of the fuel. As an indicator of the tendency of a fuel to cause corrosion, polished copper strips are placed in the fuel for 3 hours at 50°C. Then the strips are washed in a solvent and compared to the descriptions in Table B1. The test results are given as a number followed by a letter. For example, a strip that was slightly tarnished with a dark orange color would be designated as “1b.”

Table B1 Copper Strip Classifications

Classification	Designation	Description
1	a	Light orange, almost the same as freshly polished strip
	b	Dark orange
2	a	Claret red
	b	Lavender
	c	Multicolored with lavender blue orsilver
3	a	Magenta overcast on brassy strip
	b	Multicolored with red and green showing
4	a	Transparent black, dark gray or brown
	b	Graphite or lusterless black
	c	Glossy or jet black

APPENDIX C

CHEMICAL ANALYTICAL METHODS FOR BIODIESEL

1. ASTM D – 4951: Standard test method for determination of additive elements in lubricating oils by inductively coupled plasma atomic emission spectrometry (Biodiesel limit < 0.001 mass % phosphorus)

Scope - This test method covers the quantitative determination of barium, boron, calcium, copper, magnesium, phosphorus, sulfur and zinc in unused lubricating oils and additive packages.

Additive packages are blends of individual additives, which can act as detergents, antioxidants, antiwear agents, etc. Many additives contain one or more elements covered by this test, which was developed for testing oil additives to meet industry specifications. In biodiesel processing, this test is used primarily for the determination of phosphorus content. The presence of phosphorus may be due to the incomplete refining of vegetable oil or bone and proteins remaining from the rendering process in recovering animal fats. This test can also be used to determine the presence of sulfur if the ICP instrument used can operate at a wavelength of 180 nm. However, this test is not the recommended method for sulfur determination when testing to meet the specifications of B100 biodiesel as outlined in ASTM D6751. That test method (D5453) is discussed later in this module.

Summary of method – A sample is diluted (1% to 5% by mass of oil in solvent) with mixed xylenes or kerosene. An internal standard is included in the solvent and calibration standards. The solutions are run through the ICP. By comparing emission intensities of the sample to those of the standards, concentrations of the elements present are determined.

Apparatus – Required and optional apparatus are listed in the apparatus section of the standard. The primary instrument is an atomic emission spectrometer that is equipped with a quartz inductively-coupled plasma (ICP) torch and r-f generator to form the plasma. Also needed are an analytical balance and solution containers. Optional equipment includes a peristaltic pump, solvent dispenser, vortexer and ultrasonic homogenizer. Mixed xylenes, o-xylene, or kerosene can be used as solvents. Base oil (U.S.P. white oil or a lubricating base oil free of analytes) is required for the internal standard solution (several possible internal standards are listed). Calibration standard solutions containing known concentrations of the elements being determined are prepared in accordance with the ASTM Practice D 4307. Phosphorus is the only element of interest when this test method is applied to biodiesel production specifications.

Sampling – The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Lab samples are recommended to be taken in accordance to ASTM D4057, which provides procedures for sampling petroleum products from a wide variety of containers. The specific sampling technique can affect the accuracy of this test.

Preparation of apparatus – Recommendations for the operation of the atomic emission spectrometer, ICP excitation source and peristaltic pump are given in this section of the test method. There are several different adequate instruments so the recommendation is to follow the manufacturer's instructions regarding operation of the ICP unit.

Preparation of test specimens – Procedures are given for the weighing out and dissolution of oil sample specimens

Preparation of calibration standards – The user is given freedom to determine the identity and concentration of calibration standards. Guidelines are given for solution preparation and instrument check standards are suggested.

Internal Standardization – This section of the test method outlines the required use of internal standards.

Calibration – A comprehensive discussion of calibration curves and the application of internal standards to those curves in ICP spectrometry is provided in this section. After compensating for the internal standard, the calibration curve is a plot of the intensity of emission for the analyte vs. analyte concentration.

Analysis – Samples should be analyzed using the same procedure as the calibration standards. An instrument check standard should be run after every fifth test specimen to ensure that the instrument is still calibrated.

Calculations

$C = S(W1+W2+W3)/W1$

where C = analyte concentration in sample (mass %)

S = analyte concentration in test specimen (mass %)

$W1$ = sample mass (g)

W2 = diluent mass (g)

W3 = base oil mass (g)

2 ASTM D – 5453: Standard test method for determination of total sulfur in light hydrocarbons, motor fuels and oils by ultraviolet fluorescense (Biodiesel limit – 0.05 mass %)

Scope – This test method covers the determination of total sulfur in liquid hydrocarbons. It is applicable to naphthas, distillates, oils, gasoline, diesel, biodiesel and jet fuel. Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur are present. Biodiesel feedstocks typically have very little sulfur, but this test is an indicator of contamination of protein material and/or carryover catalyst or neutralization material. Summary of method – The sample is inserted into a high temperature combustion tube where sulfur is oxidized to sulfur dioxide (SO2) in an oxygen rich atmosphere. Sample combustion gases are next exposed to UV light. The SO2 is excited, from which fluorescence is emitted as it returns to its stable state. The fluorescence is detected by a photomultiplier tube and the resulting signal is a measure of the amount of sulfur contained in the sample.

Apparatus – Required and optional apparatus are discussed in this section of the standard. Primary pieces of equipment include a Quartz Combustion Tube and a UV Fluorescence Detector. Sample input systems can either be a boat inlet system or a direct injection design. Another necessity for this test is a furnace capable of holding a temperature (1075±25°C) sufficient to pyrolyze all of the sample and oxidize sulfur to SO_2. Also required is a dryer tube or permeation dryer to remove water vapor that is produced in the pyrolysis tube. Water must be removed prior to the fluorescence measurement by the detector. The test method allows the option of using a self calibrating analyzer.

Reagents – High purity, dry oxygen is used in the pyrolysis tube. Solvents such as toluene, xylene, isooctane are needed to prepare standards and dilute samples. A sulfurcontaining compound such as dibenzothiophene, butyl sulfide, or benzothiophene can be used for calibration standards. Procedures for mixing appropriate standard are provided. QC samples, representative of the samples of interest, can be used to check the validity of the testing process.

Sampling – The objective of sampling is to obtain a test specimen that is representative of the entire quantity. Lab samples should be taken in accordance with ASTM D4057, which provides procedures for sampling petroleum products from a wide variety of containers. The specific sampling technique can affect the accuracy of this test.

Preparation of Apparatus – This section of the standard test method discusses the typical operating conditions including sample inlet rate, furnace temperature, oxygen flow rate, and carrier gas flow rate.

Calibration and Standardization – This section provides the procedure for preparation of a calibration curve. Three different suggestions for curve preparation are given, based on the anticipated sulfur concentration in the sample. Again, procedures for both direct injection and inlet boat delivery into the apparatus are provided.

Procedure – The procedure allows for either gravimetric or volumetric dilution of samples and either direct injection or inlet boat delivery into the apparatus. It requires repeat instrument calibration prior to reanalysis of the sample. Also, each test specimen must be measured three times and the average response must be calculated.

Calculation – Either analyzers calibrated using a standard curve or analyzers using a self calibration routine are accepted. Sulfur content can be calculated using either the mass or volume of the test sample for either type of analyzer used.

Using analyzer with standard curve:

(using sample mass) Sulfur (ppm) = $(I-Y)/SMKg$

I = integrated detector response (counts)

Y = y-intercept of standard curve (counts)

S = slope of standard curve (counts/μg Sulfur)

M = mass of test specimen (g)

Kg = gravimetric dilution factor;mass sample/mass sample+solvent (g/g)

(using sample volume) Sulfur (ppm) = $(I-1000Y)/SVKv$

V = volume of test specimen (g)

Kv = volumetric dilution factor; mass sample/volume sample+solvent

(g/mL)

Using self calibrating analyzer:

(using sample mass) Sulfur (ppm) = 1000G/MKg

G = sulfur found in test specimen (μg)

M = mass of sample solution injected (mg)

(using sample volume) Sulfur (ppm) =1000G/VD

D = density of sample in solution (mg/μL)

V = volume of sample solution injected (μL)

3 ASTM D – 874: Standard test method for sulfated ash from lubricating oils and additives (Biodiesel limit – 0.02 mass %)

Scope – This test method determines the amount of mineral ash remaining after a fuel is burned. For biodiesel, this test is an important indicator of the quantity of residual metals in the fuel that could come from the catalyst used in the esterification process. The lower limit of this test is 0.005 mass% sulfated ash.

Terminology – Sulfated ash is the residue remaining after the sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to constant weight.

Summary of the Test Method – The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775°C until oxidation of carbon is complete. The ash is then cooled, re-treated with the sulfuric acid, and heated at 775°C to constant weight.

Apparatus – Necessary for the test method are a furnace capable of maintaining 775±25°C and evaporating dishes or crucibles. A 50 or 100 mL crucible is recommended for samples containing more than 0.02 mass% sulfated ash. A 120 or 150 mL crucible is recommended for samples containing less than 0.02 mass% sulfated ash.

Reagents – Required reagents include concentrated sulfuric acid and 50 volume% sulfuric acid in water. Isopropanol and toluene may be needed if the sample contains sufficient moisture to cause foaming and loss of material from the dish/crucible.

Sampling – It is recommended to follow the instructions in ASTM Standard Practice D4057.

Procedure – The general steps required to complete this test are:

- Prepare the sample dish by heating at 775 C for at least 10 min, cooling, and weighing;
- Weigh in the sample to be determined;
- Heat the sample until the contents will sustain a flame and burn the sample until there is no further smoke or fumes;
- If the sample has sufficient moisture to foam, discard the sample, and follow procedures given to reduct the moisture content before proceeding;
- Cool the sample, add water and sulfuric acid, and heat until no further fumes are evolved;
- Place the dish in a furnace and heat at 775 C until oxidation of the carbon is complete. Continue the cooling, acidification and heating process until successive weightings differ by no more than 1.0 mg.

Calculation – Sulfated ash is calculated as a percentage of the original sample.

Sulfated Ash (%wt) = w/W*100

w = mass of sulfated ash (g)

W = mass of sample used in test (g)

Report – Report the result to the nearest 0.001 mass% for samples below 0.02 mass% and to the nearest 0.01 mass% for higher levels.

4 ASTM D 2709 Standard test method for water and sediment in middle distillate fuels by centrifuge (Biodiesel limit – 0.05 volume %)

Scope – This test method covers the determination of the volume of free water and sediment in middle distillate fuels having viscosities at 40°C in the range of 1.0 to 4.1 mm^2/s and densities in the range of 770 to 900 kg/m3. This test is a measure of cleanliness of the fuel. For B100 biodiesel it is particularly important because water can react with the esters to make free fatty acids and can support microbial growth in storage tanks.

Summary of Test Method – A 100 mL sample of undiluted fuel is centrifuged in a tube readable to 0.005 mL. After centrifugation, the volume of water and sediment which has settled into the tip of the centrifuge tube is read to the nearest 0.005 mL and recorded as the volumetric percent water and sediment by centrifuge.

Apparatus – Centrifuge which can be controlled to give a relative centrifugal force (rcf) of 800±60 at the tip of the tubes. A table is provided that relates centrifuge diameter and rpm to rcf. Specifications and suggested suppliers for centrifuge tubes are listed.

Sampling - It is recommended to follow the sampling instructions in ASTM Standard Practice D4057. The sample for a laboratory test will normally be an aliquot of a much larger sample taken for full or partial specification testing.

Procedure – 100 mL of a well-shaken sample is poured into a centrifuge tube and spun at 800±60 rcf for 10 minutes. The volume of combined water and sediment present at the bottom of the tube is recorded to the nearest 0.005 mL.

Report – Report the volume of the combined water and sediment read from the tube as a percentage of the total sample, since 100 mL of sample was used. Results lower than 0.005% may be reported as either 0 or 0.005 volume%.

Apparatus – Centrifuge which can be controlled to give a relative centrifugal force (rcf) of 800±60 at the tip of the tubes. A table is provided that relates centrifuge diameter and rpm to rcf. Specifications and suggested suppliers for centrifuge tubes are listed.

Sampling - It is recommended to follow the sampling instructions in ASTM Standard

Practice D4057. The sample for a laboratory test will normally be an aliquot of a much larger sample taken for full or partial specification testing.

Procedure – 100 mL of a well-shaken sample is poured into a centrifuge tube and spun at 800±60 rcf for 10 minutes. The volume of combined water and sediment present at the bottom of the tube is recorded to the nearest 0.005 mL.

Report – Report the volume of the combined water and sediment read from the tube as a percentage of the total sample, since 100 mL of sample was used. Results lower than 0.005% may be reported as either 0 or 0.005 volume%.

5 ASTM D – 664 Determination of acid number by potientiometric titration (Biodiesel limit 0.80 mg of KOH/g sample)

Scope - This test method covers procedures for the determination of acidic constituents in petroleum products and lubricants that are soluble in mixtures of toluene and isopropanol. In B100 (biodiesel), the acid number is a measure of free fatty acids. The free fatty acids can lead to corrosion and are a symptom of water in the fuel or fuel oxidation.

Discussion - This test method determines the quantity of base that is required to titrate a sample from its initial reading to a reading corresponding to a basic buffer solution or an inflection point as specified in the test method. It also provides the additional information on the quantity of base required to titrate a sample from its initial reading to a reading corresponding to an acidic buffer solution or an inflection point, as specified in the test method. This quantity is reported as the strong acid number. The causes and effects of strong acids and the causes and effects of other acids can be very different. Therefore, this test method differentiates and reports the two values. Since biodiesel generally contains only weak acids, this distinction is not relevant. An alternative method that is simpler to perform and gives similar results is the American Oil Chemist's Society Official Method Cd 3a-63. This method uses phenolphthalein indicators to determine neutrality. However, since it is not included in ASTM D 6751, it should be used only for process development, not for verifying product quality.

Summary of test method - The sample is dissolved in a mixture of toluene and isopropanol that contains a small amount of water. The sample is titrated potentiometrically with alcoholic potassium hydroxide. The meter readings are plotted against the respective volumes of titrating solution and the end points are taken at well defined inflections in the resulting curve.

Terminology - Acid number is the quantity of base, expressed as milligrams KOH per gram of sample, required to titrate the sample to a specified end point.

Apparatus - Exacting specifications are given in the standard for the potentiometer, electrodes, stirrer, buret, titration beaker, and titration stand to be used. Specifications of an automatic titration apparatus accepted as an adequate substitute are also given. Samples in alcohol solution while measuring the electrode potential in mV. A curve of KOH volume vs. potential is then plotted. Detailed procedures for the manual and automatic titration methods are given, including blank titrations of solvent.

Calculations – The electrode potential curves are plotted as the volume of KOH needed to titrate the sample vs mV or pH.The end (inflection) point is chosen as the point at which the curve is most nearly vertical. A procedure is also given for curves without a definite inflection point. Figure 20 is an example of the titration curves that are produced using this method.

Acid number = 56.1M(A-B)/W

where M = concentration of KOH (moles/L)

A = volume of KOH used to reach end point corresponding to basic buffer (mL)

B = volume corresponding to A for blank titration (mL)

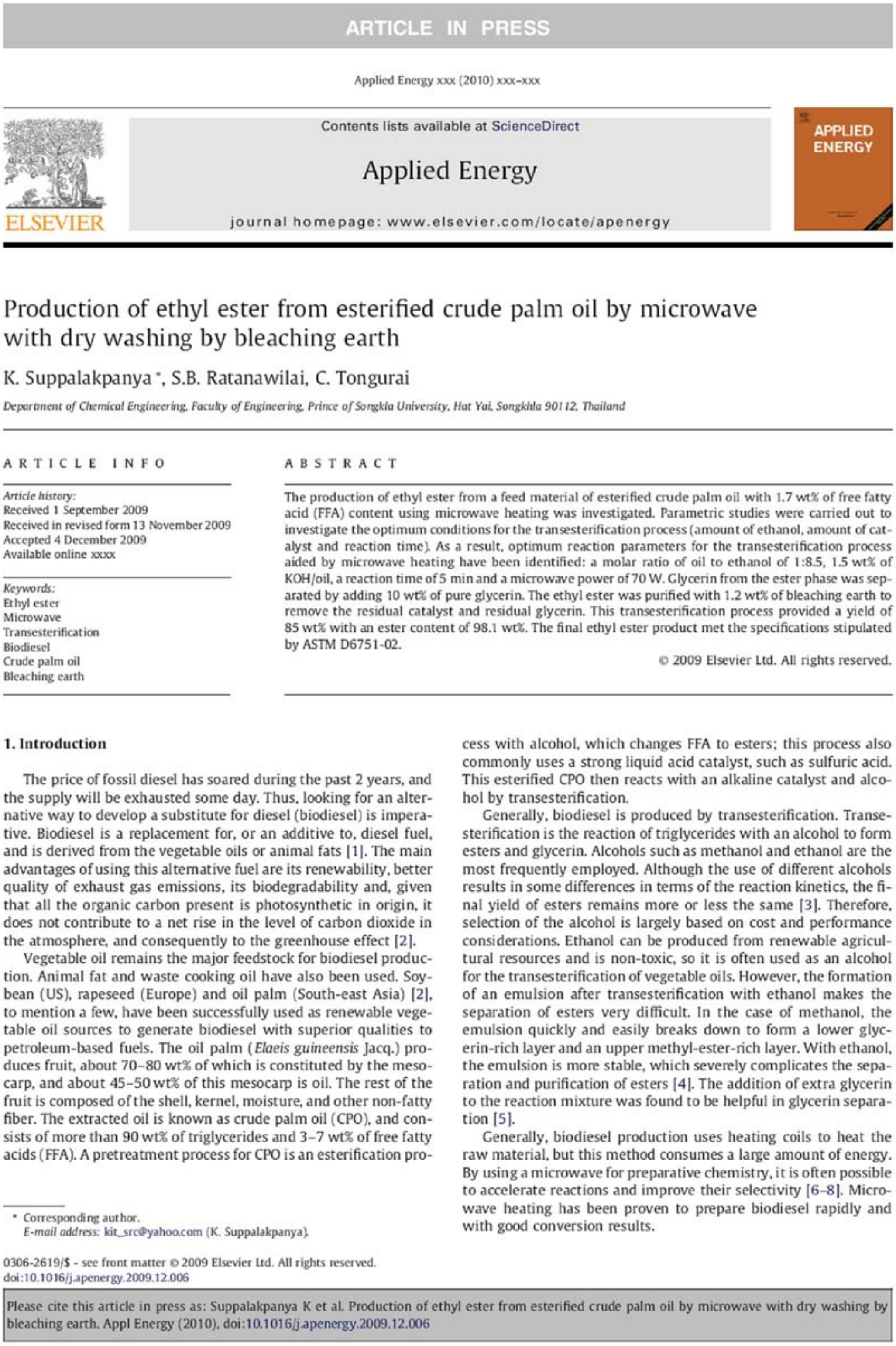
W = mass of sample (g)

APPENDIX D

REACTOR IN MICROWAVE OVEN

APPENDIX E

LIST OF PUBLICATION AND PROCEEDING



ARTICLE IN PRESS

Applied Energy xxx (2010) xxx–xxx

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth

K. Suppalakpanya *, S.B. Ratanawilai, C. Tongurai

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

A R T I C L E   I N F O

Article history:
Received 1 September 2009
Received in revised form 13 November 2009
Accepted 4 December 2009
Available online xxxx

Keywords:
Ethyl ester
Microwave
Transesterification
Biodiesel
Crude palm oil
Bleaching earth

A B S T R A C T

The production of ethyl ester from a feed material of esterified crude palm oil with 1.7 wt% of free fatty acid (FFA) content using microwave heating was investigated. Parametric studies were carried out to investigate the optimum conditions for the transesterification process (amount of ethanol, amount of catalyst and reaction time). As a result, optimum reaction parameters for the transesterification process aided by microwave heating have been identified: a molar ratio of oil to ethanol of 1:8.5, 1.5 wt% of KOH/oil, a reaction time of 5 min and a microwave power of 70 W. Glycerin from the ester phase was separated by adding 10 wt% of pure glycerin. The ethyl ester was purified with 1.2 wt% of bleaching earth to remove the residual catalyst and residual glycerin. This transesterification process provided a yield of 85 wt% with an ester content of 98.1 wt%. The final ethyl ester product met the specifications stipulated by ASTM D6751-02.

1. Introduction

The price of fossil diesel has soared during the past 2 years, and the supply will be exhausted some day. Thus, looking for an alternative way to develop a substitute for diesel (biodiesel) is imperative. Biodiesel is a replacement for, or an additive to, diesel fuel, and is derived from the vegetable oils or animal fats [1]. The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions, its biodegradability and, given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere, and consequently to the greenhouse effect [2].

Vegetable oil remains the major feedstock for biodiesel production. Animal fat and waste cooking oil have also been used. Soybean (US), rapeseed (Europe) and oil palm (South-east Asia) [2], to mention a few, have been successfully used as renewable vegetable oil sources to generate biodiesel with superior qualities to petroleum-based fuels. The oil palm (*Elaeis guineensis* Jacq.) produces fruit, about 70–80 wt% of which is constituted by the mesocarp, and about 45–50 wt% of this mesocarp is oil. The rest of the fruit is composed of the shell, kernel, moisture, and other non-fatty fiber. The extracted oil is known as crude palm oil (CPO), and consists of more than 90 wt% of triglycerides and 3–7 wt% of free fatty acids (FFA). A pretreatment process for CPO is an esterification process with alcohol, which changes FFA to esters; this process also commonly uses a strong liquid acid catalyst, such as sulfuric acid. This esterified CPO then reacts with an alkaline catalyst and alcohol by transesterification.

Generally, biodiesel is produced by transesterification. Transesterification is the reaction of triglycerides with an alcohol to form esters and glycerin. Alcohols such as methanol and ethanol are the most frequently employed. Although the use of different alcohols results in some differences in terms of the reaction kinetics, the final yield of esters remains more or less the same [3]. Therefore, selection of the alcohol is largely based on cost and performance considerations. Ethanol can be produced from renewable agricultural resources and is non-toxic, so it is often used as an alcohol for the transesterification of vegetable oils. However, the formation of an emulsion after transesterification with ethanol makes the separation of esters very difficult. In the case of methanol, the emulsion quickly and easily breaks down to form a lower glycerin-rich layer and an upper methyl-ester-rich layer. With ethanol, the emulsion is more stable, which severely complicates the separation and purification of esters [4]. The addition of extra glycerin to the reaction mixture was found to be helpful in glycerin separation [5].

Generally, biodiesel production uses heating coils to heat the raw material, but this method consumes a large amount of energy. By using a microwave for preparative chemistry, it is often possible to accelerate reactions and improve their selectivity [6–8]. Microwave heating has been proven to prepare biodiesel rapidly and with good conversion results.

---

* Corresponding author.
E-mail address: kit_src@yahoo.com (K. Suppalakpanya).

0306-2619/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apenergy.2009.12.006

Please cite this article in press as: Suppalakpanya K et al. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. Appl Energy (2010), doi:10.1016/j.apenergy.2009.12.006

Wastewater from biodiesel production contains soap, glycerin and oil, so treatment of the wastewater is necessary. However, the methods of doing so are not described in most instruction-manuals because the process is very difficult. Biodiesel wastewater purified using the water washing method still contains a substantial amount of effluents, as shown in Table 1. Significant product loss also can occur via retention during the water washing phase. Furthermore, emulsions can form when processing used cooking oils or other feeds with high FFA content, due to soap-formation. In refined vegetable oil production bleaching earth is commonly used, due to its high absorption capacity, for de-coloring vegetable oils and removing soap from vegetable products. Bleaching earth can also be used in the cleaning step of biodiesel production to improve the quality of the waste water [9].

In this paper, we describe the development of a transesterification process for the production of ethyl ester from esterified crude palm oil which uses ethanol for an alcohol, and a microwave heating system. Bleaching earth is then applied to purify the ethyl ester.

2. Method

2.1. Materials

Crude palm oil, bleaching earth and ethanol (99.5%) were acquired from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops at Prince of Songkla University. Phenolphthalein of analytical reagent grade was obtained from Lab-Chem (Pittsburgh, PA, USA). Potassium hydroxide (95%), sulfuric acid (98%) and pure glycerin (98%) were commercial grade.

2.2. Microwave system

All batch microwave tests were conducted with a Sharp model R235 compact microwave oven working at 2.45 GHz with a power of 800 W. Reactions were performed in a 250 mL boiling flask which was connected to a condenser in order to prevent ethanol loss.

2.3. Transesterification process

The transesterification process was performed on the product from the esterification process (molar ratios of oil to ethanol, 1:6, with 1 wt% of H_2SO_4, microwave power of 70 W, and a reaction time of 60 min) using KOH (0–2 wt% of KOH/oil) dissolved in ethanol (molar ratio of oil to ethanol, 1:1–1:6). The reactants were mixed in a 250 mL boiling flask equipped with a reflux condenser that was heated in the microwave oven at 70 W for 1–10 min.

2.4. Separation and purification processes

At the end of the transesterification process, pure glycerin (0–20 wt% of glycerin/oil) was added, and the resulting mixture was heated in the microwave oven at 70 W for 1 min. This resulted in the formation of an upper phase consisting of ethyl esters and a lower phase containing glycerin. After separation of the layers by sedimentation in a separatory funnel, excess ethanol in the ethyl ester phase was evaporated by heating at 80 °C, and then purified with bleaching earth (0–1.4 wt% of bleaching earth/oil), mixed for 5 min and separated by centrifuge. The residue of ethyl ester in spent bleaching earth was extracted using hexane. The collected hexane was then evaporated at 80 °C.

Table 1
Characterization of the effluent from water washing purification.

Parameter	Results
COD[a] (mg/L)	33,600
BOD[b] (mg/L)	168,000
Grease and oil (mg/L)	4030
SS[c] (mg/L)	80,480
pH	8.6

[a] Chemical oxygen demand.
[b] Biological oxygen demand.
[c] Suspended solids.

2.5. Analysis of reaction product

The glycerin content of the ethyl esters after the separation and purification processes was measured by titration (TIS 1593-2541). The purified ethyl esters were analyzed by gas chromatography (GC) using an Agilent 5890 gas chromatograph with a flame ionization detector (Agilent Technologies, Santa Clara, CA, USA) and a Stabilwax column (Restek, Bellefonte, PA, USA) of length 30 m, film thickness 0.25 μm and i.d. 0.25 mm. Fatty acid components of the ethyl esters were identified by gas chromatography–mass spectrometry (GC/MS) using an HP 5890 gas chromatograph coupled to an HP 5972 mass-selective detector (Hewlett–Packard, Palo Alto, CA, USA). The density at 15 °C was measured by the hydrometer method (ASTM D1298), the acid value was determined by titration (ASTM D664) and the water content was determined by the Karl-Fischer method. The flash point was ascertained by means of a Pensky-Martens closed tester (ASTM D93), and the viscosity was measured with a viscometer (ASTM D445). The cloud point (ASTM D2500) and the pour point (ASTM D97) were determined with pour and cloud point testers; the 95% distillation was determined with appropriate distillation equipment (ASTM D86); the ash content was measured with a furnace (ASTM D874) and the copper corrosion was measured with a copper corrosion tester (ASTM D130).

3. Results and discussion

3.1. Transesterification process

A study case of alkaline-catalyzed transesterification was run using esterified CPO that had 1.7 wt% of FFA content and a molar ratio of oil to ethanol of 1:4.5. Important variables affecting the ester content in the transesterification process are the molar ratio of oil to ethanol, the amount of alkaline catalyst, and the reaction time.

3.1.1. Effects of molar ratio of oil to ethanol

The amount of ethanol required for transesterification was analyzed in terms of the molar ratio with respect to triglyceride. Stoichiometrically, the molar ratio of triglyceride to ethanol is 1:3. However, in practice this is not sufficient to complete the reaction. Higher molar ratios are required to complete the reaction at a satisfactory rate [10,11]. Esterified CPO has initial molar ratio of oil to ethanol of 1:4.5; however, in practice this also is not sufficient to complete the reaction at a fast enough rate. Again, higher molar ratios are required. It can thus be seen that lower molar ratios require longer reaction periods. The effect of molar ratio on the wt% of ester content is shown in Fig. 1. This demonstrates that the wt% of ester content increases with an increasing molar ratio of oil to ethanol. The maximum wt% of ester content is obtained for a molar ratio of oil to ethanol of 1:8.5. Further increases in the molar ratio resulted in only a minor increase in ester content. This result is in good agreement with Encinar et al. [5], who employed a molar ratio of oil to ethanol of 1:12 for producing ethyl ester from used frying oil by a transesterification process.

Please cite this article in press as: Suppalakpanya K et al. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. Appl Energy (2010), doi:10.1016/j.apenergy.2009.12.006

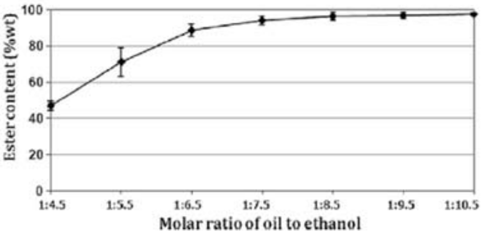


Fig. 1. Effect of the molar ratio of oil to ethanol on wt% of ester content after 5 min of reaction, with 1.5% wt/wt KOH/oil and microwave power of 70 W.

However, the used ethanol amount for transesterification is more than methanol because intermediate ethoxide is lower reactive than intermediate methoxide [3].

3.1.2. Effects of alkaline catalyst amount

The amount of alkaline catalyst used in the process also affects the wt% of ester content. Tests were performed using varying amounts of alkaline catalyst, in a range of 0–2% wt/wt KOH/oil, under reaction conditions of a 1:8.5 molar ratio of oil to ethanol, a reaction time of 5 min and a microwave power of 70 W. The effect of the amount of catalyst on the wt% of ester content is shown in Fig. 2. It was found that the transesterification reaction barely occurred without the catalyst. An appropriate amount of alkaline catalyst was found to be 1.5% wt/wt KOH/oil, giving the maximum wt% of ester content. Also, the addition of an excess amount of catalyst gave rise to the formation of an emulsion which in turn led to the formation of gels and a decreased % of ethyl ester. This result differed from that of Kulkarni et al. [12], who employed an alkaline catalyst of 0.7% wt/wt KOH/oil for producing ethyl ester from used canola oil by a transesterification process. Part of this difference may be attributed to differences in the raw material used, as well as the amount of alkaline catalyst needed to neutralize the acid catalyst in the esterification product [13].

3.1.3. Effects of reaction times

Fig. 3 shows the effects of reaction times on the wt% of ester content, comparing microwave heating and conventional heating at 70 °C. Reaction times ranged from 1 to 10 min, with other reaction parameters remaining constant (1.5% wt/wt of KOH/oil, a 1:8.5 M ratio of oil to ethanol and a microwave power of 70 W). The wt% of ester content rapidly increased within the first 1 min. Thereafter, the wt% of ester content slowly increased until the reaction times exceeded 5 min. Thus, a reaction time of 5 min was selected for this study. Conventional heating at 70 °C would require 1 h to achieve the same ester content as that produced by microwave heating with a 5 min reaction time. This is in good agreement with the findings of Issariyakul et al. [3] who employed a reaction time of 1 h and a reaction temperature of 60 °C to produce ethyl ester from waste fryer grease by a transesterification process. The present study confirms that a microwave-assisted chemical reaction significantly reduces the reaction time and increases the product yield, as has been mentioned in the literature [14–16]. This result is to be expected, since the changing electrical field activates a very small degree of variance of molecules and ions, leading to molecular friction; therefore, initiation of chemical reactions is possible. Microwave treatment induces greater accessibility of the pertinent bonds, and hence a much more efficient chemical reaction [7]. Consequently, microwave irradiation accelerates the chemical reaction, and a high product yield can be achieved within a short time. The obtained results are in good agreement with the findings of Hernando et al. [17] who employed a reaction time of 5 min and used a microwave oven to produce biodiesel from rapeseed oil by a transesterification process. In the present study, the optimum conditions for the transesterification process were identified as a 1:8.5 molar ratio of oil to ethanol, 1.5% wt/wt KOH/oil as a catalyst, a reaction time of 5 min and a microwave power of 70 W, which is in good agreement with the reported data.

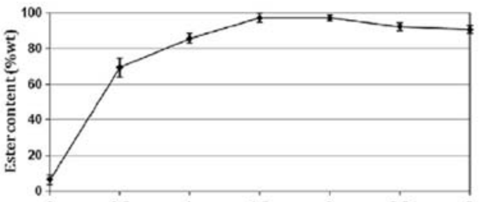


Fig. 2. Effect of alkaline catalyst amount on wt% of ester content, using a 1:8.5 M ratio of oil to ethanol, a reaction time of 5 min and microwave power of 70 W.

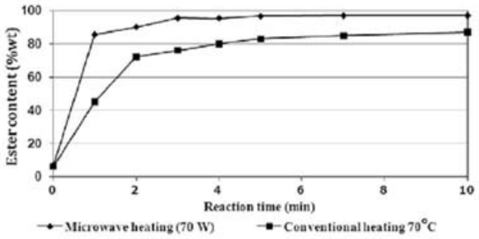


Fig. 3. Effect of reaction time of microwave heating compared to conventional heating at 70 °C on wt% of ester content, with 1.5% wt/wt KOH/oil, 1:8.5 molar ratio of oil to ethanol and microwave power of 70 W.

3.2. Separation and purification processes

At the end of the transesterification process, glycerin from the reaction had not separated from the ethyl ester by gravitation. Pure glycerin was then mixed in, and the resulting mixture was heated in a microwave oven at 70 W for 1 min. This produced the formation of an upper phase consisting of ethyl esters, and a lower phase containing glycerin. Fig. 4 shows the results of testing various wt% of pure glycerin added to the ethyl ester in order to reduce its glycerin content. The addition of 2–6 wt% of pure glycerin did not decrease the glycerin content, because the pure glycerin dissolved in the ethyl ester, and so could not induce a separation reaction. But the addition of more than 6 wt% of pure glycerin, greatly decreased the glycerin content due to separation from the ethyl ester.

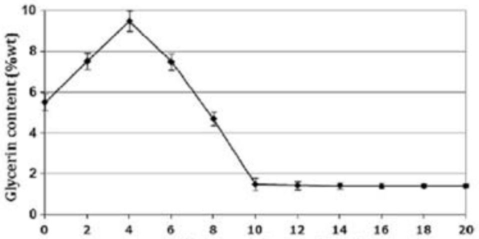


Fig. 4. Effect of adding various amounts of pure glycerin on wt% of glycerin content in ethyl ester.

Please cite this article in press as: Suppalakpanya K et al. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. Appl Energy (2010), doi:10.1016/j.apenergy.2009.12.006

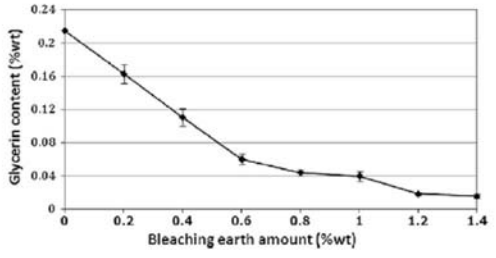


Fig. 5. Effect of bleaching earth amount on wt% of glycerin content in ethyl ester.

The optimum amount of pure glycerin was found to be 10 wt%. Adding more than 10 wt% pure glycerin had no significant additional effect on the glycerin content of the ethyl ester. This result differed from Encinar report [5], in which 25 wt% of pure glycerin was added. Part of the difference may be attributed to the differences in the process used.

Excess ethanol in the ethyl ester phase was evaporated by heating at 80 °C, followed by standing in a separatory funnel 30 min. Separation of glycerin decreased the glycerin content in the ethyl ester. This study found that the glycerin content in the ethyl ester before adding pure glycerin, after adding the optimum amount of pure glycerin, and after evaporation of ethanol was 5.49, 1.47 and 0.21 wt%, respectively.

The separated ethyl ester was purified by mixing with bleaching earth, for 5 min and then separating by centrifuge. Fig. 5 presents amounts of bleaching earth which were used to test its effect on the purification process.

As can be seen from Fig. 5, the glycerin content in ethyl ester was decreased by mixing with bleaching earth. According to ASTM D6751, biodiesel may contain up to 0.02 wt% of free glycerin content. When bleaching earth in an amount of 1.2 wt% is used, the glycerin content in ethyl ester drops below this limit, thus meeting the specifications.

Spent bleaching earth which was removed by centrifuge had adsorbed approximately 1 wt% of ethyl ester. This ethyl ester was extracted by hexane. The efficiency of extracting ethyl ester by hexane was 75%. Extracted bleaching earth was unsuitable for further purification of ethyl ester because the surface area of the extracted bleaching earth had decreased by more than 90%. However, extracted bleaching earth can be applied in cement manufacturing as a source of silicium dioxide, or by mixing with sandy oils [18].

The purified ethyl ester was analyzed by GC–MS, which indicated 97.4 wt% of ethyl ester. The fuel properties of ethyl ester in comparison with those of methyl ester standards are shown in Table 2. It can be seen that most of its salient properties fall within the limits prescribed by American standards for methyl ester.

Table 2
Properties of ethyl ester in comparison with diesel and methyl ester standards.

Properties	Unit	Test method	This work	ASTM D6751-02*
Acid value	mg KOH/g	ASTM D664	0.73	0.80 max
Ash content	wt%	ASTM D874	0.016	0.02 max
Cloud point	°C	ASTM D2500	7	−3 to 12
Copper corrosion	No.	ASTM D130	1	3 max
Density at 15 °C	kg/m^3	ASTM D4052	875.3	870–900
Distillation 95%	°C	ASTM D86	345	360 max
Ester content	wt%	EN 14103	97.4	-
Flash point	°C	ASTM D93	178	130 min
Pour point	°C	ASTM D97	4	−15 to 10
Viscosity at 40 °C	mm^2/s	ASTM 445	5.78	1.9–6.0
Water content	wt%	ASTM D6304	0.03	0.03 max

* Standard for methyl ester (adopt ASTM D6751-02 for the methyl ester to the ethyl ester) [19].

4. Conclusions

The production of ethyl ester from esterified CPO containing 1.7 wt% of FFA content and an oil to ethanol molar ratio of 1:4.5, under microwave assistance, was investigated. It was found that microwave irradiation facilitated the synthesis of ethyl ester from esterified CPO. The optimum conditions for producing ethyl ester from esterified CPO were a molar ratio of oil to ethanol of 1:8.5; 1.5% wt/wt KOH/oil as a catalyst; a reaction time of 5 min; and a microwave power of 70 W. The problem of glycerin separation was solved by mixing 10 wt% of pure glycerin into the ethyl ester to induce the glycerin from the reaction to separated. The ethyl ester phase was purified with 1.2 wt% of bleaching earth, reducing the residual amounts of glycerin and soap in the ethyl ester. This transesterification process yielded 85 wt%; its ester content was 98.1 wt%, and its fuel properties were within the limits prescribed by American standards for methyl ester.

Acknowledgments

The author gratefully acknowledges financial support from a Prince of Songkla Graduate Studies Grant and the Graduate School of Prince of Songkla University, and the provision of equipment by the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops at Prince of Songkla University.

References

[1] Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70:1–15.
[2] Barnwal BK, Sharma MP. Prospects of biodiesel production from vegetables oils in India. Renew Sustain Energy Rev 2005;9:363–78.
[3] Issariyakul T, Kulkarni MG, Dalai AK, Bakhshi NN. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. Fuel Proc Technol 2007;88:429–36.
[4] Meher LC, Sagar DV, Naik SN. Technical aspects of biodiesel production by transesterification. Renew Sustain Energy Rev 2006;10:248–68.
[5] Encinar JM, González JF, Rodríguez-Reinares A. Ethanolysis of used frying oil. Biodiesel preparation and characterization. Fuel Proc Technol 2007;88:513–22.
[6] Mazzocchia C, Modica G, Nannicini R, Kaddouri A. Fatty acid methyl esters synthesis from triglycerides over heterogeneous catalysts in presence of microwaves. CR Chimie 2004;7:601–6.
[7] Azcan N, Danisman A. Microwave assisted transesterification of rapeseed oil. Fuel 2008;87:1781–8.
[8] Tatlier M, Cigizoglu KB, Tokay B, Erdem-Senatalar A. Microwave vs. conventional synthesis of analcime from clear solutions. J Cryst Growth 2007;306:146–51.
[9] Kheang LS, Foon CS, May CY, Ngan MA. A study of residual oils recovered from spent bleaching Earth. Am J Appl Sci 2006;10:2063–7.
[10] Demirbas A. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Convers Manage 2002;43:2349–56.
[11] Meher LC, Dharmagadda VSS, Naik SN. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. Bioresour Technol 2006;97:1392–7.
[12] Kulkarni GM, Dalai AK, Bakhshi NN. Transesterification of canola oil in mixed methanol/ethanol system and use of esters as lubricity additive. Bioresour Technol 2007;98:2027–33.
[13] Ghadge SV, Raheman H. Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. Biomass Bioenergy 2005;28:601–5.
[14] Barnard TM, Leadbeater NE, Boucher MB, Stencel LM, Wilhite BA. Continuous-flow preparation of biodiesel using microwave heating. Energy Fuels 2007;2:1777–81.
[15] Saifuddin N, Chua KH. Production of ethyl ester (biodiesel) from used frying oil: optimization of transesterification process using microwave irradiation. Malaysian J Chem 2004;6:77–82.
[16] Refaat AA, El Sheltawy ST. Time factor in microwave-enhanced biodiesel production. WSEAS Trans Environ Develop 2008;4:279–88.
[17] Hernando J, Leton P, Matia MP, Novella JL, Alvarez-Builla J. Biodiesel and fame synthesis assisted by microwaves. Homogeneous batch and flow processes. Fuel 2007;86:1641–4.
[18] Ong J. Oil recovery from spent bleaching earth and disposal of the extracted material. J Am Oil Chem Soc 1983;60:314–5.
[19] Shell Comments on National Standard for Biodiesel Discussion Paper; 2003.

Please cite this article in press as: Suppalakpanya K et al. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. Appl Energy (2010), doi:10.1016/j.apenergy.2009.12.006

RSCE-SOMCHE 2008 703
Edited by Daud et al.

TRANSESTERIFICATION OF ESTERIFIED CRUDE PALM OIL BY MICROWAVE WITH DRY WASHING BY BLEACHING EARTH

K. Suppalakpanya*, S. B. Ratanawilai, C. Tongurai
Department of Chemical Engineering, Faculty of Engineering,
Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
*Email: kit_src@yahoo.com

Keywords: ethyl ester; microwave; biodiesel; bleaching earth

ABSTRACT

The production of ethyl ester by microwave using crude esterifed palm oil as a feed material was investigated in this work. Transesterification of esterified crude palm oil was carried out with a molar ratio of crude palm oil to ethanol 1:4, using 1.5 wt% of KOH as a catalyst, microwave power of 70 watts and a reaction time 5 min. The optimum condition for the purification process used bleaching earth 1 wt% of ethyl ester to remove glycerol, soap and the rest catalyst. The efficiency of extracted oil from spent bleaching earth was 75 %. This process gave a yield of 85 wt % ethyl ester with ester content 98.15 wt%. The final ethyl ester product met with ASTM D6751-02 and the Thai biodiesel quality standard which is the methyl ester standard adapted to ethyl ester.

INTRODUCTION

Biodiesel as an alternative fuel for diesel engines is becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. Biodiesel is made from renewable sources such as vegetable oils and animal fats (Veljkovic et al. 2006).

Crude Palm Oil (CPO) was the major feedstock for biodiesel production in South-East Asia (Peterson et al. 1990). CPO consists of more than 90 wt% triglyceride and 3-7 wt% free fatty acid (FFA). Neutralization of FFA can be carried out by the addition of excess alkali, but this leads to the formation of soaps and to post reaction separation problems. Thus, a preferred pretreatment process for CPO is an esterification process with alcohol for changes FFA to esters that commonly uses a strong liquid acid catalyst, such as sulfuric acid.

Generally, biodiesel is produced by transesterification which is the reaction of triglycerides with an alcohol to form esters and glycerol. Alcohols such as methanol and ethanol are the most frequently employed (Issariyaki et al. 2007). Ethanol can be produced from agricultural renewable resources. Therefore, ethanol is often used as an alcohol for the transesterification of vegetables oils (Encinar et al. 2007).

The general heating system for biodiesel production uses heating coils to heat the raw material but this method consumes high energy. Using microwave for preparative chemistry, it is possible to accelerate the rate of reactions and selectivity (Mazzocchia et al. 2004). Therefore it was possible to prepare biodiesel rapidly and with good conversions by microwave heating.

Wastewater from biodiesel production constitutes soap, glycerol and oil, so the treatment of wastewater is necessary. However, the treatment of biodiesel wastewater is not described in the instruction manual because the treatment is very difficult. In refine vegetable oil production, is a commonly used adsorbent due to its high absorption capacity for de-colored vegetable oils and remove soap in vegetable. To avoid the biodiesel wastewater, bleaching earth was used in cleaning step for decrease quantity of waste water (Kheang et al. 2006).

This paper presents the development of a transesterification process for the production of biodiesel from the esterified crude palm oil by transesterification process which used ethanol as alcohol and heating system with microwave. Applying the bleaching earth to purified the ethyl ester.

METHOD

Materials

Crude Palm Oil, bleaching earth and ethanol (99.5%) were acquired from the Specialized R&D Center for Alternative Energy from Palm Oil Crops (Thailand). Potassium hydroxide (95%), Sodium hydroxide (95%) and Sulfuric acid (98%) are commercial grade.

Microwave system

All batch microwave tests have been conducted with a Sharp, model R235 compact microwave oven working at 2.45 GHz, with a power of 70 W. Reactions were performed in 250 ml boiling flask which was connected to condenser.

EXPERIMENT PROCEDURES AND ANALYSIS

Transestericationprocess

The transesterification process was carried out with the product form the esterification process (molar ratios of oil to ethanol, 1:6 with 1 %wt of H_2SO_4, microwave power of 70 watts and reaction times of 60 min) and 1.5 %wt of KOH dissolved in ethanol (molar ratio of oil/ethanol : 1/4) were mixed in a 250 ml boiling flask equipped with a reflux condenser heated by microwave at 70 watts for 5 min. At the end of reaction, pure glycerol was added and heated by microwave at 70 watts for 1 min. After separation of the two layers by sedimentation in a separation funnel, Access ethanol was evaporated from the ethyl ester phase by heating at 80 °C and ethyl ester was left to settle to separate in a separation funnel again. The ethyl ester was cleaned by adding bleaching earth, mixed for 5 minutes and separated by centrifuge. Spent bleaching earth was extracted residue ethyl ester by hexane. The collected hexane was evaporated at 80 °C.

Analysis of reaction product

The ethyl ester was measured using gas chromatography (GC). The surface area of bleaching earth was measured by the BET surface area. Measurements of soap content by titration method, the density at 15 °C was determined by hydrometer method, the acid value was obtained by titration, water content was determined by Karl-Fischer method. The flash point was determined by Pensky-Martens Closed Tester, the viscosity was determined by viscometer and Ash content was determined by furnace.

RESULTS AND DISCUSSION

Transesterification process

The transesterification of esterified palm oil which contains 1.7 %wt of FFA, 4.5 mol of ethanol, 0.34 % wt of water and H_2SO_4 as a catalyst was carried out using KOH as a catalyst. After the end of reaction, glycerine form the reaction did not separated from ethyl ester by gravity, the pure glycerine was added and heated with microwave at 70 watts for 1 min to separated glycerine by sedimentation in separation funnel.

Figure 1 shows %wt of pure glycerine which was added in ethyl ester to reduced soap content by separated glycerine from the ethyl ester. Addition of 2-6 %wt of pure glycerine, the soap content not decreased because pure glycerine which was added in ethyl ester can not induced the glycerine from the reaction to separated from ethyl ester and it dissolved in ethyl ester. But addition of more than 8 %wt of pure glycerine, the soap content decreased greatly because glycerine separated from ethyl ester. The optimum of pure glycerine which was added in ethyl ester was 10 %wt. The added pure glycerine more than 10 %wt had no significant effect on soap content in ethyl ester.

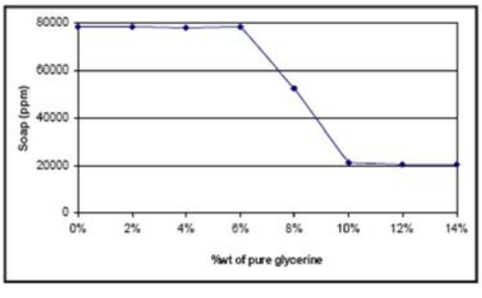


FIGURE 1 Effect of pure glycerine quantity on soap content in ethyl ester

The ethyl ester phase was heating at 80 °C for evaporate ethanol and mixture was left to settle to separate in separation funnel 30 minutes. The glycerine separated form ethyl ester and caused to decrease the soap content in ethyl ester. In this work, the soap content in ethyl ester before added glycerine, after added glycerine and after evaporated ethanol was 78465, 20799 and 3064, respectively.

Purification process

The crude ethyl ester was purified by adding bleaching earth, mixed for 5 minutes and separated by centrifuge. The bleaching earth which was used in this process is a white powder (Figure 2A), but the spent bleaching earth turned to a light brown color (Figure 2B) due to adsorption of colored compounds, soap, glycerine, residual catalyst and ethyl ester and the spent bleaching earth was extracted by hexane (Figure 2C). The figure 3 presents amount of bleaching earth which was used in purification process.

2A 2B 2C

FIGURE 2 Appearance of fresh bleaching earth (A), spent bleaching earth (B) and spent bleaching earth after extract ethyl ester by hexane (C).

Figure 3 shows the effect of bleaching earth on soap content of ethyl ester. From the figure, it can be seen that the soap content in ethyl ester decreased with increasing bleaching earth. Biodiesel which sell at Specialized R&D Center for Alternative Energy from Palm Oil Crops (Thailand) and purify by hot water has soap content in biodiesel less than 500 ppm, so the optimum condition for quantity of bleaching earth to remove soap content in ethyl ester less than 500 ppm was 1 %wt of ethyl ester.

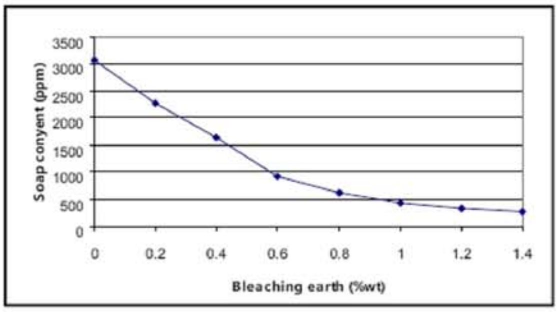


FIGURE 3 Effect of bleaching earth quantity on soap content in ethyl ester

Spent bleaching earth removed from centrifuge adsorbed approximately 90 %wt ethyl ester. This ethyl ester was extracted by hexane. The efficiency of extracted ethyl ester by hexane was 75 %. Extracted bleaching earth was unsuitable purification ethyl ester because the surface area of extracted bleaching earth decreased more than 90% compared with fresh bleaching earth. However, extracted bleaching earth can be applied in cement manufacture, as a source of silicium dioxide, or mixing with sandy oils.

When ethanol was used, the glycerol was not separated properly and hence, the amount of ethyl ester recovered was as low as 85 %wt of CPO was used for the reaction. The result of yield from this experiment is in good agreement with Issariyakul et al. [3] has 62 %wt of oil.

Characterization of ethyl ester

The fuel properties of ethyl ester in the comparison of methyl ester standards are shown in Table 1. It can be seen that most of its properties are comparable fuel properties in the limit prescribed by the latest Thai and American standards for methyl ester, except viscosity

TABLE 1 Ethyl ester in comparison with diesel and methyl ester standards

Properties	Unit	Test method	This work	ASTM D 6751-02*
Acid value	mg KOH/g	ASTM D664	0.33	0.80 max
Ash content	wt %	ASTM D874	0.0066	0.02 max
Carbon residue	wt %	ASTM D4530	0.07	0.3 max
Density at 15°C	kg/m^3	ASTM D4052	879.8	870-900
Ester content	wt %	EN 14103	98.1	-
Flash point	°C	ASTM D93	160	130 min
Viscosity at 40°C	mm^2/s	ASTM D445	5.57	1.9-6.0
Water content	wt %	ASTMD6304	0.03	0.03 max

*Standard for methyl ester (Adopt ASTM D 6751-02 for the methyl ester and adapt it to an ethyl ester standard) [10]

CONCLUSIONS

The production of ethyl ester from esterified CPO by microwave is investigated in the present study. It is found that microwave irradiation helps the synthesis of ethyl ester from triglycerides in few minutes. Adding pure glycerine solved glycerine form the reaction which was not separated from ethyl ester by gravity.

Beaching earth from edible oil processing industry could be used as adsorbent for remove soap glycerine and residual catalyst from ethyl ester. This process gave a yield of 85 wt % ethyl ester with ester content 98.1 wt %. The final ethyl ester product met with ASTM D6751-02 and the Thai biodiesel quality standard which was the methyl ester standard and adapt it to an ethyl ester standard.

ACKNOWLEDGMENT

The author gratefully acknowledges the financial support from the Prince of Songkla Graduate Studies Grant and Graduate School of Prince of Songkla University and the equipments support from Specialized R&D Center for Alternative Energy from Palm Oil Crops (Thailand).

REFERENCES

Barnard T.M., Leadbeater N.E., Boucher M.B., Stencel L.M. and Wilhite B.A. 2007. Continuous-Flow Preparation of Biodiesel Using Microwave Heating.

Daewoo electronics co., ltd. Service Manual Microwave Oven.

Encinar J.M., González. J.F., A. Rodríguez-Reinares. 2007. Ethanolysis of used frying oil. Biodiesel preparation and characterization. *Fuel Processing Technology*. **88**: 513–522.

Issariyakul. T., Kulkarni. M. G., Dalai A. K. , and Bakhshi. N. N.. 2007. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. *Fuel Processing Technology*. **88**: 429–436.

Kheang L. S., Foon C. S., May C. Y. and Ngan M. A. 2006 A Study of Residual Oils Recovered from Spent Bleaching Earth. American *Journal of Applied Sciences*.**10**: 2063-2067.

Login GR and Dvorak AM. 1994. The Microwave Tool Book. Beth Israel Hospital. 61-63.

Mazzocchia.C., Modica G., Nannicini R. and Kaddouri A.. 2004. Fatty acid methyl esters synthesis from triglycerides over heterogeneous catalysts in presence of microwaves. CR Chimie.7: 601.

Peterson C.L., Cruz R.O., Perkings L., Korus R., Auld D.L. 1990.Transesterification of vegetable oil for use as diesel fuel: a progress report; ASAE Paper No. 90-610.

Shell Comments on National Standard for Biodiesel Discussion Paper 2003.

Veljkovic.V.B., Lakicevic.S.H., Stamenkovic. O.S. and Todorovic.Z.B. 2006. Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids. *Fuel* **85**, 2671–2675.

Esterification of Free Fatty Acid in Crude Palm Oil by Continuous Microwave with Ethanol

Kittiphoom Suppalakpanya*, Sukrithira Ratanawilai, Chakrit Tongurai

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

ABSTRACT The esterification of free fatty acids (FFA) found in vegetable oils with alcohol using an acid catalyst is a promising method to convert FFA into valuable ester and obtain a FFA-free oil that can be further transesterified using alkali bases. In this work, the direct esterification reaction of FFA in crude palm oil to ethyl ester by continuous microwave was studied. The optimum condition for the continuous esterification process was carried out with a molar ratio of FFA to ethanol 1:24, using 1.25 wt% of H_2SO_4 as a catalyst, microwave power of 77 watts and a reaction time 90 min. The esterification process that has been studied shows that the amount of FFA was reduced from 7.5 % wt to values around 1.4% wt. The esterified crude palm oil is suitable to perform the transesterification process.

1. Introduction

Crude Palm Oil (CPO) consists of more than 90 wt% triglyceride and 3-7 wt% free fatty acid (**FFA**). This feedstock often contains significant quantities of free fatty acids, which make them unsuitable for existing homogeneous alkaline-catalyzed processes. Thus, a preferred pretreatment process for CPO is an esterification process with alcohol which changes FFA to esters and commonly uses a strong liquid acid catalyst, such as sulfuric acid. The esterification process is to esterify the FFA with alcohol by acid catalysis. When the FFA content is lower than 2.0 wt%, it was suitable for the raw material in transesterification process to produce biodiesel. Alcohols such as methanol and ethanol are the most frequently employed. Although the use of different alcohols presents some differences with regard to the reaction kinetics, the final yield of esters remains more or less the same [1].

Using microwave for preparative chemistry, it is often possible to accelerate the rate of reactions, and reduce the reaction time [2]. In this way, it has proved possible to prepare biodiesel rapidly and with good conversions by microwave heating.

This paper presents the continuous esterification process for decrease FFA in CPO to below 2 wt%. The product from the esterification process was keep for raw material in the transesterification process for ethyl ester production. The continuous esterification process use ethanol as the alcohol and a microwave heating system.

2. Method

2.1 Materials

Crude palm oil and ethanol (99.5%) were acquired from the Specialized R&D Center for Alternative Energy from Palm Oil Crops (Thailand). Phenolpthalein was analytical reagent grade from Labchem. Sodium hydroxide (95%) and Sulfuric acid (98%) were commercial grade.

2.2 Microwave system

All microwave tests were conducted with a Toshiba, model ER-D33SC compact microwave oven working at 2.45 GHz with a power of 1100W. Reactions were performed in 1.5 L glass reactor in the microwave oven for continuous experiments.

2.3. Experimental procedures and analysis

2.3.1. Continuous esterification process

The continuous esterification process was started by the feeding of CPO and sulfuric acid in ethanol solution into the mixing tank I. The mixture would overflow into the reactor I in microwave oven for esterification process at 110 watts. After that it was flowed into seperation tank to separation the esterified palm oil from the ethanol.

2.3.2. Purification process and analysis of reaction product

After separation in a separatory funnel for 60 min, the esterified palm oil was purified by washing with hot water. The washed oil was dried at 120 °C for 20 min. FFA in the products was measured by titration (A.O.C.S. Ca 5a-40).

3. Results and discussion

3.1. Effect of molar ratio of FFA to ethanol

---

* Corresponding author; kit_src@yahoo.com

The effect of molar ratio on the %wt of the FFA content is shown in Figure 1. The molar ratio of FFA to ethanol was varied from 1:4 to 1:32, whereupon the optimum molar ratio was found to be 1:24.

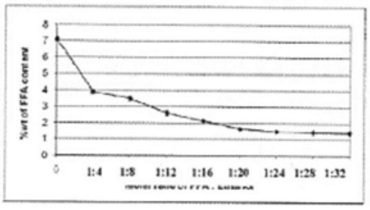


Figure 1. Effect of the molar ratio of FFA to ethanol on %wt of FFA content after 1 h of reaction, with 4% wt/wt H_2SO_4/FFA and a microwave power of 70 watts.

3.2. Effect of the amount of acid catalyst

The effect of the amount of catalyst on the %wt of FFA content is shown in Figure 2. It was found that the esterification reaction barely occurred without the catalyst. An appropriate amount of acid catalyst was found to be 4% wt/wt of H_2SO_4/FFA as this gave the lowest %wt of FFA content. Little decrease in the FFA content was seen when the amount of catalyst was increased beyond 4% wt/wt of H_2SO_4/FFA.

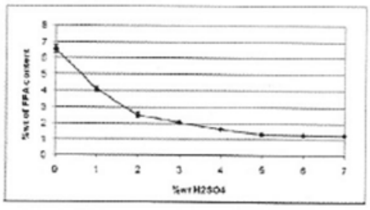


Figure 2. Effect of acid catalyst quantity on %wt FFA content with a 1:24 molar ratio of FFA to ethanol after a reaction time of 1 h at a microwave power of 77 watts.

3.3. Effects of microwave power and reaction time

Figure 3 shows the effect of reaction time on the %wt FFA content compared to conventional heating at 70 °C. From the figure show that the %wt of FFA content rapidly decreased within the first 15 min. Thereafter, the %wt of FFA content slowly decreased until the reaction time exceeded 60 min. At this point, the plot of the %wt FFA content showed a slight upward trend, which may have been due to cleavage of the triglyceride to shorter-chain organic fractions such as FFA [4]. A reaction time of 60 min was selected for this study, whereas conventional heating at 70 °C required 4 h; the latter is in good agreement with the findings of Wang et al., 2007 who employed a reaction time of 4 h and a reaction temperature of 95 °C for the esterification process. The optimum conditions for the esterification process have been identified as a 1:24 molar ratio FFA to ethanol, 4% wt/wt H_2SO_4/FFA as the catalyst, a reaction time of 1 h and a microwave power of 70 watts. At the end of the esterification process, the amount of FFA had been reduced from 7.5 wt% to 1.4 wt% which was suitable for the raw material in biodiesel production.

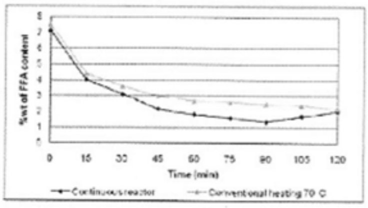


Figure 3. Effect of reaction time compared to conventional heating at 70 °C on %wt of FFA content with 5% wt/wt H2SO4/FFA and a 1:24 molar ratio of FFA to ethanol.

4. CONCLUSION

The esterification process has thus been developed to reduce the FFA content of the oil to less than 2 wt%. For the studied esterification process, the amount of FFA was reduced from 7.5 wt% to around 1.4 wt% under optimum conditions of a molar ratio of FFA to ethanol of 1:24, 5% wt/wt H_2SO_4/FFA as catalyst, a reaction time of 90 min and a microwave power of 77 watts. The esterified crude palm oil is suitable to perform the transesterification process.

5. ACKNOWLEDGMENT

The author gratefully acknowledges financial support from a Prince of Songkla Graduate Studies Grant and the Graduate School of Prince of Songkla University, and the provision of equipment by the Specialized R&D Center for Alternative Energy from Palm Oil Crops (Thailand).

6. REFERENCES

[1] T. Issariyakul, M.G. Kulkarni, A.K. Dalai, N.N. Bakhshi, Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. J. *Fuel Processing Technology*, 88, 2007, 429–436.

[2] C. Mazzocchia, G. Modica, R. Nannicini, A. Kaddouri, Fatty acid methyl esters synthesis from triglycerides over heterogeneous catalysts in presence of microwaves. *CR Chimie*, 7, 2004, 601-606.

[3] A.A. Refaat, S.T.El Sheltawy, Time factor in microwave-enhanced biodiesel production. *Transactions on Environment and Development*, 4, 2008, 279–288.

[4] Y. Wang, S. Ou, P. Liu, Z. Zhang, Z, Preparation of biodiesel from waste cooking oil via two-step catalyzed process. *Energy Conversion and Management*, 48, 2007, 184–188.

---

* Corresponding author; kit_src@yahoo.com

ISBN 978-1-84626-023-0
Proceedings of 2009 International Conference on Chemical Engineering and Applications
Singapore, 26-28 Fabruary, 2010, pp. 111-115

Production of Ethyl Ester from Esterified Crude Palm Oil by Continuous Flow Microwave

Kittiphoom Suppalakpanya[1] +, Sukritthira Ratanawilai[1], Chakrit Tongurai[1]

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

Abstract. The production of ethyl ester from a feed material of esterified crude palm oil which has 1.7 %wt of free fatty acid (FFA) content under continuous flow microwave assistance has been investigated. Parametric studies have been carried out to investigate the optimum conditions for the transesterification process (amount of ethanol, amount of catalyst and reaction time). As a result, a molar ratio of oil to ethanol of 1:8.5, 2.5 % wt/wt of KOH/oil, a reaction time of 7 min and a microwave power of 78 W have been identified as optimum reaction parameters for the transesterification process aided by microwave heating. The glycerin from the ester phase was separated by adding 10 %wt of pure glycerin. This transesterification process provided a yield of 78 %wt with an ester content of 97.8 %wt. The final ethyl ester product met with the specifications stipulated by ASTM D 6751-02.

Keywords: Ethyl ester, Microwave, Transesterification, Biodiesel, Crude palm oil

1. Introduction

The price of fossil diesel is soaring in these two years, and it will be exhausted some day. Thus, looking for an alterative way to develop a substitute for diesel (biodiesel) is an imperious task for humans. Biodiesel is a substitute for, or an additive to diesel fuel that is derived from the vegetable oils or animal fats [1]. The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions and its biodegradability [2].

Vegetable oil remains the major feedstock for biodiesel production. Animal fat and waste cooking oil have also been used. The extracted oil from oil palm is known as crude palm oil (CPO) and consists of more than 90 %wt of triglyceride and 3-7 %wt of free fatty acid (FFA). A pretreatment process for CPO is an esterification process with alcohol which changes FFA to esters and commonly uses a strong liquid acid catalyst, such as sulfuric acid. The esterified crude palm oil was reacted with alkaline catalyst and alcohol by transesterification.

Generally, biodiesel is produced by transesterification. Transesterification is the reaction of triglycerides with an alcohol to form esters and glycerin. Alcohols such as methanol and ethanol are the most frequently employed. Although the use of different alcohols results in some differences in terms of the reaction kinetics, the final yield of esters remains more or less the same [3]. Therefore, selection of the alcohol is largely based on cost and performance considerations. Ethanol can be produced from agricultural renewable resources and non toxic for human. Therefore, ethanol is often used as an alcohol for the transesterification of vegetables oils. However, the formation of emulsion after the transesterification of oil with ethanol makes the separation of ester very difficult. In the case of methanol, these emulsions quickly and easily break down to form a lower glycerin rich layer and upper methyl ester rich layer. In ethanol, these emulsions are more stable and severely complicate the separation and purification of esters [4]. The addition of extra glycerin to the reaction mixture was found helpful glycerin separation [5].

The general heating system for biodiesel production uses heating coils to heat the raw material, but this method consumes a large amount of energy. Using microwave for preparative chemistry, it is often possible

---

[+] Corresponding author. Tel.: + 66-7428-7185; fax: +66-7421-2190.
E-mail address: kit_src@yahoo.com.

to accelerate reactions and to improve their selectivity [6]. In this way, it has proved possible to prepare biodiesel rapidly and with good conversions by microwave heating.

In this paper, we describe the development of a transesterification process for the production of ethyl ester from the esterified crude palm oil by transesterification process which used ethanol as alcohol and heating system with microwave.

2. Method

2.1. Materials

Crude Palm Oil, bleaching earth and ethanol (99.5%) were acquired from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops (Thailand). Phenolphthalein was analytical reagent grade from Labchem. Potassium hydroxide (95%), sulfuric acid (98%) and pure glycerin (98%) were commercial grade.

2.2. Transesterification process

The continuous transesterification process was performed on the product from the esterification process using KOH (1-3 %wt of KOH/oil) dissolved in ethanol (molar ratio of oil/ethanol: 1:4.5 – 1:10.5) into mixing tank 1. The mixture would overflow into the reactor 1 in microwave oven for transesterification process at 78 W for 1-10 min. At the end of the reaction, 10 %wt of pure glycerol was added and flowed into the reactor 2, which resulted in the formation of an upper phase consisting of ethyl esters and a lower phase containing glycerin. The process is shown in Figure 1. After separation of the layers by sedimentation in a separatory funnel for 30 min, the ethyl esters were purified by washing with hot water. The washed ethyl esters were dried at 120 °C for 20 min.

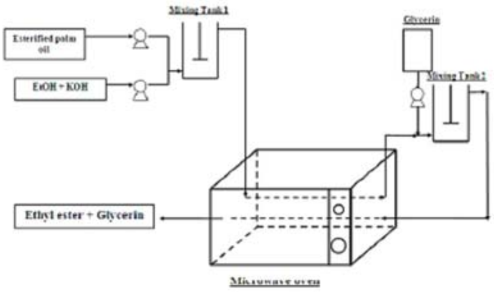


Fig. 1: The apparatus used in the continuous experiments

3. Results and discussion

A study case of alkaline-catalyzed transesterification was run using esterified CPO that had 1.4 %wt FFA content and a molar ratio of oil to ethanol of 1:4.5. Important variables affecting the ester content in the transesterification process are the molar ratio of oil to ethanol, the amount of alkaline catalyst, and the reaction time.

3.1. Effects of molar ratio of oil to ethanol

The amount of ethanol required for transesterification was analyzed in terms of the molar ratio with respect to triglyceride. Stoichiometrically, the molar ratio of triglyceride to ethanol is 1:3. However, in practice this is not sufficient to complete the reaction. Higher molar ratios are required to complete the reaction at a satisfactory rate [7]. Esterified CPO has initial molar ratio of oil to ethanol of 1:4.5; however, in practice this also is not sufficient to complete the reaction at a fast enough rate. Again, higher molar ratios are required. It can thus be seen that lower molar ratios require longer reaction periods. The effect of molar ratio on the %wt of ester content is shown in Figure 2. This demonstrates that the %wt of ester content increases with an increasing molar ratio of oil to ethanol. The maximum %wt of ester content is obtained for a molar ratio of oil to ethanol of 1:8.5. Further increases in the molar ratio resulted in only a minor increase in ester content. This result is in good agreement with Encinar et al., [8] who employed a molar ratio of oil to ethanol of 1:12 for producing ethyl ester from used frying oil by a transesterification process.

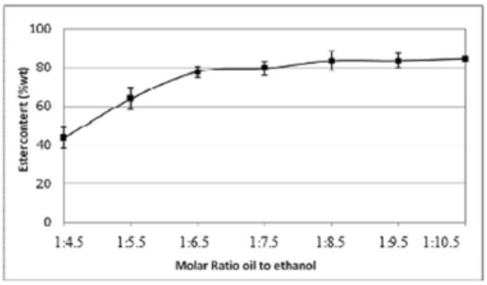


Fig. 2: Effect of the molar ratio of oil to ethanol on %wt of ester content after 5 min of reaction, with 1.5% wt/wt KOH/oil and microwave power of 78 W.

3.2. Effects of alkaline catalyst amount

The amount of alkaline catalyst used in the process also affects the %wt of ester content. Tests were performed using varying amounts of alkaline catalyst, in a range of 1-3% wt/wt KOH/oil, under reaction conditions of a 1:8.5 molar ratio of oil to ethanol, a reaction time of 5 min and a microwave power of 78 W. The effect of the amount of catalyst on the %wt of ester content is shown in Figure 3. It was found that the transesterification reaction barely occurred without the catalyst. An appropriate amount of alkaline catalyst was found to be 2.5% wt/wt KOH/oil, giving the maximum %wt of ester content. Also, the addition of an excess amount of catalyst gave rise to the formation of an emulsion which in turn led to the formation of gels and a decreased % of ethyl ester. This result differed from that of Kulkarni et al., [9] who employed an alkaline catalyst of 0.7 % wt/wt KOH/oil for producing ethyl ester from used canola oil by a transesterification process. Part of this difference may be attributed to differences in the raw material used, as well as the amount of alkaline catalyst needed to neutralize the acid catalyst in the esterification product [10].

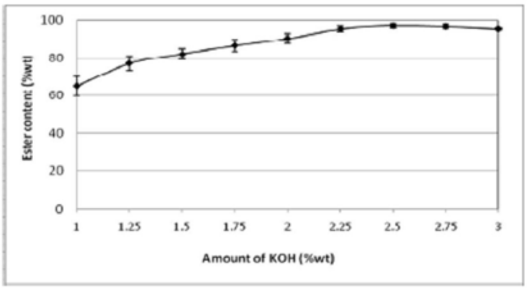


Fig. 3: Effect of alkaline catalyst amount on %wt of ester content, using a 1:8.5 molar ratio of oil to ethanol, a reaction time of 5 min and microwave power of 78 W.

3.3. Effects of reaction times

Figure 4 shows the effects of reaction times on the %wt of ester content, comparing microwave heating and conventional heating at 70 °C. Reaction times ranged from 1 to 10 min, with other reaction parameters remaining constant (2.5 % wt/wt of KOH/oil, a 1:8.5 molar ratio of oil to ethanol and a microwave power of 78 W). The %wt of ester content rapidly increased within the first 1 min. Thereafter, the %wt of ester content slowly increased until the reaction times exceeded 7 min. Thus, a reaction time of 7 min was selected for this study. Conventional heating at 70 °C would require 1 h to achieve the same ester content as that produced by microwave heating with a 5 min reaction time. This is in good agreement with the findings of Issariyakul et al., [4] who employed a reaction time of 1 h and a reaction temperature of 60 °C to produce ethyl ester from waste fryer grease by a transesterification process. The present study confirms that a microwave-assisted chemical reaction significantly reduces the reaction time and increases the product yield, as has been mentioned in the literature [11]. This result is to be expected, since the changing electrical field activates a very small degree of variance of molecules and ions, leading to molecular friction; therefore, initiation of chemical reactions is possible. Microwave treatment induces greater accessibility of the pertinent bonds, and hence a much more efficient chemical reaction [12]. Consequently, microwave irradiation accelerates the chemical reaction, and a high product yield can be achieved within a short time. The obtained results are in good agreement with the findings of Hernando et al. [6], who employed a reaction time of 5 min and used a microwave oven to produce biodiesel from rapeseed oil by a transesterification process. In the present study, the optimum conditions for the transesterification process were identified as a 1:8.5 molar ratio of oil to ethanol, 2.5% wt/wt KOH/oil as a catalyst, a reaction time of 7 min and a microwave power of 78 W.

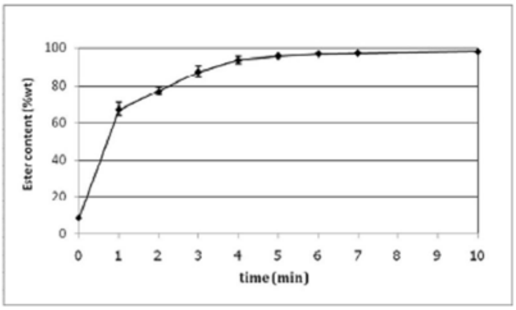


Fig. 4: Effect of reaction time on %wt of ester content, using a 1:8.5 molar ratio of oil to ethanol, with 2.5% wt/wt KOH/oil and microwave power of 78 W.

3.4. Fuel properties

The transesterification of esterified palm oil was carried out using KOH as the catalyst. When ethanol was used, the glycerin was not entirely separated and hence the amount of ethyl ester recovered was as low as 78 %wt with respect to the CPO for this reaction. This is in good agreement with the findings of Issariyakul et al. [4], who obtained 62 %wt of ethyl ester from waste fryer grease. The fuel properties of ethyl ester in comparison with those of methyl ester standards are shown in Table 1. It can be seen that most of its salient properties fall within the limits prescribed by American standards for methyl ester.

Table 1. Properties of ethyl ester in comparison with those of methyl ester standards

Properties	Unit	Test method	This work	ASTM D 6751-02*
Acid value	mg KOH/g	ASTM D664	0.33	0.80 max
Ash content	wt %	ASTM D874	0.0066	0.02 max
Cloud point	°C	ASTM D2500	8	–3 to 12
Density at 15°C	kg/m^3	ASTM D4052	879.8	870–900
Distillation 95%	°C	ASTM D86	337	360 max
Ester content	wt %	EN 14103	97.4	97.8
Flash point	°C	ASTM D93	160	130 min
Pour point	°C	ASTM D97	6	–15 to 10
Sulfur	wt %	ASTM D5453	0.0002	0.001 max
Viscosity at 40°C	mm^2/s	ASTM D445	5.57	1.9–6.0
Water content	wt %	ASTMD6304	0.03	0.03 max

*Standard for methyl ester (Adopting ASTM D 6751-02 for the methyl ester to the ethyl ester) [13]

4. CONCLUSIONS

The production of ethyl ester from esterified crude palm oil, 1.7 %wt of FFA content and molar ratio of oil/ethanol : 1:4.5 feed stock, under microwave assistance has been investigated. It has been found that microwave irradiation facilitates the synthesis of ethyl ester from esterified crude palm oil in 7 minutes. The optimum conditions for produce ethyl ester from esterified crude palm was a molar ratio of oil to ethanol 1:8.5, 2.5 %wt KOH/oil as a catalyst, a reaction time of 7 min and a microwave power of 78 W. The problem of glycerin separation was solved by mixing with 10 %wt of pure glycerin in ethyl ester to induced the glycerin from the reaction to separated from ethyl ester. This transesterification process yielded 78 %wt; its ester content was 97.8 %wt and its fuel properties were within the limits prescribed by American standards for methyl ester.

5. Acknowledgements

The author gratefully acknowledges financial support from a Prince of Songkla Graduate Studies Grant and the Graduate School of Prince of Songkla University, and the provision of equipment by the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops (Thailand).

6. References

[1] O.J. Alamu, M.A. Waheed and S.O. Jekayinfa. Effect of ethanol–palm kernel oil ratio on alkali-catalyzed biodiesel yield. *Fuel*. 2008, **87**: 1529-1533.

[2] C.L. Peterson, R.O. Cruz, L. Perkings, R. Korus and D.L. Auld. Transesterification of vegetable oil for use as diesel fuel: a progress report, ASAE Paper No. 90. 1999, 610-615.

[3] K.T. Tan, K.T. Lee, A.R. Mohamed and S. Bhatia. Palm oil: Addressing issues and towards sustainable development. *Renew Sustain Energ Rev*. 2007, **13**: 420-427.

[4] T. Issariyakul, M.G. Kulkarni, A.K. Dalai and N.N. Bakhshi. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. *Fuel Process Tech*. 2007, **88**: 429-436.

[5] C. Mazzocchia, G. Modica, R. Nannicini and A. Kaddouri. Fatty acid methyl esters synthesis from triglycerides over heterogeneous catalysts in presence of microwaves. *CR Chimie*. 2004, 7: 601-606.

[6] J. Hernando, P. Leton,M.P. Matia, J.L. Novella and Alvarez-Builla. Biodiesel and fame synthesis assisted by microwaves. Homogeneous batch and flow processes. *Fuel*. 2007, **86**: 1641-1644.

[7] A. Demirbas. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Conv Management. 2002, **43**: 2349–2356.

[8] J.M. Encinar, J.F. González and A. Rodríguez-Reinares. Ethanolysis of used frying oil. Biodiesel preparation and characterization. Fuel Proc Tech. 2007, **88**: 513–522.

[9] G. M. Kulkarni, A.K. Dalai and N.N. Bakhshi, Transesterification of canola oil in mixed methanol/ethanol system and use of esters as lubricity additive. Bioresource Tech. 2007, **98**: 2027–2033.

[10] S.V. Ghadge and H. Raheman, Biodiesel production from mahua oil having high free fatty acids. Biomass and Bioenergy. 2005, **28**: 601-605.

[11] T.M. Barnard, N.E. Leadbeater, M.B. Boucher, L.M. Stencel and B.A. Wilhite. Continuous-flow preparation of biodiesel using microwave heating. Energy & Fuels. 2007, **2**: 1777–1781.

[12] N. Azcan and A. Danisman. Microwave assisted transesterification of rapeseed oil. Fuel. 2008, **87**: 1781–1788.

[13] Shell Comments on National Standard for Biodiesel Discussion Paper, 20.

VITAE

Name Mr. Kittiphoom Suppalakpanya

Student ID 5010130002

Educational Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Science (Chemistry)	Prince of Songkla University	2001
Master of Chemical Engineering	Prince of Songkla University	2006

Scholarship Awards during Enrolment

Prince of Songkla Graduate Studies Grant 2007 - 2010

List of Publication and Proceedings

Publication

Suppalakpanya, K., Ratanawilai S.B. and Tongurai, C. 2010. Production of Ethyl Ester from Esterified Crude Palm Oil by Microwave with Dry Washing by Bleaching Earth. Applied Energy. Available online 6 January 2010.

Proceeding

1. Suppalakpanya, K., Ratanawilai S.B. and Tongurai, C. 2008. Transesterification of Esterified Crude Palm Oil by Microwave with Dry Washing by Bleaching Earth. In Proceedings of Regional Symposium on Chemical Engineering (RSCE 2008). At Impiana KLCC Hotel & Spa, Kuala Lumbur, Malaysia. 2–3 December 2008. P. 703-708.

2. Suppalakpanya, K., Ratanawilai S.B. and Tongurai, C. 2009. Esterification of Free Fatty Acid in Crude Palm Oil by Continuous Microwave with Ethanol. In Proceedings of the Thai Institute of Chemical Engineering and Applied Chemistry (TIChE 2009). At Felix River Kwai Resort, Kanchanauri, Thailand. 26-27 October 2009. P. 160-161.

3. Suppalakpanya, K., Ratanawilai S.B. and Tongurai, C. 2010. Production of Ethyl Ester from Esterified Crude Palm Oil by Continuous Flow Microwave. In Proceedings of IACSIT Applied Chemical Engineering Society (CCEA 2010). At Quality hotel, Singapore. 26-28 February 2010. P. 111-115.