Development of Biodiesel Production Processes from Various Vegetable Oils

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by

Titipong Issariyakul

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Abstract

Biodiesel is an alternative fuel to petroleum diesel that is renewable and creates less harmful emissions than conventional diesel thus the use of this fuel is a shift toward “sustainable energy”. Biodiesel can be produced from vegetable oil, animal fat, and organisms such as algae or cyanobacteria. Since vegetable oils are the major source for current commercial biodiesel, they are the focus of this thesis.

The main objective of this Ph.D. research is to develop processes suitable to produce biodiesel from various vegetable oils especially for those of non-edible oils such as used cooking oil, canola oil from greenseed, and mustard oil. An additional objective is to understand the relationship between the parent vegetable oils and the corresponding biodiesel properties.

Used cooking oil was the first vegetable oil investigated in this research. Initially, oil degradation behavior was monitored closely during frying. During 72 hours of frying, acid value and viscosity of the oil increased from 0.2 to 1.5 $mgKOH \cdot g^{-1}$ and from 38.2 to 50.6 cP, respectively. It was found that ester yield was improved by addition of canola oil to used cooking oil, i.e. addition of 20% canola oil to used cooking oil increased methyl ester yield and ethyl ester yield by 0.5% and 12.2%, respectively. At least 60% canola oil addition is needed to produce ASTM grade ethyl ester biodiesel. The optimum reaction conditions to produce biodiesel are 1% KOH loading, 6:1 alcohol to oil ratio, 600 rpm stirring speed, and either 50°C reaction temperature for 2 hr or 60°C reaction temperature for 1.5 hr for methanolysis and 60°C reaction temperature for 2 hr for ethanolysis.

Among non-edible vegetable oils, greenseed canola oil can be used in the most simple biodiesel production process. In this case, an addition of fresh vegetable oil is not required,

because chlorophyll contained in this oil did not play a crucial role in the reaction activity. Methyl ester yields derived from greenseed canola oil without and with 94.1 ppm chlorophyll content are 95.7% and 94.8%, respectively. In contrast, erucic acid contained in mustard oil created difficulties in the production process. Ester yield derived from mustard oil using the conditions mentioned above was only 66% due to the present of unconverted monoglyceride. To obtain a deeper understanding on mustard oil transesterification, its reaction kinetics was studied. In the kinetic study, transesterification kinetics of palm oil was also investigated to study the effect of fatty acid chain length and degree of saturation on the rates of the reactions. It is shown in this research that the rates of mustard monoglyceride transesterification (rate constant = 0.2-0.6 $L \cdot mol^{-1} \cdot min^{-1}$) were slower that those of palm monoglyceride transesterification (rate constant = 1.2-4.2 $L \cdot mol^{-1} \cdot min^{-1}$) due to its lower molecular polarity resulting from the longer chain of erucic acid. The activation energy of the rate determining step (in this case, conversion of triglyceride to diglyceride reaction step) of mustard transesterification was, however, 26.8 $kJ \cdot mol^{-1}$, which is similar to those of other vegetable oils as reported in literature. Despite the presence of unconverted monoglyceride, distillation can be used to obtain a high purity ester.

Several ester properties are determined by characteristics of the parent oil and choice of alcohol used in transesterification. Chlorophyll contained in greenseed canola oil, for example, has an adverse effect on biodiesel oxidative stability. The induction time for methyl ester derived from treated greenseed canola oil (pigment content = 1 ppm) was enhanced by 12 minutes compared to that derived from crude greenseed canola oil (pigment content = 34 ppm). The optimum bleaching process involves the use of 7.5 wt.% montmorillonite K10 at 60°C and stirring speed of 600 rpm for 30 minutes. In addition, it was found that induction time of treated greenseed canola ethyl ester (1.8 hr) was higher than that of methyl ester (0.7 hr), which suggests

a better oxidative stability of esters of higher alcohols. Furthermore, the use of higher alcohols instead of methanol produced materials with improved low temperature properties. For example, the crystallization temperatures of monounsaturated methyl, ethyl, propyl, and butyl esters prepared from mustard oil were -42.5°C, -51.0°C, -51.9°C, and -58.2°C, respectively. In contrast, the lubricity of biodiesel is mainly provided by its functional group which is $COOCH_3$ for methyl ester. The use of higher alcohols in transesterification results in a less polar functional group in the corresponding ester molecule, which leads to reduction in ester lubricity. Methyl ester provided the highest lubricity among all esters produced, i.e. wear reduction at 1% treat rate of methyl ester, ethyl ester, propyl ester, and butyl ester are 43.7%, 23.2%, 30.7% and 30.2%, respectively.

The outcomes of this research have been published in several scientific journals and presented at national and international conferences. The published articles and conference presentations are listed at the beginning of each chapter in this thesis.

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CHAPTER 1

Introduction and Research Overview

1.1. Introduction

Biodiesel is an alternative renewable diesel fuel that has properties comparable to diesel obtained from petroleum processing. Since biodiesel is renewable and it creates less harmful exhaust emissions when combusted compared to that of petroleum diesel, the use of this fuel is a shift towards “sustainable energy”. Biodiesel can be produced from vegetable oil, animal fat, or organisms such as algae and cyanobacteria through a chemical reaction called transesterification with short chain alcohols. Since vegetable oils are currently the major source of feedstock in commercial biodiesel production, the focus of this Ph.D. research is biodiesel production based on vegetable oils. In addition to alternative fuel, biodiesel is commonly viewed as a lubricity additive to petroleum diesel. Because biodiesel is miscible with petroleum diesel in all proportions, an addition of only 1 vol.% biodiesel to petroleum diesel improves the lubricating property of petroleum diesel [1]. Due to its various advantages especially environmental benefits, many governments worldwide encourage the use of this fuel in the form of tax incentives and mandate implementations.

In 2011, the Canadian government implemented a 2% federal mandate for biodiesel that creates demand for around 500 million litres per year of biodiesel in Canada. According to Canadian Renewable Fuels Association, the domestic biodiesel production capacity around Canada was 200 million litres per year in 2010 [2]. There is an obvious demand for domestic

biodiesel production boost in order to reduce dependency on imported biodiesel. Therefore, major growth in biodiesel industry is expected in the coming years and research and technology on biodiesel production processes will be of higher value than ever. Research done in this thesis will serve as information for researchers and biodiesel manufacturers both inside and outside Canada. More details on feedstock, production processes, and characteristics of biodiesel are extensively reviewed in Chapter 2.

1.2. Research Overview

The objective of this research is to investigate biodiesel production from various vegetable oils with special emphasis on non-edible oil. In addition, the effects of different oils used as feedstock on reaction activity as well as the resulting biodiesel properties are also studied. This research is divided into 5 phases which are discussed in Chapter 3 to Chapter 7 and are outlined as follow.

In Chapter 3, properties of used cooking oil are monitored closely during frying and biodiesel is produced from used cooking oil. The properties of biodiesel derived from used cooking oil are compared with those of biodiesel prepared from canola oil and greenseed canola oil. In an attempt to improve properties of used cooking oil biodiesel, used cooking oil is mixed with canola oil and the mixed oil is used as feedstock for biodiesel production. This process is described in Chapter 4. The optimum mixing ratio is reported along with the optimum reaction conditions. Furthermore, Differential Scanning Calorimetry (DSC) is used to measure crystallization and melting temperature as well as heat associated with crystallization and melting. In this study, the effects of lipid and alcohol feedstock used in transesterification on crystallization and melting behaviour of biodiesel are reported.

Chapter 5 is focused on biodiesel production from greenseed canola oil. The effects of chlorophyll and its derivatives on transesterification activity as well as biodiesel property are discussed with special emphasis on oxidation stability. The optimum conditions on bleaching and transesterification are reported. Biodiesel production from mustard oil is then investigated in Chapter 6. A production process to produce high quality mustard biodiesel is developed. Biodiesel lubricity is evaluated and compared to those of commercial petroleum diesel. Finally, transesterification kinetics is investigated. Mathematical model as well as MATLAB program are developed in order to simulate transesterification progress and kinetic parameters such as the rate constants and the activation energies are obtained. Transesterification kinetics of different vegetable oils are compared and discussed in Chapter 7.

Since this thesis is provided in the paper-base format, each chapter has been published in national and international scientific journals and this is mentioned at the beginning of each chapter and the contribution of the Ph.D. candidate is highlighted. Abbreviations and references are given at the end of each chapter.

References

[1] Lang X, Dalai AK, Reaney MJ, Hertz PB. Biodiesel esters as lubricity additives: effects of process variables and evaluation of low-temperature properties. Fuels International: 207-227 (2001).

[2] Canadian Renewable Fuels Association. Growing beyond oil delivering our energy future: a report card on the Canadian renewable fuels industry. www.greenfuels.org. Accessed November 2010.

CHAPTER 2

Literature Review

A part of this chapter has been submitted for publication in Renewable & Sustainable Energy Reviews:

- Issariyakul, T., and Dalai A.K. Biodiesel from vegetable oils. Renewable and Sustainable Energy Reviews (Submitted).

Contribution of the Ph.D. Candidate

Literature review was performed by Titipong Issariyakul. The content in this chapter was written by Titipong Issariyakul with discussions and suggestions provided by Dr. Ajay Dalai.

Contribution of this Chapter to the Overall Ph.D. Research

In Chapter 2, history of the use of vegetable oil related fuel is reviewed along with feedstock, production, and characteristics of biodiesel from vegetable oils. This chapter provides the overall direction of this Ph.D. research.

2.1. Abstract

Biodiesel is gaining acceptance in the market as both fuel and lubricant. It is expected that the biodiesel industry will grow rapidly worldwide in the coming years and information regarding biodiesel feedstock, its production, and characteristics will be significant. Biodiesel from vegetable oil is the focus in the present review. Since vegetable oil is currently the major source for making commercial biodiesel, selected available vegetable oils are reviewed as feedstock for biodiesel production. Production technologies including the latest catalyst developments are discussed and biodiesel characteristics and parameters influencing the corresponding biodiesel properties are revealed.

2.2. Introduction

As conventional, non-renewable, fossil-based fuel resources are depleting, research and development on alternative renewable energy is growing. Biodiesel is a promising renewable energy. Recently, a 5.54 fossil energy ratio (FER) is reported [1] which means one unit of fossil energy input is required to produce 5.54 units of biodiesel energy output from soybean oil. This FER indicates a superior energy return of biodiesel that surpasses those of other alternate fuels [2]. The FER of biodiesel is expected to increase in the coming years, due to increased crop yield, adoption of energy-saving farm practices, and continuous development technologies that enhance energy efficiency. Biodiesel has many properties that contribute to superior performance when compared to petroleum diesel. For example, biodiesel produces lower exhaust emissions than conventional diesel and it is biodegradable, non-toxic, renewable, and essentially free of

sulfur [3,4,5]. Since biodiesel is renewable and environmentally beneficial, the use of this fuel is a shift towards sustainable energy.

The history of biodiesel is as long as that of the diesel engine itself and the use of vegetable oils was investigated as early as the era when diesel engine was developed. Rudolf Diesel (1858-1913), the inventor of diesel engine, tested peanut oil as fuel for his engine. Dating from early 1920s, many vegetable oils were investigated, including palm oil, soybean oil, cottonseed oil, and castor oil. These early studies showed satisfactory performance of vegetable oil as fuel for diesel engines [6]. However, there were concerns that their higher costs as compared to petroleum fuel would prevent their prevalent uses. In spite of their performance in diesel engine, vegetable oils create engine problems when used as diesel fuel in both indirect- and direct-injection engines. The major drawback of vegetable oils is their high viscosity which causes coking, varnishing and trumpet formation on the injectors that results in poor atomization and ultimately leads to operational problems such as engine deposits [7].

Possible solutions to reduce the viscosity of vegetable oil include heating, transesterification, pyrolysis, dilution with petroleum-based fuels, and emulsification [8]. Transesterification is the most common method which yields mono alkyl esters of long chain fatty acids or fatty acid alkyl ester (FAAE). This idea originated in 1938 when it was noted that glycerine has a low calorific value and is likely to cause excess carbon deposit in the engine and, therefore, should be eliminated from glyceride oils used as diesel fuel. During that period, it was proposed that the engine should run on what was referred to as “residue fatty acid” [9]. This residue fatty acid is known today as “biodiesel”, although ester was not yet mentioned. In fact, the high molecular weight of the triglyceride molecule is responsible for much of the viscosity of vegetable oil, whereas the fatty acids are typically 10 times less viscous than their parent

vegetable oil at room temperature. During the summer of 1938, an urban bus running between Brussels and Louvain was operated on ethyl ester produced from palm oil. The engine performance was satisfactory and it was noted that the viscosity of ethyl ester was less than that of palm oil. The term “biodiesel” made its first appearance in a paper published in 1988 and this term was used exponentially thereafter [10].

Biodiesel is often defined as the mono alkyl esters of long chain fatty acids. Such esters may be prepared from acyl-glycerides (usually triglyceride) in vegetable oils via transesterification with short chain alcohols. Biodiesel is miscible in all portions with petroleum based diesel and, thus, can be effectively used as a neat biodiesel or blended with petroleum based diesel fuel [11]. The blends of biodiesel and petrodiesel are often coded to represent the percent volume of the blend. B20, for example, indicates the blend of 20 vol.% biodiesel and 80 vol.% petrodiesel. The current knowledge of biodiesel feedstock chemistry (vegetable oils), transesterification reactions, and biodiesel properties are described in the following sections.

2.3. Feedstock

Both lipid and alcohol feedstock determine the properties and method used in biodiesel production. Lipid feedstocks include vegetable oils, animal fats, and, more recently, oil from other organisms such as micro algae and cyanobacteria [12,13]. This paper focuses on vegetable triglyceride oils as lipid feedstock. The vegetable oils available for biodiesel production highly depend on climate. Rapeseed oil is utilized in European countries and Canada, soybean oil in the United States of America, and palm oil in tropical countries including Indonesia and Malaysia while coconut oil is used for synthesis of biodiesel in coastal areas. Potential inedible oils used as

lipid feedstock include jatropha oil (*Jatropha curcas*) and karanja oil (*Pongamia pinnata*) [14]. Oilseed prices and availability are important parameters to consider as biodiesel feedstock and are shown in Table 2.1.

Soybean and palm oil dominate world oilseed production while considerably less rapeseed oil production occurs. The oil content of rapeseed is >40%, while that of soybean is 21%. Palm oil is an interesting source for biodiesel production due to its low price and relatively high oil content (40%). Oil palm also achieves a higher annual oil yield compared to soybean and rapeseed.

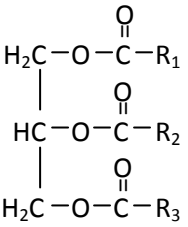
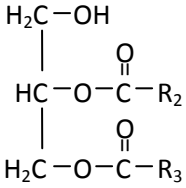
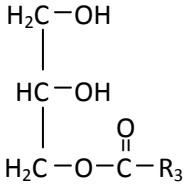
Oilseeds store lipid in organelles called oleosomes which can be broken and extracted to produce vegetable oil. The major component of vegetable oils is triacylglycerol (TAG) or triglyceride (TG) which is a molecule composed of three esters of fatty acid chain (acyl group) attached to glycerol (glycerol group). When two acyl ester groups and one hydroxyl group (–OH) are present, the molecule is called a diacylglycerol (DAG) or diglyceride (DG). Similarly, monoaclyglycerol (MAG) or monoglyceride (MG) has one acyl ester group and two hydroxyl groups. Acylglycerol is a term referred to TAG, DAG, or MAG and is depicted in Table 2.2. The acyl groups are typically unbranched fatty acids with between 10 to 24 carbon atoms. Saturated fatty acids have no double bonds between carbon atoms. When a pair of hydrogen atoms are removed from a fatty acid chain, one double bond is present and, therefore; it is called monounsaturated fatty acid. If the molecule contains two or more double bonds caused by further removal of hydrogen atoms, it is called polyunsaturated fatty acids. These fatty acids are frequently represented by a symbol such as C18:1, which indicates a fraction consisting of 18 carbon atoms and one double bond. Typical fatty acids attached to TAG found in vegetable oils are presented in Table 2.3.

Table 2.1 World oilseed production, average oil price and oil content of various oilseeds.

Plant	Oil content (%)	Oilseed production[a] (Million metric tons)	Average oilseed price[a] (U.S.D/metric ton)	Average oil price[a] (U.S.D/metric ton)	Yield (kg oil/hectare/yr)	Reference
Rapeseed	>40	46.72	375	852[b]	600 - 1000	15,16,17
Soybean	21	235.77	254	684	300 - 450	15,16,18
Sunflower seed	44-51	30.15	n/a	n/a	280 - 700	15,16,19
Palm	40	10.27	n/a	655	2500 - 4000	15,16,20
Cottonseed	18	46.02	n/a	787	n/a	15,20
Peanut	36-56	32.36	395	1253	340 - 440	15,16,21
Copra	65-68	5.28	537	n/a	n/a	15,22
Coconut	63	n/a	n/a	812	600 - 1500	15,16,20

[a]Data in 2006/2007; [b]Canola oil

Table 2.2 Molecular structure of triglyceride, diglyceride, and monoglyceride.

Triglyceride	Diglyceride	Monoglyceride
		

R_1, R_2, R_3 = fatty acid chain

Table 2.3 Structures of common fatty acids present in vegetable oils.

System name	Common name	Symbol	Formula	Double bond position[a]
Saturated				
Decanoic	Capric	C10:0	$C_{10}H_{20}O_2$	-
Dodecanoic	Lauric	C12:0	$C_{12}H_{24}O_2$	-
Tetradecanoic	Myristic	C14:0	$C_{14}H_{28}O_2$	-
Hexadecanoic	Palmitic	C16:0	$C_{16}H_{32}O_2$	-
Octadecanoic	Stearic	C18:0	$C_{18}H_{36}O_2$	-
Eicosanoic	Arachidic	C20:0	$C_{20}H_{40}O_2$	-
Docosanoic	Behenic	C22:0	$C_{22}H_{44}O_2$	-
Tetracosanoic	Lignoceric	C24:0	$C_{24}H_{48}O_2$	-
Monounsaturated				
Hexadecenoic	Palmitoleic	C16:1	$C_{16}H_{30}O_2$	9c
Octadecenoic	Petroselinic	C18:1	$C_{18}H_{34}O_2$	6c

Octadecenoic	Oleic	C18:1	$C_{18}H_{34}O_2$	9c
Octadecenoic	Asclepic	C18:1	$C_{18}H_{34}O_2$	11c
Eicosenoic	n/a[a]	C20:1	$C_{20}H_{38}O_2$	5c
Eicosenoic	Gadoleic	C20:1	$C_{20}H_{38}O_2$	9c
Eicosenoic	Gondoic	C20:1	$C_{20}H_{38}O_2$	11c
Docosenoic	Erucic	C22:1	$C_{22}H_{42}O_2$	13c
Polyunsaturated				
Hexadecadienoic	n/a[a]	C16:2	$C_{16}H_{28}O_2$	
Octadecadienoic	Linoleic	C18:2	$C_{18}H_{32}O_2$	9c12c
Octadecatrienoic	Linolenic-α	C18:3	$C_{18}H_{30}O_2$	9c12c15c
Octadecatrienoic	Linolenic-γ	C18:3	$C_{18}H_{30}O_2$	6c9c12c
Octadecatrienoic	Eleostearic	C18:3	$C_{18}H_{30}O_2$	9c11t13t
Octadecatrienoic	Calendic	C18:3	$C_{18}H_{30}O_2$	8t10t12c

[a]c = *cis* formation; t = *trans* formation; n/a = not available

Stereo isomers of unsaturated fatty acids can be arranged in *cis* and *trans* orientation. Most natural occurring fatty acids from vegetable oils have *cis*-double bonds whereas the unnatural *trans*-isomers usually only occur due to partial hydrogenation process. The Latin prefixed *cis* and *trans* describe the orientation of hydrogen atoms attached to carbon atoms at position next to a double bond. In *cis*-isomer, hydrogen atoms are attached on the same side causing a "V" shape of fatty acid chain.

The major difference between various vegetable oils is the type of fatty acids attached in the triglyceride molecule. Fatty acid compositions of various vegetable oils are provided in table 2.4. Fatty acid composition determines biodiesel fuel properties, therefore, vegetable oil fatty acid composition is important [42]. Both the degree of saturation/unsaturation and molecular weight of vegetable oils determine fuel properties. The degree of saturation/unsaturation is proportional to the iodine value while the saponification value is inversely proportional to molecular weight. Iodine value and saponification value of selected vegetable oils are provided in Table 2.5 [43].

2.3.1. Soybean Oil

Glycine max is referred to as "Soybean" or "Soya". This member of Papilionaceae is found only under cultivation. The origin of soybean is not clear, for the genus *Glycine* has two major gene centres; eastern Africa and Australia. It is believed that the genus *Glycine* was dispersed from Australia to the whole Pacific region including China via migratory birds as seed carriers. Based on historical and geographical evidence, north eastern China is considered to be the site of soybean domestication. There are a number of soy-based food products including various liquids prepared from soybean and soybean curd known as "tofu". From China, soybean spread through nearby countries including Korea, Japan, and the Southeast Asian region. More recently, soybean has been cultivated around the world. Soybean was first mentioned in USA literature in 1804. From that time until World War II, it was exclusively used as a forage crop, after which its production and economic value in the USA has grown exponentially. Today, soybean is the world's largest oilseed in terms of total production and international trade [44,45].

Table 2.4 Fatty acid compositions of vegetable oils.

Vegetable oils		Fatty acid composition (wt.%)											Reference
Common Name	Species	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:0	22:1	
Canola (Low erucic rapeseed)	*Brassica rapa*	-	-	3.1	0.2	1.3	56.6	22.4	14.0	0.4	0.2	0.1	23
Canola (Low erucic rapeseed)	*Brassica napus*	-	-	4.3	0.3	1.7	61.0	20.8	9.3	0.6	0.3	-	23
Black mustard	*Brassica nigra*	-	1.5	5.3	0.2	1.3	11.7	16.9	2.5	9.2	0.4	41.0	24
Oriental mustard	*Brassica juncea*	-	-	2.3	0.2	1.0	8.9	16.0	11.8	0.8	5.7	43.3	25
Brown mustard	*Brassica juncea*	-	-	2.2	0.2	1.2	17.4	20.5	14.1	0.7	0.5	28.1	26
Wild mustard	*Sinapis arvensis*	-	0.1	2.6	0.2	0.9	7.8	14.2	13.0	0.8	1.5	45.7	27
White mustard	*Sinapis alba*	-	-	3.1	0.2	0.7	9.1	11.7	12.5	0.7	-	46.5	26
White mustard	*Sinapis alba*	-	0.1	2.8	0.2	1.1	25.0	11.6	8.6	0.7	0.6	32.8	28
Abyssinian mustard	*Brassica carinata*	-	-	3.1	-	1.0	9.7	16.8	16.6	0.7	-	42.5	29

Soybean	*Glycine max*	-	-	10.1	-	4.3	22.3	53.7	8.1	-	-	-	30
Soybean	*Glycine max GMO*[a,b]	-	-	3.5	0.1	2.8	22.7	60.3	9.8	0.2	0.2	-	31
Soybean	*Glycine max GMO*[a,c]	-	0.1	10.9	0.1	5.7	27.5	51.5	3.0	0.5	0.4	-	31
Soybean	*Glycine max GMO*[a,d]	-	0.1	23.8	0.7	3.8	15.4	44.1	11.0	0.4	0.6	-	31
Soybean	*Glycine max GMO*[a,e]	-	-	8.0	0.1	24.7	17.2	39.2	8.3	1.5	0.7	-	31
Palm	*Elaeis guineensis*	0.3	1.2	44.3	-	4.3	39.3	10.0	-	-	-	-	32
Palm	*Elaeis oleifera*	-	0.2	18.7	1.6	0.9	56.1	21.1	-	-	-	-	32
Palm kernel	*Elaeis guineensis*	50.1	15.4	7.3	-	1.8	14.5	2.4	-	-	-	-	32
Palm kernel	*Elaeis oleifera*	29.3	25.7	10.1	-	1.8	26.4	4.5	-	-	-	-	32
Palm kernel	*Aiphanes acanthophylla*	41.5	20.5	10.2	-	3.4	15.8	7.4	-	-	-	-	33
Palm kernel	*Buttia capitata*	39.2	6.4	4.2	-	3.0	11.9	3.5	-	-	-	-	33

Palm olein[f]		0.3	1.2	40.6	0.2	4.3	41.9	11.9	0.4	0.4	-	-	34
Palm stearin[f]		0.3	1.5	61.1	0.1	4.8	25.8	6.5	0.4	0.5	-	-	34
Sunflower	*Helianthus annuus*	-	-	5.2	0.1	3.7	33.7	56.5	-	-	-	-	30
Sunflower	*Helianthus annuus GMO*[a,g]	-	-	3.1	0.1	1.5	91.5	2.1	-	0.2	0.7	0.1	31
Sunflower	*Helianthus annuus GMO*[a,g]	-	-	4.4	-	4.2	78.3	10.9	-	0.3	1.0	-	35
Sunflower	*Helianthus annuus GMO*[a,c]	-	0.1	7.5	0.1	1.9	13.3	76.0	0.1	0.1	0.4	-	31
Sufflower	*Carthamus tinctorius*	-	0.1	6.4	-	2.3	11.6	79.3	-	0.3	-	-	36
Groundnut	*Arachis hypogea*	-	-	11.2	-	3.6	41.1	35.5	0.1	-	-	-	30
Corn	*Zea mays*	-	-	11.6	-	2.5	38.7	44.7	1.4	-	-	-	30
Olive	*Olea europaea*	-	-	13.8	1.4	2.8	71.6	9.0	1.0	-	-	-	30
Cottonseed	*Gossypium hirsutum*	-	-	23.0	-	2.3	15.6	55.6	0.3	-	-	-	30

Linseed	*Linum usitatissimum*	-	-	5.6	-	3.2	17.7	15.7	57.8	-	-	-	30
Coconut	*Cocos nucifera*	50.9	21.1	9.5	-	4.9	8.4	0.6	-	-	-	-	37
Sesame	*Sesamum indicum*	-	-	9.6	0.2	6.7	41.1	41.2	0.7	-	-	-	30
Rice bran	*Oryza sativa*	-	-	22.1	-	2.0	38.9	29.4	0.9	-	-	-	38
Jatropha	*Jatropha curcas*	-	-	18.5	-	2.3	49.0	29.7	-	-	-	-	39
Karanja[f]	*Pongamia glabra*	-	-	5.8	-	5.7	57.9	10.1	-	3.5	-	-	40
Karanja	*Pongamia pinnata*	-	-	11.7	-	7.5	51.6	16.5	2.7	-	-	-	41
Neem[f]	*Azadirachta indica*	-	-	17.8	-	16.5	51.2	11.7	-	2.4	-	-	40
Sal[f]	*Shorea robusta*	-	-	6.2	-	43.0	41.3	2.1	-	5.5	-	-	40

[a]GMO = genetically modified oil; [b]low saturate; [c]high linoleic; [d]high palmitic; [e]high stearic; [f]average value; [g]high oleic

Table 2.5 Iodine value and saponification value of vegetable oils.

Oil	Saponification value	Iodine value
Low erucic rapeseed, crude	179.0	109.9
Soybean, crude	190.7	134.6
Palm, crude	200.0	56.9
Palm kernel, crude	246.4	20.7
Sunflower, winterized	190.6	135.4
Sufflower, linoleic-rich, crude	190.3	143.6
Sufflower, oleic-rich, crude	189.3	93.2
Cottonseed, crude	195.2	105.0
Linseed, crude	189.6	188.0
Corn, soap stock	195.9	105.3
Rice bran, crude	180.1	103.9
Coconut, crude	256.4	9.9
Olive, refined	192.0	84.9
Sesame, crude	188.0	109.2

The oil content in soybean seed ranges from 15 to 22% depending on cultivar and environmental conditions during seed maturity. The major fatty acids are oleic (C18:1) and linoleic (C18:2) as can be seen in Table 2.4.

2.3.2. Rapeseed Oil, Mustard Oil, and Canola Oil

The word “rape” originates from Latin word “rapum”, which means turnip and belongs to the family *Brassica* which includes turnip, mustard, cabbage, rutabaga, broccoli, and kale [46]. Rapeseed was among the first domesticated crops and was used as a source of cooking and illumination oil as early as 2000-1500 BC [47]. *Brassica* crops are among the few vegetable oil sources that can be cultivated in cool climates. The economically important crops in *Brassica* and *Sinapis* species include *Sinapis alba* (white mustard), *Brassica nigra* (black mustard), *Brassica carinata* (Abyssinian mustard), *Brassica juncea* (brown, oriental, and leaf mustard), *Brassica oleracea* (cabbage, kale, cauliflower, broccoli), *Brassica rapa* (turnip, rape), and *Brassica napus* (rape, rutabaga) [17]. Oilseeds of rapeseed have an oil content of over 40% while those of mustard have oil content as low as 20% such as that of *Sinapis alba* [48]. Oil extracted from these seeds majorly contains fatty acids of oleic acid (C18:1), linoleic acid (C18:2), and erucic acid (C22:1). When rapeseed has a erucic acid content higher than 2%, it is called high erucic acid rapeseed (HEAR), while rapeseed having erucic acid content less than 2% is referred to as low erucic acid rapeseed (LEAR) [49]. Erucic acid contained in rapeseed should be avoided in daily diets. It has been reported that cardiac fat infiltration occurs in experimental animals fed erucic acid and it was concluded that erucic acid is potentially toxic. This compound if fed in large quantities might result in heart lesions [46]. In spite of the adverse nutritional effects of erucic acid in model systems, the effects of erucic acid on humans have not been demonstrated. Nevertheless, the use of rapeseed oil containing a high erucic acid level as edible oil has continuously been objected by many organizations throughout history. The Canadian regulations state that for cooking oil, margarine, salad oil, simulated dairy product, shortening, or food

resembling margarine or shortening, the erucic and cetoleic acid may not exceed 5% of the total fatty acid [50].

Erucic acid biosynthesis is through the elongation of oleic acid. In brief, erucic acid is formed by an addition of a two-carbon fragment to oleic acid to form eicosenoic acid (C20:1), followed by an addition of another two-carbon fragment to eicosenoic acid to form erucic acid [51]. In the case of low erucic acid rapeseed (LEAR) such as *Brassica napus* (Canola Oil or Canadian Brassica), the gene that codes for the fatty acid elongation enzyme is missing leading to the accumulation of the precursor fatty acid, i.e., oleic acid. The level of erucic acid can be selected to range from less than 1% to over 60%. The percentage of erucic acid in Canadian LEAR declined between 1980 and 1989 [52]. The advent of low erucic acid rapeseed (LEAR) lead to the accepted use of LEAR for food; however, HEAR could be used in other industries such as fuel, lubricating oil, oleochemicals, and biopolymer production. In 1974, the so-called "double-low" rapeseed, that is rapeseed low in erucic acid and glucosinolate content, has become commercially available in Canada. The Canola Council of Canada trademarked the name "canola" for LEAR since this "double low" rapeseed became the major vegetable oil used in the Canadian diet. Canola oil is the fully refined, bleached, and deodorized edible oil obtained from *Brassica napus* or *Brassica rapa* with low levels of both erucic acid and glucosinolate content. Under the USA code of Federal Regulation Title 21, the erucic acid content in canola oil shall not exceed 2% of the component fatty acids [49].

2.3.3. Palm Oil

Oil palm is believed to have originated in Africa, but is cultivated most intensively in Southeast Asia especially Malaysia and Indonesia that together account for around 80% of the total world production. Palm first received its botanical name from Jacquin in 1763 as *Elaeis guineensis* [53]. The word *Elaeis* is derived from the Greek word *elaion*, meaning oil, while *guineensis* implies its origin in the Guinea coast. The genus *Elaeis* includes *Elaeis guineensis* originating in Africa, *Elaeis oleifera* originating in Central and South America, and *Elaeis odora*, previously known as *Bercella odora*, which is not cultivated. *Elaeis guineensis* is currently the main commercially grown species in Malaysia because it gives the highest yield per bunch while oil from *Elaeis oleifera* is more unsaturated and yields less oil. The fruit contains shell and one, two, or three kernels. The seed consists of layers of oily endosperm surrounded by a brown testa covered with a network of fibres. Palm affords the highest oil production per area per year (Table 2.1). There are generally two types of oil derived from palm, including palm oil derived from the mesocarp and palm kernel oil from the kernel inside the testa [22,54]. Palm oil is more saturated than soybean oil and rapeseed oil because its major fatty acids include palmitic (C16:0), stearic (C18:0), oleic (C18:1), and linoleic (C18:2) as shown in Table 2.4. Palm kernel oil is more saturated than palm oil as it mainly contains lauric (C12:0), myristic (C14:0), and oleic (C18:1) acids. Palm oil can be fractionated at ambient temperature (25-30°C) into palm olein or oleic-rich oil (liquid fraction) and palm stearin or stearic-rich oil (solid fraction). Due to the saturated fatty acids contained in this oil, it has superior oxidative stability compared to other vegetable oils.

2.3.4. Sunflower Oil

The genus *Helianthus annuus* is the botanical name for sunflower, a member of Compositae, or flowering plants, grown throughout the world. The genus name stems from the Greek words *helios,* meaning sun, and *anthos,* meaning flower. Sunflower originated in Southwest United States and Mexico [45]. Sunflowers are cultivated both for ornamental and consumption purposes. Sunflower seeds are edible and often crushed to extract oil. The major fatty acids in sunflower oil are oleic (C18:1) and linoleic (C18:2). Sunflower is considered as one of the most ancient oilseed species as its cultivation can be traced back to 3000 B.C. Prior to the advent of the soybean boom after World War II, sunflower was the major source of vegetable oil.

2.3.5. Rice Bran Oil

Rice bran is obtained when brown rice is pearled to produce white rice. The bran and yarn removed by pearling are the main source of rice oil. Lipid droplets can be extracted from rich bran using an extruder, expander, and expeller to form a bran flake or pellet followed by solvent (usually hexane) extraction in an extraction bed. The majority of oil components is triacylglyceride (TAG) with palmitic (C16:0), oleic (C18:1), and linoleic (C18:2) acids as the major fatty acids. Diacylglyceride (DAG), monoacylglyceride (MAG), and sterols may be present in minor amounts. Rice bran oil is used widely in Asian countries due to its delicate flavour and odour. It is recently gaining interest as healthy oil since it reduces serum cholesterol [55].

2.3.6. Jatropha Oil

Jatropha curcus is a member of the Euphorbiaceae family. It originated in America, but is cultivated mainly in Asia, especially India. Jatropha is well adapted to both arid and semi-arid conditions and sheds its leaves in order to survive during drought seasons [56]. It can be grown on non-cultivated degraded wasteland and is considered one of the most promising feedstock materials for biodiesel production [57]. Although Jatropha plants have minimal nutritional requirements, cultivation of Jatropha under acidic soil requires additional nutrients such as calcium and magnesium due to its preference for alkaline soils. Oil derived from Jatropha is non-edible due to curcin, a toxic compound, found in the seeds. Its oil content ranges from 35-40% in seed and 50-60% in kernel with oleic (C18:1) and linoleic (C18:2) as its major fatty acids.

2.3.7. Karanja Oil

Karanja *Pongamia pinnata* is a member of Leguminaceae family. It is an oil seed bearing tree, native to humid and subtropical environments such as those encountered in Philippines, Indonesia, Malaysia, Myanmar, Australia, India, and United States. It is highly tolerant to salinity and can be cultivated on degraded wasteland and a variety of soil types ranging from clay to sandy or stony. In addition, it plays important role in improving soil quality so that the land exhausted of nutrients can be reused for agricultural purposes [56]. The oil droplet extracted from Karanja appears yellowish orange to brown and is not edible due to the presence of toxic flavonoids [58]. Its oil content varies from 9-46% with oleic (C18:1) and linoleic (C18:2) being the major fatty acids.

2.3.8. Used Cooking Oil

The properties of used cooking oil depend highly on the origin and history of the oil. The origin of used cooking oil determines its fatty acid compositions. The history or duration that the oil exposed to water, heat, food, micro-organisms and oxygen during cooking determines its physical and chemical properties such as viscosity, water content, free fatty acid content, and the presence of polymerized and oxidized compounds.

Oil degradation during cooking occurs through three main reactions: thermolytic, oxidative, and hydrolytic reactions. Thermolytic reactions occur in the absence of oxygen and saturated fatty acids, forming alkanes, fatty acids, ketones, esters, and diacylglycerides that are decomposed at high temperatures. In addition, dimeric compounds are major products of thermolytic reactions of unsaturated fatty acids. Dimerization and polymerization of unsaturated fatty acids take place via Diels-Alder reactions. For example, a reaction between conjugated diene from linoleate and oleate can take place to produce a tetra-substituted cyclohexene [59]. In the presence of oxygen, oxidative and nonoxidative reactions will occur simultaneously.

Oxidative reactions occur in a series of initiation, propagation, and termination steps as shown in Figure 2.1. The initial step involves abstraction of hydrogen from unsaturated fatty acid to form a free radical (R·) followed by a reaction of the radical with molecular oxygen to form peroxide radicals (ROO·). The propagation phase involves intermolecular interactions, whereby the peroxide radical abstracts hydrogen from an adjacent molecule, which gives rise to hydroperoxides (ROOH) and a new free radical.

Initiation:

$$RH \rightarrow R^{\bullet} + H^{+}$$

Propagation:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + H^{+} \rightarrow ROOH$$

$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet}$$

Termination:

$$RO^{\bullet} + H^{+} \rightarrow ROH$$

$$OH^{\bullet} + H^{+} \rightarrow H_2O$$

Figure 2.1 Scheme for oxidative reaction mechanism.

Carbon-hydrogen bond dissociation energies of fatty acid are lowest at bisallylic, followed by allylic positions (see Figure 2.2). It is reported that lower bond energies for bisallylic and allylic hydrogens are 75 and 88 kcal/mol, respectively, while those of methylene hydrogens are 100 kcal/mol [60]. As a result, hydrogens at bisallylic and allylic locations are favoured sites for proton abstraction by peroxide radicals. Once formed, hydroperoxides tend to proceed toward further oxidation degradation, leading to secondary oxidation derivatives such as aldehydes, acids, and other oxygenates [59]. Hydrolytic reactions take place between the oil and water formed during food preparation. Formations of DAG, MAG, FFA, and glycerol are main derivatives from hydrolysis of TAG [61].

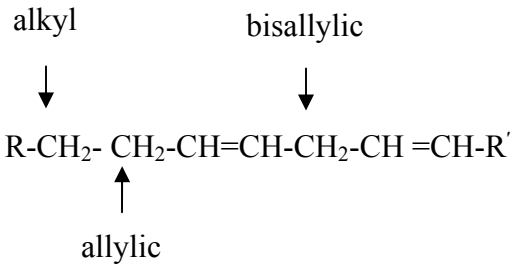


Figure 2.2 Carbon-hydrogen bond positions in fatty acids.

As a result of a combination of these reactions during food preparation, various reaction derivatives are formed leading to an increase in polar content of the oil. It is advised that used cooking oil no longer be used for edible purposes when its polar content exceeds 25% [62]. Therefore, used cooking oils were sold commercially as animal feed. However, in 2002 the European Union (EU) enforced a ban on these waste oils as animal feed because various harmful compounds are formed in used cooking oil during food preparation. When used cooking oil is mixed in feeding meals for domestic animals, these harmful compounds could be returned into the food chain through animal meats [63]. This concern has further raised interest in utilizing used cooking oil as feedstock for biodiesel production.

An obvious advantage of used cooking oil over other vegetable oils is its cheaper price. The prices of soybean, sunflower, yellow grease (FFA <20 wt.%), and brown grease (FFA >20 wt.%) are 18, 20, 9, and 5 to -5 cents/lb, respectively [64]. The negative value of brown grease price implies the cost associated with waste treatment prior to dumping. The availability of used cooking oil as a feedstock for biodiesel production is highly related to area population. Yellow grease generated in Canada is roughly equivalent to 4 kg production per person per year, meaning that approximately 124 Kilotonne of yellow grease is produced annually in Canada [65]. In comparison to used cooking oil, biodiesel produced from fresh vegetable oils would be pricier. Zhang et al. [66] reported that on average a $0.01/kg increase in canola seed cost would result in $0.03/kg increment in biodiesel prices and that raw material cost is responsible for approximately 70-95% of biodiesel production cost when fresh vegetable oil is used as feedstock. Therefore, the use of used cooking oil for feedstock for biodiesel production attracts many biodiesel producers due to its economical benefits.

2.4. Biodiesel Production

Transesterification is the most common method used to reduce viscosity of vegetable oils and produce biodiesel [7]. In addition to transesterification of TAG, biodiesel (FAAE) can be produced from free fatty acid (FFA) through esterification. Since ester is characterized by the RCOOR group (R = alkyl group), TAG is a type of ester and the reaction that converts TAG into biodiesel is known as transesterification (transforming ester). In contrast, FFA is not an ester and therefore the reaction to produce biodiesel from FFA is called esterification (making ester). Transesterification is the reaction between glycerides with short chain alcohols and is comprised of three consecutive reactions starting from TAG to DAG to MAG to glycerol, respectively (see Figure 2.3). In each step, the reaction consumes one mole of alcohol and produces one mole of ester. In total one mole of TAG reacts with three moles of alcohols to produce three moles of ester (biodiesel) and one mole of glycerol. In general, the reaction performance is influenced by various parameters such as type of alcohol, alcohol to oil molar ratio, FFA and water content, reaction temperature, reaction duration, and catalyst type. These parameters will be discussed in the following sections.

2.4.1. Effects of Free Fatty Acid and Water Content

Free fatty acid and water content in the starting materials can significantly affect ester yield and glyceride conversion in alkali-catalyzed transesterification. All starting materials including lipid feedstock, alcohol, and catalyst should be substantially anhydrous. Prolonged contact with atmospheric air of alkali catalysts will reduce catalyst efficacy through the catalyst's interaction with moisture and carbon dioxide in air. Also, it is critical that feedstock used in alkali-catalyzed

transesterification should contain free fatty acid (FFA) less than 0.5 wt.% [7]. The higher the acidity of oil, the lower is the conversion and yield in transesterification. If FFA is contained in the starting oil, extra alkali catalyst is needed to neutralize the FFA. The reaction between alkali catalyst and FFA would result in catalyst consumption as well as soap formation and water and is referred to saponification (see Figure 2.4a). Another example of saponification during transesterification is when water is present, it favours hydrolysis of glycerides to form soap and glycerol (see Figure 2.4b). In addition, water can promote hydrolysis of ester to form FFA, which lowers ester yield (see Figure 2.4c). Soap formed during saponification causes increased viscosity or gel formation, which interferes with the transesterification reaction as well as glycerol separation [58]. Ma et al. [67] studied the effects of FFA and water on transesterification of beef tallow using sodium hydroxide and sodium methoxide as a catalyst. It was reported that when 0.6% FFA was added, the yield of beef tallow methyl ester is minimal. Additional water present in the reaction mixture intensely diminished the ester yield. They concluded that FFA and water content should be maintained below 0.5 and 0.06 wt.%, respectively. Low quality feedstocks such as used cooking oil are attractive due to cheaper price. However, these feedstocks usually contain high amounts of FFA and water due to prolonged exposure of heat and contaminated moisture from food. Therefore, direct alkali-catalyzed transesterification of these oils is not applicable. Pre-treatment of these oils to remove FFA and water is usually required. Alkali refining is usually used in oil processing in order to remove FFA from oils [68]. In this process, 12% aqueous sodium hydroxide solution is required to neutralize FFA and to precipitate phosphatides. The treatment temperature and duration can be either 90°C for few seconds (short-mix process) or 40°C for 15 minutes (long-mix process).

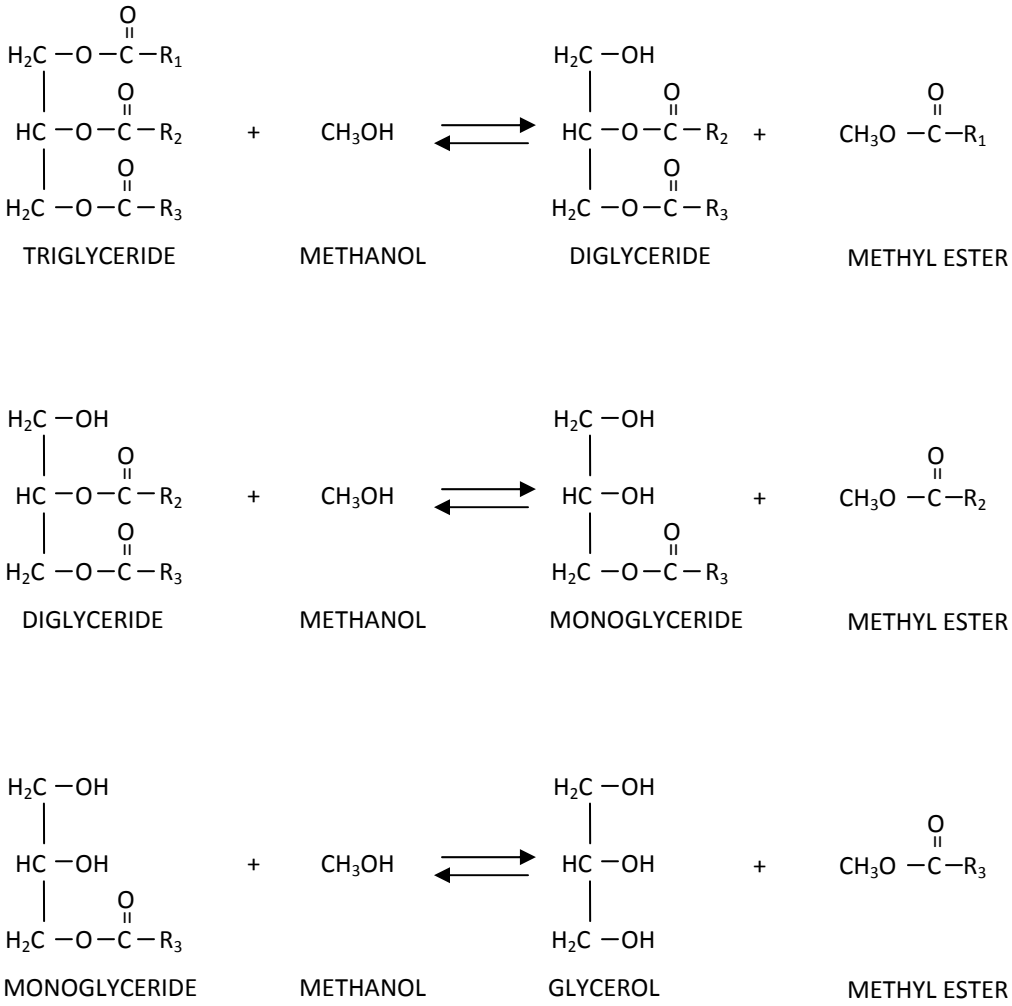
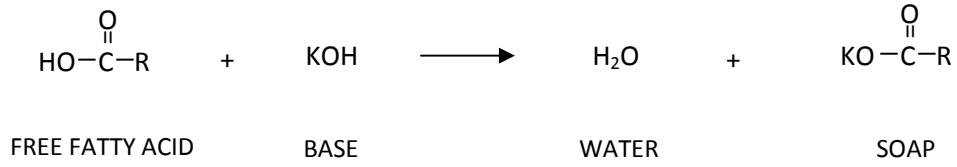
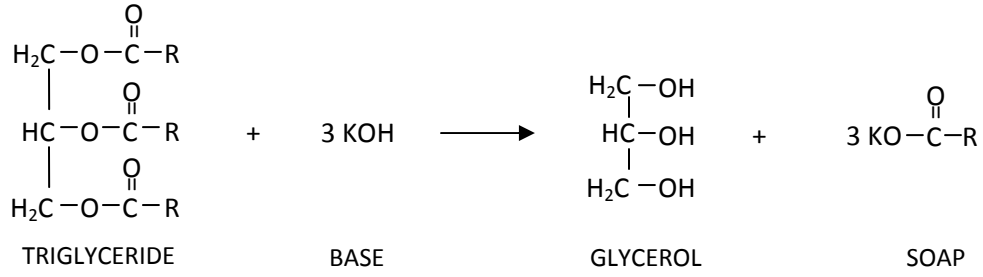


Figure 2.3 Scheme for step-wise transesterification reaction.

Reaction A:



Reaction B:



Reaction C:

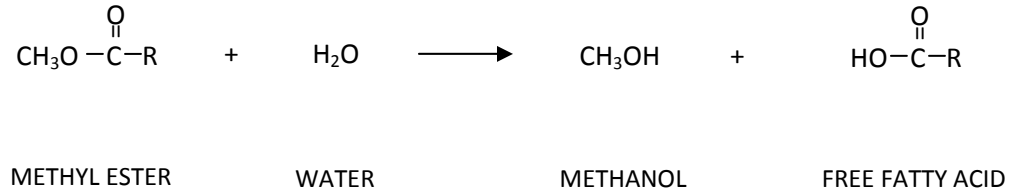


Figure 2.4 Hydrolysis and saponification during transesterification: a) saponification of free fatty acid; b) saponification of triacylglyceride; c) hydrolysis of methyl ester.

The oil-soap mixture is then centrifuged to separate the aqueous phase containing water, soap, and precipitated phosphatides. The treated oil usually has FFA reduced to <0.05% and phosphorus to <2 ppm. The disadvantage of this process is the generation of waste water.

FFA can also be removed from vegetable oils through distillation [69]. The distillation process should be performed under vacuum conditions in order to lower the operating temperature. If the operating temperature is too high, glycerides will degrade to generate more acids. The distillation temperature ranged from 100-180°C. However, this approach is less preferred due to the additional cost associated with the distillation step. Alternatively, a two-step acid-alkali esterification-transesterification process can be used [70]. In the first step, FFA is esterified with a short-chain alcohol with acid catalyst to produced ester. Since FFA is converted into ester in the first step, an alkali catalyst can be used in transesterification in the second step. A solid acid catalyst was also reported for simultaneous catalysis of esterification of FFA and transesterification of glycerides [71]. However, further research and development is required to improve conversion and ester yield.

2.4.2. Effects of Alcohol

Stoichiometrically, one mole of TAG requires three moles of alcohol in transesterification. However, due to the reversible nature of the reaction, excess alcohol is usually used in transesterification in order to shift the reaction to the product side. In general, 98% conversion can be achieved at 6:1 alcohol to oil ratio for an alkali-catalyzed reaction and an increase in alcohol used in the reaction does not increase conversion any further [72]. However, an optimum alcohol to oil ratio can be different depending on oil quality and the type of

vegetable oil used. It was reported that a maximum of 92% conversion was achieved using 10:1 methanol to oil ratio for biodiesel preparation from Karanja oil [73]. Leung and Guo [74] reported that 98% ester content can be obtained from transesterification of canola oil using 6:1 alcohol to oil ratio while transesterification of used cooking oil requires 7:1 alcohol to oil ratio to obtain 94% ester content. Transesterification of *Cynara cardunculus L.* oil requires 12:1 ethanol to oil ratio as an optimum ratio while an increase in ethanol to oil ratio to 15:1 decreases ester content [75]. Rashid and Anwar [76] also reported that a further increase in alcohol used in transesterification of rapeseed oil beyond its optimum ratio (6:1 in this case) would result in reduced ester yield. When too much alcohol is used in transesterification, the polarlity of the reaction mixture is increased, thus increasing solubility of glycerol back into the ester phase and promoting the reverse reaction between glycerol and ester or glyceride, thereby, reducing ester yield. Acid catalyzed reaction requires a higher alcohol to oil molar ratio (30:1), compared to alkali-catalyzed reactions [77-79]. In some cases, the alcohol to oil ratio is increased to 245:1 to obtain 99% conversion [80].

The type of alcohol used in transesterification can also affect reaction performance. Methanol is most commonly used in transesterification, mainly because of its economical benefit [7]. The disadvantages of using methanol are dependency on petroleum sources and a low solubility of TAG in methanol. To illustrate the immiscible behaviour of TAG in methanol, it is reported that a minimum mixing time of 3 minutes is required to sustain methanolysis of soybean oil [81]. A lag time of 2-3 minutes during methanolysis of soybean oil and sunflower oil is also reported [77,82]. This immiscibility behaviour is often referred to as mass transfer resistance or mass transfer limitation which can be overcome by several methods including the use of rigorous

mechanical stirring [83,84], a co-solvent aid [85], the use of super critical conditions [86-88], and other techniques such as microwave [89,90] and ultrasonic [91,92].

Attempts to improve the mass transfer of TAG have been made using other alcohols such as ethanol, propanol, and butanol [93-95]. Biodiesel produced using bio-ethanol is completely renewable. The main disadvantage of ethanolysis is the lower reactivity of ethoxide. When alcohol reacts with homogeneous base catalysts, alkoxides are the actual catalyst formed. If ethanol is used instead of methanol, the carbon chain length is increased which leads to a decrease in nucleophilicity and consequently a reduction in reactivity of ethoxide as compared to methoxide [96]. It was found that when waste fryer grease is transesterified with a mixture of methanol and ethanol at equal molar ratio, the resulting biodiesel contains 50% more FAME than FAEE [70], illustrating the higher reactivity of methoxide as compared to ethoxide. The lower polarity of ethanol has advantages and disadvantages on the transesterification process. On one hand, the lower polarity of ethanol alleviates the initial mass transfer resistance encountered in the case of methanolysis, hence, increasing the initial rate of the reaction. On another hand, it improves mutual miscibility of ester and glycerol, in which the catalyst resides, and promotes saponification. Therefore, in the case of ethanolysis, saponification occurs faster and soap concentration in the biodiesel phase is higher than that of methanolysis [97]. If Saponification occurred, it would result in reduced ester yield, as well as consumption of the catalyst. During ethanolysis of sunflower oil, 95% of the sodium hydroxide initially loaded in the reactor is converted into sodium soap within 5 minutes. Not only does soap formation lower ester yield, it also complicates the glycerol separation step in the biodiesel purification process. In order for phase separation to occur, an additional step such as ethanol evaporation [98] or glycerol

addition [99] is necessary. An alternative solution is to use mixtures of methanol and ethanol [70,100,101].

2.4.3. Effects of Catalyst Type

Catalyst type is one of the most important parameters in the transesterification reaction. Selection of the catalyst is a crucial step in determining the outcome of biodiesel production and is greatly dependent on the type and quality of the feedstock. Most commercial processes employ homogeneous base catalysts due to high reaction yield, short reaction time, low reaction temperature requirement, and beneficial economics of the catalysts [7]. Feedstock containing higher amounts of FFA and water, such as used cooking oil, require the incorporation of acid catalysis in the production process [70]. More recently, solid catalysts are subjected to investigation because the use of these catalysts simplifies the biodiesel purification step, eliminates waste water generation, and renders a continuous biodiesel production process possible [70,102,103]. Because a lower catalyst activity associated with heterogeneous catalysis requires a longer reaction time and higher reaction temperature compared to that of homogeneous base catalysts, further research and development is needed. Enzymatic catalysis is another alternative as it neither produces soap nor waste water, but it has expensive operating cost and strict reaction conditions [104]. On the other hand, attempts have been made to carry out non-catalytic transesterification reaction under supercritical conditions [86-88]. The process does not require catalysts and has a short reaction time; however, because it requires extreme reaction temperatures and pressures, the process is susceptible to polymerization [105]. Consequently, the

purification step becomes difficult due to increased viscosity. Each type of catalysis is discussed in the following sections.

2.4.3.1. Homogeneous Base Catalysis

Homogeneous base catalysis is most commonly used in commercial biodiesel production processes, because the process offers high reaction yield (97% or more) in a short time (10 minutes to 2 hours) with mild reaction temperatures (25-70°C). The reaction mechanism involves 3 steps as shown in Figure 2.5 [58]. The first step is the attack of alkoxide ion (methoxide ion in the case of methanol as reacting alcohol) to carbonyl carbon of the TAG molecule to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with alcohol to regenerate alkoxide ion. The last step involves the rearrangement of the tetrahedral intermediate to form alkyl ester and DAG. This mechanism can be extended to the reaction of DAG and MAG in the same manner.

Examples of homogeneous base catalysis for transesterification are presented in Table 2.6. Homogeneous base catalysis in transesterification is much faster than homogeneous acid catalysis [77]. However, homogeneous base catalysis is limited to quality of the feedstock used, i.e., acid value of lipid must be lower than 1 and all starting materials must be substantially anhydrous.

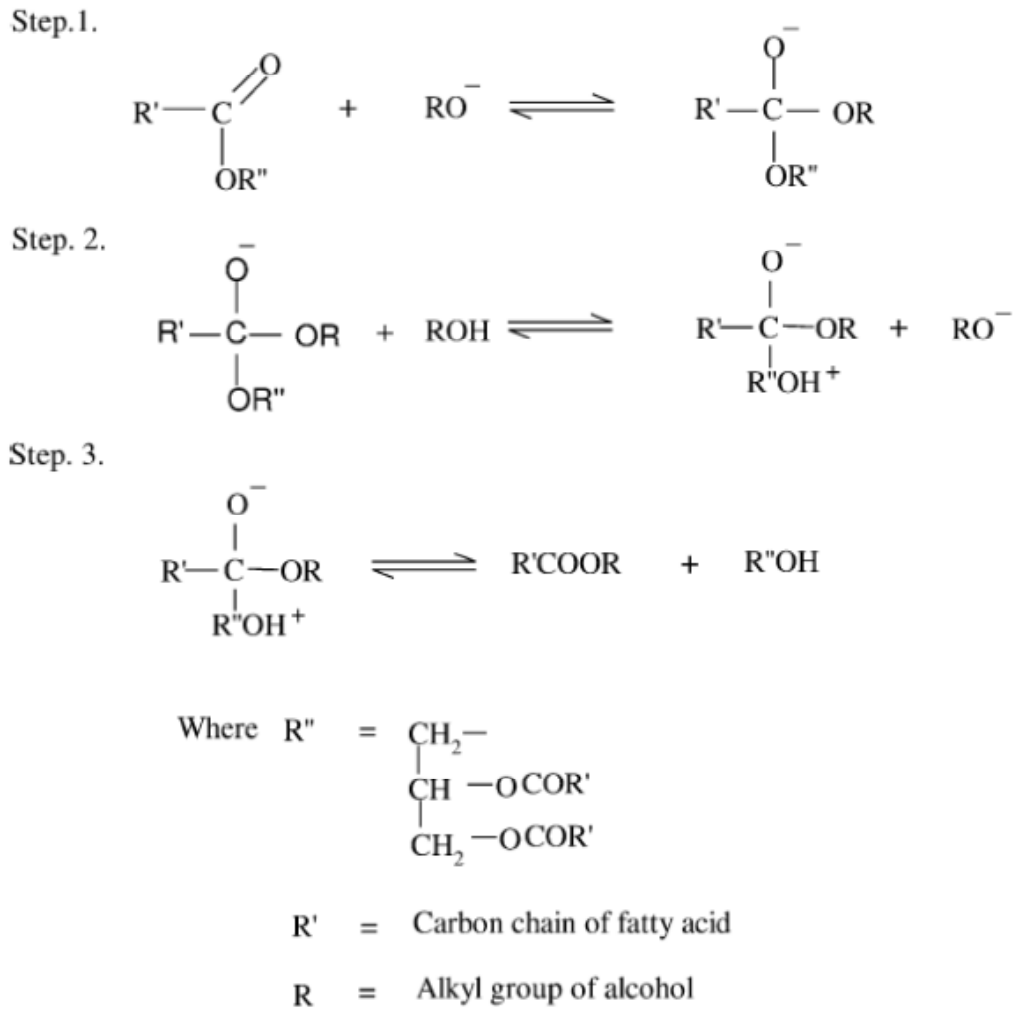


Figure 2.5 Mechanism for homogeneous base catalysis in transesterification.

Acid catalysts are more suitable if the feedstock contains higher amounts of free fatty acid and water such as used cooking oil. The most common homogeneous catalysts are hydroxides and alkoxides of alkali metals such as NaOH, KOH, $NaOCH_3$, and $KOCH_3$. Ma et al. [67] found that hydroxide of alkali metal is more effective than alkoxide as NaOH and $NaOCH_3$ reach their maximum activities at 0.3 and 0.5 wt.% with respect to beef tallow. Controversial results were reported by other researchers, as $NaOCH_3$ was reported to be more effective than NaOH [72]. In the presence of acid, water is formed from a free OH group in NaOH or KOH, while methanol is formed instead of water if $NaOCH_3$ or $KOCH_3$ is used. When water is generated, it has several adverse impacts on the transesterification reaction as discussed in Section 2.4.1.

Mahajan et al. [121] showed that when $NaOCH_3$ was used, the acid value of the reaction product was significantly lower than when NaOH was used. However, alkali metal alkoxides are less popular than hydroxides in large-scale production due to their toxicity, higher price, and disposal problems. When alkaline metal alkoxides and hydroxides are used as catalysts in methanolysis, the active catalytic species are the same, i.e., methoxide ion (CH_3O^-), concluding that these catalysts are equally effective [93]. It was also reported that at 6:1 alcohol to oil molar ratio, the use of 0.5% $NaOCH_3$ is as effective as 1% NaOH [72]. The reaction yield can also be increased by using two-step process by separating and removing glycerol at the end of the first step [122]. The increase in reaction yield, compared to the one-step process, stems from a shift in reaction equilibrium to the product side due to the removal of glycerol during the production process.

Table 2.6 Examples of homogeneous catalysis on esterification and transesterification.

Feedstock	Catalyst	Alcohol	Alcohol to oil ratio	Temperature (°C)	Duration	Conversion/yield	Year	Reference
Base catalysis								
Vegetable oils	NaOH 1% wt. CH_3ONa 0.5% wt.	methanol	6:1	60	1 h	93-99% conversion	1984	72
Beef tallow	NaOH 0.3% wt. CH_3ONa 0.5% wt.	methanol	6:1	65	15 min	60% yield	1998	67
Vegetable oils	KOH 0.5% wt. CH_3ONa 0.25% wt.	C1-C4 alcohol	6:1	25	40 min	87-96% yield	2001	93
Waste vegetable oils	KOH	methanol	-	60	1 h	95% conversion	2002	106
Vegetable oils	KOH 1% wt.	methanol	6:1	25	40 min	51-87% yield	2004	107
Pongamia pinata	KOH 1% wt.	methanol	10:1	105	1.5 h	92% conversion	2005	73
Canola oil	NaOH 1% wt.	methanol	6:1	45	15 min	98% ester	2006	74

						content		
Used fryling oil	NaOH 1.1% wt.	methanol	7:1	60	20 min	94.6% ester content	2006	74
Pongamia pinata	KOH 1% wt.	methanol	6:1	65	2 h	97-98% yield	2006	108
Canola oil	KOH 1% wt.	methanol ethanol	6:1	25-70	2 h	>90% yield	2007	100
Waste fryer grease	H_2SO_4 2% wt. KOH 1% wt.	methanol ethanol	6:1	50-60	5-6 h	97% ester content	2007	70
Jatropha	NaOH or KOH 1% wt.	methanol	3:1	-	2-4 h	-	2007	109
Mixed Canola and Used cooking oil	KOH 1% wt.	methanol ethanol	6:1	50	2 h	98% ester content	2008	99
Rapeseed	KOH 1% wt.	methanol	6:1	65	2 h	95-96% yield	2008	76
Sunflower	NaOH 1% wt.	methanol	6:1	60	2 h	97.1% yield	2008	110

Karanja	H_2SO_4/NaOH/KOH	methanol	8-9:1	45	1 h	89% yield	2008	111
Greenseed Canola oil	KOH 1%wt.	methanol ethanol	6:1	60	90 min	97% ester content	2010	101
Coriander seed oil	Ch_3ONa 0.5% wt.	methanol	6:1	60	90 min	94% yield	2010	112
Acid catalysis								
Soybean	H_2SO_4 1% wt.	butanol	30:1	117	3 h	-	1986	77
Soybean	H_2SO_4 3% wt.	methanol	30:1	60	48 h	98% conversion	1999	78
Madhuca indica	H_2SO_4 1% v/v	methanol	0.3-0.35 v/v	60	1 h	98% yield	2005	113
Rubber seed oil	H_2SO_4 0.5% by volume	methanol	6:1	45	20-30 min	-	2005	114
Tobacco seed oil	H_2SO_4 1-2%	methanol	18:1	60	25 min	91% yield	2006	115
Waste frying	H_2SO_4 3.8:1	methanol	24.5:1	70	4 h	99% yield	2006	80

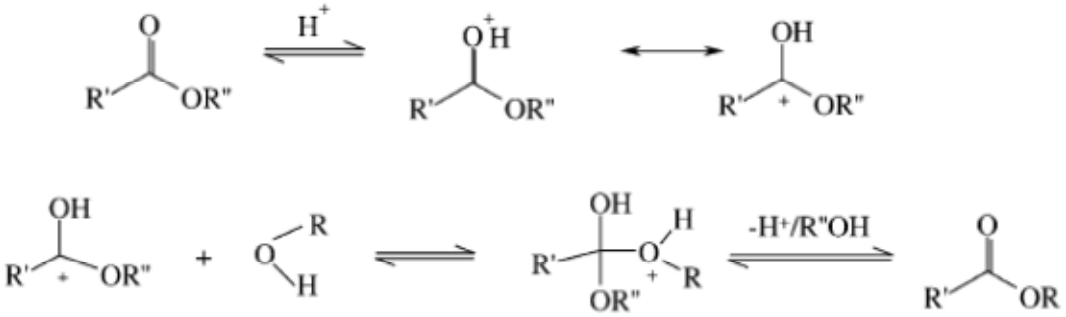
oil	mole ratio							
Calophyllum inophyllum	H_2SO_4 0.65% by volume	methanol	6:1	65	90 min	85% yield	2007	116
Zanthoxylum bungeanum	H_2SO_4 2%	methanol	24:1	60	80 min	98% yield	2008	117
Tallow	H_2SO_4 2.5% wt.	methanol	30:1	60	24 h	98.28% yield	2008	79
Canola	$AlCl_3$	methanol	24:1	110	18 h	98% conversion	2009	118
Soybean	CF_3CO_2H 2.0 M Concentration	methanol	20:1	120	5 h	98.4% ester content	2009	119
High AV oil	H_2SO_4 4% wt.	methanol	20:1	120	5 min residence time	99.5% yield	2010	120

2.4.3.2. Homogeneous Acid Catalysis

In biodiesel production from feedstock containing high FFA and water content, acid catalysis is more suitable. This approach can be used to avoid saponification and FFA is directly converted into ester through esterification while glycerides are converted into ester through transesterification. Therefore, acid catalysts can be used to catalyze both esterification and transesterification while base catalysts only catalyze transesterification but not esterification [123]. The disadvantages of homogeneous acid catalysis are that it requires a high reaction temperature, an acid-tolerable reactor, and a longer reaction time due to a slower reaction rate. The reaction mechanism is shown in Figure 2.6 [58].

The first step is protonation of the carbonyl group in the glyceride molecule, which leads to the carbocation. The attack of alcohol then produces a tetrahedral intermediate and the elimination of glycerol backbone from this intermediate leads to the formation of ester. Although saponification can be avoided, water is still being generated during esterification of FFA (see Figure 2.6). Water can then undergo hydrolysis, which is the reverse of esterification, but, unlike esterification, it can occur in the presence of either base or acid. The resulting carboxylate anion from hydrolysis shows little tendency to react with alcohol to form ester, but reacts readily with K^+ or Na^+ in the presence of base to form a stable salt. Therefore, it is essential to perform acid-catalyzed esterification and base-catalyzed transesterification separately.

Examples of homogeneous acid catalysts are H_2SO_4, H_3PO_4, HCl, BF_3, and CF_3CO_2H. Among these catalysts, H_2SO_4 is the most common catalyst due to its good catalytic activity and simplicity in H_2SO_4/MeOH preparation as concentrated liquid H_2SO_4 can be added directly to methanol (see Table 2.6). The most common H_2SO_4 concentration used in esterification is 1-2%.



$R'' = hydrogen$ for esterification and $R'' =$ OR' (or OH) / OR' (or OH) for transesterification

$R' = carbon\ chain\ of\ fatty\ acid$

$R = alkyl\ group\ of\ alcohol$

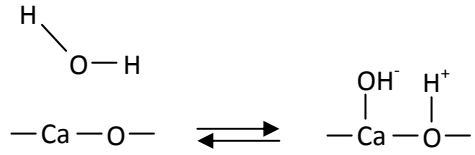
Figure 2.6 Mechanism for homogeneous acid catalysis in esterification and transesterification.

HCl/MeOH was introduced for esterification about half century ago, but is not a very popular choice due to complexity in preparation of the solution involving bubbling hydrogen chloride gas into methanol or adding acetyl chloride slowly to methanol [123], using a common concentration of 5%. BF_3/methanol is prepared by bubbling BF_3 gas into cooled methanol. BF_3 has an empty orbital that can accept a pair of electrons making it a Lewis acid. This catalyst can catalyze esterification much faster than transesterification and it is reported that FAME can be prepared from fatty acids within a very short time (10 minutes) using 6-14% catalyst loading. Due to its superior activity and short reaction time, the American Oil Chemists' Society (AOCS) has adopted BF_3 in the official method for preparing methyl ester from fatty acids (AOCS Ce 2-66). However, BF_3 is not used widely in literature as H_2SO_4 because it is expensive, toxic, and has a

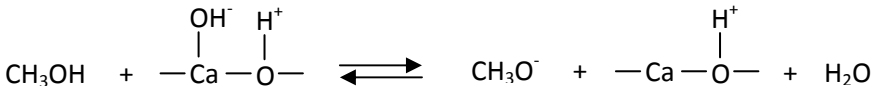
limited shelf life [123]. Diazomethane (CH_2N_2) is not classified as an acid catalyst, but rather as a strong methylation reagent. Despite its inability to catalyze transesterification, diazomethane in ether esterifies free fatty acid at a much faster rate when compared to acid catalysts. However, its shortcomings such as high toxicity, short shelf life, and potentially explosive have prevented it from being used widely like other catalysts.

2.4.3.3. Heterogeneous Base Catalysis

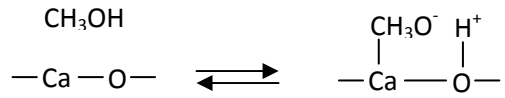
Homogeneous base catalysts have gained significant attention from numerous biodiesel researchers because the catalyst removal process is simple and does not create waste water during catalyst removal step. In addition, heterogeneous catalysts can be regenerated and reused, rendering biodiesel production in continuous processes possible. However, the use of such catalyst is limited by free fatty acid usually contained in low quality feedstock such as used cooking oil. Nevertheless, this catalyst can be used with good quality feedstock and has several advantages such as catalyst reusability, simplicity in catalyst removal, low reaction temperature requirement, and short reaction time, enticing several researchers to investigate this area. The mechanism scheme of heterogeneous base catalysis using CaO as an example catalyst is shown in Figure 2.7. The first step involves the extraction of H^+ from H_2O to form surface OH^- on the basic site of CaO (Eq. 2.1). Then H^+ is extracted from methanol to form methoxide ion and water (Eq. 2.2). Also, methanol can adsorb dissociatively on CaO (Eq. 2.3). The next step is an attack of the adsorbed methoxide ion to acylglycerol molecule to form tetrahedral intermediate (Eq. 2.4) which is protonated afterward (Eq. 2.5).



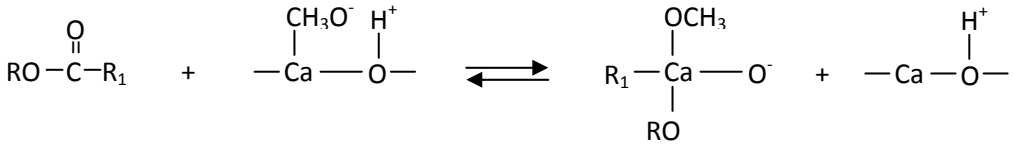
…(Eq. 2.1)



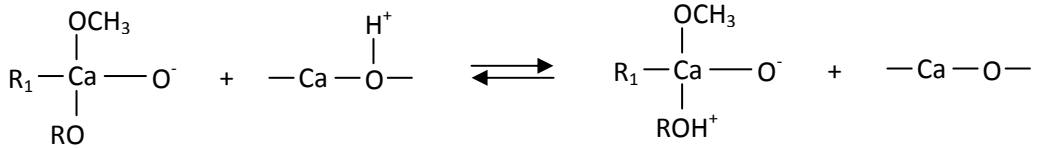
…(Eq. 2.2)



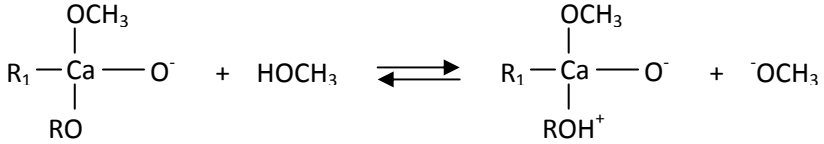
…(Eq. 2.3)



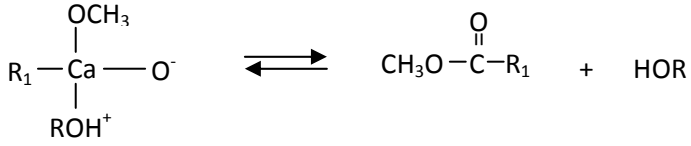
…(Eq. 2.4)



…(Eq. 2.5)



…(Eq. 2.6)



…(Eq. 2.7)

Figure 2.7 Mechanism for heterogeneous base catalysis in transesterification.

The tetrahedral intermediate can also react with methanol to generate methoxide anion (Eq. 2.6). In the last step, the rearrangement of the tetrahedral intermediate leads to the formation of methyl ester and glycerol or acylglycerol (Eq. 2.7).

Examples of heterogeneous base catalysis are illustrated in Table 2.7. Common heterogeneous base catalysts are those of alkaline earth metal oxides such as MgO, CaO, SrO, and BaO. BaO is not suitable in methanolysis because it dissolves in methanol and creates leaching problems, while SrO reacts strongly with CO_2 and water in the air to form $SrCO_3$ and $Sr(OH)_2$. The catalytic activity of MgO is not very high due to the low basic strength of MgO, leaving CaO the most attractive alkaline earth metal oxide catalyst. Alkali metals such as Li, Na, and K can be used to promote these catalysts. It has been shown that pure $LiNO_3$ is inactive and CaO alone has low activity towards transesterification of tributyrate [125]. Proper impregnation of $LiNO_3$ on CaO results in a highly dispersed monolayer Li^+ on CaO that exhibits high catalytic activity on transesterification. However, if too much $LiNO_3$ is added, the resulting catalyst is associated with the non-dissociative NO_3^- ions over the CaO surface and the formation of $LiNO_3$ multilayers. These inactive species have proven detrimental to catalytic activity of the Li/CaO catalyst. In addition, Li/CaO has higher basic strength and activity as compared to Na/CaO and K/CaO [145]. This is because the small size of the Li^+ ion makes it easier to be inserted more properly in the CaO framework creating oxygen gaps that contribute to the basic strength of the catalyst.

Table 2.7 Examples of heterogeneous catalysis on esterification and transesterification.

Feedstock	Catalyst	Alcohol to oil ratio	Temperature (°C)	Duration (h)	Yield (%)	Leaching	Year	Reference
Base catalysis								
Rapeseed	MgO	22:1	reflux	22	94	n/a	2001	124
Rapeseed	BaO	6:1	reflux	1	96	n/a	2001	124
Gylceryl tributyrate	Li/CaO	n/a	60	0.5	~100	no	2004	125
Karanja	Li/CaO	12:1	65	8	95	n/a	2006	108
Canola	K_2CO_3/Al_2O_3	11.48:1	60	2	94	yes	2007	126
Rapeseed	$K/KOH/Al_2O_3$	9:1	60	1	85	yes	2008	127
Soybean	Fe3+/Mg-Al HTC[a]	6:1	80	1	38	yes	2008	128
Jatropha	$X/Y/MgO/Al_2O_3$	10:1	reflux	3	97	n/a	2008	129
Rapeseed	K_2CO_3/Al_2O_3	15:1	50	3	99	n/a	2010	130
Sunflower	La_2O_3/ZrO_2	30:1	200	5	85	n/a	2010	131

Acid catalysis

Babassu	Amberlyst 15	300:1	60	8	74	n/a	2005	132
Soybean	$WO_3/ZrO_2/Al_2O_3$	40:1	250	20	90	n/a	2006	133
Canola (20% FFA)	TPA/HZ[b]	9:1	200	10	90	no	2006	71
Palm kernel	SO_4^{2-}/ZrO_2	6:1	200	1	95	n/a	2006	134
Cottonseed	SO_4^{2-}/TiO_2	12:1	230	8	96	n/a	2007	135
Palmitic acid	$SO_4^{2-}/ZrO_2/SiO_2$	10:1	68	6	89	n/a	2007	136
WCO[c]	ZS[d]/Si	18:1	200	10	98	no	2008	102
WCO[c] (28% FFA)	SO_3H/starch	30:1	80	8	92	n/a	2008	137
Cottonseed	SO_4^{2-}/TiO_2-SiO_2	9:1	200	6	92	n/a	2008	138
WCO[c] (15% FFA)	WO_x/Al_2O_3	n/a	110	2	97	n/a	2009	139
Palm (5% FFA)	Arene-SO_3H/SBA15	20:1	140	4	95	n/a	2010	140
WCO[c]	TPA/Nb_2O_5	18:1	200	20	92	no	2010	103
Rapeseed	Fe-Zn DMC[e]	16:1	160	8	98	n/a	2010	141
Vegetable oil	Fe-Zn DMC[e]	15:1	170	8	84-99	n/a	2010	142

Cottonseed	SO_3H/starch	20:1	80	12	97	Yes	2011	143
Vegetable oil	Fe-Zn DMC[e]	16:1	170	8	98	n/a	2011	144

[a]HTC = Hydrotalcite; [b]TPA = tungstophosphoric acid, HZ = hudrous zirconia; [c]WCO = waste cooking oil; [d]ZS = zinc stearate; [e]DMC = double metal cyanide

Alternatively, K_2CO_3 supported on Al_2O_3 can be used in transesterification. It is one of the most common catalysts in many organic chemical reactions such as isomerization, alkylation, and transesterification. This is because K_2CO_3/Al_2O_3 has strong basic strength and the catalytic activity of solid base catalysts depends greatly on basicity of the catalyst, rather than surface area [126]. The catalytic activity of K_2CO_3/Al_2O_3 is superior to metal promoted CaO and SrO and only second to alkali metal promoted BaO. Unlike alkali metal promoted BaO, the leaching of K_2CO_3/Al_2O_3 is negligible.

2.4.3.4. Heterogeneous Acid Catalysis

Heterogeneous acid catalysts are most promising for biodiesel production and are expected to dominate commercial biodiesel industries in the coming years. This is due to simplicity in the biodiesel purification step that eliminates waste water, reuseability that make continuous process possible, and the ability to handle low quality feedstock with high FFA content via simultaneous esterification and transesterification. The disadvantage of heterogeneous acid catalysts is the lower catalytic activity leading to requirements in higher reaction temperature (~200°C) and reaction time (8-20 hours). Catalyst leaching is another issue for this type of catalyst. If the catalyst leaches into biodiesel, purification will be required to remove the contaminated catalyst, and thereby, generating waste solvent and increasing biodiesel production cost. In addition, catalyst reusability or catalyst deactivation is usually studied for this type of catalyst. The simultaneous esterification-transesterification reaction mechanism is shown in Figure 2.8 [71].

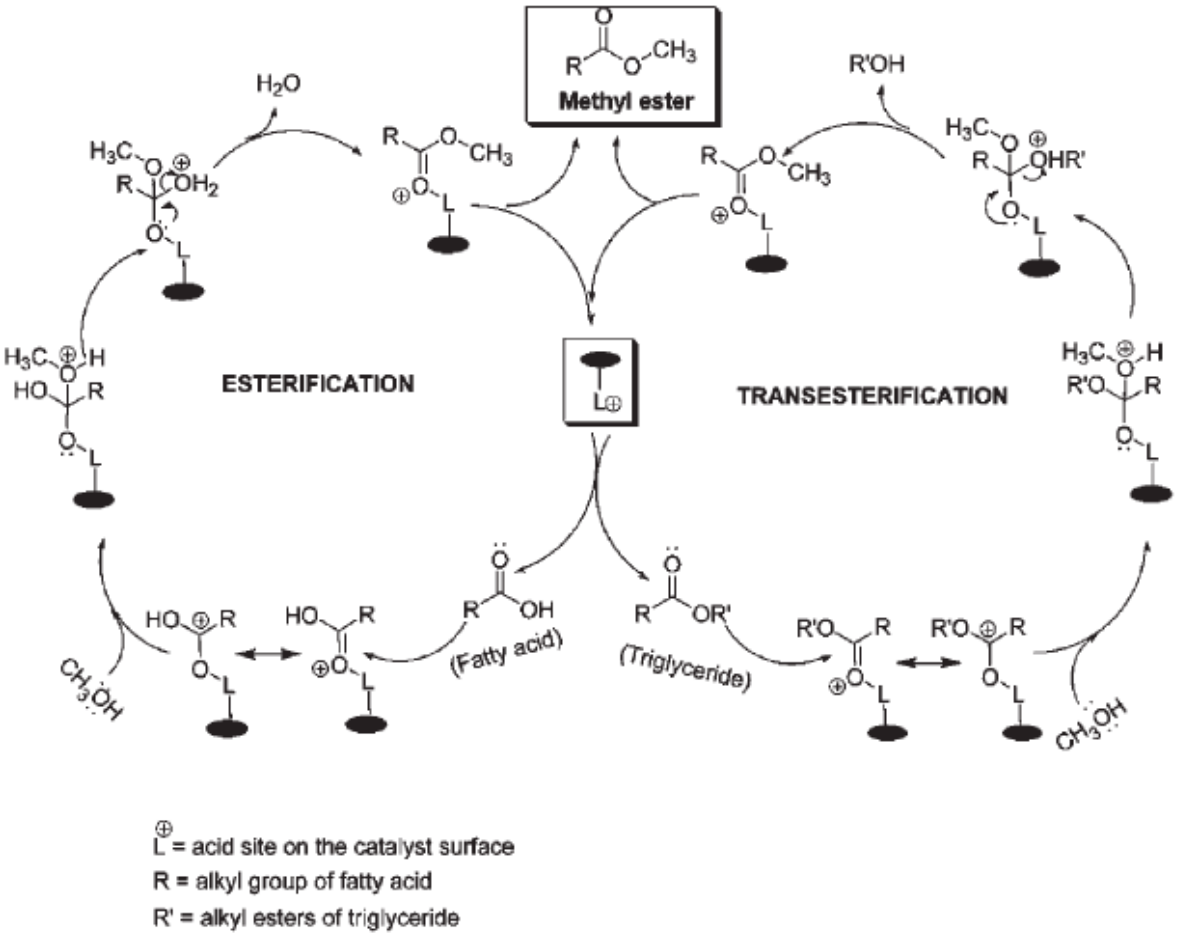


Figure 2.8 Mechanism for heterogeneous acid catalysis in esterification and transesterification.

In the esterification reaction, FFA reacts with methanol to form methyl ester. The first step involves an adsorption of FFA on the acidic site on the catalyst surface. The interaction between FFA and the acidic site leads to carbocation. An attack of methanol then produces a tetrahedral intermediate. Finally, methyl ester is formed as a result of an elimination of water molecule from the tetrahedral intermediate. In transesterification, acylglycerol including tri-, di-, and monoglyceride reacts with methanol to form methyl ester. The reaction mechanism occurs in a similar manner as that described in the esterification reaction. The formation of methyl ester stems from an elimination of diglyceride, monoglyceride, and glycerol from the tetrahedral intermediate when triglyceride, diglyceride, and monoglyceride are adsorbed in the acidic sites, respectively. Various types of heterogeneous acid catalysts are available for esterification and transesterification as shown in Table 2.7 and these catalysts are discussed as follow.

Ion-exchange resins such as Amberlyst series and Nafion silica composite solid acid catalysts are one of the first solid acid catalysts introduced for biodiesel production applications [132,146]. These resins have low catalytic activity, and therefore, require extreme reaction temperatures. Unfortunately, resins usually have low thermal stability (<140°C) and the reaction was conducted at a mild temperature of 60°C, which resulted in a low reaction conversion (74%). Alternatively, silica matrix of mesoporous solids can be used, but the catalytic activity is low. Metals such as aluminum, zirconium, titanium, or tin ions can be added to improve catalytic activity on esterification and transesterification. However, metal-doped materials tend to behave like weak acid, of which high catalytic activity is not exhibited. To improve catalytic activity of the catalyst, high dispersion of a strong acid species on interior surfaces of mesoporous supports is required.

The Tungsten-loaded catalyst is an interesting catalyst. WO_3/ZrO_2 is used as a catalyst in esterification of palm oil and a conversion of 98% is obtained [147]. Upon its formation, hydrous zirconia contains very small regions of tetragonal structure exhibiting the (101) phase that can be observed in XRD patterns. These tetragonal crystallites grow as the hydrous zirconia is thermally treated and they are transformed into the thermodynamically stable monoclinic phase during cooling. When an interacting species such as WO_3 is presented, the phase transition is somewhat hindered and the tetragonal phase is maintained. However, if too much WO_3 is added, the catalyst becomes amorphous due to excess coverage of WO_3 species on ZrO_2. The presence of the monoclinic phase of zirconia has adverse effects on catalytic activity and, therefore, the tetragonal phase is preferred. However, the presence of tetragonal zirconia is not the only criterion for good catalytic activity of the catalyst but the co-existence of amorphous WO_3 is also required. It was found that the catalytic activity of WO_3/ZrO_2 catalyst is provided by interaction between amorphous WO_3 and crystalline ZrO_2. In addition to zirconia, Al_2O_3 has been used as support due to its high surface and large pore size that can accommodate TAG molecules with long fatty acid chains. A 98% ester yield was observed from transesterification of waste cooking oil using WO_x/Al_2O_3; however, the acid value was observed at 4.7 higher than that specified in biodiesel standards [139].

The sulfated catalyst is another interesting catalyst. By using a conventional homogeneous acid H_2SO_4 as a precursor, SO_4^{2-} on ZrO_2 and TiO_2 can be obtained and the reaction yields a 95-96% conversion [134,135]. The catalytic activity of sulfated zirconia (SZ) can be further increased by dispersing it onto mesoporous silica materials such as MCM-41 or SBA-15, thus increasing dispersion and acid sites. SBA-15 is a preferred choice in esterification and transesterification due to its larger pore size facilitating the long chain fatty acids. The doped

zirconia on SBA-15 (unsulfated ZrO_2/SiO_2) shows low acidity and its acidity can be enhanced by an addition of sulfur. It is believed that an addition of sulfur causes a formation of tetragonal ZrO_2 and enhances the phase segregation by extracting zirconia to the surface of the mixed oxides and stabilizes the tetragonal phase [136]. However, if too much sulfur is added (>5%), a monoclinic phase of zirconia is formed in addition to the tetragonal phase, which should be avoided [148]. In addition, the hydrophilicity of SBA-15 surface is partially responsible to catalyst stability. In general, water formed during esterification is adsorbed on acid sites resulting in a lower concentration of acidic sites available for the reaction. However, this water can be readily adsorbed on the neighbouring silica surface of SBA-15 and some acidic sites can thus be recovered. Despite its high activity, SZ-type catalyst shows sulfate leaching problem, which is enhanced by hydrolysis. To counter this problem, chlorosulfonic acid is used as an alternate acid to sulfuric acid for SZ catalyst preparation. The catalyst was tested in esterification of acetic acid with *p-tert*-butylcyclohexanol and no leaching was observed [149]. More recently, a high reaction conversion (92-97%) was obtained using a sulphated starch catalyst [137,143]. An interesting point about starch derived catalyst is that the reaction requires a relatively low temperature (80°C); however, sulphate leaching has been observed.

Heteropolyacids (HPAs) is also later on introduced as a potential solid acid catalyst for biodiesel production. These acids are comprised of hydrogen, oxygen, metal such as tungsten, molybdenum, vanadium, and a p-block element such as silica, phosphorous, or arsenic. The two main HPA structures are Keggin ($H_nXM_{12}O_{40}$) and Dawson ($H_nX_2M_{18}O_{62}$), where X and M represent a p-block element and metal, respectively. The Keggin structure is self-assembled in acidic aqueous solution and is a preferred structure as it is thermally stable and has high acidity. In the Keggin structure, the heteroatom (X) is located at the center of the molecule, linked with 4

oxygen atoms to form tetrahedral, and surrounded by 12 octahedral MO_6 units linked to one another by neighboring oxygen bridge. This structure allows hydration and dehydration to occur without significant changes in structure and, therefore, is thermally stable and can be used in a reaction under extreme temperatures (up to 400-500°C). The disadvantages of the Keggin-type HPA are low specific surface area and solubility in polar media, but this can be overcome by dispersing it on a high surface area support. Both unsupported and MCM-41 supported HPA have been used as acid catalyst in esterification of acetic acid at 110°C giving 95% conversion [150]. It was found that the supported HPA is more active than the unsupported HPA since the high dispersion of HPA on the MCM-41 internal surface leads to a high population of available acid sites. However, MCM-41 supported HPA is more vulnerable to water than unsupported HPA because water formed during esterification leads to HPA migration to the outer surface, pore blocking, and catalyst sintering. Hydrous zirconia (HZ, $ZrO_2 \cdot nH2O$) has been used as a support for 12-tungstophosphoric acid (TPA, one of the Keggin-type HPAs). TPA/HZ was tested for its catalytic activity in esterification and transesterification of canola oil containing FFA up to 20% at 200°C for 10 hours reaction duration, giving a 90% ester yield [71]. It was found that esterification was catalyzed at a faster rate than that of transesterification. This is because the esterification route involves a simple reaction step, while the transesterification route is composed of a series of reversible reaction steps. More recently, Nb_2O_5 was reported as an effective support for TPA [103]. Under the optimized conditions of 18:1 alcohol to oil ratio, 200°C reaction temperature, 20 hours reaction duration, 92% ester yield can be obtained from transesterification of waste cooking oil without catalyst leaching.

More recently, Fe-Zn double metal cyanide catalysts (DMC) have been investigated for transesterification of vegetable oil [141,142,144]. Cyanide is a highly toxic chemical compound

containing cyano group (-C≡N). They have a general formula: $K_4Zn_4[Fe(CN)_6]_3 \cdot xH2O$ where x = 6-12 and the catalyst exhibits highest activity when x = 6. The Fe and Zn ions are linked through cyano groups. The most interesting feature of this catalyst is its hydrophobicity as it can tolerate water content in the feedstock oil up to 20% without significant loss in catalytic activity [142]. It is found that the rate of esterification is faster than that of transesterification, which is in line with other heterogeneous acid catalysts such as TPA/HZ. The catalyst is tested with various vegetable oils and shows promising catalytic activity (84-99% conversion) and can be reused without loss in catalytic activity and no purification is required for catalyst regeneration. However, when non-edible oil such as jatropha, rubber seed, and pinnai oil is used as feedstock, the acid value of the resulting biodiesel is higher than that specified in biodiesel standards, requiring further catalyst leaching investigation. Another catalyst such as zinc stearate (ZS) on silica (Si) was investigated. ZS ($Zn(C_{18}H_{35}O_2)_2$) is a zinc soap that is not soluble in polar solvents, but soluble in aromatic hydrocarbons when heated. When ZS/Si is tested on transesterification of waste cooking oil, a 98% ester yield can be obtained [102]. In addition, catalyst leaching is not detected and the catalyst can be reused without significant loss in its activity. However, the resulting biodiesel shows an acid value of 3.3, higher than those specified in biodiesel standards. In summary, further development in heterogeneous acid catalysis is required especially in terms of ester yield, acid value of the product, and catalyst leaching.

2.4.4. Effects of Reaction Time, Temperature, and the Reaction Kinetics

In general, conversion and yield increase as reaction time increases. The reaction starts with two phases: alcohol and oil. Once the reaction is initiated, DAG and MAG are formed as

the reaction intermediates and act as surfactants to enhance the mass transfer of TAG into methanol. At this point, the reaction mixture can be either one or two phase depending on the amount and type of alcohol used in the reaction, as well as reaction conditions. Then the glycerol is formed as the reaction by-product and separates out as an additional phase. If the reaction is catalyzed homogeneously, the separation of glycerol often leads to the catalyst dissolving in glycerol phase, which lowers catalyst concentration in the reaction mixture and, therefore, slower the reaction rate.

The rates of the reaction and rate constants are often used in kinetic studies in order to examine how fast the reaction proceeds. These kinetic parameters are sometimes evaluated based on the shunt (overall) reaction mechanism in which 3 moles of TAG react with 3 moles of alcohol to yield 3 moles of ester and 1 mole of glycerol [151]. Although the kinetic models can be simplified using the shunt reaction mechanism, it is highly unlikely that three molecules of methanol would simultaneously attack the TAG molecule to form three molecules of methyl ester. The shunt mechanism is easily disproved by the formation of DAG and MAG, which is widely reported in the literature. Therefore, the kinetic models should be derived based on three consecutive reversible reaction steps and the rate constants of each reaction step are usually different. The values of the rate constants indicate the rates of the corresponding reaction step, as well as reversibility of each step. Moreover, they can be used to determine the rate determining step (RDS) that controls the kinetics of overall transesterification. The proposed reaction mechanism consists of an initial mass transfer-controlled region followed by a kinetically controlled region [84,152]. The mass transfer effect is referred to the period when there is no reaction going on and yet is recorded as “reaction time” during an experiment. This period is associated with the time that the triglyceride molecule spends in order to move into the methanol

phase and collides with the methanol molecule. This period occurs at the initial part of the reaction and is often referred to as the "mass transfer-controlled region". The initial mass transfer region alters the observed kinetic data and, therefore, needs to be minimized by means of rigorous mechanical agitation [84], co-solvent aid [153], or supercritical conditions [154]. Results from the literature suggest that transesterification of vegetable oils with low alcohol to oil ratio (6:1) using homogeneous base catalysts follows second order kinetics [77,82,84,152]. The reaction step TAG to DAG is often found to be the rate-limiting step that controls the kinetics of the overall reaction. In addition, the rate constant of the reverse reaction MAG to GL is usually lowest, due to the phase separation of glycerol. However, this reaction can still take place at the glycerol-methyl ester interface rendering a small positive value of the rate constant.

Transesterification is strongly dependent on reaction temperature and is favored at high temperatures. In the mass transfer controlled region, the higher temperature leads to a higher energy state of the reacting molecules that can be translated into faster molecular vibration and movement, thus the reacting molecules have more chance to collide with one another. In the kinetically controlled region, temperature dependency of the reaction rate is often used to calculate the activation energy of the reaction by plotting logarithm of the rate constant versus the reciprocal of the reaction temperature [155]. The equation is known as the Arrhenius equation (see Equation 2.8).

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \qquad \ldots(\text{Eq. } 2.8)$$

Where k is the rate constant; A is pre-exponential factor; E_a is the activation energy; R is the gas constant; T is reaction temperature. The activation energy is referred to the minimum energy required for a reaction to take place. From Equation 2.8, if the reaction temperature is increased, the rate constant will also increase and, therefore, the reaction will proceed at a faster rate.

A homogeneous alkali-catalyzed transesterification can be performed at temperatures as low as room temperature. However, higher temperatures are usually employed, especially when an acid catalyst is used. Nevertheless, the reaction temperature should be kept below the boiling point of the corresponding reacting alcohol that is 65°C for methanol and 78°C for ethanol. However, heterogeneous acid catalysis usually requires extreme reaction temperatures (up to 220°C). If the reaction is operated at temperatures higher than the boiling point of the corresponding reacting alcohol, pressure needs to be applied to the reaction mixture to maintain the reacting alcohol in liquid state.

2.4.5. Techniques for Monitoring Transesterification

In transesterification, TAG is converted to ester step-wise through the formation of intermediates DAG and MAG. The formation of each individual compound should be monitored closely. Various techniques have been developed to monitor the reaction and an acquisition of the more detailed information requires more sophisticated, expensive, and time consuming technique and vice versa. Chromatography techniques are most commonly used because they offer comprehensive perception during the transesterification progress and detailed information required for quality control of the product. More recently, Nuclear Magnetic Resonance (NMR)

spectroscopy and Infrared (IR) spectrometry have been employed for monitoring transesterification. The cheaper methods such as thin layer chromatography (TLC) without detector, viscometer, titration, and the 3/27 conversion test have also been used; however shortcomings of these methods involve the lack of quantitative analysis.

2.4.5.1. Gas Chromatography

Chromatography is a powerful separation technique that was invented and named by the Russian botanist Mikhail Tswett, who used this technique to separate plant pigments such as chlorophylls and xanthophylls [156]. The separated species appeared as a colored band on the column, which accounts for its name (Greek "chroma" meaning color and "graphein" meaning writing). Gas chromatography in biodiesel applications is known as gas-liquid chromatography (GLC) because the separation is based on the partition of the analytes between a gaseous mobile phase and a liquid phase immobilized on the surface of an inert solid. The mixture is separated mainly by means of elution, which involves washing the analytes through a column by continuous addition of a fresh mobile phase. An illustration of chromatographic separation of a mixture containing compound A and B is given in Figure 2.9. The compound that is strongly retained by the stationary phase (component B) has a small fraction of time it spends in the mobile phase and moves slowly with the flow of the mobile phase and, therefore, has longer retention time, i.e., appears later in a chromatogram and vice versa. In biodiesel applications, this component-stationary phase interaction depends mostly on the boiling point and structure (imparting polarity) of each compound. The gaseous mobile phase is often called carrier gas and must be chemically inert, such as helium, nitrogen, argon, and hydrogen.

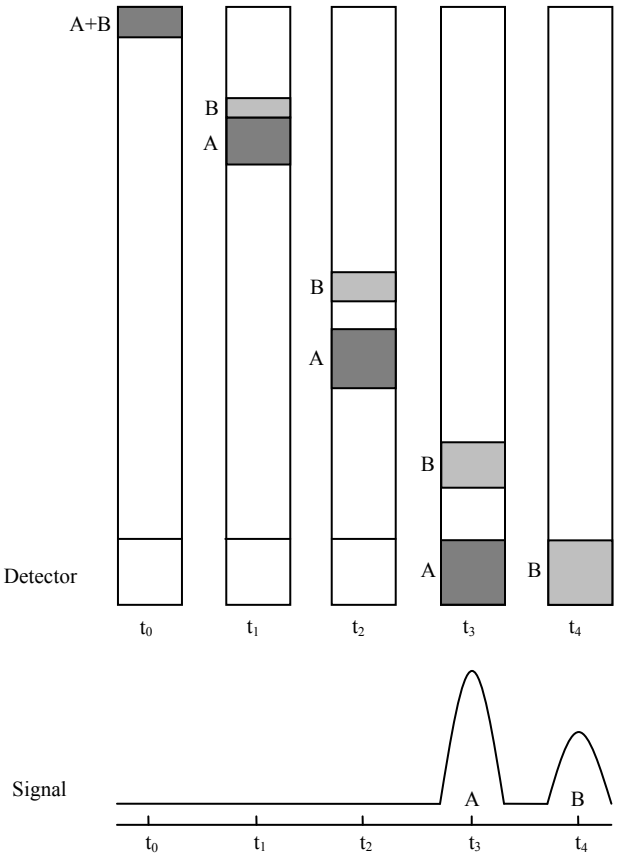


Figure 2.9 Chromatographic separation of component A and B and their corresponding output signals.

The flow rate of carrier gas creates pressure inside the column that acts as a driving force in the mobile phase that separates the analytes from one another. This pressure must be maintained constant, as its changes can affect retention time and peak shape. The program temperature is also important as heat provided in a chromatographic run determines how strongly individual components will be retained by the stationary phase, thereby affecting its elution, retention time, and peak shape. The two most common detectors are mass spectrometric detector (MSD) and flame-ionization detector (FID). A gas chromatography attached with mass spectrometric detector is often called GC-MS. In GC-MS, a compound is converted into ionic fragments, and then total ion abundance can be detected and plotted versus time or a selected mass-to-charge (m/z) ratio. A mass spectrum of selected ions obtained during a chromatographic run is known as mass chromatogram. Since each compound yields a very specific fragmentation pattern, GC-MS is a very powerful tool for identification. An example of the use of GC-MS for identification of various methyl and ethyl esters can be found in the literature [70]. The flame-ionization detector (FID) is used most widely for quantification purposes. Since most organic compounds produce ions and electrons when pyrolyzed at temperature of air-hydrogen flame, their ions can be detected and monitored by collecting these charge carriers. When these ions and electrons are released and driven towards the collector by electrode located above the flame, the resulting current is measured. Since the measuring current is in direct proportion to the number of ions and electrons released and mass of the analyte, the FID is mass-sensitive, rather than concentration-sensitive and, therefore, changes in carrier gas flow rate have only little effect on peak area. Since non-combustible gases such as H_2O, CO, CO_2, SO_2, and NO_x do not yield ions or electrons, FID is a very effective detector for organic compounds, especially those contaminated with water and oxides of carbon, nitrogen, and sulfur.

A Gas Chromatography technique has been developed to simultaneously determine glycerides and ester in a single run using a 10 to 15 m of capillary DB-5 column coated with 0.1 μm film equipped with FID [84]. TAG, DAG, MAG, and methyl ester concentrations were measured using a GC model Agilent 7890A equipped with J&W 123-5711 DB-5HT column (15 m x 320 μm x 0.1 μm; 400°C max temperature), cool on-column Inlet with track oven temperature mode, 7.6 psi, 1 μL injection volume, and FID Detector, at 380°C, 40 mL/minute H_2 flow rate, and 400 mL/minute air flow rate. The program was set to start at 50°C, ramped from 50 to 230°C at 5°C/minute, and ramped from 230 to 380°C at 30°C/minute, and held for 18 minutes with a total run time of one hour. Calibration curves showed sufficient linearity with a correlation coefficient of more than 0.99 [157]. In principle, TAG, DAG, MAG, ester, and glycerol can be analyzed on a highly inert column coated with apolar stationary phase without derivatization [58]. However, in most cases derivatization is required because diglyceride and monoglyceride contain free hydroxyl groups, causing these materials not to be quantified well in GC. Trimethylsilylation (derivatization) of DAG, MAG, and glycerol causes changes in their structure and polarity by eliminating the free hydroxyl groups and, therefore, improving peak shape and peak separation. The derivatizing agent can be either N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) or N,O-bis(trimethysilyl) trifluoroacetamide (BSTFA) and the derivatizing procedure is given in ASTM D6584 method. Internal standards such as 1,2,4-Butanetriol and 1,2,3-Tridecanolylglycerol (tricaprin) are usually used for two purposes: peak identification and quantification. In the identification step, retention time of analyte peaks are compared with those of internal standards and identified through relative retention time. This step may seem unnecessary if the corresponding standard sample is available. In quantification,

an internal standard is usually used to correct the loss of standard mixture during sample preparation and injection.

2.4.5.2. Liquid Chromatography

The main advantage of liquid chromatography (LC) over GC is its simplicity in the sample preparation step, as sample derivatization and internal standards are not required. Early LC was carried out with the gravity flow method using a glass column packed with solid particles (diameter more than 150 to 200 μm) coated with an adsorbed liquid as the stationary phase. It is well known that the column efficacies can be improved greatly by reducing the size of the packed particles, which gives rise to the new sophisticated technology using a column with packing particles having a diameter as small as 3 to 10 μm and the instrument is operated at high pressure. High performance liquid chromatography (HPLC) was then named to distinguish this new technology from the original gravity flow method. Today, all liquid chromatography is operated at high pressure and HPLC and LC are used interchangeably [156]. HPLC can be used for a wide range of chemicals and the LC mode should be selected carefully, based on solubility and molecular mass of the analytes. Ion exchange LC is used for water soluble ionic compounds, while normal phase and reverse phase LC (bonded phase LC) can be used for those soluble in organic solvent such as hexane and methanol, respectively. In bonded phase LC, the stationary liquid is not soluble in the mobile phase liquid and is kept stationary by chemical bonding resulting in highly stable packings. In early period, LC technique is based on a highly polar stationary phase and a relatively nonpolar solvent as the mobile phase and this LC mode is now known as normal phase chromatography. Later on, reverse phase chromatography is introduced,

in which the stationary phase is nonpolar and the mobile phase is a polar solvent. Bonded phase packing is classified as normal phase when the coating is polar and as reverse phase when the coating is nonpolar. In oils and fats, they are relatively nonpolar and are more soluble in hexane than methanol, therefore, normal phase LC finds its use more often than reverse phase. Size exclusive chromatography (SEC) is a separation technique based on molecular size rather than polarity of analytes. It is particularly applicable to high molecular mass species that are soluble in organic solvent such as tetrahydrofuran (THF) and, therefore, is widely used for analysis of biodiesel samples containing TAG, DAG, MAG, fatty acids, and esters. The column can be coated with hydrophilic or hydrophobic gel and is sometimes called gel permeation chromatography (GPC). The packing gel may be silica or polymer particles, containing a network of uniform pores that the solute and solvent molecules can diffuse in and that molecules of analytes are effectively trapped in. Compounds with molecular size larger than average pore size of the packing are excluded and, therefore, are the first to be eluted. Smaller molecules permeate throughout the pore maze and are trapped longer and, therefore, eluted later. Various LC are available for use with LC. The UV detector is used for absorption measurements of eluents from a chromatographic column at single or multiple wavelengths. The absorption intensity is measured and calculated for absorbance that is shown in a chromatogram as a function of time. Application of a UV detector is limited to compounds that can absorb UV at a specific wavelength, i.e., acylglycerols have weak absorbance at wavelengths higher than 220 nm [158]. A reflective index detector (RID) continuously measures reflective index of the effluent and is generally used as it is reliable. Since RID is relatively insensitive, it is not affected by flow rate, but its application is limited to measuring analytes at higher concentration as compared to other detectors. In evaporative light scattering detector (ELSD), the column effluent

is continuously evaporated and the light scattering of the resulting aerosol is measured. ELSD is significantly more sensitive than RID, with a detection limit of 0.2 ng/μL, but the mobile phase is limited to volatile components.

SEC equipped with RID has been used to quantify acylglycerols and esters of alcohol ranging from C_1 to C_4 [28]. A Hewlett-Packard 1100 series (HPLC-SEC) was used with two Phenogel 5μ 100A 300X7.80 mm 5 micron columns in series. The guard column is used to protect analytical columns by removing particulate matters and sample components that bind irreversibly to the stationary phase. The packing components are identical or similar to those of the analytical column, but the particle size is larger to minimize pressure drop. THF was used as a mobile phase at 1 mL/min for 25 min. The operating parameters used were: injection volume 5 μL; column temperature 24°C; and detector temperature 35°C. Analysis of glycerides, fatty acids, and esters was compared using HPLC equipped with various detectors, including UV detector, ELSD, and atmospheric pressure chemical ionization mass spectrometry (APCI-MS) detector [158]. The solvent systems used in this work are rather complicated and include: 1) mixtures of methanol (A) with 5:4 2-propanol/hexane (B) from 100% A to 50:50 A:B - a non-aqueous reversed phase (NARP) solvent system; and 2) mixtures of water (A), acetonitrile (B), and 5:4 2-propanol/hexane (C) in two linear gradient steps (30:70 A:B at 0 min, 100% B in 10 min, 50:50 B:C in 20 min, and last isocratic 50:50 B:C for 5 min). In APCI-MS and ELSD, the sensitivity of individual TAG decreased when the number of double bonds increased. Sensitivity of UV detection is also different for each individual TAG and APCI-MS was concluded to be the most suitable detector because it gives additional structural information of acylglycerols. Komers et al. [159] employed HPLC for quantification of TAG, DAG, MAG, and esters using UV detection at a wavelength of 205 nm. The glass column 150x3 mm with pre-column 30x3 mm,

both packed with C-18, particles with diameter 7 mm, and the mobile phase A (acetonitrile:water 80:20), B (acetronitrile), C (hexane:2-propanol 40:50) with 0 to 2 min - 100% A, 2 to 12 min - change to 100% B, 12 to 22 min - change to 50% B and 50% C, 22 to 29 min - change to 100% B, 30 to 32 min - change to 100% of B, 32 to 33 min change to initial 100% A.

2.4.5.3. Nuclear Magnetic Resonance Spectroscopy

The Nuclear Magnetic Resonance (NMR) technique involves the measurement of absorption of electromagnetic radiation in the radio frequency (~4 to 900 MHz), in which nuclei of atoms rather than outer electrons are involved in the absorption process. It is necessary to place the analyte in an intense magnetic field in order to cause nuclei to develop an energy state strong enough for absorption to occur. The most commonly used NMR technique in biodiesel analysis is proton NMR or ^{1}H NMR, in which the adsorption on protons is measured. Equivalent nuclei of proton do not interact with one another to give multiple absorption peaks, i.e., three protons in the methyl group give rise to one peak rather than splitting among themselves to give multiple peaks. Gelbard et al. [160] employed ^{1}H NMR to measure methyl ester yield from rapeseed oil transesterification. The yield was calculated based on absorption area ratio of methoxy and methylene protons. ^{13}C NMR was used in comparison to ^{1}H NMR to determine unsaturated fatty acid composition via absorption of allyic and divinyl carbons [161]. In addition, ^{1}H NMR spectra was obtained at 400 MHz for monitoring two-stage transesterification of canola oil, where the replacement of glycerol with methanol was shown [3]. More recently, polyunsaturated fatty esters were identified and quantified based on ^{1}H NMR spectra obtained at 300 MHz [162]. It was reported that the signal due to protons of the ester group OCH_3 and long

alkyl chain ($–CH_2$)n are indicated at 3.65 and 1.27 ppm, respectively, while signals from methyl groups at 0.875, 0.90 and 0.97 ppm are due to saturated, mono- and di-unsaturated, and polyunsaturated fatty acids (3 double bonds), respectively. The polyunsaturated fatty ester percentage was calculated based on integral intensity of the PUFA region from 0.9 to 1.02 ppm and the average of percentage of methyl protons present in methyl esters of unsaturated fatty acids containing three or more double bonds such as linolenic (C18:3), EPA(C20:5), DHA (C22:6) etc.

2.4.5.4. Infrared Spectrometry

Infrared (IR) spectrometry employs the unique molecular vibrational characteristics of moieties in a molecule. Dipole moment is essential in enabling IR technique. For example, a charge distribution of a molecule such as hydrogen chloride is not symmetric and has a strong dipole moment because the chlorine has a higher electron density than the hydrogen. Thus, the dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge. When hydrogen chloride vibrates, a fluctuation in its dipole moment occurs and creates a field that can interact with an electric field associated with radiation. In this technique, IR is radiated through the analyzing sample and the transmission associated with molecular absorbance is recorded. The molecular absorbance can occur only when the frequency of the radiation exactly matches the vibrational frequency of the molecule. Molecular vibration can be either stretching or bending. Stretching vibration involves continuous changes in the interatomic distance between two atoms, while bending vibration is a change in the angle between two bonds. The y-axis is commonly shown linear in transmission, but a modern

computer-based spectrometry can produce spectra that are linear to absorbance. Today, most IR instruments are that of Fourier transform (FTIR) type due to their speed, reliability, signal to noise advantage (isolating very weak signals from environmental noise), and convenience. IR regions include near IR (NIR) (wave number: 12800 to 4000 cm^{-1}), mid IR (wave number: 4000 to 200 cm^{-1}), and far IR (wave number: 200 to 10 cm^{-1}). Far IR application is limited because the sources of radiation are weak and require filters that prevent radiation from reaching the detector [156]. NIR and mid IR spectroscopy find their use in biodiesel research.

The method for monitoring transesterification can be established by recording spectra of biodiesel, the feedstock oil, and intermediate samples at 25, 50, 75% conversion [163]. NIR has been used for monitoring transesterification of soybean oil. Absorbance at 6005 and 4428 cm^{-1} gave distinguishing results of TAG and methyl ester [164]. It is found that NIR results are in good agreement with those obtained from ^{1}H NMR [165]. More recently, FTIR (mid IR) has also been used to monitor transesterification of *cyanara cardulus*, cotton, sunflower, and sesame oil [166]. The absorption peak at 1200 cm^{-1} is associated with O-CH_3 stretching, which is only presented in methyl ester and not TAG and was used primarily for quantitative purpose.

2.4.5.5. Other Methods

Since the above mentioned techniques are not always available, various cheaper methods have been used to monitor transesterification. Thin layer chromatography (TLC) has been used for separation and confirmation of various lipid classes such as glycerides, free fatty acids, and esters [167,168]. A droplet of sample is used on a TLC plate with the mobile phase consisting of a mixture of hexane, diethyl ether, and a small quantity of formic or acetic acid to ensure that

fatty acid migrates successfully. Complex lipid such as phospholipids and glycolipids, will remain at the origin point. TLC offers a simple, fast, and cheap method to confirm the formation of specific individual compounds during the course of the reaction, but these compounds are not determined quantifiably without a detection system such as flame-ionized detector (FID). With FID, these compounds can be quantified properly, but the method becomes more cost-intensive. A simpler method to estimate the progress of the reaction is a measurement of changes in viscosity of the reaction mixture [169]. The principle of this method is based on the differences in viscosity of the reactant (TAG) and the product (ester). While transesterification may be monitored using viscosity, acid value is commonly used as a means to determine progress in esterification. The so-called "3/27 conversion test" is used widely in home-made biodiesel industry, where cost-intensive techniques such as chromatography and spectroscopy are not available. This method employs the fact that methyl ester is more soluble in methanol than TAG. In the 3/27 conversion test, 3 mL of biodiesel is added to 27 mL of methanol at a temperature around 20°C and the mixture is shaken [170]. If TAG is present in the biodiesel sample, it will settle out of methanol phase as it is not soluble in the methanol. This method can be used to roughly determine TAG conversion during transesterification; however, measurement of DAG and MAG conversion is not applicable using this method.

2.4.6. Post Reaction Treatment

Transesterification products consist of biodiesel and glycerol that are contaminated with alcohol and catalyst and post-reaction purification of biodiesel is a crucial step to ensure the product quality meets standard specifications. Glycerol can be separated from biodiesel through

gravity. If a heterogeneous catalyst is used, it can be removed from biodiesel by simple filtration or centrifuge. However, removal of a homogeneous catalyst requires water and this step is called "biodiesel washing". During the washing step, water is added to biodiesel, the mixture is shaken so that catalyst and alcohol are dissolved in the aqueous phase, and the water is then drained. This step is repeated until the pH 7 of the washing water is obtained. In many cases, warm distilled water is used in order to avoid emulsion. The remaining moisture and alcohol are then evaporated. Sodium sulfate or silica gel may also be used for removal of the remaining water.

2.5. Biodiesel Quality

The use of low-quality biodiesel due to incomplete reaction or contaminants in a diesel engine could result in several engine problems [7]. In order to protect consumers from unknowingly purchasing substandard fuel, several fuel standards have been adopted for quality control. Among these standards, ASTM D6751 (the American Society for Testing and Materials) [171] and EN 14214 (European Committee for Standardization) [172] are the most referred standards for pure biodiesel and are presented in Table 2.8. In addition, AOCS (American Oil Chemists' Society) has established official test methods for biodiesel quality and these methods are also listed in Table 2.8 [173]. It is reported that FAAE can be added at a low ratio to protroleum diesel fuel without substantially changing fuel properties [3]. The low-temperature flow property of blended fuel with lower than 30% FAAE is not significantly changed from its parent petroleum diesel fuel. When FAAE that meets standard specifications is properly blended into petroleum diesel fuel and is handled according to standard techniques, the resulting fuel is of high quality and should perform well in a diesel engine.

Table 2.8 Fuel standards and test methods for pure biodiesel.

Property	AOCS method	ASTM method	EN method	ASTM Limits	EN Limits
Acid value	Cd 3d-63	ASTM D664	EN14104	0.5 max[a] (mg KOH/g)[b]	0.5 max (mg KOH/g)
Water and sediment	Ca 2e-84	ASTM D2709	EN ISO 12937	0.05 max (% vol.)	500 max (mg/kg)
Ester content	-	-	EN 14103	-	96.5 min (% mol)
MAG content	Cd 11b-91 Cd 11d-96	-	EN 14105	-	0.8 max (% mol)
DAG content	Cd 11b-91 Cd 11d-96	-	EN 14105	-	0.2 max (% mol)
TAG content	Ce 5-86 Ce 5b-89	-	EN 14105	-	0.2 max (% mol)
Free glycerol	Ca 14-56 Ca 14b-96	ASTM	EN 14105 EN 14106	0.02 (% mass)	0.02 max (% mol)

Total glycerol	Ca 14-56	ASTM	EN 14105	0.24	0.25 max
				(% mass)	(% mol)
Methanol	-	-	EN 14110	0.2 max	0.2 max
				(% vol.)	(% mol)
Ash content	Ca 11-55	ASTM D874	ISO 3987	0.02 max	0.02 max
				(% mass)	(% mol)
Sulfur	Ca 8a-35	ASTM D5453	EN ISO 20846		10.0 max
S15 grade	Ca 8b-35		EN ISO 20884	0.0015 max	(mg/kg)
				(% mass)	
S500 grade				0.05 max	
				(% mass)	
Copper strip corrosion	-	ASTM D130	EN ISO 2160	No. 3 max	1.0
					(degree of
					corrosion)
Phosphorous content	Ca 12-55	ASTM D4951	EN 14107	0.001 max	10.0 max
	Ca 12b-92			(% mass)	(mg/kg)

Sodium and Potassium, combined	Ca 15b-87	-	EN 14108 EN 14109	5.0 max (ppm)	5.0 max (mg/kg)
Calcium and magnesium, combined	Ca 15b-87	-	EN 14538	5.0 max (ppm)	5.0 mix (mg/kg)
Cetane number	-	ASTM D613	EN ISO 5165	47.0 min[a]	51.0 min
Iodine value	Cd 1-25	-	EN 14111	-	120 max (g I_2/100 g)
Linolenic acid content	-	-	EN 14103	-	12.0 max (% mol)
Polyunsatured (≥ 4 double bonds) FAME	-	-	EN 14103	-	1.0 max (% mol)
Cloud point	Cc 6-25	ASTM D2500	-	-	-
Cold soak filterability	-	ASTM D7501	-	360 max (s)	-

Carbon residue	-	ASTM D4530	EN ISO 10370	0.05 max (% mass)	0.3 max; 10% distillation residue (% mol)
Oxidative stability	Cd 12b-92	-	EN 14112	3.0 min (h)	6.0 min (h)
Flash point	Cc 9b-55	ASTM D93	EN ISO 3679	93 min (°C)	120 min (°C)
Density, 15°C	Cc 10a-25	-	EN ISO 3675 EN ISO 12185	-	860 – 900 (kg/m^3)
Kinematic viscosity, 40°C	-	ASTM D445	EN ISO 3104 ISO 3105	1.9 – 6.0 (mm^2/s)	3.5 – 5.0 (mm^2/s)
Distillation temperature, atmospheric equivalent, 90% recovered	-	ASTM D1160	-	360 max (°C)	-

Total contamination	-	EN 12662	-	24.0 max (mg/kg)

[a]For all tables: max refers to maximum and min refers to minimum
[b]Units of the corresponding limits are displayed in parentheses

Table 2.9 Fuel standards ASTM D7467 for B6 to B20 and CAN/CGSB-3.520 for B1 to B5 blended biodiesel-petroleum diesel fuel.

Property	ASTM method	ASTM Limits	CGSB Limits	
			Type A-LS[a]	Type B-LS[b]
Acid value	ASTM D664	0.3 max (mg KOH/g)	0.1 max (mg KOH/g)	0.1 max (mg KOH/g)
Water and sediment	ASTM D2709	0.05 max (% vol.)	0.05 max (% vol.)	0.05 max (% vol.)
Ash content	ASTM D482	0.01 max (% mass)	0.01 max (% mass)	0.01 max (% mass)
Sulfur			500 max (mg/kg)	500 max (mg/kg)
S15 grade	ASTM D5453	15 max (µg/g)		
S500 grade	ASTM D2622	0.05 max (% mass)		
Copper corrosion, 3 h 50°C	ASTM D130	No. 3 max	No. 1 max	No. 1 max
Cetane number	ASTM D613	40.0 min	40.0 min	40.0 min

One of the following must be met				
(1) Cetane index	ASTM D976	40.0 min	-	-
(2) Aromaticity	ASTM D1319	35.0 max (% vol.)	-	-
Cloud point	ASTM D2500 ASTM D4539 ASTM D6371	-	-	-
Electrical conductivity at point, time and temperature of delivery to purchaser	ASTM D2624	-	25.0 min (pS/m)	25.0 min (pS/m)
Carbon residue, 10% bottoms	ASTM D524	0.35 max (% mass)	0.10 max (% mass)	0.16 max (% mass)
Oxidative stability	-	6.0 min (h)	-	-
Flash point	ASTM D93	52 min (°C)	40 min (°C)	40 min (°C)

Kinematic viscosity,	ASTM D445	1.9 – 4.1	1.3 – 3.6	1.7 – 4.1
40°C		(mm^2/s)	(mm^2/s)	(mm^2/s)
Distillation temperature,	ASTM D86	343 max	290 max	360 max
atmospheric equivalent, 90% recovered		(°C)	(°C)	(°C)
Lubricity, HFRR 60°C	ASTM D6079	520.0 max	-	-
		(μm)		
Biodiesel content	ASTM D7371	6 – 20	-	-
		(% vol.)		

[a]Type A-LS is intended for use in urban transit buses and passenger automobiles or when ambient temperatures require better low-temperature properties than Type B-LS

[b]Type B-LS is intended for use in engines in services involving relatively high loads as found in industrial and heavy mobile equipment, such as intercity trucks and construction equipment, and when ambient temperatures and fuel storage conditions allow use of such fuel

In the United States, ASTM D7467 is adopted for quality control of blended fuel containing 6% to 20% FAAE and is shown in Table 2.9 [174]. It is imperative that FAAE meets the standards for pure biodiesel prior to blending. Blends up to 5% are allowable in ASTM D957 for diesel fuel and ASTM D396 for heating oil provided that FAAE meets the standards for pure biodiesel. In 2005, the Canadian General Standard Board issued standard CAN/CGSB-3.520 for biodiesel-petroleum diesel blends up to 5% in Canada (see Table 2.9) [175]. The Canadian standard is intended for quality control of Type A-LS blends used in urban transit buses and passenger automobiles and Type B-LS blends used in engines in services involving relatively high loads as found in industrial and heavy mobile equipment. The ASTM methods are adopted for testing the blended fuels.

2.5.1. Combustion Properties

The heating value of biodiesel and its parent oils is approximately 10% less than those of petroleum base diesel fuel on a mass basis [70,93,99]. However, the higher viscosity of biodiesel reduces the amount of fuel that leaks past the plungers in the diesel fuel injection pump. In addition to heat of combustion, ignition delay time is important fuel combustion characteristic. The ignition delay time is the time that passes between injection of fuel into the cylinder and onset of ignition and is characterized by cetane number (CN) [4]. The higher CN represents a shorter ignition delay time and vice versa. Cetane (hexadecane; $C_{16}H_{34}$) is a long straight-chain hydrocarbon and has been assigned a CN of 100. Most biodiesel from vegetable oils have CN higher than 51 and CN of specific ester such as that of stearic can be as high as 87, while the CN of petroleum base diesel is usually ranged at 40 to 52 [175,177]. The higher CN of biodiesel

stems from the fact that biodiesel is composed of linear chain molecules similar to that of cetane itself, while petroleum base diesel is a mixture of hydrocarbons that typically contains 8-12 carbon atoms per molecule, which is composed of 75% saturated hydrocarbon including stretch chains, branched chains, cycloalkanes, and 25% aromatics. The branched chains, cycloalkanes, and aromatics are responsible for the lower CN in petroleum base diesel. CN is usually characterized by ASTM D613. Alternatively, since the CN of biodiesel increases with chain length and decreases with the number of double bonds, CN of FAME can be estimated with reasonable accuracy using its saponification and iodine values [178]. It is worthy to note that although CN of biodiesel increases with chain length, the use of longer chain alcohols such as ethanol or butanol as reacting alcohols in transesterification yields an insignificant effect on CN of the resulting biodiesel [176].

2.5.2. Flow Properties

Fuel flow property is an important characteristic as it determines performance of fuel flow system and can be evaluated by viscosity, which measures fluid's resistance to flow. A high viscous fuel could lower the performance of fuel flow system. One of the main reasons that the use of neat vegetable oil as diesel fuel has been considered unsatisfactory and impractical is its high viscosity [7]. In order to reduce its viscosity, the glycerol backbone of TAG is required to be stripped off, usually by the transesterification reaction. The resulting FAAE has shown a significant reduction in viscosity compared to its parent oils. Due to the reduction of viscosity during transesterification, viscosity can also be used as a means to monitor the extent of the transesterification reaction [169].

Since the viscosity of diesel fuels is a strong function of temperature and usually increases at lower temperatures, operating engines at the cold climate regions is often challenging and; therefore, the low temperature flow properties of fuel should be monitored closely. These properties can be examined by cloud point (CP), pour point (PP), and cold filter pligging point (CFPP). Cloud point is the temperature at which a cloud of wax crystals first appears in the oil when it is cooled and a cloudy fuel is visible to the naked eye. At temperatures below CP, crystals grow larger and agglomerate together to the point that they prevent the fluid to flow. The lowest temperature at which the fluid will pour is defined as pour point. The CFPP is defined as the lowest temperature at which biodiesel will flow under vacuum conditions through a wire mesh filter screen within 60 sec. In addition to CP, PP, and CFPP, differential scanning calorimeter (DSC) has been used to evaluate low temperature properties of biodiesel [28,99,179]. At an adequately low temperature, crystal is formed and the heat associated with crystallization is released and measured by DSC, and the temperature is recorded as onset crystallization temperature (OCT), which is the temperature at which the first crystal is formed. In addition to OCT, DSC is used to measure melting temperature, polymorphic transition temperature (temperature at which crystal changes its form), and the corresponding endothermic and exothermic heats.

The low temperature property of biodiesel depends mainly on its composition. It is well known that unsaturated FAAE crystallized at a lower temperature than saturated FAAE, due to their different three-dimensional conformations. Saturated molecules are at minimum energy when fully extended and are well stacked, thereby strengthening intermolecular attraction force [180]. Unlike saturated ester, especially *cis*-formation, unsaturated FAAE molecules have weaker intermolecular interactions and, therefore, crystallize at a lower temperature. The *tran*-

formation fatty acids which usually occur unnaturally have a similar molecular arrangement to those saturated fatty acids and therefore would crystallize at a temperature higher than that of the corresponding *cis*-formation fatty acids. Branched molecules also have weak intermolecular force and, therefore, crystallize at low temperatures. Based on this knowledge, there have been attempts to improve low-temperature flow property of biodiesel by introducing branched structure to the originally straight-chain FAAE either by means of transesterification with branched alcohols [181] or isomerization reaction [182]. Alternatively, low temperature additives such as glyceryl ethers produced from etherification of glycerol with isobutylene or tert-butanol in the presence of solid acid catalysts, such as sulfonated carbon and amberlyst-15 have been used to improve CP biodiesel [183-185]. In addition to fatty acid compositions, transesterification intermediates, such as DAG and MAG, if present in FAAE can greatly deteriorate low-temperature flow properties of biodiesel. The transesterification intermediates, especially saturated MAG, induce stronger intermolecular force due mainly to molecular stacking and hydroxyl moiety in their molecules and, therefore, raise biodiesel low temperature properties such as CP, PP, CPFF, and OCT. In addition, it was found that the presence of saturated MAG in biodiesel induces precipitates even at temperatures higher than CP which cause problems with fuel filterability [186,187].

2.5.3. Stability

Biodiesel is susceptible to oxidation, which leads to fuel degradation; therefore oxidative stability of biodiesel is crucially important as it determines resistance to chemical changes brought about by oxidation reaction. The oxidation of biodiesel is similar to those of lipid

oxidations as discussed in Section 2.3.8. In addition to oxidation, polymerization occurs due to the presence of double bonds to form higher molecular weight products that, in turn, raises the biodiesel's viscosity. Oxidative stability of biodiesel depends greatly on fatty acid compositions and degree of unsaturation. Saturated FAAE is more stable than those of unsaturated, while polyunsaturated FAAE is at least two time more reactive to auto-oxidation than monounsaturated FAAE [188,189]. For the same number of double bonds per molecule, FAAE with longer chain or higher molecular weight would be less prone to auto-oxidation, due to the lower molar concentration of double bond [190]. As an example of this phenomenon, ethyl ester has shown higher oxidative stability compared to that of methyl ester [70,101]. In addition to the degree of unsaturation, the position at which double bonds are located in an unsaturated molecule is also an important parameter to determine oxidative stability of biodiesel. It is reported that η-3 fatty acids autoxidize faster than η-6 fatty acids [191].

Some metals can accelerate oxidation of biodiesel. It has been shown in the literature that elemental copper has strong catalytic effects on biodiesel oxidation [190] and the peroxide value of biodiesel increases more rapidly when a copper strip is immersed in a glass container of biodiesel, compared to when a steel strip is used [192]. In addition, biodiesel is prone to hydrolytic degradation in the presence of water. The hydrolytic reaction is strongly influenced by the initial acid value of biodiesel due to the catalytic effects of free fatty acid on the reaction [193]. Biodiesel with a high concentration of transesterification intermediates, i.e., DAG and MAG, has a high tendency to absorb water, therefore, promoting a hydrolytic reaction. Most vegetable oils contain natural anti-oxidant reagents, i.e., tocopherol or Vitamin E that hinder the oxidation reaction. Once the amount of anti-oxidants is depleted, the rate of oxidation grows rapidly. An addition of synthesis anti-oxidants, such as tert-butyl hydroquinone (TBHQ), 3-tert-

butyl-4-hydroxyanisole (BHA), pyrogallol (PY), and n-propyl gallate (PG) up to 1000 mg/kg may be required as these compounds have been shown to improve oxidative stability of biodiesel. The effects of another widely used anti-oxidant 2,6-di-tert-butyl-4-methyl-phenol (BHT) in the food industry is controversial when used to improve biodiesel stability [194,195]. Most biodiesel properties such as viscosity, density, CFPP, and carbon residue are not affected by the addition of anti-oxidants. However, an addition of high amounts of anti-oxidants can alter the acid value of biodiesel [196].

Oxidative stability of biodiesel is preferably determined by the Rancimat method as per EN 14112 or AOCS Cd 12b-92. During the Rancimat test, the biodiesel sample is heated to 110°C and oxygen is supplied. In the presence of oxygen at high temperatures, the oxidation reaction takes place and the oxidation derivatives are transferred to the measuring chamber containing Millipore water. The increase in conductivity of the water is detected as the oxidation derivatives are transferred into the water. The induction time is defined as the time required for the conductivity of the water to be increased rapidly and is used as an indication of biodiesel oxidative stability. Alternatively, oxidative stability of biodiesel can be evaluated by peroxide value (PV) and iodine value (IV). PV of biodiesel increases when FAAE oxidation initiates and propagates to form peroxides and hydroperoxides. However PV is not a very suitable parameter for determining oxidative stability because its value drops during further degradation of hydroperoxides to form secondary oxidation derivatives [192,197]. IV indicates the degree of unsaturation in terms of mg Iodine per 100 g sample and is often used to correlate with oxidative stability of the test sample. The major flaw of this method as an oxidative stability indicator is that it does not take into account the positions at which double bonds are located in a molecule, which is a proven contributing factor for autoxidation of fatty acids [191]. Pressurized

differential scanning calorimeter (PDSC) has also been used to determine oxidative stability of biodiesel. Since oxidation is an exothermic reaction, the reaction heat makes it possible to use DSC to monitor the biodiesel oxidation process. Operating DSC at high pressure helps to increase the number of mole of oxygen available for the reaction, thereby accelerating oxidation to take place at lower temperature [198]. The results from the DSC method are in line with those obtained from the Rancimat method and it requires lesser amounts of sample and shorter analyzing time [199]. DSC was concluded to be a reliable alternative method to determine oxidative stability of biodiesel.

2.5.4. Lubricity

The lubricating property of fuel is defined as the quality that prevents wear when two moving metal parts come into contact with each other [200]. Oxygen and nitrogen containing compounds are responsible for the natural lubricating property of diesel fuel [201]. In petroleum refineries, processes such as hydrotreating usually used to remove sulfur also destroy heterocyclic oxygen and nitrogen containing compounds, which are responsible to providing lubricity to the fuel [202]. Consequently, this typically ultra-low sulfur diesel fuel exhibits poor lubricity. ASTM D6079 is typically used to evaluate lubricating property of biodiesel and diesel fuel by the High-Frequency Reciprocating Rig (HFRR). In this method, the ball and disk are submerged in the test fluid and rubbed against each other for 75 minutes at 50 Hz to generate a wear. At the end of the test, the wear diameter is measured on the ball and the high wear diameter indicates poor lubricating property of the test fluid and vice versa. It was shown that the blended mustard biodiesel-petrodiesel samples have superior lubricating property as

compared to those of commercial diesel fuels purchased from different gas stations (Esso, Shell, Petro-Canada, Co-op) [28]. This is explained by the presence of $COOCH_3$ moeity in methyl ester, while the lower lubricating performance of esters prepared from higher alcohols is explained by an absence of $COOCH_3$ moeity. It was reported that the order of oxygenated moiety that provides lubricity are COOH > OH > $COOCH_3$ > C=O > C-O-C [203].

Although biodiesel lubricating property is tested, compared with petroleum based diesel, and reported widely in the literature, the tribological mechanism of biodiesel is still not available. Nevertheless, the tribological mechanism of other model compounds such as zinc dialkyl-dithiophosphate (ZDDP) [204] may be useful in explaining lubricity behaviour of biodiesel. Initially, lubrication fluids are used to generate hydrostatic and hydrodynamic pressures to support the load. This condition is referred to as the elastohydrodynamic lubrication (EHL) regime where the fluid pressure is used to provide lubrication. Further increase in contact pressure causes thickness of fluid film to decrease. When the average thickness of fluid film falls below the average surface roughness, the boundary lubrication (BL) regime is applied. Under the BL regime, the temperature is usually high enough to cause chemical reactions between the lubricant and the solid surface to take place, resulting in a chemical film that protects the surface. The reaction yields metallic-organo compounds that polymerize to form higher molecular weight products. These polymers (MW = 3000-5000) are critical in providing lubrication to the contacting surfaces. Petroleum diesel is a mixture of hydrocarbons that typically contains 8-12 carbon atoms per molecule, with 75% saturated hydrocarbon and 25% aromatics. The reaction rate between petroleum diesel and the contacting surfaces in a diesel engine is insufficient to form a film quickly enough. Unlike petroleum diesel, biodiesel contains a polar functional group such as $–COOCH_3$ in case of FAME in its molecule. This functional group promotes reactivity

between biodiesel and metal surfaces forming a chemical film quickly enough to protect the surfaces. However, if the reaction rate is too rapid, chemical corrosion can occur causing an increase in wear.

The proposed chemical solution model of biodiesel blends in petroleum based diesel involves aggregation of biodiesel molecules in reverse micelle formation (polar group in the inside and hydrocarbon tail on the outside) if the biodiesel concentration is high enough (see Figure 2.10). Outside the reverse micelle of FAAE lays a free molecular region in which each molecular species competes freely for adsorption on the solid surface. When these free molecules are depleted, the reverse micelle dissociates to release more free species. This model is used to explain how lubricant maintains its functionality throughout its lubricating life. In addition to polar head, the hydrocarbon chain has great impacts on biodiesel lubricating properties. Hydrocarbon chain length, degree of branching, and the presence of double bonds all influence how the lubricant pack themselves on the solid surface resulting in the packing density. Low packing density film allows lubricating molecules to move about, hence providing flexibility and longevity of the lubricant. On the other hand, high packing density film has mechanical strength necessary for load-bearing ability. Increase in hydrocarbon chain length results in lower packing density film that improves lubricating longevity, but the load-bearing ability is decreased. In addition, an increase in alkyl chain length leads to a reduction in molar concentration of the functional group, resulting in a slower rate of the reaction between the lubricant and the solid surface.

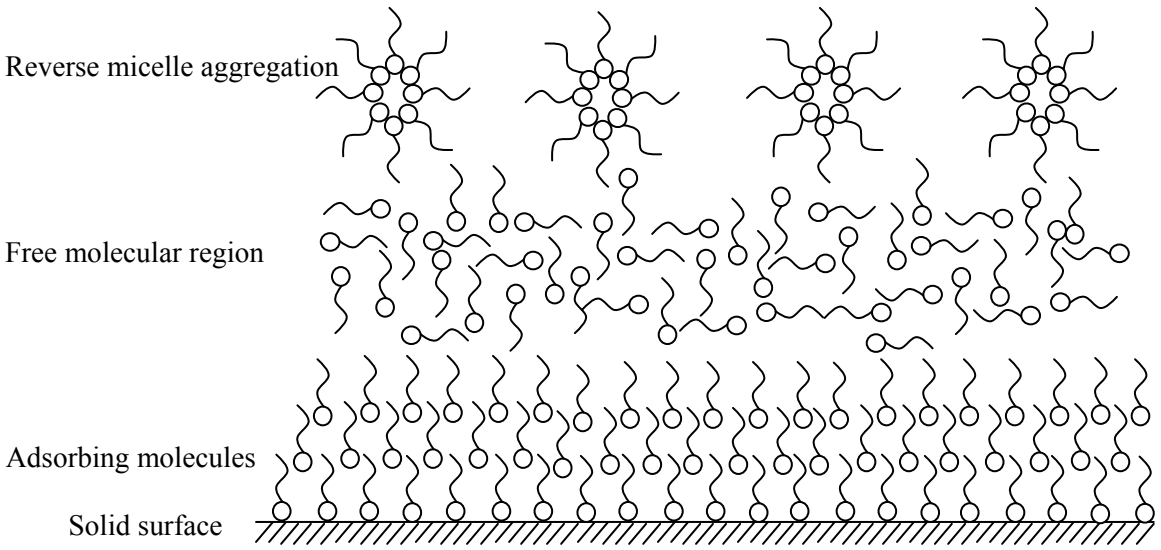
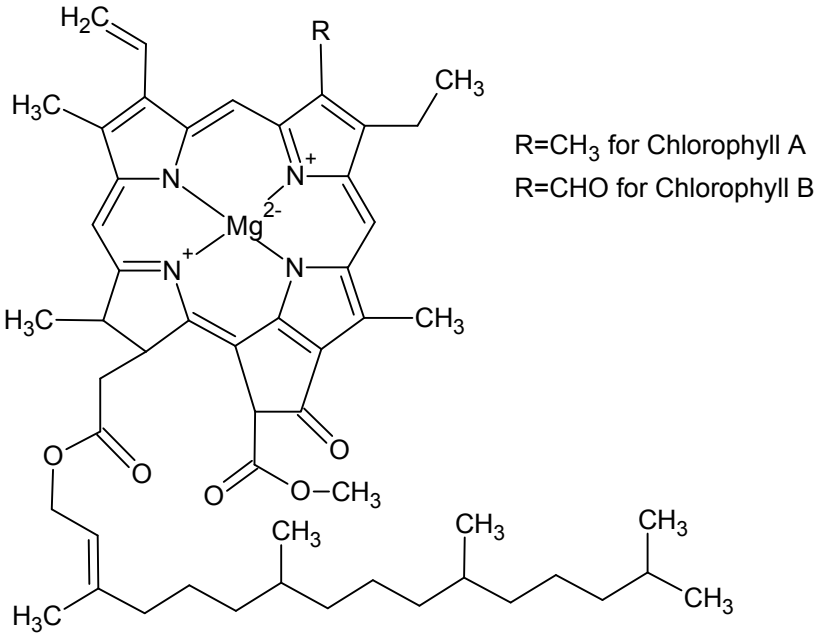


Figure 2.10 Chemical solution model for biodiesel blends.

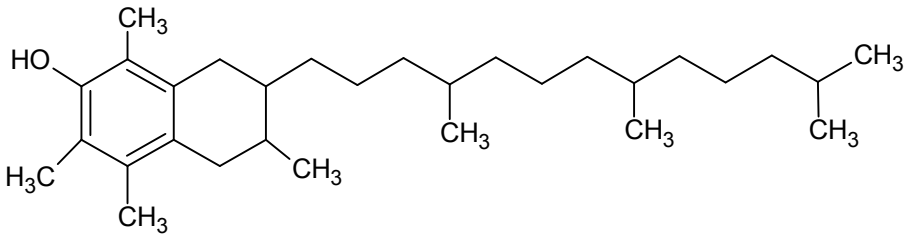
However, if the chain length is insufficient, FAAE would lose its durability as a lubricant. A good lubricating biodiesel should compose of varieties of FAAE to provide molecular mobility as well as solid adhesion strength.

2.5.5. Minor Components

Minor components usually presented in vegetable oil are presented in Figure 2.11. A comprehensive database of lipid classification including these minor components can be found in the literature [205]. These components affect biodiesel characteristics differently.



(a)



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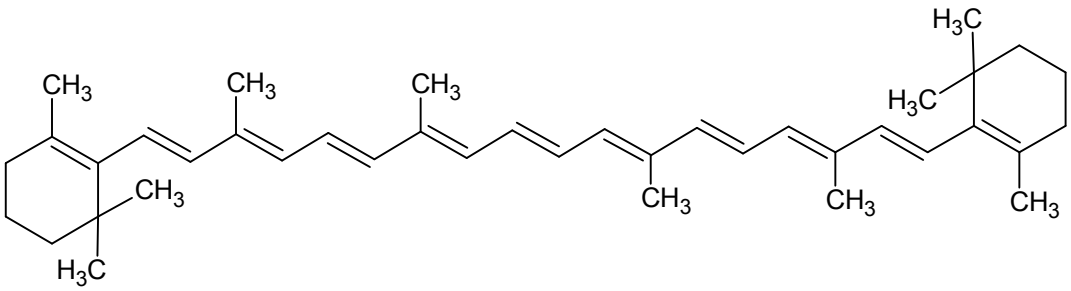

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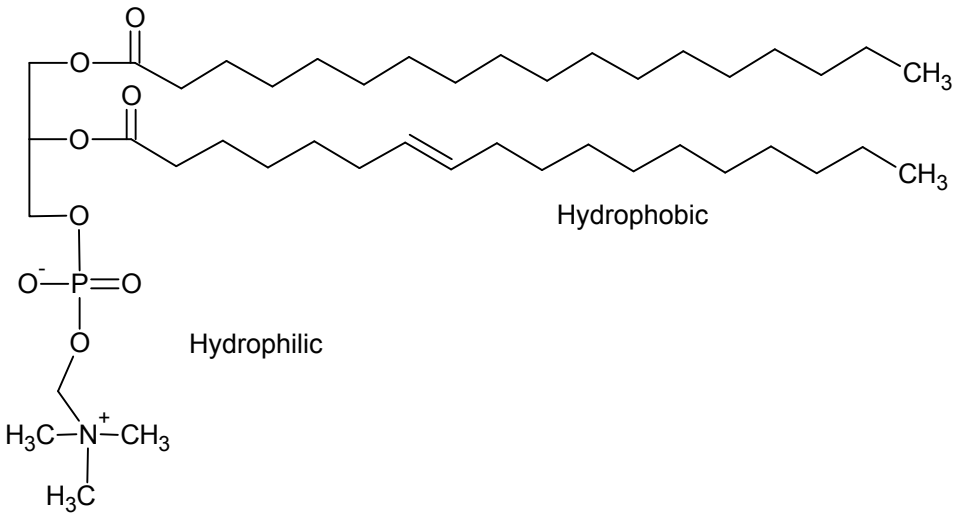

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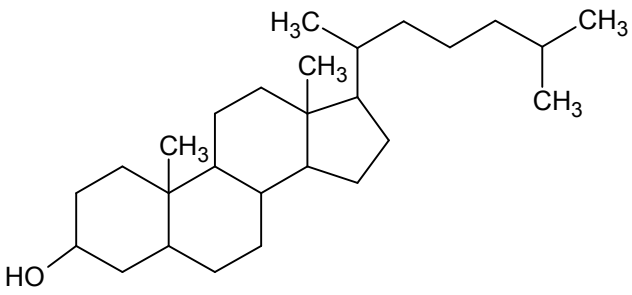

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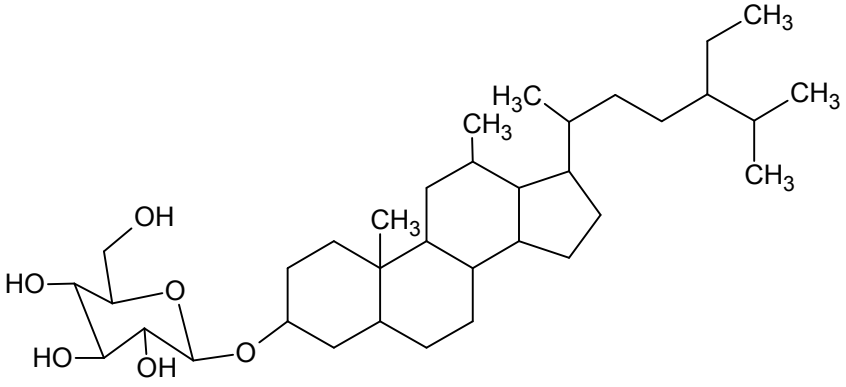

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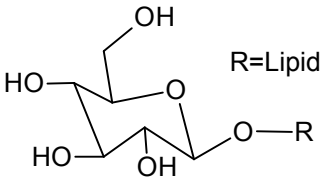
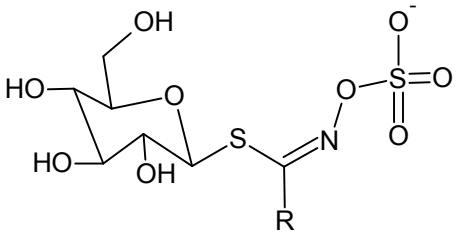


(g)



(h)

Figure 2.11 Minor components in vegetable oils: a) chlorophyll; b) α-tocopherol or vitamin E; c) β-carotene; d) phospholipid; e) sterol; f) sterol glycoside (β–sitosterol-β-D-glucopyranoside); g) glycolipid; h) glucosinolate.

2.5.5.1. Pigments

Chlorophylls and their derivatives (see Figure 2.12) have been reported for their detrimental effects on biodiesel stability [101] because it is an effective photoreceptor. Chlorophyll is responsible for green colour in plants such as canola oil. In fact, if canola oil contains higher amounts of chlorophylls, the oil is downgraded, has lower economic value, and is labelled as greenseed canola oil [206]. Chlorophyll can generally be categorized into 2 types: Chlorophyll A (contains $–CH_3$ as its functional group) and Chlorophyll B (contains –CHO as its functional group). For plant growth, these two types of chlorophylls absorb sunlight at a slightly different wavelength, thereby complimenting each other [207]. In addition, chlorophyll can degrade into various compounds depending on the surrounding conditions (see Figure 2.12). In the presence of weak acids, magnesium ion is removed and chlorophyll degrades to pheophytin. Chlorophyllase is found mostly in plants such as ferns, mosses, and algae, and can act as a catalyst for the removal of phytol tail from a chlorophyll molecule to form chlorophyllide. It is reported that chlorophyll derivatives could be converted to compounds capable of being prooxidants, thus giving deleterious effect on the stability of vegetable oils [208]. In contrast, tocopherols such as α-tocopherol or vitamin E, are presented naturally in most vegetables and are reported widely for their antioxidative activity [194,195,209,210].

In addition to chlorophylls, carotenoids are organic pigments that naturally occur in plants and can be categorized into two classes, xanthophylls (contain oxygen) and carotenes (purely hydrocarbons and contain no oxygen). The most common carotenoid in vegetable oils such as palm oil is β-carotene as depicted in Figure 2.11. β-Carotene is responsible for the red-orange colour in plants and fruits and the colour darkens at elevated temperatures.

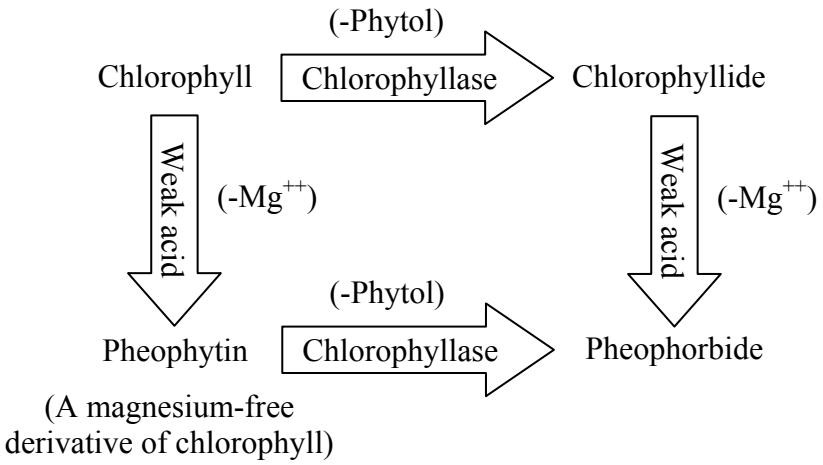


Figure 2.12 Chlorophylls degradation pathways.

Most carotenoids are known for their anti-oxidant activity as they are efficient free radical scavengers and, therefore, enhance biodiesel oxidative stability [209,211]. However, they could interfere the biodiesel production process especially in homogeneous base catalyzed transesterification as the mechanism involves the attack of alkoxide ions to the carbonyl carbon of the triglyceride molecule.

2.5.5.2. Lecithin and Phospholipids

Lecithin is a mixture of various phospholipids that contains hydrophilic head and hydrophobic tails. Figure 2.11 shows molecular structure of phospholipid possessing hydrophilic and hydrophobic property in its molecule. The hydrophilic head is negatively charged with a phosphate group and possibly another polar group, while the hydrophobic tails usually consist of

fatty acid chains. Because phospholipids consist of both a polar head and nonpolar tails, it acts as a co-solvent in transesterification, enhancing vegetable oils' solubility in alcohols. However, phosphorous can be carried over from vegetable oils, i.e., phospholipid, and can poison catalysts used for exhaust emissions.

2.5.5.3. Phytosterols

Phytosterols refer to all sterols of plant origins. The chemical structure of sterols is composed of an alkyl chain attached to a sterol nucleus and is presented in Figure 2.11. Most phytosterols contain 28 to 30 carbon atoms and 1-2 carbon-carbon double bonds (one in the sterol nucleus and possibly one in the alkyl chain) in their molecule. It can be found as free sterol, acylated (sterol esters), alkylated (sterol alkyl ethers), sulfated (sterol sulfate), or linked to a glycoside moiety (sterol glycosides), and acylated sterol glycosides. During transesterification, acylated sterol glycosides are converted into sterol glycosides (SG) due to the alkaline catalysts. Therefore, SG concentration in biodiesel is usually higher than that found in the vegetable oil feedstock. The chemical structure of an SG is depicted in Figure 2.11. SG in biodiesel can accelerate precipitate formation, even above biodiesel's cloud point, and possibly block fuel filters due to its polarity and limited solubility. Among several sterols, SG has been found as the major component in biodiesel precipitates. Either GC or HPLC may be used to detect and quantify the presence of SG.

2.5.5.4. Glycolipids

Glycolipids are lipids with carbohydrates attached. Examples of glycolipids are sterol glycoside (SG) and glucosinolate, as they are lipids attached to carbohydrate. The chemical structure of glucosinolate is shown in Figure 2.11. Glucosinolate is the major source of sulfur contained in biodiesel. Sulfur, like Phosphorus, is a potential catalyst poison and it oxidizes during combustion to produce SO_2 and SO_3 that rapidly converts to sulfuric acid in the presence of water, which leads to acid rain. Glucosinolates can be found in rapeseed oil, while canola oil has low amounts of glucosinolates (see Section 2.3.2). Therefore, one can expect lesser amounts of sulfur content in biodiesel produced from canola oil compared to that derived rapeseed oil.

2.6. Biodiesel Production in Canada

Biodiesel production in Canada was below 50 million litres per year in 2005. In December 2006, the federal government announced an intention to mandate 2% renewable content in diesel fuel, which would create approximately 500 million litres per year of biodiesel demand across the country. This announcement was a major driving force for the tremendous growth in Canadian biodiesel industry. Canadian biodiesel production capacity increased to ~150 million litres per year in 2008 and ~200 million litres per year in 2010 [212]. The implementation date of the 2% federal mandate for biodiesel was later set at July 1, 2011 [213]. Prior to this federal mandate, there were a number of provincial renewable fuel mandates, such as 2% in Alberta and Manitoba and 3% in British Columbia. The current major Canadian biodiesel plants using various feedstocks are listed in Table 2.10, indicating that the current total Canadian biodiesel production is 205.9 million litres per year [212].

Table 2.10 Biodiesel plants in Canada.

Plant	Status	Feedstock	Capacity (million litres per year)	City	Province
BioStreet Canada	Proposed plant	Oilseed	22	Vegreville	Alberta
Canadian Bioenergy Corporation – Northern Biodiesel Limited Partnership	Proposed plant	Canola	265	Lloyminster	Alberta
FAME Biorefinery	Demonstration facility	Canola, camelina & mustard	1	Airdire	Alberta
Kyoto Fuels Corporation	Under construction	Multi-feedstock	66	Lethbridge	Alberta
Western Biodiesel Inc.	Operational	Multi-feedstock	19	Calgary	Alberta
City-Farm Biofuel Ltd.	Operational	Recycled oil/tallow	10	Delta	British Columbia

Consolidated Biofuels Ltd	Operational	Yellow Grease	10.9	Delta	British Columbia
Bifrost Bio-Blends Ltd.	Operational	Canola	3	Arborg	Manitoba
Eastman Bio-Fuels Ltd.	Operational	Canola	5	Beausejour	Manitoba
Speedway International Inc.	Operational	Canola	20	Winnipeg	Manitoba
Bioversel Sarnia	Proposed plant	Multi-feedstock	170	Sarnia	Ontario
BIOX Corporation	Operational	Multi-feedstock	66	Hamilton	Ontario
BIOX Corporation (Plant 2)	Proposed plant	Multi-feedstock	67	Hamilton	Ontario
Methes Energies Canada	Operational	Yellow Grease	5	Mississauga	Ontario
Methes Energies Canada	Under construction	Multi-feedstock	50	Sombra	Ontario
Noroxel Energy Ltd.	Operational	Yellow Grease	5	Springfield	Ontario
Biocardel Quebec Inc.	Proposed plant	Multi-feedstock	40	Richmond	Quebec

Bio-Lub Canada.com	Operational	Yellow Grease	10	St-Alexis-des-Monts	Quebec
QFI Biodiesel Inc.	Operational	Multi-feedstock	5	St-Jean-d'Iberville	Quebec
Rothsay Biodiesel, A member of Maple Leaf Foods Inc.	Operational	Multi-feedstock	45	Sainte-Catherine	Quebec
TRT-ETGO	Proposed plant	Vegetable Oil	100	Bécancour	Quebec
Milligan Bio-Tech Inc.	Operational	Canola	1	Foam Lake	Saskatchewan

The feedstock for biodiesel production includes animal fats and waste vegetable oils (yellow grease), with only a small quantity of canola oil used to produce biodiesel. A fraction of Canadian canola oil is shipped to the United States for production of biodiesel, which is then shipped back to Canada to meet the mandate. In addition, Germany imports canola oil from Canada for their biodiesel production process and biodiesel usage. The Canadian biodiesel production industry is relatively new compared to that in the United States and many European countries, since the first provincially mandated market was established in 2009. The new Canadian 2% renewable fuel standard (RFS) requirement is anticipated to drive biodiesel production and market growth for the sustainable future.

2.7. Conclusions

It is expected that biodiesel will be in high demand in the coming years as conventional diesel additives. The use of vegetable oils as feedstock will play a major role in supplying biodiesel to various sectors, such as agriculture and transportation. The use of different vegetable oil may affect production processes and costs, as well as the resulting biodiesel characteristics. For example, used cooking oil requires pre-treatment prior to traditional alkali-catalyzed transesterification. Palm oil may be selected in tropical countries due to its high oxidative stability, but canola oil is a preferred choice in cold-climate countries due to its resistance to freeze at low temperatures. Therefore, selection of vegetable oil and production technology is vital for the growth in biodiesel industries. In order to make an effective decision, in-depth information and understanding on biodiesel from vegetable oils is essential.

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CHAPTER 3

Oil Degradation during Frying and its Effect on the Corresponding Biodiesel Yield and Oxidative Stability

A part of this chapter has been published in the following conference proceeding:

- Issariyakul, T., and Dalai A.K. Utilization of used cooking oil, canola oil, and greenseed canola oil for biodiesel production. The 8th World Congress of Chemical Engineering, Montreal Quebec, Conference Proceeding Paper (2009).

Contribution of the Ph.D. Candidate

Experiments were conducted by Titipong Issariyakul. The content in this chapter was written by Titipong Issariyakul with discussions and suggestions provided by Dr. Ajay Dalai.

Contribution of this Chapter to the Overall Ph.D. Research

Used cooking oil is one of the main focused feedstock for biodiesel production in the overall Ph.D. research. The aim of this chapter is to illustrate how various properties of used cooking oil such as acid value and viscosity change during frying process. Furthermore, yield and oxidative stability of biodiesel prepared from used cooking oil are measured and compared with those prepared from canola and greenseed canola oil.

3.1. Abstract

Biodiesel is a fuel derived from a renewable source such as vegetable oils, and emits less pollutants and greenhouse gases as compared to petro-fuel. The use of this fuel is an environmental friendly shift towards sustainability due to its renewability and low harmful emissions. Due to high price of food-grade vegetable oils and the food vs. fuel concern, non-food grade oils have gained tremendous interests as a feedstock to produce biodiesel. Used cooking oil is generated in everyday-life around the world and therefore is a potential source for biodiesel production. Extended-life canola oil was used to fry food for duration of 72 hours to make used cooking oil. An increase in viscosity and acid value of the oil was observed as a result of oil degradation during the frying process. Used cooking oil, RBD (refined, bleached, deodorized) canola oil, and greenseed canola oil was transesterified to produce fatty acid methyl ester (FAME). The transesterification was conducted with methanol (6:1 alcohol to oil molar ratio) using KOH as a catalyst at 1 wt.% with respect to oil. The reaction temperature was maintained at 60°C for 1.5 h at the stirring speed of 600 rpm. During this study it was observed that FAME from RBD canola oil has higher ester percentage (97.3%) as compared to those derived from used cooking oil (95.1%) and greenseed canola oil (94.8%). This is because canola oil has negligible acid value whereas used cooking oil and greenseed canola oil have acid value of 1.5 and 3.8 mgKOH/g, respectively.

3.2. Introduction

Biodiesel or fatty acid methyl ester (FAME) is an alternative fuel arising from concerns of depleting sources of fossil fuels and environmental issues. Biodiesel properties are comparable to those of fossil-based diesel fuel and can be produced from animal fats or

vegetable oils thus they are renewable. Recently, there are concerns regarding food versus fuels controversy of which crops for energy and food compete with each other in many ways (agricultural landing, skilled labour, water, fertilizers etc.) [1,2]. Moreover, the high price of biodiesel derived from food-grade vegetable oils makes it difficult to compete economically with the fossil-based diesel. A less expensive, non food-grade vegetable oil can be a potential feedstock for biodiesel production.

In recent years, attempts to utilize used cooking oil (UCO) as a feedstock for biodiesel production have been made to overcome the economic problem [3,4]. This is because the cost of yellow grease (16.5 ¢/lb) is lower than that of canola oil (34 ¢/lb) [5]. Yellow grease is defined as used cooking oil containing free fatty acid (FFA) less than 20%. FFA, if present, could cause the side saponification reaction which consumes catalyst and generates soap leading to low yield and low quality of FAME. In the present work, extended-life canola oil was used to fry food over 72 hours. Observations have been made and presented to demonstrate oil degradation during frying process. The fried oil was then transesterified to produce FAME.

Another interesting feedstock for biodiesel production is greenseed canola oil. Greenseed canola is an immature canola seed of which its colour appears green. The green colour is due to high level of chlorophyll content in the seeds. In addition, chlorophyll is retained in canola seeds if the seeds are exposed to frost condition during seed development. According to Canadian Grain Commission (CGC), Canola seeds are divided into 3 grades. No. 1 Canola is the best quality canola seed which contain less than 2% greenseed, with less than 25 ppm chlorophyll content and can be sold at around $500 per metric ton [6]. No.2 Canola and No.3 Canola are the lower canola seeds as they contain 26-45 ppm and 46-100 ppm chlorophyll, respectively. The price of green seeds drops by around $10 to $15 per grade per metric ton [7]. As the level of

chlorophyll content increases, the selling value of the seed drops and cannot be used for edible purpose. Therefore, greenseed canola oil can be considered as a non-food grade feedstock and hence making it a good feedstock for biodiesel production. The objective of this work is to study the feasibility of used cooking oil and greenseed canola oil as feedstock for biodiesel production.

3.3. Materials

Extended-life canola oil was obtained from Dow Chemical Inc., Canada. Greenseed canola oil was obtained from Milligan Bio-Tech Inc., Foam Lake, Saskatchewan, Canada. RBD (refined, bleached, deodorized) canola oil was purchased from a local grocery store. Anhydrous methanol (MeOH) (99.8%) and potassium hydroxide (KOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were purchased from Sigma-Aldrich, MO, USA. F.A.M.E. mix rapeseed oil reference standard was obtained from SUPELCO, PA, USA.

3.4. Experimental Procedures

3.4.1. Frying Process for Extended-Life Canola Oil

The extended-life canola oil was used for food frying for 8 h per day for 9 days consecutively giving a frying load of 72 h. A 2 L of oil was poured into a fryer. Before frying, the oil was heated to 176.67°C for 1 h then 200 g of food was fried at 176.67°C. For the first batch of each day, pork sausage was used for day 1, 2, 3, and 4, marinated chicken was used for day 5, 6, and 7, and marinated pork was used for day 8 and 9. Pre-fried potatoes (“no-name” brand) were fried in batch 2 to batch 8 each day. The potatoes were fried for 10 min and the meats were fried for 20 min. The temperature of the oil was kept constant at 176.67°C for 8 h

each day. At the beginning of each day except the first day, 200 mL of fresh oil was added into the fryer. At the end of each day 60 mL of the oil was sampled.

3.4.2. Transesterification

FAME was produced by means of KOH-catalyzed transesterification from a 100 g of feedstock, which are used cooking oil, greenseed canola oil, and RBD canola oil. A 1% KOH based on the total amount of oil was used in each case as a catalyst. In each case, the feedstock was initially placed in a Parr reactor and heated to 60°C. The reactor consists of a ~300 mL (6.3 cm inside diameter and 10.2 height) stainless steel vessel equipped with a temperature and stirring speed control unit. A mixture of methanol (6:1 methanol to oil molar ratio) and KOH (1 wt.% with respect to oil) was then added to the reactor. The temperature and stirring speed of the reaction mixture were maintained constant for 1.5 h at 60°C and 600 rpm, respectively. After the reaction, the transesterification product was allowed to settle in a separating funnel for glycerol separation. Afterward, distilled water was heated and used in the washing step to remove KOH remained in the FAME phase. In this step, the water was added to the ester phase and the mixture was shaken. The mixture was then allowed to settle in a separating funnel and the aqueous phase was removed. The washing was completed after around 10 times of washing when the washing water became clear and its pH was approximately 7. Unreacted methanol and water was then removed using BÜCHI rotavapor. Biodiesel was finally passed through the anhydrous sodium sulphate, which was previously dried in an oven at 100°C for 1 hour, to remove traces of moisture.

3.4.3. Characterization

The ester phase collected from each experiment was analyzed for its ester content using a Hewlett-Packard 1100 series HPLC with refractive index detector and two Phenogel 5u 100A 300X7.80 mm 5 micron columns in series protected with guard column, equipped with ChemStation for LC 3D, Agilent Technologies. THF was used as a mobile phase at 1 mL/min for 25 min. The operating parameters were as follows: injection volume 5 µL; column temperature 24°C; and detector temperature 35°C. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were used for the HPLC calibration (see Appendix A). Fatty acid compositions of esters were determined using Agilent Technologies 6890N Network GC System equipped with GC ChemStation software with FID detector and RESTEK 10638 Stabilwax column. The injection volume was 2 µL and the program was started at 160°C, hold for 1 min, ramped to 240°C at 4°C/min and hold for 24 min. SUPELCO FAME Mix Rapeseed Oil standard was used as a reference for GC calibration (see Appendix B). The oxidative stability of biodiesel was measured as induction time using Metrohm 743 Rancimat instrument. Viscosity was measured by Brookfield DV-I Viscometer. Acid value was determined as per the method AOCS Te 1a-64.

3.5. Results and discussions

3.5.1. Oil Degradation during Frying

The sampled oil was characterized every 8 h of frying to study the properties changed in this oil during the frying process. Acid value and viscosity of the oil with error bars are shown in Figures 3.1 and 3.2, respectively. A number of reactions took place during the frying process

including thermolytic and oxidative reactions [8,9] resulting in the formation of oxidation derivations composing of various acids and polymerized materials. These oxidative derivatives caused an increase in acid value and viscosity as shown in Figures 3.1 and 3.2.

In order to determine oxidative stability of biodiesel, Rancimat instrument was used. During the Rancimat test, the sample was heated (110°C in this case) and the oxygen was supplied. In presence of oxygen at high temperature, the oxidation reaction took place and the oxidation derivatives were transferred to the measuring chamber containing Millipore water. The increase in conductivity of the water was detected as the oxidation derivatives were transferred into the water.

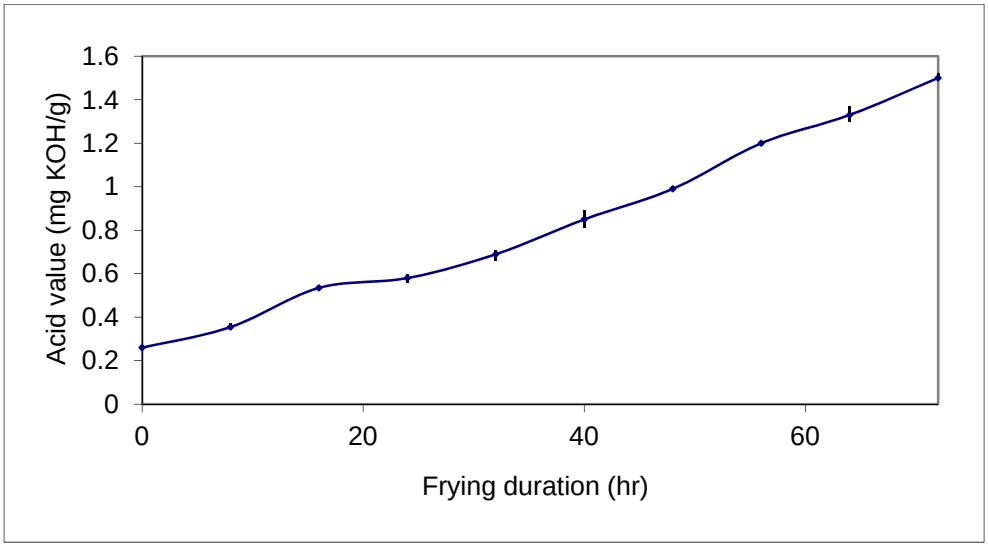

Figure 3.1 Acid value of extended-life canola oil during the frying process.

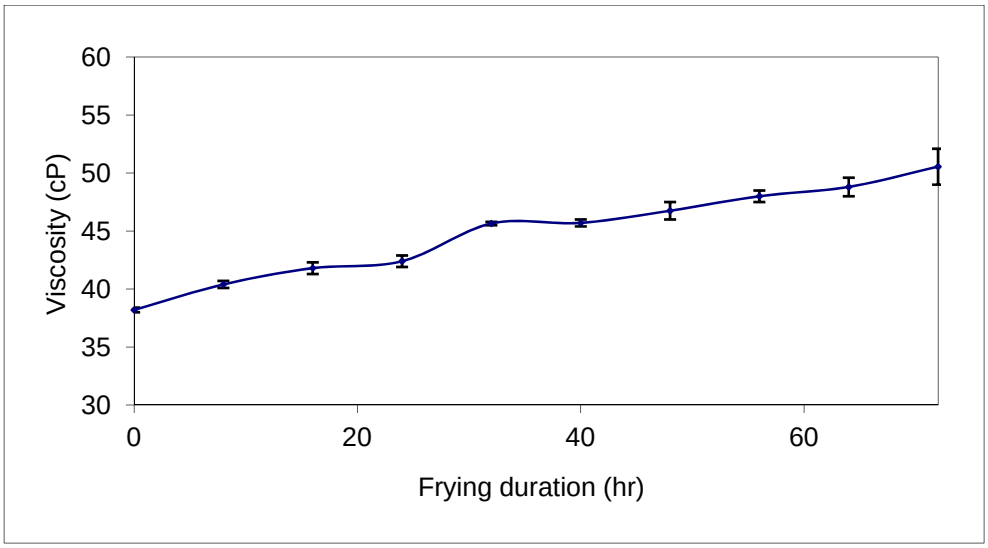

Figure 3.2 Viscosity @40°C of extended-life canola oil during the frying process.

The induction time is defined as the time required for the conductivity of the water to be increased rapidly and was used as an indication of oxidative stability of a sample. Table 3.1 shows induction time and acid value of the feedstock oil. Table 3.2 shows fatty acid compositions of each oil. The Rancimat results indicate that the aged oil has lower stability (induction time = 12.2 h) as compared to the fresh oil (induction time = 20.5 h). This is because the oxidation reaction took place during the frying period. The aged extended-life canola oil has a longer induction time as compared to RBD canola oil (8.2 h) or greenseed canola oil (11.5 h) due to its fatty acid composition profile. Table 3.2 shows that the used extended-life canola oil has less degree of unsaturation (lower linolenic acid) as compared to RBD canola oil or greenseed canola oil, thus increasing oxidative stability.

Table 3.1 Induction time and acid value of the feedstock oil.

Oil type	Induction time (hr)	Acid value (mg KOH/g)
“no name” RBD canola oil	8.2	0.2
Fresh extened-life canola oil	20.5	0.2
Aged extended-life canola oil (72hr)	12.2	1.5
Greenseed canola oil	11.5	3.8

3.5.2. Transesterification and Ester Analysis

The change in the FAME percentage during transesterification of the aged oil, greenseed canola oil and RBD canola oil is shown in Figure 3.3. Product compositions of biodiesel produced after transesterification of RBD canola, greenseed canola, and used cooking oil at 60°C for 1.5 h are given in Table 3.3. Ester percentage increased as transesterification proceeded towards the equilibrium. The higher ester percentage was achieved when the fresh RBD canola oil was used as compared to the aged oil (used cooking oil) or greenseed canola oil. This is due to possible occurrence of the saponification reaction when the aged oil or greenseed canola oil was used as a feedstock. This is because the acid value of the aged oil (AV = 1.5) and greenseed canola oil (AV = 3.8) was higher than that of the fresh oil (AV = 0.2).

Table 3.2 Fatty acid compositions of RBD canola oil methyl ester (CME), greenseed canola oil methyl ester (GME), and used cooking oil methyl ester (UME).

Structure	Compound name	CME (%ME)	GME (%ME)	UME (%ME)
C14:0	Myristic ester	0.06	0.07	0.09
C16:0	Palmitic ester	4.36	4.60	5.73
C16:1	Palmitoleic ester	0.16	0.26	0.02
C16:2	n/a[a]	0.08	0.08	0.07
C16:3	n/a[a]	0.09	0.15	0.08
C18:0	Stearic ester	1.96	2.01	2.30
C18:1 z9	Oleic ester	60.92	55.51	63.95
C18:1 z11	Asclepic ester	2.89	3.59	2.41
C18:2	Linoleic ester	18.70	20.93	20.05
C18:3	Linolenic ester	6.79	9.41	2.16
C20:0	Arachidic ester	0.59	0.66	0.53
C20:1	Eicosenoic ester	1.12	1.34	1.22
C22:0	Behenic ester	0.22	0.41	0.03
Total saturated fatty acid		7.19	7.75	8.68
Total monounsaturated fatty acid		65.09	60.7	67.6
Total polyunsaturated fatty acid		25.66	30.57	22.36

[a]n/a = not available

Table 3.3 Product compositions of esters produced from RBD canola, greenseed canola, and used cooking oil (transesterification at 60°C for 1.5 h).

Biodiesel	Triglyceride (%)	Diglyceride (%)	Monoglyceride (%)	Ester (%)
UME	0.9	2.8	1.2	95.1
GME	1.3	2.4	1.5	94.8
CME	0.0	1.7	1.0	97.3

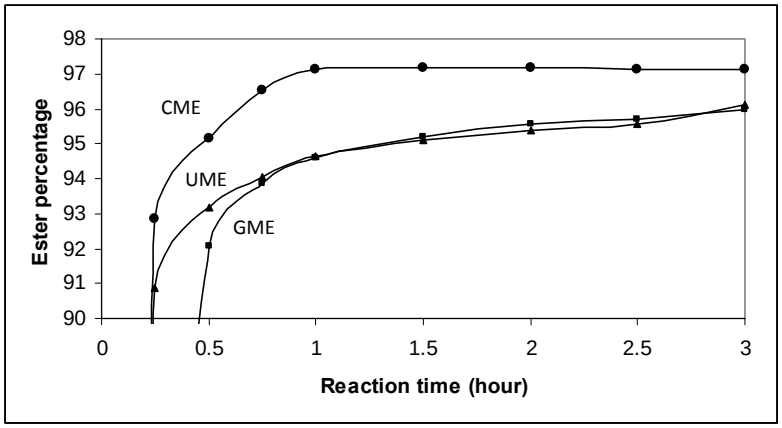

Figure 3.3 Change in ester percentage during transesterification of used cooking oil, greenseed canola oil and RBD canola oil.

A Rancimat plot of canola oil methyl ester (CME) is given in Figure 3.4 as an example to demonstrate oxidative stability of an oil sample. In Rancimat test, conductivity of distilled water is measured as a function of time. When the oil sample in another container is oxidized, the oxidation derivatives are transferred to the distilled water causing an increase in the conductivity of the water. The induction time is defined as the time that the conductivity of the water begins to increase rapidly. The induction time of biodiesel is shown in Figure 3.5. It was reported that the oil stability increase with the decrease in the degree of unsaturation [10]. Figure 3.5 shows that UME has longer induction time (3.4 h) compared to CME (1.85 h) or GME (0.5 h). This is because the UME has significant lower level of the highly unstable compound, linolenic acid (C18:3, containing three double bonds), (2.16%) as compared to that contained in CME (6.79%) or GME (9.41%). The total poly unsaturated compounds in UME (22.36%) are also lower than those contained in CME (25.66%) or GME (30.57%). In addition, it is found that biodiesel has lower oxidative stability when compared to their parent oils. This is because triglyceride, in general, has higher viscosity than ester. The higher viscosity is believed to be hindrance factor preventing oxygen and oxidation derivative compounds to move freely in the oil medium, thereby limiting the mass transfer of these compounds and retarding oxidation reaction.

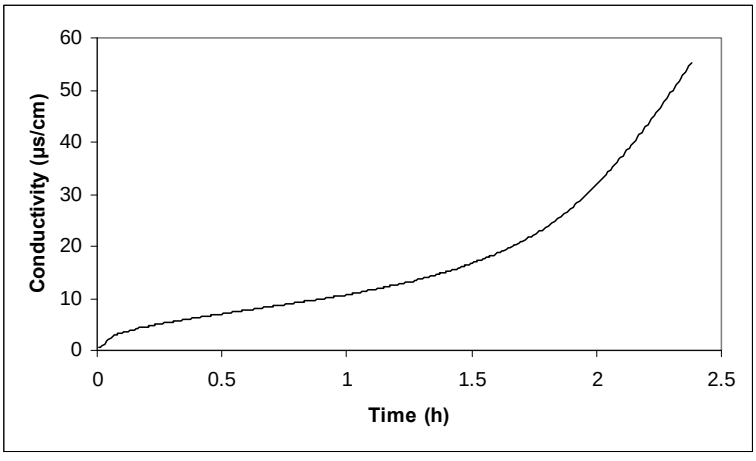

Figure 3.4 Oxidative stability plot of RBD canola oil methyl ester (CME).

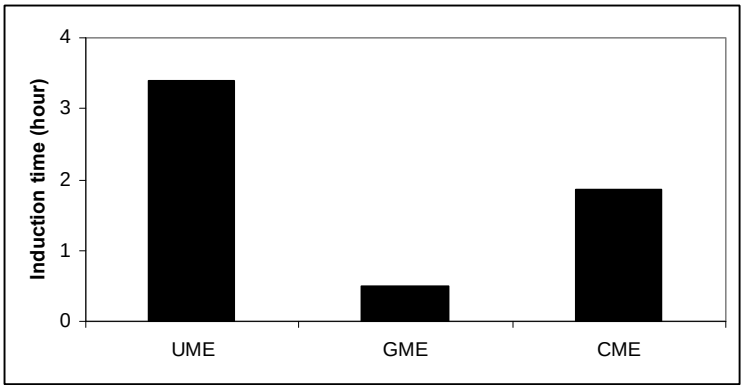

Figure 3.5 Induction time of esters produced from used cooking oil, greenseed canola oil, and RBD canola oil.

3.6. Conclusions

Oxidation derivatives such as various acids and polymerized materials are formed during frying. The formation of such compounds leads to an increase in viscosity and acid value of the frying oil. In addition, the frying process deteriorates the oil's oxidative stability and this is exhibited by the lower induction time of the used oil (12.2 h) as compared to that of the fresh oil (20.5 h). Due to this increase in acid value, the biodiesel yield produced from used oil (95.1%) is lower than that of fresh RBD canola oil (97.3%). Biodiesel yield is even lower (94.8%) when a feedstock with higher acid value such as greenseed canola oil is used (AV = 3.8). This finding suggests that biodiesel yield is reciprocally related to acid value of the corresponding feedstock oil. Oxidative stability of biodiesel is in the order of UME > CME > GME. This is because fatty acid composition is found to be the major factor determining oxidative stability. The used oil has significantly lower level of the highly unstable compound, linolenic acid (C18:3, containing three double bonds), as compared to that contained in RBD canola oil or greenseed canola oil and therefore shows highest oxidative stability.

It is noteworthy that UCO from different sources have different properties such as fatty acid compositions and acid value that potentially cause changes in ester yield and properties. To illustrate this point, UCO from another source (campus cafeteria) was used as feedstock for biodiesel production and the results were discussed in Chapter 4.

Abbreviations

AV	Acid value
CME	Canola oil methyl ester
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GME	Greenseed canola oil methyl ester
HPLC	High performance liquid chromatography
KOH	Potassium hydroxide
ME	Methyl ester
MeOH	Methanol
THF	Tetrahydrofuran
UCO	Used cooking oil
UME	Used cooking oil methyl ester

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CHAPTER 4

Biodiesel Production

from Canola Oil and Used Cooking Oil

A part of this chapter has been published in Chemical Engineering Journal:

- Issariyakul T., Kulkarni M.G., Meher L.C., Dalai A.K., and Bakhshi N.N. Biodiesel production form mixtures of canola oil and used cooking oil. Chemical Engineering Journal 140: 77-85 (2008).

In addition, a portion of this chapter was presented in the following conferences:

- Issariyakul T., Kulkarni M.G., Meher L.C., and Dalai A.K. Biodiesel Production form Canola Oil and Used Cooking Oil with Methanol and Ethanol. Auto21 Network Centre of Excellence, Highly Qualified People Poster Competition, Windsor, Ontario, Canada (2007).
- Issariyakul T., Kulkarni M.G., Dalai A.K. and Bakhshi N.N. Biodiesel from Waste Cooking Oil. The University of Saskatchewan Research Day, Saskatoon Saskatchewan, Canada (2008).

Contribution of the Ph.D. Candidate

Experiments were conducted by Titipong Issariyakul. The content in this chapter was written by Titipong Issariyakul with discussions and suggestions provided by Drs. M.G. Kulkarni, L.C. Meher, Ajay Dalai, and N.N. Bakhshi.

Contribution of this Chapter to the Overall Ph.D. Research

It was found from the last chapter that biodiesel content is reduced when used cooking oil is employed as feedstock. In addition, biodiesel obtained from used cooking oil has inferior quality due to the higher glyceride content. In this chapter, attempts are made to improve biodiesel content and quality by means of an addition of canola oil to the used cooking oil feedstock. Ethanol is also used in transesterification in comparison with methanolysis. In addition to ester content, other important fuel characteristics such as viscosity, acid value, water content, heating value are evaluated with special emphasis on low temperature property of biodiesel.

4.1. Abstract

Used cooking oil (UCO) was mixed with canola oil at various ratios in order to make use of used cooking oil for production of biodiesel and also lower the cost of biodiesel production. Methyl and ethyl esters were prepared by means of KOH-catalyzed transesterification from the mixtures of both the oils. Water content, acid value and viscosity of most esters met ASTM standard except for ethyl esters prepared from used cooking oil. Canola oil content of at least 60% in the used cooking oil/canola oil feedstock is required in order to produce ethyl ester satisfying ASTM specifications. Although ethanolysis was proved to be more challenging, ethyl esters showed reduced crystallization temperature (-45.0°C to -54.4°C) as compared to methyl esters (-35.3°C to -43.0°C). A somewhat better low-temperature property of ester was observed at higher used cooking oil to canola oil ratio in spite of similar fatty acid compositions of both oils.

4.2. Introduction

Biodiesel is a well known alternative, renewable fuel which provides less harmful emissions when compared with the conventional fossil-based diesel fuel. The most common method to produce biodiesel is transesterification of vegetable oils or animal fats with a short-chain alcohol [1]. High purity methyl ester can be achieved by transesterification of fresh vegetable oils with methanol in presence of an alkaline catalyst [2,3]. Transesterification of canola oil (CO) produces ester whose properties are comparable with those of conventional diesel fuels [3]. It has also been reported that the lubricity of diesel fuel can be enhanced by 60% with the addition of 1 vol.% canola-derived methyl ester [4].

However, the main drawback of this fuel is the high cost of feedstock which leads to the high price of biodiesel. A comparison of biodiesel price with that of diesel fuel can be used to depict severity of economic barrier of biodiesel. According to S&T Consultants Inc. and Meyers Norris Penny LLP [5], in 2004, the price of biodiesel in the United States, on average, was 2.22 US$/US gallon while diesel fuel cost at 1.21 US$/US gallon. This economical factor has been undermining biodiesel business for decades.

In more recent years, attempts to utilize used cooking oil (UCO) as a feedstock for biodiesel production have been made to overcome the economic problem. The cost of yellow grease, which is 16.5 ¢/lb, is lower than that of canola oil, which is 34 ¢/lb [6]. However, due to high free fatty acids (FFA) and water content in used cooking oils, they cannot be directly transesterified using an alkaline catalyst, which otherwise, gives low yield and low quality of biodiesel. This is because the side saponification reaction consumes catalyst and generates soap which causes problems in producing high quality biodiesel. Transesterification of used cooking oils with an alkaline catalyst can be done only when the FFA and water content have been removed through different pre-treatment processes [7,8]. Alternatively, acid catalyst may be used instead of base catalyst in order to prevent the emergence of this saponification [9]. However, this approach requires a longer reaction time, a higher operating temperature, and an acid-resistible reactor. It is obvious that exploitation of used cooking oils requires a more sophisticated technology and a more complicated process, which increase the cost of biodiesel production process.

Even though several attempts have been made to produce biodiesel from various fresh vegetable oils and used cooking oils, the combination of these two sources as feedstock for biodiesel production is relatively unexplored. It was anticipated that the addition of fresh

vegetable oil, i.e., canola to used cooking oil would improve yield and quality of biodiesel produced from direct alkali-catalyzed transesterification. The purpose of this study is to optimize canola to used cooking oil ratio to produce high yield and quality biodiesel while maintaining a simple and low cost alkali-catalyzed transesterification process. This study could provide an alternative means to make use of UCO for a low-cost biodiesel production process.

4.3. Materials

UCO was obtained from the campus cafeteria, University of Saskatchewan, Saskatoon, Canada. Commercial grade canola oil (CO) was purchased from a local grocery store. The characteristics of these oils are discussed in Section 4.5.1. Anhydrous methanol (MeOH) (99.8%) and potassium hydroxide (KOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany. Anhydrous ethanol (EtOH) was obtained from Commercial Alcohol Inc., Brampton, Ontario, Canada. Sulfuric acid (H_2SO_4) was procured from EM Science, Darmstadt, Germany. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were purchased from Sigma-Aldrich, MO, USA.

4.4. Experimental Procedures

4.4.1. Transesterification

Canola oil methyl ester (CME), canola oil ethyl ester (CEE), used cooking oil methyl ester (UME), and used cooking oil ethyl ester (UEE) were produced by means of KOH-catalyzed transesterification from a 100 g of feedstock. The same method was also used for the production of methyl and ethyl ester from mixed feedstock. In the present work, 80:20, 60:40, 40:60, 20:80 ratio of UCO and CO was used to produce 80UME (methyl ester produced from 80 g of UCO

and 20 g of CO), 60UME (methyl ester produced from 60 g of UCO and 40 g of CO), 40UME (methyl ester produced from 40 g of UCO and 60 g of CO), and 20UME (methyl ester produced from 20 g of UCO and 80 g of CO), respectively. Ethyl esters were also produced from the same set of feedstock. The feedstock was initially placed in a Parr reactor (Parr Instrument Company, Illinois, USA) and heated to 50°C at atmospheric pressure. A mixture of alcohol (methanol or ethanol at 6:1 alcohol to oil molar ratio) and KOH (1 wt.% with respect to oil) was then added to the reactor. The temperature and stirring speed of the reaction mixture were maintained constant for 2 hours at 50°C and 600 rpm, respectively.

After the reaction, the transesterification product was allowed to stand in a separating funnel for glycerol separation. Due to a strong emulsion in the case of ethanolysis products, glycerol was not separated only by gravity. In order to separate glycerol from ethyl ester phase, approximately 10 g of pure glycerol was added into the transesterification product and the separatory funnel was shaken vigorously and the product was allowed to stand. Glycerol layer separated from ester layer within an hour.

To avoid the formation of emulsion, tannic acid solution (0.1 wt.%) was used in the washing step, thereby neutralizing the excess base catalyst. The pH of washing water was measured by pH-indicator strips from EMD Chemicals Inc., Gibbstown, N.J. throughout the washing process. The pH of washing water was initially very high at approximately 10 due to dissolved KOH. After 7-8 times of washing, the washing water became clear and its pH was approximately 7.7. The washing process was continued until the approximate pH of 7 was achieved.

Unreacted methanol and water was removed using BÜCHI rotavapor at ~90°C. The process was continued until the constant weight was observed. Biodiesel was finally passed

through the anhydrous sodium sulphate, which was previously dried in an oven at 100°C for 1 hour, to remove traces of moisture.

4.4.2. Characterization

The percentage of triglyceride, diglyceride, monoglyceride, and ester were analyzed by Gel Permeation Chromatography (GPC) using a Hewlett-Packard 1100 series HPLC with refractive index detector and two Phenogel (5μ 100A 300X7.80 mm) columns in series protected with guard column. The data were collected by ChemStation software, Agilent Technologies. Tetrahydrofuran (THF) was used as a mobile phase at 1 mL/min for 25 min. The operating parameters were as follows: injection volume 5 μL; column temperature 24°C; and detector temperature 35°C. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were used for the calibration (see Appendix A). The esters were characterized for their properties such as water content (AOCS Ca 2e-84), acid value (AOCS Te 1a-64), heating value (ASTM D240-92), density (ASTM D5002-94), viscosity (ASTM D2500), and fatty acid compositions (AOCS Ce 1-62).

Thermal analysis of biodiesel esters was performed by a Differential Scanning Calorimeter (DSC) from PerkinElmer, Inc., Connecticut, U.S.A. equipped with Pyris software thermal analysis and a cryofill filled with liquid nitrogen as a cooling device. The rate of cooling and heating can cause major differences in calorimetric peaks and traces in a DSC thermogram. This is because different shape of biodiesel crystal, thus different peak position can be formed as a result of different cooling rate. In the present work, a standard cooling rate of 5°C/min [4,10] was used. The program used for thermal analysis was set as follows: 1) hold at 30°C for 5 min;

2) cool from 30°C to -80°C at 5°C/min; 3) hold at -80°C for 5min; and 4) heat from -80°C to 30°C at 5°C/min.

4.5. Results and Discussions

4.5.1. Feedstock Analysis

Saponification value (SV) is the mg KOH required to saponify 1 g of oil. Number of mole of oil was approximated from SV and average molecular weight of oil was then calculated from mass of oil divided by number of mole of oil. The saponification value of CO and UCO was 193.0 and 178.4, respectively. Based on saponification value, molecular weight of feedstock with 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 UCO to CO ratio were 943, 929, 915, 900, 886, and 872 g/mol, respectively. It is believed that the higher molecular weight of UCO was due to the formation of polymerized compounds such as polymerized triglycerides during the frying process [11]. The frying process contributed to the formation of FFA, which can be demonstrated in terms of acid value (AV). The acid value of UCO was 2.5 mgKOH/g while that of CO was significantly lower (0.4 mgKOH/g). Figures 4.1a and 4.1b show HPLC chromatograms of CO and UCO, respectively. It can be seen that CO composed mainly of triglyceride (16.2 min) and trace amounts of diglyceride (16.9 min) while UCO composed of triglyceride, diglyceride, and monoglyceride (18.4 min). Diglyceride and monoglyceride were probably products of triglyceride decomposition during the frying process. In addition, a small peak at 14.7 min in UCO chromatogram indicates existence of molecules with higher molecular weight than that of triglyceride. Such compounds might be polymerized compounds. These compounds affect overall properties of UCO such as molecular weight and viscosity.

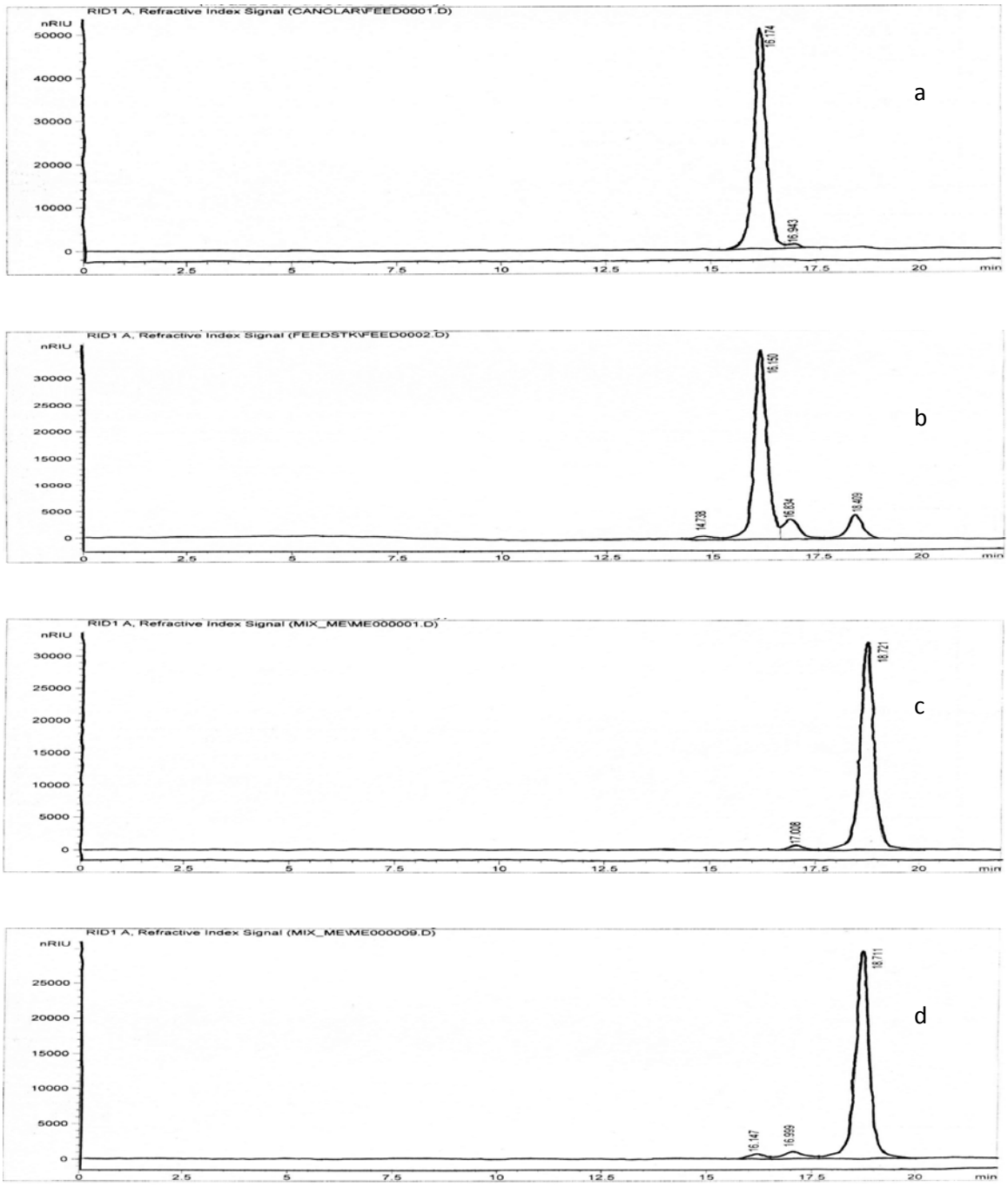

Figure 4.1 HPLC chromatograms: a) canola oil; b) used cooking oil;

c) canola oil methyl ester; d) used cooking oil methyl ester.

The higher AV and viscosity of UCO compared to those of CO as shown in Table 4.2 suggest that the quality of UCO is lower than that of fresh CO.

4.5.2. Product Analysis

Feedstock for this study were various mixtures of UCO and CO with UCO to CO weight ratio of 100:0, 80:20, 60:40, 40:60, 20:80, 0:100. All feedstock were transesterified with methanol and ethanol. Figures 4.1c and 4.1d show HPLC chromatograms of CME and UME, respectively. The chromatogram of CME (see Figure 4.1c) does not show a peak of triglyceride at 16.1 min. The disappearance of triglyceride peak in chromatogram of CME indicates the complete conversion of triglyceride to an ester. However, a peak of triglyceride is present in UME chromatogram (see Figure 4.1d) indicating incomplete transesterification due to interference of saponification. The saponification occurred due to the reaction of free fatty acid present in feedstock with base catalyst producing soaps. These soaps interfere with the separation of glycerol and also induce emulsion afterward. Glycerol is not detected in biodiesel indicating complete glycerol separation from esters. Ester percentages in the biodiesel as analyzed by the HPLC are shown in Figure 4.2. The ester percentage in both methyl and ethyl ester tend to increase with CO percentage in feedstock mixture. These results strengthen our hypothesis that the addition of CO would help to improve biodiesel yield.

The amounts of ester collected from each experiment are shown in Figure 4.3a. Reproducibility of the recovery of esters is ~5%. In comparison with methyl ester yield obtained from pure UCO feedstock, the higher methyl ester yield was obtained with the addition of CO to the feedstock mixture. In the case of ethyl ester, a higher amount of CO (at least 60 wt.%) was required to improve ethyl ester yield. Considering UCO, the lower ester yield was observed due

to the fact that UCO was a compilation of various compounds such as triglyceride, diglyceride, and monoglyceride. Therefore, a 100 g of UCO contains less moles of triglyceride when compared to a 100 g of CO.

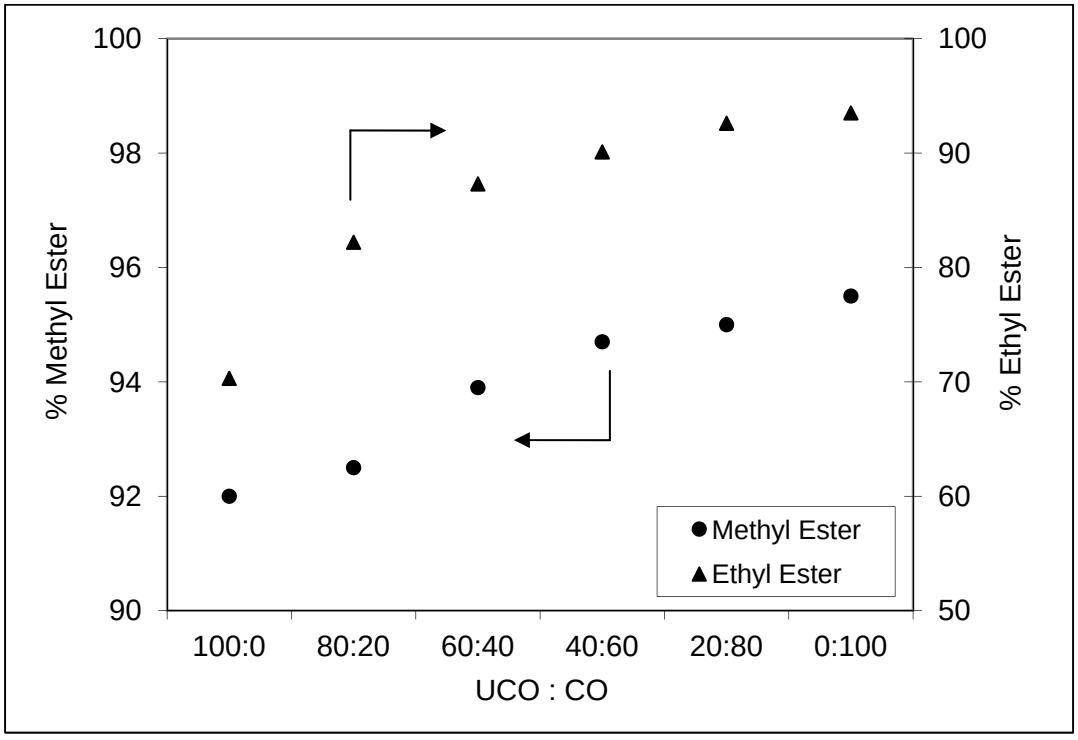

Figure 4.2 Ester percentage as analyzed by HPLC analysis: ● methyl ester; ▲ ethyl ester (reaction conditions: alcohol to oil ratio 6:1, temperature 50°C).

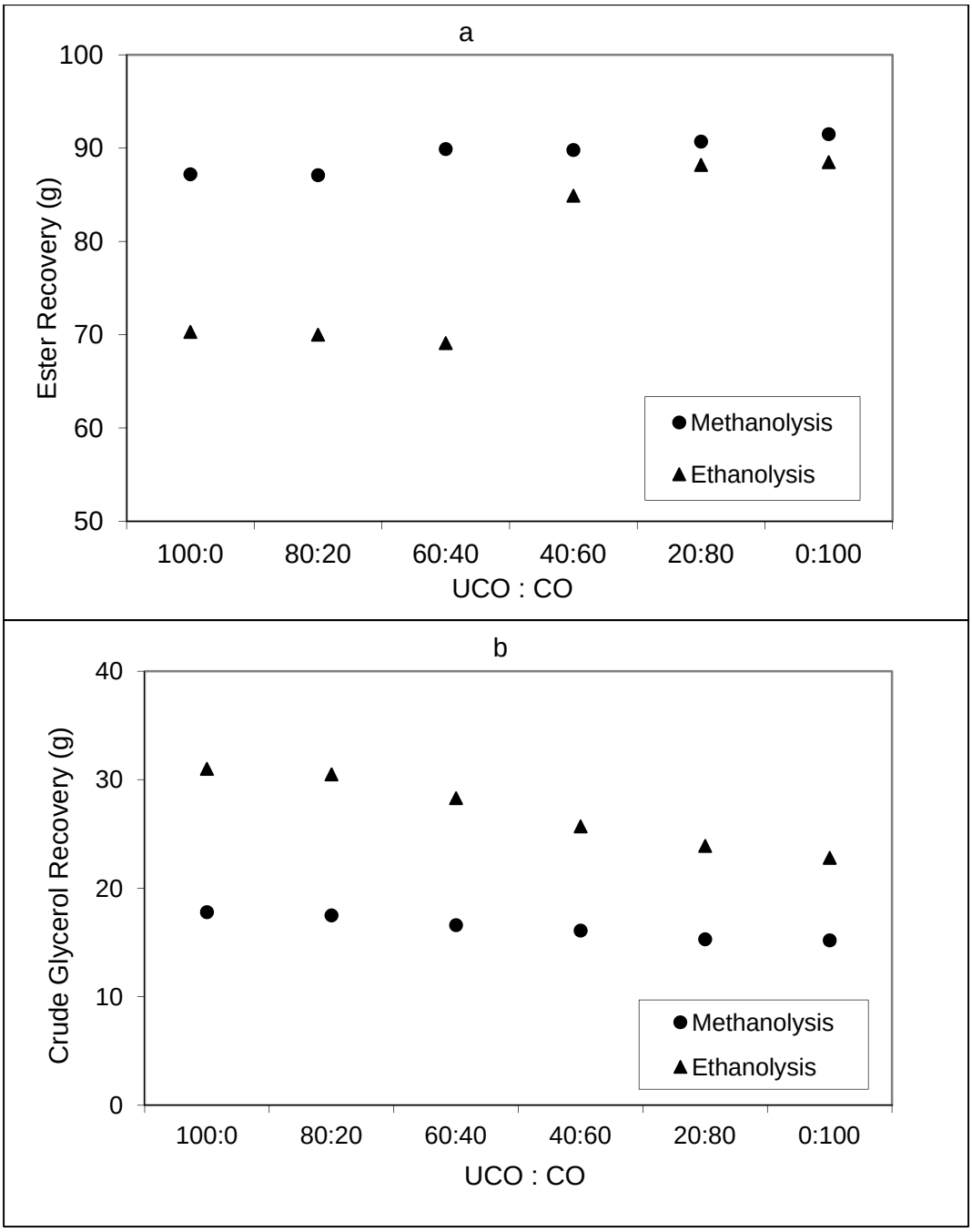

Figure 4.3 Amounts of ester and glycerol collected from transesterification of 100 g of feedstock: a) ester recovery; b) glycerol recovery; ● methanolysis; ▲ ethanolysis (reaction conditions: alcohol to oil ratio 6:1, temperature 50°C).

Diglyceride and monoglyceride contained in UCO have higher glycerol to acyl-group molar ratio than triglyceride (glycerol to acyl-group molar ratio of triglyceride, diglyceride, and monoglyceride are 0.33, 0.5, and 1, respectively). As a result, the same amount of feedstock containing mainly triglyceride (CO) would have more moles of acyl-group than that containing a mixture of triglyceride, diglyceride and monoglyceride (UCO). Theoretically, one mole of acyl-group gives one mole of biodiesel ester, therefore the higher yield of esters was observed at a lower UCO to CO ratio. Dmytryshyn et al. [2] also reported a low ester yield (approximately 50 – 60%) when UCO was used as a feedstock.

Figure 4.3b displays the amount of glycerol collected at different UCO to CO ratios. Although less ester yield was obtained at higher UCO to CO ratio, the glycerol recovery was opposite to this trend. Based on the concept of glycerol to acyl-group molar ratio in feedstock, a 100 g of UCO would have more moles of glycerol group than a 100 g of CO. Therefore, glycerol was collected at a larger amount when a higher UCO to CO ratio was used as a feedstock.

The percentage of tri-, di-, and monoglyceride in each ester are presented in Table 4.1. The percentage of these acylglycerols in ester phase increased as amount of UCO in feedstock increased. This observation is predictable as Table 4.2 shows that UCO has higher acid value thus higher free fatty acid content compared to CO. Alkali catalyst (KOH) was consumed by reacting with free fatty acid to form soap, which leads to lower conversion and consequently higher level of acylglycerols. The higher amount of these glycerides in ethyl esters compared to methyl esters indicates lower glyceride conversions in case of ethanolysis than that of methanolysis. This is due to the higher methanol reactivity towards transesterification as compared to ethanol [12].

Table 4.1 Triglyceride, diglyceride, and monoglyceride percentage in esters.

Type of ester	Triglyceride (wt.%)	Diglyceride (wt.%)	Monoglyceride (wt.%)	Total glycerin (wt.%)
UME	1.6	3.4	1.3	1.0
80UME	1.3	3.1	1.2	0.9
60UME	0.3	2.5	1.1	0.7
40UME	0.0	2.5	1.1	0.7
20UME	0.0	2.1	1.1	0.6
CME	0.0	1.7	0.9	0.5
UEE	8.5	11.3	9.3	5.0
80UEE	3.9	7.1	6.5	3.1
60UEE	2.5	5.4	5.5	2.5
40UEE	1.3	3.9	4.6	1.9
20UEE	0.6	2.9	3.6	1.4
CEE	0.0	2.3	3.1	1.2

Table 4.2 Characteristics of esters.

Type of ester	Water content (% vol.)	Heating value (MJ/kg)	Density (g/cm^3)	Viscosity @40°C (mm^2/s)	Acid value (mgKOH/g)
UME	0.03	39.1	0.86	4.9	0.5
80UME	0.03	39.2	0.86	4.9	0.4
60UME	0.02	39.6	0.86	4.8	0.4
40UME	0.03	39.5	0.86	4.6	0.4
20UME	0.04	40.0	0.86	4.6	0.4
CME	0.05	39.1	0.86	4.4	0.5
UEE	0.07	39.3	0.87	8.8	1.5
80UEE	0.04	39.6	0.86	6.4	1.2
60UEE	0.03	39.8	0.86	5.8	1.0
40UEE	0.03	39.7	0.86	5.5	0.5
20UEE	0.04	40.2	0.86	5.1	0.4
CEE	0.04	40.3	0.86	4.9	0.5
Canola oil	--	39.7	0.90	38.2	0.4
Used cooking oil	0.02	--	0.90	44.7	2.5
Summer diesel fuel	--	45.5	--	--	0.002
ASTM	0.05 max	--	--	1.9 - 6.0	0.5 max

Total glycerin content (GL_T) is defined as $GL_T = GL + 0.26(MG) + 0.15(DG) + 0.1(TG)$ [13]. GL_T of the prepared esters are above the ASTM limit (0.24% max) suggesting that purification of these esters is required. The purification process will be discussed in Section 4.5.4.

4.5.3. Characterizations of the Esters

The esters obtained from transesterification were characterized and their properties are presented in Table 4.2. Water content of all esters met ASTM standard except for ethyl ester prepared from UCO. The densities of all esters were considerably lower than those of their parent oils and were not significantly related to UCO to CO ratio. Acid value of all methyl esters met the ASTM standard. In contrast, acid value of UEE was very high at 1.5 mgKOH/g and did not meet the ASTM standard. This might be due to the un-reacted FFA in UCO. However, with the addition of CO up to 60% in the feedstock, the acid value of ethyl ester was reduced to 0.5 mg KOH/g, which meets the ASTM standard. The viscosities of both CO and UCO were very high at 38.2 and 44.7 mm^2/s, respectively. Viscosities of esters were significantly lower than those of their parent oils and met the ASTM standard (with an exception of some esters). Viscosity of esters decreased with a decrease in UCO to CO ratio as UCO itself was more viscous than CO. The viscosity of UEE was very high and did not meet the standard. This is due to lower reactivity of ethanol as compared to methanol [12] resulting in the presence of unconverted acylglycerols. Low ester percentage in UEE as shown in Figure 4.2 helps to strengthen this concept. The ester content can be improved by the addition of CO in the feedstock. By adding CO up to 40%, an ethyl ester with a satisfiable level of viscosity at 5.8 mm^2/s was obtained. The further reduction of viscosity can be accomplished if more CO was used in the feedstock. Heating values of all esters were approximately the same value, which are

roughly 10% lower than that of the reference diesel fuel. These results are in substantial agreement with those reported in the literature [3].

Table 4.3 shows boiling points of each biodiesel esters, their corresponding feedstock, and a reference diesel fuel. The boiling points at 90% off of feedstock were very high (654.2°C for CO and 726.9°C for UCO). The boiling points of UCO were higher than that of CO due to its high molecular weight constituent such as polymerized acylglycerols. When transesterification was carried out, it is possible for these polymerized compounds to give rise to polymerized esters which have a higher molecular weight and boiling point than a monomer ester. Table 4.3 also showed that esters derived from UCO have higher boiling point than those derived from CO. The boiling points of esters have a tendency to decrease when more CO was used in the feedstock. As expected, boiling points of ethyl esters were obtained at higher value when compared to the corresponding methyl ester. For example, boiling point at 90% off of CME was 365.3°C while the corresponding boiling point for CEE was observed at 372.8°C. This is because ethyl ester generally has higher molecular weight and boiling point as compared to methyl ester. The unusual high boiling point of UEE is due to presence of unconverted acylglycerols as a result of incomplete transesterification as discussed earlier.

4.5.4. Ester Purification

The ester percentages in ethyl esters are less than those of methyl esters as shown in Figure 4.2. The ethyl esters were purified by means of column chromatography as described by Meher et al. [14]. After purification, ethyl esters showed improvement in ester percentage with decrease in total glycerin content (GL_T) as presented in Table 4.4.

Table 4.3 Boiling point distribution (°C) of esters.

%off	10	20	30	40	50	60	70	80	90
UCO	610.3	617.5	625.2	635.3	648.1	664.3	683.6	704	726.9
CO	599.7	606.3	608.8	611.8	615	619	624.8	635.2	654.2
UME	355.7	358.2	359.9	361.2	362.3	363.2	364.2	365.9	409.3
80UME	357.5	361.2	363.6	365.5	367.1	368.6	369.8	370.9	372.1
60UME	357	360.7	363.2	365.1	366.8	368.2	369.5	370.6	371.8
40UME	355.5	358	359.5	360.7	361.7	362.6	363.5	364.3	365.6
20UME	355	357.6	359.2	360.5	361.6	362.6	363.5	364.3	365.2
CME	354	355.7	356.7	357.6	358.4	359	359.6	360.2	365.3
UEE	363.9	365.3	366.4	367.3	370.8	515.7	600.6	611	639.4
80UEE	363.8	365.6	366.8	367.8	368.6	369.3	370	389	542.7
60UEE	363.3	364.9	365.9	366.8	367.5	368.1	368.7	369.6	426.1
40UEE	364.8	367.3	368.9	370.2	371.3	372.2	373.1	374.6	416.9
20UEE	364.4	366.6	368.1	369.3	370.2	371.1	371.9	372.6	373.6
CEE	364.3	366.3	367.7	368.8	369.7	370.5	371.2	371.9	372.8
Diesel fuel	175	185	195	218	242	260	285	320	365

Table 4.4 Characteristics of purified ethyl esters.

Type of ester	Ester content (wt.%)	Total glycerin (wt.%)	Acid value (mgKOH/g)	Viscosity @40°C (mm^2/s)
UEE (prior to purification)	70.3	5.0	1.5	8.8
UEE	89.4	1.18	0.5	3.1
60UEE	95.7	0.54	0.5	2.0
40UEE	97.7	0.35	0.6	2.7
CEE	96.5	0.47	0.5	2.5

The acid values and viscosities of the purified esters reduced significantly. This is due to the improvement of the purity of ethyl esters after purification of the esters.

4.5.5. Thermal Analysis by Differential Scanning Calorimetry (DSC)

The low-temperature flow property of biodiesel is very important for its use in a cold-climate country. This is because when a blended diesel fuel is used at a low temperature, the biodiesel portion of the blend crystallizes and separates out from diesel fuel. This crystal can create problems to engine flow system, undermine engine operation, and eventually cause engine to stop running. Therefore, a satisfactory attribute of biodiesel low-temperature properties should be warranted prior to its commercial use. Such property is conventionally characterized by cloud point (CP) and pour point (PP).

More recently, DSC has been used to determine the low-temperature property of biodiesel [4]. Each fatty acid ester such as palmitic methyl ester, stearic methyl ester, oleic

methyl ester, etc. is miscible with each other at room temperature and therefore shows no heat change when mixed. However, crystallization or polymorphic transition (a change in structural geometry when solid) of a given ester could exhibit heat change, which is possible to monitor using a DSC. It is reported in the literature that enthalpy of crystallization of triglycerides can be measured using a DSC [15]. In addition, it has been also reported that polymorphic transition of triglyceride usually occurs after a melting of the first habit (a shape of crystal). Lee et al. [10] reported that branched-chain esters have lower crystallization temperature than that of conventional straight-chain esters. They reported a good correlation between crystallization temperature measured by a DSC and CP and PP of the biodiesel samples.

In this study, a typical DSC thermogram of CME is shown in Figure 4.4 and fatty acid compositions of CME and UME are presented in Table 4.5. The top and bottom curves in Figure 4.4 are heating and cooling curves, respectively. Fatty acid composition in Table 4.5 is used to explain the DSC results, which is discussed as follows. The initial concentration of a given fatty acid methyl ester (palmitoleic methyl ester, oleic methyl ester, linoleic methyl ester, etc.) in CME was lower than its saturated concentration at 30°C, thus crystallization is not possible. When the sample temperature was reduced, the saturated concentration and solubility of each component was also reduced. At a certain point, the saturated concentration reduced to the point lower than its actual concentration, thereby making crystallization of the corresponding component possible [16]. The major peak at -35.3°C appeared as a result of exothermic crystallization of monounsaturated fatty acid methyl esters. These esters were a major portion of CME as GC analysis showed a result of 63.2%. The small peak right after exothermic crystallization of monounsaturated fatty acid methyl ester at -40.7°C was probably due to its

polymorphic transition. It is well known that unsaturated ester crystallized at lower temperature than saturated ester. This is because they have different three-dimensional conformations.

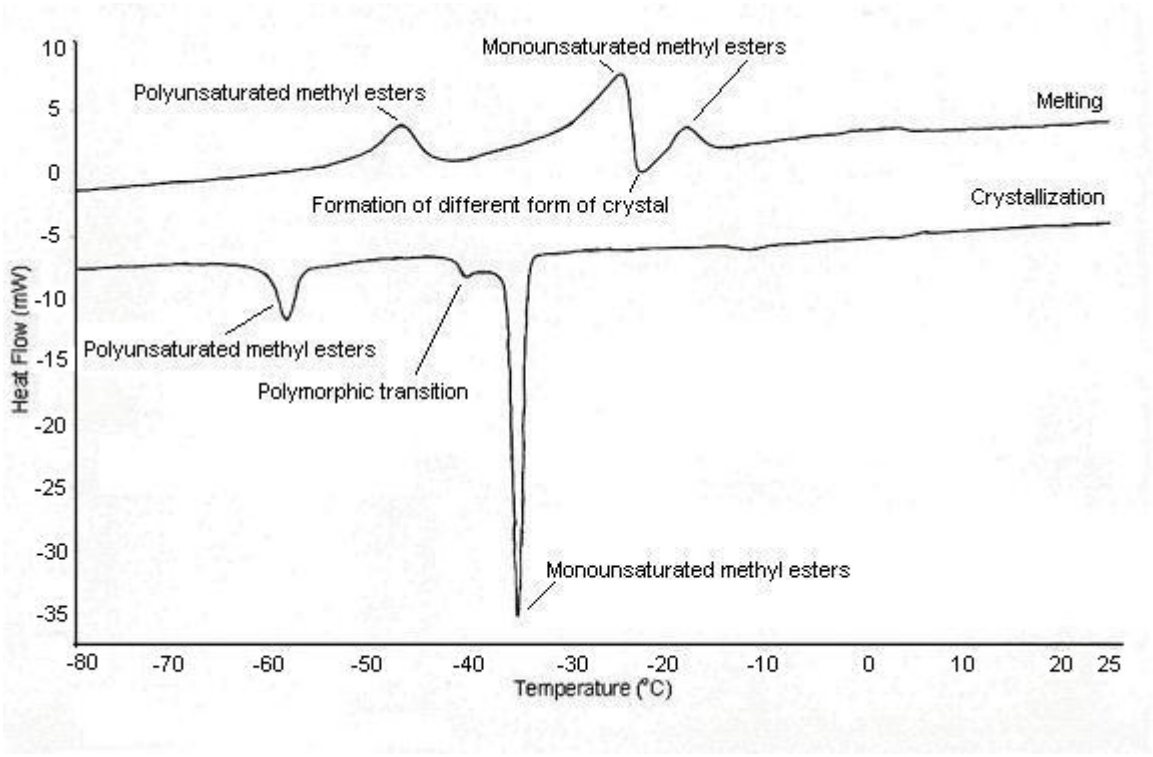

Figure 4.4 Typical DSC thermogram of canola oil methyl ester.

Table 4.5 Fatty acid compositions of canola oil methyl ester and used cooking oil methyl ester.

Structure	Compound name	Percentage in canola oil methyl ester	Percentage in used cooking oil methyl ester
C14:0	Myristic methyl ester	0.05	0.08
C16:0	Palmitic methyl ester	4.23	5.31
C16:1 z7	n/a[a]	0.03	0.04
C16:1 z9	Palmitoleic methyl ester	0.23	0.36
C16:2	n/a[a]	0.07	0.06
C16:3	n/a[a]	0.11	0.10
C18:0	Stearic methyl ester	1.89	2.76
C18:1 z9	Oleic methyl ester	57.75	56.94
C18:1 z11	Asclepic methyl ester	3.58	2.17
C18:2	Linoleic methyl ester	19.09	19.03
C18:3	Linolenic methyl ester	8.71	6.54
C20:0	Arachidic methyl ester	0.67	0.67
C20:1 z5	n/a[a]	0.04	0.10
C20:1 z11	Gondoic methyl ester	1.37	1.42
C20:2	n/a[a]	0.14	0.16
C22:0	Behenic methyl ester	0.36	0.36
C24:0	Lignoceric methyl ester	0.04	0.14
C24:1 z15	Tetracosenoic methyl ester	0.18	0.17
C26:0	Hesacosanoic methyl ester	0.04	0
Total saturated fatty acid		7.27	9.32
Total monounsaturated fatty acid		63.17	61.20
Total polyunsaturated fatty acid		19.41	19.34

[a]n/a = not available

Saturated ester molecules are in its minimum energy when fully extended and are well stacked, thereby strengthening intermolecular attraction force [17]. Unlike saturated ester, especially cis-formation, unsaturated ester molecules have weaker intermolecular interactions and therefore crystallize at a lower temperature. This explains exothermic crystallization of polyunsaturated fatty acid methyl esters at lower temperature of -58.6°C. These observations are consistent with those reported in the literature in which crystallization temperature of saturated compounds were higher than that of unsaturated compounds [4]. Endothermic peaks on the heating curve at -47.0°C and -24.6°C represent melting point of polyunsaturated and monounsaturated fatty acid methyl ester crystals, respectively. These crystals melted at temperature above their corresponding crystallization temperature. This finding conforms with those found in literature indicating that the melting temperature is higher than crystallization temperature of the same component [4,15]. After the melting of monounsaturated fatty acid methyl ester crystal, a different crystal shape of the same component can be formed. This behaviour is shown by exothermic crystallization peak at -22.6°C on the heating curve. Another endothermic peak at -17.8°C is due to melting of the recently formed crystal of methyl ester. A similar behaviour has been reported in the literature [15].

Figure 4.5 displays comparative cooling DSC thermograms of UME, 40UME, and CME, respectively. The major crystallization temperature of UME (-43°C) is lower than that of CME (-35.3°C). As discussed earlier, these peaks represent monounsaturated fatty acid methyl ester of each UME and CME. The literature suggests that crystallization temperature of linear, long-chain esters decrease with increase in the carbon chain length if number of double bond is the same [4]. The comparison has been made for samples with different fatty acid compositions (esters from canola oil and rapeseed oil) and the difference of the peak temperature was obvious

(>20°C). In this study, the chain length difference between monounsaturated fatty acid methyl ester of UME and CME is trivial and so does the peak temperature difference.

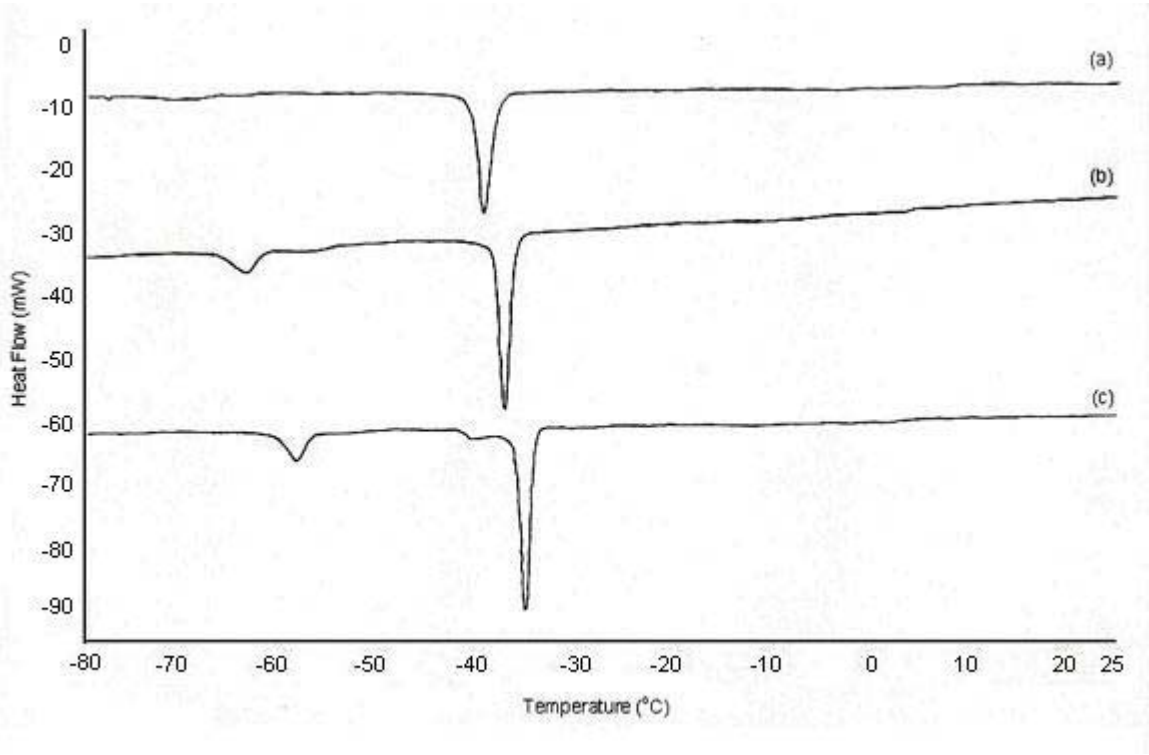

Figure 4.5 Cooling curves of DSC thermogram:

a) used cooking oil methyl ester; b) 40:60 UCO:CO methyl ester; c) canola oil methyl ester.

Polymerized methyl ester in UME is another possible reason contributed to this difference. It is possible for a polymerized methyl ester to form a crystal shape such that is having a poor molecular stacking and poor intermolecular interactions. A detailed study is required to acquire a better understanding on this phenomenon. The major peak temperature of 40UME fell between those of UME and CME. This is because 40UME was produced from a mixture of UCO and CO.

Table 4.6 summarizes major peak temperature and total heat associated with melting and crystallization of esters. As expected, ethyl esters have lower major peak temperature than

methyl esters. This is a typical observation as ethyl esters are known to have a lower cloud point than methyl ester [3].

Table 4.6 Major peak temperature and heat associated to crystallization and melting of esters.

Ester	Major crystallization peak temperature (°C)	Major melting peak temperature (°C)	Total heat associated with crystallization of ester (kJ/kg)	Total heat associated with melting of ester (kJ/kg)
UME	-43.0	-27.8	49.6	55.0
80 UME	-41.1	-27.4	70.4	74.4
40 UME	-37.4	-26.4	71.4	77.4
20 UME	-36.8	-26.2	76.1	78.9
CME	-35.3	-24.6	84.0	88.8
UEE	-54.4	-30.0	38.1	30.6
80 UEE	-51.3	-25.8	48.1	44.6
40 UEE	-45.6	-19.5	51.3	49.0
20 UEE	-45.7	-20.6	58.5	56.1
CEE	-45.0	-19.6	60.2	58.1

The heat associated with crystallization of esters prepared from UCO was lower than that of esters prepared from CO. This might be due to polymerized esters prepared from UCO, which cause an increase in average molecular size of the ester, thereby affecting its total heat of crystallization. The heat associated with crystallization is approximately equivalent to the heat associated with crystal melting. The difference between heat associated with melting and crystallization might be because some polymorphs crystallized or melted during the period of time outside DSC scan. However, those polymorphs are habits of minor components as the calorimetric peaks of major components are presented within the range of DSC scan and the total heat differences were trivial. These findings show that DSC provided an accurate means of monitoring crystallization of biodiesel esters.

4.6. Conclusions

Used cooking oil is an economical feedstock for the production of biodiesel. However, the production process using this feedstock is usually more complicated than that using fresh oil feedstock. Nevertheless, the utilization of used cooking oil for a single step KOH-catalyzed transesterification is possible with addition of a certain amount of canola oil. Methyl and ethyl esters were prepared at different used cooking oil to canola oil ratio and were characterized extensively for their properties. Methanolysis products showed satisfactory properties. In contrast, canola oil of at least 60% was required to achieve a high quality ethyl ester (UCO:CO ratio of 40:60). Based on the feedstock cost discussed in the earlier part, if the feedstock consists of 40% UCO instead of pure canola oil, the feedstock cost will be reduced by ~20%. Due to the reduction of feedstock cost and economical operating cost of a single step transesterification, production of biodiesel from mixture of canola and used cooking oil is a promising alternative.

Although ethanolysis was proved to be more challenging, ethyl ester showed a better low-temperature property. The low-temperature property difference between esters derived from used cooking oil, canola oil and mixtures of both oils were trivial as fatty acid compositions of both oils were similar.

Although the process optimization and ester characteristics using UCO as feedstock were discussed in this chapter, availability of UCO is highly depended on human population and food consumption habit. Therefore, availability of UCO may be fluctuated and other inedible oils may play important role in biodiesel industry. Hence, these inedible vegetable oils should be investigated as potential feedstock for biodiesel. Thus, greenseed canola oil was studied as feedstock for biodiesel production and the results are presented in Chapter 5.

Abbreviations

AV	Acid value
CEE	Canola oil ethyl ester
CME	Canola oil methyl ester
CO	Canola oil
CP	Cloud point
DG	Diglyceride
DSC	Differential scanning calorimeter
EtOH	Ethanol
FFA	Free fatty acid
GL	Glycerol
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
KOH	Potassium hydroxide
MeOH	Methanol
MG	Monoglyceride
PP	Pour point
TG	Triglyceride

THF	Tetrahydrofuran
UCO	Used cooking oil
UEE	Used cooking oil ethyl ester
UME	Used cooking oil methyl ester

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CHAPTER 5

Biodiesel Production from Greenseed Canola Oil

A part of this chapter has been published in Energy & Fuels Journal:

- Issariyakul T., and Dalai A.K. Biodiesel production from greenseed canola oil. Energy & Fuels 24: 4652-4658 (2010).

In addition, a portion of this chapter was presented in the following conferences:

- Issariyakul T., Jacobson K., Dalai A.K. and Bakhshi N.N. Biodiesel from Canola Oil, Greenseed Canola Oil, and Waste Cooking Oil. Auto21 Network Centre of Excellence, Highly Qualified People Poster Competition, Hamilton, Ontario, Canada (2009).

Contribution of the Ph.D. Candidate

Experiments were conducted by Titipong Issariyakul. The content in this chapter was written by Titipong Issariyakul with discussions and suggestions provided by Dr. Ajay Dalai.

Contribution of this Chapter to the Overall Ph.D. Research

Greenseed canola is an off-grade canola that available in Canadian market at low cost due to high chlorophyll content. The main objective is to make use of this low cost greenseed canola oil as feedstock for biodiesel production. The effects of pigments including chlorophyll and pheophytin on transesterification activity as well as biodiesel oxidative stability are investigated in this chapter.

5.1. Abstract

Greenseed canola oil is low grade oil with green colour. Due to the high level of chlorophyll, this oil is considered as “waste product” and cannot be used for edible purposes. In this research, biodiesel was produced from canola oil and greenseed canola oil via KOH-catalyzed transesterification with methanol, ethanol and mixture of methanol and ethanol. The reaction was conducted at 60°C and stirring speed of 600 rpm for 90 minutes. Prior to transesterification, greenseed canola oil was bleached to remove pigments using various adsorbents at different conditions. The optimum bleaching material was found to be montmorillonite K10. The pigment content was reduced from 94 ppm to 0.5 ppm with using 7.5 wt.% of this material at 60°C and stirring speed of 600 rpm for 30 minutes. Biodiesel derived from the treated greenseed canola oil showed an improvement in oxidative stability (induction time = 0.7 h) as compared to that derived from crude greenseed canola oil (induction time = 0.5 h). These pigments, however, did not have a significant impact on transesterification activity.

5.2. Introduction

Biodiesel is an alternative fuel arising from concerns of depleting sources of fossil fuels and environmental issues. Biodiesel properties are comparable to those of fossil-based diesel fuel and it can be produced from animal fats or vegetable oils thus they are renewable. Recently, there are many concerns regarding the use of food crops as feedstock for fuel production. Using crops for energy and food compete with each other in many ways (agricultural land, skilled labour, water, fertilizers etc.) [1,2,3]. Moreover, the high price of biodiesel derived from food-grade vegetable oils makes it difficult to compete economically with the fossil-based diesel. A less expensive, non food-grade vegetable oil is a potential feedstock for biodiesel production.

The present chapter focuses on biodiesel production from greenseed canola oil. Greenseed canola is an immature canola seed. The green colour is present in greenseed due to high level of chlorophyll, which is retained in canola seeds if the seeds are exposed to frost during seed development. According to Canadian Grain Commission (CGC), Canola seeds are graded into 3 catagories. No. 1 Canola is the best quality canola seed which contains less than 2% greenseed containing less than 25 ppm chlorophyll content, and can be sold at C$ 250 per ton. No.2 Canola and No.3 Canola are the lower grade seeds as they contain 26-45 ppm and 46-100 ppm chlorophyll, respectively. The price of No. 2 and No.3 Canola are C$ 225/ton and C$ 190/ton, respectively [4,5]. As the level of chlorophyll content increases, the selling price of the seed drops and it cannot be used for edible purposes. Therefore, greenseed canola oil can be considered as a non-food grade feedstock and can be used for biodiesel production.

Chlorophyll is an effective photoreceptor and can generally be categorized into 2 types: Chlorophyll A (contains $–CH_3$ as its functional group) and Chlorophyll B (contains –CHO as its functional group). For plant growth, these two types of chlorophylls absorb sunlight at slightly different wavelength, thereby complimenting each other in photosynthesis [6]. It is reported that chlorophyll gives adverse effect on oil stability [5]. In addition, chlorophyll can degrade into various compounds depending on the surrounding conditions [7]. In presence of weak acids, magnesium ion is removed and chlorophyll degrades to pheophytin. Chlorophyllase can act as a catalyst for the removal of phytol tail from a chlorophyll molecule to form chlorophyllide. It is reported that chlorophyll derivatives could be converted to compounds that are capable of being prooxidants, thus giving deleterious effect on the stability of vegetable oils [8]. Ward et al. [7] reported that the major pigments contained in canola and greenseed canola are chlorophylls and

pheophytins. In order to remove these pigments, various kinds of clay and activated carbon can be used to adsorb chlorophylls and pheophytins [5,9,10].

The alcohols commonly used in transesterification are short-chain alcohols, i.e., methyl, ethyl, propyl, butyl alcohol. It is reported that the use of mixture of alcohols has certain advantages. When the mixture of methanol and ethanol was used for transesterification, the alcohol-oil solubility was improved by ethanol and the reaction equilibrium was improved by methanol [11]. Although there are several research works in the literature focused on chlorophyll adsorption and biodiesel production from canola oil, information on both technologies combined is scarce. The objectives of this work are to produce biodiesel from greenseed canola oil and to study the effects of pigments on transesterification activity and ester oxidative stability.

5.3. Materials

Greenseed canola oil was provided by Milligan Bio-Tech Inc., Foam Lake, Saskatchewan, Canada. Commercial grade canola oil was purchased from a local grocery store. Montmorillonite K10 and KSF Clay (adsorbent) were obtained from Alfa Aesar, Massachusetts, United States. Activated carbons (adsorbent) were prepared in our laboratory from bio-char obtained from Dynamotive Energy Systems Corp., Vancouver, Canada, Ensyn Corp., Delaware, United States, and Advanced Biorefinery Inc., Ontario, Canada and from char obtained from Luscar Ltd., Alberta, Canada. Anhydrous methanol (MeOH) (99.8%) and potassium hydroxide (KOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany. Anhydrous ethanol (EtOH) was obtained from Commercial Alcohol Inc., Brampton, Ontario, Canada. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were purchased

from Sigma-Aldrich, MO, USA. Fatty acid methyl esters (FAME) mix rapeseed oil reference standard was obtained from SUPELCO, PA, USA.

5.4. Experimental Procedures

Initially, the oil feedstock was analyzed for pigment content and acid value. Experimental procedure for this research includes 3 steps: bleaching of greenseed canola oil, transesterification, and ester characterization.

5.4.1. Bleaching of Greenseed Canola Oil

For bleaching of greenseed canola oil, greenseed canola oil was treated with 8 types of adsorbents. These adsorbents composed of 3 types of clay (Montmorillonite K10, Montmorillonite KSF, Attapulgus Clay) and 5 types of activated carbons (AC) (obtained from Dynamotive Energy Systems Corp., Luscar Ltd. (granular and powder), Ensyn Corp., and Advanced Biorefinery Inc.). In the treatment process, 100 g of greenseed canola oil was placed in a Parr reactor (Parr Instrument Company, Illinois, USA) and the oil was heated slowly. When the oil temperature reached at 60°C, the adsorbent was added to the reactor and the stirring speed was kept constant at 600 rpm. The parameters studied are type of adsorbents (8 kinds as mentioned above), treatment duration (0.5, 1, 1.5, 2 h), and adsorbent loading (1, 2.5, 5, 7.5, 10 wt.% loading). UV-260 Shimadzu spectrometer was used to determine pigments content. The calculation method was described by Lichtenthaler [12]. An attempt has been made to regenerate Montmorillonite K10 using solvent extraction technique [13]. The solvents used in this step include methanol (MeOH), hexane, tetrahydrofuran (THF), and chloroform. Initially, the used clay was mixed with a solvent at 30:70 clay to solvent weight ratio. The mixture was then stirred

at 45°C, 600 rpm for 30 minutes. The liquid portion was separated from solid portion by filtration. These steps were repeated twice prior to drying the clay at 100°C for 24 hours.

5.4.2. Transesterification

For transesterification step, a series of methyl ester and ethyl ester were produced by means of KOH-catalyzed transesterification from a 100 g feedstock, which are canola oil, crude greenseed canola oil, treated greenseed canola oil, mixture of canola oil and treated greenseed canola oil (50 g of canola oil and 50 g of treated greenseed canola oil). Esters from the mixture of methanol and ethanol were also prepared from the same set of feedstocks. A 1% KOH based on the total amount of oil was used in each case as a catalyst. In case of using only one alcohol (methanol or ethanol), the feedstock was initially placed in a Parr reactor and heated to 60°C. Alcohol (6:1 alcohol to oil molar ratio) and KOH (1 wt.% with respect to oil) were then added to the reactor. In case of ester preparation from mixture of alcohols (methanol + ethanol), 3 moles of methanol and 3 moles of ethanol were used for each mole of oil in order to set 6:1 total alcohol to oil molar ratio. The temperature and the stirring speed of the reaction mixture were maintained constant for 1.5 h at 60°C and 600 rpm, respectively.

After the reaction, the transesterification product was allowed to settle in a separating funnel for glycerol separation. Due to strong emulsion in the case of ethanolysis products, glycerol could not be separated only by gravity. In order to separate glycerol from ethyl ester, an approximately 10 g of pure glycerol was added into the transesterification product and the separatory funnel was shaken vigorously and the product was allowed to settle. Glycerol layer was then separated from ester layer within an hour. Distilled water was heated and used in the washing step. A strong emulsion was usually formed in case of ethyl ester preparation. To avoid

the formation of emulsion, tannic acid solution (0.1 wt.%) was used in the washing step, thereby neutralizing the excess base catalyst. Unreacted methanol and water was removed using BÜCHI rotavapor. Biodiesel was finally passed through the anhydrous sodium sulphate, which was previously dried in an oven at 100°C for 1 hour, to remove traces of moisture. All biodiesel produced in this step are shown in Table 5.1.

Table 5.1 Biodiesel samples.

Sample	Alcohol used	Feedstock
CGME[a]	Methanol	Crude greenseed canola oil
TGME[a]	Methanol	Treated greenseed canola oil
CME[a]	Methanol	Canola oil
TGCME[a]	Methanol	Treated greenseed canola oil + canola oil (50:50)
CGEE[a]	Ethanol	Crude greenseed canola oil
TGEE[a]	Ethanol	Treated greenseed canola oil
CEE[a]	Ethanol	Canola oil
TGCEE[a]	Ethanol	Treated greenseed canola oil + canola oil (50:50)
CGMEE[a]	MeOH+EtOH (50:50)	Crude greenseed canola oil
TGMEE[a]	MeOH+EtOH (50:50)	Treated greenseed canola oil
CMEE[a]	MeOH+EtOH (50:50)	Canola oil
TGCMEE[a]	MeOH+EtOH (50:50)	Treated greenseed canola oil + canola oil (50:50)

[a]See abbreviation section

5.4.3. Characterization

For analysis part, the ester phase collected from each experiment was analyzed for ester and glycerides content using a Hewlett-Packard 1100 series HPLC with refractive index detector and two Phenogel 5u 100A 300X7.80 mm 5 micron columns in series protected with guard column, equipped with ChemStation for LC 3D, Agilent Technologies. THF was used as a mobile phase at 1 mL/min for 25 min. The operating parameters used were as follows: injection volume 5 µL; column temperature 24°C; and detector temperature 35°C. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were used for the HPLC calibration (see Appendix A). Fatty acid compositions of esters were determined using Agilent Technologies 6890N Network GC System equipped with GC ChemStation software with FID detector and RESTEK 10638 Stabilwax column. The injection volume was 2 µL and the temperature program was started at 160°C, held for 1 min, ramped to 240°C at 4°C/min and then was held for 24 min. SUPELCO FAME Mix Rapeseed Oil standard was used as a reference for GC calibration (see Appendix B). The oxidative stability of biodiesel was measured as induction time using Metrohm 743 Rancimat instrument. Brookfield DV-I Viscometer was used to measure the viscosity of esters. Sulfur content of biodiesel was determined using Antek N/S Analyzer equipped with Antek model 9000NS combustion analyzer, Antek model 735 controlled rate sample drive, Antek model 740 multi-matrix sample inlet, and Antek model 738 robotic auto-sampler. Acid value and iodine value were determined as per the method AOCS Te 1a-64 and AOCS Tg 1a-64, respectively.

5.5. Results and Discussions

5.5.1. Bleaching

The objective of bleaching of greenseed canola oil is to remove pigments from the oil. The pigments present in the oil are chlorophyll A (ChA), Chlorophyll B (ChB), Pheophytin A (PhA), and Pheophytin B (PhB). Table 5.2 shows initial pigments content and acid value of canola oil and greenseed canola oil. Canola oil has negligible amounts of pigments and acid value while greenseed canola oil has total initial pigment content and acid value of 94 ppm and 3.8 mg KOH/g, respectively. To remove these pigments, greenseed canola oil was bleached according to the process discussed in Section 5.4.1.

Table 5.2 Initial pigment content and acid value in canola oil and greenseed canola oil.

Feedstock	ChA[a] (ppm)	ChB[a] (ppm)	PhA[a] (ppm)	PhB[a] (ppm)	Total (ppm)	AV[a] (mg KOH/g)
Canola oil	0.0	0.1	0.0	0.0	0.1	0
CGO[a]	26.0	2.7	56.6	8.8	94.1	3.8
TGO[a]	0.2	0.0	0.2	0.1	0.5	3.0

[a]See abbreviation section

Table 5.3 shows bleaching performances of various adsorbents selected in this study. Greenseed canola oil was treated at 60°C using 1 wt.% adsorbent loading and stirring speed of 600 rpm for 30 minutes. The reproducibility of this experiment is within ± 3 ppm of total pigment content. Different materials have different pigment adsorption capability.

Table 5.3 Physical properties and performance of various adsorbents for pigment adsorption[a].

Adsorbent	ChA[b] (ppm)	ChB[b] (ppm)	PhA[b] (ppm)	PhB[b] (ppm)	Total (ppm)	% Pigment adsorbed	BET surface area[c] (m^2/g)	Average pore width[c] (A^o)
CGO[b]	26.0	2.7	56.6	8.8	94.1	0	n/a	n/a
Montmorillonite K10	18.2	2.2	39.1	7.3	66.7	29.1	250.1	57.8
Montmorillonite KSF	25.8	3.0	56.5	9.1	94.3	0	1.5	57.4
Attapulgus Clay	25.4	3.0	55.8	8.8	93.1	1.1	n/a	n/a
Dynamotive Energy Systems AC[b]	21.7	3.1	48.8	6.6	80.1	14.9	454.0	23.0
Luscar AC[b] (powder)	18.9	3.3	43.4	5.5	71.2	24.4	312.9	17.1
Luscar AC[b] (granular)	24.2	2.8	53.4	8.1	88.6	5.9	n/a	n/a
Ensyn AC[b]	19.9	12.3	41.6	14.7	88.4	6.1	524.6	21.9
Advanced Biorefinery AC[b]	19.0	3.5	43.1	6.2	71.9	23.6	n/a	n/a

[a]Treatment condition: stirring speed 600 rpm; treatment temperature 60°C; treatment duration 30 mins; adsorbent loading 1% (w/w); [b]See abbreviation section; [c]Analysis was conducted on the bleaching materials

It was found that montmorillonite K10 is the most suitable adsorbent for the bleaching of greenseed canola oil with 29% pigment adsorbed. This is due to the relatively high surface area of K10 as compared to KSF (see Table 5.4). Despite the high surface area of activated carbons (ACs), these materials were not suitable for the removal of pigments from greenseed canola oil due to the narrow pore width of ACs.

Table 5.4 Properties and performance of regenerated montmorillonite K10.

Sample	BET Surface area (m^2/g)	Average pore diameter (A°)	% Pigment adsorbed
MeOH-treated K10	0.8	1774.9	13
Hexane-treated K10	24.2	133.5	31
THF-treated K10	51.3	93.9	53
Chlorform-treated K10	0.2	14.4	12

The effect of treatment duration on greenseed oil is shown in Table 5.5. It was found that the treatment duration of 30 min is sufficient for the bleaching of greenseed canola oil using montmorillonite K10. The increase in treatment duration shows no significant improvement in the bleaching of greenseed canola oil. The effect of percent adsorbent loading on the pigment removal from greenseed oil is shown in Table 5.6. It was found that 7.5 wt.% montmorillonite K10 loading is required for the maximum pigments adsorption from greenseed canola oil. The optimum condition for the bleaching of greenseed canola oil is the use of montmorillonite K10 at 7.5 wt.% loading, at 60°C and stirring speed of 600 rpm and treatment time of 30 min. After the

treatment process, the pigment content of greenseed canola oil was reduced from 94.1 ppm to 0.5 ppm. A minor reduction on acid value of greenseed canola oil was observed (from 3.8 to 3.0, see Table 5.2).

Table 5.5 Performance of montmorillonite K10 at various bleaching durations for pigment adsorption[a].

Treatment duration (hr)	ChA[b] (ppm)	ChB[b] (ppm)	PhA[b] (ppm)	PhB[b] (ppm)	Total (ppm)	% Pigment adsorbed
0	26.0	2.7	56.6	8.8	94.1	0
0.5	18.2	2.2	39.1	7.3	66.7	29.1
1	18.2	3.8	39.1	9.1	69.5	26.1
1.5	17.2	2.2	38.4	4.2	66.9	28.9
2	17.7	2.5	43.3	7.8	65.7	30.1

[a]Treatment condition: stirring speed 600 rpm; treatment temperature 60°C; adsorbent loading 1% (w/w);
[b]See abbreviation section

An attempt was made to regenerate montmorillonite K10 (K10). The spent K10 was regenerated based on the method discussed in Section 5.4.1. The regenerated K10 was analyzed for the BET surface area and average pore width using BET analysis. The regenerated K10 was then reused to remove pigments from greenseed oil using 7.5 wt.% loading, stirring speed of 600 rpm, at treatment temperature of 60°C for 30 min. The performance of regenerated K10 is shown in Table 5.4. Due to its relatively high BET surface area, the THF-treated K10 exhibited the highest pigments adsorption performance (53%) among all the regenerated K10.

Table 5.6 Performance of montmorillonite K10 at various percent loading for pigment adsorption[a].

% Adsorbent loading	ChA[b] (ppm)	ChB[b] (ppm)	PhA[b] (ppm)	PhB[b] (ppm)	Total (ppm)	% Pigment adsorbed
0	26.0	2.7	56.6	8.8	94.1	0
1	18.2	2.2	39.1	7.3	66.7	29.1
2.5	7.7	1.5	14.8	5.1	29.1	69.1
5	2.0	0.7	3.2	2.1	8.0	91.5
7.5	0.2	0.0	0.2	0.1	0.5	99.5
10	0.2	0.0	0.2	0.1	0.5	99.5

[a]Treatment condition: stirring speed 600 rpm; treatment temperature 60°C; treatment duration 30 mins;
[b]See abbreviation section

Although greenseed canola oil was removed from the spent K10, chlorophyll was not entirely removed from this bleaching material. A significant drop in pigments adsorption capability of these regenerated K10 is observed.

5.5.2. Transesterification

For biodiesel production, all vegetable oils were transesterified using the method discussed in Section 5.4.2. Figure 5.1 shows the ester formation during transesterification reaction at 50 and 60°C. Each experiment was conducted twice and the solid lines represent the average values from observed values. It is clear that reaction at 60°C is faster than that performed at 50°C and the reaction duration of 90 min is sufficient to complete the reaction. The error bars shown in Figure 5.1 indicate that the reproducibility of this experiment is within 1%.

Table 5.7 shows the percentage of triglyceride, diglyceride, monoglyceride and ester as well as percent ester recovery. Triglyceride, diglyceride, monoglyceride and ester percentage were determined using HPLC and percent ester recovery was defined as the ratio of the amounts of ester phase recovered to the amounts of the feedstock multiply by 100.

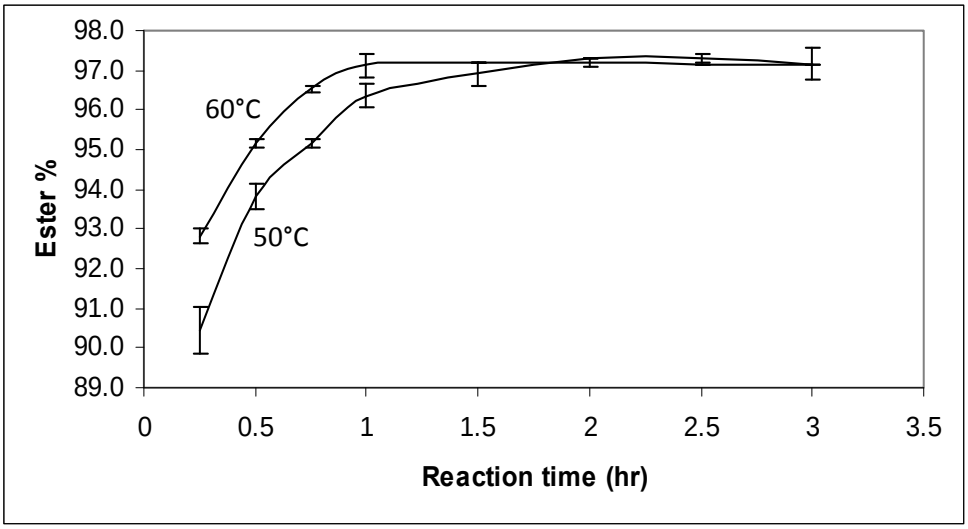

Figure 5.1 Ester formation during transesterification of canola oil using methanol at 50 and 60°C.

Table 5.7 Percent (w/w) of triglyceride, diglyceride, monoglyceride, ester, and percent ester recovery.

Biodiesel	Triglyceride	Diglyceride	Monoglyceride	Ester	Ester recovery
CGME[a]	1.3	2.4	1.5	94.8	82.6
TGME[a]	0.9	2.2	1.3	95.7	84.7
CME[a]	0.0	1.7	1.0	97.3	90.0
TGCME[a]	0.0	2.0	1.2	96.8	86.0
CGEE[a]	11.7	10.7	7.6	70.0	63.8
TGEE[a]	7.0	9.3	9.3	74.4	65.2
CEE[a]	0.4	2.4	4.1	93.1	82.8
TGCEE[a]	2.8	6.1	7.6	83.4	68.8
CGMEE[a]	0.0	2.5	2.4	95.1	79.2
TGMEE[a]	0.0	2.2	2.2	95.6	74.0
CMEE[a]	0.0	2.2	2.2	95.7	81.4
TGCMEE[a]	0.0	2.3	2.5	95.3	83.5

[a]See abbreviation section

Methyl esters are obtained at higher ester percentage compared to ethyl esters (see Table 5.7), in line with that reported in the previous chapter. This is because of the relative higher reactivity of methoxide ion compared to ethoxide ion leading to higher amount of methyl ester formation [11,14]. The percent ester recovery was not reached to 100 mainly due to the loss of oil during washing step. This loss was higher during the production of ethyl esters as the emulsion was strongly formed in these cases. A comparable ester percentage was observed in case of methyl ester and mixed methyl-ethyl ester. This finding indicates that mixed methyl-ethyl

alcohol is suitable for production of biodiesel from canola oil, greenseed canola oil and the mixture of both oils. The low ester percentage in case of ethanolysis can be improved by adjusting reaction conditions or using the purification method described in the literature [15]. There was no distinct difference between crude greenseed canola oil ester percentage and treated greenseed canola oil ester percentage. This finding implies that pigments did not play a significant role in transesterification reaction.

5.5.3. Biodiesel Properties

Table 5.8 shows fatty acid compositions of canola oil methyl ester (CME), crude greenseed canola oil methyl ester (CGME), treated greenseed canola oil methyl ester (TGME), canola oil ethyl ester (CEE), and treated greenseed canola oil methyl ethyl ester (TGMEE). Oleic acid was found to be the dominant fatty acid in all esters. The results in this table are comparable to those reported in the previous chapter (see table 4.5). Greenseed oil contains higher unsaturated compounds as compared to canola oil. The fatty acid compositions of CGME are similar to those of TGME. This finding indicates that the treatment process did not alter fatty acid compositions of greenseed canola oil. In addition, fatty acid compositions of CME are comparable to those of CEE. This finding suggests that fatty acid composition of ester prepared from the same oil remains the same regardless of the type of alcohol used in transesterification. A clear fatty acid composition of biodiesel prepared from mixed alcohols was not obtained due to the peak overlapping between methyl and ethyl esters of various fatty acids in the GC chromatogram. When the treated greenseed canola oil was transesterified with the mixed methanol/ethanol, methyl esters were formed in the higher amounts compared to ethyl esters. For example, the amounts of methyl oleate and ethyl oleate formed during transesterification were

36.20 and 19.95%, respectively. This result confirms that methanol has higher reactivity towards transesterification than ethanol.

Table 5.8 Fatty acid compositions of selected esters.

Structure	Compound name	CME[a] (%ME[a])	CGME[a] (%ME[a])	TGME[a] (%ME[a])	CEE[a] (%EE[a])	TGMEE[a] (%ME[a]/%EE[a])
C14:0	Myristic ester	0.06	0.07	0.06	0.05	trace
C16:0	Palmitic ester	4.36	4.60	4.54	4.45	3.08/n.a.[b]
C16:1	Palmitoleic ester	0.16	0.26	0.24	0.26	n.a.[b]/0.10
C16:2	n.a.[b]	0.08	0.08	0.08	0.07	trace
C16:3	n.a.[b]	0.09	0.15	0.12	0.11	0.07/trace
C18:0	Stearic ester	1.96	2.01	1.94	1.95	1.29/n.a.[b]
C18:1 z9	Oleic ester	60.92	55.51	55.05	61.09	36.20/19.95
C18:1 z11	Asclepic ester	2.89	3.59	3.47	2.98	n.a.[b]/1.27
C18:2	Linoleic ester	18.70	20.93	21.16	18.82	13.45/7.60
C18:3	Linolenic ester	6.79	9.41	9.76	6.85	6.06/3.36
C20:0	Arachidic ester	0.59	0.66	0.73	trace	0.42/0.23
C20:1	n.a.[b]	1.12	1.34	1.41	1.17	0.88/0.49
C22:0	Behenic ester	0.22	0.41	0.43	trace	0.21/trace
Total saturated fatty acid		7.19	7.75	7.7	6.45	n.a.[b]
Total monounsaturated fatty acid		65.09	60.7	60.17	65.50	n.a.[b]
Total polyunsaturated fatty acid		25.66	30.57	31.12	25.85	n.a.[b]

[a]See abbreviation section; [b]n.a. = not available

The additional biodiesel properties such as acid value, iodine value, viscosity @40°C and sulfur content are presented in Table 5.9. The acid value of CME was 0.2 which meets the ASTM specification (AV < 0.5). The acid values of CGME and TGME were both 0.4 which reflect the higher initial acid value of greenseed canola oil (AV=3.0-3.8) as compared to that of canola oil (AV = 0) but still meet the ASTM specification. The acid value of methyl ester prepared from the mixture of both oils fell in between that of canola oil methyl ester and greenseed oil methyl ester. The higher acid values of esters prepared with mixed alcohol and especially ethanol were probably because of the tannic acid solution that was used in the washing step instead of pure distilled water as a result of the formation of strong emulsion in these cases. Iodine value of canola oil methyl ester (IV = 109.5) was lower than those of greenseed oil methyl esters (IV = 111.0, 111.6). This is because canola oil has less unsaturated compounds compared to greenseed canola oil (see Table 5.8). The equivalent iodine value of CGME and TGME is due to their similar fatty acid compositions as shown in Table 5.8. Iodine value of methyl ester prepared from the mixture of both oils fell in between that of CME and TGME. The lower iodine values of ethyl esters compared to methyl esters suggested that ethyl esters have lower degree of unsaturation compared to methyl esters. This can be explained using the concept of molar concentration of double bonds as described by Knothe and Dunn [16]. If methyl and ethyl esters have the same number of double bonds per molecule, ethyl ester which has higher molecular weight would has lower molar concentration of double bonds leading to the lower degree of unsaturation. The iodine values of esters prepared with mixed methanol-ethanol fell in between those prepared with methanol and ethanol as expected. Viscosities of esters prepared from methanol and mixed methyl-ethyl alcohol are in the range of 4.8 – 5.2 cSt, which meet the ASTM specification (viscosity between 1.9 – 6.0 cSt). The high viscosities of ethyl esters were

due to lower triglyceride conversion. These esters contain higher amounts of glycerides, therefore the higher viscosities were observed. Sulfur contents of all esters were less than 1 ppm which meet the ASTM specification (sulfur < 15 ppm).

Table 5.9 Acid value, iodine value, viscosity @40°C and sulfur content of esters.

Biodiesel	Acid value (mg KOH/g)	Iodine value (mg I_2/100g)	Viscosity @40°C (cSt)	Sulfur content (ppm)
CGME[a]	0.4	111.6	5.1	< 1
TGME[a]	0.4	111.0	4.8	< 1
CME[a]	0.2	109.5	4.8	< 1
TGCME[a]	0.3	110.9	4.9	< 1
CGEE[a]	3.0	108.1	9.2	< 1
TGEE[a]	5.1	107.1	9.0	< 1
CEE[a]	0.4	103.0	5.3	< 1
TGCEE[a]	2.3	104.7	6.9	< 1
CGMEE[a]	0.6	108.5	5.1	< 1
TGMEE[a]	0.5	109.0	5.2	< 1
CMEE[a]	0.5	102.3	5.0	< 1
TGCMEE[a]	0.5	106.7	5.0	< 1

[a]See abbreviation section

5.5.4. Oxidative Stability

In order to determine oxidative stability of biodiesel, Rancimat instrument was used. During the Rancimat test, the sample was heated to 110°C and the oxygen was supplied. In the presence of oxygen at high temperature, the oxidation reaction took place and the oxidation derivatives were transferred to the measuring chamber containing Millipore water. The increase in conductivity of the water was detected as the oxidation derivatives were transferred into the water. The induction time is defined as the time required for the conductivity of the water to be increased rapidly and was used as an indication of biodiesel oxidative stability.

A typical Rancimat plot is shown in Figure 5.2 and the Rancimat results are presented in Figure 5.3. CME exhibited higher stability than those of CGME and TGME. This is because of the higher degree of unsaturation (poly unsaturated compounds = 31.12%; IV = 111.0) of greenseed oil derived methyl ester (GME) as compared with CME (poly unsaturated compounds = 25.66%; IV = 109.5). This finding suggests that the oil stability increases with the decrease in the degree of unsaturation, in line with that reported in the literature [17]. TGME showed a slightly higher induction time as compared to CGME. CGME and TGME are similar in both fatty acid compositions and iodine value but the difference in pigment content was significant as can be seen in Table 5.10 (34 ppm for CGME and 1 ppm for TGME). This result indicates that pigments have adverse effects on biodiesel stability, which is fit well with those reported in the literature [5,18]. It is also observed from Table 5.2 and 5.10 that pigment content was reduced during transesterification (from 94 ppm to 34 ppm). This result is anticipated as it is reported that chlorophyll can be removed during alkali-catalyzed transesterification in form of water-soluble chlorophyllin salt [5]. CEE showed longer induction time compared to CME, which stems from the lower double bond molar concentration of CEE than that of CME. The interpretation of the

induction time of esters prepared with mixed methanol-ethanol requires complete fatty acid compositional analysis of these esters. Most of the esters exhibit low oxidative stability and did not meet the ASTM specification (3 h induction time). Schober and Mittelbach [19] reported that the induction time of rapeseed oil methyl ester and distilled rapeseed oil methyl ester without an addition of antioxidant were 4.56 and 2.03 h, respectively. This report suggests that FAME prepared from rapeseed family has poor oxidative stability and an addition of antioxidant to FAME is required.

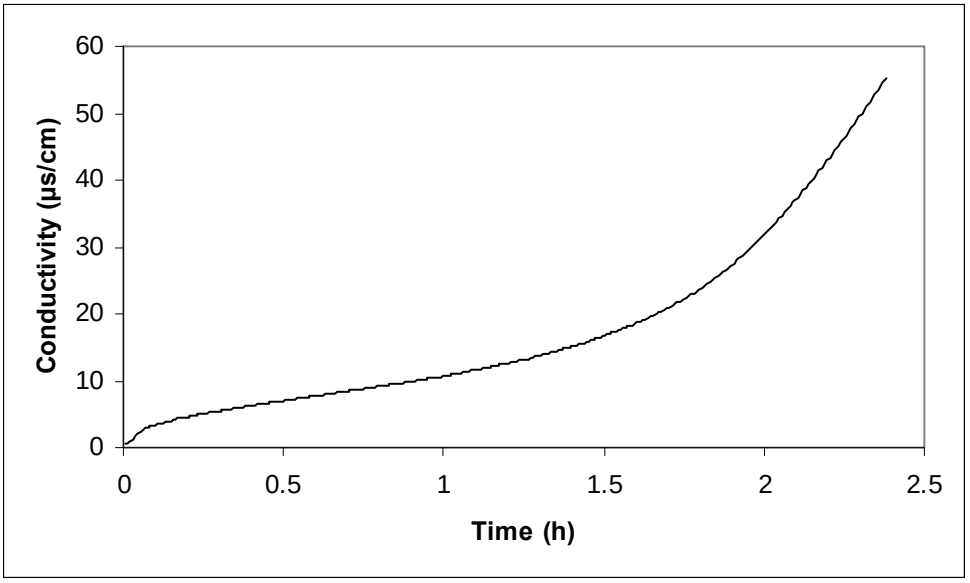

Figure 5.2 A conductivity-time plot for oxidative stability determination of canola oil methyl ester.

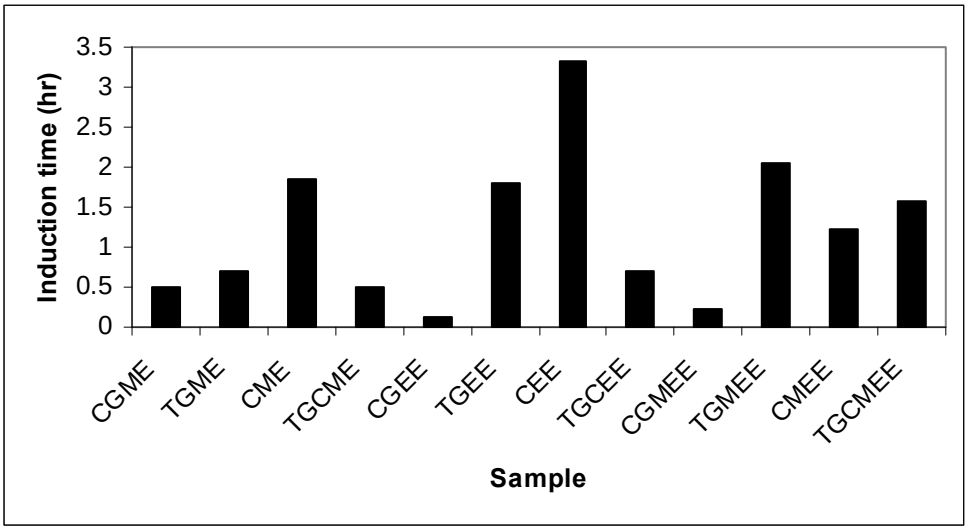

Figure 5.3 Induction time of esters prepared from canola oil and greenseed canola oil.

An attempt was made to combine the bleaching of greenseed canola oil with transesterification reaction into a single step. Crude greenseed canola oil was transesterified with methanol as per the method described in Section 5.4.2. In addition, 7.5 g of montmorillonite K10 was added to the reactor at the beginning of the reaction. The ester formed during the reaction and pigment content at the end of the reaction are shown in Figure 5.4. The results suggest that the combination of bleaching of greenseed canola oil and transesterification leading to a lower transesterification activity as well as an impairment of the sorption of pigments. This can be explained by the sorption phenomenon of potassium in montmorillonite as described by Muravyov and Sakharov [20]. Montmorillonite, by nature, has high negative potential and suitable size of interlayer spacing for the sorption of potassium. If potassium is trapped in the interlayer of montmorillonite, less catalyst would be available for transesterification resulting in tremendous drop in ester percentage (see Figure 5.4). In addition, when the potassium cation

enters the region between montmorillonite layers, it will polarize the adjacent laters, which prevents the sorption of other ions such as those of pigments in greenseed canola oil.

Table 5.10 Pigment content of esters.

Biodiesel	ChA[a] (ppm)	ChB[a] (ppm)	PhA[a] (ppm)	PhB[a] (ppm)	Total (ppm)
CGME[a]	9.1	2.3	16.8	5.9	34.0
TGME[a]	0.2	0.2	0.3	0.3	1.0
CME[a]	0.2	0.4	0.3	0.4	1.3
TGCME[a]	0.1	0.1	0.1	0.1	0.4
CGEE[a]	14.4	1.5	29.2	6.0	51.1
TGEE[a]	0.2	0.3	0.3	0.5	1.4
CEE[a]	0.3	0.6	0.5	0.6	2.0
TGCEE[a]	0.2	0.3	0.3	0.4	1.3
CGMEE[a]	12.5	1.0	24.7	5.3	43.5
TGMEE[a]	0.4	0.7	0.7	0.8	2.7
CMEE[a]	0.8	1.3	1.3	1.4	4.7
TGCMEE[a]	0.1	0.2	0.1	0.2	0.5

[a]See abbreviation section

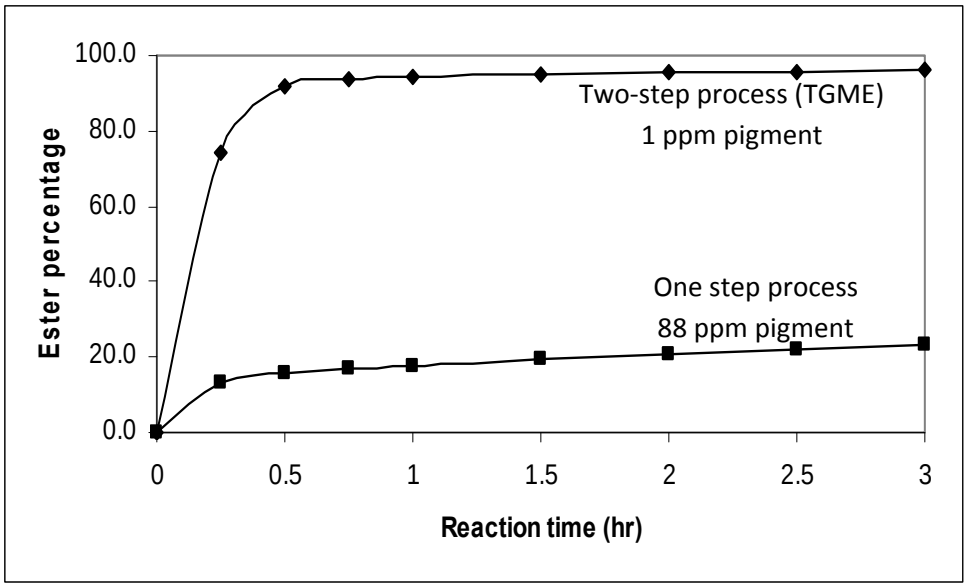

Figure 5.4 Ester formation during transesterification of greenseed canola oil and pigment content of ester at the end of the reaction.

5.6. Conclusions

Greenseed canola oil is a potential feedstock for biodiesel production due to its low price. Although greenseed canola oil contains high amounts of pigments such as chlorophyll and pheophytin, these pigments do not play a vital role in transesterification and therefore high ester percentage biodiesel can be obtained from crude greenseed canola oil. However, biodiesel derived from crude greenseed canola oil contains high amounts of these pigments and it, in turn, exhibits reduced oxidative stability. Therefore, it is suggested that crude greenseed canola oil is bleached prior to transesterification. The optimum conditions in the bleaching process is the use of 7.5 wt.% montmorillonite K10 at 60°C and stirring speed of 600 rpm for 30 min. After the bleaching process, the pigment content of greenseed canola oil was reduced from 94 ppm to 0.5 ppm. This bleaching process did not alter fatty acid compositions of the oil. Since montmorillonite K10 is readily obtainable at low cost, regeneration of this clay is not

recommended. A combination of bleaching of greenseed canola oil and transesterification reaction into a single step results in a serious drop in catalytic activity as well as adsorbent performance and therefore is not recommended.

In addition to greenseed canola oil, mustard oil is interesting inedible oil as feedstock for biodiesel production. Therefore, it was investigated for biodiesel production and the results are discussed in Chapter 6.

Abbreviations

AC	Activated carbon
AV	Acid value
CEE	Canola ethyl ester
CGEE	Crude greenseed ethyl ester
CGME	Crude greenseed methyl ester
CGMEE	Crude greenseed methyl & ethyl ester
CGO	Crude greenseed canola oil
ChA	Chlorophyll A
ChB	Chlorophyll B
CME	Canola methyl ester
CMEE	Canola methyl & ethyl ester
EtOH	Ethanol
FAME	Fatty acid methyl ester
HPLC	High performance liquid chromatography
IV	Iodine value
KOH	Potassium hydroxide
MeOH	Methanol

PhA	Pheophytin A
PhB	Pheophytin B
TGCEE	Treated greenseed & canola ethyl ester
TGCME	Treated greenseed & canola methyl ester
TGCMEE	Treated greenseed & canola methyl & ethyl ester
TGEE	Treated greenseed ethyl ester
TGME	Treated greenseed methyl ester
TGMEE	Treated greenseed methyl & ethyl ester
TGO	Treated greenseed canola oil
THF	Tetrahydrofuran

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CHAPTER 6

Biodiesel Production from Mustard Oil

A part of this chapter has been published in Journal of the American Oil Chemists' Society:

- Issariyakul, T., Dalai A.K., and Desai P. Evaluating esters derived from mustard oil (*Sinapis alba*) as potential diesel additives. Journal of the American Oil Chemists' Society 88: 391-402 (2011).

Contribution of the Ph.D. Candidate

Experiments were conducted by Titipong Issariyakul. The content in this chapter was written by Titipong Issariyakul with discussions and suggestions provided by Dr. Ajay Dalai and Mr. Pete Desai.

Contribution of this Chapter to the Overall Ph.D. Research

Mustard oil is a non-edible vegetable oil due to high level of erucic fatty acid. Chapter 6 focuses on the use of mustard oil as feedstock for biodiesel production and evaluating mustard oil-derived biodiesel as a lubricity additive to petroleum based diesel. Biodiesel production process is developed in order to produce high quality mustard oil-based biodiesel. Extensive biodiesel characteristics are evaluated with special emphasis on its lubricity.

6.1. Abstract

Biodiesel was produced from mustard oil utilizing transesterification with methanol, ethanol, propanol, and butanol at 6:1 alcohol to oil molar ratio, using KOH as a catalyst at 1 wt.%. The maximum ester content achieved by this method was only 66%. Distillation was then used to purify the ester, raising the ester content to 99.8%. Alternatively, mustard oil methyl ester (MME) can be mixed with esters derived from canola oil or soybean oil to achieve an ASTM quality biodiesel. Biodiesel derived from mustard showed great potential as lubricity additive for regular diesel fuel. With an addition of 1% MME, lubricity of diesel fuel was improved by 43.7%. It is also found that methyl ester is the best lubricity additive among all esters (methyl-, ethyl-, propyl-, and bytyl-ester). MME can be used at -16°C without freezing whereas monounsaturated compounds (oleic, eicosenoic, and erucic esters) largely present in esters derived from mustard oil can tolerate -42°C to -58°C. Monounsaturated esters derived from higher alcohols such as butyl alcohol demonstrated a superior low temperature tolerance (-58°C) as compared to that derived from lower alcohol such as methyl alcohol (-42°C).

6.2. Introduction

Conventional fossil-based fuels are not renewable and are destined to exhaustion. Furthermore, the price of these fuels tends to rise every year, which inspires the use of alternative renewable fuels. Biodiesel, commonly produced from vegetable oils such as canola oil and soybean oil [1,2], is one of the most promising renewable fuels and use of this fuel is a shift towards sustainable energy. Transesterification, a series of consecutive, reversible reactions as shown in Figure 6.1 [3], is commonly used to produce biodiesel from vegetable oils. With arising concerns regarding the use of food crops as feedstock for fuel production, non-food grade oils

are gaining tremendous attention from researchers around the world. High erucic acid rapeseed (HEAR) oil or mustard oil is an interesting feedstock for biodiesel production.

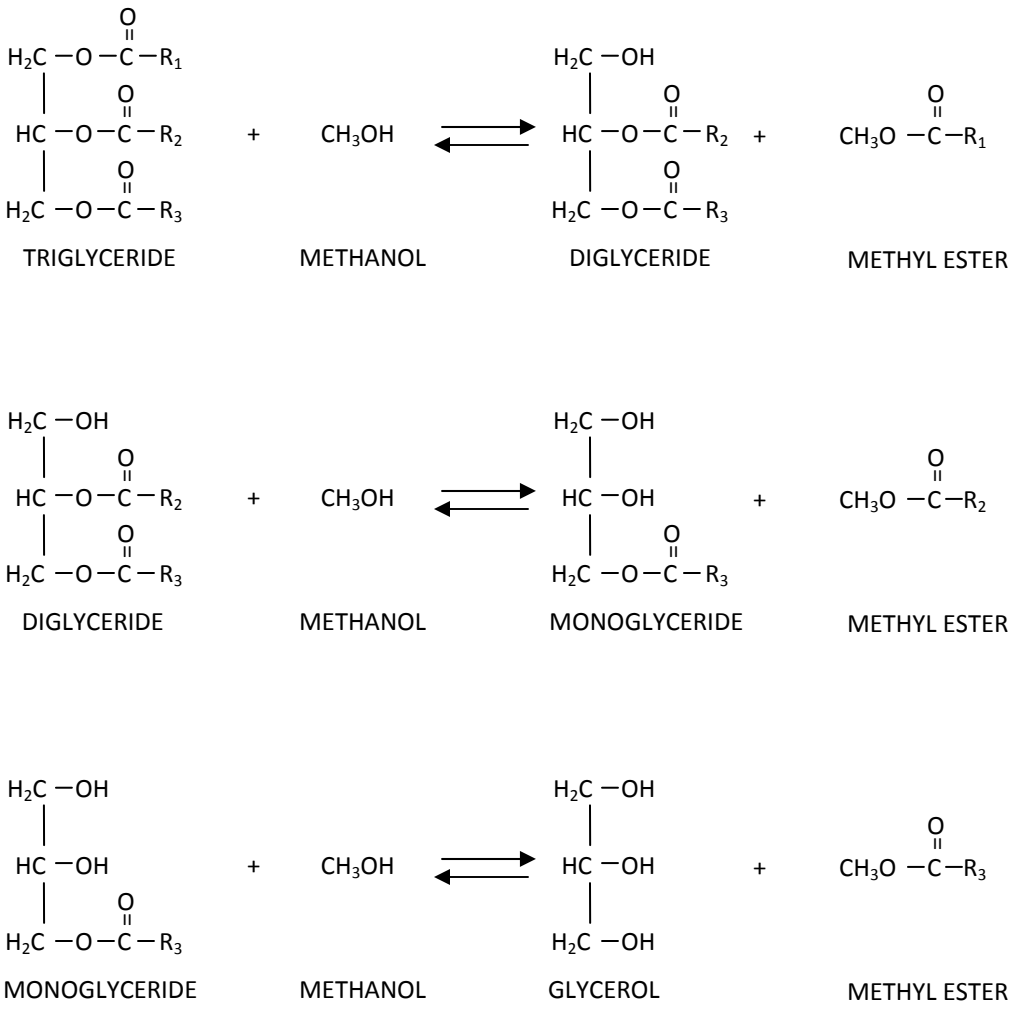


Figure 6.1 Transesterification reaction scheme.

Mustard oil can be extracted from *Brassica nigra* (Black Mustard), *Brassica carinata* (Abyssinian Mustard), *Brassica juncea* (Brown, Oriental, and Leaf Mustard), *Sinapis arvensis* (Wild Mustard), and *Sinapis alba* (White Mustard). These seeds can have oil content over 40% in which the dominant fatty acids include oleic acid (C18:1), linoleic acid (C18:2), and erucic acid (C22:1). The erucic acid results from the addition of a two-carbon fragment to oleic acid to form eicosenoic acid (C20:1), followed by addition of another two-carbon fragment to eicosenoic acid to form erucic acid [4]. In the case of low erucic acid rapeseed (LEAR) such as *B. napus* (Canola Oil or Canadian Brassica), the genetic elongation ability of fatty acids is blocked, leading to the accumulation of the precursor fatty acid, i.e., oleic acid. The level of erucic acid can be genetically modified ranging from less than 1% to over 60%. A study showed a declining trend in erucic percentage in Canadian LEAR during 1980s [5].

Many researchers report that cardiac fat infiltration in experimental animals is caused by erucic acid present in high erucic acid rapeseed (HEAR) and thus conclude erucic acid as toxic compound. This compound if fed in large quantities would result in heart lesions [6]. Since there are fewer experiments done on the effects of erucic acid on people compared to the number of experiments on animals, the effects of erucic acid on human health is not fully understand. Historically, the use of rapeseed oil with high erucic acid level as edible oil has been objected by many organizations. The Canadian regulations state that in cooking oil, margarine, salad oil, simulated dairy product, shortening or food that resembles margarine or shortening, the erucic and cetoleic acid may not excess 5% of the total fatty acid [7]. The advent of LEAR leads to a "phase out" of HEAR from the foodmarket, but HEAR can still be used in other industries such as fuel, lubricating oil, oleochemicals, and biopolymer production.

Canadian mustard seed production has ranged from 105,000 tonnes in 2001-2002 to 306,000 tonnes in 2004-2005. In 2006, the total world mustard exports were 315,000 tonnes, 55% of which were Canadian mustard. In 2006-2007, Saskatchewan dominated Canadian mustard seed production, with 78% of total production. The area seeded for mustard in 2006 in Saskatchewan was 280,000 acres, which yielded 776 pounds per acre [8]. These data show that mustard seed is available in large quantity in Canada. Because it contains a high level of erucic acid, mustard oil does not meet Canadian specifications for edible purpose, but it could be a viable feedstock for biodiesel production. Information related to biodiesel production from mustard oil is necessary for pilot scale production. However, there is no literature available on biodiesel production from vegetable oil of *Sinapis'* family. Furthermore, the properties of biodiesel derived from mustard oil could be different from that derived from canola oil, due to the difference in fatty acid compositions. In the present chapter, biodiesel was produced from mustard oil and the resultant fuel was evaluated as a diesel additive, using various characterization techniques to demonstrate its distinctive properties as compared to that derived from canola oil.

6.3. Materials

Commercial grade canola oil and soybean oil were purchased from a local grocery store. Mustard oil was provided from Mustard Capital Inc., Saskatoon, SK, Canada. Anhydrous methanol (MeOH) (99.8%), anhydrous ethanol (EtOH), and potassium hydroxide (KOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany. Propanol and 1-butanol were purchased from Sigma-Aldrich, Canada. Diesel fuels were purchased from four gas stations (Esso, Shell, Petro-Canada, Co-op) in Saskatoon, SK, Canada in December 2009. Reference

standard chemicals including methyl oleate, triolein, diolein, and monoolein were purchased from Sigma-Aldrich, MO, USA. Fatty acid methyl esters (FAME) mix rapeseed oil reference standard was obtained from SUPELCO, PA, USA. The reference diesel fuel used in lubricity testing of biodiesel was that specified in ASTM D6079-04 and was purchased from Haltermann Products, Hamburg, Germany.

6.4. Experimental Procedures

6.4.1. Transesterification

In the present chapter, two types of mustard oil were donated by Mustard Capital Inc. including *S. alba* (White Mustard) and *B. juncea* (Oriental Mustard). The fatty acid compositions and acid value (AV) of these mustard oils were analyzed. *S. alba* was chosen in this study due to its high erucic acid content (see Table 6.1).

Fatty acid methyl ester was produced from canola oil, soybean oil and mustard oil via transesterification reaction using KOH as a catalyst. A 100g sample of the oil was initially placed in a Parr reactor (Parr Instrument Company, IL, USA) and heated to 60°C. A mixture of methanol (6:1 alcohol to oil molar ratio) and KOH (1 wt.% with respect to oil) was added to the reactor. The temperature and stirring speed of the reaction mixture were maintained constant for 1.5 hours at 60°C and 600 rpm, respectively. The same procedure was applied to the production of ethyl-, propyl-, and butyl-esters.

After the reaction, the glycerol was separated from the ester phase by gravity in a separatory funnel. Heated distilled water was used to remove KOH, soap, and alcohol remained in the ester phase. BÜCHI rotavapor was then used to remove the remaining alcohol and water in ester phase. To remove traces of moisture, the biodiesel was passed through the anhydrous

sodium sulphate, which was previously dried in an oven at 100°C for 1 hour. The biodiesel produced from mustard oil was mixed with the purified biodiesel produced from the canola and soybean oils, at various ratios, as shown in Table 6.2.

Table 6.1 Fatty acid compositions and AV of *S. alba* and *B. juncea.*

Structure	Compound name	*S. alba* (wt.%)	*B. juncea* (wt.%)
C14:0	Myristic ester	0.05	0.06
C16:0	Palmitic ester	2.80	3.01
C16:1	Palmitoleic ester	0.16	0.14
C16:2	n/a[a]	0.06	0.03
C18:0	Stearic ester	1.09	1.31
C18:1 z9	Oleic ester	24.98	16.92
C18:1 z11	Asclepic ester	1.10	1.38
C18:2	Linoleic ester	11.64	20.82
C18:3	Linolenic ester	8.61	12.85
C20:0	Arachidic ester	0.70	0.75
C20:1	n/a[a]	10.44	10.70
C22:0	Behenic ester	0.57	0.43
C22:1	Erucic ester	32.81	25.76
AV (mg KOH/g sample)		0.85	3.1

[a]n/a = not available

Table 6.2 Mixtures of esters produced from canola, soybean and mustard oil.

Sample	Mustard ME[a] (wt.%)	Canola ME[a] (wt.%)	Soybean ME[a] (wt.%)
CME[a]	0	100	0
MIX1	0.75	99.25	0
MIX2	1.5	98.5	0
MIX3	3	97	0
MIX4	6	94	0
MIX5	12	88	0
MME[a]	100	0	0
SME[a]	0	0	100
MIX6	0.75	0	99.25
MIX7	1.5	0	98.5
MIX8	3	0	97
MIX9	6	0	94
MIX10	12	0	88

[a]see abbreviation section

6.4.2. Distillation of Transesterification Products

Distillation of the transesterification products of mustard oil was performed as per ASTM D 1160-06. In this step, transesterification products derived from mustard oil were distilled using a spinning band distillation unit (Model: 24/100 A) equivalent to 80 theoretical plates from B/R Instrument Corp., Easton, MD, USA. For methyl-, ethyl-, and propyl-ester production, the heating unit was set at 14% resulting in 200°C pot temperature and 170°C head temperature. The reflux ratio and operating pressure were set at 50 and 667 Pa, respectively. For butyl-ester production, the heater, reflux ratio, and pressure were set at 17%, 50, and 67 Pa, respectively, resulting in 250°C pot temperature and 180°C head temperature.

6.4.3. Characterization

Table 6.3 summarizes the standard methods used in this study for fuel characterization. The purified methyl ester was analyzed for ester and glycerin content using a Hewlett-Packard 1100 series HPLC with a refractive index detector and two Phenogel 5µ 100A 300X7.80 mm 5 micron columns in series protected with a guard column and equipped with a ChemStation for LC 3D, Agilent Technologies. THF was used as a mobile phase at 1 mL/min for 25 min. The operating parameters used were as follows: injection volume 5 µL; column temperature 24°C; and detector temperature 35°C. Reference standard chemicals including methyl oleate, triolein, diolein, monoolein, and glycerol were used for the HPLC calibration (see Appendix A). Fatty acid compositions of esters were determined using Agilent Technologies 6890N Network GC System equipped with GC ChemStation software with an FID detector and RESTEK 10638 Stabilwax column. The injection volume was 2 µL and the temperature program was started at

160°C, held for 1 min, ramped to 240°C at 4°C/min and then held for 24 min. The SUPELCO FAME Mix Rapeseed Oil standard was used as a reference for GC calibration (see Appendix B).

Table 6.3 Analysis of transesterification products.

Property	Unit	Method
Ester and glycerides content	mass%	HPLC
Fatty acid compositions	mass%	AOCS Ce 1-62
Boiling point distribution	°C	ASTM D 6352-04
AV	mg KOH g^{-1}	AOCS Te 1a-64
Water content	ppm	ASTM D 6304-07
Sulfur content	ppm	ASTM D 5453-09
Phosporous content	ppm	ASTM D 4951-09
Viscosity	cSt	ASTM D 445-09
Lubricating property	μm,% reduction	ASTM D 6079-04
Oxidative stability	minutes	EN 14112
Low temperature property	°C, J g^{-1}	DSC

The lubricating properties of the biodiesel and biodiesel blends were tested as per the High-Frequency Reciprocating Rig (HFRR) ASTM D6079-04 method. The test sample was placed in a sample container onto a metal surface. The ball surface was in contact with the metal surface at 50 Hz for 75 minutes, and the wear scar diameter on the ball surface was then measured using a microscope. A Rancimat instrument was used to determine oxidative stability

of the biodiesel, according to the EN 14112 method (see Table 6.3). During the Rancimat test, the sample was heated (110°C in this case) and oxygen was supplied. In presence of oxygen at high temperature, the oxidation reaction took place and the oxidation derivatives transferred to a measuring chamber containing Millipore water. As the oxidation derivatives were transferred into the water, an increase in conductivity of the water was detected. The induction time is defined as the time required for conductivity of the water to increase rapidly, and was used as an indication of biodiesel oxidative stability. The low temperature properties of the fuels were examined by a Differential Scanning Calorimeter (DSC) from PerkinElmer, Inc., CT, USA, equipped with Pyris software thermal analysis and a cryofill filled with liquid nitrogen as a cooling device. After sample encapsulation, the sample chamber was held at 30°C for 5 min and then cooled from 30°C to -110°C at 5°C/min.

6.5. Results and Discussions

6.5.1. Feedstock Analysis

Fatty acid compositions and AV of *S. alba* and *B. juncea* are shown in Table 6.1. Having a higher erucic acid (32.81%) compared to that of *B. juncea* (25.76%), *S. Alba* was chosen as the feedstock for this study. The AV of this oil was not high (0.85), hence base-catalyzed transesterification was a viable option.

The physical and chemical properties of vegetable oils were evaluated, according to the methods presented in Table 6.4. Both water content and AV of all three oils were low enough for effective KOH-catalyzed transesterification reactions (water content <500 ppm and AV <1). The HPLC analyses of the canola, soybean, and mustard oils suggest that these three oils contain mainly triglyceride and a small amount of diglyceride. In conclusion, all these vegetable oils

consist mainly of triglyceride, with a minor percentage of other compounds such as diglyceride, free fatty acid, and water.

Table 6.4 AV, water content, ester and glyceride content of vegetable oils.

Sample	Canola oil	Soybean oil	Mustard Oil
AV[a] (mg KOH g^{-1})	0.26	0.28	0.85
Water content (ppm)	288	290	299
Viscosity@40°C (cSt)	33.2	29.3	37.5
Phosporous content (ppm)	n/a	n/a	29.6
Sulfur content (ppm)	1.9	1.2	1.7
TG[a] (wt.%)	96.62	99.86	97.04
DG[a] (wt.%)	3.25	0	2.54
MG[a] (wt.%)	0	0	0
FFA[a] (wt.%)	0.13	0.14	0.42

[a]see abbreviation section

6.5.2. Transesterification products of mustard oil

Ester obtained from transesterification of mustard oil was discussed in this section. Figure 6.2 shows ester formation as well as triglyceride (TG), diglyceride (DG), and monoglyceride (MG) percentages during transesterification of mustard oil. The KOH-catalyzed transesterification occurred rapidly and the major portion of ester was formed during the first 30 minutes of the reaction. The reaction was completed within 60 minutes and only 64% of ester was formed. TG and DG were observed at negligible amounts; however, there was a high

percentage of MG contained in the transesterification products. Transesterification occurs in a series of consecutive, reversible reactions consisting of the conversion of TG to DG, DG to MG, and MG to glycerol (GL) as shown in Figure 6.1. The HPLC results implied that TG and DG were smoothly converted to DG and MG, respectively. On the other hand, MG was not able to convert to form ester and GL easily, leading to an accumulation of MG compound in the transesterification products. A product with a high MG percentage was not suitable for use as fuel and required upgrading.

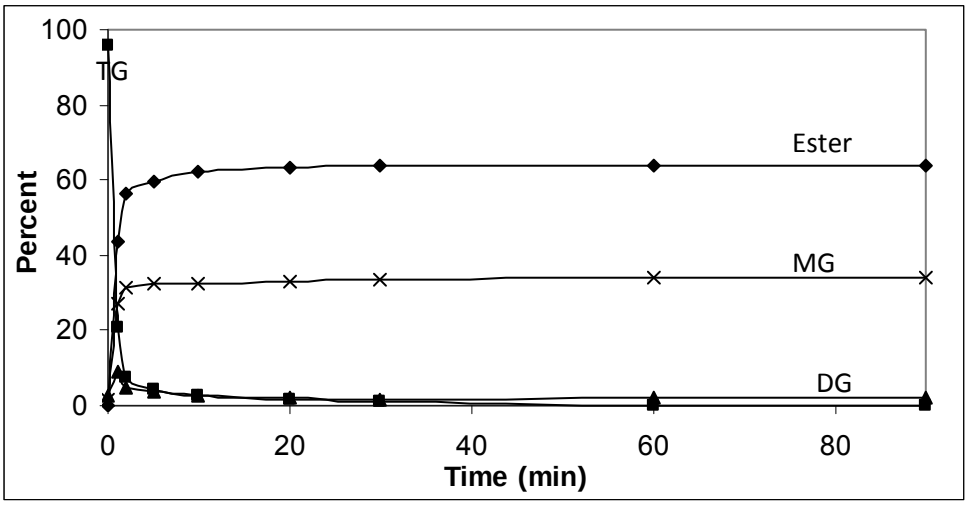


Figure 6.2 Ester and glyceride content during transesterification of mustard oil.

6.5.3. Mixtures of Esters derived from Canola, Soybean and Mustard Oil

In order to meet ASTM specifications prior to its use in a diesel engine, the mustard oil methyl ester (MME), was blended with canola oil methyl ester (CME) and soybean oil methyl ester (SME) at various ratios as shown in Table 6.2. To discriminate the effects of MME percentage on ester properties, the blend ratios were studied as low as 0.75% MME up to 12% MME. The ester and glyceride content of the mixed and pure esters derived from the canola,

soybean, and mustard oils are shown in Table 6.5. Unlike mustard oil, the canola and soybean oils can easily be transesterified to produce an ASTM-grade biodiesel. All the blended esters showed low values of water content and AV meeting the ASTM specifications, but the total glycerol content of the higher MME percent blends did not. Total glycerin content can be calculated from triglyceride, diglyceride, monoglyceride and glycerol content using the equation: total glycerin content (GL_T) = GL + 0.26(MG) + 0.15(DG) + 0.1(TG) [9]. To meet the ASTM specification of total glycerol content, the MME content of biodiesel blend must not exceed 1.5 wt.%. Although, MME can be blended with high purity esters derived from canola and soybean oils, the percentage of MME allowed in a blend was significantly low. An alternate means of using mustard oil as feedstock for biodiesel production has been explored and discussed in the following sections.

6.5.4. Esters Production from Mustard Oil

In an attempt to improve purity of ester produced from mustard oil, three hypotheses were made related to glycerol formation, catalyst impurity, and high activation energy.

1. Glycerol formation - It was hypothesized that glycerol was formed during transesterification and the catalyst was transferred into the glycerol phase. As a result, less catalyst was available in alcohol phase where reaction took place, hence hindering ester yield. In response to this hypothesis, a two-step reaction was performed. After 60 minutes of the reaction, the glycerol was removed, followed by an addition of a mixture of methanol and KOH (6:1 methanol to oil molar ratio; 1 g of KOH). Addition of methanol/KOH mixture was expected to compensate the catalyst loss to the glycerol phase. Moreover, it was anticipated that the removal of glycerol would shift the reaction to product side, thereby enhancing ester yield.

Table 6.5 Water content, AV, ester and glyceride content of biodiesel derived from canola, soybean, and mustard oil.

Sample	Water content (ppm)	AV[a]	%FFA[a]	%TG[a]	%DG[a]	%MG[a]	%Ester	%Total Glycerol
CME[a]	416	0.29	0.15	0	1.39	0	98.46	0.21
MIX1[b]	422	0.24	0.12	0	1.41	0	98.47	0.21
MIX2[b]	460	0.37	0.18	0	1.41	0	98.41	0.21
MIX3[b]	486	0.40	0.20	0	1.43	2.06	96.31	0.75
MIX4[b]	282	0.40	0.20	0	1.40	2.68	95.72	0.91
MIX5[b]	353	0.40	0.20	0	1.41	3.84	94.56	1.21
MME[a]	369	0.60	0.30	0	1.28	33.68	64.75	8.95
SME[a]	443	0.30	0.15	0	0.41	0	99.44	0.06
MIX6[b]	383	0.32	0.16	0	0.41	0	99.43	0.06
MIX7[b]	448	0.36	0.18	0	0.41	0	99.41	0.06
MIX8[b]	416	0.36	0.18	0	0.44	1.68	97.70	0.50
MIX9[b]	460	0.32	0.16	0	0.44	2.25	97.15	0.65
MIX10[b]	467	0.41	0.20	0	0.45	2.97	96.37	0.84
ASTM D6751	500 max	0.5 max	-	-	-	-	-	0.24

[a]see abbreviation section; [b]See Table 6.2

The ester formation during this two-step reaction is shown in Figure 6.3. The final ester content was 66% which was only 2% higher than the one step process, suggesting that the glycerol formation during transesterification has a minor effect on ester yield.

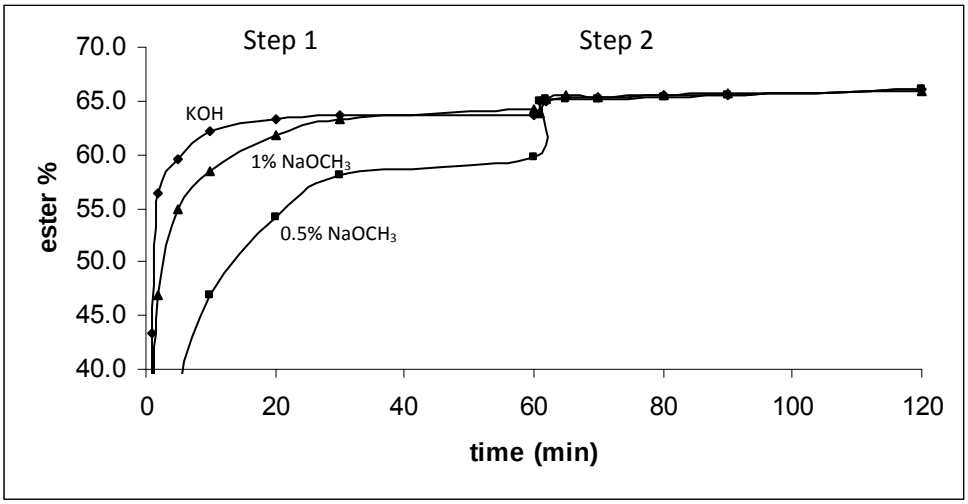


Figure 6.3 Ester formation during transesterification of mustard oil using CH_3ONa and KOH as a catalyst.

2. Catalyst impurity - KOH, which was purchased from EMD chemicals Inc. and used as a catalyst in this study, contains approximately 15% of water. Water, if present in the reaction system, could hydrolyze ester to form FFA, which intensifies saponification and lowers ester yield. Being anhydrous, sodium methoxide (CH_3ONa) was reported for its high activity towards transesterification of rapeseed, flaxseed, and sunflower oil [10] and was chosen as a catalyst for this study. CH_3ONa loading selected in this study was 0.5 and 1 wt.% with respect to mustard oil. Ester formation during transesterification of mustard oil using CH_3ONa compared to that using KOH as a catalyst is shown in Figure 6.3. The results suggested that the reaction occurred faster when higher catalyst loading was used. However, the final ester percentage in both cases

was 66%, which was equal to that when KOH was used as a catalyst. This finding indicated that the hydrolysis of ester during transesterification was insignificant and water contained in KOH was at an acceptable level for transesterification.

3. Activation energy - Based on the HPLC analysis of the final transesterification products derived from mustard oil (see Figure 6.2), TG and DG content was negligible, but MG was present in large amounts (33%). It can be assumed that the first two reactions in Figure 6.1 (TG to DG and DG to MG) were completed, whereas the conversion of MG to GL was minimal. Based on the principle of activation energy, a minimum energy provided to the reaction must exceed the activation energy of the corresponding reaction to allow it to take place. To provide adequate energy overcoming the activation energy, the reaction was performed at elevated temperature and pressure (150°C and 3.4 MPa). The reaction was carried out for 4 hours. Figure 6.4 shows the ester formation during elevated temperature and pressure transesterification of mustard oil. The ester percentage at the end of the reaction was only 63%. A high purity biodiesel was not achieved and an alternative means of obtaining high purity ester was required.

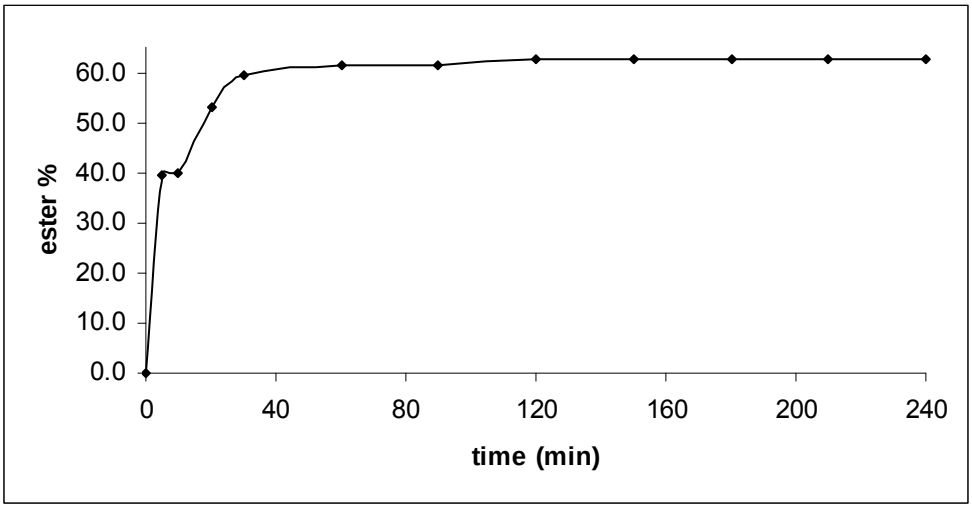


Figure 6.4 Ester formation during transesterification of mustard oil at elevated temperature and pressure (150°C, 3.4 MPa).

Since all three hypotheses could not explain transesterification behaviour of *S. alba*, it was believed that the low ester yield obtained from transesterification of *S. alba* was probably due to steric effects of long chain erucic fatty acid hindering the reaction. Figure 6.5 shows the boiling point distribution of esters derived from canola and mustard oils. It was clear that MME has higher boiling points as compared to CME, due to the high level of heavy portion (high MW compounds). This heavy portion could be either MG or methyl erucate, which boil at a higher temperature than the typical methyl oleate found in CME. To identify the heavy portion, the following reason is given. If the heavy portion in Figure 6.5 was erucic ester, this ester would be left out from the rest of the ester portion during distillation. However, results from Table 6.6 suggest the opposite. It was found that the major ester in MME was methyl erucate (31.57%). Therefore the heavy portion as shown in Figure 6.5 is more likely to be MG instead of methyl erucate. The data from Figure 6.5 suggest that ester and MG have distinctive range of boiling temperature and, therefore, can be separated from each other by means of distillation.

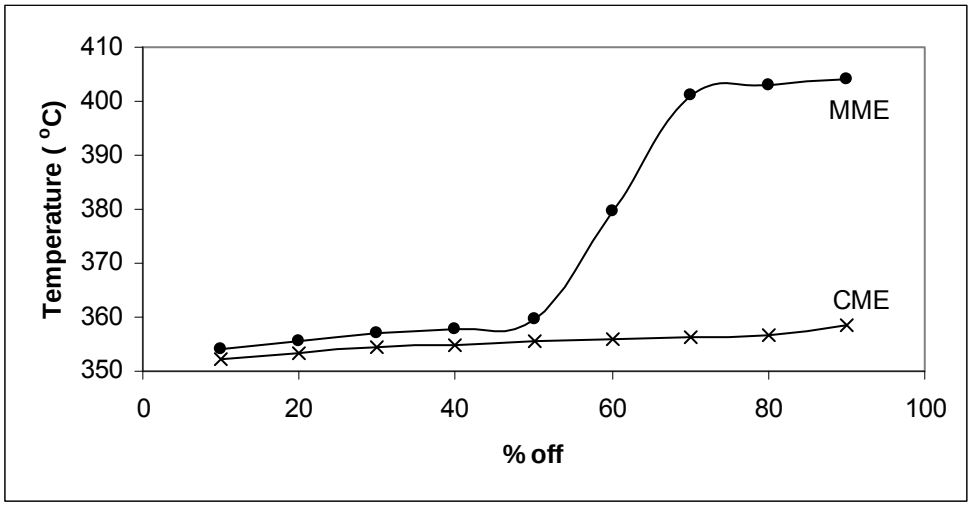


Figure 6.5 Boiling point distribution of canola and mustard oil methyl ester using simulated distillation unit.

Table 6.6 Fatty acid compositions of mustard, canola, and soybean oil methyl ester.

Structure	Compound name	MME[a]	CME[a]	SME[a]
C14:0	Myristic ester	0	0.06	0.10
C16:0	Palmitic ester	2.84	4.24	11.56
C16:1	Palmitoleic ester	0.21	0.22	0.15
C16:2	n/a[b]	0.04	0.07	--
C18:0	Stearic ester	1.11	2.00	4.32
C18:1 z9	Oleic ester	25.30	61.36	22.82
C18:1 z11	Asclepic ester	0.93	2.78	1.38
C18:2	Linoleic ester	11.54	18.43	51.93
C18:3	Linolenic ester	8.58	6.72	5.95
C20:0	Arachidic ester	0.68	0.70	0.34
C20:1	n/a[b]	10.34	1.30	0.25
C22:0	Behenic ester	0.48	0.38	0.34
C22:1	Erucic ester	31.57	--	--

[a]see abbreviation section; [b]n/a = not available

6.5.5. Distillation of Transesterification Products Derived from Mustard Oil

Due to the difference in boiling points between ester and MG, the transesterification products derived from mustard oil containing mainly ester and MG were distilled, as per the method described in the experimental procedures section. The HPLC chromatograms of undistilled MME, distilled MME (DMME), and residual from distillation of mustard oil butyl

ester (MBE) are presented in Figure 6.6, and shows that undistilled MME contained mainly ester and MG, whereas MME after distillation contained only ester. The mustard oil ethyl ester (MEE), mustard oil propyl ester (MPE), and mustard oil butyl ester (MBE) were also distilled, using the method described in the experimental procedures section. The chromatograms of these esters were somewhat similar to that of MME, but the esters were completely separated from monoglyceride; therefore, high purity esters were achieved. Since the oil samples were exposed to high temperature (200°C - 250°C) for a long period of time (~ 6 hours), it was likely that polymerization took place during distillation process. These polymerized compounds had high molecular weight and were left in the residual portion during distillation (see Figure 6.6c).

6.5.6. Characterization of Mustard Biodiesel

Properties from the mustard biodiesel (methyl, ethyl, propyl and butyl ester) and its parent oil are summarized in Table 6.7. Fatty acid compositions of CME, SME, and MME are shown in Table 6.6. The results suggested that the major fatty acid in canola, soybean, and mustard were oleic (C18:1), linoleic (C18:2), and erucic acid (C22:1) acid, respectively, in line with those found in literature [3,11].

The molecular weights of esters and mustard oil (MO) were calculated from fatty acid compositions corresponding to each sample. The AV of DMME and DMEE met the ASTM specifications, but was higher for butyl-ester synthesis, which was probably due to the severe operating conditions used in the distillation step. At high temperature, it was likely that some ester and monoglyceride degraded into acids resulting in the apparently higher AV.

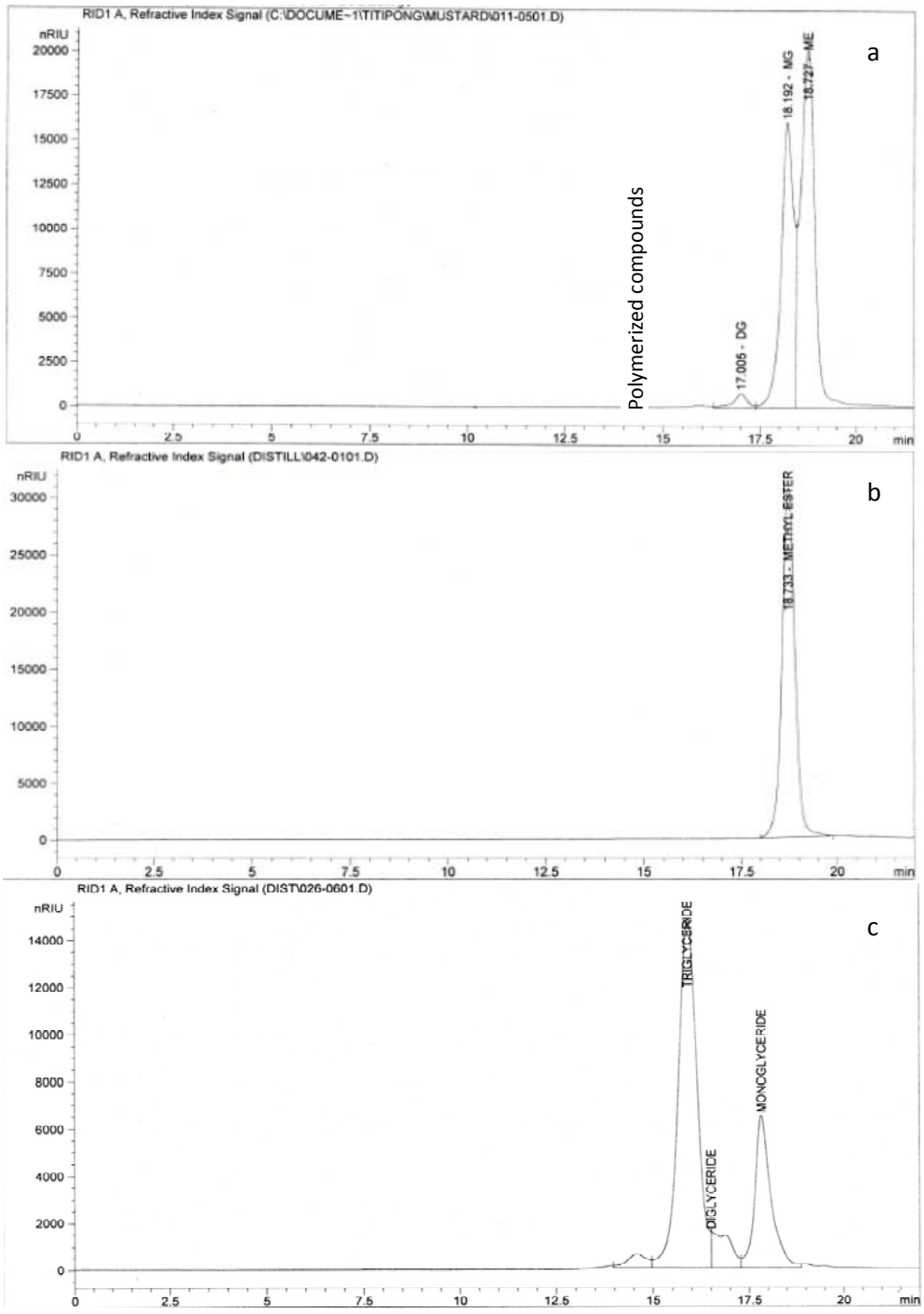


Figure 6.6 HPLC chromatograms of (a) undistilled mustard oil methyl ester; (b) distilled mustard oil methyl ester; and (c) residual from distillation of mustard oil butyl ester.

Table 6.7 Properties of mustard oil and biodiesel produced from mustard oil.

Property	MO[a]	DMME[a]	DMEE[a]	DMPE[a]	DMBE[a]	ASTM D6751
MW cal ($g\ mol^{-1}$)	947	317	331	345	359	n/a
AV[a] ($mg\ KOH\ g^{-1}$)	0.9	0.4 (0.1)[b]	0.5 (0)[b]	0.6 (0.1)[b]	4.0 (0.2)[b]	0.5
Free fatty acid (mass%)	0.4	0.2	0.3	0.3	2.0	n/a
Triglyceride (mass%)	96.9	0	0	0	0	n/a
Diglyceride (mass%)	2.5	0	0	0	0	n/a
Monoglyceride (mass%)	0	0	0	0	0	n/a
Free glycerol (mass%)	0	0	0	0	0	<0.02
Total glycerol (mass%)	10.1	0	0	0	0	<0.24
Ester (mass%)	0	99.8	99.7	99.7	98.0	n/a
Water (ppm)	241 (58)[b]	231 (44)[b]	62 (45)[b]	187 (10)[b]	345 (30)[b]	<500

Sulfur	1.7	0	14.7	9.5	10.4	15
(ppm)	(0.2)[b]	(0)[b]	(0.7)[b]	(0)[b]	(0.3)[b]	
Phosphorous	30	9	4	10	8	10
(ppm)						
Density @40°C	0.9	0.9	0.9	0.9	0.9	n/a
(g mL^{-1})						
Kinematic viscosity @40°C	37.5	4.2	4.5	5.0	5.5	1.9 –
(cSt)	(0.3)	(0.2)	(0.1)	(0.2)	(0.2)	6.0
Wear reduction, HFRR, 1% ester	n/a	43.7	23.2	30.7	30.6	n/a
(%)		(4.2)	(5.3)	(2.4)	(4.6)	
Induction time, 110°C	n/a	3	7	7	9	>180
(min)						
Onset crystallization temperature	n/a					n/a
(°C)						
Saturated compounds		-16.4	-16.5	-12.3	-16.6	
		(0.8)	(0.1)	(1.6)	(0)	
Monounsaturated compounds		-42.5	-51.0	-51.9	-58.2	
		(0.8)	(0.2)	(0.2)	(0)	
Polyunsaturated compounds		-65.4	-93.5	n/a	n/a	
		(0.8)	(1.2)			

Heat of crystallization ($J\ g^{-1}$)	n/a				n/a
Saturated compounds		8.4	8.9	14.7	3.6
		(0.5)	(0.5)	(0.7)	(0.4)
Monounsaturated compounds		46.7	59.0	48.5	36.8
		(2.1)	(0.5)	(0.4)	(0.1)
Polyunsaturated compounds		23.6	11.6	n/a	n/a
		(0.3)	(0.6)		

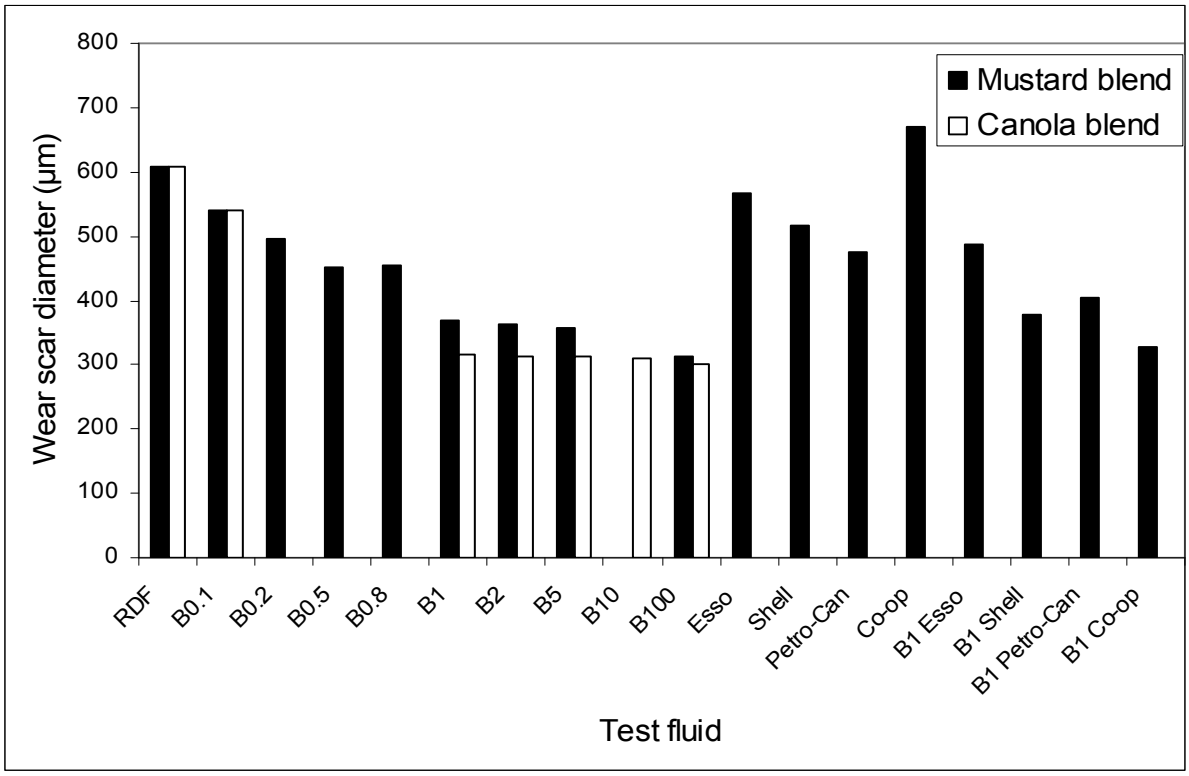
[a]see abbreviation section; [b]The numbers in parentheses are corresponding standard deviation values of 3-4 runs

Since esters were separated from glycerides and polymerized compounds during distillation, the total glycerol content of distilled esters were null, hence rendering ultra high purity esters. In comparison with the data obtained from HPLC using RID, DMME was analyzed for free and total glycerol as per ASTM D6584. Free glycerol was not detected in the GC chromatogram; however, total glycerol was measured at 0.121 mass%. These data suggested that the amount of free and total glycerol contained in the distilled ester was trivial and the quality of DMME met the ASTM specification. Water, sulfur, and phosphorous content of all esters were within the range specified in ASTM D6751. Viscosity of esters was reduced significantly from their parent oil (viscosity of MO = 37.5 cSt) due to transesterification and distillation, and met ASTM specifications.

6.5.7. Lubricity

The lubricating property of fuel is defined as the quality that prevents wear when two moving metal parts come into contact with each other [12]. Oxygen and nitrogen containing compounds are responsible for the natural lubricating property of diesel fuel [13]. In petroleum refineries, the processes such as hydrotreating usually utilized to remove sulfur also destroy heterocyclic oxygen and nitrogen containing compounds [14]. Consequently, this typically ultra-low sulfur diesel fuel exhibits poor lubricity. ASTM D6079-04 was used to evaluate lubricating property of biodiesel and diesel fuel by the High-Frequency Reciprocating Rig (HFRR). In this method, the high wear diameter indicates poor lubricating property of the test fluid and vice versa. In the present chapter, biodiesel samples were blended with the reference diesel fuel and HFRR results were observed. Figure 6.7 shows that the lubricity of the blended fluid increased with an increase in biodiesel percentage. The improvement in lubricity was insignificant when the biodiesel percentage exceeds 1% of regular diesel, therefore, it was concluded that a 1% biodiesel blend was the optimum ratio.

The biodiesel derived from canola oil was somewhat superior in lubricating property as compared to that obtained from mustard oil. However, the biodiesel produced from mustard oil showed great potential as a diesel fuel additive to improve its lubricating property. At 0.1 and 1% distilled mustard oil methyl ester (DMME) blended with diesel fuel, the wear scar diameter was reduced by 11.1 and 43.7%, respectively. The results from Table 6.7 suggest that methyl ester was the best lubricity additive among all esters (methyl-, ethyl-, propyl-, and butyl-ester). This is because the lubricity of biodiesel is provided by the polarity-imparting oxygen atoms and the nature of which the oxygen atom is bound in the molecule.



see abbreviation section

Figure 6.7 Lubricity properties of methyl esters derived from mustard oil and canola oil blended with reference diesel fuel using high frequency reciprocating rig (HFRR) method.

It was reported that the order of oxygenated moiety that provides lubricity are COOH > OH > $COOCH_3$ > C=O > C-O-C [15]. In the case of methyl ester, the lubricity was provided mainly by the $COOCH_3$ moeity. In contrast, the lubricity of ethyl, propyl, and butyl esters was possibly contributed by the ketone group (C=O moiety), due to the lack of $COOCH_3$ moeity in their molecules. Therefore, methyl ester exhibited a better lubricating property when compared to ethyl, propyl, and butyl ester. In addition, four commercial diesel samples were purchased from different gas stations (Esso, Shell, Petro-Canada, Co-op) and tested for their lubricity. The viscosity at 40°C of these commercial diesel fuels were within the range of 2.2-2.4 cSt. The results from Figure 6.7 show that DMME/RDF blends had a lubricating property superior to that

of the purchased commercial diesel fuels. The lubricity of these commercial diesel fuels can be improved by the addition of DMME (see Figure 6.7).

6.5.8. Oxidative Stability

Oxidative stability is an important property as it determines stability of biodiesel. It was reported that the oil stability increases with a decrease in the degree of unsaturation [16]. In this study, the rancimat plot of esters derived from mustard oil is presented in Figure 6.8. The stability of DMBE was higher than those of DMME, DMEE, and DMPE due to its longer carbon chain length. The longer chain provides a lower double bond concentration per molecule, hence lowering degree of unsaturation and thus increasing stability.

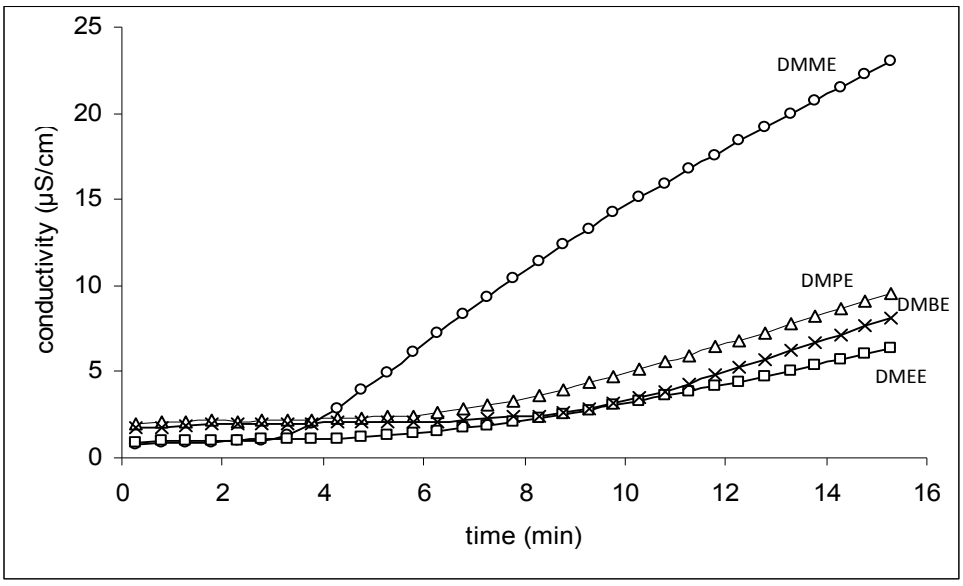


Figure 6.8 A conductivity-time plot for oxidative stability determination of esters derived from mustard oil.

6.5.9. Crystallization

Low temperature property of biodiesel determines how well biodiesel can be operated and stored in a cold environment and therefore is of special importance in cold climate regions. When temperature is reduced to a certain point, a portion of the biodiesel or biodiesel blends begins to crystallize, which can create problems with the engine flow system and eventually cause the engine to cease. Differential scanning calorimetry (DSC) is an effective means to determine the low temperature property of esters with good correlation to cloud point and pour point of biodiesel [2,17]. Figure 6.9 represents a DSC thermogram of esters derived from mustard oil in this study. The exothermic crystallization of saturated, monounsaturated and polyunsaturated esters appeared as peaks in the corresponding DSC thermogram. Crystallization of saturated compounds occurred at higher temperatures due to the arrangement of the molecules. Saturated compounds are well stacked and hence strengthening the intermolecular attractive forces. On the other hand, the *cis*-formation in unsaturated molecules causes distance between molecules and weakens the intermolecular attractive forces, which causes these compounds to crystallize at lower temperatures [2]. The onset crystallization temperatures as well as heats associated with crystallization of each compound are reported in Table 6.7. The crystallization temperature of ester tended to decrease when a higher alcohol was used in transesterification. For unsaturated compounds, if the number of double bonds is the same, a molecule with a higher carbon chain length would have poorer molecular stacking and therefore poorer intermolecular interactions leading to a lower crystallization temperature.

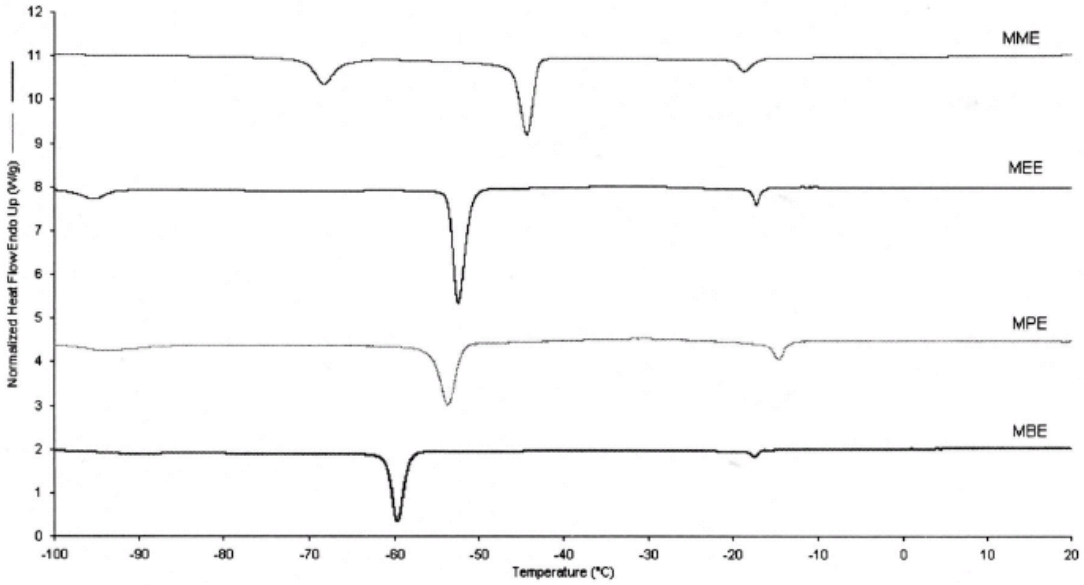


Figure 6.9 DSC thermogram of esters derived from mustard oil.

The low temperature property of biodiesel can be improved by using higher alcohols, i.e., cloud point and pour point of ethyl ester were reported to be lower than those of methyl ester [17,18]. Based on this concept, the freezing points of polyunsaturated compounds in propyl- and butyl-ester would be extremely low and were outside of the DSC scan in this study. Heat from crystallization of monounsaturated compounds was highest as compared to that of saturated and polyunsaturated compounds. This was because the major fatty acids in mustard oil were erucic and oleic acid at 31.6 and 25.3%, respectively (see Table 6.6). Because they both contain one double bond per molecule, these two compounds were considered as monounsaturated. When a large amount of monounsaturated compounds is present in the oil sample, exothermic heat associated to crystallization of these compounds will be higher, as evidenced from the data in tables 6.6 and 6.7. DSC was also used to study petro-diesel and DMME/petro-diesel blends (1% biodiesel). However, crystallization peaks were not observed on any DSC thermograms in this

study. Therefore, it is believed that the crystallization points of these fuels are extremely low and are below the range of DSC scan of 30°C to -110°C. This finding suggests that the fuel can be used without freezing in winter conditions at the optimum biodiesel-diesel blend (1% biodiesel).

6.6. Conclusions

Mustard oil was not suitable for use in direct KOH-catalyzed transesterification. Glycerol formation, hydrolysis and saponification have minor effects on transesterification of mustard oil. Mustard oil methyl ester can be mixed with canola or soybean oil methyl esters up to 1.5 wt.% to obtain an ASTM quality biodiesel. Alternatively, distillation can be used to purify esters derived from mustard oil. The distilled esters were extremely pure in ester content. Properties of distilled methyl and ethyl ester satisfy the ASTM specifications. An improvement was required for a specific property of a specific ester such as AV of butyl ester. Esters derived from mustard oil showed great potential as a lubricity additive to diesel fuel. The optimum ester percentage in a biodiesel-diesel blend was 1% of which wear scar diameter was reduced by 43.7%. Methyl ester was the best lubricity additive among all the esters (methyl-, ethyl-, propyl-, and butyl-ester), and lubricity of the biodiesel-diesel blend was superior to that of commercial diesel fuels. Methyl ester derived from mustard oil did not freeze until the temperature reached -16°C. Monounsaturated compounds (oleic, eicosenoic, and erucic esters) which are largely present in esters derived from mustard oil can tolerate temperatures of -42°C to -58°C. The freezing point of monounsaturated esters can be reduced by using higher alcohols like butyl alcohol as the reactive alcohol. The freezing point of monounsaturated butyl and methyl esters was -58°C and -42°C, respectively. For B1 blend, the fuel can be used at low temperature without freezing.

It is found that mustard MG was more difficult to be transesterified into methyl ester. The kinetic data would be useful to extend our understanding on this topic. Therefore, the kinetics of transesterification was studied and discussed in Chapter 7.

Abbreviations

AV	Acid value
BX	Biodiesel blended with petro diesel at x percent biodiesel
CME	Canola oil methyl ester
DG	Diglyceride
DMBE	Distilled mustard oil butyl ester
DMEE	Distilled mustard oil ethyl ester
DMME	Distilled mustard oil methyl ester
DMPE	Distilled mustard oil propyl ester
DSC	Differential scanning calorimeter
EtOH	Ethanol
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GL	Glycerol
HEAR	High erucic acid rapeseed
HFRR	High-frequency reciprocating rig
HPLC	High performance liquid chromatography
KOH	Potassium hydroxide

LEAR	Low erucic acid rapeseed
MBE	Mustard oil butyl ester
ME	Methyl ester
MEE	Mustard oil ethyl ester
MeOH	Methanol
MG	Monoglyceride
MME	Mustard oil methyl ester
MO	Mustard oil
MPE	Mustard oil propyl ester
RDF	Reference diesel fuel
SME	Soybean oil methyl ester
TG	Triglyceride

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CHAPTER 7

Transesterification Kinetics of Vegetable Oils

A part of this chapter has been accepted for publication in The Canadian Journal of Chemical Engineering:

- Issariyakul, T., and Dalai A.K. Comparative kinetics of transesterification for biodiesel production from palm oil and mustard oil. The Canadian Journal of Chemical Engineering (Accepted).

In addition, a portion of this chapter was presented in the following conferences:

- Issariyakul T., and Dalai A.K. Kinetics of transesterification of palm oil. The 60th Canadian Chemical Engineering Conference, Saskatoon, Saskatchewan, Canada (2010).
- Issariyakul T., and Dalai A.K. Comparative kinetics of transesterification for biodiesel production from palm oil and mustard oil. The 61th Canadian Chemical Engineering Conference, London, Ontario, Canada (2011).

Contribution of the Ph.D. Candidate

Experiments were conducted by Titipong Issariyakul. The content in this chapter was written by Titipong Issariyakul with discussions and suggestions provided by Dr. Ajay Dalai.

Contribution of this Chapter to the Overall Ph.D. Research

Kinetic study of transesterification is an important part of the Ph.D. research. In order to study transesterification kinetics, mustard oil is selected because kinetic data of mustard oil transesterification is not available in the literature. Research work in this chapter is extended to a study of an effect of saturation/unsaturation fatty acids on transesterification kinetics. In order to study this effect, palm oil is also chosen due to its high saturated fatty acid (palmitic acid, C16:0) content.

7.1. Abstract

The kinetics of palm oil and mustard oil transesterification are compared. Transesterification of palm oil and mustard oil using KOH as a catalyst was performed at various reaction temperatures ranging from 40°C to 60°C. The reaction steps are reversible and transesterification is favoured at elevated temperatures. The reaction step of triglyceride to diglyceride is the rate determining step (RDS) that controls kinetics of overall transesterification with activation energies of 30.2 and 26.8 kJ/mol for palm oil and mustard oil transesterification, respectively. It is found that percentage of saturated compounds play a vital role on transesterification kinetics.

7.2. Introduction

Biodiesel has drawn tremendous attentions from scientists around the world. It is considered as one of the most promising alternative renewable bio-fuels that can be used as substitutes and additives for the conventional non-renewable petroleum diesel. The use of biodiesel is simple yet effective as it is miscible with petroleum diesel in all proportions and it can be used in diesel engine with no requirement for engine modifications. Biodiesel is derived from lipid feedstock such as vegetable oils and animal fats. Mustard oil is selected in this chapter because its kinetic data is much needed in the coming years for Canadian biodiesel industry. This is because of the fact that the new 2% federal mandate for biodiesel in Canada in 2011 requires approximately 500 million litres per year of biodiesel demand across the country while the Canadian biodiesel production capacity is only 200 million litres per year in 2010 [1]. To fill up the biodiesel production capacity, the domestic mustard is anticipated to play a vital role as there is a bountiful supply of Canadian mustard available (306,000 tonnes per year of production

capacity in Canada) on top of the fact that mustard oil is non-edible [2]. Although, process optimization for biodiesel production from mustard oil as well as fuel properties have been extensively investigated in the previous chapter, kinetic data for transesterification of such oil are not available in the literature and are urgently needed. The kinetic data of mustard oil transesterification presented in this chapter will not only benefit Canadian biodiesel industry but also biodiesel manufacturers outside Canada employing mustard oil as feedstock. In addition to being one of the world's most productive vegetable oils, palm oil is also selected in this research due to the uniquely high saturated content to study an effect of saturated and unsaturated content as well as chain length distribution on kinetic of transesterification. Furthermore, palm oil is reported to have more economical advantages when compared to canola and soybean oil [3].

Biodiesel can be produced via a reversible chemical reaction called "transesterification" which is shown in Figure 7.1. Transesterification is the reaction between glycerides with short chain alcohols and it is comprised of three consecutive reactions starting from triglyceride (TG) to diglyceride (DG) to monoglyceride (MG) to glycerol (GL), respectively. In each step, the reaction consumes one mole of alcohol and produces one mole of ester. In the present chapter, methanol and KOH were used as a reacting alcohol and catalyst, respectively.

The rate constants of each reaction step are usually different. The values of the rate constants indicate the rates of the corresponding reaction step as well as reversibility of each step. Moreover, they can be used to determine the rate determining step (RDS) that controls the kinetics of overall transesterification. Therefore, the kinetic data are of crucial importance for the design for process development.

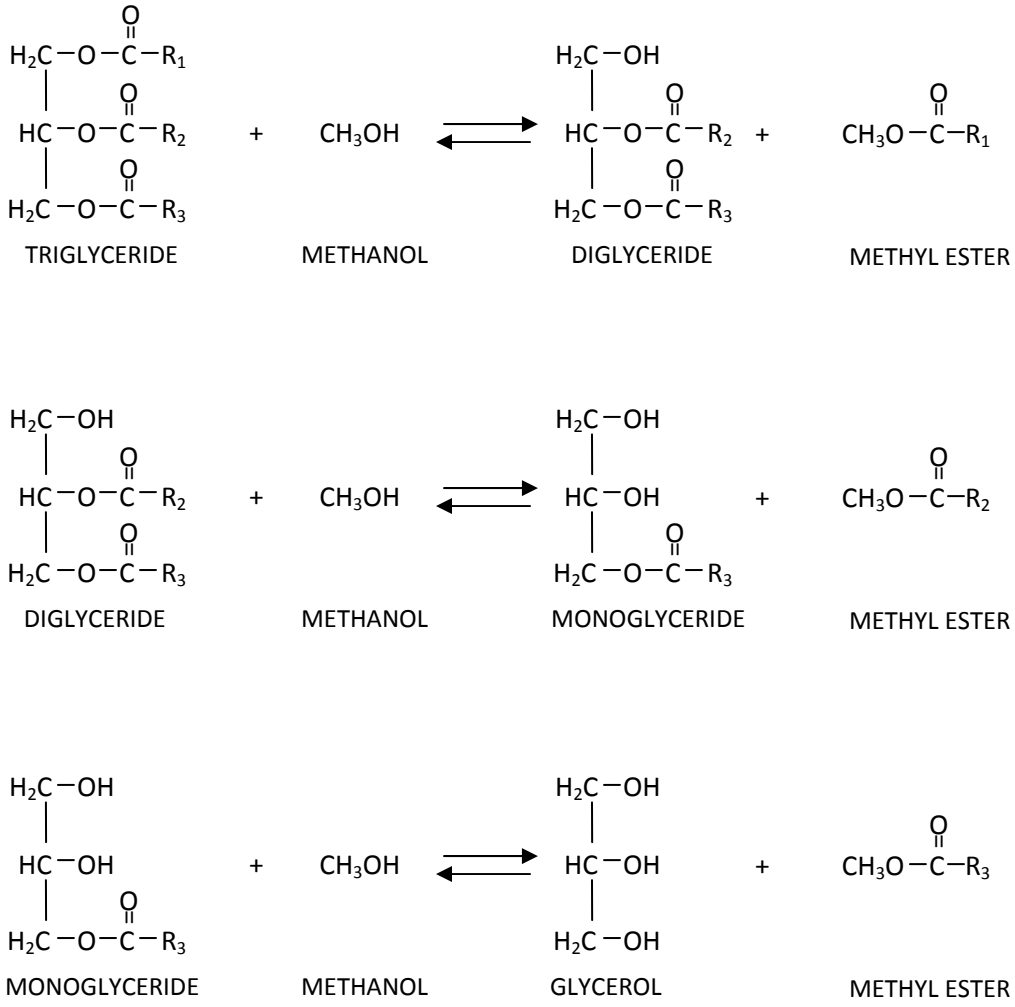

Figure 7.1 Scheme for step-wise transesterification reaction.

Results from literature suggest that transesterification of vegetable oils with low alcohol to oil molar ratio (6:1) using homogeneous base catalysts follows second order kinetics [4-7]. The proposed reaction mechanism consists of an initial mass transfer-controlled region followed by kinetically controlled region [6,7]. The initial mass transfer region alters the observed kinetic data and therefore need to be minimized by means of rigorous mechanical agitation [7], co-solvent aid [8,9], or supercritical conditions [10].

The kinetic models can be derived by applying rate law [11] to each reaction step shown in Figure 7.1. The rate constants can then be calculated using a numerical method. Computer programming such as MATLAB program is often used for this purpose. Although there are many kinetic studies on transesterification reaction reported in the literature, the details on computer programming are inadequately elucidated. The complicated nature of transesterification along with the lack of clear explanation on computer programming has resulted in hardship and frustration in kinetic study of this reaction system. Consequently, many research groups have simplified the reaction system using assumptions of shunt reaction [12] and irreversible reaction [13]. The shunt reaction mechanism employs the overall transesterification reaction as shown in Figure 7.2. Although, the kinetic models can be simplified using shunt reaction mechanism, it is highly unlikely that three molecules of methanol would simultaneously attack the triglyceride molecule to form three molecules of methyl ester (ME). The shunt mechanism is easily disproved by the formation of diglyceride and monoglyceride which is widely reported in the literature. In the case of irreversible reaction, it is assumed that the values of all reverse rate constants are zero. In the case when the values of all reverse rate constants are adequately low, the simulated results based on this assumption may seem to fit with experimental data. However, many studies have suggested that the values of all reverse rate

constants are not zero and therefore the reactions are proven reversible [4-7,14,15]. Therefore, the kinetic models should be derived based on three consecutive reversible reaction steps. In the present chapter, the kinetics of transesterification of palm oil and mustard oil with methanol using KOH as a catalyst are compared. This study includes preliminary analysis of lipid feedstock, experimental development, kinetic modelling, MATLAB programming, and kinetic parameters interpretation.

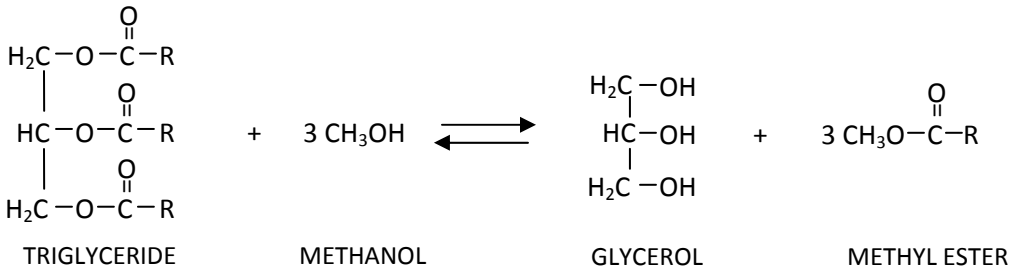

Figure 7.2 Scheme for transesterification based on shunt reaction mechanism.

7.3. Materials

Food grade palm oil (*Palm Olein*, Oleen Brand) was purchased from a grocery store in Thailand. Mustard oil (*Sinapis Alba*) was provided from Mustard Capital Inc., Saskatoon, SK, Canada. Anhydrous methanol (MeOH) (99.8%) and potassium hydroxide (KOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany. Dichloromethane, centrifuge and centrifuge tubes were purchased from VWR International, Canada. Reference standard chemicals including triolein, diolein, monoolein, and methyl oleate were purchased from Nu-Chek Prep, Inc. MN, USA. Grain FAME mix and monoglyceride stock solution, 1,2,4-Butanetriol (internal standard

1) and 1,2,3-Tridecanolylglycerol (tricaprin) (internal standard 2) were purchased from Sigma-Aldrich, ON, Canada.

7.4. Experimental Procedures

7.4.1. Feedstock Analysis

A food-grade palm oil and mustard oil were used in this chapter. The fatty acid composition of palm oil and mustard oil were evaluated using the GC method described in Section 7.4.4. Table 7.1 summarizes fatty acid composition of palm oil and mustard oil. The data from this table suggest that palmitic and oleic are largely presented in palm oil at 37 and 43 wt.%, respectively while oleic and erucic are largely present in mustard oil at 25 and 33 wt.%, respectively. Average values of molecular weight of palm oil and mustard oil, which were calculated based on fatty acid compositions, are 853 and 947 g/mol, respectively and are presented in Table 7.2 along with other properties. Afterward, the average molecular weight of palm oil and mustard oil were used to calculate an amount of methanol required for each experiment. TG and DG concentrations obtained via GC method are 0.97 and 0.15 mol/L for palm oil and 0.52 and 0.01 mol/L for mustard oil, respectively. The acid value (0.2 – 0.8 mgKOH/g) and water content (255 - 299 ppm) of both oils are sufficiently low to neglect side reactions, e.g. saponification and esterification.

Table 7.1 Fatty acid composition (wt.%) of palm oil and mustard oil.

Structure	Compound name	Palm	Mustard
C14:0	Myristic ester	1.14	0.05
C16:0	Palmitic ester	37.08	2.80
C16:1	Palmitoleic ester	0.22	0.16
C16:2	n/a[a]	0	0.06
C18:0	Stearic ester	3.89	1.09
C18:1 z9	Oleic ester	42.93	24.98
C18:1 z11	Asclepic ester	0.72	1.10
C18:2	Linoleic ester	12.20	11.64
C18:3	Linolenic ester	0.52	8.61
C20:0	Arachidic ester	0.06	0.70
C20:1	n/a[a]	0.33	10.44
C22:1	Erucic ester	0	32.81
	Saturated compounds	42.17	4.64

[a]n/a = not available

Table 7.2 Chemical properties of palm oil and mustard oil.

Property	Palm	Mustard
Average molecular weight (g/mol)	853	947
Triglyceride (mol/L)	0.97	0.52
Diglyceride (mol/L)	0.15	0.01
Acid value (mgKOH/g)	0.2	0.8
Water content (ppm)	255	299

7.4.2. Transesterification

Transesterification of palm oil and mustard oil were conducted using a stirred reactor equipped with temperature and stirring speed controller model 4848 from Parr Instrument Company, IL, USA. For each experiment, 150 grams of oil was placed in the reactor. Methanol (6:1 alcohol to oil molar ratio) was mixed with KOH (1 wt.% with respect to oil) in a conical flask. The oil was first heated to 4-5°C above the reaction temperatures. The alkaline methanol solution was then poured into the reactor vessel bringing the temperature down to the desired reaction temperature ranging from 40°C-60°C. Finally, the reactor was sealed, the mechanical agitation was started, and the time was marked as initial point (t=0).

7.4.3. Sample Preparation

The reaction samples (5 mL) were taken from the reactor vessel during transesterification at 1, 2, 4, 6, 8, 10, 20, and 30 minute. The samples were immediately mixed with 5 mL of 0.01 N aqueous HCl solutions. During this period, HCl reacted with the catalyst KOH to produce water

soluble potassium salt (KCl). The KOH catalyst was neutralized and thereby stopping the transesterification reaction. The mixtures were centrifuged to form a two phase mixture; oil phase and aqueous phase. Emulsion is formed in between these two phases and its thickness varies proportionally with the amount of diglyceride and monoglyceride formed in the reaction mixture. Since diglyceride and monoglyceride are partly trapped inside the emulsion layer, the sample taken directly from the oil phase at this stage is not a good representative of the reaction mixture at a specific time. The compounds in aqueous phase are water, HCl, and KCl none of which is of our interest in this study, and therefore the aqueous phase was discarded. Dichloromethane (DCM) was used to extract organic compounds and sodium sulfate anhydrous which is previously dried in an oven was used for further removal of water. The sample was then centrifuged, DCM was evaporated. Part of methanol was removed along with the aqueous phase and the remaining methanol was evaporated along with DCM.

The samples were then directly diluted with DCM for GC injection without derivatization due to the following reason. In GC, the mixture is separated mainly by boiling point and structure (imparting polarity). In some cases, derivatization is required because diglyceride and monoglyceride contain free hydroxyl groups, causing these materials not to be quantified well in GC. Derivatization of these compounds cause a change in their structure and polarity therefore improving peak shape and peak separation. Therefore, an experiment was set up by derivatizing a sample containing TG, DG, MG, and ME using N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) as a derivatizing agent. The derivatizing procedure is followed as per that specified in ASTM D6584 method excepting that DCM was used as a solvent instead of n-heptane. Shifts in retention time were observed but not peak shape or peak separation and most importantly the

resulting concentration of each compound was not affected. Therefore, it is concluded that under analyzing conditions and column used in this research, derivatization is not required.

7.4.4. Characterization

Acid values and water content were measured by means of titrations as per AOCS Te 1a-64 method and ASTM D 6304-07 method. Fatty acid compositions analysis was performed on a gas chromatography (GC) model Agilent 7890A using J&W 122-2362 DB23 column (60 m x 250 μm x 0.25 μm; 250°C max temperature), Split-splitless Inlet at 260°C, 23.3 psi, 100:1 Split ratio, 1 μL injection volume, and FID Detector, at 260°C, 40 mL/minute H_2 flow rate, and 400 mL/minute air flow rate. The program was set to start at 140°C and hold for 5 minutes, then ramp from 140°C to 240°C at 4°C/minute and hold for 10 minutes with a total run time of 40 minutes. In order to measure TG, DG, MG, and ME content, the organic phase was analyzed by a GC model Agilent 7890A equipped with auto sampler using J&W 123-5711 DB-5HT column (15 m x 320 μm x 0.1 μm; 400°C max temperature), cool on-column Inlet with track oven temperature mode, 7.6 psi, 1 μL injection volume, and FID Detector, at 380°C, 40 mL/minute H_2 flow rate, and 400 mL/minute air flow rate. The program was set to start at 50°C, ramp from 50°C to 230°C at 5°C/minute, and ramp from 230°C to 380°C at 30°C/minute and hold for 18 minutes with a total run time of one hour. For calibration methods of GC, 5 standards of each compound (TG, DG, MG, and ME) were prepared at 5 different concentrations. Each standard was injected 3 times into the GC and an average value was used to generate 5-point calibration curves for each component. All calibration curves yield r^2 of more than 0.99 (see Appendix C). In general, internal standards are used for 2 purposes, peak identification and quantification. For

identification, 1,2,4-Butanetriol and 1,2,3-Tridecanolylglycerol (tricaprin) were used as internal standards along with TG, DG, MG, and ME standards mentioned in Section 7.3.

Methanol concentrations were calculated based on a concept of number of mole of methanol consumed equals to number of mole of methyl ester formed. Based on the concept of number of mole of glycerol group in the reaction mixture is constant, glycerol concentrations were calculated from Equation 7.1 as follow:

$$n_{TG0} + n_{DG0} + n_{MG0} = n_{TGi} + n_{DGi} + n_{MGi} + n_{GLi} \quad \text{…(Eq.7.1)}$$

where; n_{TG0} is initial number of mole of triglyceride, n_{DG0} is initial number of mole of diglyceride, n_{MG0} is initial number of mole of monoglyceride, n_{TGi} is number of mole of triglyceride at time = i, n_{DGi} is number of mole of diglyceride at time = i, $n_{T=MGi}$ is number of mole of monoglyceride at time = i, and n_{GLi} is number of mole of glycerol at time = i.

7.4.5. The Kinetic Model

The sequential reaction scheme shown in Figure 7.1 can be divided into six irreversible reactions.

$$TG + MeOH \xrightarrow{k1} DG + ME \quad \text{…(r1)}$$

$$DG + ME \xrightarrow{k2} TG + MeOH \quad \text{…(r2)}$$

$$DG + MeOH \xrightarrow{k3} MG + ME \quad \text{…(r3)}$$

$$MG + ME \xrightarrow{k4} DG + MeOH \quad \text{…(r4)}$$

$$MG + MeOH \xrightarrow{k5} GL + ME \quad \text{…(r5)}$$

$$GL + ME \xrightarrow{k6} MG + MeOH \quad \text{…(r6)}$$

Where; TG is triglycerides, DG is diglycerides, MG is monoglycerides, GL is glycerol, MeOH is methanol, and ME is methyl ester.

Upon applying rate law to these reactions, six differential equations can be written as

$$\frac{dTG}{dt} = -k_1[TG][MeOH] + k_2[DG][ME] \quad \ldots(\text{Eq. 7.2})$$

$$\frac{dDG}{dt} = k_1[TG][MeOH] - k_2[DG][ME] - k_3[DG][MeOH] + k_4[MG][ME] \quad \ldots(\text{Eq. 7.3})$$

$$\frac{dMG}{dt} = k_3[DG][MeOH] - k_4[MG][ME] - k_5[MG][MeOH] + k_6[ME][GL] \quad \ldots(\text{Eq. 7.4})$$

$$\frac{dME}{dt} = k_1[TG][MeOH] - k_2[DG][ME] + k_3[DG][MeOH] - k_4[MG][ME] + k_5[MG][MeOH] - k_6[ME][GL] \quad \ldots(\text{Eq. 7.5})$$

$$\frac{dGL}{dt} = k_5[MG][MeOH] - k_6[ME][GL] \quad \ldots(\text{Eq. 7.6})$$

$$\frac{dMeOH}{dt} = -k_1[TG][MeOH] + k_2[DG][ME] - k_3[DG][MeOH] + k_4[MG][ME] - k_5[MG][MeOH] + k_6[ME][GL] \quad \ldots(\text{Eq. 7.7})$$

In addition; $k_i = k_{ic}C_{cat} + k_{in}$ …(Eq. 7.8)

Here, i = 1, 2, 3, 4, 5, 6 and k_1, k_3, k_5 are forward rate constants and k_2, k_4, k_6 are reverse rate constants. In addition, the rate constants are influenced from catalyzed and non-catalyzed reactions, thus k_i represents effective rate constants, k_{ic} represents rate constants for catalyzed reactions, k_{in} represents rate constants for non-catalyzed reactions, and C_{cat} is the catalyst concentration. In this study, the reactions were performed at mild temperature (40-60°C), hence it is assumed that the rate constants for non-catalyzed reactions are insignificant and can be neglected. In addition, the catalyst concentration used in this study is considered as a constant (1 wt.%), thus the effective rate constants can be directly estimated from Equations 7.2 to 7.7. It is noted that both primary and secondary DG can be formed from TG. However, the formation of

secondary DG is sterically hindered and, therefore, it is assumed that primary DG is the major DG formed in this study. Hence, all DG mentioned in this chapter is referred to primary DG.

7.4.6. The MATLAB Program

In order to estimate the values of the rate constants, a computer program was developed by incorporating regression and differential equation solvers using MATLAB version 7.7.0.471. The backgrounds in MATLAB programming can be found in MATLAB textbooks [16,17]. The program consists of 5 functions which are "inputvalue" for entering experimental data, "KinODE" for storing differential equations, "err" for defining error function, "main" for executing the program, and "plotgraph" for generating graph. These functions are written in MATLAB program as shown in Appendix D.

Initially, the experimental data were inserted in the "inputvalue" function. *C* was then defined as concentrations of each species at various times in time and species dimension matrix. Equations 7.2 to 7.7 were stored in the function "KinODE". These differential equations were solved using a built-in MATLAB command *"ode45"* which employs 4^{th} and 5^{th} order Runge-Kutta formular. The *Cerror* metrix was defined as the differences between experimental values and calculated values.

$$C_{error} = | C_{cal} - C_{exp} | \qquad \text{…(Eq. 7.9)}$$

Where *Ccal* and *Cexp* are matrices that store output elements from calculation and experimental value elements, respectively. The error function output "err" was then defined as a summation of all elements in *Cerror* matrix. This error function output was then minimized

using another built-in MATLAB command *"fminsearch"* which employs the Nelder-Meade simplex algorithm [18]. The *"fminsearch"* command accepted input vector *KI*, i.e. initial guess values of k_1 to k_6, and returned scalar err and minimized it. The *"fminsearch"* command is not a preferred choice for solving problems of sum of squares; therefore the error function was defined based on sum of absolute values in the matrix *Cerror* instead of squares of each species in vector form (see Equation 7.9). The initial guess values are crucially important as improper guess values lead to a stiff problem. When the problem is stiff, the returned *C* values change rapidly between each step size, therefore the program must take a smaller step to obtain satisfactory results which leads to a change in dimension of metrix *Ccal*, rendering *Cerror* undefined. The most effective way to avoid this problem is to choose initial guess values appropriately. Alternatively, *"fminunc"* which uses a different algorithm based on quasi-Newton or interior-reflective Newton method may be used to find the minimum value of the error function.

The rate constants of each reaction step varied with reaction temperature. The Arrhenius equation (Equation 7.10) shows temperature dependency of the rate constant.

$$k = Ae^{(\frac{-E_a}{RT})} \qquad \ldots(\text{Eq. } 7.10)$$

Where k is the rate constant; A is pre-exponential factor; E_a is the activation energy; R is the gas constant; T is reaction temperature. From this equation, the activation energy can be calculated by plotting logarithm of the rate constant versus the reciprocal of the reaction temperature [11].

7.5. Results and Discussions

7.5.1. The Mass Transfer Effect

The observed rate, also known as "apparent rate", obtained from experimental data is influenced by mass transfer effect. In a kinetic study, the experiment should be conducted in such a way that the observed rate is representative of the kinetic rate, which is achieved when the mass transfer effect is minimal. The mass transfer effect is the period that there is no reaction going on and yet is recorded as "reaction time" during an experiment. This period is associated with the time that triglyceride molecule spends in order to move into methanol phase and collides with methanol molecule. This period occurs at the initial part of the reaction and is often referred to as "mass transfer-controlled region". In some cases, the effect of mass transfer is visible as shown in Figure 7.3a. When an experiment was conducted at agitation speed of 200 rpm, triglyceride takes long time to move into methanol phase and to collide with methanol molecule. During this period, there is little to no reaction taking place and the mass transfer effect is shown in terms of low TG conversion. In contrast, when the reaction was performed at agitation speed of 600 rpm, the TG conversion increased immediately indicating that the mass transfer effect was reduced. Figure 7.3b shows the effect of agitation speed (200, 400, 600, 800 rpm) on TG conversion. An increase in stirring speed helps with mass transfer in the reaction mixture but it is not associated with kinetics of the reaction. Therefore, if the reaction is mass transfer controlled, an increasing in stirring speed would cause an increase in TG conversion. However, if the reaction is kinetically controlled, stirring speed will have no effect on the observed TG conversion.

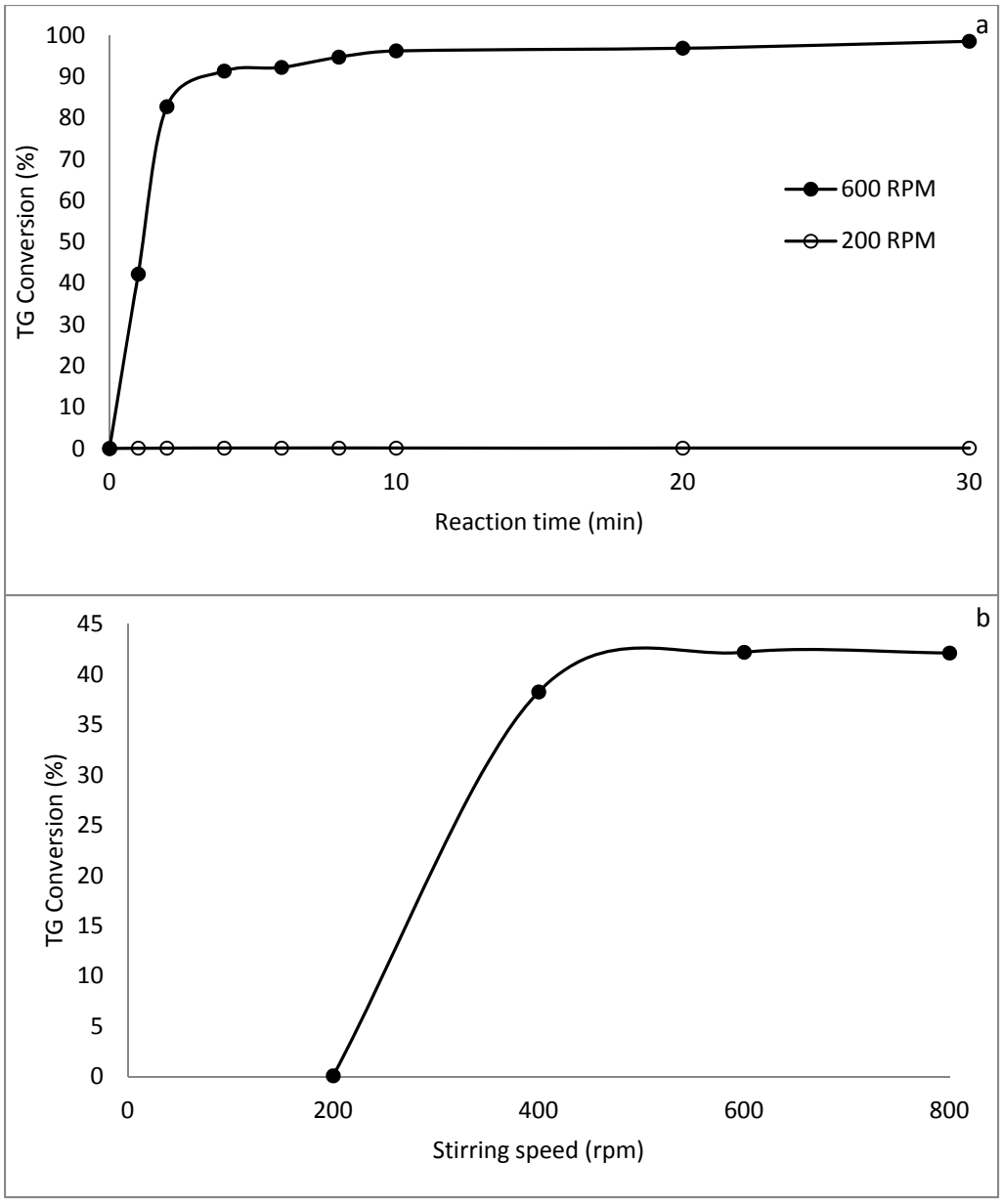

Figure 7.3 Effect of stirring speed during palm oil transesterification at 60°C on

a) TG conversion using 200 and 600 rpm;

b) TG conversion at 1 minute using 200, 400, 600, and 800 rpm.

The results in Figure 7.3b indicate that mass transfer is minimized at 600 rpm and any increase in agitating speed beyond 600 rpm causes no change in TG conversion. Therefore, it is concluded in this work that a stirring speed at 600 rpm is sufficient to neglect the effects of mass transfer and for calculating kinetics of the reaction.

The use of solvent is another approach to reduce the mass transfer effect. However, it was not included in the present chapter due to the following reason. An addition of solvent causes change in concentrations of each component, and "apparent rate of the reaction" is altered. As a result, the apparent rate obtained from a study using solvent is not relevant to processes without using solvent that currently employed in this research and by many biodiesel manufacturers. An addition of solvent helps to improve mass transfer usually occurred only during the first few minutes of the reaction. The added costs of using solvent seem unnecessary when the reaction gets close to equilibrium within less than 10 minutes without solvent as shown in this chapter. In addition, although the reaction mixture is rendered single phase via addition of solvent, triglyceride molecules still need time to move and collide with methoxide prior to reaction and therefore the mass transfer effect is not eliminated, consequently the observed rate is still "apparent rate". Therefore, an addition of solvent is believed to be an unnecessary complication and not being used in this chapter and by many kinetic studies [4-7,19].

7.5.2. Repeatability

Repeatability is one of the most important factors in this experiment. Each reaction was conducted three times at the same condition and the average values were used in the kinetic models. Figure 7.4 shows actual and average data for a typical transesterification run, which illustrates that the experimental errors for each experiment are trivial. The concentrations of the

reaction mixture during palm oil and mustard oil transesterification are shown in Figure 7.5. It is observed that the initial changes during the first 10 minutes of the reaction are most vital whereas the concentration changes after 10 minutes of the reaction are relatively insignificant. This observation is expected due to the nature of the rapid rate of KOH-catalyzed transesterification.

7.5.3. The Rate Constants and Activation Energies

Figure 7.6 shows experimental versus simulated data obtained from the MATLAB programs during reaction at 60°C. It is observed that the simulated curves adequately fit with the experimental data. The pearson's correlation coefficients are calculated based on an equation reported in literature [20] and found to be more than 0.9. An increasing trend in the rate of methyl ester formation with reaction temperature found in Figure 7.7 confirms that the reaction is favoured at higher temperatures, in line with those reported in literatures [6,7,9,10,21].

The main difference between palm and mustard oil that has most influence on kinetics of transesterification is their fatty acid compositions (see Table 7.1). The two main differences in fatty acid compositions between palm and mustard oil are amount of saturated compound and chain length distribution. The rates of each reaction steps are affected differently by these properties, i.e., TG to DG reaction step is affected by the amount of saturated compound while MG to GL reaction step is more influenced by the chain length distribution. Palm oil has more saturated compounds (42.2%) compared to mustard oil (4.6%) making it more stable due to structural arrangement and molecular stacking, which is resulted in stronger intermolecular forces and therefore more difficult to transesterify. Consequently, for each reaction temperature, the rate constants of TG to DG reaction step (k_1) in palm oil transesterification are lower than those in mustard oil transesterification as shown in Table 7.3.

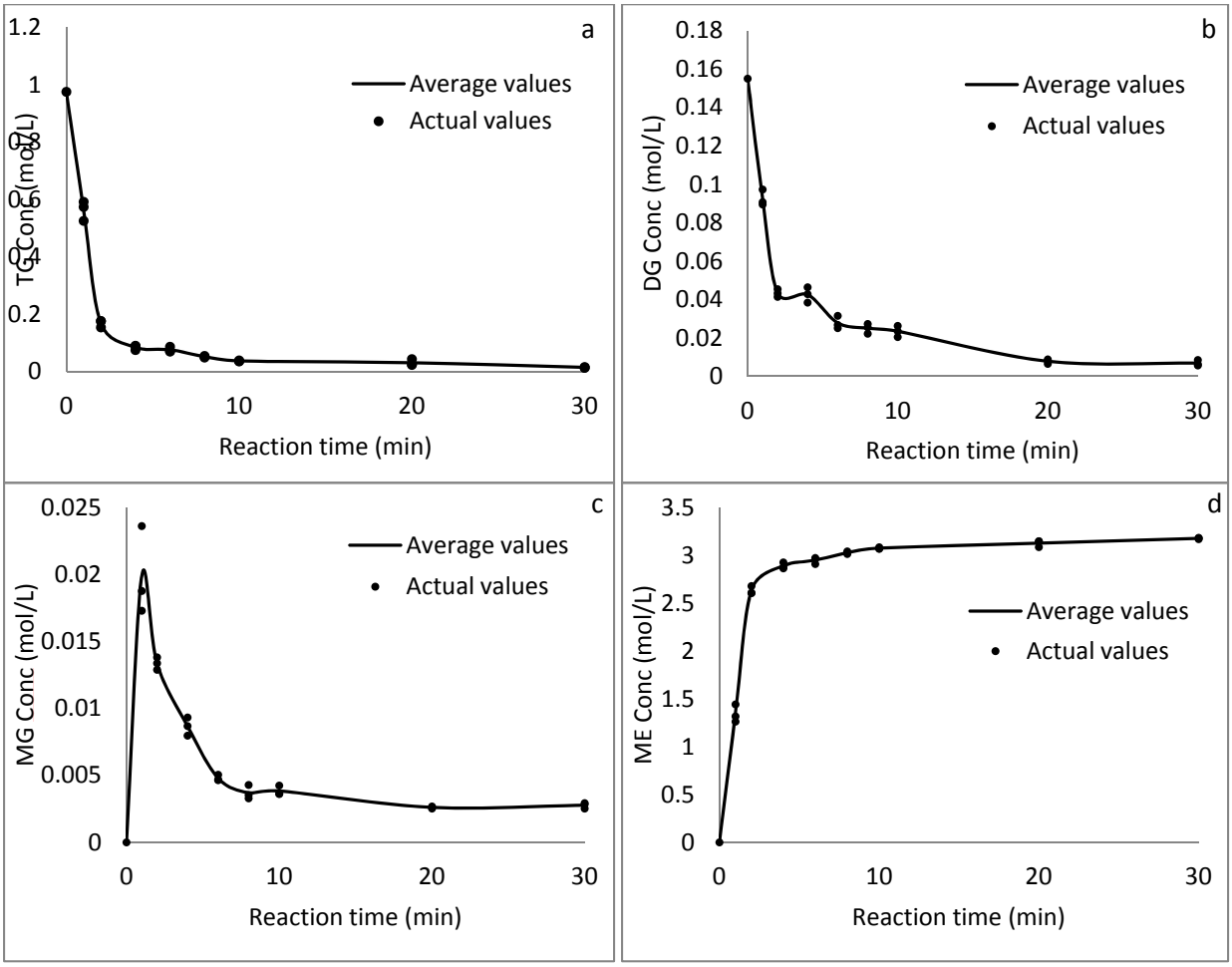

Figure 7.4 Concentrations change during palm oil transesterification at 60°C and 600 rpm:

a) triglyceride concentration; b) diglyceride concentration;

c) monoglyceride concentration; d) methyl ester concentration.

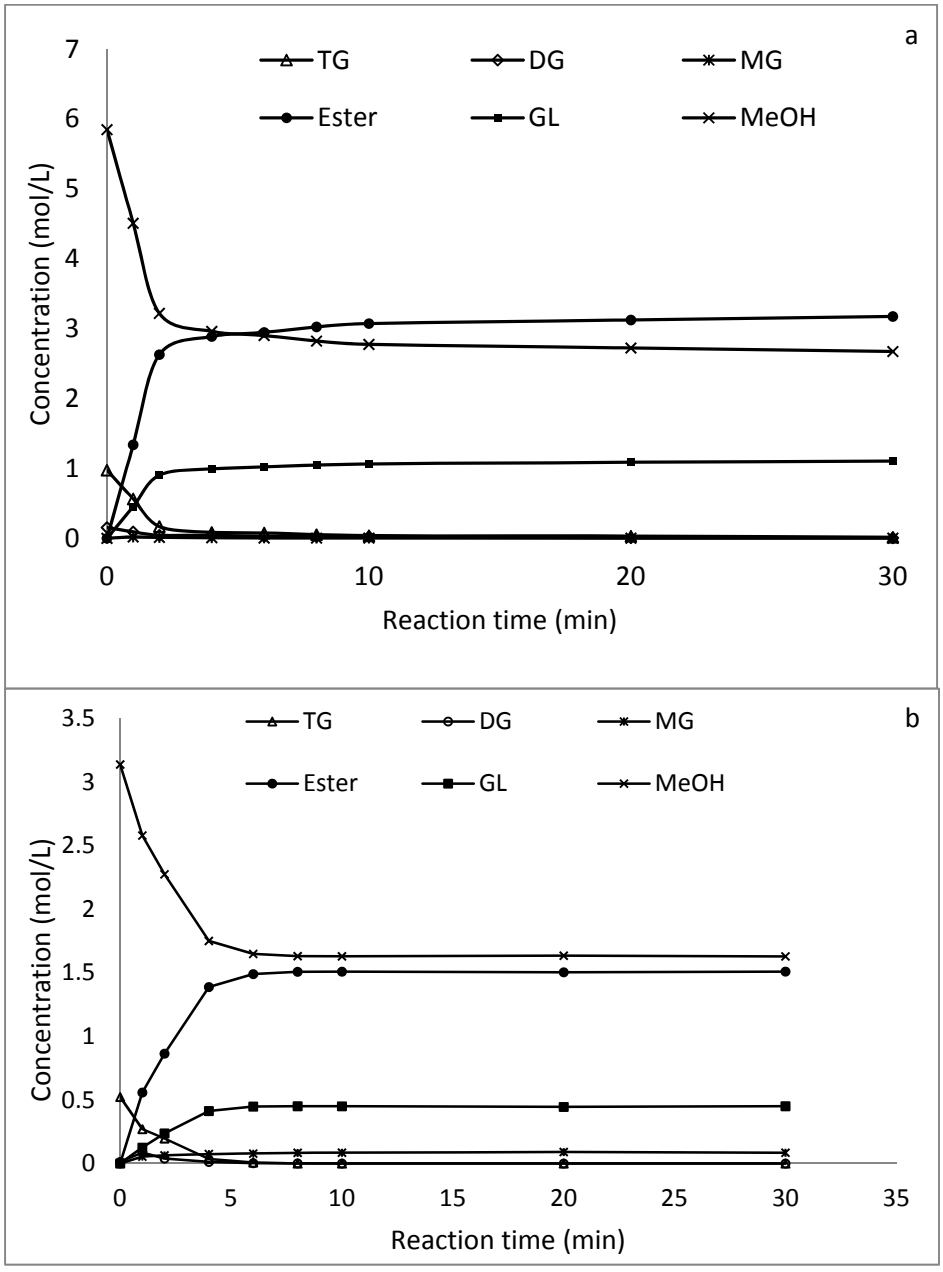

Figure 7.5 Concentrations of the reaction mixture during

a) palm oil; b) mustard oil transesterification at 60°C and 600 rpm.

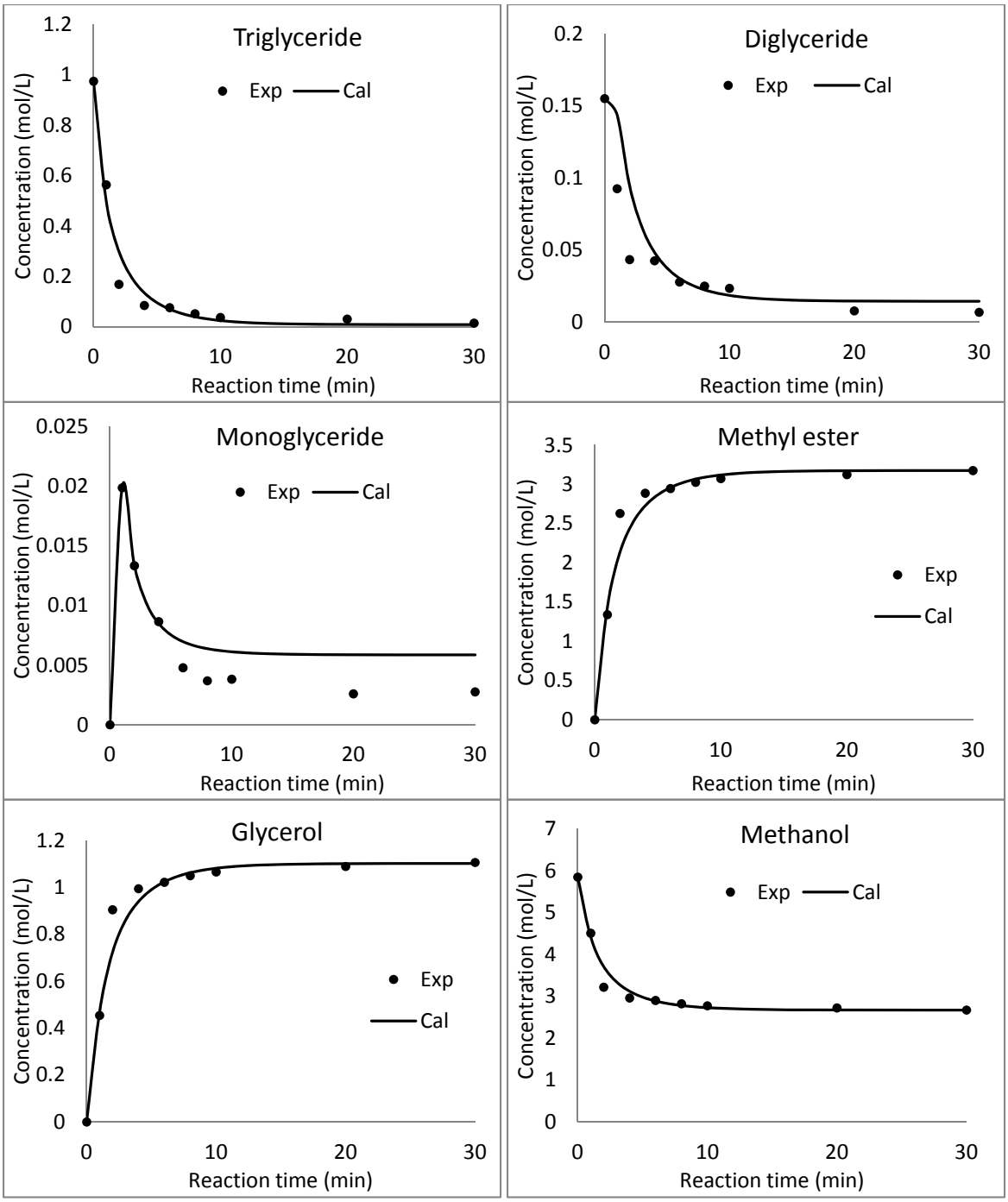

Figure 7.6 Experimental and simulated data during palm oil transesterification at 60°C: a) triglyceride concentration; b) diglyceride concentration; c) monoglyceride concentration; d) methyl ester concentration; e) glycerol concentration; f) methanol concentration.

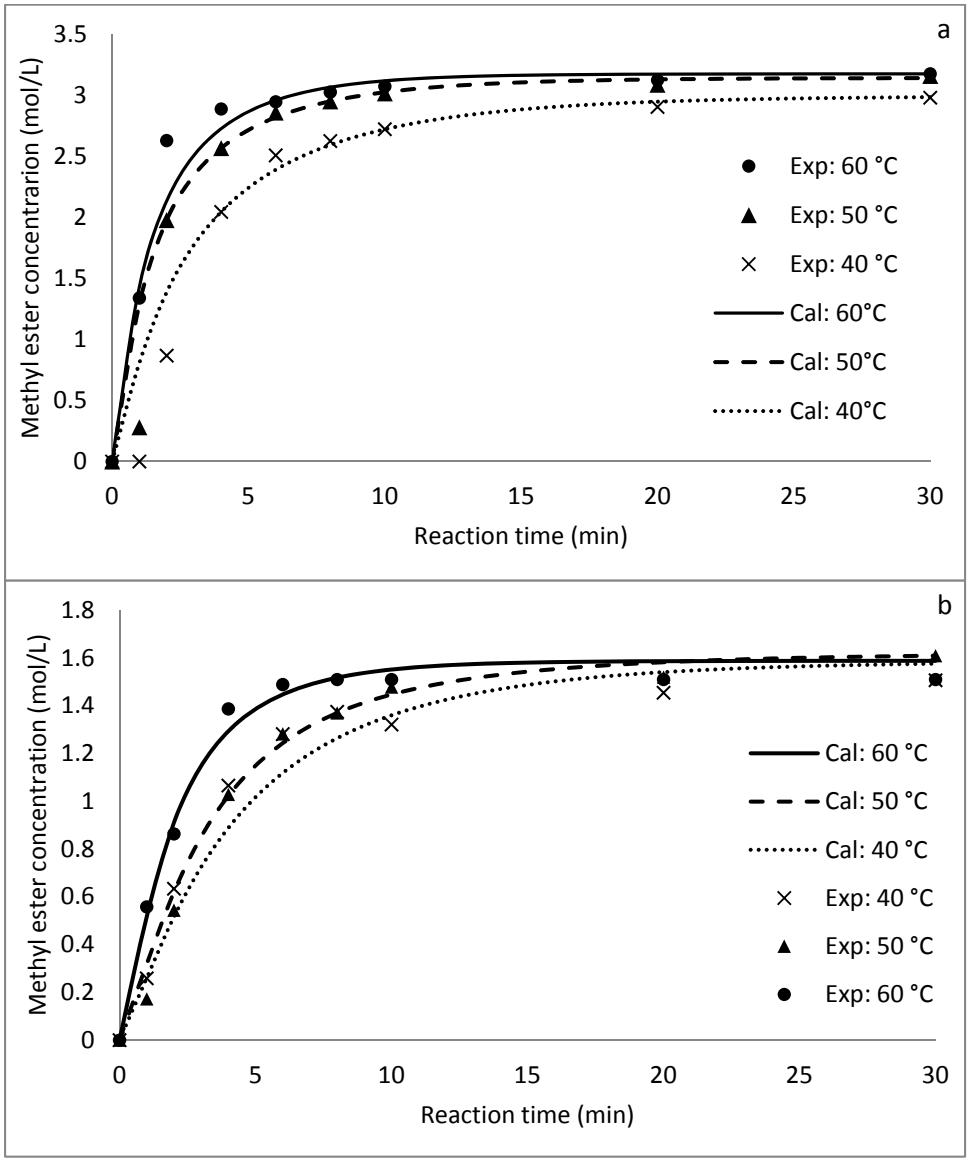

Figure 7.7 Experimental and simulated methyl ester concentrations during a) palm oil; b) mustard oil transesterification.

Table 7.3 The rate constants of each reaction step during transesterification.

Reaction	Direction	Rate constant	Palm oil			Mustard oil		
			40°C	50°C	60°C	40°C	50°C	60°C
TG ↔ DG	Forward	k_1	0.07	0.12	0.14	0.11	0.14	0.21
	Reverse	k_2	0.10	0.17	0.06	0.10	0.11	0.02
DG ↔ MG	Forward	k_3	0.31	0.61	0.60	0.55	0.63	1.04
	Reverse	k_4	0.64	1.52	1.24	0	0	0
MG ↔ GL	Forward	k_5	1.15	2.56	4.18	0.19	0.26	0.64
	Reverse	k_6	0.02	0.01	0.02	0	0.04	0.01

In contrast, mustard oil has unique fatty acid composition containing erucic acid as the main fatty acid (see Table 7.1). This specific fatty acid has untypically long carbon chain, thus rendering lower molecular polarity compared to palm oil. Due to the lower molecular polarity, MG of mustard oil has lower tendency to attract methoxide for reaction to form ME and GL. This phenomenon is exhibited in terms of lower rate constants of MG to GL reaction step (k_5) of mustard oil transesterification compared to those of palm oil (see Table 7.3).

Although it is well know that transesterification is a reversible reaction, further understanding on this regard can be obtained from a kinetic study. Each reverse rate constant gives information to reversibility of the corresponding reaction step. It is observed that the values of reverse rate constants are not zero (except k_4 in mustard oil transesterification) which indicates that the reaction steps of TG to DG, DG to MG, and MG to GL are reversible. The exceptionally low values of k_6 indicate that the reaction step of MG to GL is less reversible. This observation is

due to phase separation of glycerol from oil phase; however the reverse reaction can still take place at the glycerol-methyl ester interface rendering a small positive value of k_6. The rate constants k_5 of mustard oil transesterification are significantly lower than those of palm oil transesterification due to the effect of chain length distribution discussed above. Once formed, MG has a better chance to proceed with the forward reaction step by reacting with methanol to form GL rather than to reverse the reaction step by reacting with ME to form DG. Therefore, the reverse rate constants are lower than the forward rate constants. Since the forward reaction step is very slow (low value of k_5), the reverse rate constants (k_4) are unnoticeable (see Table 7.3). In addition, it is found that the rate constant k_1 is the lowest among forward rate constants indicating that the reaction step involving TG to DG is the rate determining step (RDS) that controls the kinetic of overall transesterification of palm oil and mustard oil. Moreover, when the reaction temperature is increased, the rate constant of RDS is also increased. This finding indicates that the reaction is favoured at higher reaction temperatures.

Activation energies (E_a) of the rate determining step were calculated from Arrhenius plots (see Figure 7.8) and are presented in Table 7.4. The activation energy is the minimum energy required for a reaction to take place. The activation energies of TG to DG reaction step for palm oil transesterification are reported at various values ranging from 27.3 to 61.5 kJ/mol [22,23]. In the present chapter, the activation energy of RDS of plam oil transesterification is found to be 30.2 kJ/mol, which is within the range reported in the literature and is also comparable to that reported for sunflower oil transesterification (31.6 kJ/mol) [7]. The lower activation energy of RDS of mustard oil transesterification is observed at 26.8 kJ/mol. The two main factors that affect kinetics of transesterification are amount of saturation compounds affecting TG to DG reaction step and chain length distribution affecting MG to GL reaction step.

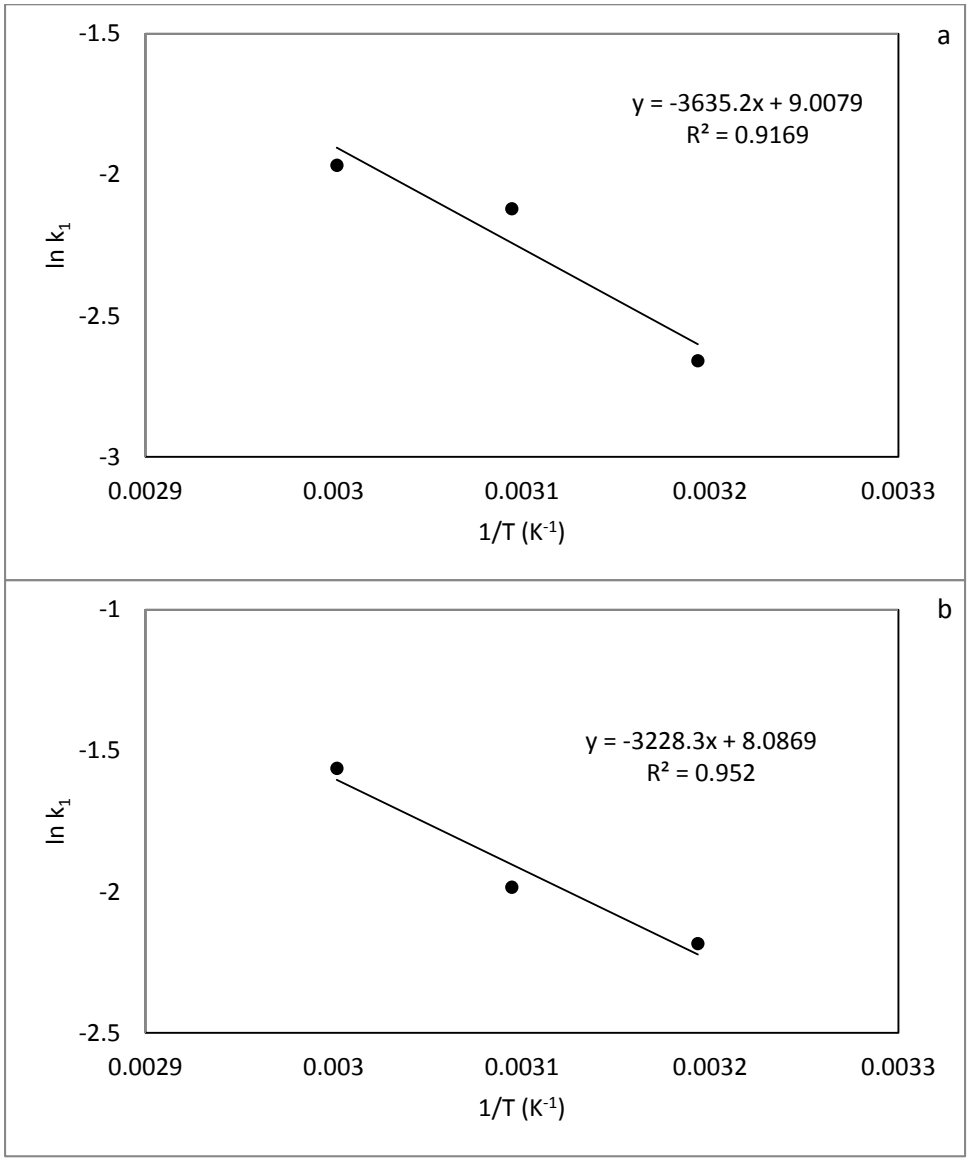

Figure 7.8 Arrhenius plots of the rate determining step:

a) palm oil transesterification; b) mustard oil transesterification.

Table 7.4 Activation energy of the rate determining step of transesterification.

Feedstock	Activation energy (kJ/mol)
Palm oil	30.2
Mustard oil	26.8
Sunflower oil [7]	31.6

It is found in this chapter that percentage of saturation compounds is more important in transesterification kinetics because of TG to DG reaction step being RDS. Therefore, palm oil which has higher percentage of saturated compounds is more difficult to transesterify as compared to mustard oil and this is shown in terms of the higher E_a of palm oil transesterification.

7.6. Conclusions

The transesterification kinetics depends greatly on fatty acid composition of vegetable oils that affects percentage of saturated compounds and chain length distribution. Although both parameters play a vital role in transesterification kinetics and affect each reaction step differently, percentage of saturated compounds is concluded to be more important factor in this work. This is because the TG to DG reaction step that was found to be RDS of the reaction is mostly affected by the percentage of saturated compounds rather than chain length distribution. This finding is manifested in terms of the higher activation energy of TG to DG reaction step in palm oil transesterification (30.2 kJ/mol) that has higher percentage of saturated compounds

compared to that of mustard oil transesterification (26.8 kJ/mol). In addition, it was found that the reaction steps are reversible and transesterification is favored at elevated temperature. Also, the mass transfer effect is minimized and the reaction is kinetically controlled when an agitation speed of 600 rpm is used for around 185 g of the reaction mixture.

Abbreviations

DCM	Dichloromethane
DG	Diglyceride
Ea	Activation energy
FAME	Fatty acid methyl ester
GC	Gas chromatography
GL	Glycerol
HPLC	High performance liquid chromatography
KCl	Potassium chloride
k_i	Rate constant of the reaction step i in Section 7.4.5.
KOH	Potassium hydroxide
ME	Methyl ester
MeOH	Methanol
MG	Monoglyceride
MSTFA	N-Methyl-N-trimethylsilyltrifluoroacetamide
RDS	Rate limiting step
TG	Triglyceride

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CHAPTER 8

Conclusions and Recommendations

8.1. Conclusions

It is found that a high quality biodiesel can be obtained from non-edible oils. Used cooking oil (UCO) is one of the most attractive feedstock to both researchers and commercial manufacturers. The properties such as acid value (AV) and viscosity of used cooking oil change constantly during the course of cooking. This property change depends on cooking environment such as type of food, cooking temperature and cooking duration. In addition, used cooking oil with different origin can exhibit different properties. It is shown in this thesis that fatty acid composition of used cooking oil originated from extended life canola oil is different than that of used cooking oil originated from canola oil, i.e., used cooking oil originated from extended life canola oil has lower degree of unsaturation than that originated from canola oil. Not only fatty acid compositions, but AV of each oil is different, i.e., AV of UCO are 1.5 and 2.5 $mgKOH \cdot g^{-1}$, respectively. All properties such as fatty acid compositions, AV, water content, and minor components contained in the oil are required to be taken into account when used as biodiesel production feedstock as they affect the reaction conversion as well as biodiesel properties. It is found that the optimum condition for biodiesel production are 1% KOH loading, 6:1 alcohol to oil ratio, 600 rpm stirring speed, and either 50°C for 2 h or 60°C for 1.5 h for methanolysis and 60°C for 2 h for ethanolysis. Under the optimum condition, methyl ester yield derived from UCO were 92-95%. The effects of these inferior properties such as higher acid value of used cooking

oil on reaction conversion can be reduced by mixing it with edible oil such as canola oil. It is found in this thesis that addition of 20% canola oil to used cooking oil increased methyl ester yield and ethyl ester yield by 0.5% and 12.2%, respectively. At least 60% canola oil addition is needed to produce ASTM grade ethyl ester biodiesel.

Greenseed canola oil does not have high acid value problem but it has high chlorophyll content. Bleaching of greenseed canola oil prior to transesterification is found to help improve oxidative stability of biodiesel. It is found that a 12 minutes enhancement in induction time was observed from methyl ester derived from treated greenseed canola oil (pigment content = 0.5 ppm) as compared to that derived from crude greenseed canola oil (pigment content = 94.1 ppm). The optimum bleaching process involves the use of 7.5 wt.% montmorillonite K10 at 60°C and stirring speed of 600 rpm for 30 minutes. In addition, it was found that induction time of treated greenseed canola ethyl ester (1.8 h) was higher than that of methyl ester (0.7 h), which suggests a better oxidative stability of esters of higher alcohols. However, bleaching and transesterification cannot be combined into a single step due to sorption of the KOH catalyst on the bleaching clay.

Due to high erucic acid content in mustard oil, it is considered as non-edible oil. It was more difficult to transesterify monoglyceride of this oil compared to that of edible oil such as canola oil and soybean oil. The ester yield was only 66% and unconverted monoglyceride was around 30%. Distillation was used in order to achieve a high quality mustard biodiesel and no trace of unconverted monoglyceride can be seen in HPLC chromatogram of mustard biodiesel after distillation. The resulting biodiesel exhibits great potential as lubricating additive especially mustard oil methyl ester. Wear reduction at 1% treat rate of methyl ester, ethyl ester, propyl ester, and butyl ester are 43.7%, 23.2%, 30.7% and 30.2%, respectively.

From the kinetic study, it is generally concluded that different vegetable oils with different fatty acid compositions can be transesterified at different reaction rate and difficulty. More specifically, mustard monoglyceride is found to be transesterified at a slower rate (rate constant = 0.2-0.6 $L \cdot mol^{-1} \cdot min^{-1}$) when compared to palm monoglyceride (rate constant = 1.2-4.2 $L \cdot mol^{-1} \cdot min^{-1}$) due to its molecular arrangement and lower molecular polarity resulting from the longer chain of erucic acid. However, the triglyceride counterpart which controls the kinetics of the overall reaction suggests differently, i.e., the activation energies of palm oil and mustard oil transesterification are 30.2 and 26.8 kJ/mol, respectively, due to the higher degree of saturation of palm oil.

8.2. Recommendations

1. Since various non-edible oils require different production processes, an economical analysis of these processes can be greatly valuable.
2. A study on energy balance of each process should serve as vital information for biodiesel consumers, manufacturers, and policy makers.
3. In Chapter 5, the effect of chlorophyll on oxidative stability is reported. It is recommended that effects of antioxidant addition are investigated. In addition, greenseed canola oil can be mixed with highly stable oil such as palm oil to improve biodiesel oxidative stability.
4. Profound understanding on biodiesel lubricity requires further research such as a study on the rate of biodiesel-metal surface reaction and micelle formation/deformation during lubricating duration. Scanning electron microscope (SEM) may be used to look at transfer films and surface wear of the HFRR sample to extract more information on the lubricating property of biodiesel.
5. Effects of alcohol used on transesterification kinetics can be useful. For example, competitive kinetics of methanolysis and ethanolysis in mixed methanol-ethanol can be investigated.
6. Heterogeneous catalysis has strong tendency to dominate biodiesel industry and therefore a development of novel heterogeneous catalysts is recommended.
7. Epoxidation of ester may be investigated to enhance low temperature properties of biodiesel.

APPENDIX A

HPLC Calibration

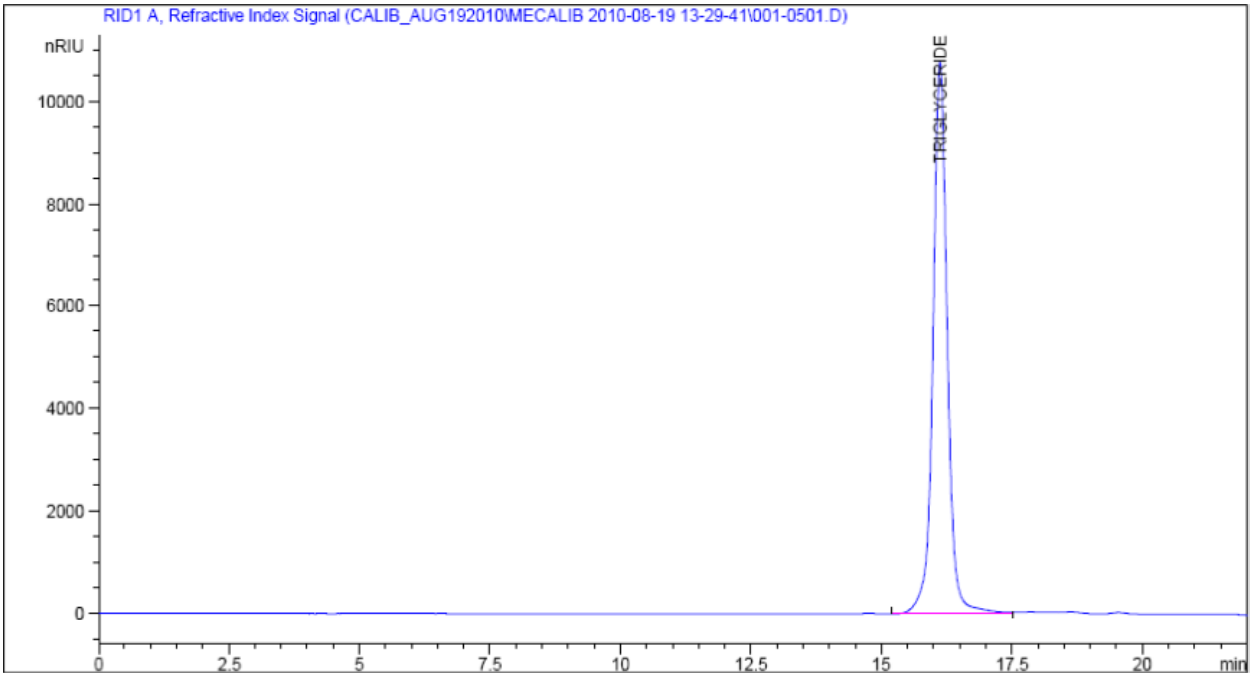


Figure A1 Chromatogram of a triolein standard.

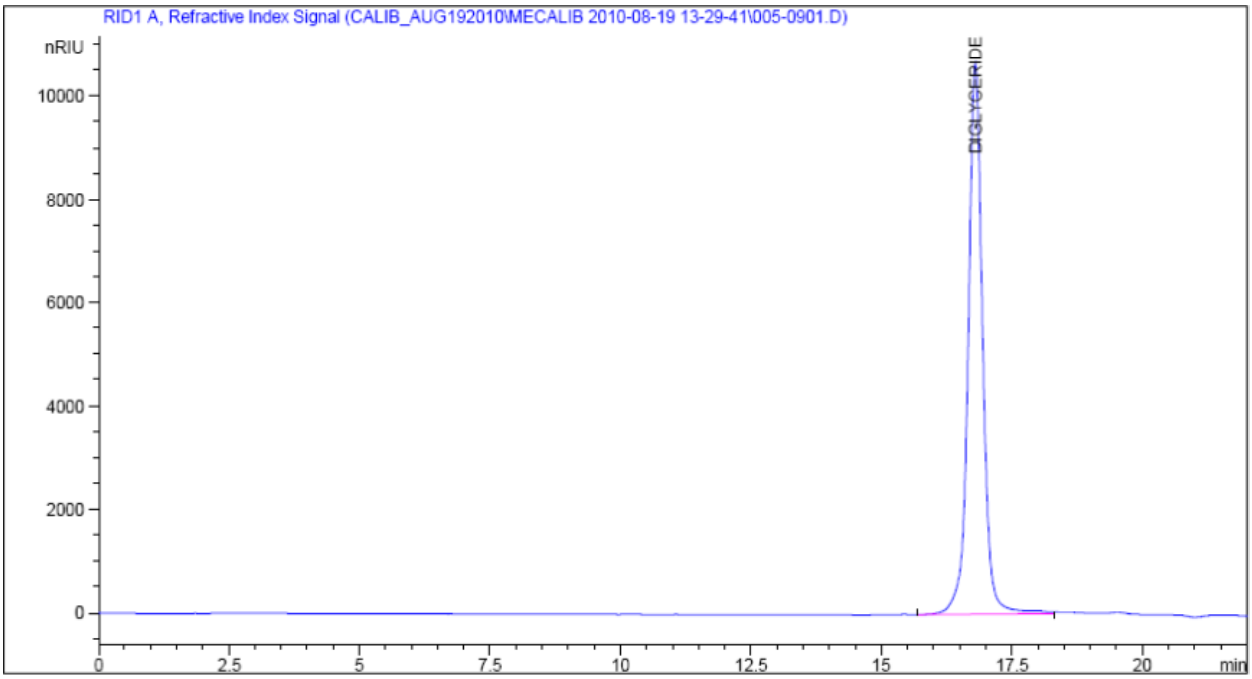


Figure A2 Chromatogram of a diolein standard.

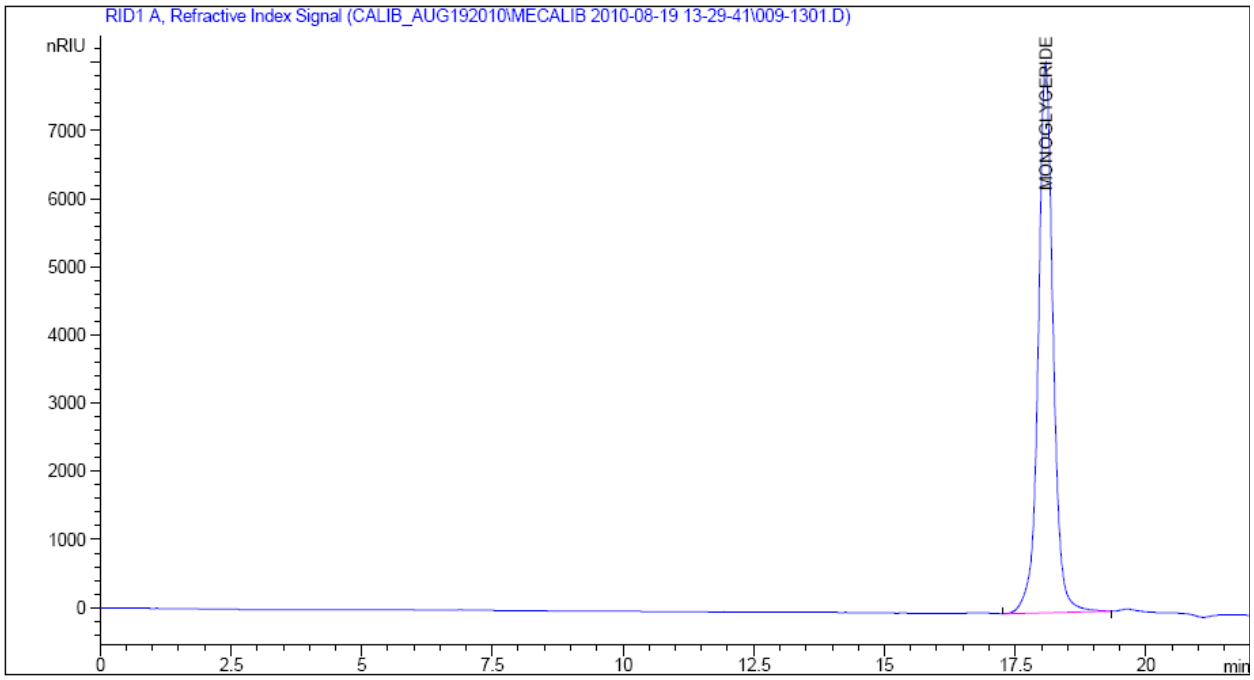


Figure A3 Chromatogram of a monoolein standard.

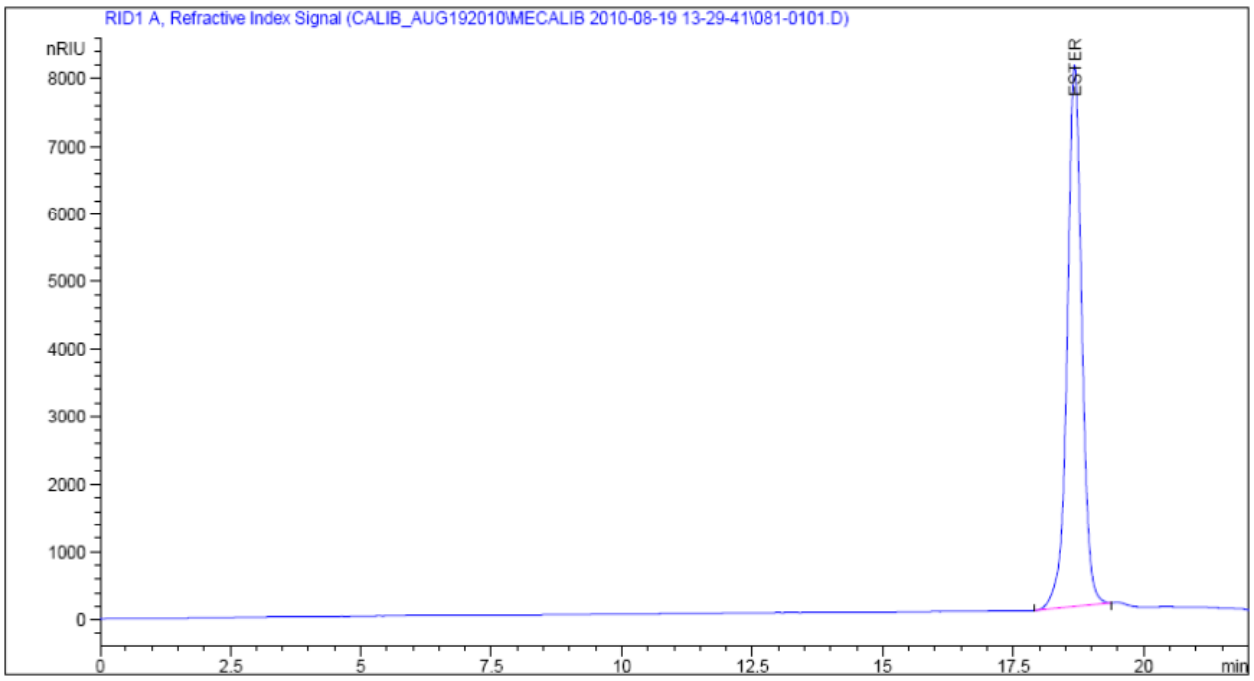


Figure A4 Chromatogram of a methyl oleate standard.

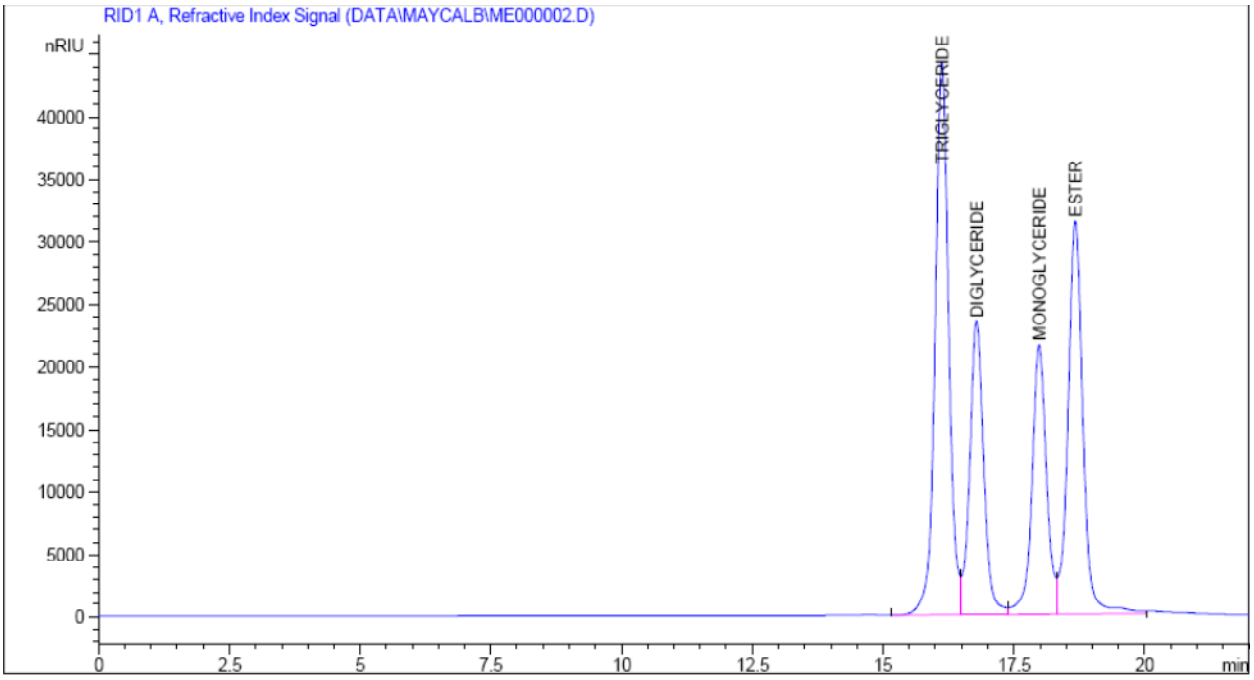


Figure A5 Chromatogram of a standard mixture.

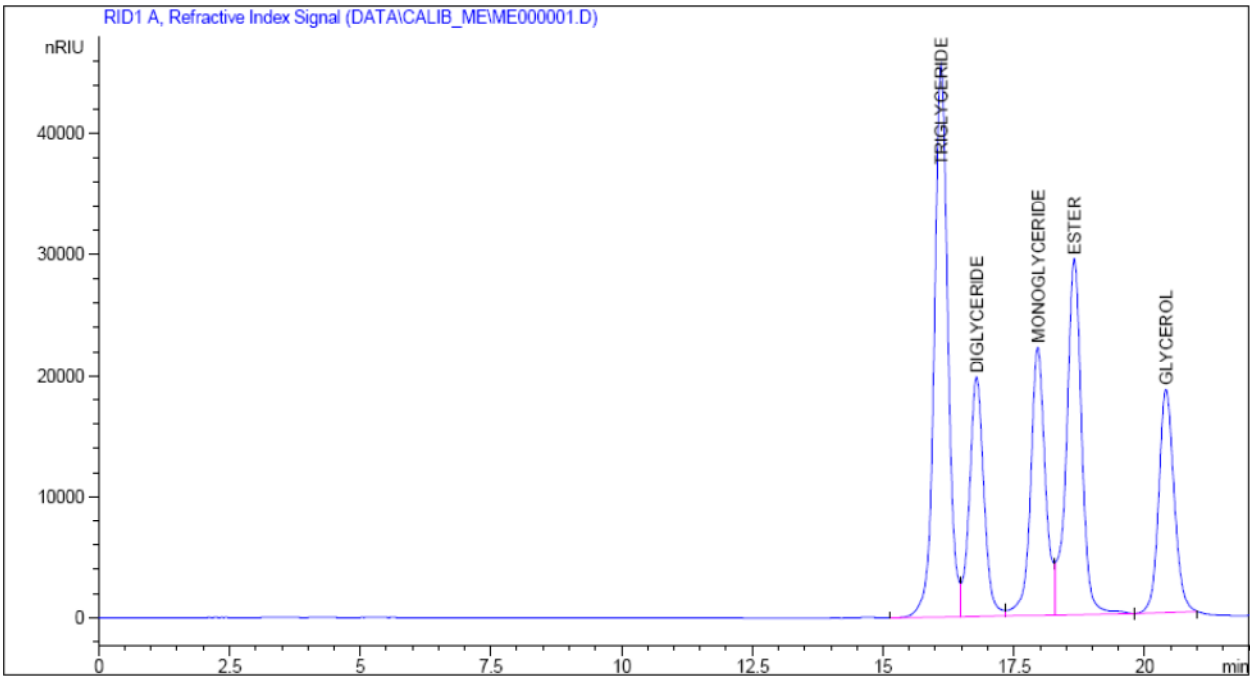
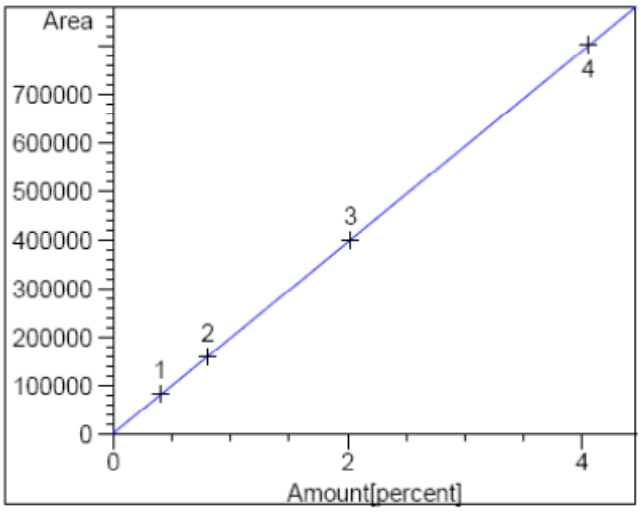
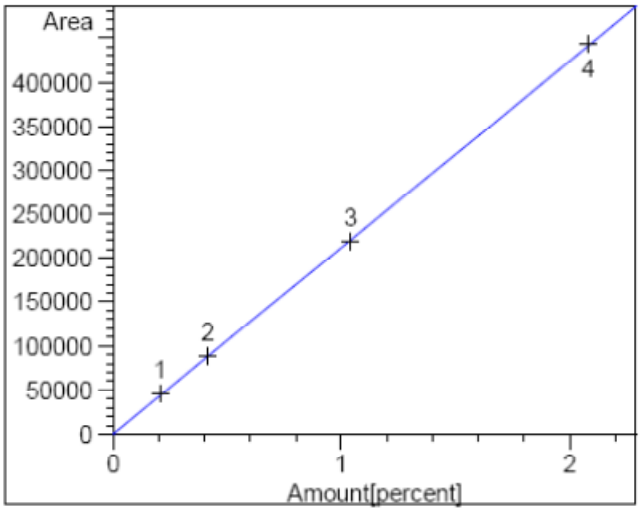


Figure A6 Chromatogram of a standard mixture with glycerol.



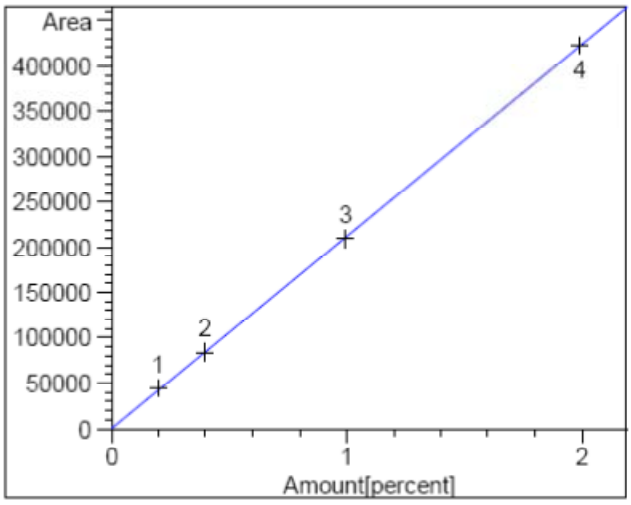

```
TRIGLYCERIDE at exp. RT: 16.123
RID1 A, Refractive Index Signal
Correlation:           0.99998
Residual Std. Dev.: 2614.13150
Formula: y = mx + b
      m: 197955.15092
      b:    699.21511
      x: Amount
      y: Area
```

Figure A7 Triglyceride calibration curve.



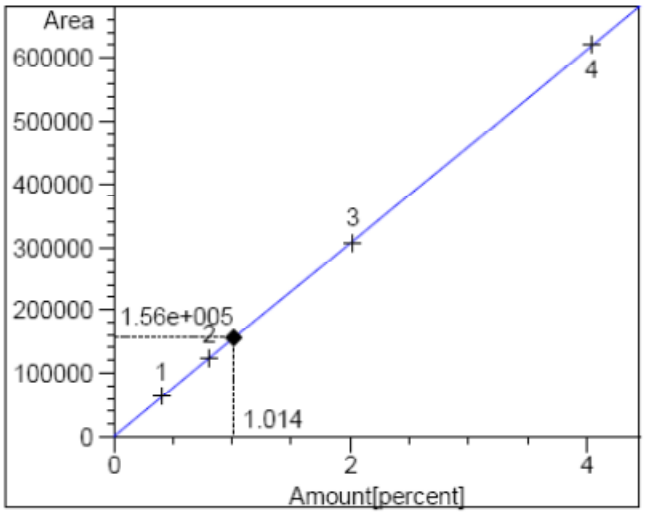
DIGLYCERIDE at exp. RT: 16.791
RID1 A, Refractive Index Signal
Correlation: 0.99996
Residual Std. Dev.: 1885.34863
Formula: y = mx + b
m: 211937.55984
b: 377.50963
x: Amount
y: Area

Figure A8 Diglyceride calibration curve.



MONOGLYCERIDE at exp. RT: 17.992
RID1 A, Refractive Index Signal
Correlation: 0.99994
Residual Std. Dev.: 2091.75390
Formula: y = mx + b
m: 212092.11947
b: 394.39863
x: Amount
y: Area

Figure A9 Monoglyceride calibration curve.



ESTER at exp. RT: 18.600
RID1 A, Refractive Index Signal
Correlation: 0.99996
Residual Std. Dev.: 2587.94326
Formula: y = mx + b
m: 153458.57304
b: 327.44842
x: Amount
y: Area

Figure A10 Ester calibration curve.

APPENDIX B

FAME Standard for GC Analysis

	Component FAME	Wt. %
1.	Caprylic (C8:0)	1.9
2.	Capric (C10:0)	3.2
3.	Lauric (C12:0)	6.4
4.	Tridecanoic (C13:0)	3.2
5.	Myristic (C14:0)	3.2
6.	Myristoleic (C14:1n9c)	1.9
7.	Pentadecanoic (C15:0)	1.9
8.	Palmitic (C16:0)	13.0
9.	Palmitoleic (C16:1n9c)	6.4
10.	Heptadecanoic (C17:0)	3.2
11.	Stearic (C18:0)	6.5
12.	Elaidic (C18:1n9t)	2.6
13.	Oleic (C18:1n9c)	19.6
14.	Linoleic (C18:2n6c)	13.0
15.	Arachidic (C20:0)	1.9
16.	cis-11-Eicosenoic (C20:1)	1.9
17.	Linolenic (C18:3n3)	6.4
18.	Behenic (C22:0)	1.9
19.	Erucic (C22:1n9)	1.9

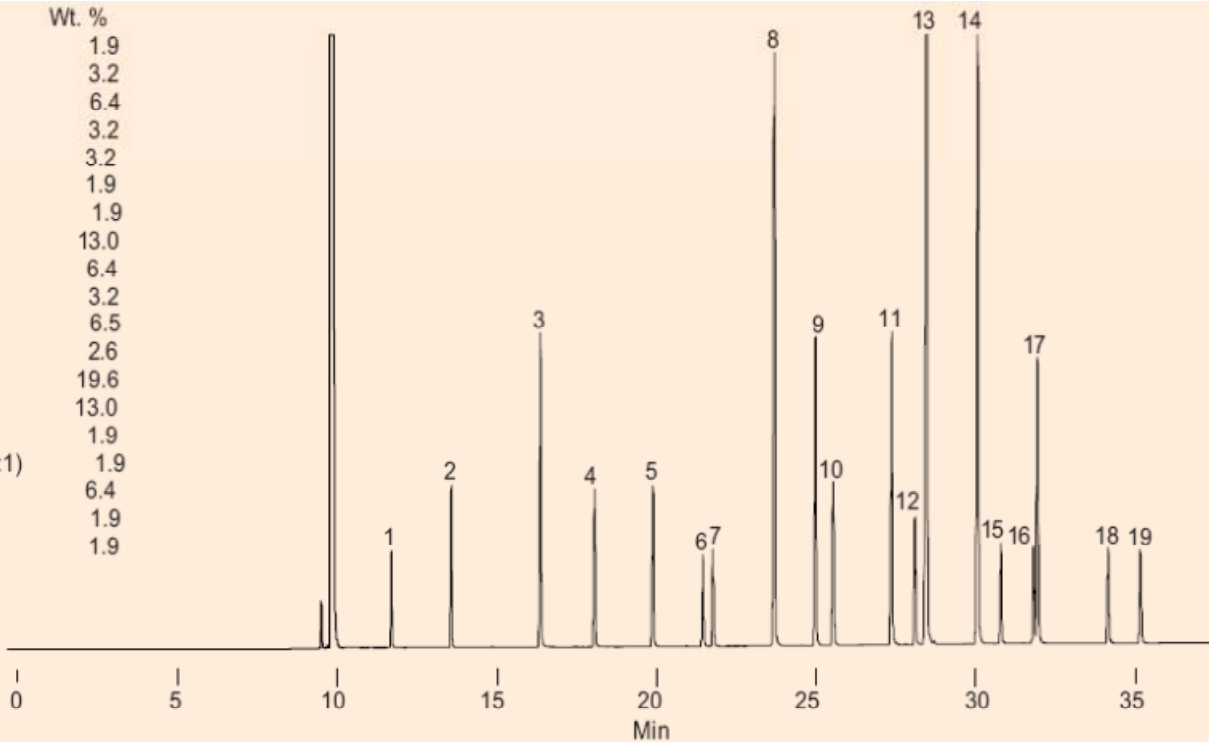


Figure B1 Chromatogram of FAME standard (10 mg/mL FAME in methylene chloride).

APPENDIX C

GC Calibration

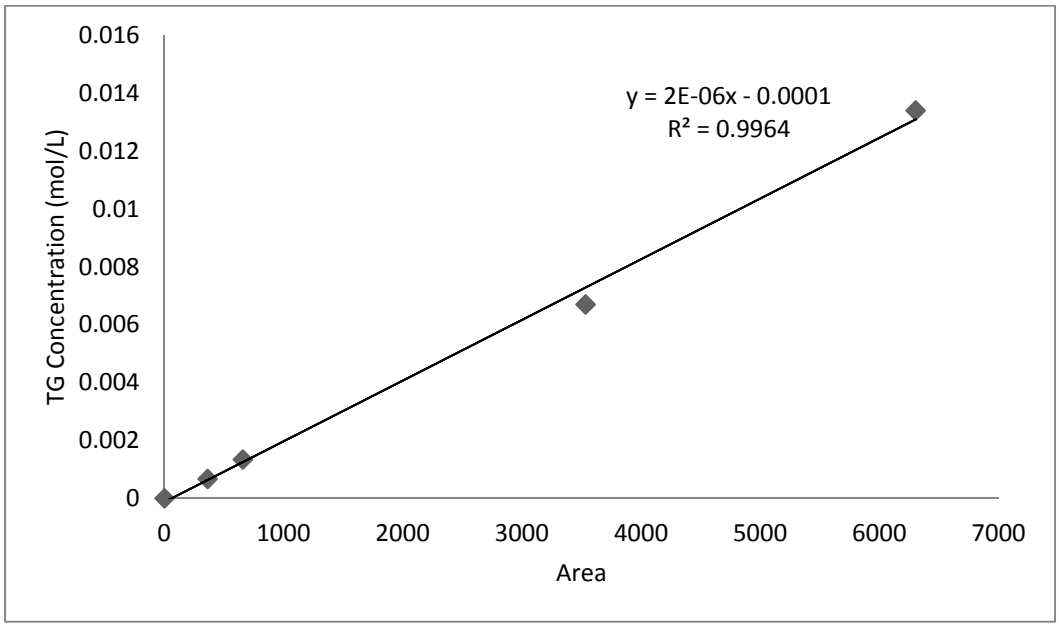


Figure C1 Triglyceride calibration curve.

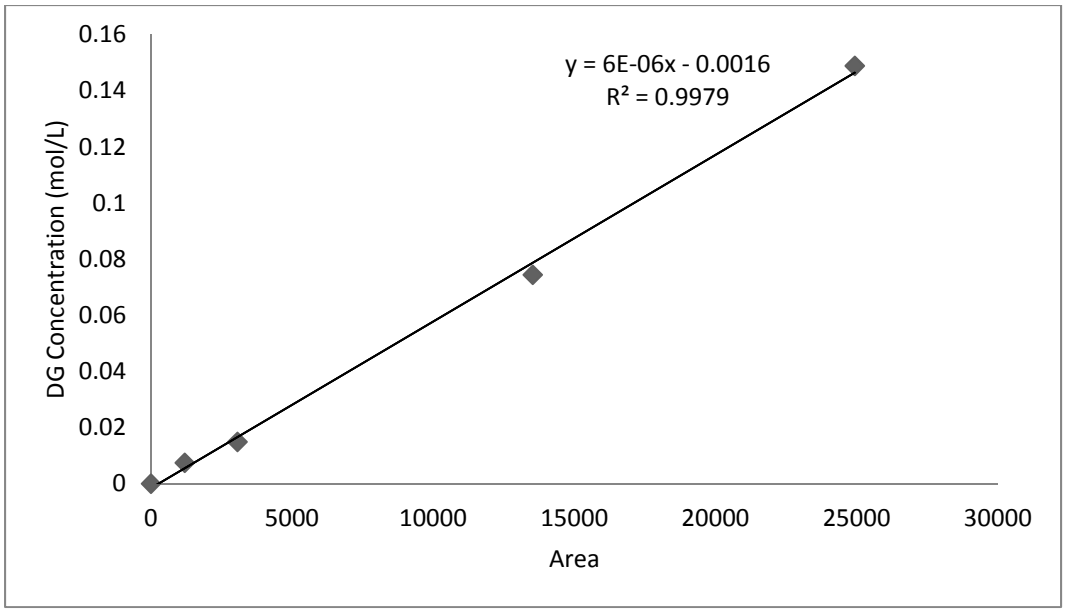


Figure C2 Diglyceride calibration curve.

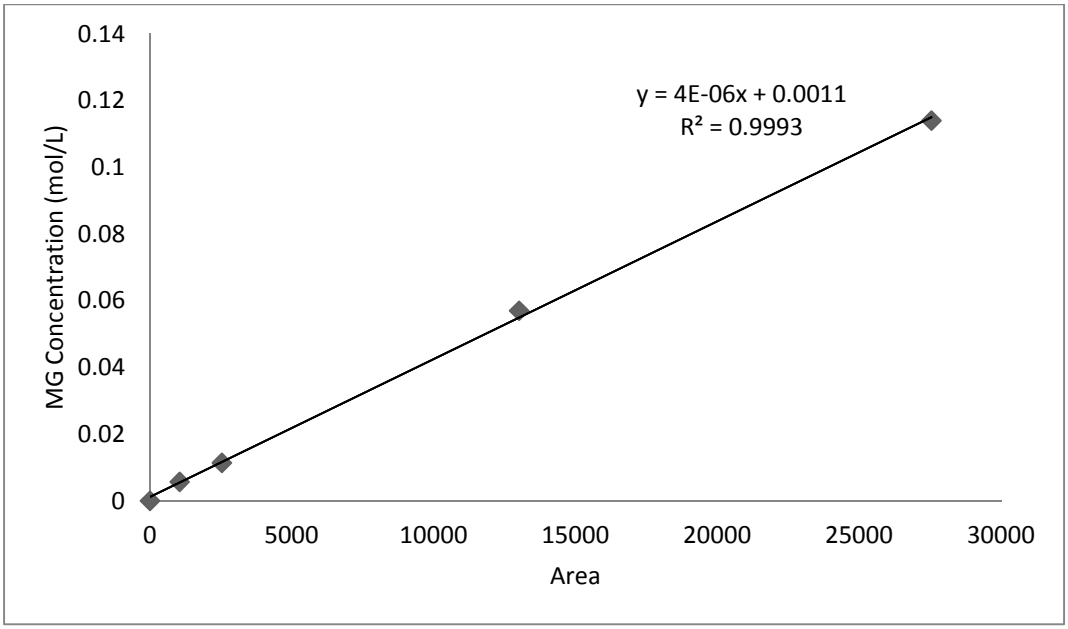


Figure C3 Monoglyceride calibration curve.

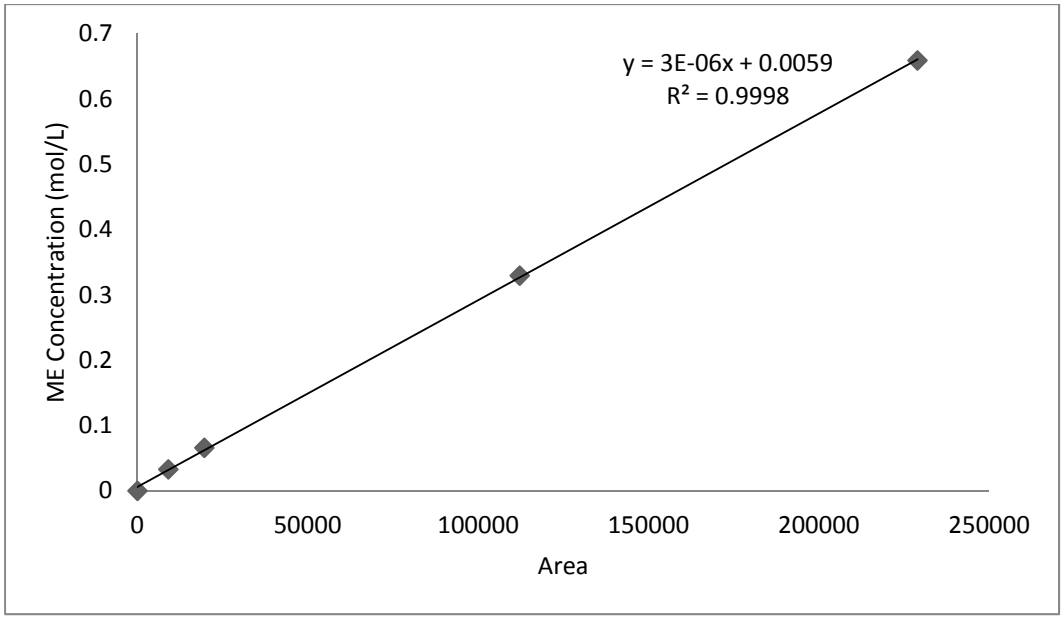


Figure C4 Ester calibration curve.

APPENDIX D

MATLAB Program for Transesterification Kinetics

MATLAB Function for Inserting Experimental Data

Function Name – inputvalue

```
% ********** Reaction Time; Unit – Minutes **********

texp=[0 1 2 4 6 8 10 20 30];


% ********** Concentrations; Unit – mol/L **********

TG=[0.97482 0.56344 0.168453333 0.084426667 0.075804 0.051533333 0.036813333
0.030453333 0.0142];

DG=[0.155 0.0925 0.043333333 0.042533333 0.0278 0.025 0.023433333 0.0078 0.006833333];

MG=[0 0.01988 0.013346667 0.008653333 0.004786667 0.003693333 0.003826667 0.0026
0.00276];

ME=[0 1.33926 2.629086667 2.88746 2.946661333 3.026166667 3.073326667 3.1249
3.175433333];

GL=[0 0.454 0.904686667 0.994206667 1.021429333 1.049593333 1.065746667 2.72402
2.673486667];

MeOH=[5.84892 4.50966 3.219833333 2.96146 2.902258667 2.822753333 2.775593333
1.088966667 1.106026667];
```

MATLAB Function for Ordinary Differential Equations

Function Name – KinODE

```
function dCdt=KinODE(t,Cinput,K)
global k1 k2 k3 k4 k5 k6;

% ************ Define Concentration and Rate Constant Parameters **************
C1 = Cinput(1);
C2 = Cinput(2);
C3 = Cinput(3);
C4 = Cinput(4);
C5 = Cinput(5);
C6 = Cinput(6);
k1 = K(1);
k2 = K(2);
k3 = K(3);
k4 = K(4);
k5 = K(5);
k6 = K(6);

% ************ Ordinary Differential Equations **************
dCdt = [-k1*C1*C6+k2*C2*C4;...
    k1*C1*C6-k2*C2*C4-k3*C2*C6+k4*C3*C4;...
    k3*C2*C6-k4*C3*C4-k5*C3*C6+k6*C4*C5;...
    k1*C1*C6-k2*C2*C4+k3*C2*C6-k4*C3*C4+k5*C3*C6-k6*C4*C5;...
    k5*C3*C6-k6*C4*C5;...
    -k1*C1*C6+k2*C2*C4-k3*C2*C6+k4*C3*C4-k5*C3*C6+k6*C4*C5];
```

MATLAB Function for Error Function

Function Name – err

```
function error=err(KI)
run inputvalue

% ************ Define Concentration and Step Time **************
CExp = [TG; DG; MG; ME; GL; MeOH];
Cini = CExp(:,1);
tspan = (0:1:30);

% ************ Solving Ordinary Differential Equations **************
[t,C] = ode45(@KinODE,tspan,Cini,[],KI);
disp(C);

TGc=C(:,1)';
DGc=C(:,2)';
MGc=C(:,3)';
MEc=C(:,4)';
GLc=C(:,5)';
MeOHc=C(:,6)';

TGcal=[TGc(t==0),TGc(t==1),TGc(t==2),TGc(t==4),TGc(t==6),TGc(t==8),TGc(t==10),TGc(t
==20),TGc(t==30)];
DGcal=[DGc(t==0),DGc(t==1),DGc(t==2),DGc(t==4),DGc(t==6),DGc(t==8),DGc(t==10),DGc
(t==20),DGc(t==30)];
```

```
MGcal=[MGc(t==0),MGc(t==1),MGc(t==2),MGc(t==4),MGc(t==6),MGc(t==8),MGc(t==10),
MGc(t==20),MGc(t==30)];

MEcal=[MEc(t==0),MEc(t==1),MEc(t==2),MEc(t==4),MEc(t==6),MEc(t==8),MEc(t==10),ME
c(t==20),MEc(t==30)];

GLcal=[GLc(t==0),GLc(t==1),GLc(t==2),GLc(t==4),GLc(t==6),GLc(t==8),GLc(t==10),GLc(t
==20),GLc(t==30)];

MeOHcal=[MeOHc(t==0),MeOHc(t==1),MeOHc(t==2),MeOHc(t==4),MeOHc(t==6),MeOHc(t
==8),MeOHc(t==10),MeOHc(t==20),MeOHc(t==30)];

Ccal = [TGcal; DGcal; MGcal; MEcal; GLcal; MeOHcal];


% ********** Define Error Parameter **********

CError = abs(Ccal-CExp);

n=1;

error = sum(sum(CError))/n;
```

MATLAB Function for Main Function

Function Name – main

```
clear
run inputvalue

% ************ Initial Guess for Rate Constants **************
KI = [0.4 0.02 0.8 2 4 0.005];

% ************ Regression **************
[k,fval] = fminsearch(@err,KI);

% ************ Optional Regression Command **************
%[k,fval] = fminunc(@err,KI);


% ************ Define Concentration and Step Time **************
CExp = [TG; DG; MG; ME; GL; MeOH];
Cini = CExp(:,1);
tspan = (0:1:30);

% ************ Solving Ordinary Differential Equations **************
[t,C]=ode45(@KinODE,tspan,Cini,[],k);
TGc=C(:,1)';
DGc=C(:,2)';
MGc=C(:,3)';
MEc=C(:,4)';
```

```
GLc=C(:,5)';

MeOHc=C(:,6)';

TGcal=[TGc(t==0),TGc(t==1),TGc(t==2),TGc(t==4),TGc(t==6),TGc(t==8),TGc(t==10),TGc(t
==20),TGc(t==30)];

DGcal=[DGc(t==0),DGc(t==1),DGc(t==2),DGc(t==4),DGc(t==6),DGc(t==8),DGc(t==10),DGc
(t==20),DGc(t==30)];

MGcal=[MGc(t==0),MGc(t==1),MGc(t==2),MGc(t==4),MGc(t==6),MGc(t==8),MGc(t==10),
MGc(t==20),MGc(t==30)];

MEcal=[MEc(t==0),MEc(t==1),MEc(t==2),MEc(t==4),MEc(t==6),MEc(t==8),MEc(t==10),ME
c(t==20),MEc(t==30)];

GLcal=[GLc(t==0),GLc(t==1),GLc(t==2),GLc(t==4),GLc(t==6),GLc(t==8),GLc(t==10),GLc(t
==20),GLc(t==30)];

MeOHcal=[MeOHc(t==0),MeOHc(t==1),MeOHc(t==2),MeOHc(t==4),MeOHc(t==6),MeOHc(t
==8),MeOHc(t==10),MeOHc(t==20),MeOHc(t==30)];

Ccal = [TGcal; DGcal; MGcal; MEcal; GLcal; MeOHcal];


% ************ Number of Data Point for each Species **************

N = 9;


% ************ Pearson Correlation Coefficient **************

for i = 1:6

r(i) = (N*sum(CExp(i,:).*Ccal(i,:))-sum(CExp(i,:))*sum(Ccal(i,:)))/sqrt((N*sum(CExp(i,:).^2)-
(sum(CExp(i,:)))^2)*(N*sum(Ccal(i,:).^2)-(sum(Ccal(i,:)))^2));

end
```

```
% ********** Display Simulation Results **********
run plotgraph
disp(C);
disp('Rate constants: k1, k2, k3, k4, k5, k6');
disp(k);
disp('Pearson correlation coefficient: TG, DG, MG, ME, GL, MeOH');
disp(r);
```

MATLAB Function for Graphical Display

Function Name – plotgraph

```
% ************ Example for Plotting TG Concentrations **************

plot(texp,CExp(1,:),'ro',texp,TGcal,'bo',t,C(:,1),'b-');

legend('experimental values','simulated values');
xlabel('time(min)');
ylabel('concentration(mol/L)');
```

APPENDIX E

Preliminary Economic Analysis

It was found from this thesis that an ASTM grade biodiesel can be produced from various feedstocks including canola oil, used cooking oil, greenseed canola oil, mustard oil, and soybean oil. It can be assumed that ASTM grade biodiesel may be sold at the same price regardless of feedstock used in the production processes; therefore, the feedstock cost is the major factor determining economic feasibility of biodiesel. The cost of feedstocks used in this research is presented in Table E1. Based on the data presented in Table E1, used cooking oil (UCO) seems to have an economical advantage over other vegetable oils. Economical analysis of biodiesel production from fresh vegetable oil and UCO has been reported in literature [1]. It is shown that the production process of biodiesel derived from UCO has higher fixed capital cost due to the added cost of acid-pretreatment unit. However, the production cost of biodiesel derived from fresh vegetable oil (palm oil in this study) was much higher than that derived from UCO, i.e., 7491 Euros/day for palm oil vs 3822 Euros/day for UCO. This is because the price of palm oil, which was 7054 Euros/day, is accounted for more than 90% of the total production cost while the price of UCO was only 3037 Euros/day. The payback investment period of biodiesel production process from palm oil and UCO was 12 and 10 years, respectively. Therefore, it was concluded that UCO has an economical advantage as feedstock for biodiesel production.

As part of life cycle analysis (LCA), global warming potential (GWP) analysis shows that for the production of 1 ton of biodiesel from UCO, the pretreatment of UCO and transesterification of UCO created 75 and 225 kg CO_2 equivalent, respectively, while the collection and delivery of UCO did not contribute to the GWP [2]. Moreover, LCA shows that the biodiesel production process using UCO as feedstock has lower environmental impact than those using fresh vegetable oil as feedstock [1].

Despite the seemingly economical and environmental attraction of UCO, its price and availability can be fluctuated and the cheapest and lowest quality UCO may not always be available in large quantity. Therefore, utilization of other inedible oils will also play a vital role in biodiesel industry.

Table E1 Prices of feedstocks for biodiesel production.

Feedstock	Price (CDN $/Tonne)	Reference
Rapeseed oil	1314[a]	3
Soybean oil	1222[a]	4
Greenseed canola oil	n/a[b]	-
Mustard oil	550[a]	5
Used cooking oil[c]	-110 to 110	6

[a]Data in 2011.
[b]The price of greenseed canola oil is not available because greenseed canola oil is usually converted into canola oil prior to distribution, however the canola greenseed price may be dropped by up to $30 per tonne [7] when compared to canola seed due to an increased oil-refining cost.
[c]This is referred to brown grease that have FFA >20%.

References

[1] Varanda MG, Pinto G, Martins F. Life cycle analysis of biodiesel production. Fuel Processing Technology 92: 1087-1094 (2011).

[2] Peiro LT, Lombardi L, Mendez GV, Durany XG. Life cycle assessment (LCA) and exergetic life cycle assessment (ELCA) of the production of biodiesel from used cooking oil (UCO). Energy 35: 889-893 (2010).

[3] Indexmundi website: http://www.indexmundi.com/commodities/?commodity=rapeseed-oil&currency=cad. Accessed November 2011.

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