Development of a Green Heterogeneous-Catalyzed Process for the Production of ASTM-Standard Biodiesel from Multi-Feedstocks

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Biodiesel is a nontoxic, renewable, and biodegradable alternative green fuel for petroleum-based diesel. However, the major obstacle for the production of biodiesel at an industrial scale is the high production cost, which is related to the relative high price of the conventional "1st generation feedstocks" (refined vegetable oils) used. As a result, various alternative feedstocks, also known as "2nd generation feedstocks" are being evaluated as possible substitutes for the refined vegetable oil, such as used vegetable oil, animal fats, and waste oils and fats. However, there is a great need to develop a green process which can be used for multiple feedstocks. This shows the universal ability of the process to be adopted as per availability of local feedstock.

In this study, three feedstocks, for biodiesel production namely soybean oil, yellow grease, and crude *jatropha* oil have been explored. A 2nd generation heterogeneous-catalyzed process has been developed for successful conversion of high free fatty acid (FFA) feedstocks into biodiesel. In the first phase of this research, we have applied a single-step second generation heterogeneous-catalyzed process to produce biodiesel from soybean oil with added palmitic acid as a model feedstock.

Second phase of this research is the application of this process using real feedstock. Therefore, we have developed a novel green technology for the production of biodiesel using a simple and environmentally green single-step solid acid-catalyzed process to produce high quality biodiesel from multi-feedstocks including yellow grease (used in industrial-scale biodiesel process). It was found that FFAs in the yellow grease were converted to biodiesel with 95% conversion using 12-tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Furthermore, the yellow grease was successfully transesterified with 87.3 mass% ester content. Analysis based on the ASTM D974, and EN 14103 standards confirmed the production of high-purity biodiesel from yellow grease with only 3% linolenic ester, which is far below the limit of EN 14103.

The recycling studies shows even after 5 reaction cycles, catalyst activity remains at 97% of the fresh catalyst. This demonstrates the reusability of this new solid acid catalyst. This green technology has a potential for industrial scale production of biodiesel from high FFA feedstocks.

Due to the high cost of edible oils and growing concern of food for oil, *jatropha* oil has been considered as one of the most promising potential feedstocks for the production of biodiesel in Asia, Africa, Europe, South America, and now is gaining momentum in North America. Therefore, in the third phase of this research study, a process for the synthesis of biodiesel from crude *jatropha* oil as the 2nd generation feedstock using TPA with 30% loading supported on neutral alumina as versatile green solid acid catalyst in a single-step has been developed. To the best of our knowledge, this is the first report on the development of a single-step solid acid-catalyzed process for the production of biodiesel from crude *jatropha* oil.

Due to an increase in the commercial use of biodiesel and biodiesel blends, both ASTM D6751 and EN 14214 include the acid number (AN) as an important quality parameter. Currently, ASTM D974 and D664 analytical methods for acid number analysis of biodiesel are time consuming, expensive, and environmentally not friendly. Therefore, ASTM D974 has been modified and a green analytical method has been developed. This extensive study has demonstrated that this new method is a reliable method for the determination of AN and could be used for establishing the specifications of AN for biodiesel and biodiesel blends ranging from B1 to B20 in quality standards. Using green chemistry approaches, the ASTM D974 has been modified and used for the determination of AN of bio-feedstock for biodiesel was studied. This method could also be used as in-process quality control tool for monitoring biodiesel production process. The ASTM reference standard method D664, a potentiometric method, has major problems such as the use of excess toxic solvents, large sample size, mediocre reproducibility, tedious process for cleaning electrodes, and relatively long analysis

time. Therefore, a new proposed method based on green chemistry approaches, has been developed to determine the acid number of biodiesel and biodiesel blends using small sample size and reduced toxic titration solvent. This proposed green analytical method could be used for the determination of AN of biodiesel and biodiesel blends in R&D as well as industrial quality control laboratories as a simple, time-efficient, cost effective and environmentally friendly method.

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Saving the best for the last, I am deeply indebted to my parents, Mr. Aziz and Mrs. Saeeda for their endless love, patience, and support during this work and throughout my life. This work would not have been possible without my parents' encouragement, and prayers for my success. This is not my achievement; in fact this is the achievement of my sweet parents.

This thesis is especially dedicated to

My Lovely Parents

for their love, support and encouragement

throughout the course of this

Intellectual, Creative and Meticulous work.

And,

Today Whatever Good I Have, All from Them.

In the name of

ALLAH

The Most Compassionate, The Most Merciful

He is Allah (the Almighty God):

the Creator, the Inventor, the Designer,

to Him belong the most beautiful names.

Whatever is in the heavens and earth

is exalting Him.

And He is the Exalted in Might, the Wise

(Qur'an 59:24)

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing Materials
ASTM D6751	Specification for biodiesel (B100) blend stocks for distillate fuels
ASTM D6584	Test method for determination of free and total glycerin in b-100 biodiesel methyl esters by gas chromatography
ASTM D664	Method for acid number of petroleum products by potentiometric titration
ASTM D975	Standard test method for acid and base number by color-indicator titration
B100	100% Biodiesel
B20	20% Biodiesel, 80% Petroleum diesel
B10	10% Biodiesel, 90% Petroleum diesel
B5	5% Biodiesel, 95% Petroleum diesel
BET	Brunauer, Emmett, Teller
CBG	Chemically Bound Glycerol
CJO	Crude *jatropha* oil
DG	Diglyceride
EN14214	Fatty acid methyl esters (FAME) for diesel engines, requirements and test methods
EN14105	Fat and oil derivatives–fatty acid methyl esters (fame)–determination of free and total glycerol and mono-, di- and triglyceride content
EN14103	Determination of ester and linolenic acid methyl ester
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FID	Flame ionization detector
GC	Gas chromatography
Gl	Glycerol
HPA	Heteropoly acid
id	internal diameter
ME	Methyl Ester

MG	Monoglyceride
OA	Oleic acid
OSI	Oil Stability Index
PA	Palmitic acid
SBO	Soybean oil
SA	Stearic acid
TG	Triglyceride
USDA	United States Department of Agriculture

Nomenclature

Symbol	Description	Units
MW	Molecular weight	g/mol
m	Mass	kg, g
t	Time	day, hour, min, s
V	Volume	litre (L), milliliter (mL), microliter(µL)
PV	Pore volume	cm^3
T	Temperature	Celcius (°C), Kelvin (K)
P	Pressure	kPa, Mpa, psi
R^2	Linearity	
k	chemical reaction rate constant	sec^{-1} ,min^{-1}
E	Molar Energy	kJ/mole, J/mole
E_a	Activation Energy	kJ/mole
A	pre-exponential factor	L $mol^{-1}s^{-1}$ or $M^{-1}s^{-1}$(for 2^{nd} order) and s^{-1}(for 1^{st} order)
M	Molarity (molar concentration)	mol/L
N	Normality	mol/L
R	Gas constant	8.314 J/mol K.

Greek

ω	Angular velocity	rpm (revolutions per minute)

Subsripts

a_i	initial acid number
a_t	acid number at time t
CBG_i	initial chemically bound glycerin
CBG_t	chemically bound glycerin at time t

Symbol	Description
RSD	Relative Standard
STD	Standard Deviation
max	maximum
AVE	average

CHAPTER 1
INTRODUCTION

1.1 Global energy consumption and alternative energy sources

Oil depletion is one of the most important problems of the 21st century. According to recent estimates, the world's oil reserves could be diminished by 2050 if the current rate of energy consumption persists (Demirbas, 2003). In addition to depletion of fossil fuels, growing world's population, rapid urbanization and higher living standards create ever increasing demands for alternative energy sources. Meeting energy needs is not only a problem for under-developed countries, even developed countries are not able to meet the current fuel demands despite increasing energy production manifold.

In the past few decades, fossil fuels such as petroleum, natural gas and coal have played an important role as major energy resources worldwide. However, energy resources are non-renewable and are projected to be exhausted in the new future. In Canada, on average, Ontario and Quebec utilize about 60% of the gasoline consumed in Canada. The western provinces account for about 32% of Canada's gasoline consumption, while the Atlantic province and the Territories consume the remaining 8% (Natural Resources Canada, 2009).

The impact of fossil fuel-based energy technologies on the environment and global climate has recently been recognized worldwide and is the major driving force in the search for renewable energy sources. Therefore, to meet energy needs and keep the global environment as clean as possible, it is crucial to develop green energy technologies that are renewable, sustainable and environmentally benign. Biofuels and biomass-based energy are potential major contributors of energy in the next century. Approximately, 90% of the biofuel market is dominated by bioethanol and biodiesel (Wikipedia Biofuel, 2012).

1.2 Biodiesel as an alternative diesel fuel

Biodiesel is considered to be a promising replacement for conventional diesel fuel. It has similar properties to fossil diesel and is considered a "green" fuel (Ma *et al.*, 1999). Biodiesel offers many advantages since it is safe, renewable (Korbitz, 1999) and biodegradable (Sheehan *et al.*, 1988 and 1998). It contains insignificant amounts of sulfur and has high lubricity that extends the life of diesel engines. In addition, it has a higher cetane number (above 60 compared to only 40 for regular diesel), a high flash point (> 130°C) and emits 70% fewer hydrocarbons, 80% less carbon dioxide and 50% less particles (Kiss *et al.*, 2006) than does regular diesel. Although, biodiesel increases nitrogen oxide (NO_x) (EPA, 2002), but it still will not increase the level of carbon dioxide in the atmosphere and will minimize the intensity of the greenhouse effect (Vicente *et al.*, 2004; Antolin *et al.*, 2002). Therefore, biodiesel is a very promising alternative fuel source for diesel engines.

1.3 Global biodiesel production

At present, biodiesel production has grown the fastest among biofuels on a percentage basis. Globally, industrial production of biodiesel has significantly increased from about 550 million gallons to almost 5 billion gallons during the period from 2004 to 2009 (Energy Information Administration, EIA, International Energy Statistics, Biodiesel Production tables, 2012). In European Union, biodiesel production has more than doubled. During the same period, Germany, France, and Italy have been the top three leading biodiesel producing countries (Energy Information Administration, EIA, International Energy Statistics, Biodiesel Production tables, 2012). The European Union and the United States are the major producers of biodiesel with 55% and 10% of the world's biodiesel production, respectively (Energy Information Administration, EIA, Petroleum and Other Liquids Navigator, Biodiesel Overview, 2012). The United States has increased biodiesel production more than 5-fold over the same time period (Energy Information Administration EIA, Petroleum and Other Liquids Navigator, Biodiesel Overview, 2012).

A total of 158 biodiesel production facilities have been established in 42 states across the US (National Biodiesel Board, 2012) with a total biodiesel production capacity of 2.7 billion gallons (EIA, Annual Energy Outlook, 2011), significantly more than the 310 million gallons of biodiesel produced in the U.S. in 2010 (EIA, Petroleum and Other Liquids Navigator, Biodiesel Overview, 2012).

Presently, industrial scale production of biodiesel is also growing exponentially all across Canada. Recently, Canada's biodiesel industry has been looking to expand its production capacity from 130 million liters (34 million gallons) to between 500 and 600 million liters in order to meet the Canadian mandate of 2 percent renewable content in diesel by 2011. In order to help achieve this goal, the Canadian government under the administration of Natural Resources Canada will invest up to $1.5 billion over nine years in support of biofuel production in Canada until March 2017 (Schill, 2009).

1.4 Biodiesel production technologies

In industrial processes, a highly refined vegetable oil widely used as the feedstock contains primarily triglycerides (TGs), which will react with low molecular weight alcohols (e.g. methanol and ethanol) and homogenous alkali catalysts (such as NaOH and KOH) through a transesterification process. The resulting products are biodiesel and glycerol.

In order to overcome the high production cost of biodiesel mainly due to its high price, 1st generation feedstock from a refined vegetable oil could be substituted with a more economical 2nd generation feedstock such as waste oils and fats that contain a low to moderate amount of free fatty acids (FFAs), moisture and other impurities. This makes biodiesel production very challenging due to the undesirable by-products of water and FFAs. Hence, pretreatment stages are required to reduce acid concentrations and water to meet the requirements of standard biodiesel manufacturing. The step involves an acid catalyzed pre-esterification combined with water separation.

The acid catalysts are used not only for esterification reaction, but also for TG transesterification. Thus, this acid catalyst performs two tasks simultaneously, FFA esterification and TG transesterification. Generally, heterogeneous catalysts also known as 2^{nd} generation catalysts are more suitable in general industrial processes because of their non-corrosive nature, ease of separation and recyclability as compared to conventional 1^{st} generation homogeneous catalysts. Also, the use of solid catalysts are preferable because their use reduces the number of reaction and separation steps required in the conversion of oils and fats to biodiesel, resulting in more economical processing and higher quality ester products and glycerol yield (Suwannakarn, 2008).

1.5 Motivation

Based on a literature review, a major barrier in the commercialization of biodiesel production from vegetable oil is its high manufacturing cost, due to expensive virgin vegetable oils (Haas, 2005 & 2006; Kulkarni *et al*., 2006a). In addition, a major challenge for the commercialization of biodiesel is to meet biodiesel quality standards requirement set by ASTM D6751 and EN 14214 for its use as a transportation fuel. Reaching complete conversion of the TG is a challenge in the light of the chemical equilibrium of the reaction. Currently, most of the heterogeneous processes reported in the literature yield biodiesel with high levels of triglyceride (TG), diglyceride (DG) and monoglyceride (MG), which involve a loss of reactants as well as a failure to meet the "bound glycerol" levels required by the ASTM standard. In addition, the residual TG, DG and MG may result in the production of glycerin over time, which would further violate the ASTM D6571 standards as provided in Appendix-A (Cao *et al*., 2008). However, to the best of our knowledge, most of the studies on biodiesel production focused on its yield without providing detailed analytical results on its quality.

To date, most of the studies on biodiesel synthesis have focused on either homogenous base-catalyzed processes employing refined or pre-treated vegetable oils. Fatty acid esterification as well as transesterification using solid acids is not yet well established in industry since it is

much more difficult to find a suitable solid acid catalyst for esterification of long-chain acids compared to shorter acids such as acetic acid and that is also highly active for transesterification (Kiss *et al*., 2006). Despite the fact that esterification is a well-known reaction that has been extensively studied in the literature, the further development of novel solid acid catalysts with high catalytic activity and reusability is necessary. Furthermore, the scope of this intensive search should be more expanded into real life complex cases such as esterification of long chain fatty acids and esterification of FFAs in the presence of triglyceride, a typical industrial process scenario using 2nd feedstocks.

With over 10 years of commercial use in Europe, biodiesel has now proved its value as a fuel for diesel engines (Wilson, 2002; IEA, 2002; Vermeersch, 2001). Increasing biodiesel consumption requires optimized production processes allowing high production capacities, simplified operations, high yields and the absence of special chemical requirements and waste streams (Bournay *et al*., 2005).

From the above discussion, it is clear that the introduction of a solid acid catalyst in biodiesel production could reduce its price, and make it competitive with diesel from an economic point of view (Di Serio *et. al.*, 2007). Therefore, a need exists for a systematic research study to develop a green 2nd generation heterogeneous acid-catalyzed process for the production of ASTM-standard biodiesel from both 1st generation (edible vegetable oils) and 2nd generation feedstock (non-edible *jatropha* oil as well as waste oils and fats).

Due to an increasing interest and the use of biodiesel around the world, the assurance of biodiesel quality is of paramount interest to the successful commercialization and market acceptance of biodiesel. Therefore, various biodiesel standards have been established around the world, including the United States (ASTM D6751) and Europe (EN 14214) (Knothe, 2006).

As discussed previously, the production of biodiesel from high FFA content feedstock is gaining momentum around the world due to its economical, commercial and environmental benefits (Baig and Ng, 2010). This requires an accurate determination of acid number (AN) to monitor the progress of the biodiesel production process. AN determination is a facile method for monitoring fuel quality (Knothe, 2006). Analytical methods for AN determination can be divided into two titration categories: potentiometric and colorimetric. Two major ASTM test methods for AN determination exist: ASTM D664 and ASTM D974 (Baig and Ng, 2011; Baig and Ng, 2012). However, both methods require a large sample size to analyze, excessive use of toxic solvents, production of a large amount of waste and are expensive. Furthermore, due to the growing use of the 2nd generation non-edible feedstock which generally contains high amount of FFA, it is very critical to determine the FFA content of bio-feedstock for biodiesel. The selection of appropriate biodiesel process technology depends on the accurate determination of FFA content of the feedstock for the biodiesel. In order to develop a green biodiesel production process, it is essential to use green analytical methods for biodiesel analysis. Therefore, a secondary objective of this research is to develop green analytical methods for acid number analysis of biodiesel and bio-feedstock with high FFA content.

1.6 Research objectives

Based on the problems associated with the conventional 1st generation homogeneous catalyzed process as well as the 2nd generation base-catalyzed heterogeneous processes, the overall goal of this study is to design and develop a 2nd generation single-step heterogeneous acid-catalyzed process for simultaneous esterification and transesterification in the production of ASTM-standard biodiesel from multi-feedstock including 1st generation (edible vegetable oils) and 2nd generation feedstock (non-edible *jatropha* oil as well as waste oils and fats) with high FFA content. The development of time-efficient, reliable and low cost analytical methods for an accurate determination of AN to monitor the acid number of biodiesel and bio-feedstock for biodiesel will also be required. Therefore, the second objective of this research is to develop green analytical methods for acid number analysis of

biodiesel and bio-feedstock for biodiesel to ensure the use of appropriate biodiesel process technology and the quality of biodiesel.

The research objectives will be met by the following set of approaches:

1. Development of a heterogeneous (solid) acid catalyst which can effectively catalyze esterification and transesterification simultaneously.
2. Validation of ASTM standard methods for the quantitative analysis of in-process and finished biodiesel products.
3. Investigation of the major process parameters including oil to alcohol molar ratio, type of reaction temperature, amount of catalyst, catalyst loading, rate of mixing, co-solvent, nature of catalyst support, calcination temperature, water and FFA content in the feedstock.
4. Kinetic study of the heterogeneous process to determine the kinetic parameters.
5. Recycling studies of the heterogeneous catalyst for industrial applications.
6. Hydrolysis studies to control the process chemistry for processing feedstocks with high FFA content.
7. Application of the process to multi-feedstock including 1st generation (edible vegetable oils), and 2nd generation feedstock (non-edible *jatropha* oil as well as waste oils and fats).
8. Development of green analytical methods for the determination of acid number of biodiesel, biodiesel blends, and bio-feedstock for biodiesel.

1.7 Outline of the thesis

A basic overview of current biodiesel problems' is discussed in Chapter 1. Chapter 2 and 3 present a detailed literature review on current research directions on those problems and preliminary experimental work, respectively. Chapter 4 presents the development of a single-step solid acid-catalyzed process for the production of biodiesel from a model feedstock with high FFA content (Baig and Ng, 2010). Chapter 5 presents biodiesel production from multi-feedstock for global applications. Chapter 6 presents the production of biodiesel from *jatropha* oil as 2nd generation non-edible bio-feedstock. Chapter 7 describes the development of a technique to determine the acid number of biodiesel and biodiesel blends (Baig and Ng,

2011). Chapter 8 presents a simple and green analytical method for acid number analysis of biodiesel and biodiesel blends based on potentiometric technique (Baig *et al.*, 2013). Chapter 9 presents a development of an efficient method for the determination of acid number of biodiesel and its feedstock with high FFA content. Lastly, chapter 10 presents the general conclusions of this work.

CHAPTER 2
BACKGROUND AND REVIEW OF LITERATURE

For many years, the world has utilized energy resources based on fossil fuel such as petroleum, natural gas and coal. Globally, petroleum diesel continues to be a major fuel worldwide. Canada consumes ~23 million tons (~26 billion liters) of diesel annually, of which 46% is utilized in the transportation sector. The United States consumes 178 million tons of diesel fuel annually, while global consumption is 934 million tons of diesel fuel per year (Holbein, 2004).

In the last few decades, a significant amount of research has been carried out to find new renewable and sustainable energy sources to substitute petroleum-based fuels that will become depleted in the future. The development of energy efficient biofuel production technologies aimed at reducing the chemical costs and increasing the production efficiency is becoming important in a world that is increasingly becoming "green".

Thus, one potential and promising renewable source of energy is biodiesel not only due to its environmental and technology advantages, but also because it offers extra societal and environmental benefits, e.g. creation of new jobs, rural revitalization and minimized greenhouse effects and global warming.

2.1 Vegetable oil as diesel fuel

Vegetable oils have long been promoted as possible substitutes for diesel fuel. Historically, Rudolph Diesel, the inventor of the diesel engine, used peanut oil in his engine as early as 1900 (Peterson, 1986). The first diesel engine in Argentina in 1916 used the castor oil as fuel (De Vedia, 1944).

The use of vegetable oils as diesel fuel offer several advantages: (1) heat content (80% of diesel fuel), (2) easy availability and (3) renewability. However, the use of vegetable oil as fuel has several disadvantages: (1) higher viscosity, (2) lower volatility and (3) the reactivity of unsaturated hydrocarbon chains (Pryde, 1983) which causes problems especially with direct-injection engines. These problems include (1) carbon deposits, (2) oil ring sticking and (3) thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils (Ryan, 1984).

2.2 Biodiesel

Biodiesel is defined by ASTM D6751 as a fuel contained of mono alkyl esters of long chain fatty acids originating from a renewable lipid feedstock such as vegetable oil or animal fat (Marchetti *et al*., 2008). If methanol is used as a reactant, it will produce a mixture of fatty acid methyl esters (FAME).

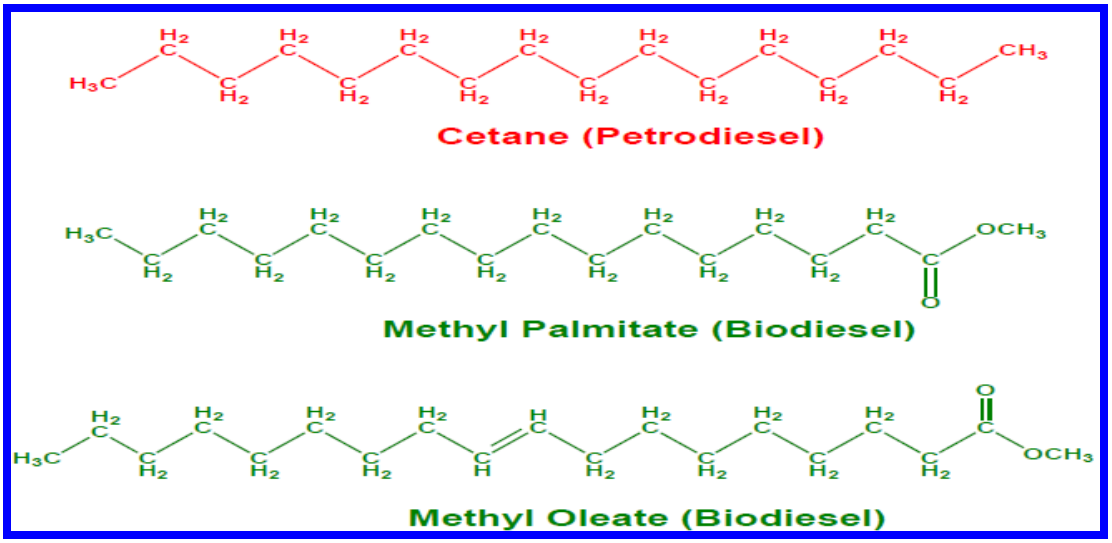


Figure 2.1 Molecular structures of petroleum-based diesel and several types of biodiesel.

Although, biodiesel increases nitrogen oxide (NO_x) (EPA, 2002), however, it offers several advantages which are: 1) the presence of oxygen (~10%) improves combustion and reduces emission of carbon monoxide (CO) and hydrocarbon, 2) a higher cetane number (above 60 compared to only 40 for regular diesel) and a higher flash point (> 130°C) resulting in better

and safer performance with 70% fewer hydrocarbons, 80% less carbon dioxide, and 50% less particles (Kiss *et al*., 2006) released in comparison to regular diesel, and 3) higher lubricity extends the engine life and reduces the frequency of engine part replacement.

A great structural similarity exists between biodiesel and petrodiesel molecules as shown in Figure 2.1, where methyl palmitate and methyl oleate are examples of typical biodiesel molecules and cetane represents a typical petrodiesel molecule. Based on the feedstock, biodiesel contains different proportions of fatty acid methyl esters. Table 2.1 shows the chemical composition of common fatty acids and their methyl esters that are present in biodiesel (Singh, 2007).

Table 2.1 Chemical structures of common fatty acids and methyl esters.

Fatty acid/Formula/ Molecular weight (g.mol^{-1})	**Common acronym**	**Methyl ester/Formula/ Molecular weight (g.mol^{-1})**
Palmitic acid/$C_{16}H_{32}O_2$/ 256.428	C16:0	Methyl Palmitate/$C_{17}H_{34}O_2$/ 270.457
Stearic acid/$C_{18}H_{36}O_2$/ 284.481	C18:0	Methyl Stearate/$C_{19}H_{38}O_2$/ 293.511
Oleic acid/$C_{18}H_{34}O_2$/ 282.465	C18:1	Methyl Oleate/$C_{19}H_{36}O_2$/ 296.495
Linoleic acid/$C_{18}H_{32}O_2$/ 280.450	C18:2	Methyl Linoleate/$C_{19}H_{34}O_2$/ 294.479
Linolenic acid/$C_{18}H_{30}O_2$/ 278.434	C18:3	Methyl Linolenate/$C_{19}H_{32}O_2$/ 292.463

Several factors play roles in the cost of biodiesel, such as the cost of feedstock (raw materials) and their processing (Nelson *et al.*, 1994). These factors will be discussed in more detail in the following sections.

2.3 First generation feedstock

Currently, more than 95% of biodiesel production throughout the world is made from conventional 1st generation feedstocks (Gui *et. al.*, 2008). These refined edible oils are originated from sources such as canola, soybean, rapeseed and corn oils.

This conventional 1st generation of feedstock consists of 90-98% triglycerides (TG), while the rest contains small amounts of diglycerides (DG), monoglycerides (MG), free fatty acids (FFA), water, sterols, phospholipids, odorants and other impurities.

The chemical structure of TG, as shown in Figure 2.2, is built from three fatty acid molecules and one glycerin molecule. In one mole of TG, the weights of bound fatty acids are in the range from 650 g to 790 g and the weight of glycerin is about 41 g.

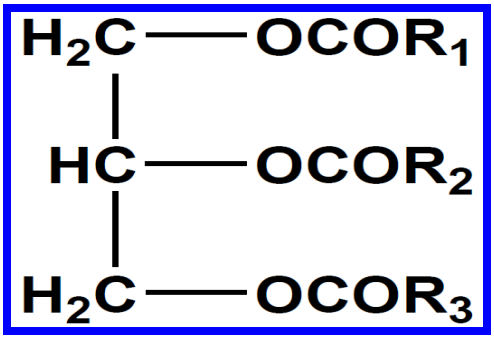


Figure 2.2 Chemical structure of triglyceride.

Thus, the characteristics of oils and fats are influenced by the bound fatty acids containing most of the reactive groups in the TG molecules.

2.4 Second generation feedstock

Generally, the price of 1st generation feedstocks (i.e. vegetable oils) is higher than other oils because they are refined/edible oils and also used as food resources. Consequently, feedstock cost plays a vital role in the economics of biodiesel (Noordam *et al.*, 1996; Haas, 2005; Haas *et al.*, 2006; Kulkarni *et al.*, 2006a; Marchetti *et al*., 2007; Gui *et. al*., 2008; Fan *et. al*., 2009;

Leung *et. al*., 2010; Baig and Ng, 2010; Balat, 2011, Baig *et. al.*, 2011). Therefore, it is essential to reduce the cost of the feedstock for the long-term commercial viability of biodiesel. One way to reduce the cost of biodiesel is to use inexpensive feedstocks that are non-edible oils, although they contain high amounts of FFA varying from 3% to 40% (Ma *et al*., 1999; Srivastava *et al*., 2000; Baig, 2003; Nabel *et al.*, 2006; Kulkarni *et. al.*, 2006a; Issariyakul *et. al.*, 2007; Ngo *et. al.*, 2008; Meng *et. al.*, 2008; Vyas *et. al*., 2010; Koh *et al.*, 2011). Examples of 2nd generation feedstocks are waste/used cooking oil and fats, and *jatropha curcas*.

Table 2.2 Oil sources and yields (Pure Energy Systems Wiki, Fitzgerald, 2006)

Oil	**Yield (gallon/acre/year)**
Corn	15
Soybean	48
Sunflower	102
Rapeseed	127
Jatropha	202
Palm	635

Jatropha produces inedible oils, and can be grown in arid land that may not be suitable for other crops and would require minimal irrigation requirements. The Caribbean, Africa, India, Pakistan and the Philippines are some of the best places to grow *jatropha* economically. Furthermore, as shown in Table 2.2, *jatropha* has a higher yield compared to many 1st generation feedstocks. Palm trees cannot be grown at all geographic locations whereas soybeans can be grown. Soybean has lower yield compared to rapeseed, but it requires considerably less fertilizer than does of rapeseed since it can fix nitrogen.

FFA can contain 4-24 carbon atoms with some degree of unsaturation (typically 1-3 C-C double bonds). In fact, fats are more saturated than oils, leading to a higher melting point and higher viscosity. Consequently, biodiesel produced from saturated fats have a higher cloud and gel points, which is unsuitable for use in cold climates compared to those generated from

The FFA contents of different feedstocks are listed in Table 2.3 (Gerpen, 2004).

Table 2.3 The FFA contents of different feedstocks.

Feedstock	**% FFA**
Refined vegetable oils	< 0.05%
Crude vegetable oil	0.3 – 0.7%
Restaurant waste grease	2 – 7%
Animal Fat	5 – 30%
Trap Grease	40 – 100%

unsaturated oils. Hence, food-grade vegetable oils containing low FFA levels are currently used for commercial biodiesel production. Some examples of waste greases are yellow grease containing 15% FFA or less and brown grease with higher percentage of FFA (i.e. 33% FFA). These greases and waste oils and fats are attractive feedstocks for biodiesel synthesis because they are widely available and low in cost (Canakci *et al.*, 2001; Zhang *et al.*, 2003; Baig, 2003; Nabel *et al.*, 2006; Issariyakul *et. al.*, 2007; Ngo *et. al.*, 2008; Meng *et. al.*, 2008)

The choice and suitability of fats and oils as feedstock for biodiesel results from their molecular structure and high energy content. Long chain, saturated, un-branched hydrocarbon chains in fatty acids are preferred due to their stability against oxidation.

Fatty acids are usually identified by the length of their carbon chains and the number of double bonds (unsaturation level). For instance, C18:3 (linolenic acid) indicates the presence of 18 carbon atoms and 3 double bonds.

Table 2.4 presents several fatty acid compositions and their methyl ester content obtained from different vegetable oils and animals fats available in the market that have been used widely as biodiesel feedstock (Knothe, 1997; Kulkarni *et. al.*, 2006b; Singh, *et al.*, 2007; Ngo *et. al.*, 2008; Meng *et. al.*, 2008).

Table 2.4 Composition of Various Fats and Oils (wt.%) (Knothe, 1997).

Carbon: Double bond	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	**20:0**	**22:1**
Oil/fat	**Myristic**	**Palmitic**	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**	**Arachidic**	**Erucic**
Soybean		6-10	2-5	20-30	50-60	5-11		
Corn	1-2	8-12	2-5	19-49	34-62	Trace		
Peanut		8-9	2-3	50-65	20-30			
Olive		9-10	2-3	73-84	10-12	Trace		
Cottonseed	0-2	20-25	1-2	23-35	40-50	Trace		
Hi Linoleic safflower		5.9	1.5	8.8	83.8			
Hi Oleic Safflower		4.8	1.4	74.1	19.7			
Hi Erucic Rapeseed		3.0	0.8	13.1	14.1	9.7	7.4	50.7
Butter	7-10	24-26	10-13	28-31	1-2.5	0.2-0.5		
Lard	1-2	28-30	12-18	40-50	7-13	0-1		
Tallow	3-6	24-32	20-25	37-43	2-3			
Linseed Oil		4-7	2-4	25-40	35-40	25-60		
Tung Oil		3-4	0-1	4-15		75-90		
Yellow Grease	1.3	17.4	12.4	54.7	8.0	0.7	0.3	0.5

2.5 Chemistry of biodiesel production

2.5.1 Transesterification

Different methods exist for biodiesel production and application such as direct use and blending, micro emulsions, thermal cracking (Pyrolysis) of vegetable oil and transesterification (Ma *et al.*, 1999; Srivastava *et al.*, 2000). Among these, the most common methods of biodiesel production are transesterification (alcoholysis) and esterification. The majority of the biodiesel production around the world is carried out by the conventional base-catalyzed transesterification. Transesterification reaction is a reversible reaction that involves the reaction between triglyceride (TG) molecule as a primary compound in vegetable oils and

a low molecular weight alcohol (i.e. methanol or ethanol) with the help of alkaline catalyst (i.e. NaOH or NaOMe) producing biodiesel (fatty acid methyl esters) and glycerol (byproduct) as shown in Figure 2.3 (Bournay *et al.*, 2005).

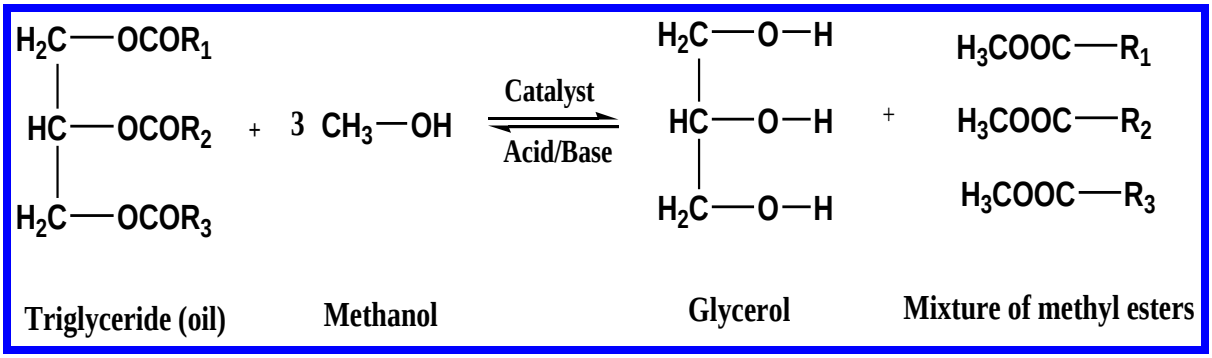


Figure 2.3 Overall transesterification reaction for vegetable oils.

The stoichiometric reaction requires 1 mole of triglyceride and 3 moles of alcohol. The excess of alcohol (i.e. methanol or ethanol) is used to drive the reversible reaction forward to increase the yields of the alkyl esters and to assist phase separation from the formation of glycerol. Methanol is preferably used because of its lower cost. The presence of acid or basic catalyst increases the rate of reaction. In general, basic catalyst is more favorable for transesterification because it is more effective and lower temperature required.

The conventional homogeneous base-catalyzed method offers several advantages because it can be operated under mild conditions with minimal side reactions and fast reaction time. However, the presence of water and free fatty acids (FFAs) in feedstocks combined with the basic homogeneous catalyst can produce soap, which causes serious problems in product separation and hinders catalytic activity.The overall process occurs as a sequence of three consecutive and reversible reactions in which di- and monoglycerides are formed as intermediates, as shown in Figure 2.4 (Singh *et al.*, 2007).

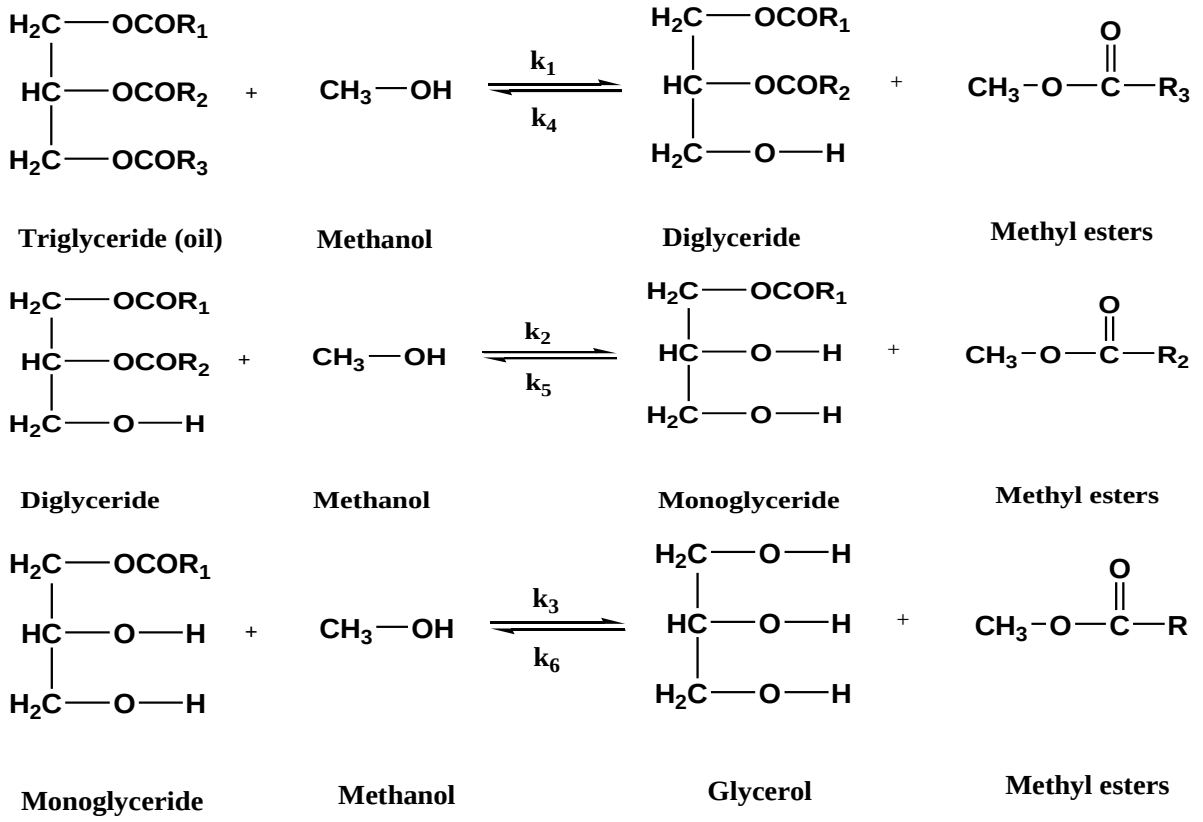


Figure 2.4 Sequential reactions of triglycerides.

Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. Transesterification has been studied in various vegetable oils including soybean, rapeseed and sunflower (Noureddini, 1997; Freedman *et al.,* 1984).

When homogeneous Brönsted basic catalyst, i.e. NaOH, KOH or Na_2CO_3, is mixed with alcohol, the actual catalyst formed is the alkoxide group shown in Equation (**2.1**), which attacks the carbonyl carbon atom of the triglyceride molecule (Ma *et al.*, 1999; Lotero *et al.*, 2006). Frequently, an alkoxide ($NaOCH_3$, $KOCH_3$) is directly used as catalyst.

$$Na^+OH^- + CH_3OH \rightarrow H_2O + CH_3O^-Na^+ \quad \textbf{(2.1)}$$

2.5.2 Esterification

For the 2nd generation feedstocks containing high levels of FFAs, esterification is the main reaction that reduces the amount of FFA present in the feedstock by converting FFAs to biodiesel and thus makes the feedstock suitable for conventional base-catalyzed transesterification.

Esterification is a reversible reaction between carboxylic acids and alcohol in the presence of strong acid catalyst resulting in the formation of ester product and water as shown in Figure 2.5.

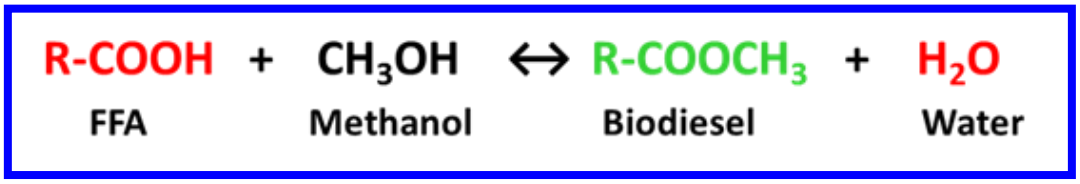


Figure 2.5 Overall esterification reaction for vegetable oils.

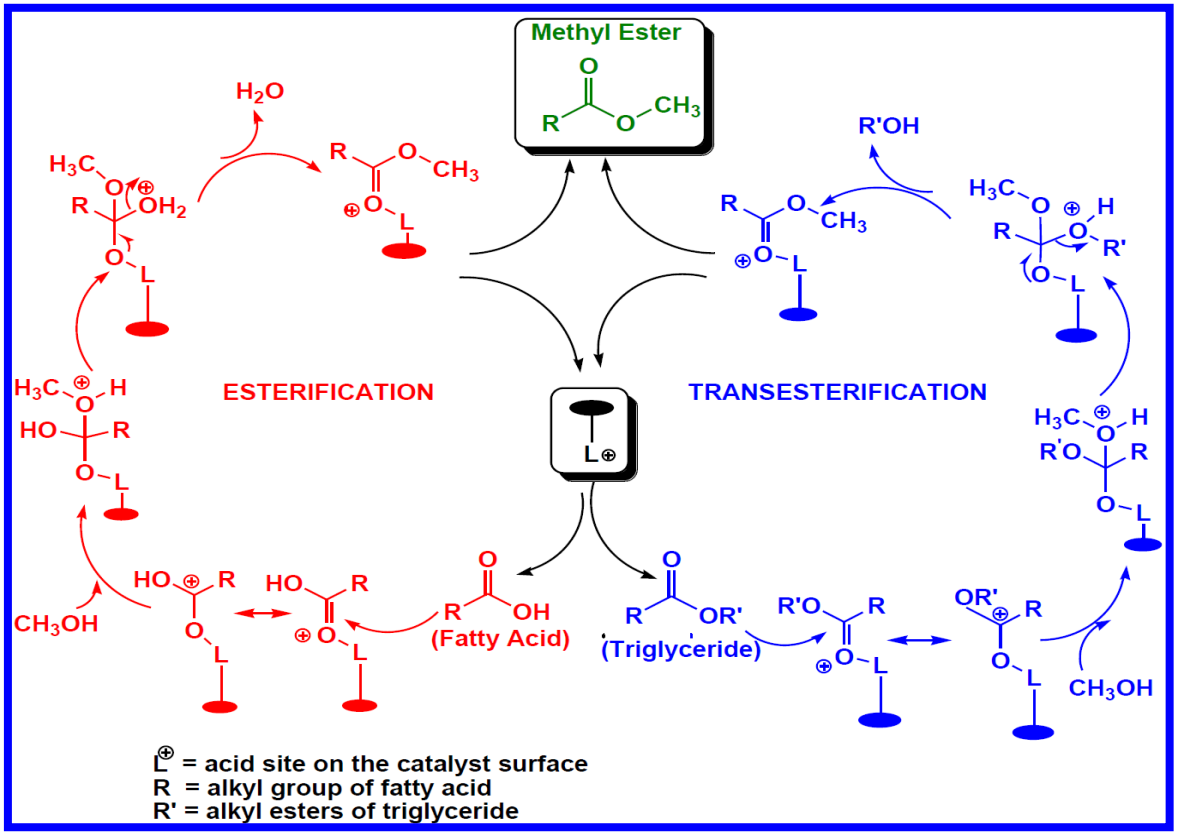
Due to an increased in the use of feedstocks with high amount of FFAs, applications of 1st generation (homogeneous) and 2nd generation (heterogeneous) acid catalysis have been extensively studied due to their tolerance to multi-feedstocks, high biodiesel yield, lower production cost, and potential for reuse.

2.5.3 Simultaneous esterification and transesterification

Acid catalysts can catalyze not only esterification, but also the transesterification of TG. Therefore, acids can simultaneously catalyze both, esterification and transesterification (Lotero *et al*., 2005; Zhang, *et al*., 2003a; Zhang, *et al*., 2003; Zheng, *et al*., 2006). However, the rates of reaction with acid catalysts are 3 orders of magnitude slower than that with basic catalysts (Freedman, 1986).

The reaction mechanism of simultaneous esterification and transesterification using a Lewis acid is shown in Scheme 1.1 (Kulkarni *et al.*, 2006c). The esterification takes place between

free fatty acids (RCOOH) and methanol (CH_3OH) whereas transesterification takes place between monoglyceride (RCOOR) (taken as representative of triglycerides in this case) and methanol adsorbed on acidic site (L+) of catalyst surface. The interaction of the carbonyl oxygen of free fatty acid or monoglyceride with acidic site of the catalyst forms carbocation. The nucleophilic attack of alcohol to the carbocation produces a tetrahedral intermediate (Scheme 1.1) (Kulkarni *et al.*, 2006c).



Scheme 1.1 Reaction mechanism of simultaneous esterification and transesterification.

During esterification, the tetrahedral intermediate eliminates a water molecule to form one mole of ester ($RCOOCH_3$). The transesterification mechanism can be extended to tri- and di-glyceride. It is well known that transesterification is a stepwise reaction. In the reaction sequence the triglyceride is converted stepwise to di- and monoglyceride and finally glycerol. The tetrahedral intermediate formed during reaction eliminates di-, monoglyceride and

glycerol when tri-, di- and monoglyceride come in contact with the acidic sites, respectively, to give one mole of ester ($RCOOCH_3$) in each step. Hence, the final product in esterification and transesterification steps is methyl ester (Kulkarni *et al.*, 2006c).

Also, as shown in Scheme 1.1, the catalyst is regenerated after the simultaneous esterification and transesterification reactions. The use of excess alcohol is desirable to drive the reaction forward and maximize the ester yield (Kulkarni *et al.*, 2006c).

In the biodiesel processing step, the presence of FFAs and water leads to undesirable side reactions such as hydrolysis when waste oils and fats are used as feedstock for biodiesel, making the process more challenging and complex. Therefore, it is crucial to conduct systematic studies to evaluate the emerging 2^{nd} generation feedstocks for sustainable biodiesel production in the future.

2.6 Biodiesel production technologies

The primary commercial biodiesel production process utilizes homogeneous base catalysts such as alkaline metal alkoxides (Schwab *et al.*, 1987) or hydroxides (Tanabe *et al.*, 1999). This process consists of transesterification followed by downstream processing involving separation (biodiesel and glycerol, biodiesel and methanol), neutralization of the homogeneous base catalysts, washing steps and the recovery of catalyst and unused methanol. Homogeneous catalysts lead to a better reaction rate compared to heterogeneous catalysts. However, complicated downstream processing results in low production efficiency.

The requirement to recover excess amounts of alcohol and catalyst leads to higher costs and greater energy consumption (Corma *et al.*, 2006). Moreover, the washing step to remove homogenous catalysts discharges a massive amount of waste water, which is not environmentally benign (Fukufa *et al.*, 2001).

A schematic flow chart of the conventional 1st generation homogeneous base catalyzed process using 1st generation feedstock (e.g. vegetable oil) is shown in Figure 2.6. When the amount of FFA in the feedstock exceeds 0.5% especially when 2nd generation feedstocks are used, this approach is not recommended because the sodium hydroxide catalyst reacts with FFA to form soaps as shown in equation **(2.2)** (Naik *et al.*, 2008). The soap causes downstream processing problems associated with emulsion formation (Ma *et al.*, 1999, Huber *et al.*, 2006).

$$\text{R-COOH} + \text{NaOH} \rightarrow \text{R-COONa} + \text{H}_2\text{O} \qquad \textbf{(2.2)}$$

Also, as shown in Figure 2.6, the homogeneous base catalyzed transesterification process requires complex downstream neutralization, separation, and washing steps making the purification of the biodiesel more challenging (Marchetti *et al*., 2007).

In order to address these problems, several alternative methods have been proposed to produce biodiesel from feedstock containing high FFA content (Kawahara *et al.*, 1979). Following are the some of the more effective methods which have been reported in the literature (Fukuda *et al.*, 2001; Haas *et al.*, 2002; Di Serio *et al.*, 2005; Lotero *et al.*, 2005; Kulkarni *et al.*, 2006c; Kumari *et al.*, 2007).

2.6.1 Removal of free fatty acid (FFA) from the feedstock

This method involves the removal of free fatty acid (FFA) present in the feedstock by saponification reaction. In this reaction, FFAs react with the base (NaOH/KOH in water) to produce soap. Then, the pure feedstock is separated from the soap by centrifugation.

This strategy is useful for feedstocks containing less than 2 wt.% FFA. Generally, the 2nd generation feedstocks contain higher levels of FFAs, e.g., yellow grease (≤ 15%), *jatropha* oil (≤ 20%), animal fats (≤ 30%) and brown grease (≤ 70-85%). In these cases, so much FFA must be removed from these feedstocks that biodiesel yields will be much lower, making this approach infeasible for industrial-scale production.

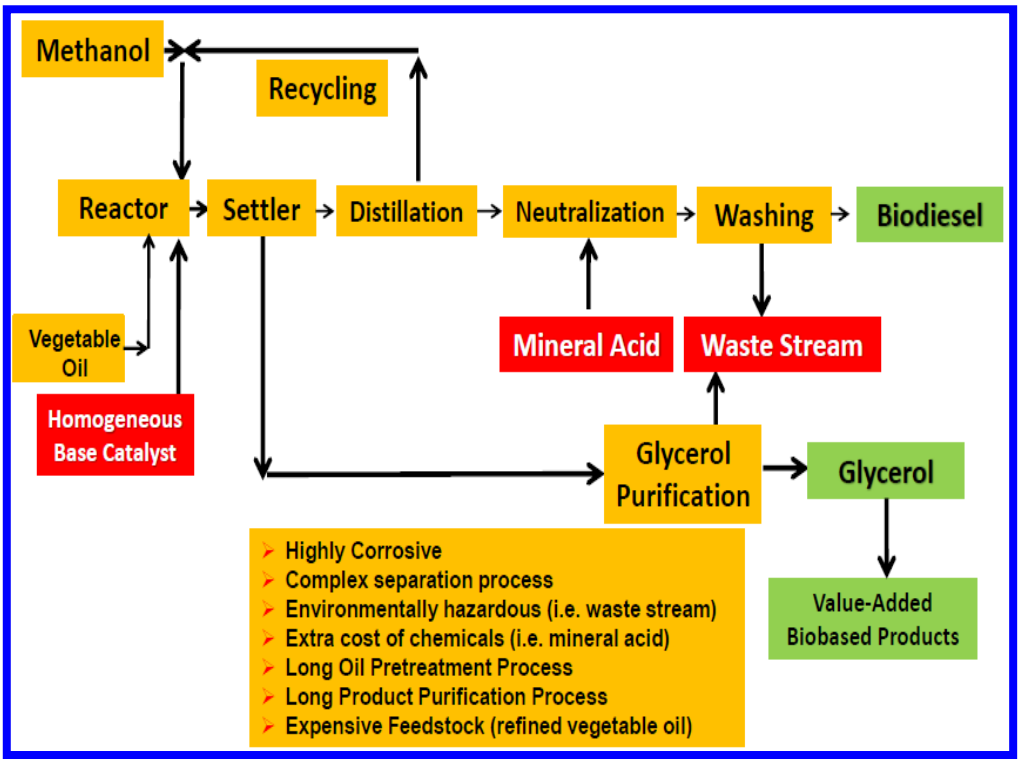


Figure 2.6 Schematic flow chart of homogeneous base-catalyzed reaction using 1st generation feedstock (e.g. vegetable oil).

2.6.2 First generation process technologies

Currently, most of the industrial processes use multi-step process technologies to produce biodiesel from 2nd generation feedstocks. These technologies involve two or more steps to convert waste oils and fats into biodiesel. In a typical two-step process, the first step involves the conversion of FFAs present in the feedstock to biodiesel by 1st generation homogeneous acid-catalysis followed by a homogeneous base-catalysis to convert triglyceride into biodiesel (Baig, 2003; Zhang *et al.*, 2003; Ramadhas *et al.*, 2005; Nebel *et al.*, 2006; Kumartiwari *et al.*, 2007; Rashid *et al.*, 2008).

However, these 1st generation homogeneous-catalyzed technologies are not preferable for the production of biodiesel from multi-feedstocks at industrial scale due to the tedious downstream processing, refining and complex separation steps and higher production cost that are required (Ilham *et al.*, 2010; Olutoye *et al.*, 2011).

2.6.2.1 Acid catalyzed esterification and transesterification

Homogeneous acid-catalyzed transesterification has not attracted much attention for industrial-scale production of biodiesel compared to the base-catalysis. This is mainly due to the fact that homogeneous acid-catalysis is about 4000 times slower than base-catalysis (Canacki *et al*., 2001). However, due to an increase in the use of 2nd generation feedstock containing high levels of FFAs, the acid-catalyzed transesterification holds an important advantage over base-catalyzed transesterification: presence of FFAs in the feedstock should not significantly affect the performance of the acid catalyst. The acid catalyst has the ability to simultaneously catalyze both esterification and transesterification. For this reason, the use of acid catalysts for the production of biodiesel from 2nd generation feedstocks with high FFA content has attracted more attention.

The reaction mechanism of simultaneous esterification and transesterification using acid catalysts is different from that of conventional base-catalysis which enables esterification of FFA as well as transesterification of triglycerides. The protonation of the carbonyl oxygen is the key step of the reaction, which makes the carbonyl more electrophilic. This highly electrophilic carbon can attract the alcohol directly instead of requiring a stronger nucleophile, such as the methoxide ion that operates in the base-catalyzed mechanism. The reaction mechanism of simultaneous solid acid-catalyzed esterification and transesterification has already been shown in Scheme 1.1 (section 2.5.3).

2.6.2.2 Acid and alkali catalyzed two-step transesterification

Acidic and alkaline catalysts have their own advantages and disadvantages in the transesterification of waste cooking oil. Therefore, looking at the characteristics of both catalysts, many researchers have used both acidic and alkaline catalysts for the synthesis of biodiesel from waste cooking oil using a two-step process (Baig, 2003; Kulkarni *et al.*, 2006b). An acidic catalyst can be used initially to convert FFA to esters and decrease the FFA level to $\leq$ 1%. In the second stage, the transesterification of oil can be performed using an alkaline catalyst (Lotero *et al.*, 2005; Kulkarni, *et al.*, 2006b).

However, the two-step method also faces the problem of catalyst removal in both steps. The problem of catalyst removal in the first step can be avoided by neutralizing the acidic catalyst, using extra alkaline catalyst in the second step. However, this requires extra catalyst that adds to the cost of the biodiesel. Furthermore, this alternative encounters problems linked with the corrosive action of the liquid acid catalyst and the high quantity of byproduct obtained (Lotero, *et al.*, 2005; Di Serio *et al.*, 2005).

2.6.2.3 Limitations of conventional 1st generation homogeneous-catalyzed process

Whether an acidic or basic catalyst is used, 1st generation homogeneous-catalysis involves the use of a soluble catalyst (NaOH, KOH or H_2SO_4) that tends to contaminate the biodiesel product and glycerol by-product. When NaOH is used as catalyst, sodium methoxide produced is dissolved in the final product mixture, mostly in the glycerol phase and partly in the biodiesel phase.

Also, due to the hydrolysis by water formed when $NaOCH_3$ is present, a small fraction of the triglycerides is always wasted as soap. From an industrial perspective, it is challenging to separate the $NaOCH_3$ and the soap from the final product mixture. It requires an extensive series of water washing steps. Furthermore, due to homogeneous nature of the catalyst, the catalyst is ultimately wasted, as regeneration is very expensive and fresh catalyst has to be constantly used.

Also, conventional 1st generation homogeneous catalysis generates a large amount of waste. Water is one of the most expensive resources in biodiesel plants. Also, due to repeated water washing steps, the water remaining in the biodiesel has to be removed which requires additional heating. As a result, additional processing units are required before the produced biodiesel goes through the final finishing process.

Glycerol is a value-added byproduct of biodiesel production. For every 10 kg of biodiesel, about 1 kg of glycerol is also produced. Glycerol is a valuable commodity chemical product

used in many industries including pharmaceuticals, cosmetics, food, beverages and paints. However, due to the significant increase in biodiesel production more glycerol is produced than is currently required in industry. This has made the glycerol market volatile with its price expected to drop significantly. However, glycerol can be used as a feedstock to produce value-added bio-based commodity products. However, this requires high purity glycerol which is challenging to produce using conventional 1st generation homogeneous-catalysis. The purity of glycerol produced using conventional 1st generation homogeneous catalysis process is only about 80% since it is contaminated with catalyst, soap and water. Due to this low purity, it can only be sold at a lower price to glycerol refineries or must be disposed. In order to purify the glycerol, the use of vacuum distillation is generally required. For these reasons, great interest exists to develop a green heterogeneous-catalysis second-generation process to produce not only high quality biodiesel but also high purity glycerol.

In summary, traditional 1st generation homogeneous catalysis has many limitations including complex downstream separation steps, extensive water washing, generating waste streams, various processing units and lower quality of glycerol. These limitations make these methods undesirable for industrial applications. Therefore, the development of an industrial-scale process for biodiesel product which is simple, green, efficient and robust is highly desirable.

2.6.3 Second generation process technologies

For these reasons, research has focused on the development of 2nd generation heterogeneous-catalysis technologies for the production of biodiesel. The goal then is to develop a second generation process to produce high quality biodiesel and valuable byproduct, glycerol. Furthermore, it should entail a simplified process which does not involve neutralization and washing steps and a simplified process which does separation of catalyst is relatively easy.

2.6.3.1 Solid base-catalyzed process

Various heterogeneous base catalysts have been developed such as zeolites, alkaline earth oxides and metal loaded alumina (Ono *et al*., 1997; Hattori, 2001; Handa *et al*., 1999). These

base catalysts can selectively catalyze triglycerides to biodiesel without interference from of FFAs and therefore increase the biodiesel yield. However, feedstocks consisting of a significant amount of FFAs of solid base catalysts are less effective since they are not able to convert FFAs to biodiesel by esterification.The schematic flow chart for solid base catalysis is shown in Figure 2.7.

Solid base-catalysis is a better alternative than homogeneous base-catalysis because it is simpler and more environmentally friendly by generating less amount of waste water. However, it still suffers from such drawbacks as an expensive feedstock (refined vegetable oil) and a low tolerance to water and FFA in feedstocks (Bournay *et al.*, 2005). These limitations can be overcome by using 2nd generation acid-catalyzed process which can simultaneously catalyze both esterification and transesterification.

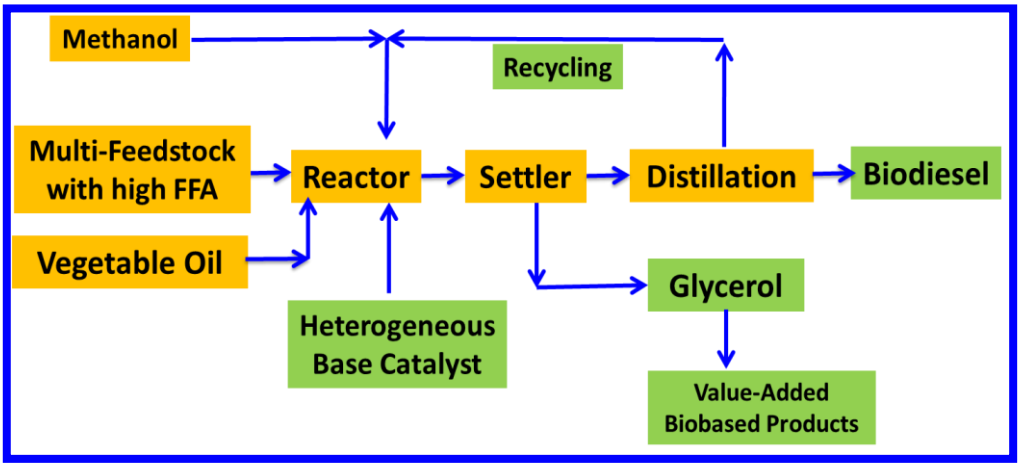


Figure 2.7 Schematic flow chart of solid base-catalyzed process.

2.6.3.2 Solid acid-catalyzed process

Currently, the majority of the biodiesel production around the world is carried out by using homogeneous base catalysis because it is kinetically much faster than heterogeneously catalyzed transesterification and is economically viable. However, due to the separation problems and product quality concerns, extensive research on heterogeneous catalysis towards the biodiesel production is ongoing all over the world.

During the last decade, many industrial processes have shifted towards solid acid catalysts (Harmer *et al.*, 2002; Toda *et al.*, 2005; Zong, *et al.*, 2007; Di Serio *et al.*, 2008; Yan *et al*., 2010). The major advantage of solid acid catalysts is that no polluting by-products are formed and no separation of catalyst from the biodiesel product is required. In addition to lower separation costs, less maintenance is required since these catalysts are not corrosive. In contrast to liquid acids that possess well defined acid properties, solid catalysts contain sites with a range of acidities (Clark *et al.*, 2000). Usually they are categorized by their Brønsted or Lewis acidity, the strength and number of sites and textural properties of the support (Kiss *et al*., 2006).

At low temperatures, the activity of acid catalysts for transesterification is normally quite low. Thus, it is necessary to increase the reaction temperature above 170°C to achive acceptable reaction rates (Di Serio *et al.*, 2008). Sulfonic acid resins cannot be used at these temperatures and can be used only for esterification where they perform well at temperatures below 120°C (Steinigeweg *et al.*, 2003; Tesser *et al.*, 2005; Pasias *et al.*, 2006). Propylsulfonic acid-functionalized mesoporous silica showed good performance for FFA esterification in beef tallow. Starting from an initial concentration of 7% FFA, a final FFA concentration of 0.3% was achieved within 60 min at 120°C with a methanol/FFA weight ratio of 20:1 and an FFA/catalyst weight ratio of 9:1 (Mbaraka *et al.*, 2006). The same catalyst reused in a successive run lost its original activity because of the adsorption of organic polar impurities present in beef tallow (Mbaraka *et al.*, 2006).

Esterification catalysts can be prepared by the incomplete carbonization of natural products such as sugar, starch, or cellulose and their successive sulfonation (Toda *et al.*, 2005; Zong *et al.*, 2007). The “sugar catalyst” has higher activity for oleic acid esterification than other acid solids most likely because of the higher concentration of acid sites on the surface.

It was reported that the sugar catalyst still retained a high proportion (93%) of its original catalytic activity in the methyl oleate formation reaction even after more than 50 cycles of successive reuse. This catalyst also gave higher yields (90% after 15 h at 80°C) biodiesel production from waste oils (FFA conc = 27.8% w/w) than other acid solids (Zong *et al.*, 2007). However, this catalyst has been found to be successful only for esterification (Toda *et al.*, 2005).

Ferric sulfate has been shown to have a good catalytic activity for esterification of FFAs contained in waste cooking oil. After calcination at 460°C to remove the adsorbed organic substance, this catalyst can be reused with the same performance as fresh ones (Wang *et al.*, 2006 & 2007). However, since ferric sulfate is soluble in methanol, a small amount of the solid catalyst remains dissolved in the oil phase after methanol distillation. Thus, it is not clear if ferric sulfate acts as a homogeneous or heterogeneous catalyst (Di Serio *et al.*, 2008). The sulfated carbon-based (carbon fiber, mesoporous carbon) catalysts also exhibited lower activity compared to the other catalysts and so cannot be seriously considered for industrial scale applications (Kiss *et al.*, 2006).

Catalysts with small pores, such as zeolites, are not suitable for biodiesel manufacturing because of the diffusion limitations of the large fatty acid and ester molecules. Ion-exchange resins such as Nafion and Amberlyst are active strong acids, but have a low thermal stability. This is problematic as the reaction must be carried out at high temperatures to achieve high reaction rates (Kulkarni *et al.*, 2006c).

Since acid catalysts can simultaneously catalyze both esterification of FFAs and transesterification of TGs, they can help in processing low-cost, low-quality feedstocks (generally high in FFAs) and thereby lower overall production costs (Lotero *et al.*, 2005 & 2006; Kulkarni *et al.*, 2006a). However, few research studies dealing with transesterification reactions catalyzed by solid acids have been reported in the literature, while most papers have been devoted to esterification reactions (Lotero *et al.*, 2005 & 2006). The major reason

that solid acid catalysts have not been considered for transesterification is due to their slow rates compared to the esterification reaction.

A challenge exists in finding a suitable solid acid catalyst which can simultaneously catalyze both esterification and transesterification. For industrial scale processes, such a catalyst must fulfill several conditions that may not seem so important on a laboratory scale. The catalyst should be very active and selective (as by-products formed in secondary reactions are likely to render the process uneconomical), water-tolerant (water by-product may deactivate the catalyst) and stable at relatively high temperatures. In addition, it should be an inexpensive material that is readily available on an industrial scale (Kiss *et al.*, 2006). Considering these conditions, a strong Brønsted acid with increased hydrophobicity and high thermal stability (up to 200–250°C) is desirable. Hydrophobic surfaces are preferable for conducting organic reactions in water to avoid water blocking the solid acid surface and preventing the adsorption of organic materials. This feature is particularly very important for the production of biodiesel with a feedstock containing FFA and water. An ideal solid acid catalyst for the transesterification of waste cooking oil should consist of an interconnected system of large pores, a moderate to high concentration of strong acid sites and a hydrophobic surface (Lotero *et al.*, 2005).

Heteropolyacids (HPAs) have been extensively studied as acid and oxidation catalysts for a wide range of reactions (Kozhevnikov, 1995, 1998 & 2003; Okuhara *et al.*, 1996; Misono *et al.*, 1990). Industrially, they have found application in several processes such as the oxidation of methacrolein tomethacrylic acid, oxidation of ethylene to acetic acid and hydration of olefins (Okuhara *et al.*, 1996). Heteropolyacids (HPAs) are found to be active solid acid catalysts for many homogeneous and heterogeneous acid-catalyzed reactions since they have strong Brønsted acidity better than H_2SO_4, easier separation and reusability, higher proton mobility and higher selectivity (Cavani, 1998; Kozhevnikov, 1998; Mizuno *et al.*, 1998). HPAs are well known to be active toward liquid phase esterification and transesterification; they are often used as catalysts in the food and chemical industry.

The major disadvantages of HPA are their low specific areas and solubility in polar media, but can be overcome by dispersing them on high surface area supports (Kulkarni *et al.*, 2006a). In this way, HPAs can be made to be ecofriendly with high thermal stability and high surface area. As examples, silica (Pizzio *et al.*, 2003; Bielanski *et al.*, 2003; Dias *et al.*, 2006), activated carbons (Dupont *et al.*, 1995; Chimienti *et al.*, 2001; Vazquez *et al.*, 2002), zeolites (Mukai *et al.*, 1997; Haber *et al.*, 2003), polymers (Choi *et al.*, 2001; Castanheiro *et al.*, 2003 & 2005) have been used as supports.

HPAs are promising green catalysts since most are environmentally friendly. Tungstophosphoric acid supported on zirconium oxide (Kulkarni *et al.*, 2006a) and other solid supports, such as activated carbon, silica (Rao *et al.*, 2006; Mizuno, *et al.*, 1998; Vazquez *et al.*, 2002) have been used as catalysts in the esterification of palmitic acid with methanol.

On the basis of this literature review, it is imperative that more work is needed to find robust enough solid catalysts that are selective towards esterification and transesterification. Therefore in an attempt to develop a strong solid acid catalyst that can simultaneously catalyze esterification and transesterification reactions.

Our objective is to evaluate the activity of a supported HPA solid acid catalyst (30% tungstophosphoric acid supported on neutral alumina, HPA/nAl_2O_3) suggested and provided by Professor Ng for the production of biodiesel from feedstocks with high FFA content. I have studied the effect of calcinations temperature, HPA loading and the method of preparation on the activity of this catalyst (HPA/n-Al_2O_3) for the production of biodiesel for the feedstocks described in this thesis.

Selection of Catalyst:

Since past decades, acid catalysis by heteropoly acids (HPAs) and other related polyoxometalate compound is an increase research field of importance in the literature due to

variety of structures and compositions (Misono *et al.*, 1990; Corma, 1995; Okuhara *et al.*, 1996; Kozhevnikov, 1998; Sharma and Patel, 2006; Bhatt *et al.*, 2007; Nakajo, 2008; Bhatt and Patel, 2008; Bhatt *et al.*, 2008; Brahmkhatri and Patel, 2010; Brahmkhati and Patel, 2011). HPAs provide the flexibilities to tuning their chemical properties such as acidities and reactivates based on the selection of an appropriate support material (Brahmkhati and Patel, 2011). There are several advantages economically and environmentally for HPAs that makes them catalyst of choice for solid acid catalysis. HPAs are not only widely employed for fundamental research as model system, providing unique opportunities for mechanistic studies on the molecular level (Kozhevnikov, 1998) but are becoming vital for applied catalysis as well.

Solid HPAs possess purely Bronsted acidity and are considered stronger than conventional solid acids such as SiO_2-Al_2O_3, H_3PO_4/SiO_2, and HX and HY zeolites (Furuta *et al.*, 1979; Misono *et al.*, 1982). The acid strength of crystalline HPAs decreases in the order of PW > SiW ≥ PM0 > SiMo (Kozhevnikov, 1987; Misono, 1987, 1988). Furthermore, HPAs have a fairly high thermal stability. The Keggin-type PW, SiW, PMo, and SiMo decompose at 465, 445, 375 and 350°C, respectively (Kozhevnikov, 1998). Due to these advantages, several industrial processes based on HPA catalysis have been developed and commercialized (Misono *et al.*, 1990).

The major disadvantage of bulk HPAs is to have a low specific surface area (1-5m^2/g) (Kozhevnikov, 1987; Misono, 1987, 1988; Ono, 1992). This has been address by using supported HPAs (Nakajo, 2008). Also, one of the major challenges for catalyzing transesterification reaction of triglyceride is the mass transfer limitations. This can also be overcome by the use of structure promoters or catalyst supports. These support material can provide more specific surface area, access to active sites where reaction can take place (Aroua *et. al.*, 2009). Acidity and catalytic activity of supported HPAs mainly depends on the nature of support, the HPA loading, and conditions of pre-treatment. Incorporation of HPA into zeolite pores for shape - selective catalysis has been remains challenging since

conventional zeolites are not suitable due to their pores are too small to adsorb large (12 Å) HPA molecules (Kozhevnikov, 1998). Also, the acid strength of PW is significantly reduced when supported on activated carbon (Kozhevnikov, 1998). For HPAs, generally, acid and neutral supports are considered suitable as support since basic supports tend to decompose HPA (Kozhevnikov, 1987; Kozhevnikov, 1995) due to acid base interactions. The use of alumina is widely used industrially as adsorbent, drying agent, filler, reagent, catalyst and catalyst support (Palmieri *et. al*., 2005). It is material of choice due to its abundant availability and low cost. Neutral alumina is most commonly utilized to carry out surface organic chemistry (Kabalka and Pagni, 1997). Furthermore, in contrast to clays and zeolites, alumina does not contain accessible channels or cavities and shows large surface area and highly porous exteriors available to substrates (Palmieri *et. al*., 2005).

Therefore, TPA based supported catalyst (tungstophosphoric acid with supported on neutral alumina) with modifications is anticipated to be an active catalyst to produce biodiesel from multi-feedstocks by catalyzing both, esterification and transesterification reactions.

2.7 Proposed method of research

Based on the literature, our research strategy is focused on the development of a single-step solid acid-catalyzed process, for both esterification and transesterification to produce biodiesel from economical multi-feedstocks (edible and non-edible), as shown in Figure 2.8.

Advantages of this method are that it is a single-step integrated process that simultaneously catalyzes esterification and transesterification, makes use of an inexpensive multi-feedstock, can produce high quality biodiesel and pure glycerol from multi-feedstocks (soybean oil, yellow grease and *jatropha* oil) requires no waste water treatment stream and is a green process (uses waste and non-food grade oil to produce a sustainable fuel).

2.8 Analytical methods for biodiesel analysis

With the increasing interest and use, the assurance of fuel properties and quality has become a paramount interest for the successful commercialization and market acceptance of biodiesel. Accordingly, biodiesel standards have been established or are being developed in various countries and regions around the world, including the United States (ASTM D 6751), Europe (EN 14214), Brazil, South Africa, Australia and elsewhere (Knothe, 2006 and 2008). This section details the specifications of biodiesel standards in ASTM D6751 and EN 14214, the standards commonly used as references or bases for other standards and their analysis. The specifications of the ASTM biodiesel standard are presented in Appendix-A (ASTM, 2006).

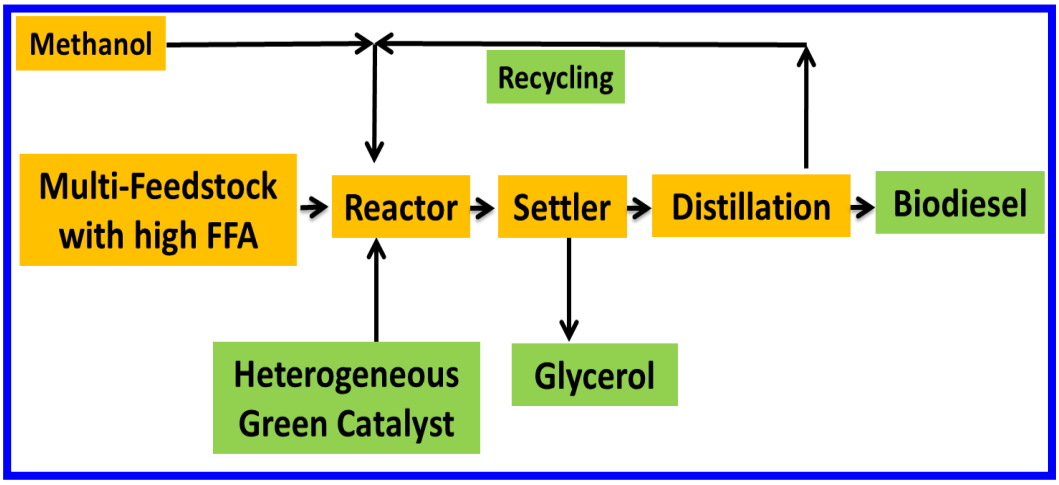


Figure 2.8 Proposed novel process for the production of biodiesel from multi-feedstocks.

2.8.1 Glyceride content analysis

During the transesterification process, intermediate monoglyceride (MG) and diglyceride (DG) are formed, small amounts of which can remain in the final biodiesel product. Besides these partial glycerols, unreacted triglyceride (TG) as well as un-separated glycerol, free fatty acid (FFA), residual alcohol and catalyst can contaminate the final product. The contaminants can lead to severe operational problems, such as engine deposits, filter clogging or fuel deterioration. Therefore, standards such as those in Europe (EN 14214; EN 14213

when using biodiesel for heating oil purposes) and the United States (ASTM D6751) limit the amount of contaminants allowed in biodiesel fuel (Knothe, 2006).

To meet the requirements of biodiesel standard ASTM D6751, the determination of concentrations of individual compounds in biodiesel is not necessary, but the quantification of classes of compounds is required (e.g. free glycerin and total glycerin). For the determination of total glycerol, it does not matter which kind of acylglycerol (MG, DG or TG) or free glycerol is present. However, in addition to free glycerin and total glycerin, European standard, EN14214, also required quantification of individual compounds (MG, DG and TG) and it does not matter which FA is (are) attached to the glycerol backbone as long as the limits of the individual acylglycerol species (in case of) or free glycerol are met. Acylglycerols are quantifiable as classes of compounds by GC (Knothe, 2006).

2.8.2 Linolenic acid methyl ester content

The content of methyl linolenate is restricted in EN 14214 because of the propensity of methyl linolenate to oxidize. However, the limit (12%) is set so as not to exclude high-oleic rapeseed oil, the major biodiesel source in Europe, as feedstock. The method EN 14103 used for this determination is the same as used for ester content (Knothe, 2006).

2.8.3 Free fatty acid (FFA) and acid number

In 2001, an American Society of Testing of Materials (ASTM) standard, (D6751), was set for biodiesel with regard to the lower alkyl esters of fatty acid (FA) (ASTM, 2006). This was followed soon by a European standard EN 14214 (DIN, 2003). One of the most critical quality parameters of biodiesel, particularly from the viewpoint of producers, is the acid number, which is the number of milligrams of potassium hydroxide that is required to neutralize a 1 g sample.

In the case of biodiesel, the acid number is derived almost exclusively from the FA content which can be formed by the hydrolysis of ester linkages in both the TG feedstock and the

biodiesel during its manufacture. The ASTM Task Force on Biodiesel recently lowered the ASTM D6751-allowed acid number of biodiesel from 0.80 to 0.50 to harmonize with the European standard (Howell, 2005). ASTM D974 is a method for measuring the acid number of petroleum oils (ASTM, 1997). It uses *p*-naphtholbenzein as the indicator in an isopropanol/toluene mixture. The change of this indicator from orange to green at the end point can be seen even in the colored samples.

The acid number is a facile parameter for monitoring fuel quality. The acid number is described in ASTM D6751 and can be measured using method ASTM D664 and in EN 14214 using method EN 14104. However, D664 is based on a potentiometric method which suffers from mediocre reproducibility (ASTM, 2001), a problem acknowledged in the ASTM standard itself. The problem is likely due to the variability of electrodes. ASTM D974 makes use of a non-aqueous titration with KOH in isopropanol and *p*-naphtholbenzoin as indicator and is suitable even for the colored samples. Analytical results have been more consistent using ASTM D974 than ASTM D664. Therefore, ASTM D974 would be the more appropriate method than ASTM D664 in the biodiesel standard D6751 (Mahajan *et al.*, 2006). EN 14104 also involves titration; with a dilute ethanolic KOH solution and phenolphthalein as indicator.

2.9 Studies for commercialization

Based on the literature review and preliminary results, development of heterogeneous acid-catalysis for the production of ASTM-standard biodiesel from waste oils and fats will be complemented by studying important process parameters such as:

1. oil-to-alcohol molar ratio.
2. temperature.
3. amount of catalyst and catalyst loading.
4. FFA content.
5. water content.
6. use of co-solvent.

2.9.1 Oil-to-alcohol molar ratio

As seen in the literature review (Freedman *et. al*., 1984; Boocock *et. al.*, 1998; Kulkarni *et al.*, 2006b; Cao *et. al*., 2008) as well as in preliminary experiments, a high oil-to-alcohol molar ratio will favor the fast conversion of free fatty acid (FFA) and triglyceride (TG) into methyl ester (ME). Therefore, the effect of oil-to-alcohol molar ratios in the range from 1:6 to 1:40 will be investigated (as shown in Table 2.5).

2.9.2 Temperature

Another important parameter which can influence the yield of biodiesel is temperature. A rise in the reaction temperature can increase the rate of reaction. However, when the reaction is carried out above 200°C, polymeric products were found to form by the degradation of triglycerides and unsaturated fatty acids due to exposure of oil to high temperature for long reaction times. Since this is not desirable during biodiesel production, the optimum reaction temperature was reported to be 200°C (Peng *et al.*, 2008; Kulkarni *et al.*, 2006c).

A decrease in reaction temperature is favorable with respect to industrial applications since this will lower energy consumption and pressure requirements. Therefore, in this study, experiments will be conducted at 150°C, 175°C, 200°C and 225°C. The data so collected will also be used for kinetic studies.

Table 2.5 Process variables and conditions for biodiesel production.

S. No.	Process Variables	Conditions
1	Oil to alcohol molar ratio	1:6 - 1:40
2	Temperature	150°C - 225°C
3	Amount of catalyst	1% - 10%
4	Catalyst loading	10% - 40%
5	FFA content	0% - 25%
6	Water Content	0.1% - 1%

2.9.3 Amount of catalyst and catalyst loading

The common reason for the change in the value of the catalyst-to-oil weight ratio is the change in contact conditions between oil and catalysts which in turn changes the average

activation of catalysts. In general, as the catalyst-to-oil weight ratio increases, the probability of contact between oil and active centers also increases (Singh *et al.*, 2007).

By increasing the amount of catalyst used, the reaction rate can be further increased (Kiss *et al.*, 2006). Therefore, this can speed up the process which potentially can make this catalyst suitable for reactive distillation applications where high activity is required in a short time.

In the preliminary studies, the amount of catalyst used was 3 wt.%. In proposed studies, catalyst amounts in the range of 1% - 10% will be used as shown in Table 2.5. Also, catalyst loading plays a vital role for the efficient use of support material. In preliminary studies, catalyst loading was about 30%. However, in literature, catalyst loading up to 70% has been reported (Mizuno and Misono, 1998; Clark and Wilson, 2000; Kulkarni *et al.*, 2006c; Semwal *et. al*., 2011). Therefore, to attain the maximum conversion over shorter reaction times, the use of higher catalyst loading has been suggested. In the proposed research, the effects of catalyst loadings of 30% and 40% will be evaluated.

2.9.4 Free fatty acid (FFA) content

As recommended in the literature (Chapter 2) and demonstrated by the preliminary experimental results (Chapter 3), the use of inexpensive feedstocks with high FFA content will significantly reduce the cost of biodiesel and remove the major barrier for the commercialization of biodiesel (Haas 2005; Haas *et al.*, 2006; Kulkarni *et al.*, 2006a). Therefore, in the proposed studies, feedstocks with high FFA contents will be used. This parameter is very crucial to evaluate the effectiveness of our proposed process for a wide range of feedstock (Kulkarni *et al.*, 2006a).

2.9.5 Water content

Water is a major process variable that can significantly impact the quality of methyl ester. For traditional base-catalyzed transesterification reactions, highly anhydrous feedstocks and reagents (water free or maximum water content of < 0.06%) are required (Ma *et al.*, 1999;

Komer *et al.*, 2001) in order to prevent the hydrolysis of methyl ester (biodiesel) into fatty acids (Ma *et al.*, 1999; Huber *et al.*, 2006), and reduce the acid number. Also, in esterification reaction, water is inevitably produced during esterifications. This water can also deactivate catalyst (as seen in literature review). Also, waste frying oil can contain about 0.1% water (Cao *et al.*, 2008). Therefore, the catalyst tolerance also needs to be evaluated towards water content. Due to this very important process chemistry, the effect of water contents of 0.1, 0.5 and 1% will be evaluated.

2.9.6 Use of co-solvent

During typical homogeneous base-catalyzed transeterification, the reaction mixture exists in two phases. Mass transfer has been found to be a major limitation due to the nature of the two-phase system (alcohol-rich and oil-rich phase) (Boocoock *et al.*, 1998). To overcome this mass transfer limitation, tetrahydrofuran (THF) has been used as a co-solvent to dissolve both oil and methanol to form a single phase. The rate of reaction increased significantly after THF was added to the system. However, THF does not take part in the reaction and has to be recovered completely. The purification of methanol for reuse is difficult as the boiling point of methanol (65°C) and THF (67°C) are close.

Another approach is the use of mixed alcohols (Issariyakul *et al*., 2007). In order to make use of ethanol as a co-solvent to improve the solubility of oil in methanol, mixtures of methanol and ethanol have been used for transesterification. The addition of ethanol to methanol significantly improved the rate of the reaction, particulary in the initial stages. Even a small amount of ethanol (molar ratio of methanol: ethanol 5:1) improved the initial rate of the reaction. The addition of ethanol improved the solubility of oil in methanol, which ultimately increased the rate of the reaction.

Although ethanol helps to improve the solubility of oil in methanol and also partly takes part in the reaction, the rate of ethanolysis is slower than the rate of methanolysis. The slower reaction rate of ethanol can be explained by the reaction mechanism of alkaline catalyzed

transesterification. The alkoxide anions formed in the preliminary step attack the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate in the first step of the reaction. Since this is the rate-determining step of transesterification, the rate of transesterification is determined by the reactivity of the alkoxide anion. The reactivity of methoxide is higher than that of the ethoxide anion. Since the nucleophilicity of the alkoxide anion decreases as the carbon chain length increases, leading to a decrease in the reactivity of alkoxide anion (Kulkarni *et. al*., 2006a). This causes a lesser amount of ethyl esters to form compared to methyl esters when a mixture of methanol/ethanol is used for transesterification of canola oil. Although the formation of ethyl ester is slow, the overall rate of formation of ester was fast since equilibrium was achieved. The fast rate of formation of ester was due to the better solubility of oil in a mixture of alcohols. Therefore, we propose to evaluate the effect of co-solvent (and/or mixed alcohol) on the reaction. It is expected that it can result in faster reaction rates as well as reduce the need for mechanical mixing.

2.10 Catalyst recycling

The catalyst recycling is an important step as it reduces the cost of the process (Semwal *et al*., 2011). The efficiency of the catalysts also depends on their reusability. Therefore, catalyst recycling studies have been proposed to investigate the reuse of catalyst for up to 5 consecutive runs (or more depending on its catalytic activity after a few runs).

2.11 Hydrolysis (selectivity and side reactions)

Typically, a higher alcohol-to-oil (or acid) ratio favors transesterification (or esterification) to form biodiesel. However, in the presence of an excess of alcohol, the use of an acid catalyst may lead to side reactions such as etherification or dehydration. The selectivity will be assessed by testing the formation of side products in a suspension of catalyst in alcohol under reflux conditions for 24 h (Kiss *et al.*, 2006).

CHAPTER 3
PRELIMINARY EXPERIMENTAL WORK

The overall goal of this research is to develop a heterogeneous acid-catalyzed chemical process to produce ASTM-standard biodiesel from multi-feedstocks (Chapter 4, 5 and 6). Therefore, preliminary studies were conducted to accomplish the overall goal by focusing on three objectives to assess the feasibility of producing biodiesel from waste oils and fats using a solid acid catalyst. In order to meet the specifications of biodiesel quality standards (ASTM and CEN), it is very important to use recommended standard analytical methods (ASTM and CEN). Therefore, in this research studies, the first objective is to apply ASTM analytical methods (ASTM D6584) and EN 14103 to quantify the quality of biodiesel (ASTM International D6751, 2006; European committee for Standardization EN 14214, 2003). Hence, the application and the validation of ASTM-standard analytical methods for in-process and final biodiesel products were carried out to develop valid analytical methods to obtain reliable experimental results. The second objective is to focus on the esterification of major free fatty acid (FFA) in vegetable oils to biodiesel using a homogeneous acid catalyst which will provide a benchmark for comparison with a novel heterogeneous solid acid catalyst with sulfuric acid in real medium (vegetable oil) (Chapter 4, 5 and 6). Finally, the third objective of the preliminary studies is to study the kinetics in order to evaluate the new solid acid catalyst for the production of biodiesel from feedstock containing high FFA content (Chapter 4). Therefore, the preliminary results obtained for this research study will be discussed in more detail in this section.

Subsections 3.1.1 and 3.1.2 present the preliminary results of ASTM D6584/EN 1405 method validation for glyceride determination and EN 14103 for ester and linolenic acid methyl ester determination, respectively. The results of the second phase of preliminary studies focusing on the production of biodiesel using homogeneous acid catalysis are

discussed in Section 3.2. Finally, the results of the final phase of the preliminary studies focusing on the kinetic studies for the production of biodiesel using a heterogeneous solid acid catalyst are provided in Section 3.3.

3.1 Validation of analytical methods for biodiesel analysis (ASTM D6584/EN14105 for glyceride determination and EN 14103 for ester and linolenic acid methy ester determination)

3.1.1 Introduction

Before biodiesel can be sold as a fuel or blending stock, it must first meet a defined standard. ASTM standard D6751 and European Committee of Standardization (CEN) standard EN 14214 set similar specifications for biodiesel blending and motor fuels (ASTM International and European Committee for Standardization, 2003). In each standard, an important specification is a limit on the amounts of free glycerin and glycerides in biodiesel. Free glycerin is a by-product of biodiesel production. Monoglycerides, diglycerides and triglycerides are partially reacted oils that may be contaminants in the finished biodiesel. High amounts of free glycerin can cause problems due to separation. High amounts of glycerides and glycerin can result in increased engine deposits. Table 3.1 shows the limits of glycerin set by each standard.

ASTM and CEN have defined several physical and chemical test methods to meet the standard specifications. An important chemical test measures the free glycerin and glyceride content in B100. Two gas chromatographic methods, EN 14105 and D6584, were developed to make this measurement (ASTM International, 2003 and European Committee for Standardization, 2003). Both are nearly identical in sample preparation, instrument configuration, operating conditions and reporting. Since glycerin and glycerides are polar and have high boiling points, they must first be derivatized to improve their volatility and reduce

Table 3.1 Free and total glycerin specifications for biodiesel.

	EN14214		ASTM D6571	
	Limit (% m/m)	Test method	Limit (% m/m)	Test method
Free glycerin	0.02 max	EN14105	0.020 max	D6584
Monoglycerides	0.80 max	EN14105	NA	D6584
Diglycerides	0.20 max	EN14105	NA	D6584
Triglycerides	0.20 max	EN14105	NA	D6584
Total glycerin	0.25 max	EN14105	0.240 max	D6584

3.1.2 Experimental procedures

3.1.2.1 Materials

For ASTM D6584, Agilent Technologies biodiesel standards used contained glycerin, monoolein, diolein, triolein, butanetriol (internal standard #1) and tricaprin (internal standard #2) at concentrations specified in the ASTM D6584 method (ASTM International, 2003). The derivatization agent, N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was supplied by Agilent Technologies, Canada.

For EN 14103, methyl heptadecanoate, heptanes and rapeseed FAME standard mixture were purchased from Sigma-Aldrich (AnalR).

3.1.2.2 Method

For ASTM D6584, five GC calibration standards were prepared by mixing aliquots of the individual stock standards in proportions specified by the ASTM D6584 method. After mixing, 100 µL of the derivatization agent N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was added to each calibration standard. After 20 minutes, 8 mL of reagent grade n-heptane was added to each calibration standard.

Sample preparation followed the procedure in the ASTM and CEN methods using internal standards. This involves addition of 100 µL addition of each internal standard and MSTFA derivatization reagent in 0.1 g of sample in a 20 mL vial. Then, the procedure followed as for

the standards mentioned above. These final reaction mixtures were directly injected into the gas chromatograph.

Samples were analyzed for TG, DG, MG and glycerol content using GC as per ASTM D6584. The GC system consists of an Agilent 7890 Series gas chromatograph equipped with a cool on column injection system with electronic pneumatics control (EPC), a capillary flame-ionization detector (FID), auto injector, and Agilent Chem Station software. An analytical column DB-5ht (15 m x 0.32 mm id x 0.1 µm film) with high-temperature retention gap deactivated fused-slica tubing (1 m x 0.53 mm) and He as carrier gas was used. Detailed GC conditions are shown in Table 3.2.

Table 3.2 GC operating conditions.

Cool-on-column inlet	
Mode	Ramped
Initial temperature	oven track, approx 50°C
Pressure	7.6 psi helium
Injection amount	1 µL
Initial column flow	3.0 mL/min, constant pressure mode
FID temperature	380°C
Oven temperature program	50°C for 1 min,
15°C/min to 180,	hold 0 min
7°C/min to 230,	hold 0 min
30°C/min to 380,	hold 10 min

For EN 14103, 250 mg of sample was weight out into a 20 mL vial to which 5 mL of methyl heptadecanoate solution was then added using a pipette as per EN 14103.

Samples were analyzed for ester content and linolenic acid ester content using GC as per EN 14103. The GC system consisted of a Agilent 7890 Series gas chromatograph equipped with a split/splitless injection system with electronic pneumatic control (EPC), a capillary flame-ionization detector (FID), auto injector and Agilent Chem Station software. An analytical HP INNOWAX column (30 m x 320 µm id x 0.25 µm film of polyethylene glycol) was used. Detailed GC operating conditions are shown in Table 3.3.

Table 3.3 GC operating conditions as per EN 14103.

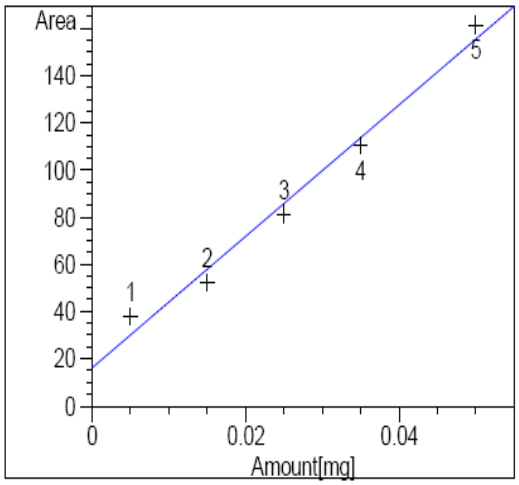
Split/splitless inlet	
Inlet Temperature	250°C
Split Ratio	80:1
Pressure	7.6 psi helium
Injection volume	1 µL
Column flow (He)	1.5 mL/min, constant flow mode
FID temperature	300°C
H_2 Flow	40 mL/min
Air Flow	40 mL/min
Make up (He) Flow	40 mL/min
Oven Program	210°C hold 9 min, to 230°C at 20°C/min, hold 10 min

3.1.3 Results and discussion

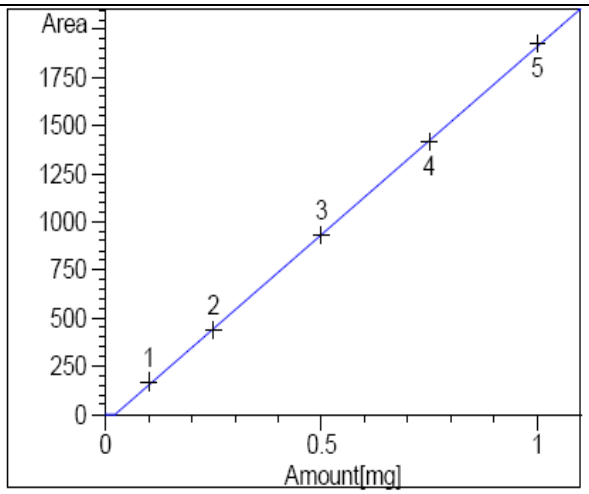
Using the approach detailed in the ASTM D6584 and CEN methods, the amount of glycerin in each sample was calculated with the calibration functions derived from the glycerin calibration curve.

After running the standards, the Agilent ChemStation was used to calculate linear calibration curves for glycerin, monoolein, diolein, and triolein. The curves for each compound showed excellent linearity. These curves are shown in Figure 3.1. The correlation coefficients (R^2) for each compound exceeded the specification of 0.99 set forth in the ASTM and CEN methods. Likewise, the amount of monoglycerides, diglycerides, and triglycerides was determined from the monoolein, diolein, and triolein calibration functions, respectively as shown in Figure 3.1.

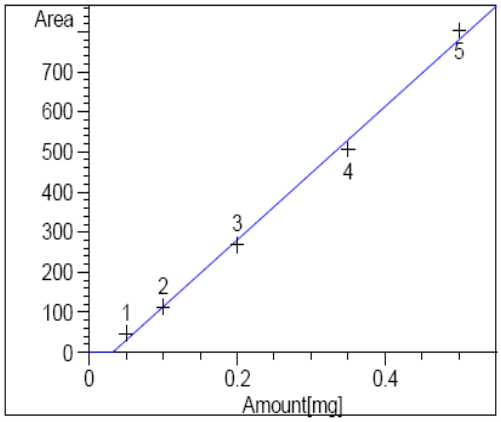
Figure 3.2 shows the typical chromatograms obtained for samples of soybean biodiesel. The large peaks observed in each chromatogram are the FAMEs present in the samples (C16 and C18). Also, it shows the regions of the soybean chromatogram based on retention times, where glycerin, monoglycerides, diglycerides and triglycerides elute. A sample analytical results report as per ASTM D6584 is presented in Appendix B.



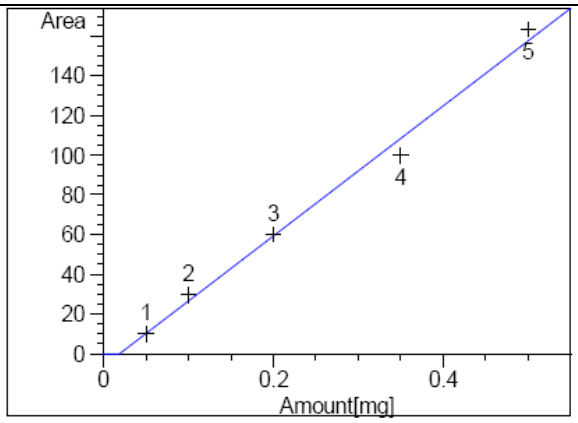
Glycerin Calibration Correlation R^2: 0.99173



Monoolein Calibration Correlation R^2: 0.99986



Diolein Calibration Correlation R^2: 0.99790



Triolein calibration Correlation R^2: 0.99602

Figure 3.1 Calibration curve as per ASTM D6584.

Peak identification for each compound is made using the relative retention times published in the ASTM D 6584. The retention time of the first internal standard, 1,2,4-butanetriol was used to identify glycerin. The retention time of the second internal standard tricaprin was used to identify the monoglycerides, diglycerides and triglycerides.

Precision of the analysis was measured by running ten successive analyses of the same sample run on the same day by a single operator on the same instrument. Table 3.4 lists the amounts of glycerin and glycerides found in each sample and relative standard deviation data. With respect to accuracy, the linearity has already been demonstrated in Figure 3.1 with R^2 values of over 0.99.

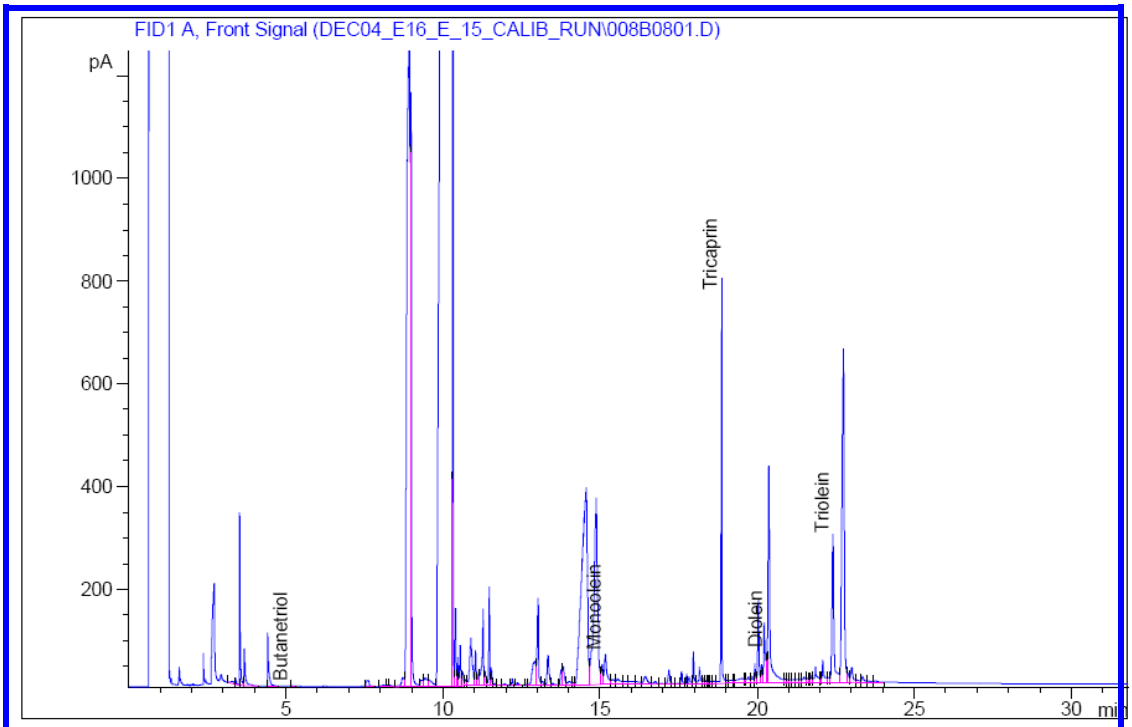


Figure 3.2 GC chromatograms showing typical analysis of free and total glycerins in soybean methyl ester (biodiesel) sample.

Rapeseed oil contains almost all major FFA components which are generally found in feedstocks including vegetable oils, animal fats, waste oils and fats. Therefore, rapeseed FAME mixture (standard) was used to validate the method by measuring individual FAME components using GC as shown in Figure 3.3.

GC analysis showed that major fatty acid components in the mixture were separated with high resolution and identified as myristic acid (C14:0), palmitic acid (C16:0), palmitoleic

acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), arachidic acid (C20:0), eicosenoic (C20:1), behenic acid (C22:0), erucic acid (C22:1), lignoceric acid (C24:0) and nervonic acid (C24:1).

Table 3.4 Relative standard deviation data for ASTM D6584.

Run	Glycerol	Monoolein	Diolein	Triolein	Total
1	0.007	2.052	0.535	0.222	0.641
2	0.007	2.055	0.555	0.197	0.642
3	0.007	2.055	0.552	0.191	0.641
4	0.007	2.062	0.549	0.188	0.643
5	0.007	2.065	0.550	0.187	0.643
6	0.007	2.059	0.549	0.191	0.642
7	0.007	2.066	0.550	0.192	0.644
8	0.007	2.065	0.552	0.191	0.644
9	0.007	2.065	0.551	0.191	0.644
10	0.007	2.061	0.552	0.191	0.643
Average	0.007	2.0605	0.5495	0.1941	0.6427
STD	-9.1428E-19	-0.005	-0.0054	-0.0101	-0.0012
%RSD	1.30611E-14	0.24454	0.98282	5.22841	0.18041

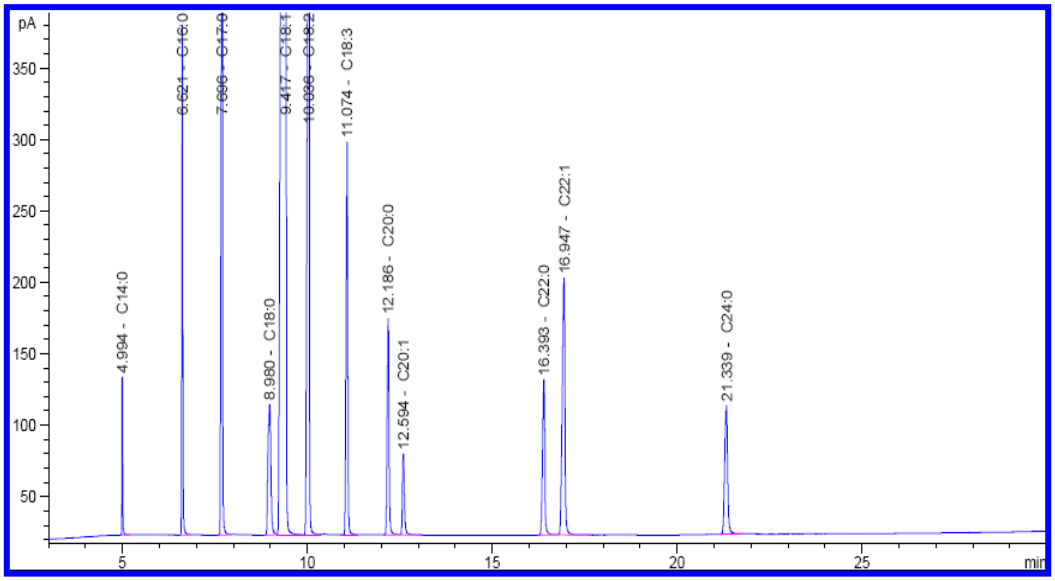


Figure 3.3 Chromatogram of rapeseed FAME mixture.

Table 3.5 Repeatability and relative standard deviation data (% RSD) for ester and linolenic acid (C18:3) methyl ester analysis as per EN 14103.

Run No	Ester Content %	C18:3 ME Content %
1	103.07	4.95
2	103.03	4.94
3	103	4.94
4	102.98	4.94
5	102.93	4.94
6	102.91	4.94
7	102.97	4.94
8	102.9	4.94
9	102.89	4.94
10	102.84	4.94
STDEV	0.0705	0.0032
AVE	102.952	4.941
% RSD	0.07	0.06

Table 3.6 Repeatability and relative standard deviation data (% RSD) for FAME analysis as per EN 14103.

Component FAME		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Average	STD	%RSD
Myristic acid	C14:0	0.83898	0.86217	0.86252	0.86235	0.86253	0.86651	0.85918	0.01003	1.16755
Palmitic acid	C16:0	3.62119	3.63325	3.63687	3.63857	3.63952	3.64450	3.63565	0.00798	0.21941
Stearic acid	C18:0	2.76594	2.77458	2.77334	2.77311	2.77166	2.76893	2.77126	0.00325	0.11711
Oleic acid	C18:1	55.0568	54.96038	54.96306	54.95808	54.97534	54.98312	54.98279	0.03750	0.06821
Linoleic acid	C18:2	11.1225	11.10300	11.10379	11.10527	11.10613	11.10873	11.10824	0.00728	0.06557
Linolenic acid	C18:3	4.54788	4.54241	4.54268	4.54194	4.54225	4.54144	4.54310	0.00238	0.05239
Arachidic acid	C20:0	2.80237	2.8133	2.81194	2.81350	2.80840	2.80617	2.80928	0.00446	0.15858
Gadoleic acid	C20:1	1.0815	1.08418	1.08260	1.08347	1.08125	1.08170	1.08245	0.00118	0.10900
Behenic acid	C22:0	2.75811	2.77666	2.77563	2.77264	2.76901	2.76386	2.76932	0.00722	0.26054
Erucic acid	C22:1	4.67531	4.6993	4.69738	4.69568	4.69237	4.68499	4.69084	0.00912	0.19434
Lignoceric acid	C24:0	2.62456	2.64329	2.64052	2.64426	2.63674	2.63301	2.63706	0.00742	0.28142
Methyl heptadecanoic acid	C17	8.10484	8.10748	8.10968	8.11113	8.11479	8.11613	8.11068	0.00429	0.05293

Table 3.5 shows excellent repeatability for measurement of the ester content (0.07%) and C18:3 content (0.06%), meeting the specifications of EN 14103 (1.6% for ester content and 0.1% for C18:3 content). The average ester content value of 102.95% is is within ±3% to the theoretical ester content value of 99.3% demonstrated good accuracy.

As shown in Table 3.6, measurement of the individual components of the rapeseed FAME mixture exhibit very good reproducibility with maximum RSD of 0.2% (except for C14 which has % RSD ~ 1.2%).

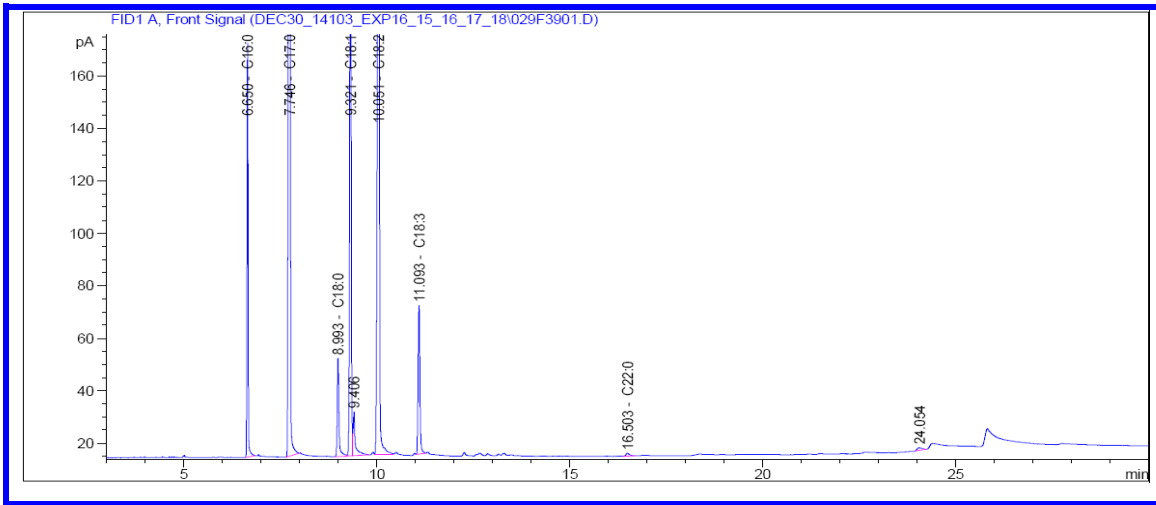


Figure 3.4 GC Chromatograms showing typical analysis of Ester and Linolenic Ester content in soybean methyl ester (biodiesel) sample.

Figure 3.4 shows typical chromatograms obtained for samples of soybean biodiesel. The large peaks observed in each chromatogram correspond to the FAMEs present in the samples (C16 and C18). Also, it shows the regions of the soybean chromatogram based on retention times where the different FAMEs of soybean oil elute.

3.2 Production of biodiesel using homogenous acid catalyst

3.2.1 Introduction

The transesterification of the triglycerides contained in vegetable oil with alcohol to yield fatty acid methyl ester (noted FAME or biodiesel) is typically catalyzed in industrial units by homogeneous bases. Free fatty acids (FFA) are a strong poison to these catalysts and also lead to the formation of soap with the resulting separation difficulties. The FFA content is

low (i.e. < 1 wt.%) in refined oil, but can exceed 10 wt.% for some crude and recycled oils and greases. The combined esterification of FFA and transesterification of various vegetable oils with methanol has been carried out over lewis solid acids, but require relatively high reaction temperatures (> 140°C). The esterification of FFA with CH_3OH using a solid catalyst located in a reactor prior to that of the transesterification unit is a promising method to convert FFA into valuable FAME.

However, further investigation is required, in particular regarding the use of (1) long-chain acids, which is a better representative FFA found in raw and recycled oils and (2) real reaction media such as vegetable oils instead of organic solvents. The latter point is of particular importance since the blockage of the catalyst surface and pores by the high molecular weight triglycerides comprising the oil could be a serious cause of deactivation (Ni, 2007). Therefore, the present work, is initailly, aimed at studying the kinetics of the esterification of major FFA (palmitic acid, stearic acid, and oleic acid) generally found in vegetable oils (i.e. soyabean oil) using homogenous acid catalysts (sulphuric acid). Later, a solid acid catalyst will be used in the kinetic studies.

Contrary to situations at high dilution in tetrahydrofuran (Liu, 2006) or in pure FFA medium (Ramu, 2004**)**, in which methanol is fully soluble, the low miscibility of the oil and methanol phases constitutes a major challenge in the type of work reported here. Experiments were conducted using palmitic acid (PA), stearic acid (SA) and oleic acid (OA), in real feedstock media (soybean oil) with homogeneous catalyst (sulphuric acid) in a glass batch reactor. All experiments were performed in triplicates.

3.2.2 Experimental procedures

3.2.2.1 Materials

All the chemicals used were supplied by Sigma-Aldrich and were analytical grade.

3.2.2.2 Method

Thirty milliliters of a mixture of soybean oil (SBO) containing 10 wt.% of FFA (PA, SA or OA, as specified in particular experimental condition) were placed in a three-neck 100 mL round bottom-flask fitted with a tap water-cooled reflux condenser. No organic solvent was used. Nine milliliters of methanol mixed with a known amount of concentrated sulfuric acid (2 wt.%) were then added to the oil. The reaction mixture was stirred at low rpm (50-100) to increase the dispersion of the reactants, that were not fully miscible at the temperature used (i.e. 60°C). The reaction was carried out at ambient pressure. Due to the effects of the vaporization and condensation of MeOH within the apparatus, the precision on the temperature of reaction (measured directly in the reaction mixture) was about ± 1°C.

3.2.3 Results and discussion

The conversion of the major FFAs (PA, SA and OA) which was found in most vegetable oils (including soybean oil) was measured as a function of time at 60°C in concentrated sulfuric acid as shown in Figures 3.5, 3.6 and 3.7. It was found that in all three cases over 95% conversion of FFA was achieved in 40 min. Similar conversion of FFA were obtained during heterogeneous-catalyzed simultaneous esterification and transesterifications (refer to chapter 4, 5 and 6).

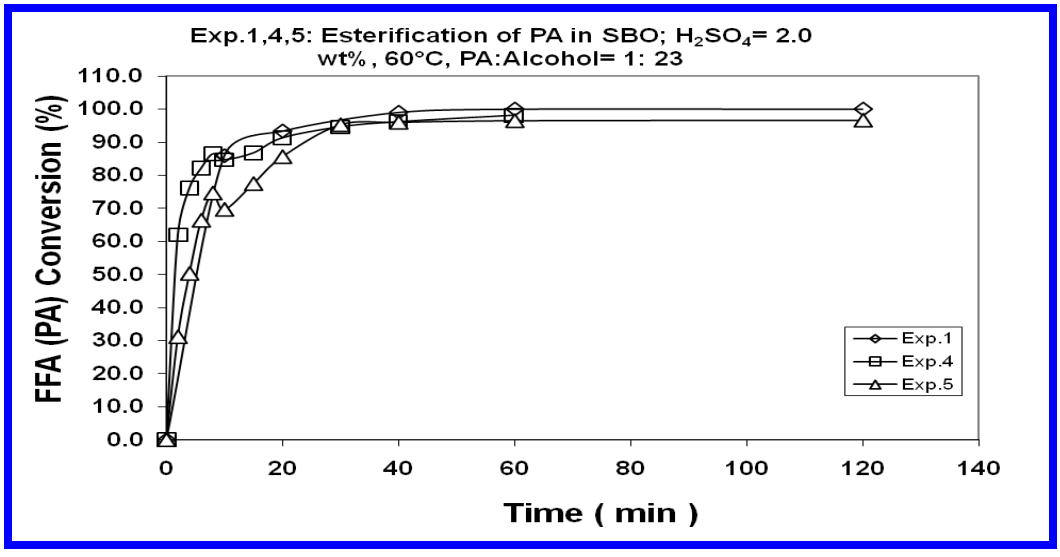


Figure 3.5 FFA (PA) conversion as a function of reaction time.

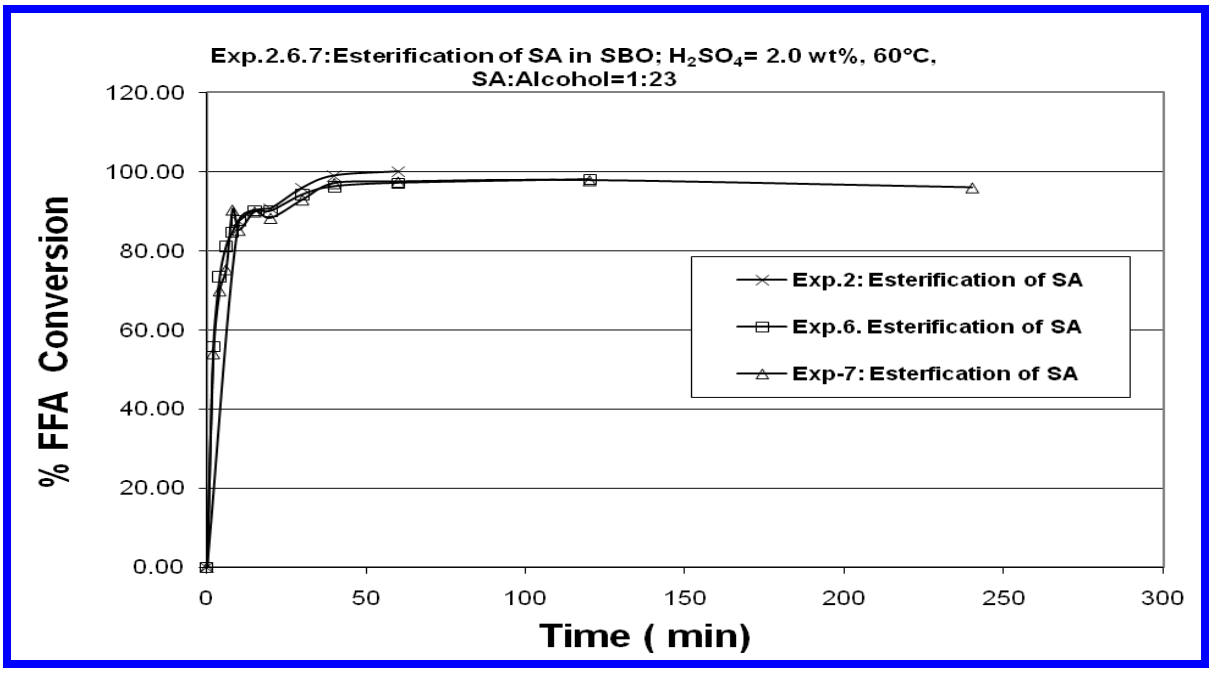


Figure 3.6 FFA (SA) conversion as a function of reaction time.

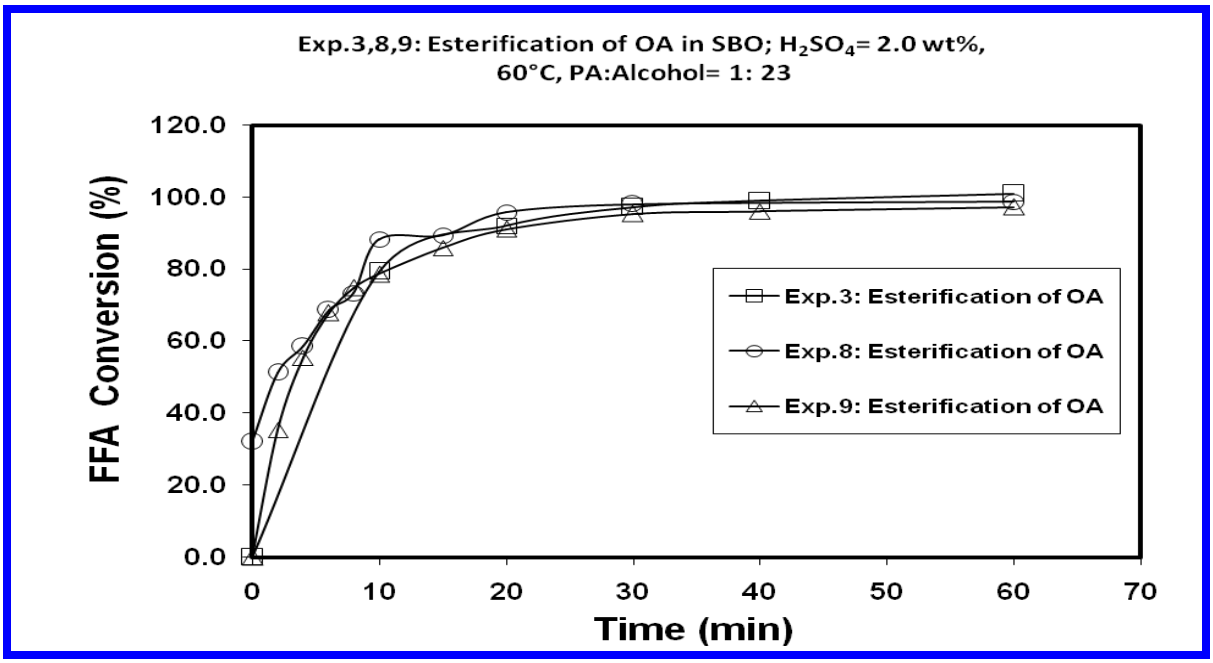


Figure 3.7 FFA (OA) conversion as a function of reaction time.

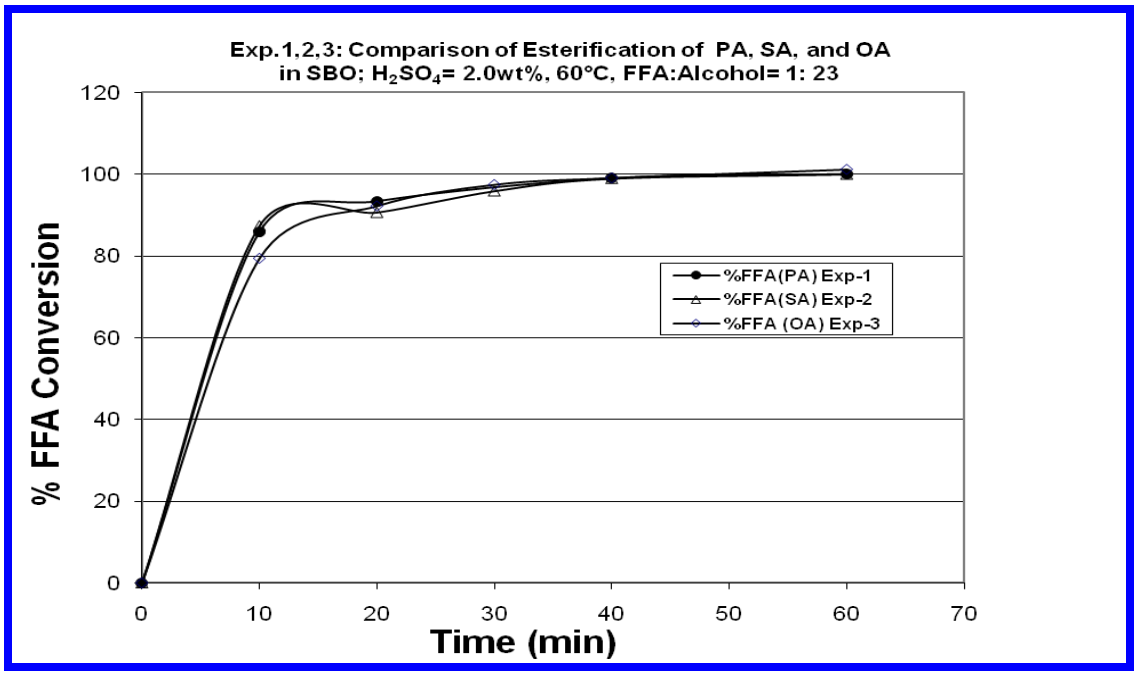


Figure 3.8 Comparison of major FFA (PA, SA, and OA) as a function of time.

3.3 Kinetics of transesterification

A study of the kinetics of transesterification provides parameters that can be used to predict the extent of the reaction at any time under particular conditions. As mentioned in the literature review, various kinetic models have been proposed due to the complex nature of transesterification reaction. For our experimental data, the best kinetic model was a pseudo second-order model based on the kinetics of TG hydrolysis (Dandik and Aksoy, 1992). According to this model, the second-order reaction rate for TG (as in Equation **3.1**) is written as follow (Smith, 1981):

$$\frac{-d[TG]}{dt} = k[TG]^2 \qquad \textbf{(3.1)}$$

Integration of Equation 3.1 yields:

$$k_{TG} \cdot t = \frac{1}{[TG]} - \frac{1}{[TG_0]} \quad \textbf{(3.2)}$$

Similarly, rate equations for DG and MG conversion are:

$$k_{DG} \cdot t = \frac{1}{[DG]} - \frac{1}{[DG_0]} \quad \textbf{(3.3)}$$

$$k_{MG} \cdot t = \frac{1}{[MG]} - \frac{1}{[MG_0]} \quad \textbf{(3.4)}$$

where,

k = is the overall pseudo rate constant

t= is the reaction time

TG_0 = is the initial triglyceride concentration

DG_0= is the initial diglyceride concentration

MG_0= is the initial monoglyceride concentration

If this model is valid, a plot of reaction time (t) *vs* 1/[TG] should yield a straight line. As shown in Figure 3.9, for TG, DG and MG, straight lines were obtained in all cases for initial stages of the reaction (0-3 h). This finding is similar to that reported in the literature (Darnoko, 2000).

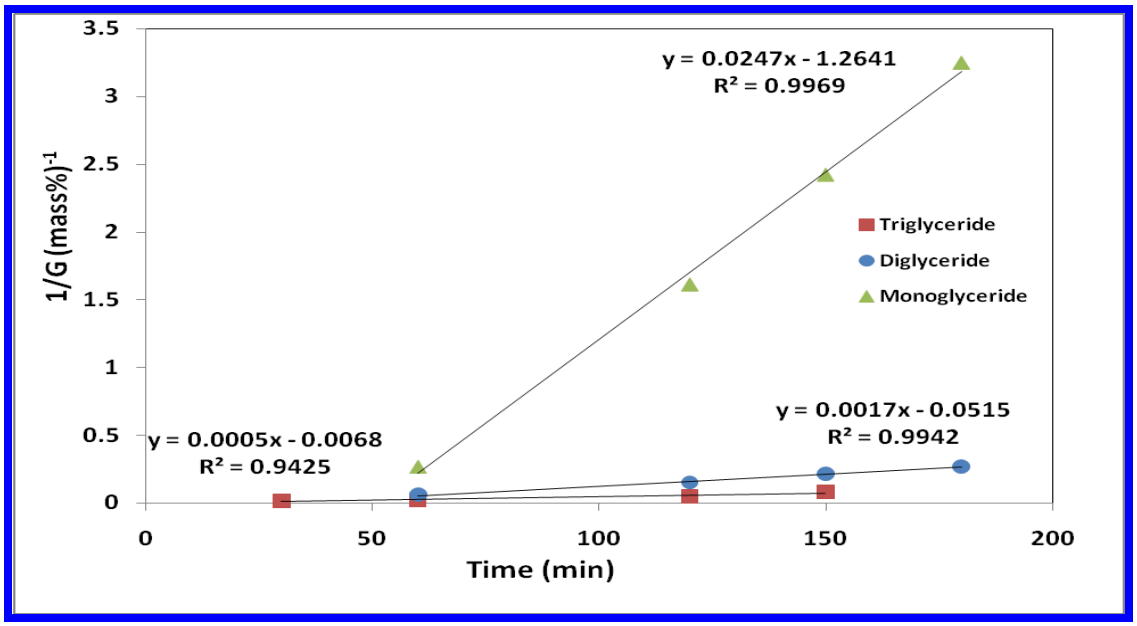


Figure 3.9 Pseudo second-order reaction model of triglyceride, diglyceride, and monoglyceride transesterification (Eq. 3.2, 3.3 and 3.4). Reaction conditions: MeOH-to-SBO molar ratio 1:24, reaction temperature 200°C, stirring speed 700 rpm, 600 psi, catalyst loading 3%.

The values of the rate constants for the three steps with the corresponding correlation coefficient are listed in Table 3.7.

Table 3.7 Reaction rate constant k (mass%.min^{-1}) for triglyceride (TG), diglyceride (DG) and monoglyceride (MG).

Glyceride	**Reaction Rate Constant, k (mass%.min^{-1})**	**R^2**
TG → DG	0.0005	0.9425
DG → MG	0.0017	0.9942
MG → GL	0.0247	0.9969

It is observed that the rate constants k decrease in the following order $k_{MG} > k_{DG} > k_{TG}$ as shown in Table 3.7. Similar pattern has been reported in the literature for the kinetics of palm oil transesterification using a homogeneous base catalyst (Darnoko, 2000).

CHAPTER 4
A SINGLE-STEP SOLID ACID CATALYZED PROCESS FOR THE PRODUCTION OF BIODIESEL FROM HIGH FREE FATTY ACID FEEDSTOCKS[1]

Overview

Biodiesel is a non-toxic, renewable and biodegradable alternative green fuel for petroleum-based diesel. However, the major obstacle for the commercial production of biodiesel is the high cost of raw material i.e. refined vegetable oils. This problem can be addressed by using low cost feedstocks such as waste oils and fats. However, these feedstocks contain high amounts of free fatty acids (FFA) which cannot be used for the production of biodiesel using a traditional homogeneous alkali-catalyzed transesterification process. A solid acid catalyst, tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina, was evaluated for the production of biodiesel from soybean oil (SBO) containing up to 25 wt.% palmitic acid (PA). It was demonstrated that this solid acid simultaneously catalyzed esterification and transesterification. The total glycerin, ester content and acid numbers were determined according to ASTM D6584, EN 14103 and ASTM D974 standards, respectively. It was found that at 200°C, 1:27 oil-to-alcohol molar ratio and 3 wt % of catalyst, a high quality biodiesel with an ester content of 93.95 mass % was produced from a soybean oil feedstock containing 10% PA in 10 h. The PA and chemically bound glycerin (CBG) [includes triglyceride (TG), diglyceride (DG), and monoglyceride (MG)] conversion of 92.44% and 99.38% were obtained, respectively. The effect of process parameters such as catalyst amount, oil-to-alcohol molar ratio and FFA content in the feedstock has been investigated. This single-step solid acid catalyzed process has potential for industrial scale production of biodiesel from high free fatty acid feedstocks.

[1] Adapted from Aijaz Baig and Flora T.T. Ng "A single-step solid acid-catalyzed process for the production of biodiesel from high free fatty acid feedstocks", Energy Fuels (2010) 24(9):4712-4720.

4.1 Introduction

Petroleum diesel continues to be a major fuel worldwide. Canada consumes ~23 million tonnes (~26 billion liters) of diesel annually, of which 46% is utilized in the transportation sector. The United States consumes 178 million tonnes of diesel fuel annually, while global consumption is 934 million tonnes of diesel fuel per year (Holbein *et al.*, 2009). The development of energy efficient biofuel production technologies aimed at reducing reagent costs and increasing production efficiency is becoming important in a world that is increasingly becoming "green". Vegetable oils have long been promoted as possible substitutes for diesel fuel. Historically, Rudolph Diesel, the inventor of the diesel engine, used vegetable oil in his engine as early as 1900 (Peterson,1986). Major advantages of vegetable oils as diesel fuel are their (1) liquid nature, (2) heat content (80% of diesel fuel), (3) easy availability and (4) renewability. However, the use of vegetable oils as fuel results in several problems especially with direct-injection engines due to their higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains (Pryde, 1983). These problems include (1) coking on injectors, (2) carbon deposits, (3) oil ring sticking and (4) thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils (Ryan *et al.*, 1984). Over the last few decades, a substantial amount of research has been carried out in order to find new renewable and sustainable energy sources as substitutes for petroleum-based fuel as indicated by the exponential increase in the number of research publications. One promising renewable source of energy is biodiesel defined by ASTM as the mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat (Marchetti *et al.*, 2008). Biodiesel, also known as fatty acid methyl ester (FAME), is a green fuel that has many advantages over conventional diesel fuel.

Biodiesel is safe, renewable, non-toxic and biodegradable and contains insignificant amounts of sulfur. In addition, biodiesel increases lubricity and extends the life of diesel engines (Ma *et al.*, 1999). Furthermore, it has a high cetane number (above 60 compared to only 40 for

regular diesel and flash point (> 130°C), while emitting 70% fewer hydrocarbons, 80% less carbon dioxide and 50% less particles (Kiss *et al.,* 2006). Due to its environmentally friendly nature, biodiesel is rapidly gaining momentum worldwide as an alternative fuel source for diesel engines.

The methods of biodiesel production and application include direct use and blending, microemulsions, thermal cracking (pyrolysis) of vegetable oil and transesterification (Ma *et al*., 1999). Currently, most biodiesel is produced by the traditional alkali-catalyzed transesterification of triglycerides of refined/edible vegetable oils using methanol and an alkaline catalyst (NaOH, NaOMe), which also yields glycerol as a byproduct, as shown in Figure 4.1 (Bournay *et al.,* 2005)

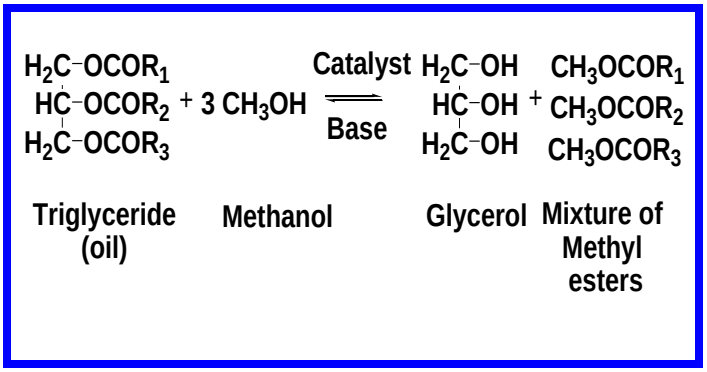


Figure 4.1 Overall transesterification reaction for the conversion of vegetable oils to methyl esters.

The stoichiometric reaction requires one mole of triglyceride (TG) and three moles of alcohol. However, excess alcohol is used to drive the reversible reaction forward to increase the yields of the alkyl esters and to assist phase separation from the glycerol (GL).

The overall process is a sequence of three consecutive and reversible reactions in which di- and monoglycerides are formed as intermediates as shown in Figure 4.2 (Singh *et al.,* 2007). Diglycerides (DG) and monoglycerides (MG) are converted by the same mechanism to a mixture of alkyl esters and glycerol.

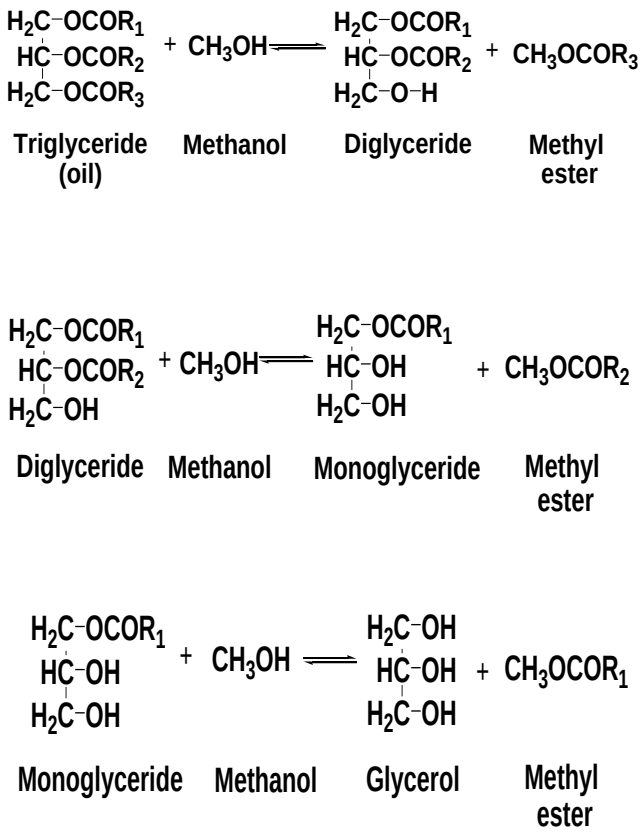


Figure 4.2 Sequential reaction of triglycerides, where R1, R2, R3 represents alkyl groups from 14-24 carbon atoms.

The major obstacle for the production of biodiesel at an industrial scale is the high production cost, which is related to the relatively high price of the refined vegetable oils used. Generally, 76-80% or a major part of the biodiesel from vegetable oils cost accounts for the cost of feedstock (Marchetti *et al.,* 2007). The cost of feedstock can vary from one bio-feedstock to another such as 1.28 USD L^{-1} for rapeseed, 0.70 USD L^{-1} for soybean and 0.13 USD L^{-1} for yellow grease (Sivasamy *et al.,* 2009). Furthermore, the production cost of biodiesel is also becoming more significant, particularly when feedstock with high FFA content is used. The production costs of diesel fuel from petroleum have been becoming ever more competitive with those of biodiesel. For example, the cost of biodiesel produced from rapeseed oil is 1.75 USD L^{-1} which includes the price of rapeseed oil at 1.60 USD L^{-1}.

On the other hand, for waste oil, the cost of bio-feedstock, 0.53 USD L^{-1}, is much less as compared to the processing cost of 0.64 USD L^{-1} (Sivasamy *et al.*, 2009). This demonstrates the need of new innovative technologies with reduced processing cost when inexpensive high free fatty acids feedstocks are used for the production of biodiesel.

The problem of the high cost of refined vegetable oil has been addressed by evaluating various alternative feedstocks such as used vegetable oil, animal fats and refurbished oils and fats in which the amount of free fatty acids (FFA) varies from 3% to 40% (Ma *et al.*, 1999, Srivastava *et al.*, 2007). High free fatty acid feedstocks such as yellow grease (FFA ≤ 15%) and brown grease (FFA > 15%) are inexpensive, readily available and renewable, making them promising feedstocks for biodiesel production (Zafiropoulos *et al., 2*007). However, when the amount of FFA in the feedstock exceeds 0.5%, the use of the traditional homogeneous base catalyzed transesterification process, which employs NaOH as catalyst, is not recommended since catalyst and the raw material will be consumed by saponification between FFA and base as shown in Equation **4.1**. The soap so formed causes downstream processing problems associated with product separation due to emulsion formation (Ma *et al.,* 1999).

$$\text{R-COOH} + \text{NaOH} \rightarrow \text{R-COONa} + \text{H}_2\text{O} \qquad (\mathbf{4.1})$$

Furthermore, it requires complex downstream neutralization, separation and washing steps which make the purification of the biodiesel more challenging (Peterson, 1986). This problem can be overcome by using an acid catalyst which is insensitive to FFA and is better than the alkaline catalyst for processing vegetable oil with > 1% FFA (Freedman *et al.*, 1984). Furthermore, an acid catalyst can catalyze both esterification and transesterification reactions (Lotero *et al.*, 2005; Kulkarni *et al.*, 2006a).

Esterification reaction involves the reaction of FFA with methanol in the presence of an acid catalyst to produce FAME and water.

$$\text{R-COOH} + \text{R'-OH} \leftrightarrow \text{R-COO-R'} + \text{H}_2\text{O} \qquad (\mathbf{4.2})$$

where R and R' are the alkyl groups of the FFA and alcohol, respectively. Esterification is an equilibrium reaction causing the equilibrium to be shifted in the forward direction when an excess of alcohol is used. As can be seen from Equation 4.2, the water produced in the esterification reaction can hydrolyze the FAME to produce FFA which is highly undesirable. The only but major disadvantage of an acidic catalyst is a slower reaction rate (Freedman *et al.,* 1984).

Acidic and alkaline catalysts have their own advantages and disadvantages in the transesterification of high free fatty acid feedstocks. Therefore, both acidic and alkaline catalysts have been used in a two-step process for the synthesis of biodiesel from refurbished waste oils and fats (Baig, 2003). However, the two-step process (or similar multi-step process) also faces the problem of catalyst removal in both steps. The problem of catalyst removal in the first step can be avoided by neutralizing the acidic catalyst, using extra alkaline catalyst in the second step. However, this results in extra consumption of the catalyst that adds to the cost of the biodiesel. Furthermore, this process has problems linked with the corrosive action of the liquid acid catalyst and to the high quantity of byproduct obtained (Lotero *et al.,* 2005; Di Serio *et al.,* 2005). Therefore, homogeneous catalysts, whether acidic or basic, have major limitations as mentioned above.

Despite the major limitations of homogeneous catalysts, most of the current worldwide biodiesel production is carried out by using homogeneous alkali catalysis because it is much faster than heterogeneously catalyzed transesterification and is economically viable. Due to the separation problems and product quality concerns, extensive research on heterogeneous catalysis for biodiesel production is ongoing all over the world. However, solid base catalyzed processes still have major limitations as they require expensive refined vegetable oil as feedstock and are sensitive to water and FFA content in the feedstock (Bournay *et al.,* 2005; Kouzu *et al.,* 2009). Therefore, during the last decade, many industrial processes have shifted towards solid acid catalysts (Harmer, 2002). Solid acid catalysts are generally preferred for chemical transformations in industrial processes due to their ease of separation

from a reaction mixture. In addition, solid catalysts can potentially be regenerated, and are environmentally benign since they can be reused. Furthermore, they are considered safe for industrial operations since solid acid catalysts do not contaminate ground waters in case of a spillage. A solid catalyst also will produce a higher purity by-product glycerol (glycerin) stream due to much simpler downstream separation since no washing or neutralizing is required for the product stream. Due to these advantages, solid acid catalysts are attractive for the production of biodiesel from oil containing FFA (Lotero *et al.,* 2005; Kulkarni *et al.*, 2006a; Lotero *et al.,* 2006). However, little research dealing with transesterification reactions catalyzed by solid acids has been reported in the literature, while many papers have been devoted to esterification using solid acid catalysts (Lotero *et al.,* 2005; Lotero *et al.,* 2006). This is due to the fact that acid catalyzed esterification is much faster as compared to transesterification. However, it must be pointed out that in some cases the data obtained with simple model molecules cannot be used to predict the behavior of oils/fats and fatty acids (Lotero *et al.,* 2006).

Apart from a few reports (Kiss *et al.,* 2006; Kulkarni *et al.,* 2006a; López *et al.,* 2007; Suwannakarn *et al.,* 2009; Yan *et al.,* 2009) on solid acid-catalyzed esterification and transesterification of model compounds and feedstock with high FFA content, utilization of solid acids for biodiesel production from high FFA content feedstocks has not been explored in depth to our knowledge. Development of a catalyst which is highly active for transesterification remains challenging. Another challenge is the quality of biodiesel produced from high free fatty acid feedstocks using solid acid catalysts.

With the increasing interest and use, the assurance of fuel properties and quality has become of paramount interest to the successful commercialization and market acceptance of biodiesel. Accordingly, biodiesel standards have been established or are being developed in various countries and regions around the world, including the United States (ASTM D6751), Europe (EN 14214), Brazil, South Africa, Australia and elsewhere (Knothe, 2006 and 2008). ASTM standard D6751 and European Committee of Standardization (CEN) standard EN

14214 set similar specifications for biodiesel blending and motor fuels (ASTM International D6751, 2006, European committee for Standardization EN 14214, 2003). Both standards describe two important specifications. First, a limit is placed on the acid number and second the amounts of free glycerin and glycerides in biodiesel are restricted. Free glycerin is a by-product of biodiesel production. Mono-glycerides (MG), diglycerides (DG) and triglycerides (TG) are partially reacted oils that may be contaminants in the finished biodiesel. High amounts of free glycerin can cause problems due to phase separation. High amounts of glycerides and glycerin can result in serious engine problems due to their deposition in engine. However, complete conversion of triglyceride is a challenge in light of the chemical equilibrium of the reaction.

Currently, most of the heterogeneous processes (whether solid acid or solid base) reported in the literature yield biodiesel with high levels of triglyceride, diglyceride and monoglyceride, which implies a lower yield of biodiesel as well as failure to meet the bound glycerol levels required by the ASTM standard. Furthermore, glycerin may form over time due to the presence of residual glycerin moieties (i.e. TG, DG, and MG), which result in further deviation from the specifications of ASTM D6571 standards.

However, most of the studies on biodiesel production have not reported on these important parameters which measure the product quality of commercial biodiesel. Furthermore, most of the studies reported in the literature used various analytical methods. As a result, due to the lack of the use of standard analytical methods, the quality of the biodiesel reported in various studies may not be comparable. Furthermore, in order to meets the specifications of biodiesel quality standards such as ASTM and CEN, it is very important to use their recommended standard analytical methods (ASTM and CEN).

Therefore, in this research studies, ASTM analytical methods (ASTM D974 and ASTM D6584) and EN 14103 have been used to quantify the quality of biodiesel (ASTM International D6751, 2006, European committee for Standardization EN 14214, 2003).

In this paper, a single-step solid acid catalyzed process for the production of biodiesel from high free fatty acid feedstocks is reported. The activity of a solid acid catalyst, tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina, has been evaluated for esterification and transesterification as well as for simultaneous esterification and transesterification using ASTM and CEN standard methods. The effect of process parameters such as catalyst amount, oil-to-alcohol molar ratio and FFA content in the feedstock on the product quality has been investigated.

4.2 Experimental procedures

4.2.1 Materials

The soybean oil used was a food-grade President's Choice product, purchased from Zehrs Supermarket (Waterloo, ON, Canada). The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): palmitic acid (99%), 2-propanol (anhydrous, 99.5%), toluene (anhydrous, 99.8%), *p*-naphtholbenzein (indicator grade), 0.1N KOH (volumetric standard, in isopropanol), methyl heptadecanoate, *n*-heptanes and a rapeseed FAME standard mixture. Agilent Technologies biodiesel standards were used containing glycerin, monoolein, diolein, triolein, butanetriol (internal standard #1), and tricaprin (internal standard #2) at concentrations specified in the ASTM D 6584 method. The derivatization agent for silylation, N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), was also obtained from Agilent Technolgoies.

4.2.2 Catalyst preparation

The catalyst ($H_3PW_{12}O_{40}\cdot nH_2O$ supported on neutral alumina) was synthesized by a wet impregnation method. A series of catalysts containing 10–40% 12-tungstophosphoric acid (TPA) supported on neutral alumina were synthesized by wet impregnation method. Required amounts of TPA were dissolved in 100 mL of deionized water. The resultant solution was added slowly drop wise to the support (n-Al_2O_3). The mixture was stirred for 35 h using a magnetic stirrer. After this, the water was evaporated and the resultant catalyst powder was dried at 100°C for 10 h. The final catalyst was calcined at 300°C for 5 h in the air. For more details, please refer to Appendix G.

4.2.3 Equipment

Esterification and transesterification with the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) was carried in a fully automated high-pressure high-temperature batch reactor (PARR Instrument, 4843, Moline, Illinois, USA). The equipment consisted of a high pressure cylindrical chamber, a heater, a water line (in order to control the temperature), a sampling outlet, and a stirrer.

4.2.4 Procedures

Simultaneous Esterification and Transesterification.

The feedstock for simultaneous transesterification and esterification of soybean oil (SBO) containing 10% free fatty acids (palmitic acid) was prepared manually by mixing 90 parts of soybean oil and 10 parts of palmitic acid (PA) by mass (or otherwise stated). The reaction was carried out in a 300 cm^3 Parr reactor (Parr Instrument Co.) equipped with a temperature controller. Initially, the reactor was charged with soybean oil and methanol and finally the solid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).When the reaction was carried out above 200°C, polymeric products could be formed by the degradation of triglycerides and unsaturated fatty acids due to exposure of oil to high temperature for long reaction times (Kulkarni *et al.*, 2006c). Since the formation of polymeric compounds is not desirable during biodiesel production, 200°C has been selected as the optimum reaction temperature for simultaneous esterification and transesterification reactions. The reactor was pressurized (depending on the reaction temperature) to ensure that at the desired reaction temperature the reactants were in the liquid phase. A temperature of 200°C and a pressure of 600 psi were selected for experiments experiments (or otherwise as stated). Once the reaction mixture reached the desired reaction temperature, then the mixing of the reaction was started and this point was taken as time zero for the reaction. All the reactions were carried out for a total reaction time of 10 h unless otherwise stated. Samples were taken at regular time intervals and the solid acid catalyst was separated by centrifugation to limit further reaction. For initial samples only two phases were formed up to

6 h: ester-rich phase (bottom layer) and methanol-rich phase (top layer). However, later samples contained a third phase at the bottom, which is mainly glycerol. The reason for the absence of glycerol phase during the initial stages may be due to the production of small amount of glycerol at the earlier stage of the reaction or/and glycerol remained at the bottom of the reactor. Glycerol was separated by centrifuge. Samples from the ester-rich phase were analyzed without any post experiment treatment such as water washing. Samples from the ester-rich phase were analyzed using an Agilent 7980A GC system as per ASTM D6584 (as validated in Chapter 3; section 3.1) for the determination of free glycerin (glycerol) and chemically bound glycerin (mono-, di-, and triglycerides) in the biodiesel.

Five GC calibration standards were prepared by mixing aliquots of the individual stock standards in proportions specified by the ASTM D6584 method. After mixing, 100 µL of the derivatization agent, N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was added to each calibration standard. After 20 min, 8 mL of reagent grade n-heptane was added to each calibration standard. Sample preparation followed the procedure in the ASTM and CEN methods using internal standards. This involves addition of 100 µL addition of each internal standard and MSTFA derivatization reagent in 0.1 g of sample in a 20 mL vial. After 20 min, 8 mL of reagent grade n-heptane was added to each sample. These final reaction mixtures were directly injected into the gas chromatograph. An Agilent 7890A GC system equipped with a 7683 auto injector, cool-on-column inlet with electronic pneumatic control (EPC), FID detector, and a DB-5ht capillary column was used for the total glycerin analysis as per ASTM D6584. The ester content were determined by the same GC system with HP-INNOWax column (30m x 320mm x 0.25µm) using a split/splitless inlet as per EN 14103 (as validated in Chapter 3; section 3.1). A few samples were treated with water washing to remove the residual methanol and glycerol for ester content analysis which resulted in an increase of 15% ester content. Therefore, results for ester content were adjusted, accordingly. Also, the methanol rich-phase (top layer) was also analyzed which also show the presence of the esters.

The FFA content was determined as per ASTM D974. The conversion of free fatty acid was calculated using Equation **4.3** (Marchetti *et al.*, 2007).

$$\text{FFA conversion}(\%) = \left(\frac{a_i - a_t}{a_i} \right) \times 100 \qquad \textbf{(4.3)}$$

where a_i is the initial acid number of the mixture and a_t is the acid number at time t as specified in ASTM D6751.

A schematic of the experimental procedure flow is shown in Figure 4.3.

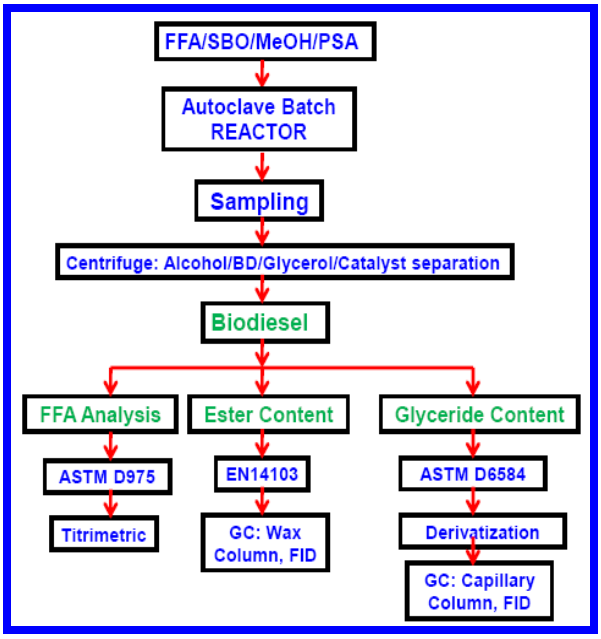


Figure 4.3 Process flow chart for experimental work.

Similarly, the conversion of chemically bound glycerin (CBG), which is the sum of TG, DG, and MG, was calculated from the difference between the CBG content at time zero and at time t as follows:

$$\text{CBG conversion}(\%) = \left(\frac{CBG_i - CBG_t}{CBG_i} \right) \times 100 \qquad \textbf{(4.4)}$$

Experiments were performed with oil-to-alcohol molar ratios of 1:27 and 1:40, catalyst loadings of 1 wt.%, 3 wt.% and 10 wt.%, and FFA (PA) contents of 10 wt.% and 25 wt.% in the feedstock.

Esterification. Esterification of palmitic acid (PA) was performed in the absence of triglyceride (soybean oil) using the same procedure and reaction conditions as for the transesterification reaction. A PA-to-alcohol molar ratio of 1:79 (which is equivalent to oil-to-alcohol molar ratio of 1:27 as used for transesterification) was used.

Transesterification. Transesterification of soybean oil (SBO) was performed in the absence of free fatty acid (PA) using the same procedure and reaction conditions as for the simultaneous esterification and transesterification reaction. The molar oil-to-alcohol ratios of 1:6, and 1:24 were evaluated. A blank reaction without catalyst was also performed as a control experiment.

4.3 Results and discussion

4.3.1 Transesterification

Transesterification of soybean oil was performed using 3wt.% of solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) at 200°C and an oil- to-methanol molar ratio of 1:24, while being stirred at 600 rpm for 5.5 h. Methanol has been selected as alcohol due to its relatively low cost, easy availability and higher reaction rates compared to 1-propanol or 2-ethylhexanol (Kiss *et al.*, 2006).

The typical chromatograms obtained for samples of soybean biodiesel as per ASTM D6584 and EN 14103 (as validated in Chapter 3; section 3.1) are shown in Figure 4.4 and Figure 4.5, respectively. In GC chromatogram as per ASTM D6584, the large peaks observed in each chromatogram are the FAMEs present in the samples (C16 and C18). Also, it shows the regions of the soybean chromatogram based on retention times, where glycerin, monoglycerides, diglycerides, and triglycerides elute. Peak identification for each compound is made using the relative retention times in the ASTM method.

The retention time of the first internal standard, 1, 2, 4-butanetriol, was used to identify glycerin. The retention time of the second internal standard, tricaprin, was used to identify the monoglycerides, diglycerides, and triglycerides.

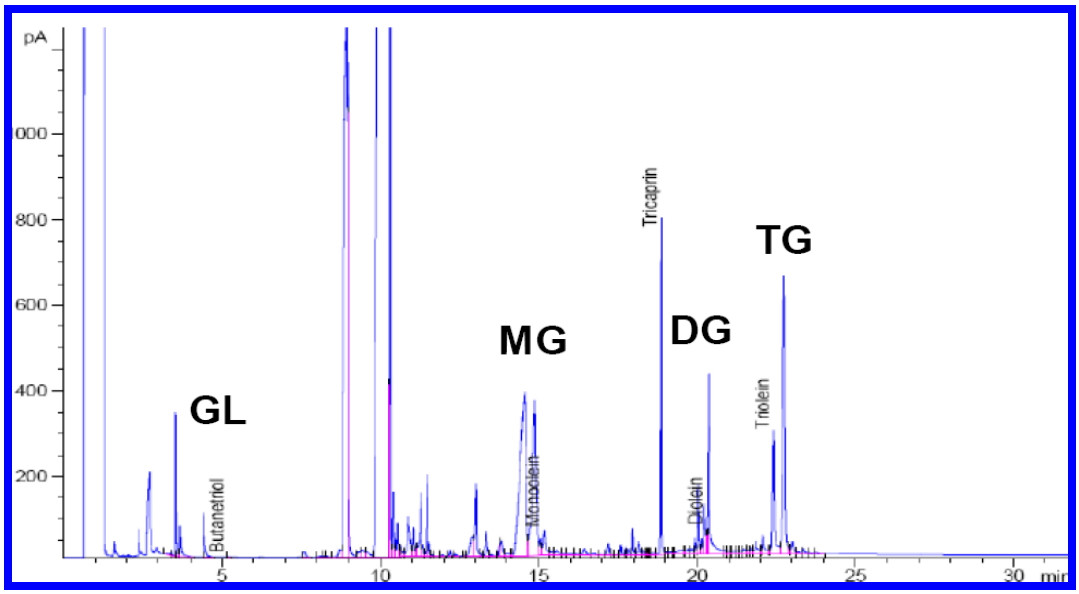


Figure 4.4 GC Chromatograms showing typical analysis of free and total glycerin in soybean methyl ester (biodiesel) sample as per ASTM D6584.

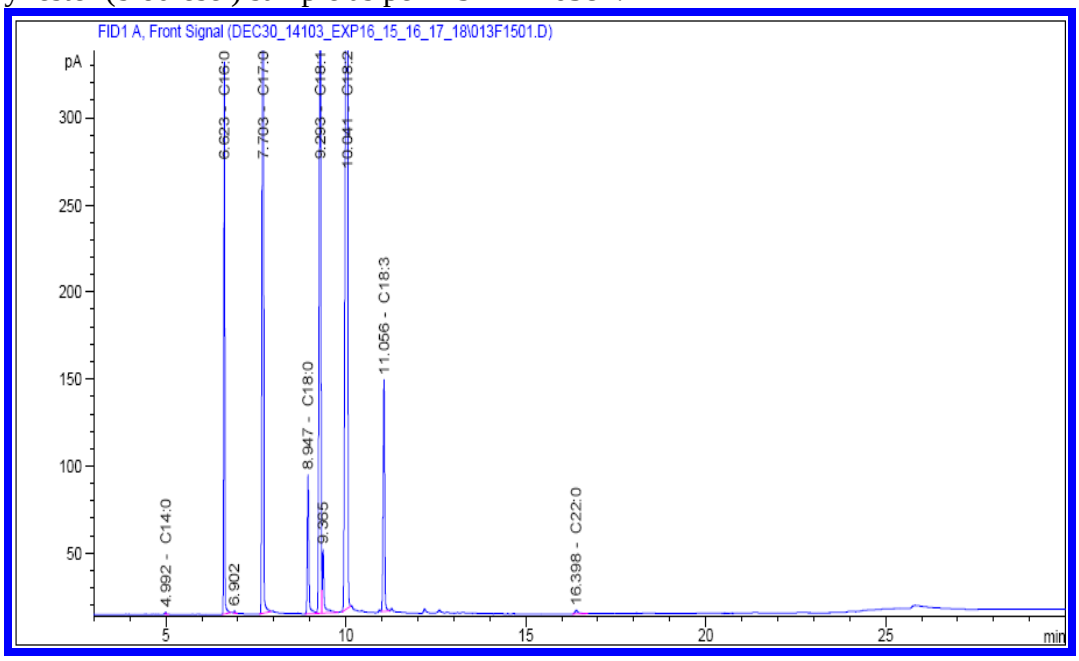


Figure 4.5 GC Chromatograms showing typical analysis of ester content in soybean methyl ester (biodiesel) sample as per EN 14103.

Figure 4.5 shows the typical chromatograms obtained for samples of soybean biodiesel as per EN 14103. The large peaks observed in each chromatogram are the FAMEs present in the samples (C16 and C18). Also, it shows the regions of the soybean chromatogram based on retention times, where different FAME (from C14 to C24 carbon chains including saturated and unsaturated) of soybean oil elutes.

The temporal evolution of reactants, intermediates and products for the transesterification of soybean oil with the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) is presented in Figure 4.6. As the reaction proceeds, TG concentration decreases quite quickly in the first hour producing FAME and also some MG and DG. MG and DG are intermediates which are further converted to FAME with time. It was found that within 10 h, the CBG concentration was only 0.68 mass%. The concentrations of MG and DG increase at the beginning of the reaction (within first one hour of the reaction) but then decrease showing that DG and MG are intermediates. Kinetics results (as shown in Chapter 3) confirm these trends of chemical bound glycerides (TG, DG and MG).

This reaction profile is similar to the homogeneous alkali catalyzed transesterification of palm oil reported in the literature (Darnoko *et al.*, 2000). To our knowledge, this is the first time such data have been reported for the transesterification using a solid acid catalyst.

In order to keep the reactants in the liquid phase, high pressure was used in the experiments (e.g. 600 psi). However, due to the high temperature and pressure operating conditions, a possibility exists that triglyceride is converted by subcritical methanol. A blank experiment was performed without catalyst to investigate whether there is any conversion occurs in the absence of a catalyst. These runs confirmed that subcritical methanol catalyzed the reaction to some extent. However, it is clear that the catalyzed reaction yielded a higher ester content of 75.45 mass % and a chemically bound glycerin (CBG) content of 1.015 mass % as compared to only 38.90 mass % of methyl ester in the ester-rich phase with a CBG content of 9.73 mass % when no catalyst was used (Figure 4.7).

4.3.2 Esterification

The esterification reaction is of great importance due not only to the possible increase on the biodiesel production, but also because it will affect the properties of future biodiesel (Marchetti *et al.*, 2007). According to stoichiometry, one mole of FFA requires only one mole of alcohol. Since esterification is an equilibrium reaction, an increase in alcohol concentration will shift the equilibrium towards the production of biodiesel and will also increase the rate of esterification.

To investigate the catalytic activity of this solid acid catalyst, a reaction was performed at a PA-to-methanol molar ratio of 1:79 (which is equivalent to oil-to-alcohol molar ratio of 1:27 used for transesterification based on molar ratio of soybean oil and PA) at 200°C with stirring at 600 rpm. After 10 hours of reaction, a 94.3% conversion of PA was achieved which is similar to the PA conversion of ~ 95% using sulfuric acid as a homogeneous catalyst (as shown in Chapter 3, section 3.2.3). This was similar to the conversion of PA achieved in the presence of soybean oil (92.4%). This shows that esterification of FFA is not inhibited in the presence of triglycerides due to huge excess of methanol in feed.

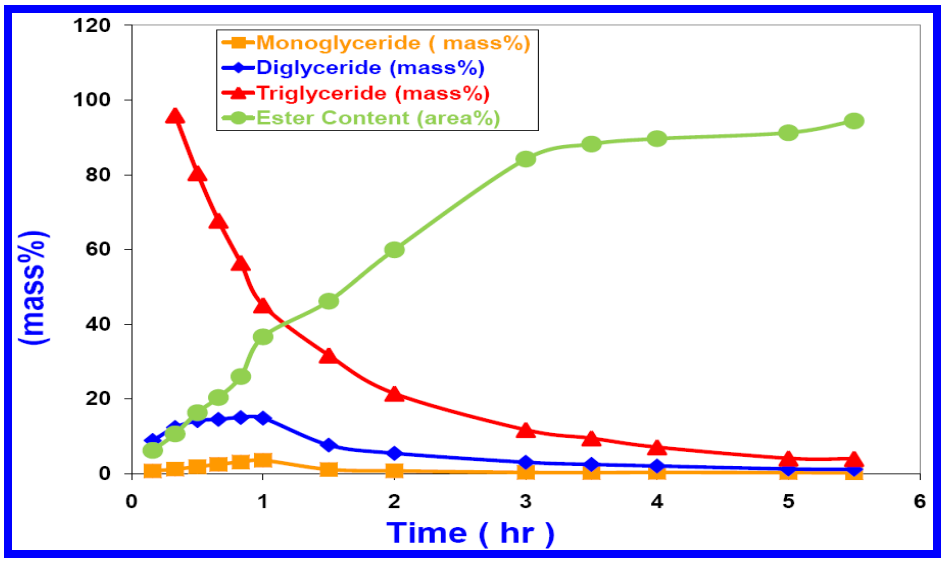


Figure 4.6 Reaction profiles for the transesterification of soybean oil using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: oil-to-alcohol molar ratio 1:24, reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%.

4.3.3 Simultaneous esterification and transesterification

After successful application of this solid acid catalyst for esterification and transesterification reaction, the next important aspect is the application of this catalyst for the production of biodiesel via simultaneous esterification and transesterification. A mixture of SBO with 10 wt %.PA (and 25 wt.%) was used as a model feedstock for the production of biodiesel from a low cost industrial feed stock which contains high amount of FFA.This solid acid catalyst showed promising activity towards simultaneous esterification and transesterification of SBO with 10 wt % PA. In about 10 hours, PA and CBG conversions of 92.4% and 99.4%, respectively were achieved with a CBG content of 0.62 mass% in a single-step process as shown in Figure 4.8.

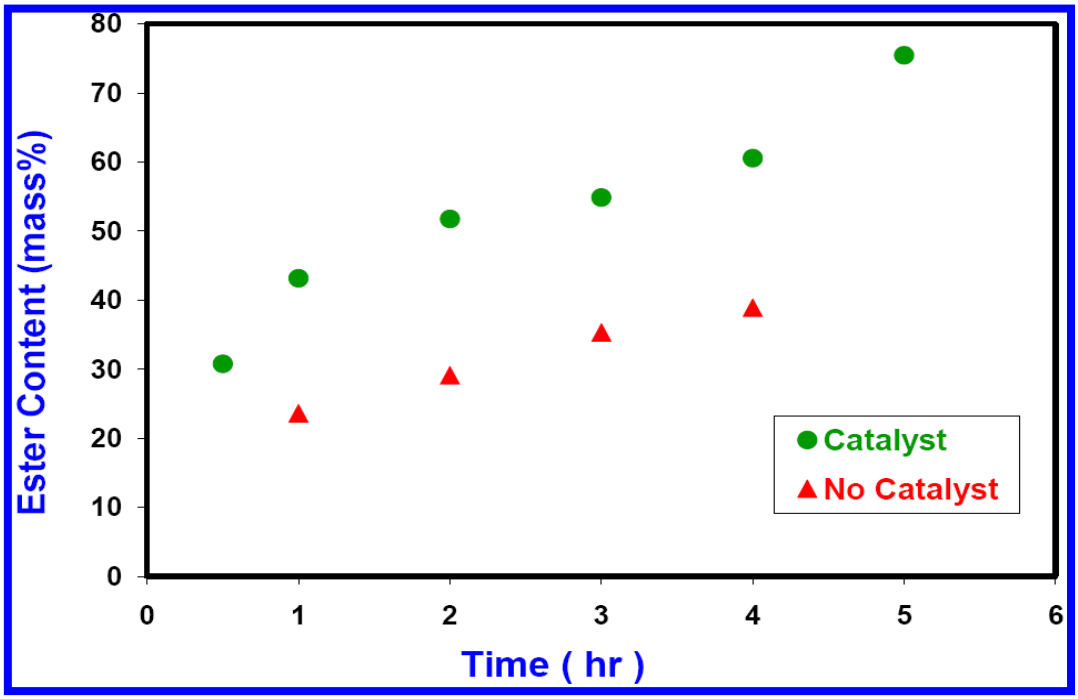


Figure 4.7 Transesterification of SBO for biodiesel production using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst with 3 wt.% catalyst and without catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:24, stirring speed 600 rpm.

This result of PA conversion is similar to the PA conversion of ~ 95% using sulfuric acid as a homogeneous catalyst (as shown in Chapter 3, section 3.2.3). CBG is rapidly converted to ME similar to that observed in previous work on transesterification of soybean oil and sunflower oil using homogeneous base-catalysis (Freedman *et al.*, 1984). After 30 min, 80% of CBG was converted to ME and after 3 h, equilibrium was achieved at about 95% CBG conversion. Similarly, the progress of esterification of FFA to ME can be monitored through the decrease in acid number.

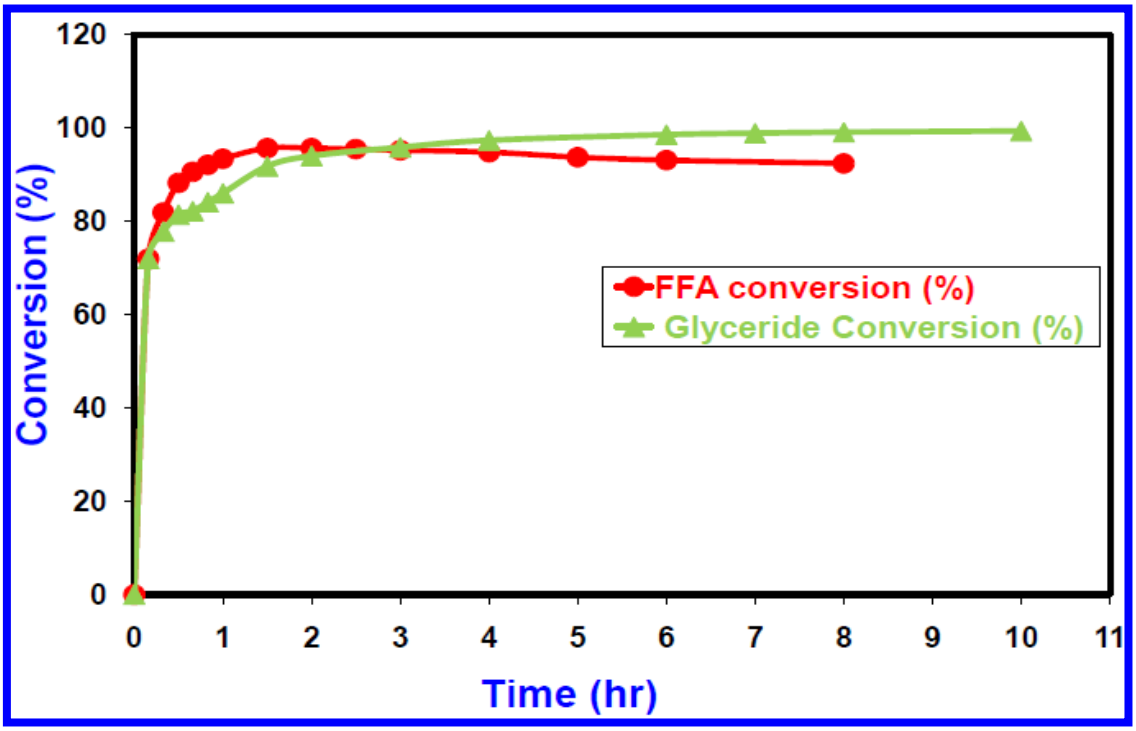


Figure 4.8 FFA and glyceride (CBG) conversion as a function of time for the simultaneous esterification and transesterification for biodiesel production from soybean oil containing 10 wt.% PA using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%.

As discussed in the literature review, the rate of esterification is faster as compared to transesterification as shown in Figure 4.8. The acid number of 0.850 mg KOH/g was achieved in less than 2 h of reaction time as shown in Figure 4.9. Both esterification and

transesterification took place simultaneously by converting the FFA and reducing the glyceride (CBG) content as shown in Figure 4.10. It can be seen from Figure 4.10 that as reduction of CBG occurs simultaneously with rise in ME content. These results are very promising since the product quality is very close to the specification of ASTM D6751 which limits the CBG content to a maximum value of 0.24 mass % and an acid number of 0.5 mg KOH/g. The acid number can be reduced to meet ASTM specifications through water stripping, a common processing step for the industrial production of biodiesel.

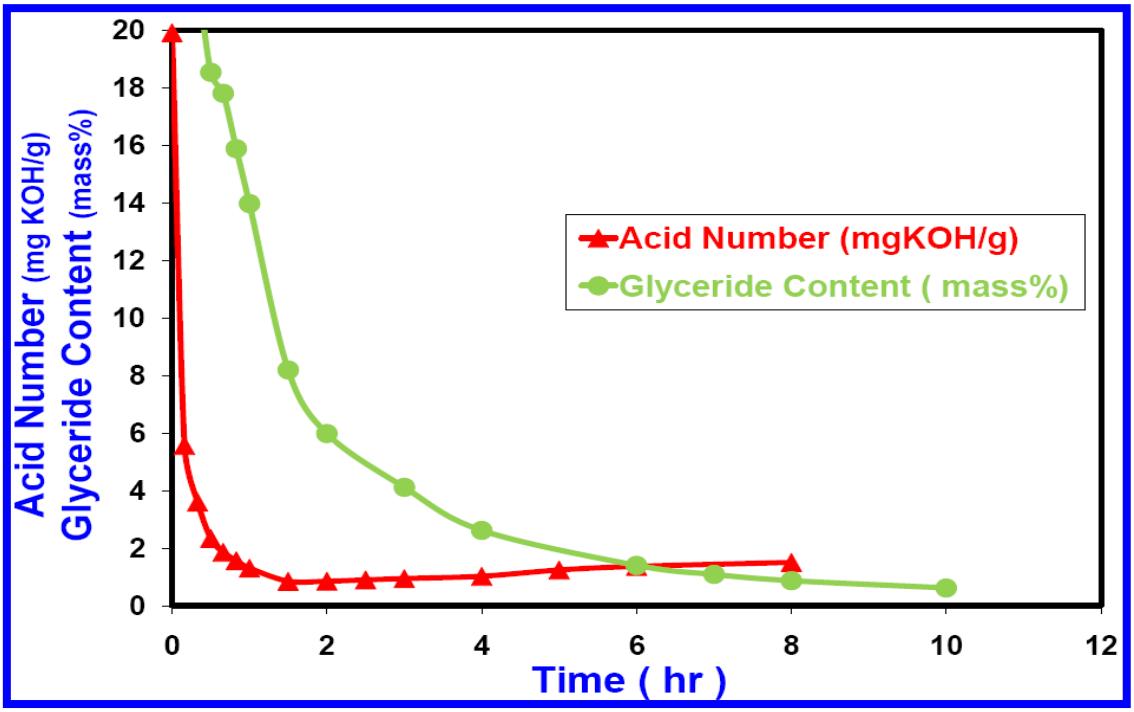


Figure 4.9 Acid number and glyceride (CBG) content as a function of time for simultaneous esterification and transesterification of SBO with 10% PA using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to- alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%.

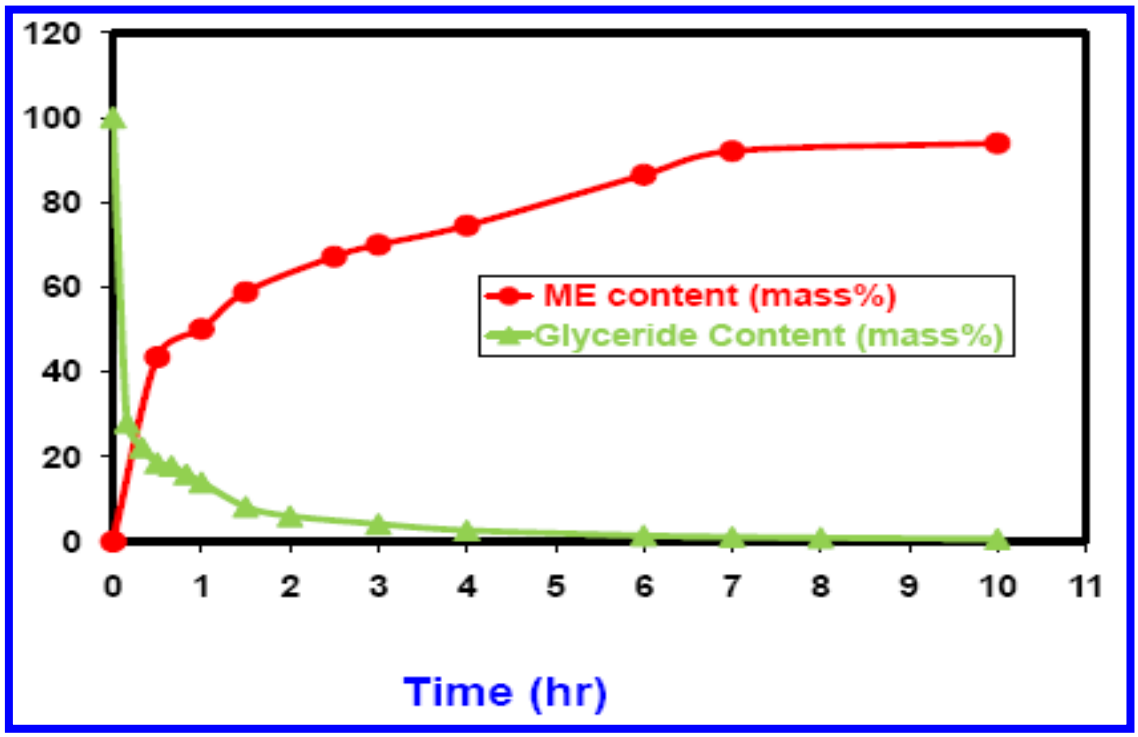


Figure 4.10 Methyl ester (ME) and glyceride (CBG) content as a function of time for simultaneous esterification and transesterification of SBO with 10 wt % PA using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%.

4.3.4 Effect of feed-to-alcohol molar ratio

The oil-to-alcohol molar ratio is one of the most important parameters that affect the yield of alkyl esters (Kulkarni *et al.*, 2006b and 2006c). To examine its effects, transesterification of soybean oil was performed using 3 wt.% of catalyst at 200°C and oil-to-methanol molar ratios of 1:6 and 1:24.

In the preliminary studies, the effect of the oil-to-alcohol molar ratio was investigated. It was found that an increase in the oil-to-alcohol molar ratio from 1:6 to 1:24 reduced CBG

concentration 5.25 mass % to 0.77 mass % over a 5 h reaction time, as shown in Figure 4.11. This shows that excess amount of methanol favors the conversion of CBG and shifts the equilibrium towards the forward direction, which is in accordance with the reported literature (Marchetti *et al.*, 2007; Freedman *et al.*, 1986).

The excess methanol added to the reactor can be collected and reused. However, even at 1:6 of oil-to-methanol ratio, the CBG content was reduced to 0.66 mass % was achieved which is similar to that achieved at a molar ratio of 1:24 after 5 h. This value of 0.66 mass% can be reduced further by water washing and distillation, typical post-processing steps.These results are very promising and closely approach the product quality stipulated by the ASTM D6751 standard.

For simultaneous esterification and transesterification, soybean oil with PA contents of 10 wt.% and 25 wt.%, were used as feedstock. Experiments were performed using 3 wt.% of catalyst at 200°C at stirring speed of 600 rpm at oil-to-methanol molar ratios of 1:27 and 1:40. The oil-to-methanol ratio was found to have little effect on the ester content in the ester-rich phase as shown in Figure 4.12. This is similar to that observed when only transesterification occurs. This demonstrates that this acid catalyzed process does not require a very high oil-to-methanol ratio.

4.3.5 Effect of catalyst amount

The amount of catalyst required for any process has significant economical and environmental effects. In general, higher concentration of catalyst increases the rate of reaction and thus results in a higher product yield. However, it is preferable to use the minimum amount of catalyst to reduce costs as well as minimizing the use of chemicals which makes a process green.

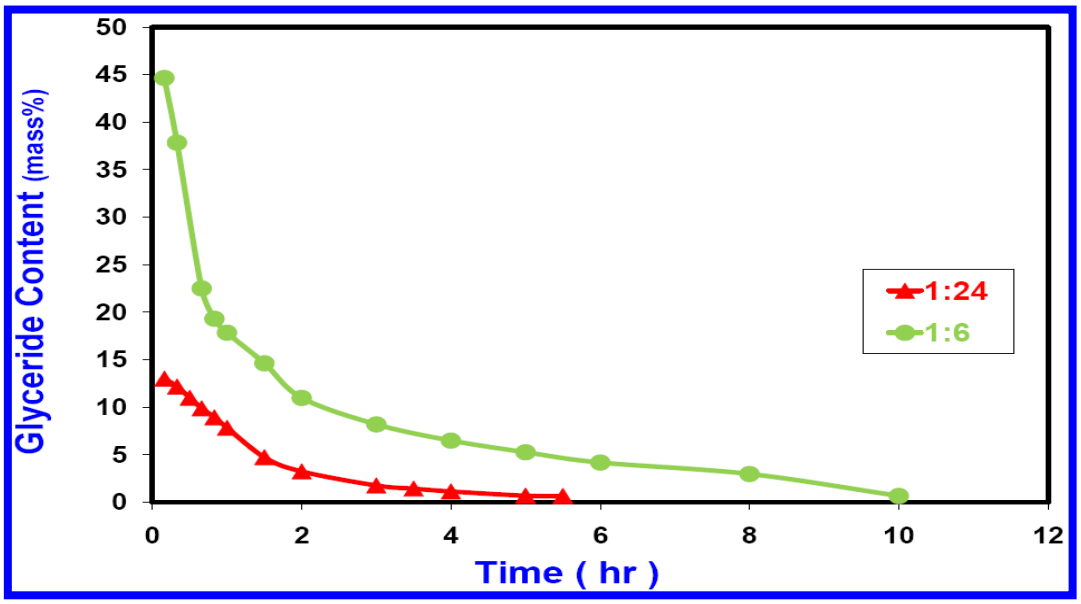


Figure 4.11 Effect of oil to alcohol molar ratio on glyceride (CBG) conversion in the transesterification of soybean oil using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: molar ratio of oil-to-alcohol (1:6 and 1:24), reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%.

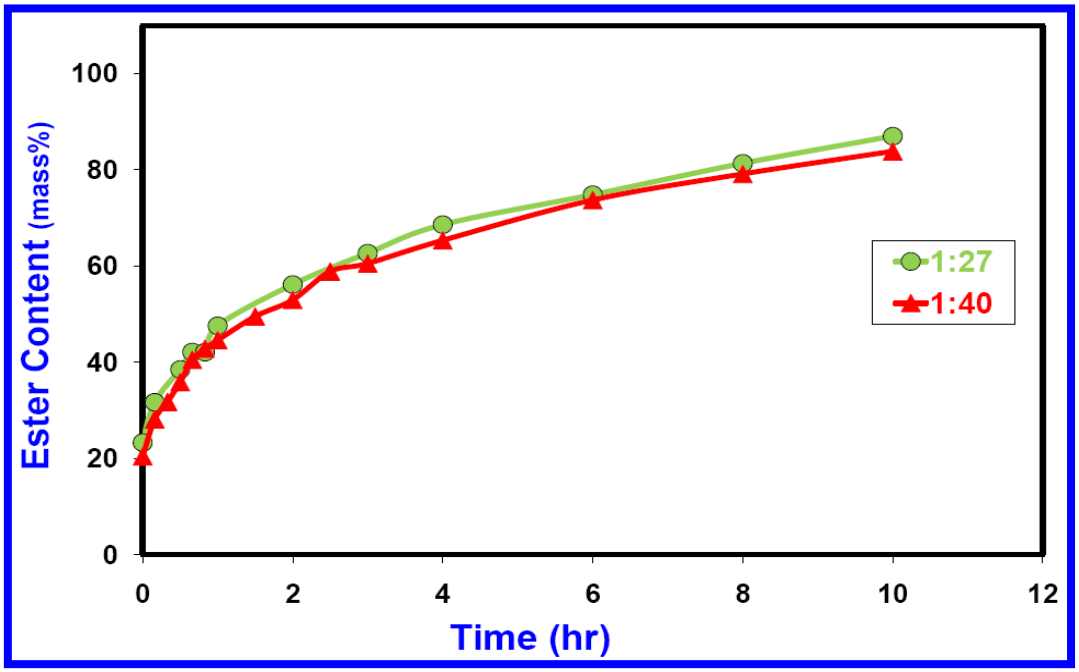


Figure 4.12 Effect of oil to methanol molar ratio on ester content in the ester-rich phase as a function of time for the simultaneous esterification and transesterification from soybean oil containing 10 wt.% PA. Reaction conditions: molar ratio of oil-to-alcohol (1:27 and 1:40), reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%.

Therefore, in the present work, the effect of the amount of catalyst on simultaneous esterification and transesterification has been studied. The experiments were performed using 1 wt.%, 3 wt.% and 10 wt.% of the catalyst at 200°C and 600 rpm stirring speed at a oil-to-methanol molar ratio of 1:27 using soybean oil with 10 wt.% PA as feedstock. An increase in the amount of catalyst from 3 wt.% to 10 wt.% increased the initial rate of formation of ester in the ester-rich phase as expected and apparently an equilibrium conversion of PA was achieved at about 4 h (Figure 4.13).

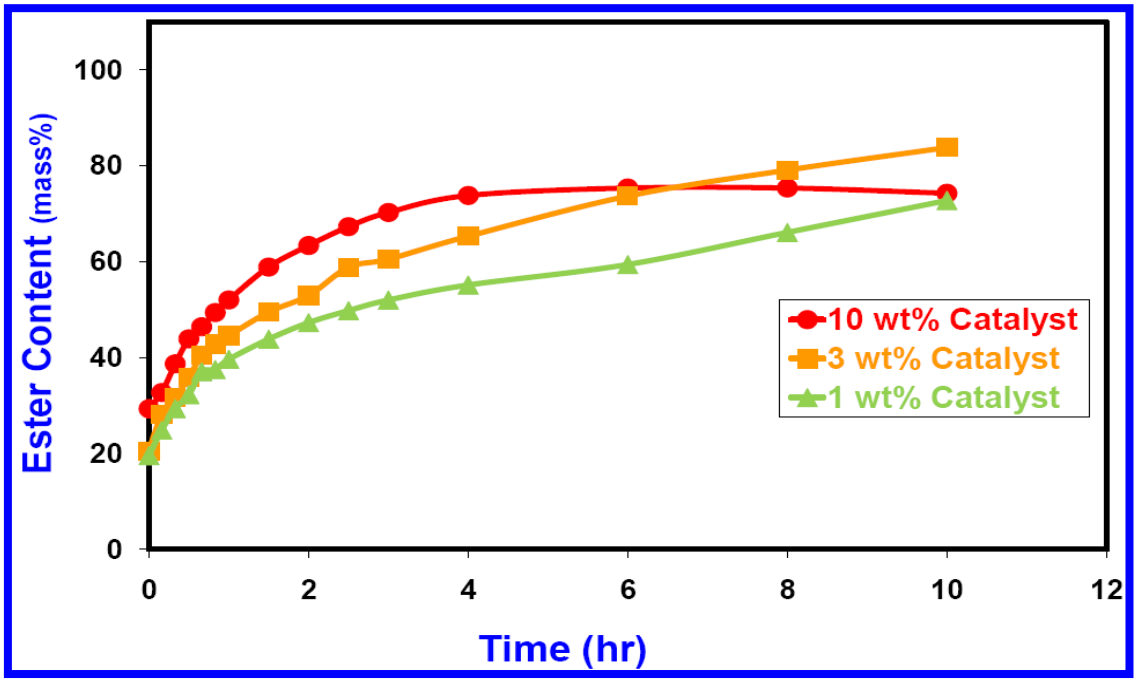


Figure 4.13 Effect of the amount of catalyst on ester content in the ester-rich phase as a function of time using 10 wt.% PA in SBO as feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst (1, 3, and 10 wt.%).

An experiment was also carried out at 1 wt.% catalyst. It is interesting to note that the initial rate of reaction with 1 wt.% catalyst is similar to that for 3 wt.% and 10 wt.% catalyst and after 10 h, the ester content in the ester-rich phase was the same as that for the 10 wt.%

catalyst. This shows that this catalyst is quite active to convert a model waste oil feedstock to biodiesel using a relatively low amount of catalyst. It is noted that the ester content using 3 wt.% eventually exceeds that obtained using 10 wt.% catalyst. Also, it appears that the ester content obtained with only 1 wt.% catalyst would exceed that obtained with 10 wt.% catalyst if the reaction time had been extended past 10 hours.

4.3.6 Effect of free fatty acid content of feedstock

The effect of free fatty acids (FFA) in the feedstock is very important as FFA may have adverse effects on the catalyst activity or the ester yield (Ma *et al.,* 1999). Therefore, the effect of free fatty acid level on the ester yield was investigated.

In the present work, FFA levels of 10 wt.% (yellow grease) and 25 wt.% (brown grease) were studied by adding 10 wt.% and 25 wt.% of PA to pure soybean oil, respectively. The reaction was performed using the optimized reaction conditions such as reaction temperature of 200°C, 1:27 molar ratio of oil-to-alcohol, and 3 wt.% catalyst. It should be noted that esters were formed during the time required to reach the desired reaction temperature (e.g. ~25 min for 200°C). Once the reaction mixture reached the desired reaction temperature, then the mixing of the reaction was started and this point was taken as time zero for the reaction.

It is found that the initial ester content in the ester rich-phase was increased with an increase in FFA level in the feedstock from 10 wt.% to 25 wt.%, which demonstrates the simultaneous occurrence of esterification and transesterification.

Figure 4.14 shows that after 10 h of reaction, the yield of esters reached about 84 wt % in both cases, when the PA content of soybean oil was 10 wt.% and 25 wt.%. It is important to note that even though a higher initial ester was obtained when 25 wt.% PA was used, after 6 h, the ester content were the same for both experiments suggesting equilibrium conversion was attained. A higher amount of FFA will produce a higher amount of .water. Water. is

considered to inhibit transesterification since it can hydrolyze the biodiesel product as well as could deactivate the catalyst to catalyze transesterification reaction. However, in our experimental results, it demonstrated that our catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) is tolerant to the water produced in the esterification of FFA as well as the water present in the feedstock. More studies are required to elucidate the effect of FFA on the processing of waste oil containing FFA.

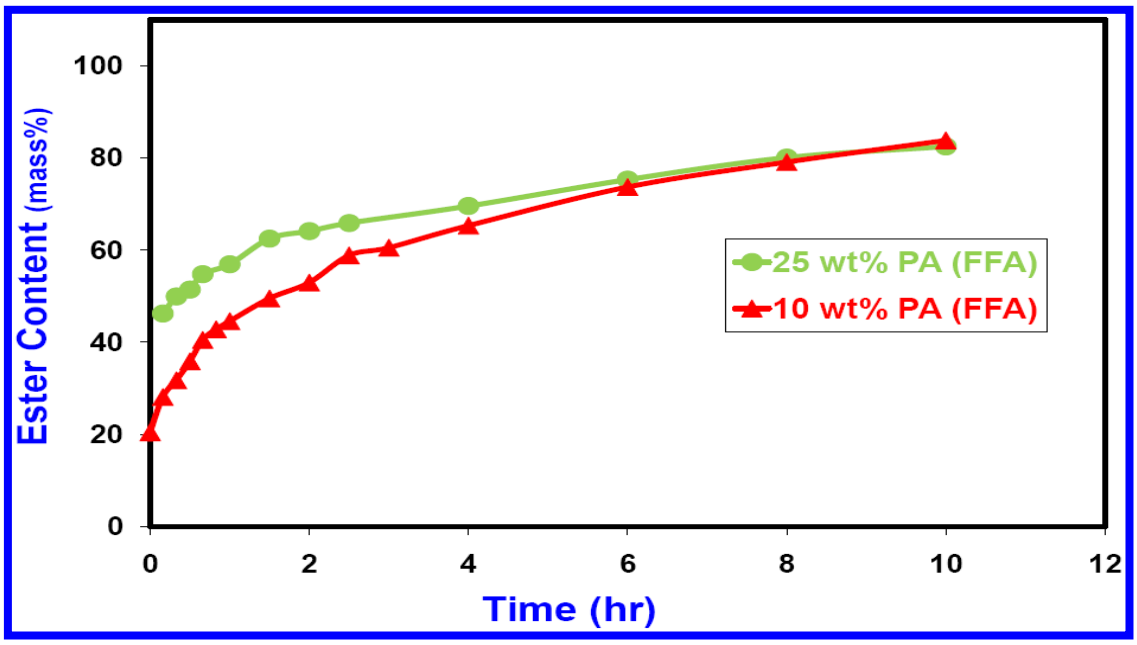


Figure 4.14 Effect of free fatty acids on ester content in the ester-rich phase as a function of time using 10 wt.% and 25 wt.% PA in SBO as feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst.Reaction conditions: reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%.

It was observed that the FFA conversions are similar for both 10 wt.% PA and 25 wt.% PA as shown in Figure 4.15.

This demonstrates that this acid catalyzed process, can convert high amount of FFA to FAME (similar to the FFA conversion of ~ 95% using sulfuric acid as a homogeneous catalyst as shown in Chapter 3, section 3.2.3). Furthermore, this process is insensitive

towards the the FFA level in the feedstock and the water produced during esterification.

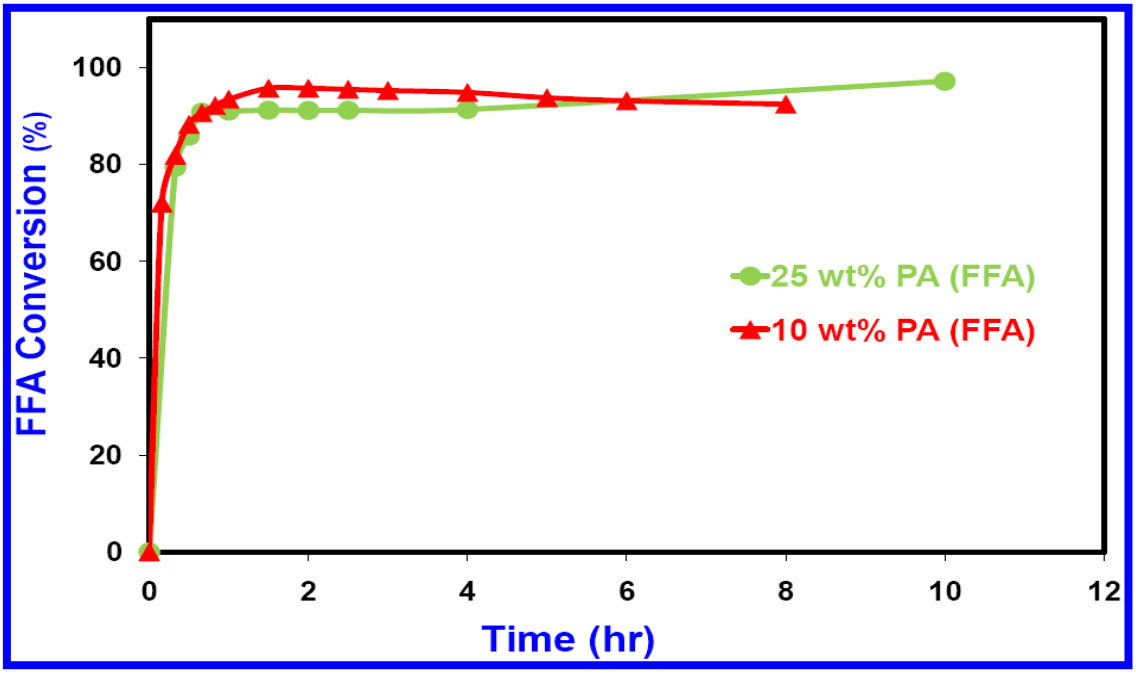


Figure 4.15 Effect of free fatty acids on FFA conversion as a function of time using 10 wt.% and 25 wt.% PA in SBO as feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%.

This shows the advantage of this single-step solid acid catalyzed process over a homogeneous acid or base catalyzed process, in which an increase in FFA level resulted in decrease in FAME yield. However, the initial amount of ester content was higher with 25 wt.% PA as compared to with 10 wt.% PA. This is due to the fact that, in the case of Figure 4.14 on page 92, the ester content (mass %) are measured which produced from both, FFA conversion (by esterification) and triglyceride conversion (by transesterifications). The initial ester content obtained with 25% FFA and 75% oil-triglyceride are higher than with 10% FFA and 90% oil-triglyceride due to the fact that esterification is faster than transesterification. With 25% FFA, the amount of triglyceride is less than the amount of triglyceride present in feedstock with 10% PA (i.e. 90% triglyceride), so the contribution to methyl ester content increased due to a faster formation of methyl ester from the feedstock with 25% PA as compared to only 10% PA by the esterification reaction.

The increase in the ester yield was due to the higher esterification rate of PA compared to the transesterification of triglycerides. This might be due to two possible reasons. First, fatty acids, particularly unsaturated ones, are more soluble in alcohol than triglycerides. The second reason is probably related to the reaction mechanism of esterification and transesterification. It appears that an increase in the FFA content in the feedstock will increase the biodiesel yield.

This result is very promising and suggests the feasibility of using low cost feedstocks with high FFA content for the commercial production of biodiesel. It was reported that biodiesel played a co-solvent role (Noureddini *et al.,* 1997). The biodiesel generated by a reaction between soybean oil and methanol improves the miscibility of the two substances and accelerates the reaction, which increases the level of FFA conversion. Furthermore, methanolysis of FFAs proceeds via simple esterification while triglycerides proceed via transesterification which consists of number of consecutive, reversible reactions. Due to these reasons, the rate of transesterification of triglycerides is slower than esterification of fatty acids. The lower rate of transesterification than esterification has previously been confirmed (Warabi *et al.,* 2004). It should be noted that the presence of 10 wt.% PA in SBO reduced the rate of TG conversion as shown in Figure 4.16. However, even with 10 wt.% PA, the glyceride (CBG) content (0.62 mass %) is similar to the transesterification of SBO only (0.65 mass %) at an extended reaction time of 10 h. Thus, it can be concluded from these results that the activity of this solid acid catalyst was not affected by the presence of higher amounts of free fatty acids even up to 25 wt.%. The presence of water produced during the esterification reaction apparently did not deactivate the catalyst. This finding has commercial importance since yellow grease, a potential feedstock for biodiesel production, contains up to 15% FFA and the synthesis of biodiesel from this feedstock using alkali catalysts is quite difficult (Freedman *et al.,* 1986).

Based on our studies on model waste oil feedstocks (soybean oil containing PA), it can be concluded that this solid acid catalyzed process potentially could be used for the production of biodiesel from feedstocks containing FFA such as yellow grease (≤ 15% FFA), brown grease (> 15% FFA) and tall oil (70% FFA).

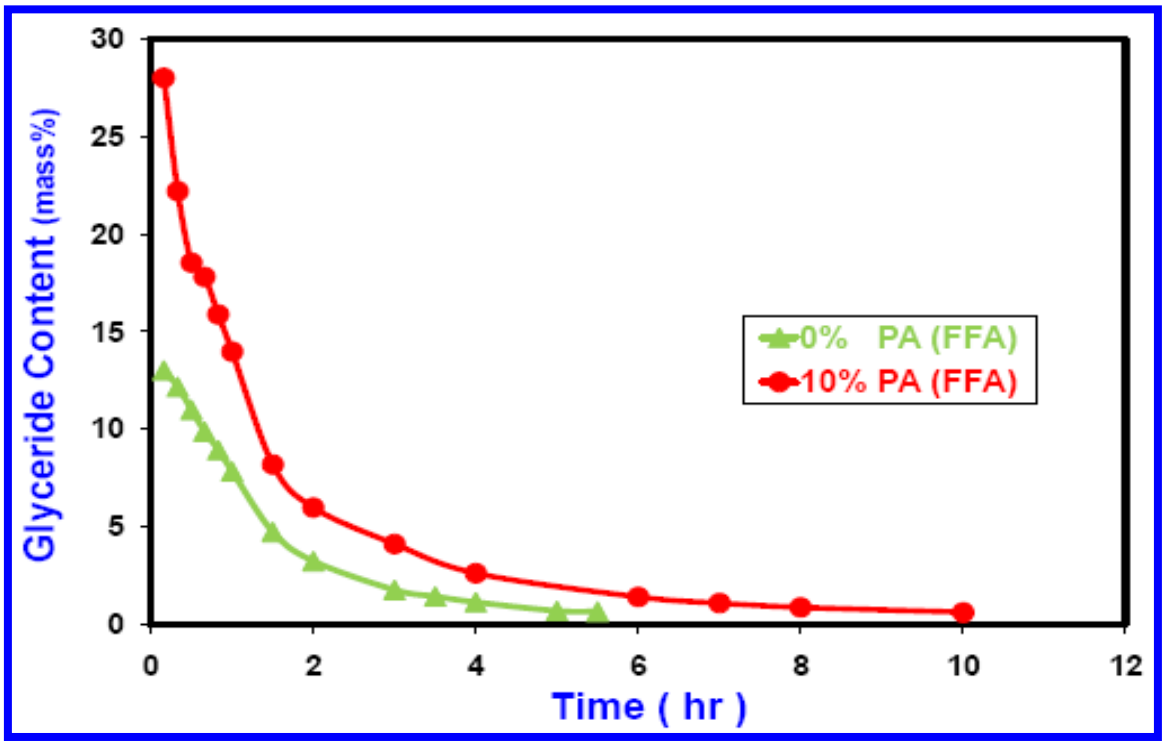


Figure 4.16 Effect of FFA content on glyceride (CBG) content in the ester-rich phase in transesterification of SBO using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: oil-to-alcohol molar ratio 1:24 (with 10 wt.% FFA is 1:27), reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%.

4.4 Conclusion

In summary, the present study showed PA was converted to biodiesel with 95% conversion using a solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina). Furthermore, SBO was successfully transesterified with 99% CBG conversion. Due to the promising activity towards esterification and transesterification, this solid acid catalyst was used for simultaneous esterification and transesterification of soybean oil

containing 10% PA. Over 95% conversion of PA and 99% conversion of CBG (SBO) were achieved. The PA conversion is similar to the PA conversion of ~ 95% using sulfuric acid as a homogeneous catalyst as shown in Chapter 3, section 3.2.3.

This catalyst is suitable to catalyze not only the esterification reaction but also the transesterification reaction. GC analysis based on the ASTM D974, ASTM D6584 and EN 14103 standards confirmed the production of high-purity biodiesel from feedstock with high FFA content. The total glycerin, ester content, and acid numbers were determined according to ASTM D6584, EN 14103, and ASTM D974, respectively.It was found that at 200°C, a 1:27 oil-to-alcohol molar ratio and 3 wt.% of catalyst, a high quality biodiesel with an ester content of 93.95 mass % was produced from a feedstock (soybean oil containing 10% PA) in 10 h. The conversion of PA and chemically bound glycerin (CBG) [includes triglyceride (TG), diglyceride (DG), and monoglyceride (MG)] were found to be 92.4% and 99.4%, respectively. The final product, without any post treatment, contains CBG, free glycerin, total glycerin, and acid number values of 0.616 mass %, 0.767 mass %, 1.383 mass %, and 1.505 mg KOH/g. These values can be reduced further by water washing, a typical post-processing step. This single-step solid acid catalyzed process has the potential for the production of biodiesel from high FFA feedstocks.

CHAPTER 5

A NOVEL SECOND-GENERATION GREEN TECHNOLOGY FOR THE PRODUCTION OF BIODIESEL FROM MULTI-FEEDSTOCKS FOR GLOBAL APPLICATIONS

Overview

Biodiesel is a green, nontoxic, renewable and biodegradable alternative fuel for petroleum-based diesel. However, the major obstacle for the production of biodiesel at an industrial scale is the high production cost, expensive 1st generation feedstocks, limited local availability and complex production processes. Currently, the amount of unsaturation in the fatty acid methyl ester (biodiesel) remains a major problem for the stability of biodiesel. This problem can be addressed by using a feedstock such as yellow grease that already possess a fatty acid profile suitable for biodiesel with enhanced stability to meet quality standards requirements for industrial scale production. Therefore, we have developed a novel technology for the production of biodiesel using a simple and environmentally green single-step heterogeneous-catalyzed process to produce high quality biodiesel from multi-feedstocks including yellow grease with enhanced stability for global applications. It was found that FFA present in yellow grease was converted to biodiesel with 95% conversion. Furthermore, yellow grease was successfully transesterified to produce an ester content of 87.3 mass %. This heterogeneous-catalyzed process is suitable not only for esterification but also for transesterification. Biodiesel analysis based on the ASTM D974 and EN 14103 standards confirmed the production of high-purity biodiesel from yellow grease with only 3% linolenic ester, which is far below the limit of 12% defined by EN 14214.

As part of process development, the effects of major parameters including feed-to- alcohol molar ratio, catalyst loading, nature of catalyst support, use of co-solvent, rate of mixing water content in the feedstock and reaction temperature have been studied and optimized.

Furthermore, it is critical to ensure hydrolysis of oil (triglyceride) and biodiesel does not take place. Therefore, a systematic study of hydrolysis of vegetable oil (soybean) and biodiesel showed that hydrolysis of vegetable oil and biodiesel did not occur until 220°C, far above the optimum operating temperature of 200°C. Experimental kinetic data were analyzed using a first-order kinetic model. The apparent activation energy and Arrhenius constant values were found to be 42.3 kJ/mole and 9.4801 sec^{-1}, respectively. Furthermore, surface properties were studied as part of the recycling studies to evaluate the changes in the catalyst surface which could also affect its overall activity. The recycling studies show no significant change in the catalytic activity of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) even after five reaction cycles. It was found that catalyst activity remained at 97% of the fresh catalyst. Then, the catalyst was cleaned and regenerated between the reaction cycles. For purposes of industrial applications, extensive recycling studies were performed in which solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) was used without any treatment between the runs. No significant decrease in the catalyst activity for esterification and transesterification was observed even after at least 12 runs. This demonstrates the reusability of the catalyst for an industrial production process. Due to the high catalytic activity, reusability and the low cost, this green 2^{nd} generation technology has potential for industrial-scale production of biodiesel from multi-feedstocks for global applications.

5.1 Introduction

One of the major challenges in 21^{st} century is the world energy crisis due to an increase in world population and demand for energy in developed and emerging economies (Pérez-Lombard *et al.*, 2008). As a result, worldwide research has been focused on the development of alternative sustainable energy sources to overcome the depletion of fossil fuels. One promising alternative of diesel fuel is biodiesel which is gaining momentum around the world. Biodiesel is a nontoxic, renewable, and biodegradable alternative green fuel for petroleum-based diesel. However, the major obstacle for the production of biodiesel at an

industrial scale is the high production cost, which is related to the relatively high price of the 1st generation feedstocks (refined vegetable oils) used. Generally, 70-95% or a major part of the biodiesel production cost is due to the high cost of the feedstock (Kulkarni *et. al.*, 2006a; Marchetti *et al*., 2007; Gui *et. al*., 2008; Fan *et. al*., 2009; Leung *et. al*., 2010; Baig and Ng, 2010; Balat, 2011, Baig *et. al.*, 2011). Therefore, the source of feedstock for the production of biodiesel should fulfill two requirements: price (low feedstock and production costs; more than 80% of the production cost corresponds to the feedstock cost) and local availability (large and constant production volume) (Sivasamy *et al*., 2009). However, still more than 95% of the world's biodiesel is produced from edible vegetable oils (Gui *et al*., 2008), which increases the demand for vegetable oil production throughout the world (Gustone, 2009).

Globally, the recent rapid increase in the production of biodiesel and government mandates for the use of green alternative fuels have necessitated research into the development of alternative biodiesel feedstocks as the traditional 1st generation feedstocks (canola/rapeseed, soybeans, palm) could not address this growing demand (Moser, 2009). As a result, various 2nd generation feedstocks have been considered as possible substitutes for refined vegetable oil such as used vegetable oil, animal fats and waste oils and fats in which the amount of FFA varies from 3% to 40% (Ma *et al.*, 1999; Hass, 2005; Parawira, 2009). The FFA content of various feedstocks and the fatty acid compositions of some of the vegetable oils and animals fats that have been used as biodiesel feedstock are listed in Table 5.1 and Table 5.2, respectively (Knothe, 1997).

Currently, the amount of unsaturation in the fatty acid methyl ester (FAME) remains a major problem for biodiesel stability. Structural features such as degree of unsaturation influence the oil stability index (OSI).

Fatty acid methyl esters that have a greater number of methylene-interrupted double bonds undergo oxidative degradation at faster rates than those that have a lower number of double

bonds (Holman and Elmer, 1974; Knothe, 2008). This has been confirmed based on the OSI values of methyl esters of stearic (> 40 h), oleic (2.5 h), linoleic (1.0 h) and linolenic (0.2 h) acids (Knothe, 2008; Moser 2008). It would be expected that the biodiesel produced from feedstocks relatively low in polyunsaturated fatty acid content will have superior oxidative stability (Moser, 2009). Thus, long, saturated and unbranched hydrocarbon chains in fatty acids are preferred due to their stability towards oxidation.

Table 5.1 Free fatty acid content of various feedstocks.

Feedstock	**% FFA**
Refined vegetable oils	< 0.05%
Crude vegetable oil	0.3 – 0.7%
Restaurant waste grease	2 – 7%
Animal Fat	5 – 30%
Trap Grease	40 – 100%

A higher degree of unsaturation can result in the oxidation of biodiesel, which affects its stability during storage. Due to these problems, in biodiesel quality standards such as EN 14214, the amount of linolenic ester (C18:3) has been restricted to the maximum value of 12%. However, this limit has been set to accommodate the use of rapeseed oil (high linolenic C18:3 content) which is one of the major crops produced in European Union as a feedstock for biodiesel production. Therefore, a decrease in C18:3 is highly desirable to enhance the stability of biodiesel. This problem can be addressed by using a feedstock such as yellow grease that already possesses a fatty acid profile suitable with enhanced stability that meets quality standard requirements for industrial- scale production (Knothe, 2006).

Yellow grease (used waste cooking oil) is an inexpensive alternative to the expensive 1st generation feedstocks (pure vegetable oil) for biodiesel production (Kulkarni *et al.*, 2006a) and is considered as a promising 2nd generation feedstock. Compared to vegetable oils, these

waste cooking oils and fats could be a good choice as feedstocks for the production of biodiesel since they are much cheaper than virgin vegetable oils (2-3 times) (Phan, 2008; Wen, 2009).

Yellow grease is produced from vegetable oil or animal fat that has been heated and used for cooking. Restaurant waste oils and rendered animal fats are less expensive than food-grade canola and soybean oil (Canackci *et al.*, 2003). The waste cooking oil/waste fryer grease (WFG) is categorized by its free fatty acid (FFA) content. For example, if the FFA content of waste cooking oil is < 15%, then it is called "yellow grease"; otherwise, it is called "brown grease". The price of yellow grease varies from US $0.04 to $0.10/kg and that of brown grease from US $0.05 to $0.010/kg (Azocar *et al.*, 2010). Currently, all these waste oils are sold commercially as animal feed. However, since 2002, the European Union (EU) has enforced a ban on feeding these mixtures to animals because many harmful compounds are formed during frying. Moreover, if the waste cooking oil is used as an additive to feed mixtures for domestic animals, then it could allow the return of harmful compounds back into the food chain through the animal meat (Cvengros and Cvengrosova, 2004). Also, the disposal of waste cooking oil is problematic because this may contaminate environmental water. Many developed countries have set policies that penalize the disposal of waste oil through the water drainage (Dorado *et al.*, 2002). Due to these reasons, the waste cooking oil must be disposed of safely or be used in a way that is not harmful to human beings. Therefore, the production of biodiesel from waste cooking oil is one of the better ways to utilize it efficiently and economically.

Another motivation to use alternative feedstocks (i.e. waste oils and fats) is the growing concern for the use of vegetable oil for fuel instead of food (Canadian Bioenergy Corp,2008). Besides that, the use of varied feedstock for the production of biodiesel will lead to self-sustaining economies making countries less vulnerable to international political crises (Sivasamy *et al*., 2009).

Table 5.2 Composition of various oils and fats (wt %) (Knothe, 1997)

Carbon: Double bond	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	**20:0**	**22:1**
Oil/fat	**Myristic**	**Palmitic**	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**	**Arachidic**	**Erucic**
Soybean		6-10	2-5	20-30	50-60	5-11		
Corn	1-2	8-12	2-5	19-49	34-62	Trace		
Peanut		8-9	2-3	50-65	20-30			
Olive		9-10	2-3	73-84	10-12	Trace		
Cottonseed	0-2	20-25	1-2	23-35	40-50	Trace		
Hi Linoleic safflower		5.9	1.5	8.8	83.8			
Hi Oleic Safflower		4.8	1.4	74.1	19.7			
Hi Erucic Rapeseed		3.0	0.8	13.1	14.1	9.7	7.4	50.7
Butter	7-10	24-26	10-13	28-31	1-2.5	0.2-0.5		
Lard	1-2	28-30	12-18	40-50	7-13	0-1		
Tallow	3-6	24-32	20-25	37-43	2-3			
Linseed Oil		4-7	2-4	25-40	35-40	25-60		
Tung Oil		3-4	0-1	4-15		75-90		
Yellow Grease	1.3	17.4	12.4	54.7	8.0	0.7	0.3	0.5

Globally, the amount of waste cooking oil generated varies from country to country, depending on the use of vegetable oil. In the EU, an estimate of the potential amount of waste cooking oil collected is ~700,000−1,000,000 tonnes/yr (Supple *et al*., 2002). Also, on an average, 9 pounds of yellow grease per person are produced annually in the United States (Wiltsee, 1998).

In Canada, ~120,000 tonnes (240 million lbs) of yellow grease are produced every year (Zhang *et al.*, 2003), which can potentially produce 118.2 million liters of biodiesel per year. Projections indicate that 100-200 million litres of biodiesel can be produced annually from yellow grease alone (Ridley, 2004). Also, 1000 million lbs of animal fat are produced per

year which can be used to produce 492 million liters of biodiesel per year (Biodiesel Advisory Council, 2005). This amount is sufficient to produce the amount of biodiesel in Canada that meets the B5 requirement of 610 million liters per year (Holbein *et al.*, 2004). Hence, a substantial portion of the biodiesel (of the 5% requirement in Canada) can be replaced by biodiesel obtained from waste cooking oil. The total amount of waste frying oil produced in North America, Europe and some Asian countries has reached 16.6 Mton (Gui *et al*., 2008). The use of waste oils and fats alone could supply the total demand for FAME production per year (Azocar *et al*., 2010).

Most of the processes reported in the literature have focused on the use of model compounds. It must be pointed out that in some cases, the data obtained with simple model molecules cannot be used to predict the behavior of oils/fats and fatty acids because the polar and steric effects of the alpha-substituent group can greatly influence the reactivity.

According to the best of our knowledge, a systematic in-depth study of development of heterogeneous-catalyzed single-step process for biodiesel production from industrial-scale untreated real waste feedstocks such as crude yellow grease has not been explored in depth apart from a few reports on heterogeneous-catalyzed esterification and transesterification of model compounds and feedstock with high FFA content. In this study, the yellow grease used was a mixture of waste cooking oils and animal fats collected by a commercial waste collection company across Canada (Rothsay, Ontario, Canada). Yellow grease served as a multi-feedstock for this study. However, waste oils and fats (e.g. used cooking oils, yellow grease) contains high amount of FFA. Biodiesel production from these inexpensive feedstocks is more challenging than using 1st generation homogeneous catalysis since it involves multi-step processing, oil pretreatment, neutralization of waste homogeneous catalyst, water washing of the crude biodiesel and glycerol and the treatment of waste generated, which are time consuming and costly (Bournay *et al.*, 2005).

Furthermore, homogeneous catalysis is generally limited to batch-mode processing (Jothiramalingam *et al*., 2009). Also, conventional base-catalyzed process is sensitive to FFA and water, and so can be used only for expensive refined vegetable oils with less than 0.5% FFA and 0.06% water content (Freedman *et al*., 1984; Ma *et al.*, 1999). Therefore, a great need exists to develop innovative 2nd generation heterogeneous-catalyzed technologies, which can be used for inexpensive waste feedstock using simple, efficient and less expensive manufacturing process (Baig and Ng, 2010). The use of a solid acid catalyst for transesterification reaction has many important benefits such as its greater tolerance towards the presence of FFA in the feedstocks (Kulkarni *et al*., 2006c; Vyas *et. al*., 2010; Koh *et al.*, 2011). Also, the use of solid acid catalyst is environmentally friendly because of simple product separation and purification and possibility of regeneration and reuse that make the biodiesel production cost-effective (Dossin *et. al*., 2006).

Furthermore, in contrast to homogeneous-catalyzed process, the 2nd generation heterogeneous-catalyzed processes can be run in either batch or continuous mode giving flexibility to continue with current batch manufacturing processes or to retrofit their manufacturing process with a (Yan *et al.*, 2010).

Therefore, the problem associated with the 1st generation homogeneous-catalyzed process has been addressed by using a 2nd generation heterogeneous-catalyzed process for the production of biodiesel from oil containing FFA (Baig and Ng, 2010). However, most of the processes reported in the literature used a particular feedstock such as soybean oil, canola oil, palm oil, and used cooking oil. Moreover, a green process which can be used for multiple feedstocks would be very beneficial and enable different local feedstocks to be processed. Besides that, the use of varied feedstock for the production of biodiesel will lead to self-sustaining economies, making the countries less vulnerable to international political crises (Sivasamy *et al*., 2009).

In the development of an industrial process for global applications, catalyst activity, catalyst life and feedstock flexibility are the three major factors that tremendously affect the economics of the biodiesel (Yan *et al.*, 2010). The production of biodiesel from a model feedstock, soybean oil with added FFA, in a single-step solid acid-catalyzed process has already been demonstrated in Chapter 4 (Baig and Ng, 2010). As a second phase of the process development, the application of solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) is evaluated using a real industrial feedstock (yellow grease).

In this research, we have developed a novel 2nd generation multi-feedstock technology for the production of biodiesel using a simple and environmentally green single-step heterogeneous-catalyzed process to produce high quality biodiesel from multi-feedstocks, as shown schematically in Figure 5.1 and 5.2. This technology can be used for multi-feedstocks whether 1st generation or 2nd generation, with unlimited FFA content.

Furthermore, catalytic activity, catalyst recycling, and feedstock flexibility are investigated for the production of biodiesel for processing multi-feedstocks including yellow grease. Also, as a part of process development, major process parameters including catalyst loading, feed-to-alcohol molar ratio, reaction temperature, rate of mixing, the nature of support, water content and use of co-solvent have been investigated. Moreover, extensive recycling studies were performed to evaluate the reusability of the catalyst for industrial applications. This is one of the major features of a heterogeneous catalyst in order to be considered for an industrial process.

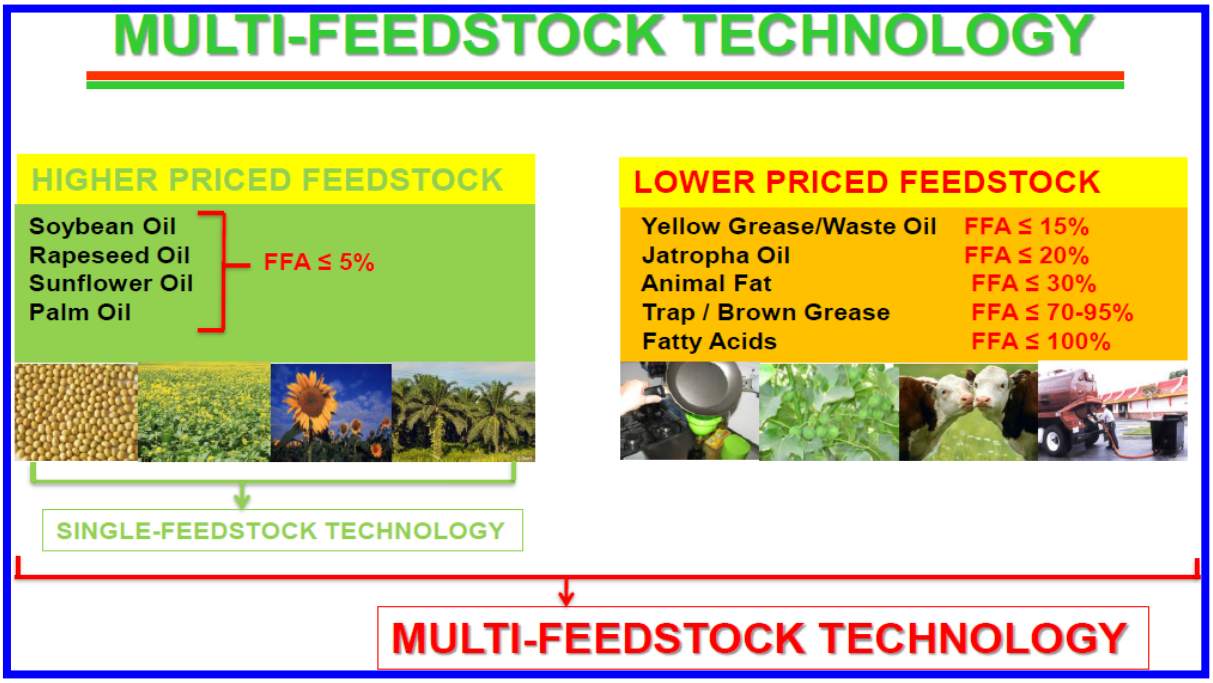


Figure 5.1 Schamatic presentation of multi-feedstock biodiesel technology to produce biodiesel from 1st and 2nd generation feedstocks.

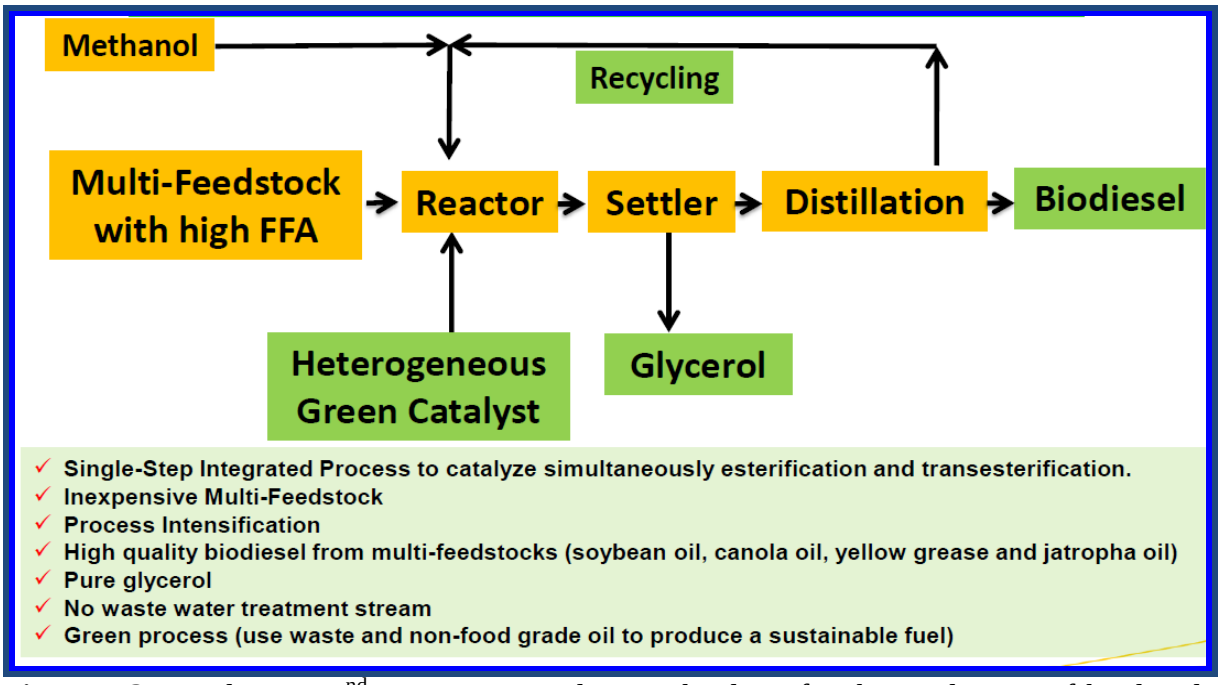


Figure 5.2 Novel green 2nd generation catalytic technology for the production of biodiesel from multi-feedstocks.

5.2 Experimental procedures

5.2.1 Materials

The yellow grease used was from waste oil and fat and obtained from Rothsay Biodiesel (Quebec, Canada). The following chemicals were obtained from Sigma-Aldrich Chemical Company (Milwaukee, WI): 2-propanol (anhydrous, 99.5%), toluene (anhydrous, 99.8%), *p*-naphtholbenzein (indicator grade), 0.1 N KOH (volumetric standard, in isopropanol), methyl heptadecanoate, n-heptanes, and rapeseed FAME standard mixture.

5.2.2 Catalyst preparation

The catalyst (12-tungstophosphoric acid, $H_3PW_{12}O_{40}{\cdot}nH_2O$ supported onto neutral alumina) was prepared with catalyst loadings of 10% to 40% as discussed earlier in section 4.2.2. For more details, please refer to Appendix-G.

5.2.3 Equipment

The esterification and transesterification with a new solid acid catalyst was carried in a fully automated high-pressure, high-temperature batch reactor (PARR Instrument, 4843, Moline, Illinois, USA). The equipment consisted of a high pressure cylindrical chamber, heater, water line (in order to control the temperature), sampling outlet and stirrer.

5.2.4 Procedures

Simultaneous Esterification and Transesterification.

Yellow grease with 9.1% FFA content was used as feedstock for simultaneous transesterification and esterification. The reaction was carried out in a 300 cc Parr reactor (Parr Instrument Co.) equipped with a temperature controller. Initially, the reactor was charged with yellow grease and methanol. A fresh solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) was added to the reaction vessel (or otherwise as stated). The reactor was pressurized (depending on the reaction temperature) to ensure that at the desired reaction temperature the reactants were in the liquid phase. A temperature of 200°C and a pressure of 600 psi were selected for experiments (or otherwise as stated). Once the reaction mixture reached the desired reaction temperature, then the

mixing of the reaction was started and this point was taken as time zero for the reaction. All the reactionswere carried out or a total reaction time of 10 h unless otherwise stated. Samples were taken at regular time intervals. Methanol was evaporated under reduced pressure using a rotary evaporator.Then, introduced into a centrifuge to remove the solid catalyst. A glycerol phase did not appear in earlier samples presumably since so little formed and/or it was remained at the bottom of the reactor. Samples from the ester-rich phase were analyzed without any post-experiment treatment such as water washing.

GC Analysis

Samples from the ester-rich phase were analyzed for methyl ester (ME) formation at a pre-determined interval of time using an Agilent 7980A GC system equipped with a 7683 auto injector, a flame ionization detector and a capillary column for sample injection to determine the ester content with a HP-INNOWax column (30 m x 320 mm x 0.25 µm) using a split/splitless inlet as per EN 14103 (as validated in Chapter 3; section 3.1). The GC oven was operated at 230°C and Helium was used as carrier gas.

Quantitative analysis of % methyl ester (ME) was performed using European standard EN 14103:2003. The % ME yield was calculated using equation (**5.1**). Free fatty acids in the samples were determined using stock solution (methyl heptadecanoate and n-heptane).

$$\%\ of\ ME = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad \textbf{(5.1)}$$

where,

$\sum A$ = Total peak area from the methyl esters in C_{14} to $C_{24:1}$

A_{EI} = Peak area corresponding to methyl heptadecanoate (C_{17})

C_{EI} = Concentration of metyl heptadecanoate (C_{17}) solution (mg/mL)

V_{EI} = Volume of metyl heptadecanoate (C_{17}) solution (mL)

m = Mass of the sample (mg)

Acid Number Analysis

The acid number was determined and calculated by using equation (**5.2**) as per ASTM D974 (Baig and Ng, 2011):

$$Acid\ \ Number, mg\ \ of\ \ KOH\ \ / g = \left[\frac{(A-B) \times M \times 56.1}{W} \right] \qquad \textbf{(5.2)}$$

where,

A = KOH solution required for titration of the sample (mL)

B = KOH solution required for titration of the blank (mL)

M = molarity of the KOH solution,

W = weight of the sample used (g)

The FFA content was determined as per ASTM D974 (Baig and Ng, 2011). The conversion of free fatty acid was calculated using Equation (**5.3**):

$$\text{FFA conversion}(\%) = \left(\frac{a_i - a_t}{a_i} \right) \times 100 \qquad \textbf{(5.3)}$$

where a_i is the initial acid number of the mixture and a_t is the acid number at time t as specified in ASTM D6751.

5.3 Results and discussion

5.3.1 Effect of feed-to-alcohol molar ratio

The feed-to-alcohol molar ratio is one of the most important parameters that affects the yield of methyl esters. Generally, an increase of the initial oil-to-alcohol molar ratio enhances the ester yield (Kafuku *et al.*, 2010; Regit *et. al*., 2011; Keera *et. al*., 2011). With respect to the type of alcohol, methanol and ethanol can both be used for the production of biodiesel via transesterification. Industrially, methanol is derived from natural gas, while ethanol is obtained from ethylene. Ethanol can also be produced from renewable resources such as wheat and sugar cane.

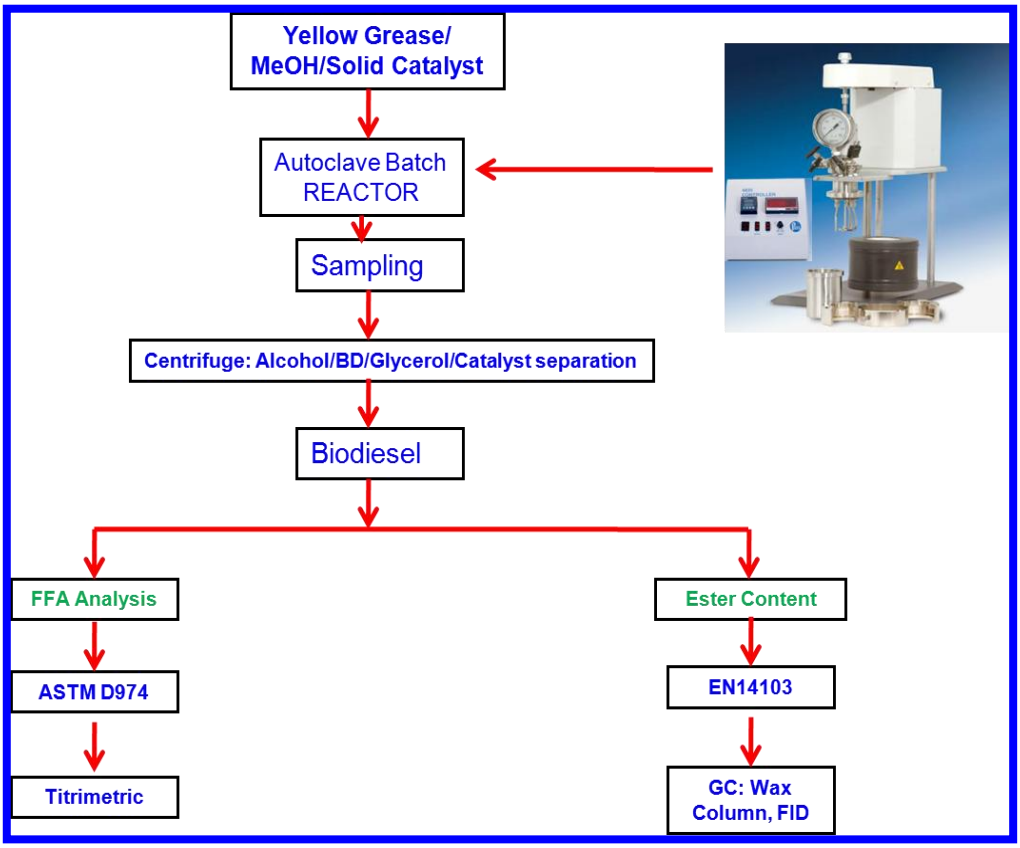


Figure 5.3 Process flow chart for experimental work.

Furthermore, ethanol is more hygroscopic than methanol which is not a desirable property. Also, the use of ethanol can cause excessive emulsion formation making separation of final products difficult, especially, if waste vegetable oil is used as the feedstock (Zhou, 2000). Due to its lower cost, methanol is the most commonly used alcohol for biodiesel production (Barnwal *et al.*, 2005; Jain *et al.*, 2009). Therefore, methanol has been selected for this research study.

Stoichiometrically, the feed-to-alcohol molar ratio required for transesterification is 1:3. However, the use of excess methanol is required to shift the equilibrium of triglyceride transesterification in the forward direction to favor the formation of FAME. Generally,

heterogeneous catalyzed transesterification is well known for its slow reaction rate. In the literature, higher triglyceride-to-alcohol molar ratios have been used to increase the rate of transesterification (such as 1:15, 1:40, 1:70, and even 1:275 molar ratios) (Xie *et al*., 2005; Cao *et al*., 2008; Zheng *et al*., 2006). The effect of the feed-to-alcohol molar ratio for the production of biodiesel from yellow grease using the tungstophosphoric acid catalyst with 30% loading supported on neutral alumina are shown in Figures 5.4 and 5.5. This solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) showed promising activity towards simultaneous esterification and transesterification of yellow grease with 9.1% FFA. The rate of esterification is higher as compared to transesterification for all molar ratios. The time evolution of the conversion of yellow grease to methyl ester at various molar ratios (1:6, 1:18, and 1:27) is shown in Figure 5.5. It can be clearly seen that as the ratio increases, so does the ester yield particularly after 2 hrs. After 10 h, methyl ester yields of 58.76%, 72.20% and 80.34% were obtained at molar ratios of 1:6, 1:18 and 1:27, respectively. The excess methanol used during the production process can be recovered and reused. Therefore, 1:27 has been selected as the optimum feed-to-methanol molar ratio for simultaneous esterification and transesterification reactions.

5.3.2 Effect of catalyst loading

A common effect of changing the catalyst-to-oil mass ratio is the change in contact conditions between oil and catalyst, which in turn changes the average activation of catalysts. In general, as the catalyst-to-oil weight ratio increases, the probability of contact between oil and active centers also increases (Singh *et al.*, 2007). Hence, by increasing the amount of catalyst used, the reaction rate and conversion after a certain time can be further increased (Kiss *et al.*, 2006). Also, catalyst loading plays a vital role for the efficient use of support material. Initially, the catalyst loading used was 30%. However, catalyst loading up to 70% has been reported in previous studies. Therefore, to obtain the maximum conversion over shorter reaction times, the use of a higher catalyst loading is suggested.

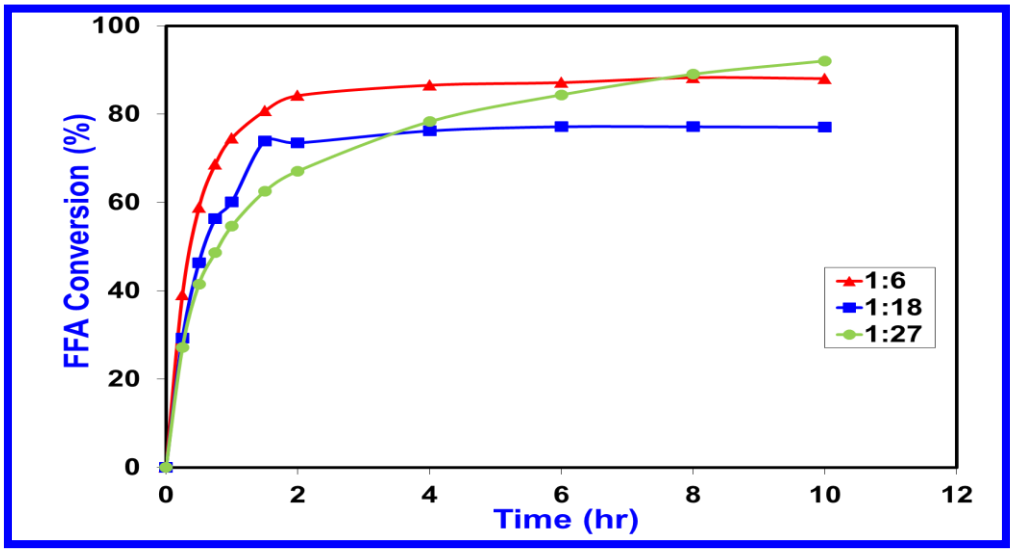


Figure 5.4 Effect of feed to alcohol molar ratio on FFA conversion as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: molar ratio of feed-to-alcohol (1:6, 1:18, and 1:27), reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

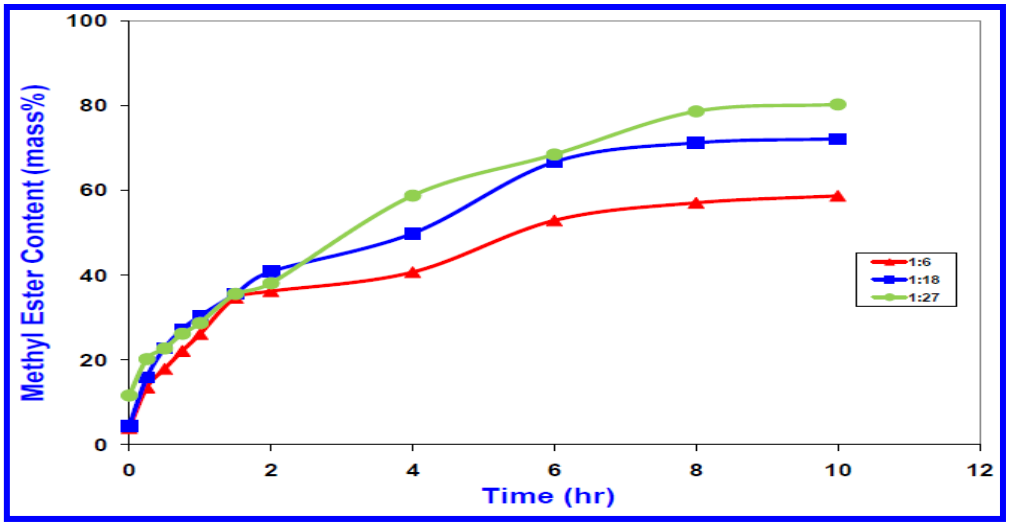


Figure 5.5 Effect of feed-to-alcohol molar ratio on ester content in the ester-rich phase as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: molar ratio of feed-to-alcohol (1:6, 1:18 and 1:27), reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

An objective is to to determine whether this catalyst is suitable for reactive distillation applications where high activity is required in a short time. Therefore, the effect of catalyst loading has been studied at 10%, 20%, 25%, 30% and 40% as shown in Figure 5.6. The amount of catalyst 3 wt.% means 3 g of the catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) for 100 g of the feed. Catalyst loading means how much active is supported on the support. For example, 30% catalyst loading means 30 g of active (e.g. tungstophosphoric acid) is supported on 70 g of the support (e.g. neutral alumina). It was found that as the catalyst loading increases, ester yield also increases as shown in Figure 5.6. This may be due to an increase in accessible acidic sites (because of higher surface area) which are responsible for catalyzing the esterification and transesterification reaction. However, the maximum ester yield was obtained when catalyst loading of 30% was used. Therefore, this catalyst loading has been selected as optimum.

As shown in Table 5.3, the surface area decreases as the % increase in catalyst loading increases. However, above 30% loading, a significant drop in the surface areas occurs, leading to a decrease in catalyst activity. This may be due to the pore blockage of the catalyst surface (Srilatha *et al*., 2010).

Table 5.3 Relationship between the catalyst loading and the surface area of the catalysts.

Catalyst (PSA)	Surface Area (m^2/g)
10%	114.5
20%	97.9
25%	90.7
30%	77.6
40%	33.9

Scanning electron micrographs of catalyst surfaces with loading between 0% and 40% are shown in Figure 5.7. It is clearly demonstrates in Figure 5.7 that the size of the solid acid

catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) increases as does the loading %. These SEM images confirm the phenomenon of agglomeration of particles (Srilatha *et al*., 2010). Therefore, SEM results further support that at high catalyst loading (e.g. 40%), bulk nature was attained.

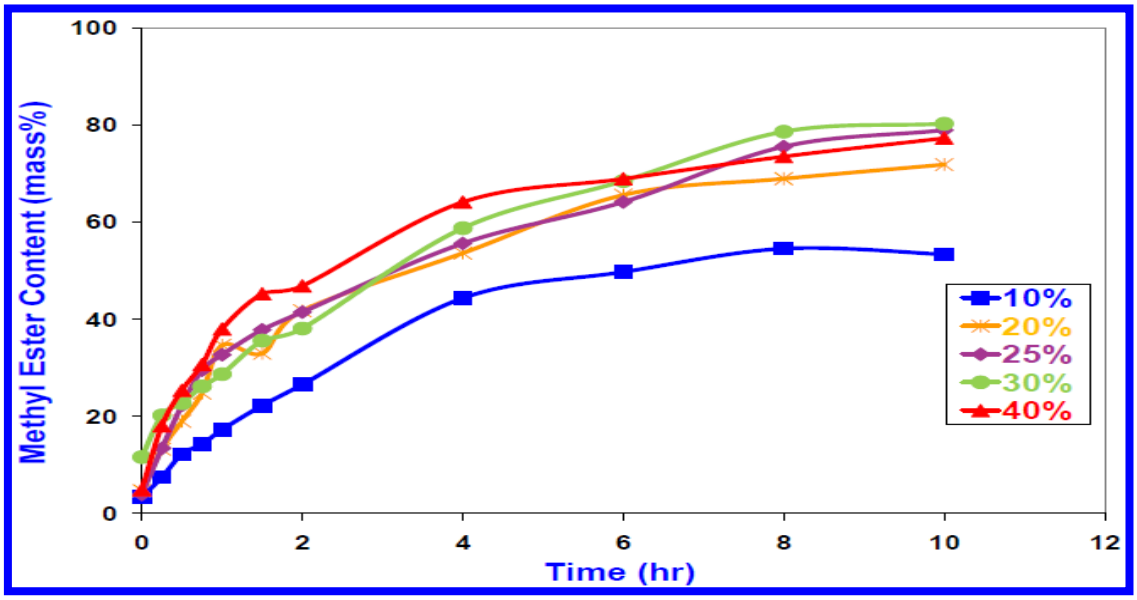


Figure 5.6 Effect of catalyst loading on ester content in the ester-rich phase as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: catalyst loadings (tungstophosphoric acid supported on neutral alumina with 10%, 20%, 25%, 30% and 40% loading), reaction temperature 200°C), molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%.

5.3.3 Effect of nature of support

The activity of a heterogeneous (solid) catalyst mainly depends on its structural characteristics such as its nature, specific surface area and pore size. The catalyst performance can also be significantly improved by using a catalyst support as the carrier which provides a higher specific surface area (Zabeti *et. al.,* 2009). Generally, for heterogeneous catalyst, the main role of the support is to provide a high surface area for the active component that is responsible for catalyzing the reaction.

An acidic support, acidic alumina (acidic Al_2O_3), has also been evaluated to improve the acidic properties of catalyst. Furthermore, one of the major challenges of acid-catalyzed transesterification is its slow rate compared to that of conventional 1st generation homogeneous base-catalysis. Therefore, a basic support, basic alumina (basic Al_2O_3), has also been evaluated in attempt to combine the acidity of active catalyst and basicity of support.

Results for the study of the effect of support for the production of biodiesel from yellow grease using solid acid catalysts (tungstophosphoric acid with 30% loading supported on neutral, acidic, and basic alumina) are shown in Figures 5.8 and 5.9. The FFA conversion of FFA presents in the yellow grease using neutral alumina as support is similar to the FFA conversion of ~ 95% using sulfuric acid as a homogeneous catalyst as shown in Chapter 3, section 3.2.3. It is found that for 24 h reaction time, neutral, acidic, and basic supports provide ester yields of 87.81%, 81.06%, and 79.59%, respectively, as shown in Figure 5.8.

Although, the initial activities of all supports (acidic Al_2O_3, basic Al_2O_3, and neutral Al_2O_3) were similar, however, the order of overall catalytic activity of catalysts is as follows: 30% tungstophosphoric acid /neutral Al_2O_3 > 30% tungstophosphoric acid /acidic Al_2O_3 > 30% tungstophosphoric acid / basic Al_2O_3. The reason for the low ester yield using basic support could be its deactivation due to its reaction with FFA present in the feedstock. For esterification reaction, no significant difference was observed. However, FFA conversion when a neutral Al_2O_3 was used was higher than when acidic Al_2O_3 and basic Al_2O_3 were used as supports (Figure 5.8).

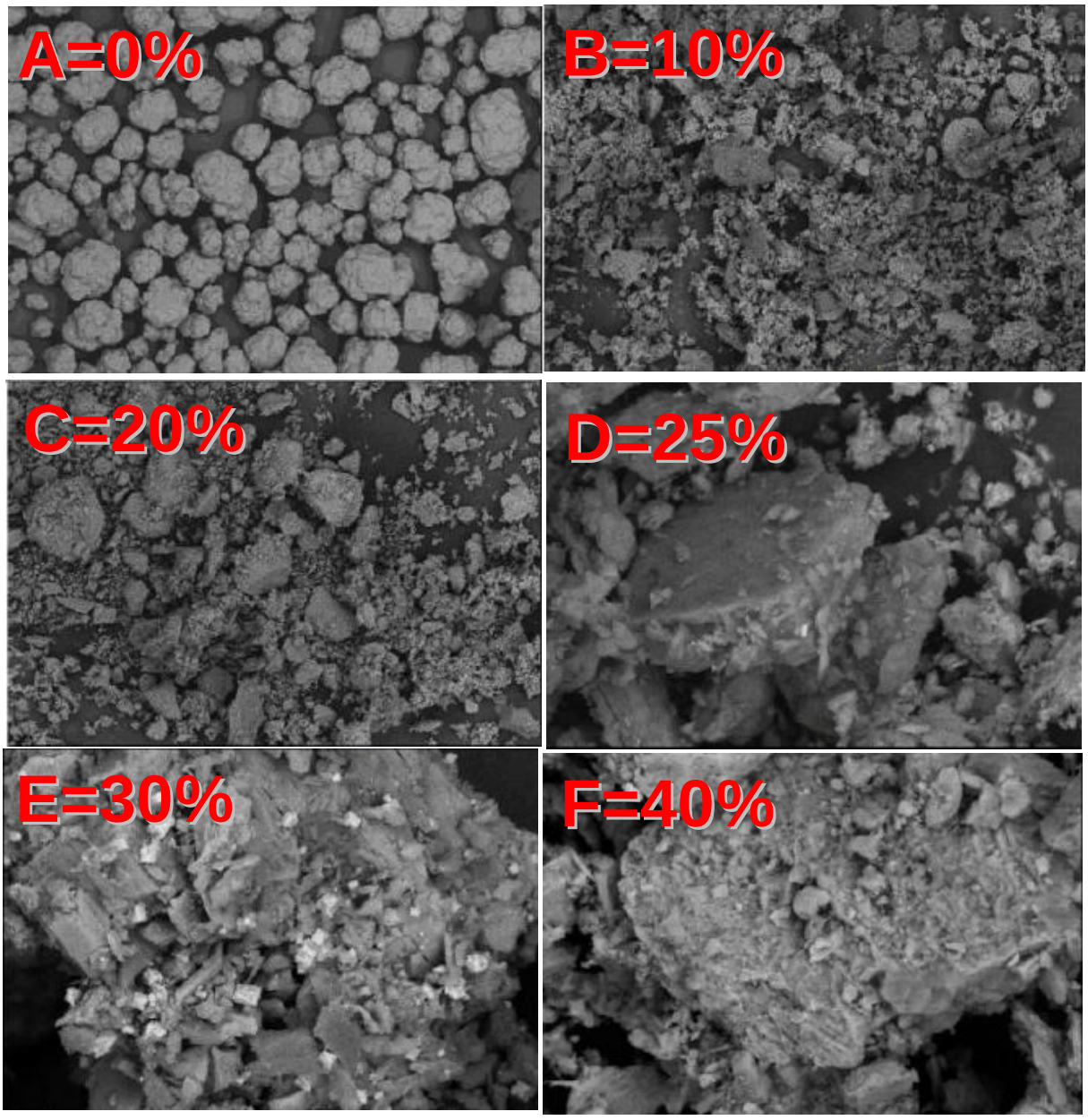


Figure 5.7 Scanning electron micrographs of (A) 0 wt.% catalyst, (B) 10 wt.% catalyst, (C) 20 wt.% catalyst, (D) 25 wt.% catalyst, (E) 30 wt.% catalyst and (F) 40 wt.% catalyst.

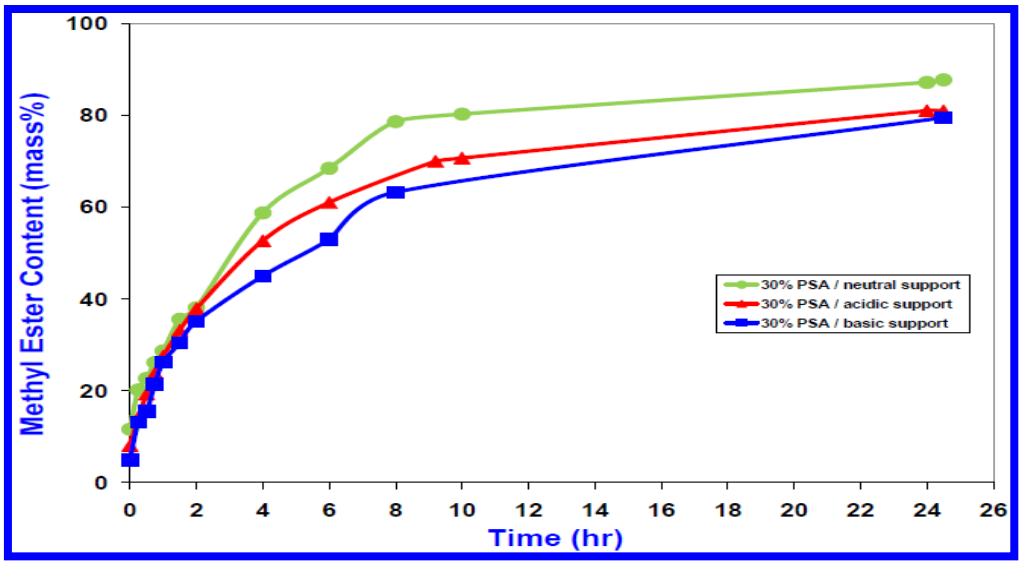


Figure 5.8 Effect of nature of support (neutral, acidic and basic) on ester content in the ester-rich phase as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: molar ratio of feed-to-alcohol (1:27), reaction temperature 200°C, stirring speed 600 rpm, 3 wt.% PSA solid acid catalysts (tungstophosphoric acid with 30% loading supported on neutral, acidic, and basic alumina).

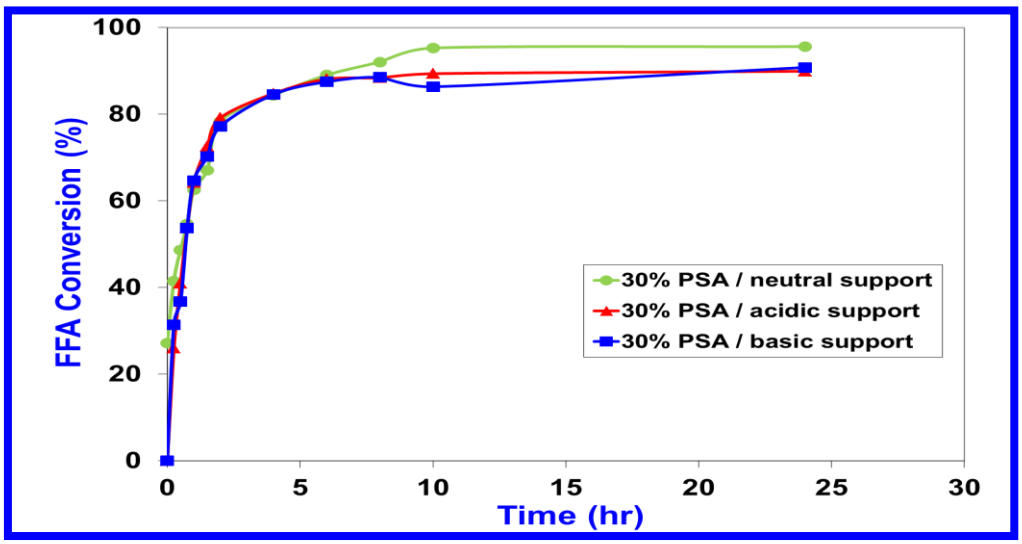


Figure 5.9 Effect of nature of support (neutral, acidic, and basic) on FFA conversion as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: molar ratio of feed-to-alcohol (1:27), reaction temperature 200°C, stirring speed 600 rpm, 3 wt.% PSA solid acid catalysts (tungstophosphoric acid with 30% loading supported on neutral, acidic and basic alumina).

5.3.4 Effect of co-solvent

Typically, the reaction mixture exists in two phases during transesterification. Mass transfer has been reported to be one of the major limitations due to such a two-phase system (alcohol-rich and oil-rich phase) (Boocook *et al.,* 1998). To overcome this mass transfer limitation, tetrahydrofuran (THF) has been used as a co-solvent so that both phases can be recombined into a single one. It was reported that the rate of reaction increased significantly after THF was added to the system. The advantage of using THF as co-solvent is its inert nature and boiling point (67°C) close to the boiling point of methanol (65°C), which makes separation and recovery more efficient. Also, it could help to reduce the rate of mixing which ultimately results in low energy consumption and improves the economical feasibility of the process.

Therefore, THF has been selected as a co-solvent to study its effect on mass transfer of transesterification. Its effect on the production of biodiesel from yellow grease using solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) is shown in Figures 5.10 and 5.11. The results show that the presence of THF decreases the ester yield. With and without THF as a co-solvent, the ester yields of 78.59% and 87.25%, respectively, were obtained after 24 h. However, it appeared at high mixing rate (i.e. 600 rpm) external mass transfer has been overcome (as reported in the literature) and the use of THF causes the rate of ester formation to slow down. This may be attributed to the deactivation of the catalyst due to the absorption of THF on catalyst surface.

5.3.5 Effect of rate of mixing

To address the external mass-transfer limitations on simultaneous esterification and transesterification, the effect of rate of mixing has been studied using 400, 600, and 800 rpm as shown in Figure 5.12. It can be seen that when rate of mixing increased from 400 to 600 rpm, the ester yield was also increased.The maximum ester yield was obtained at 600 rpm. It was found that the external diffusion control was negligible for stirrer speed greater than 600 rpm. Therefore, 600 rpm has been selected as the optimum stirrer speed.

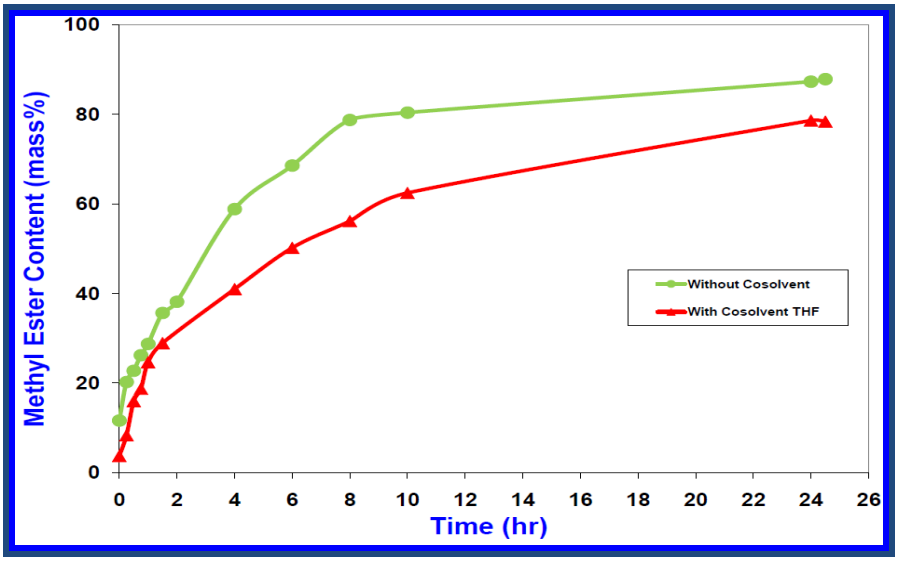


Figure 5.10 Effect of THF as co-solvent on ester content in the ester-rich phase as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: molar ratio of feed-to-alcohol (1:27), volume ratio of alcohol-to-THF (1:1), reaction temperature 200°C, stirring speed 600 rpm, 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

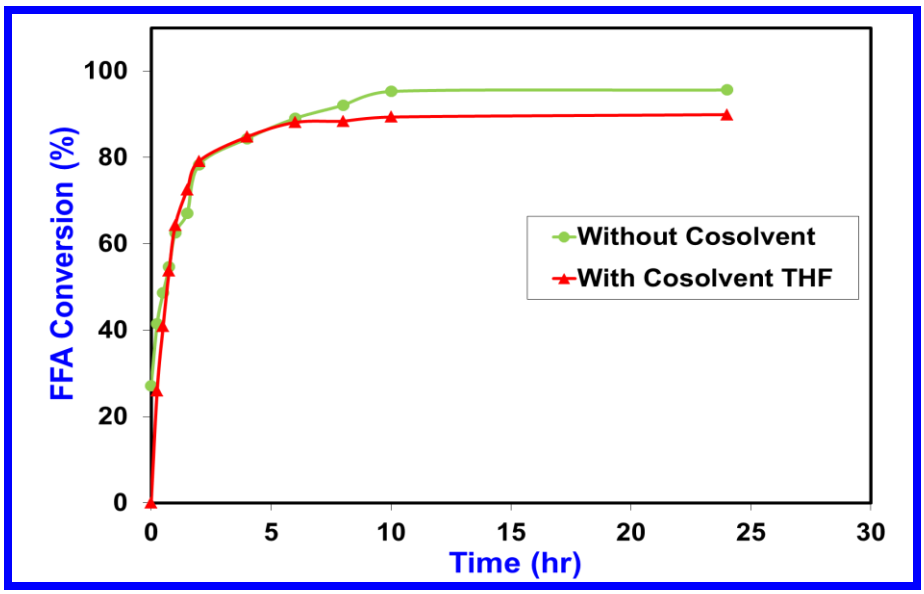


Figure 5.11 Effect of THF as co-solvent on FFA conversion as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: molar ratio of feed-to-alcohol (1:27), volume ratio of alcohol-to-THF (1:1), reaction temperature 200°C, stirring speed 600 rpm, 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

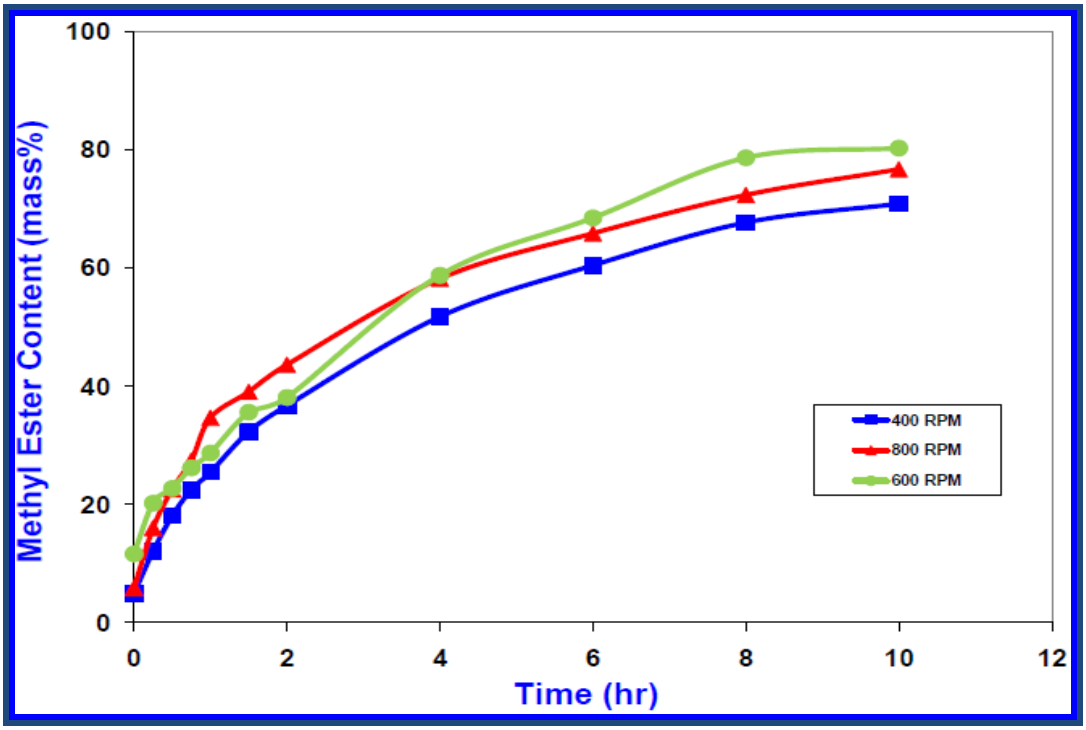


Figure 5.12 Effect of rate of mixing on ester content in the ester-rich phase as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: rate of mixing (400, 600 and 800 rpm), reaction temperature 200°C), molar ratio of feed-to-alcohol 1:27, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

5.3.6 Effect of water

Generally, FFA and water are considered to be poisons for conventional homogeneous acid and base-catalyzed biodiesel production processes (Freedman *et al*., 1984; Ma *et al*., 1998). In order to study the effects of water, 5% water was added to the feedstock (yellow grease). Effects of water on FAME yield are shown in Figure 5.13. It was found that the addition of water decreased the rate of reaction and caused less FAME to form. This may be due to the deactivation of the catalyst by the adsorption of water on its surface. However, even with this decrease in FAME yield, the performance is still better than for conventional homogeneous sulfuric acid and sodium hydroxide based processes in which FAME yields decreased to 78% and 11%, respectively (Canakci *et al.*, 1999; Fukuda *et al.*, 2001, Kulkarni *et al.*, 2006c).

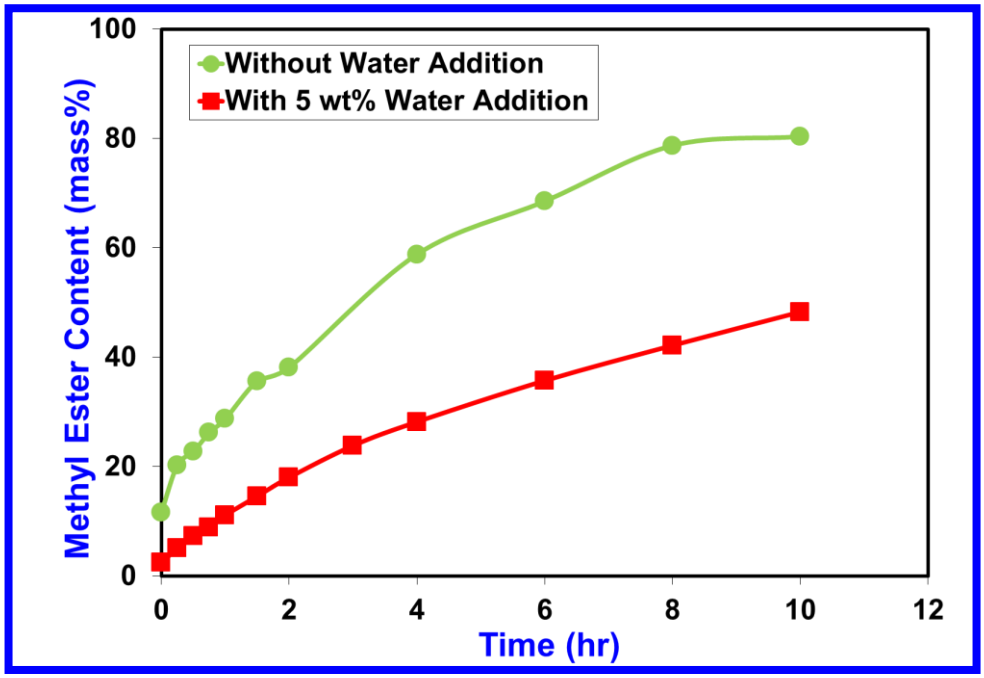


Figure 5.13 Effect of water content on ester content in the ester-rich phase as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock with 5% water addition. Reaction conditions: rate of mixing (400, 600 and 800 rpm), reaction temperature 200°C), molar ratio of feed-to-alcohol 1:27, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

5.3.7 Effect of glycerol on biodiesel yield

Since transesterification of triglyceride is a reversible reaction, the removal of glycerol produced during the reaction should shift the equilibrium towards the direction of ester formation. Furthermore, this becomes more critical in the case of batch reactors.

In order to achieve biodiesel at European specifications, which required > 96.5% methyl ester yield, removal of glycerol has been shown to increase the conversion of triglyceride to methyl ester by about 4% when transesterification was conducted in two successive stages of reaction and glycerol separation (Bournay *et al.*, 2005).

Therefore, as a part of process development, an experiment (in duplicate) was carried out in two successive stages with the removal of glycerol for simultaneous esterification and transesterification of yellow grease using solid acid catalyzed process with reaction conditions: reaction temperature 200°C, 1:27 molar ratio of feed-to-alcohol, stirring speed 600 rpm, catalyst 3 wt.%, 600 psi, 24 h reaction time. At the end of the first step after 24 h reaction time, glycerol and methanol were separated. Then, the final product of this first step was used as feedstock for the second step using the fresh catalyst and methanol under the same reaction conditions as used in the first step. It was found that ester yields after 1^{st} and 2^{nd} steps were 82.62 mass % and 85.77 mass %, respectively. The removal of glycerol from the reaction may shift the reaction in forward direction, i.e. an increase in the formation of methyl ester (Bournay et. al., 2005).The maximum yield of 86.89 mass % was achieved using this two stage process.

5.3.8 Effect of reaction temperature

One important process parameter for the production of biodiesel is temperature, which can influence the yield. Furthermore, a change in reaction temperature for both transesterification and esterification would be expected to influence the reaction rates. A decrease in reaction temperature is favorable with respect to the industrial applications as it will result an economical process with less energy consumption and low pressure requirement. Therefore, the effect of temperature on esterification and transesterification has been studied at 150°C, 175°C, 200°C, 225°C as shown in Figure 5.14 and 5.15, respectively. These will also provide the data for kinetic studies.

The conversion of FFA during esterification at 175, 200 and 225°C is shown in Figure 5.14. It can be seen that as the temperature increases, the rate of esterification also increases. However, an equilibrium conversion of about 95% is obtained at 175 and 200°C. At 225°C, the rate of FFA conversion was initially higher than at 175°C and 200°C, but begins to decrease after 6 h. This may be due to the hydrolysis of methyl ester (ME) to FFA by water produced by esterification, which shifts the equilibrium in the backward direction.

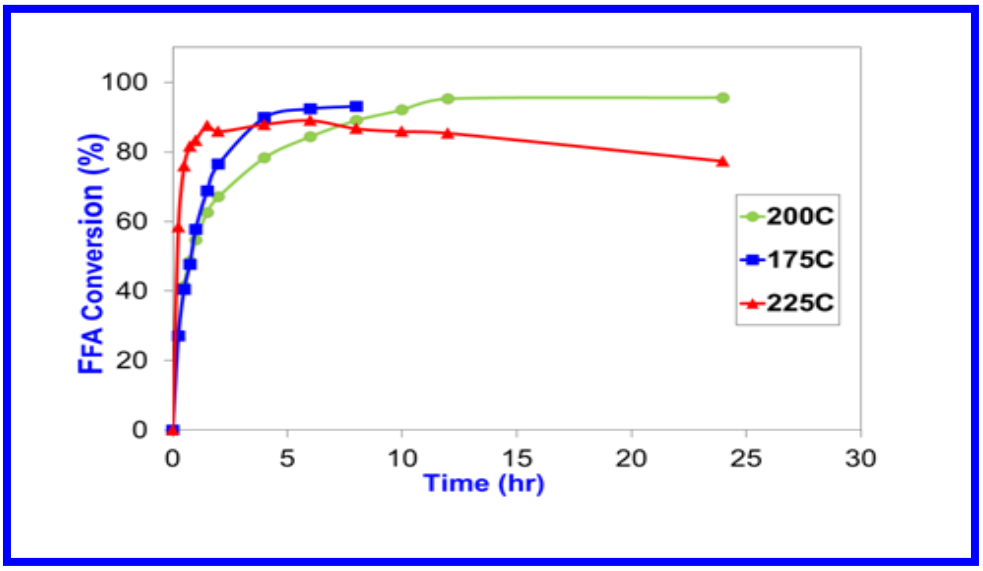


Figure 5.14 Effect of temperature on the conversion of FFA as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: reaction temperature (175, 200 and 225°C), molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

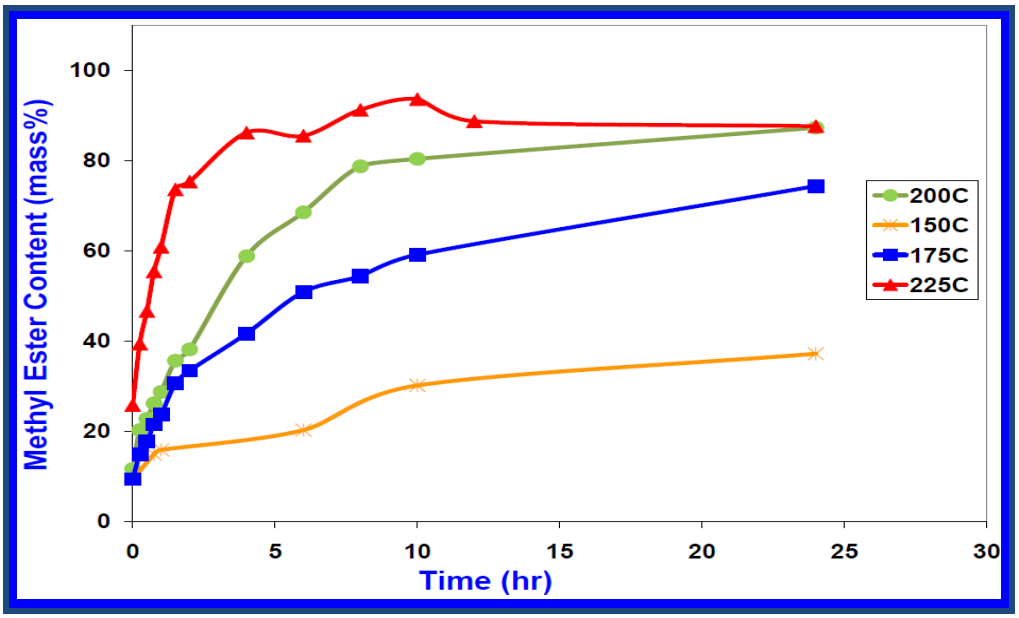


Figure 5.15 Effect of temperature on ester content in the ester-rich phase as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: reaction temperature (150°C, 175°C, 200°C and 225°C), molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

The effect of temperature on ester content during simultaneous esterification and transesterification for the production of biodiesel from yellow grease is shown in Figure 5.15. It was found that an increase in reaction temperature resulted in an increase in the ester content. Ester contents of 37.18%, 74.35%, 87.81%, and 87.61% were obtained at 150°C, 175°C, 200°C and 225°C after 24 h reaction time, respectively. Although the rates of both esterification and transesterification increased as temperature rose, esterification already remained faster than transesterification at all temperatures as shown in Figure 5.14 and 5.15. Differences in the rates could be attributed to the easier interaction of small free fatty acid molecules with alcohol as compared to triglyceride (very large molecule) as well as other steps of esterification and transesterification. However, when the reaction was carried out above 200°C, polymeric products could be formed by the degradation of triglycerides and unsaturated fatty acids due to exposure of oil to high temperature for long reaction times (Kulkarni *et al.*, 2006c). Since the formation of polymeric compounds is not desirable during biodiesel production, 200°C has been selected as the optimum reaction temperature for simultaneous esterification and transesterification reactions.

5.3.9 Optimum conditions for simultaneous esterification and transesterification

Results for the production of biodiesel from yellow grease using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst is shown in Figures 5.16 and 5.17. This solid acid catalyst showed promising activity towards simultaneous esterification and transesterification of yellow grease with 9.1% FFA.

It was found that FFA presents in yellow grease were converted to biodiesel with 95% conversion using solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) which is similar to the FFA conversion of ~ 95% using sulfuric acid as a homogeneous catalyst (as shown in Chapter 3, section 3.2.3).. Furthermore, yellow grease was successfully transesterified with ester content of 87.25 mass % in the ester-rich phase. This catalyst is suitable to catalyze not only the esterification reaction but also the

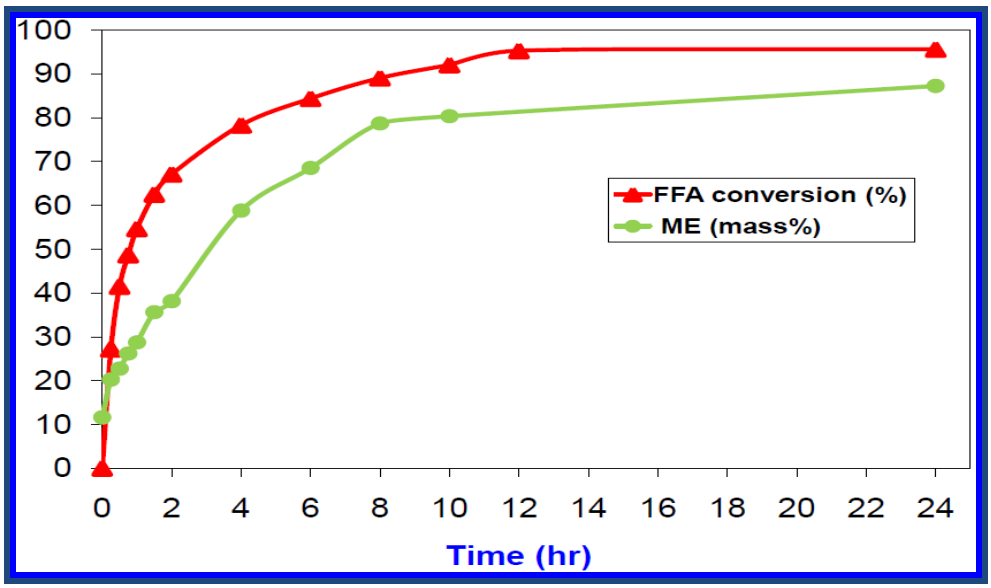


Figure 5.16 FFA conversion and ME (mass %) content as a function of time for simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

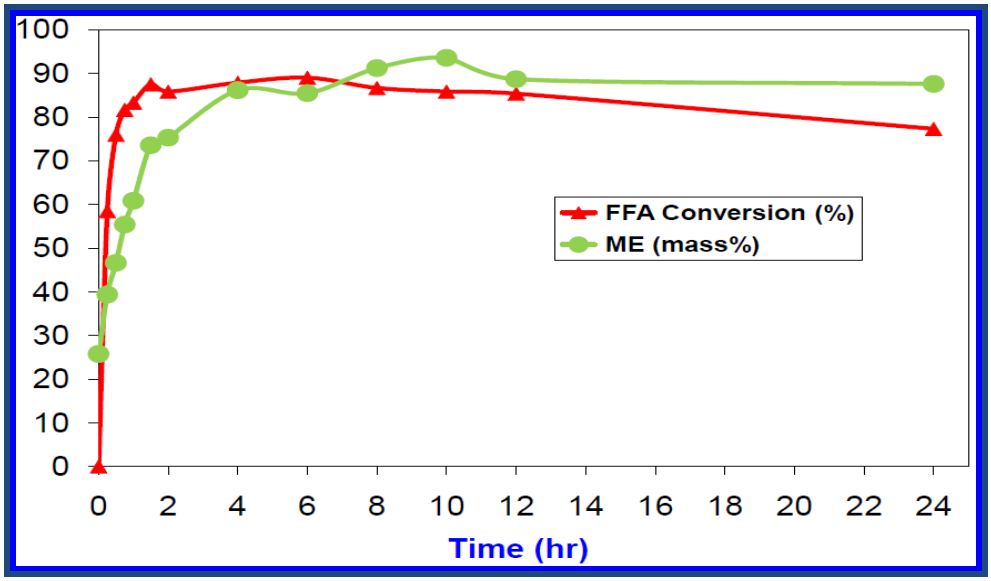


Figure 5.17 FFA conversion and ME (mass %) content as a function of time for simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: reaction temperature 225°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

transesterification reaction. Biodiesel analysis based on the ASTM D974 and EN 14103 standards (as validated in Chapter 3; section 3.1) confirmed the production of high-purity biodiesel from yellow grease.

5.3.10 Composition of biodiesel produced from yellow grease

Yellow grease (feedstock) and the biodiesel produced from yellow grease using single-step solid acid catalyzed process are shown in Figure 5.18 and 5.19, respectively.

Figure 5.18 Yellow grease (feedstock).

Figure 5.19 Biodiesel produced from yellow grease.

FAME (wt %)										
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
0	0.00	18.42	10.78	49.58	21.21	0.00	0	0.00	0.00	0.00
0.25	0.00	17.25	9.94	50.82	20.31	3.05	0	0.00	0.00	0.00
0.5	1.01	16.78	9.63	49.66	19.85	3.07	0	0.00	0.00	0.00
0.75	1.00	16.49	9.47	49.62	19.76	3.02	0	0.00	0.65	0.00
1	0.99	16.35	9.40	49.46	19.70	3.01	0	0.56	0.53	0.00
1.5	1.01	16.41	9.42	49.76	19.81	3.04	0	0.55	0.00	0.00
2	1.01	16.36	9.38	49.81	19.84	3.04	0	0.55	0.00	0.00
4	1.02	16.21	9.27	49.79	19.85	3.02	0	0.84	0.00	0.00
6	1.03	16.07	9.17	49.65	19.87	2.99	0.38	0.84	0.00	0.00
8	1.03	16.04	9.14	55.41	23.34	2.97	0.38	0.84	0.00	0.00
10	1.02	15.86	9.03	49.31	19.75	3.58	0.37	0.83	0.24	0.00
24	1.03	15.90	9.04	49.60	19.79	3.41	0.37	0.85	0.00	0.00
24.5	1.03	15.92	9.03	49.52	19.74	3.54	0.37	0.85	0.00	0.00

Table 5.4 Composition of FAME produced from yellow grease as feedstock using solid-acid catalyzed process as a function of time. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 800 rpm, 3 wt.% of solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

Our results for FAME composition at t=0 as shown in Table 5.4 are in accordance with the literature reported compositions of feedstocks (yellow grease) as shown in Table 5.2.

The typical chromatograms obtained for samples of yellow grease-based biodiesel as per EN 14103 (as validated in Chapter 3; section 3.1) is shown in Figure 5.20. The large peaks observed in the chromatogram are the FAMEs present in the samples (C16 and C18). Also, it shows the regions of the chromatogram where different FAME (from C14 to C24 carbon chains including saturated and unsaturated) of yellow grease elute.

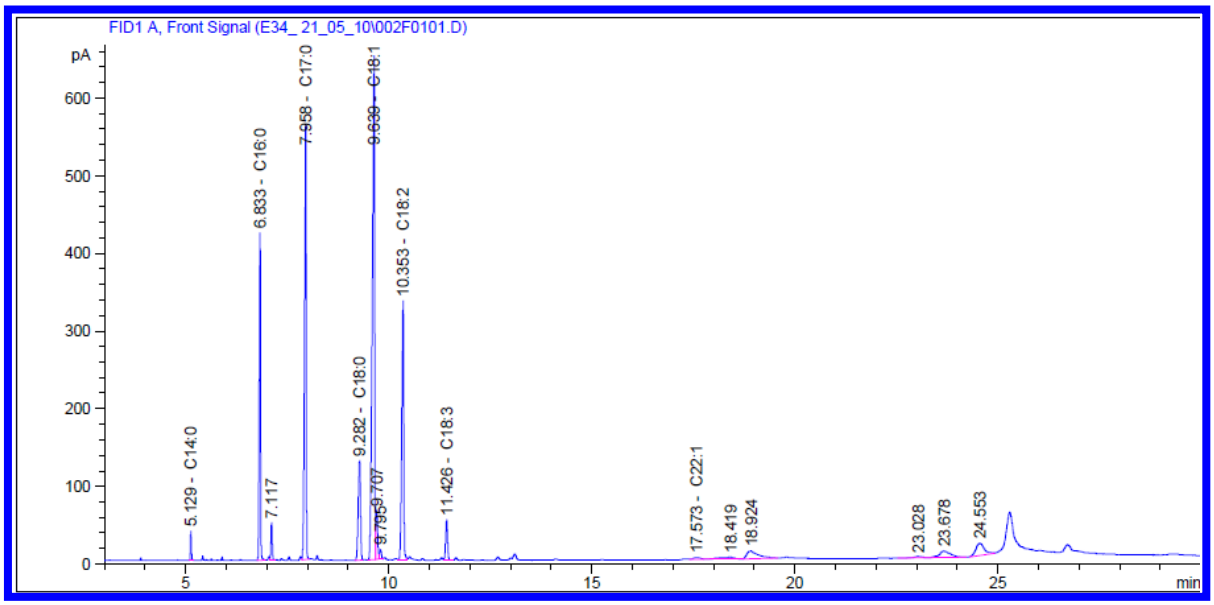


Figure 5.20 GC chromatogram showing typical analysis of ester content in the yellow grease methyl ester (biodiesel) sample as per EN 14103.

Furthermore, a higher amount of unsaturation in FAME remains a major challenge for the stability of biodiesel. A higher degree of unsaturation can result in oxidation of biodiesel, which affects its stability during storage. Due to these problems, in biodiesel quality standards such as EN 14103, the amount of linolenic ester (C18:3) has been restricted to the maximum value of 12%. However, this limit has been set to accommodate the use of rapeseed oil (high linolenic C18:3 content), which is one of the major crops produced in European Union as a feedstock for biodiesel production. However, a decrease in C18:3 is highly desirable to enhance the stability of biodiesel.

As shown in Table 5.4 and 5.7, it can be seen that soybean oil contains higher amount of C18:2 (51.5%) and C18:3 (7%). On the other hand, FAME produced from yellow grease contains only 20% and 3% of C18:2 and C18:3, respectively. Therefore, yellow grease could be used as an economical feedstock to produce biodiesel with enhanced stability to meet quality standards requirements for industrial scale production of biodiesel.

5.4 Kinetic studies

Although the importance of biodiesel as an alternative fuel has grown during the last twenty years, the chemical kinetics of transesterification, very important for process design, remains controversial. A study of kinetics of transesterification will provide parameters that can be used to predict the extent of the reaction at any time under particular conditions.

In this study, a single-step kinetic model for overall transesterification reaction (including simultaneous esterification) was used (Srilatha *et al*., 2010). When the overall transesterification reaction (including simultaneous esterification) is considered as first-order, then a plot of –ln (1-x) versus time should be linear with a slope equal to the rate constant k as per reported literature. The term "x" is the biodiesel yield (methyl ester content; mass %) and it is measure as per EN 14103. Plots of –ln (1-x) versus time at different temperatures are shown in Figure 5.21. All plots validating a first-order model yield straight lines with good values of R^2.

The rate constants as a function of temperature were determined by taking the slope of the plot of ln (k) *vs* 1/T. This method was based on the Arrhenius equation, which relates reaction coefficients to temperature:

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

where,

A= is the Arrhenius pre-factor and Ea= is the activation energy of the reaction.

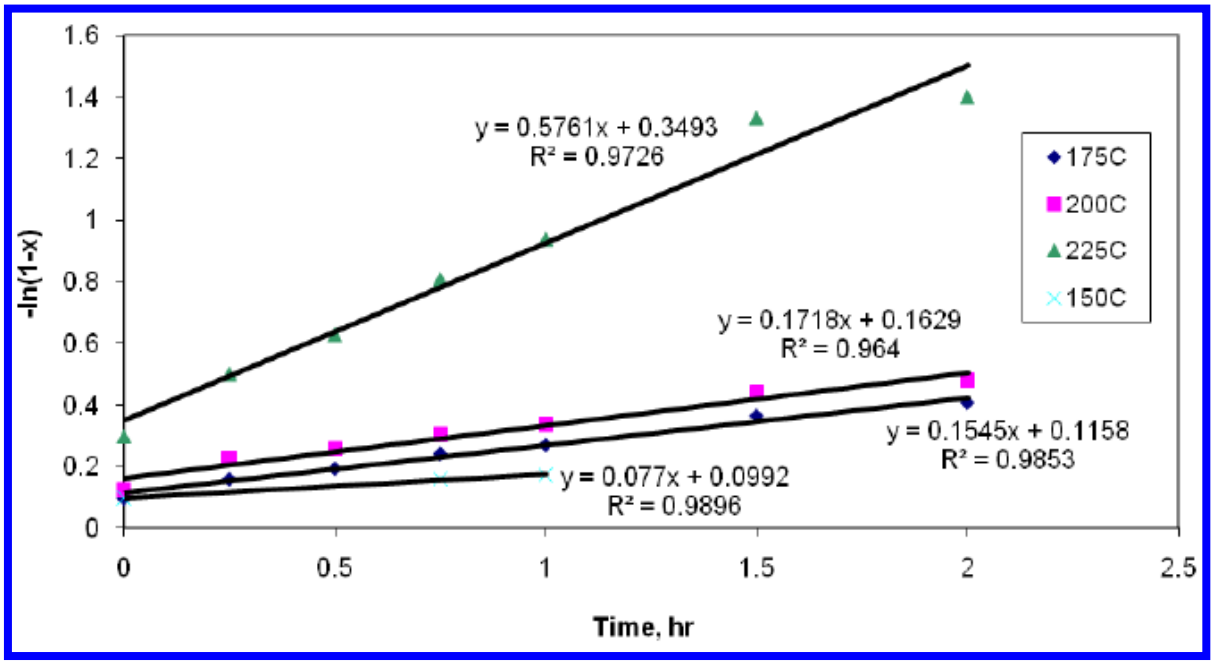


Figure 5.21 Plots of –ln (1-x) versus time at different temperatures. Reaction conditions: molar ratio of feed-to-alcohol (1:27), reaction temperature (150°C, 175°C, 200°C and 225°C), stirring speed 600 rpm, 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

By taking the ln of both sides of the equation,

$$\ln(k) = -\frac{E_a}{RT} + \ln(a)$$

This equation is linear with respect to 1/T. If k is determined for varying temperatures, the plot of ln (k) *vs* 1/T should produce a straight line of slope –Ea/R, as shown in Figure 5.22. The values of rate constants at the four reaction temperatures over a reaction time (0–2 h) with the corresponding correlation coefficient are listed in Table 5.5. It can be seen that, in the case of 0-2 h initial period, the rate constants values have good R^2 values. The activation energy as calculated from the slope of the Arrhenius plot in Figure 5.20 was 42.6 kJ/mole. Activation energy could help to determine whether the reaction rate is diffusion limited (mass transfer limited) or it is controlled by the chemic step where the catalyst is being used to its maximum capacity (Shringarpure *et al*., 2011). According to the literature (Bond,

1974), the activation energy for diffusion limited (mass transfer limited) reactons is as low as 10-15 kJ/mol, where, a truly chemical step governed reaction show activation energy excess of 25 kJ/mol. In our catalytic process, the observed activation energy is 42.6 kJ/mol, and hence, it could be concluded that the rate of reaction is truly governed by chemical step.

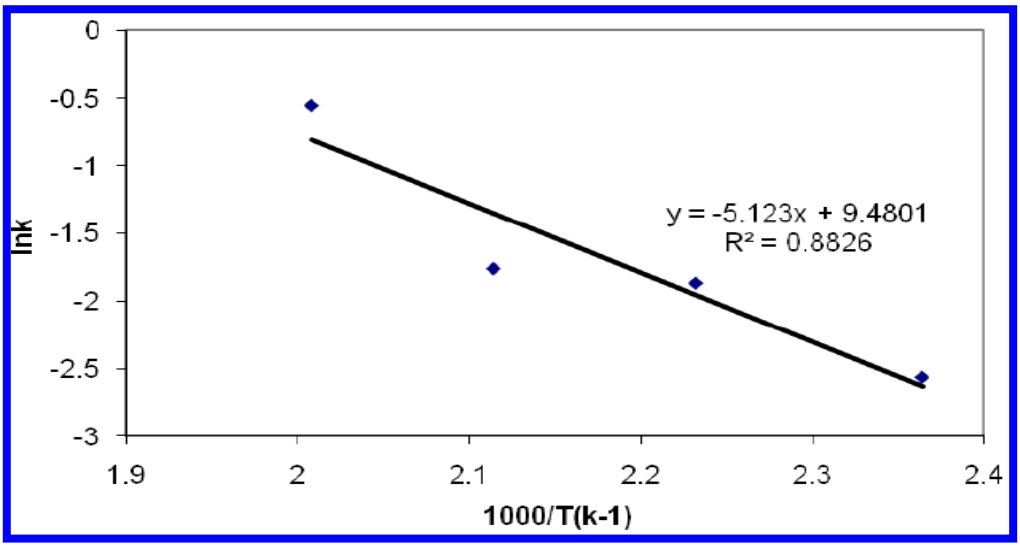


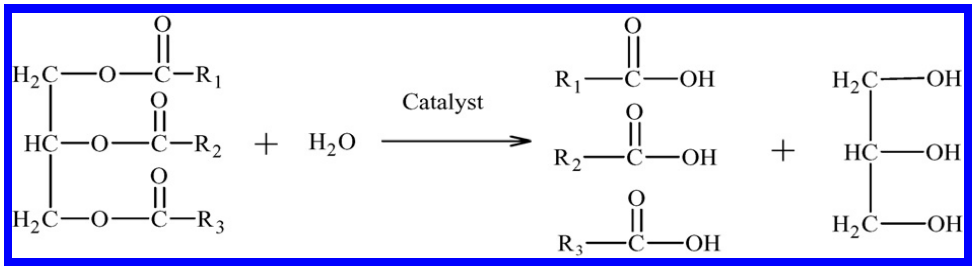
Figure 5.22 Arrhenius plot of ln *k* versus 10^3/T for simultaneous esterification and transesterification. Reaction conditions: molar ratio of feed (yellow grease)-to-alcohol (1:27), reaction temperature (150°C, 175°C, 200°C and 225°C), stirring speed 600 rpm, catalyst 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

Table 5.5 Kinetic parameters, rate constants, activation energy, and Arrhenius constant.

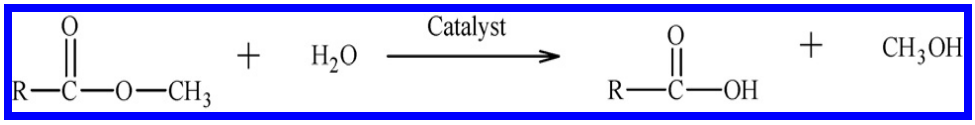
Temperature	Rate Constant		Activation Energy and Arrhenius Constant	
	K (mass%.min^{-1})	R^2	Ea (kJ/mole)	A (sec^{-1})
150° C	0.0770	0.9896	42.6	9.4801
175° C	0.1545	0.9853		
200° C	0.1718	0.9640		
225° C	0.5761	0.9726		

5.5 Hydrolysis studies

The presence of water in the waste feedstock makes it very challenging to control the process chemistry of biodiesel production due to the hydrolysis reactions as shown in Scheme-5.1. Waste oils and fats such as yellow grease contain a high amount of water. The presence of water can result in the hydrolysis of both triglycerides (feedstock) and FAME (biodiesel). The hydrolysis of triglyceride produces free fatty acids and glycerol as in Equation (**5.2**), whereas the hydrolysis of FAME also produces FFA in addition to methanol as in Equation (**5.3**).



(**5.2**)

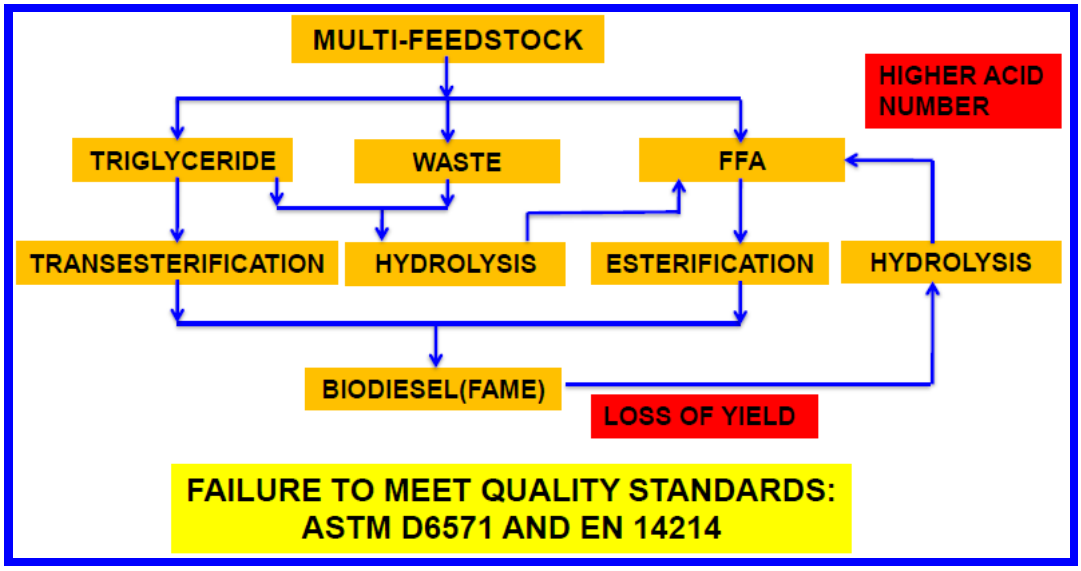


(**5.3**)

These side reactions are highly undesirable as they not only increases the acid number (FFA), but also consume FAME product. This could lead to quality standards, such as ASTM D6571 and EN 14214. Therefore, it is very important to develop a process in which the hydrolysis of fatty acid methyl esters and triglycerides is minimum.

Hydrolysis of food-grade soybean oil in the presence and the absence of the catalyst change the FFA content. Fortunately, the hydrolysis of soybean oil was found not to occur even at

temperatures below 220°C, as shown in Figure 5.23 and 5.24. Figure 5.25 and 5.26 confirm that hydrolysis of biodiesel did not take place below 200°C as there was no significant decrease in methyl ester and increase in FFA until 220°C. Therefore, for our proposed process, a temperature of 200°C is considered optimum to minimize the extent of hydrolysis.



Scheme 5.1 Process chemistry for the production of biodiesel from multi-feedstocks (transesterification, esterification, and hydrolysis).

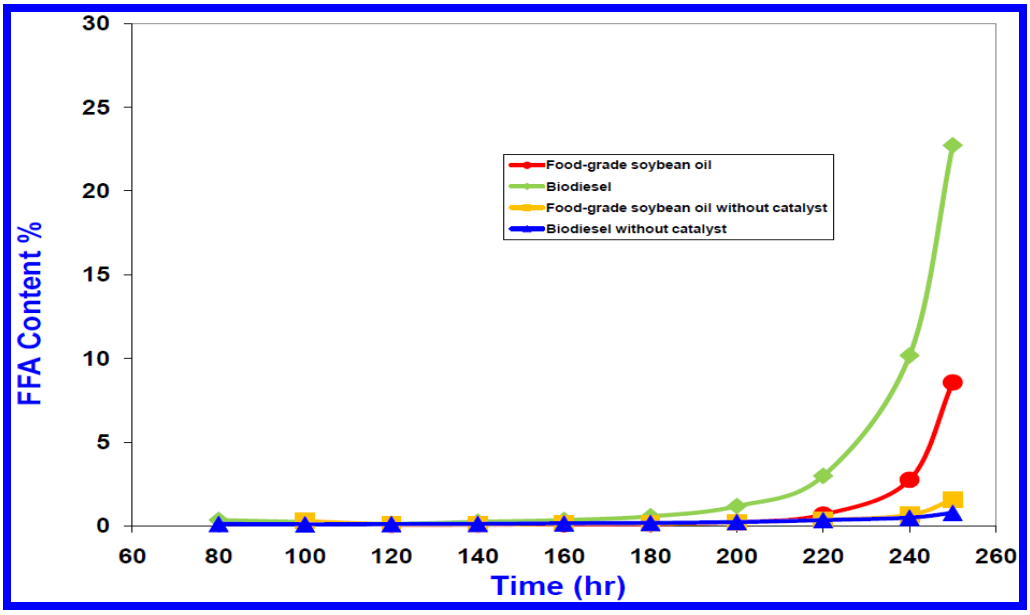


Figure 5.23 Hydrolysis of food-grade soybean oil and biodiesel in the presence and the absence of catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

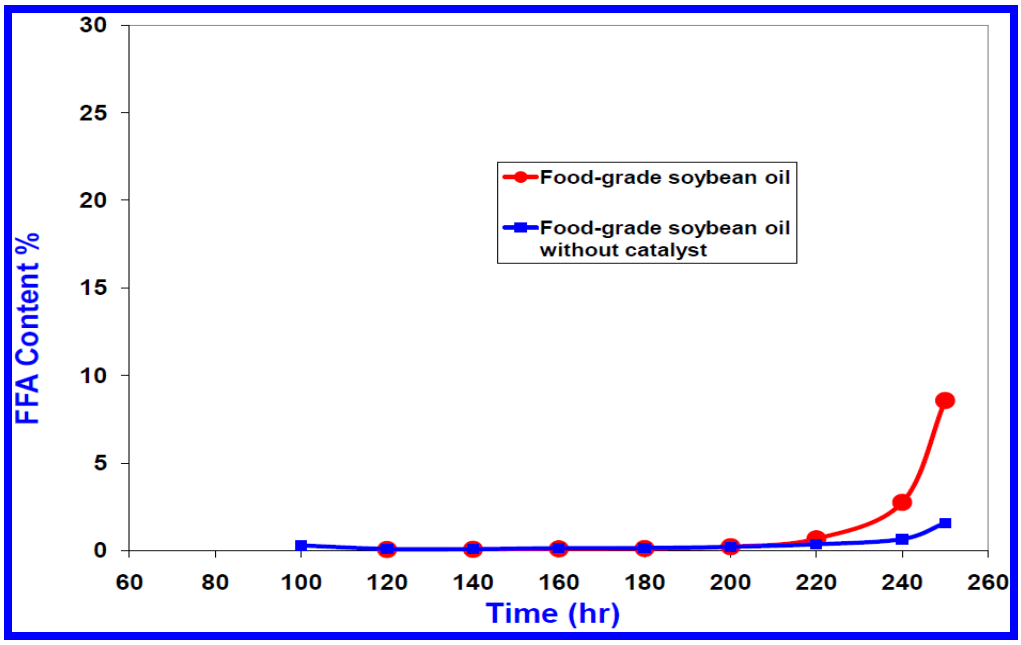


Figure 5.24 Hydrolysis of food-grade soybean oil in the presence and the absence of catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

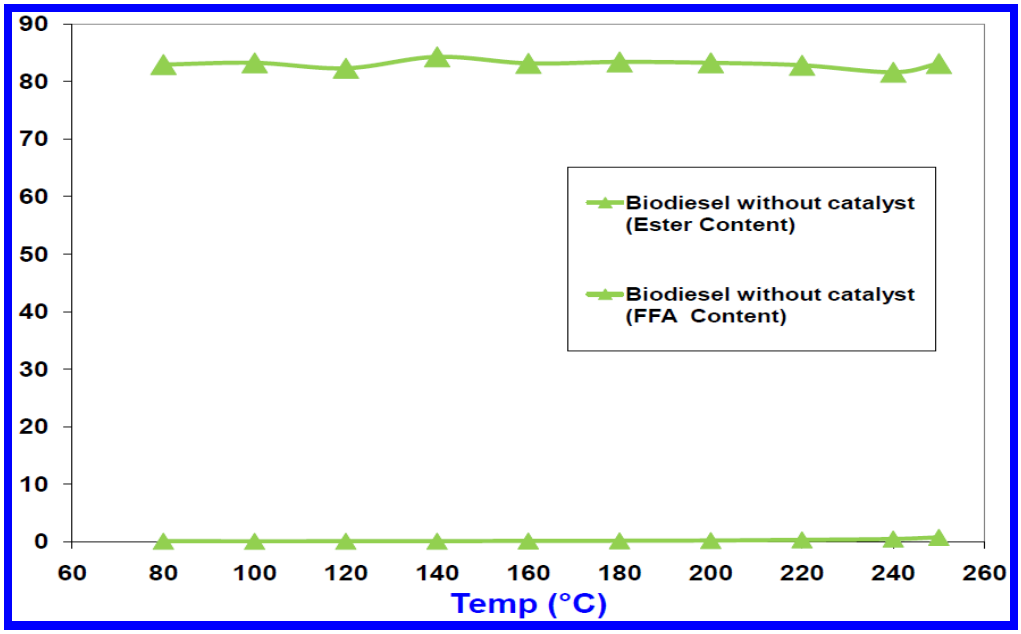


Figure 5.25 Hydrolysis of biodiesel in the presence and the absence of catalyst. Free Fatty Acid content (%) as a function of temperature.

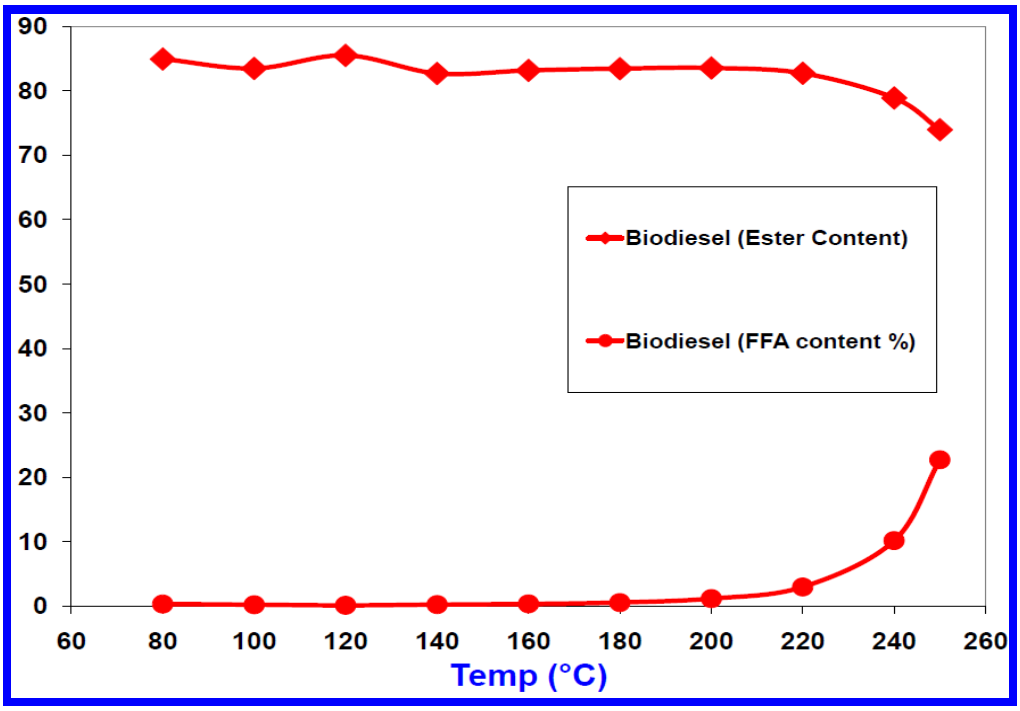


Figure 5.26 Hydrolysis of biodiesel in the presence and the absence of catalyst. Methyl ester content (mass %) as a function of temperature.

5.6 Recycling studies

Recycling of heterogeneous catalysts is one of the major features which make them attractive for industrial applications. In order to be considered for an industrial process, the efficiency of heterogeneous catalysts also depends on their reusability.

Identifying solid catalysts that show promising activity in short term tests is only a start. The commercial success of the catalyst at industrial-scale would be dictated by how long the catalyst can remain active. Catalyst life is more crucial than any other feature of the method. Catalyst life, recyclability and cost are essential features in order to be successful for commercial use since these features have a direct impact on overall cost of the process (Semwal *et al.*, 2011). Therefore, catalyst performance was studied over 5 cycles to yield the results shown in Figure 5.27.

After the first use and before every subsequent reuse, the catalyst was separated from the reaction mixture by filter and then by centrifuge from the reaction mixture. After separation, the catalyst was stirred in 100 mL of a mixture of methanol and hexane (volume ratio 1:1) for 3 h to remove any polar and non polar compounds present on the catalyst surface. Then, the catalyst was soaked in 100 mL of the solvent mixture (as stated before) for 6 h and then dried at 100°C for 10 h before using it for simultaneous esterification and transesterification. These experiments were repeated under optimum reaction conditions, i.e. oil-to-alcohol molar ratio of 1:27, reaction temperature of 200°C, mixing rate of 600 rpm, and 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

The recycling studies showed no considerable change in the catalytic activity of the catalysts even after five reaction cycles as shown in Figure 5.27. After 5 cycles, the catalyst activity remained at 96.6% of original level. The catalytical activities of the fresh and spent catalyst remained almost the same demonstrating that the spent catalyst could be regenerated.

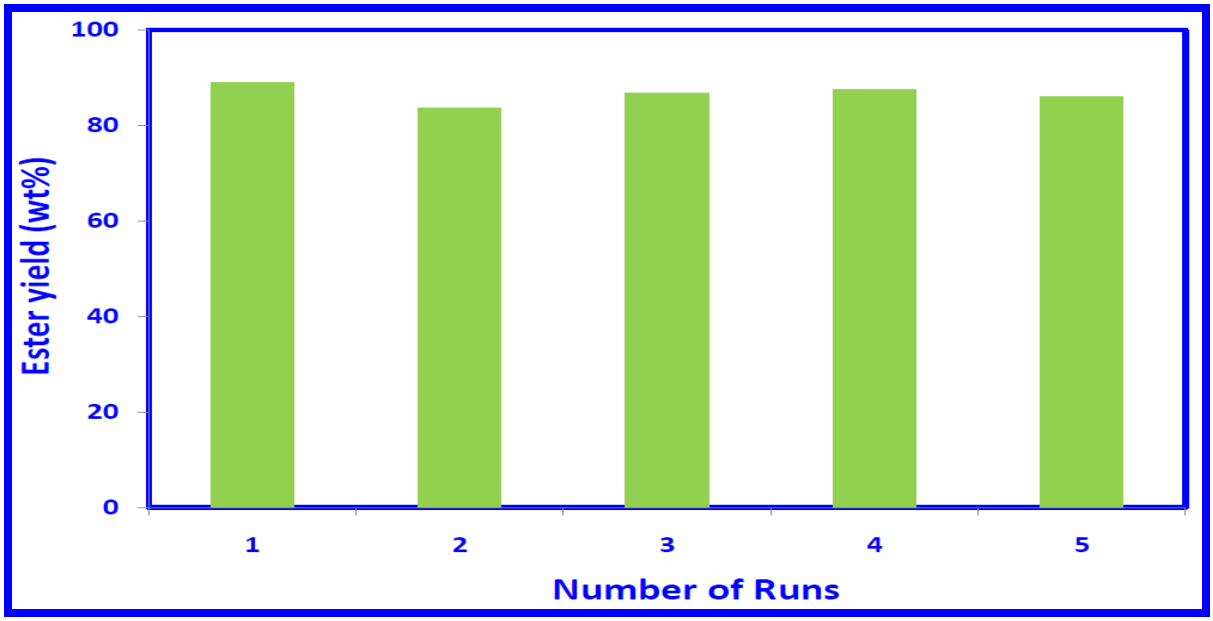


Figure 5.27 Recycling studies of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina). Reaction conditions: Reaction conditions: molar ratio of feed-to-alcohol (1:27), reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%.

To further investigate the effect of cycles on the catalyst, the physiochemical properties of the fresh catalysts and spent catalysts were measured. The surface area and porosity of recycled solid acid catalysts (tungstophosphoric acid with 30% loading supported on neutral alumina) after each of runs 1-4 are shown in Figure 5.28. Table 5.6 shows the values of BET specific area (S_{BET}), external surface area (S_{ext}), average pore diameter (D_{ave}) and pore volume (V_{pore}). The specific surface area and average pore diameter were determined using the BET method, while microporous volume and external surface area were determined by the t-method, using a standard isotherm.

These results show that the specific surface area and the pore volume decreased significantly after the first run as compared to fresh catalyst. This is expected due to the accumulation on surface and/or blockage of pores by large molecules (such as triglycerides) on catalyst. However, after the first run, both the surface area and pore volume increased with each run, presumably due to cleaning procedures after each run to remove polar and non-polar compounds from the catalyst surface. This finding is supported by the slight decrease in catalyst activity after the 1st run (Figure 5.27) which remained largely unchanged thereafter.

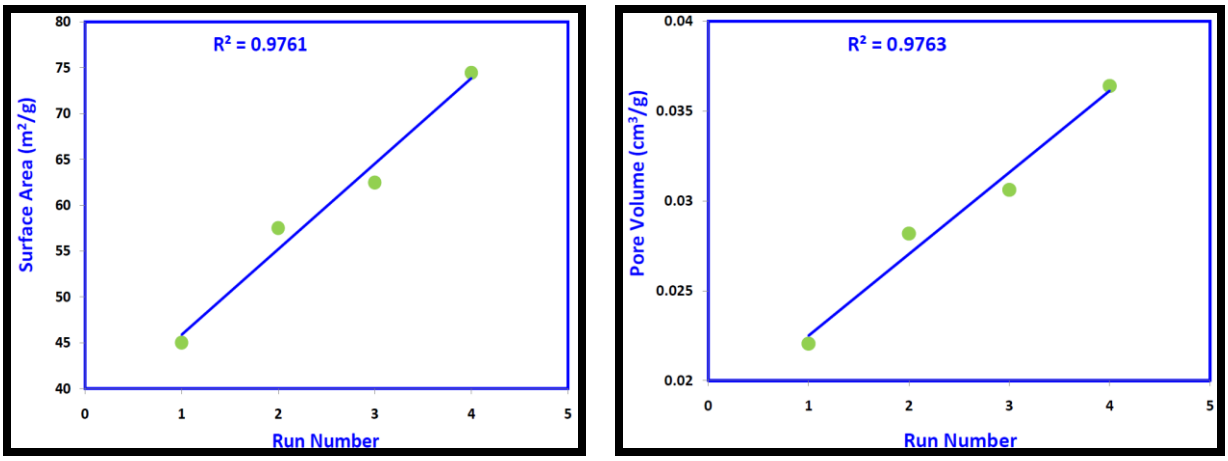


Figure 5.28 Surface area and pore volume of recycled catalyst as a function of number of runs.

The FAME composition during all recycling experiments was remained the same as show in Figure 5.29.

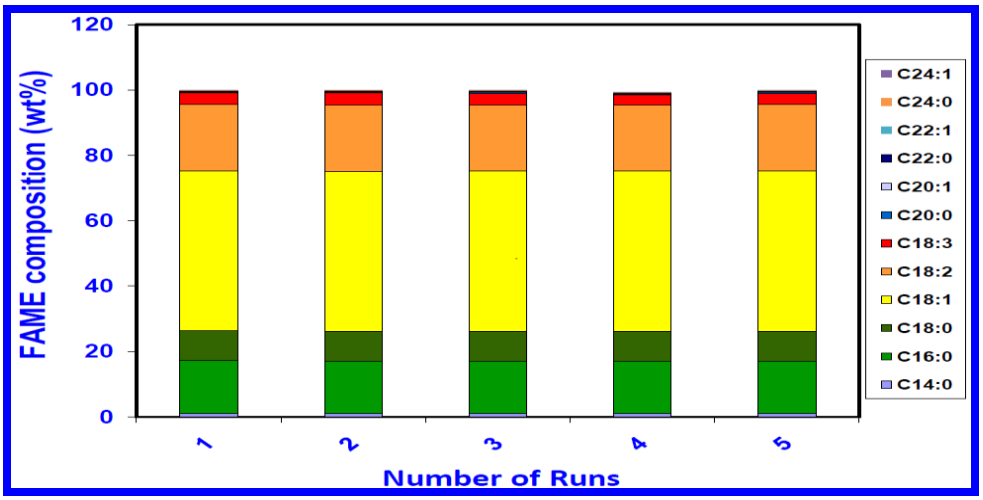


Figure 5.29 FAME compositions as a function of number of runs.

In order to simulate a real industrial application, an extensive recycling study was performed by using the catalyst for successive 12 runs without any cleaning or treatment between the runs. Even after 12 runs, the catalyst retained its original catalytical activitiy for both esterification and transesterification (Figure 5.30).

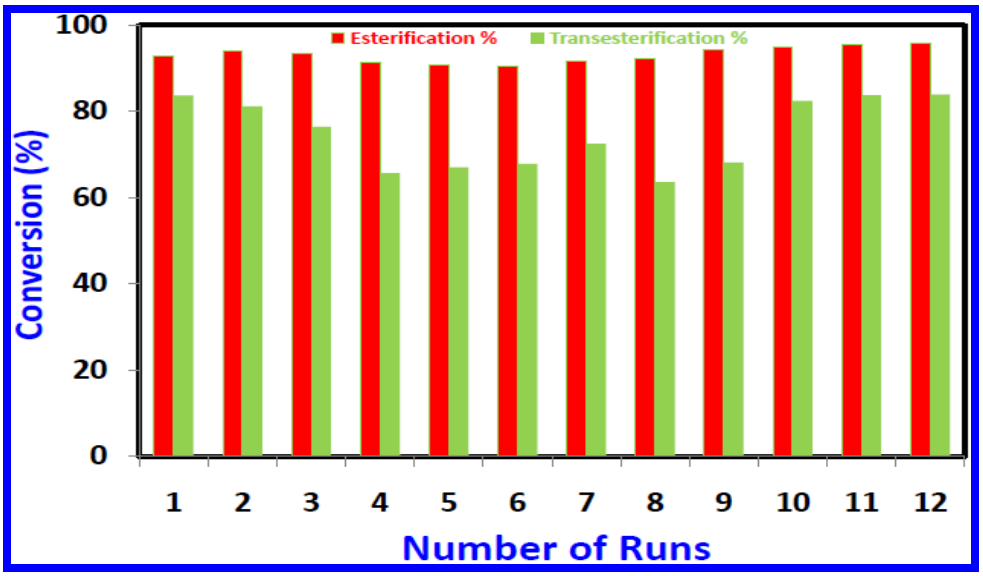


Figure 5.30 Recycling studies of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina). Reaction conditions: Reaction conditions: molar ratio of feed-to-alcohol (1:27), reaction temperature 200°C, stirring speed 600 rpm, catalyst 3 wt.%

Table 5.6 Textural properties and physicochemical characterization of recycled catalyst.

	Surface Area [a] (m^2/g)	External surface area[b] (m^2/g)	Average Pore Diameter [c] (°A)	Pore Volume [d] (cm^3/g)
Fresh Catalyst	107.4232	98.6782	19.8588	0.053332
After Run-1	45.0165	47.1805	19.5961	0.022054
After Run-2	57.5188	60.8600	19.5994	0.028183
After Run-3	62.480	65.458	19.6024	0.030619
After Run-4	74.4562	80.5980	19.5552	0.0364000

[a] BET; [b] t-Method ; [c] Average BET pore diameter; [d] Single point total pore volume.

Composition of FAME:

The composition of fatty ester in the biodiesel dictates its final fuel properties. Since each bio-feedstock has a unique chemical composition, the biodiesel produced from different feedstocks will in turn have different properties. Important properties of biodiesel that are directly influenced by fatty ester composition are its oxidative and storage stability (Moser, 2009).

The composition of FAME produced from soybean oil and yellow grease are shown in Tables 5.7 and 5.8. FAME produced from yellow grease has higher amount of saturated compounds compared to that produced from soybean oil. For example, the percentages of methyl palmitate (C16:0) and methyl stearate (C18:0) when yellow grease was used as feedstock were approximately 16.5% and 9.5% compared to 10.4% and 4.1% when soybean oil was used. The FAME produced from a feedstock, should have similar composition of FAME as in the feedstock used for biodiesel production.

Our results for FAME composition shown in Table 5.7 and 5.8 are in accordance with the literature reported compositions feedstocks produced from soybean oil and yellow grease reported in the literature (Table 5.2). Furthermore, higher amount of unsaturation in FAME remains a major challenge for the stability of biodiesel.

Table 5.7 Composition of FAME produced using soybean oil as feedstock using solid-acid catalyzed process as a function of time. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

	FAME (wt%)									
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
0.5	0.00	10.72	4.10	26.90	51.58	6.41	0	0.00	0.30	0.00
1.0	0.03	10.52	4.20	26.76	51.39	6.83	0	0.00	0.28	0.00
2.0	0.03	10.41	4.15	26.70	51.40	7.05	0	0.00	0.26	0.00
3.0	0.04	10.28	4.02	26.13	51.65	7.35	0.24	0.00	0.25	0.00
4.0	0.04	10.12	4.01	25.95	51.74	7.38	0.24	0.19	0.24	0.00

A higher degree of unsaturation makes the biodiesel more prone to oxidation of biodiesel which affects its stability during storage. Due to these problems, the amount of linolenic ester (C18:3) is been restricted in biodiesel quality standards such as EN 14103 to a maximum value of 12%. However, this limit has been set to accommodate the use of rapeseed oil (high linolenic C18:3 content) which is one of the major crops produced in the European Union as a feedstock for biodiesel production. However, a lower C18:3content is highly desirable to enhance the stability of biodiesel. It can be seen that soybean oil produce higher biodiesel with C18:2 (51.5%) and C18:3 (7%) levels (Table 5.7). On the other hand, FAME produced from yellow grease (Table 5.8) contained only 20% and 3% of C18:2 and C18:3, respectively. Therefore, yellow grease could be used as an economical feedstock to produce biodiesel with enhanced stability that meets quality standards for industrial scale production.

5.7 Conclusion

This heterogeneous-catalyzed process has shown promising results simultaneously for both esterification and transesterification reactions. GC analysis based on the ASTM D974 and EN 14103 standards confirmed the production of high-purity biodiesel from multi-feedstock (yellow grease). As part of process development, the effects of parameters including catalyst

loading, feed to alcohol molar ratio, reaction temperature, rate of mixing, nature of support and co-solvent have been studied and optimized. The optimized process parameters are: 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina), 200°C, 600 rpm, 1:27 feed-to-alcohol molar ratio. This solid acid catalyst exhibited excellent catalytical activity for the production of environmentally friendly biodiesel in high yields, which can be accounted for by the high acidity of this catalyst. Also, recycling and kinetic studies were performed and kinetic parameters such as rate constants, activation energy and Arrhenius constant were determined.

Table 5.8 Composition of FAME produced using yellow grease as feedstock using solid-acid catalyzed process as a function of time. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 800 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

FAME (wt %)										
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
0	0.00	18.42	10.78	49.58	21.21	0.00	0	0.00	0.00	0.00
0.25	0.00	17.25	9.94	50.82	20.31	3.05	0	0.00	0.00	0.00
0.5	1.01	16.78	9.63	49.66	19.85	3.07	0	0.00	0.00	0.00
0.75	1.00	16.49	9.47	49.62	19.76	3.02	0	0.00	0.65	0.00
1	0.99	16.35	9.40	49.46	19.70	3.01	0	0.56	0.53	0.00
1.5	1.01	16.41	9.42	49.76	19.81	3.04	0	0.55	0.00	0.00
2	1.01	16.36	9.38	49.81	19.84	3.04	0	0.55	0.00	0.00
4	1.02	16.21	9.27	49.79	19.85	3.02	0	0.84	0.00	0.00
6	1.03	16.07	9.17	49.65	19.87	2.99	0.38	0.84	0.00	0.00
8	1.03	16.04	9.14	55.41	23.34	2.97	0.38	0.84	0.00	0.00
10	1.02	15.86	9.03	49.31	19.75	3.58	0.37	0.83	0.24	0.00
24	1.03	15.90	9.04	49.60	19.79	3.41	0.37	0.85	0.00	0.00
24.5	1.03	15.92	9.03	49.52	19.74	3.54	0.37	0.85	0.00	0.00

Experimental kinetic data analyzed using a first-order kinetic model yielded an apparent activation energy and Arrhenius pre-exponential term of 42.3 kJ/mole, and 9.4801 sec^{-1}, respectively. Furthermore, the change in catalyst surface properties over repeated used and regeneration cycles were measured to evaluate their effect on the overall activity of the

catalyst. These studies showed that no considerable change in the catalytic activity even after five reaction cycles. After 5 reaction cycles, catalyst activity remained 96.6% of the original level. In summary, FFA present in yellow grease was converted to biodiesel with 95% conversion using the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina). Furthermore, yellow grease was successfully transesterified to yield an ester content of 87.25 mass % in the ester-rich phase.

Furthermore, this catalyst appears suitable to catalyze both the esterification and transesterification reactions. Analysis based on the ASTM D974 and EN 14103 standards confirmed the production of high-purity biodiesel from yellow grease.

These results are very promising and suggest the feasibility of using low cost feedstock with high FFA content for the industrial production of biodiesel using this green single-step process as compared to current multi-step industrial processes. Due to the high catalytic activity, reusability and low cost, this heterogeneous catalysis process has potential for industrial scale production of biodiesel from multi-feedstocks.

CHAPTER 6

A DIRECT METHOD FOR THE SYNTHESIS OF FATTY ACID METHYL ESTER (FAME) FROM CRUDE *JATROPHA* OIL AS SECOND GENERATION FEEDSTOCK.

Overview

Due to the high cost of edible oils and growing concern over the use of food for oil, the commercial production of biodiesel is in a great need of new inexpensive second-generation feedstocks which do not compete with food. Recently, *jatropha* oil has been considered as one of the most promising potential feedstocks for the production of biodiesel in Asia, Africa, Europe, South America, and now is gaining momentum in North America due to its advantages over edible oils. The amount of unsaturation in the fatty acid methyl ester (biodiesel) remains a major problem for the stability of biodiesel. This problem can be addressed by using a feedstock such as *jatropha* oil that already possess a fatty acid profile suitable to produce biodiesel with enhanced stability to meet quality standards requirements for industrial scale production of biodiesel. Currently, most of the biodiesel from *jatropha* oil either is produced by a complex homogeneous-catalyzed multi-step process or requires pre-treatement prior to a heterogeneous base-catalyzed process.

Currently, to produce biodiesel from crude *jatropha* oil becomes technically, economically, and environmentally more challenging using 1st generation homogeneous-catalysts since this involves multi-step time consuming and costly processing, oil pretreatment, neutralization of waste homogeneous catalyst, water washing of the crude biodiesel and glycerol, and treatment of waste generated. Therefore, single-step heterogeneous-catalysis for both esterification and transesterification would be an ideal solution for biodiesel production from non-edible oils such as *jatropha curcas* oil (JCO). Therefore, we have developed a novel 2nd generation method for the synthesis of fatty acid methyl esters (FAME) using a simple and

environmentally direct single-step heterogeneous-catalyzed process to produce high quality biodiesel from crude *jatropha* oil. It was found that FFAs present in crude *jatropha* oil were converted to biodiesel with 93.63% conversion of free fatty acids. Furthermore, crude *jatropha* oil was successfully transesterified with ester content of 91.44 mass %. This process is suitable to catalyze not only esterification but also transesterification reaction. Biodiesel analysis based on the ASTM D974 and EN 14103 standards confirmed the production of high-purity biodiesel from crude *jatropha* oil with only 0.17% linolenic ester which is far below the 12% limit defined by EN 14214. The effects of the amount of catalyst, calcination temperature of catalyst, rate of mixing and use of co-solvent (THF) on FAME content and FFA conversion have been studied and optimized. Due to high catalytic activity and low cost, this method has the potential for industrial-scale production of biodiesel from crude *jatropha* oil as 2nd generation non-edible feedstock. To the best of our knowledge, this is the first report on the development of a direct single-step solid acid-catalyzed process for the production of biodiesel from untreated crude *jatropha* oil.

6.1 Introduction

Since the beginning of the 21st century, the demand for petroleum has risen rapidly mainly due to an increase in the industrialization and modernization of the world. Globally, ever rising prices of conventional fossil-based fuels and potential shortage in the future have led to serious concerns about energy security (Juan *et al*., 2011). Growing energy demands, depletion of conventional energy resources and environmental concerns have directed research to find alternative renewable and sustainable resources (Butler, 2006; Kularni *et. al.* 2006a).

The important factors to be considered in the selection of biodiesel feedstock are (1) the chemical composition of the fat or oil, (2) the cost and its availability, (3) transport and pretreatment. The chemical composition is important to determine the amount of free fatty acid (FFA) in the oil which is an important factor for biodiesel production (Olutoye *et al*., 2011).

It is an established fact that globally, the availability of feedstock for biodiesel production varies considerably according to geographical location and climate (Olutoye *et al*., 2011). Currently, the 1st generation feedstocks, edible oils, are widely used for biodiesel production (more than 95%) (Gui *et. al.*, 2008). For example, rapeseed oil is mainly used as feedstock in Europe. On the other hand, palm oil predominates in tropical countries, such as Malaysia. In the United States, soybean oil and animal fats are primarily used (Craven, 2011; Joshi *et al*., 2010; Karmakar *et al*., 2010). According to Food and Agricultural Organizations' report, currently esculent plants such as rapeseed oil (84%), sunflower (13%), palm (1%) and soybean and others (2%) (Thoenes, 2006) are used for biodiesel production. The use of these edible oils for biodiesel production have become more challenging due to increasing global food demand and high feedstock cost (Kullkarni *et. al.* 2006a; Marchetti *et al*., 2007; Gui et. al., 2008; Fan *et. al.*, 2009; Leung *et. al*., 2010; Baig and Ng, 2010; Baig *et. al*., 2011; Balat, 2011). Furthermore, the use of virgin forest and arable land for large-scale biodiesel production has resulted in deforestation and ecological imbalance (Butler, 2006). Hence, the production of biodiesel from edible oils is not considered sustainable. In order to overcome these drawbacks, research has started to focus on non-edible oil for biodiesel production due to their advantages over 1st generation bio-feedstocks (edible oils) as shown in Figure 6.1. Also, the use of varied feedstock for the production of biodiesel will lead to self-sustaining economies, making the countries less vulnerable to international political crises (Sivasamy *et al*., 2009).

However, the potential of non-edible oils for biodiesel production has not been investigated in depth. Recently, non-edible oils such as *jatropha* oil, sea mango and castor oil have been considered to be renewable and sustainable feedstocks for biodiesel production (Gui *et al*., 2008; Ramezani *et al*., 2010). Among non-edible plants, *jatropha* is the most advantageous feedstock for biodiesel production in terms of its economical, sociological and environmental impact (Juan *et al*., 2011). *Jatropha curcas* belongs to the Euphorbiaceae family. The name *jatropha* is derived from the Latin words "*jatros*" (doctor) and "*trophe*" (food) due to its

medicinal benefits. Due to its leaf-shedding activity, the *jatropha* plant is highly adaptable in harsh environments because the decomposition of shed leaves provides nutrients for the plant and reduces water loss during the dry season. Thus it is well adapted to various types of soils, including those that are deficient in nutrition. The *jatropha* plant also has the ability to tolerate a wide range of climates and rainfall (Juan *et al*., 2011). As a drought-resistant plant, it is a good candidate for eco-restoration in wastelands (Juan *et al*., 2011). *Jatropha* cultivation in wastelands would help the soil to regain its nutrients and assist in carbon restoration and sequestration (Juan *et al*., 2011).

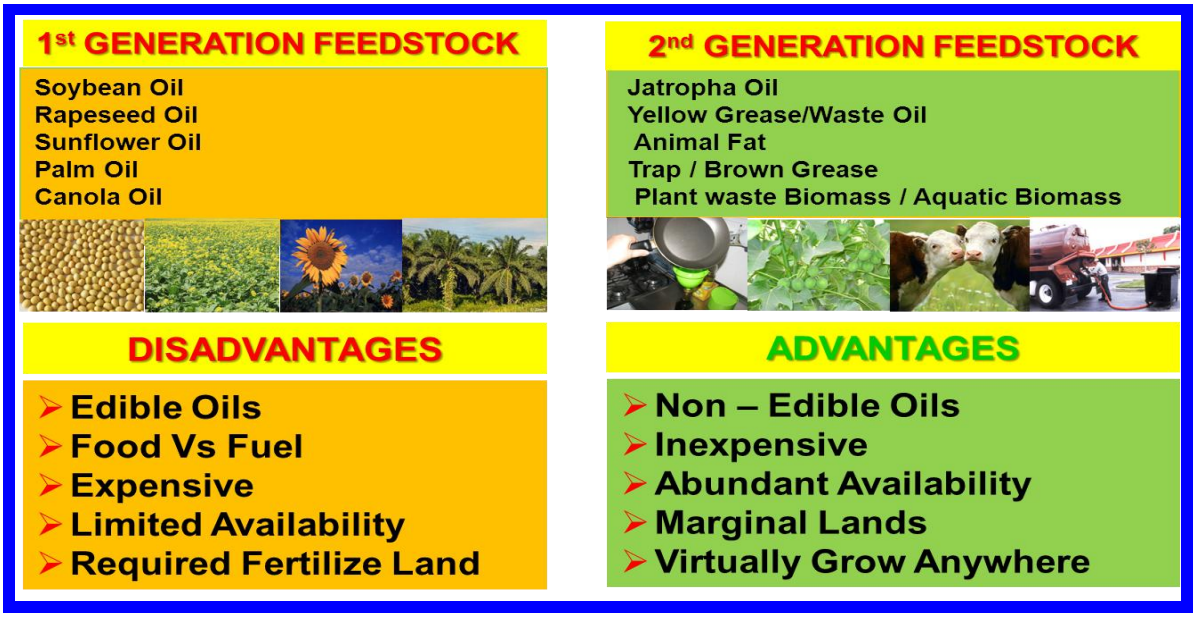


Figure 6.1 1st generation bio-feedstock *vs* 2nd generation bio-feedstock.

Jatropha curcas plant is a drought resistant, multipurpose and oil seed-bearing non-edible plant (Achten *et al*., 2007; Becker *et al*., 2008). It is cultivated in Central and South America, South-east Asia, India and Africa. It is easy to establish, grows almost everywhere even in gravelly, sandy and saline soils. It produces seeds for 50 years with a high oil content of about 37%. *Jatropha* plant has higher oil content, oil yield and heating value as compared to other non-edible plants (Table 6.1) (Gui *et al*., 2008; Fassinou *et al*., 2010).

Table 6.1 Oil Content and production of non-edible oil seeds (Singh *et al*., 2010).

Species	Oil Fraction (%)	Seed Yield (x 10^6 tones/year)	Oil Yield (tones/ha/year)
Jatropha	50-60	0.20	2.0-3.0
Mahua	35-40	0.20	1.0-4.0
Pongamia (Karanja)	30-40	0.06	2.0-4.0
Castor	45-50	0.25	0.5-1.0
Linseed	35-45	0.15	0.5-1.0
Others	10-50	0.50	0.5-2.0

Jatropha oil has valuable properties such as a low acidity, better stability than soybean oil, lower viscosity than castor oil and better cold properties than palm oil due to its fatty acid composition (Table 6.2). Also, *Jatropha* oil has a higher cetane number than diesel which makes it a good alternative fuel with no modifications required of engines (Tapanes *et al*.; 2008; Divakara *et al*., 2010; Jain *et al*., 2010). Since *jatropha* oils consist of mainly oleic and linoleic acids, which are unsaturated fatty acids, the biodiesel produced has good low temperature properties (Koh *et al*., 2011).

Jatropha is not only a 2nd generation non-edible feedstock, but also offers many benefits such as: 1) land improvement and additional ecological advantages, 2) carbon dioxide sequestration, 3) medicinal properties, 4) economical benefits to rural communities and 5) use of residue for biogas production (Van Ejick *et al*.; 2008; Gubitz *et al*.; 1999; Sarin *et al*., 2010).

Due to advantages of non-edible oils over edible oils as feedstock for biodiesel, non-edible oils are gaining attention as potential feedstock. However, these non-edible oils, such as *jatropha*, have high amount of FFA which significantly reduces biodiesel yield during conventional base-catalysis transesterification. The acid value of *jatropha* oil varies from 0.92 mg KOH/g to 28 mg KOH/g (Leung *et. al*., 2010; Acthten *et. al*., 2008).

Table 6.2 Fatty Acid Composition of *jatropha curcas* oil (Jain *et al*., 2010).

Fatty Acid	**Formula**	**Systematic Name**	**Structure**	**% Amount**
Palmitic Acid	$C_{16}H_{32}O_2CH_3(CH_2)_{14}COOH$	Hexadecanoic acid	C_{16}	14.1
Palmitolileic Acid	$C_{16}H_{30}O_2CH_3(CH_2)_5CH=CH-(CH_2)_7-COOH$	Cis-9 Hexadecanoic acid	$C_{16:1}$	0.5
Stearic Acid	$C_{18}H_{38}O_2CH_3(CH_2)_{16}COOH$	Octadecanoic acid	C_{18}	6.8
Oleic Acid	$C_{18}H_{34}O_2CH_3(CH_2)_7CH=CH-(CH_2)_7-COOH$	Cis-9-Octadecanoic acid	$C_{18:1}$	38.6
Linoleic Acid (L)	$C_{18}H_{32}O_2CH_3(CH_2)_4CH=CH-CH_2-CH=CH-(CH_2)_7COOH$	Cis-9-cis-12 Octadecanoic acid	$C_{18:2}$	36.0
Linolenic Acid	$C_{18}H_{30}O_2CH_3(CH_2)_4CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_4COOH$	Cis-6-cis-9-cis-12 Octadecanoic acid	$C_{18:3}$	0.2
Arachidice Acid	$C_{20}H_{40}O_2CH_3(CH_2)_{18}COOH$	Eicosanoic acid	C_{20}	0.2
Gadolic Acid	$C_{20}H_{36}O_2$		C_{24}	3.6

Crude *jatropha* oil usually has a FFA content up to 15% which is beyond the acceptable limit for conventional base-catalysis (Berchmans *et al*., 2008). This problem has been addressed by using a two-step process (Baig, 2003; Zhang *et al*., 2003; Ramadhas *et al.*, 2005; Nebel *et al.*, 2006; Kulkarni *et al.*, 2006b; Kumartiwari *et al.*, 2007; Rashid *et al.*, 2008; Berchmans *et al*., 2008; Jain *et al.*, 2010).

The two-step process involves acid-catalyzed esterification followed by base-catalyzed transesterification (Jain *et al.*, 2010; Wang *et al.*, 2012). However, the two step (or multi-steps) process increases the complexity and cost of production of biodiesel from the particular feedstock used (Ilham *et al*., 2010; Olutoye *et al*., 2011).

The production of biodiesel from crude *jatropha* oil is technically, economically and environmentally more challenging using a 1st generation homogeneous-catalyzed process

since this requires multi-step processing, oil pretreatment, neutralization of the waste homogeneous catalyst, water washing of the crude biodiesel and glycerol and treatment of the waste generated, which makes the purification of the biodiesel more challenging to meet the biodiesel quality standards (Bournay *et al.*, 2005; Baig and Ng 2011; Baig *et. al.*, 2012) as shown in Figure 6.2.

Some of the limitations of homogeneous-catalysis could be addressed by using heterogeneous base-catalyzed process. Heterogeneous catalysis has gained momentum for biodiesel production over the last decade (Harmer *et al.*, 2002; Toda *et al.*, 2005; Kulkani *et al.*, 2006c; Zong *et al.*, 2007; Di Serio *et al.*, 2008; Yan *et al.*, 2010). In contrast to homogeneous catalysts, heterogeneous catalysts do not required complex downstream washing and separation, can be recycled and are environmentally benign. They are also potentially inexpensive. Heterogeneous catalysts can easily be customized and tuned to acquire desired catalytic properties so that the presence of FFA or water does not adversely after the biodiesel production process.

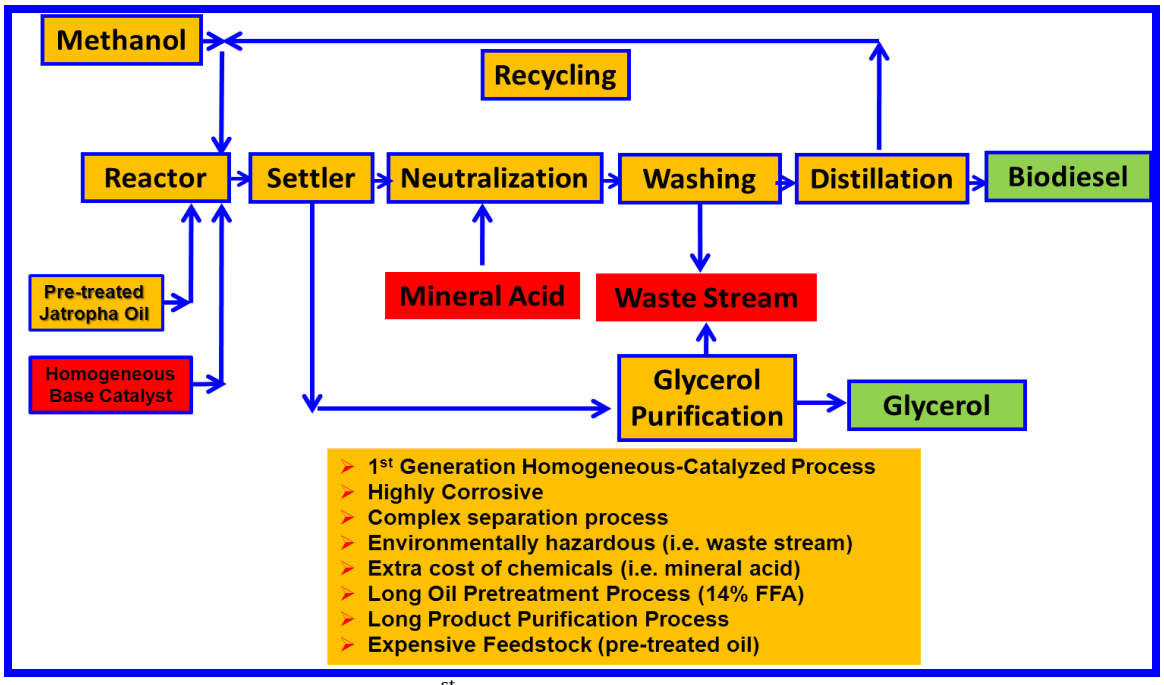


Figure 6.2 Conventional 1st generation homogeneous base-catalyzed process.

Due to the limitations of homogeneous-catalysis, it was suggested that the use of heterogeneous catalyst in each step of two-step process would help to overcome these problems (Juan *et al*., 2011). However, even when a mixture of solid acid and base catalysts has been used, their deactivation was observed when exposed to atmosphere (Endalew *et al*., 2011).

Hence, the use of two or more catalysts is still considered complex and inefficient for industrial-scale applications for the production of biodiesel. According to the reported literature, a completely heterogeneous two-step process has not been developed yet (Ivana *et al.*, 2012). Therefore, single-step heterogeneous-catalysis for simultaneous esterification and transesterification would be an ideal solution for biodiesel production from non-edible oils such as *jatropha curcas* oil (JCO) (Endalew *et al*., 2011).

Most of the processes reported in the literature have focused on using conventional homogeneous base-catalysis two-step or multi-step homogeneous-catalysis, heterogeneous base-catalysis or mixture of acid and base heterogeneous catalyzed process (Ono *et al*., 1997; Hattori, 2001; Handa, *et al*., 1999; Jain *et al.*, 2010; Juan *et al*., 2011; Endalew *et al*., 2011). However, all these processes are complex and not efficient enough to be considered for industrial-scale production of biodiesel. Furthermore, all reported processes to date require the use of pre-treated *jatropha* oil and not the crude *jatropha* oil (CJO). The price of crude *jatropha* oil is much lower than refined deodorized *jatropha* oil (RDO), which has a FFA content above 1% (Juan *et al*., 2011). Therefore, in order to produce biodiesel for industrial scale, inexpensive crude *jatropha* oil should be used.

When focusing on *jatropha curcas* oil as the feedstock for the synthesis of *jatropha* biodiesel, acid-catalyzed transesterification has rarely been conducted or proposed by other researchers since alkali-catalysis is considered to be the most favorable (Koh *et al*., 2011). This demonstrates the great need of development of innovative 2nd generation heterogeneous-catalyzed technologies for alternative inexpensive waste feedstocks using simple, time-

efficient and inexpensive manufacturing processes (Baig and Ng, 2010). Furthermore, in contrast to homogeneous-catalysis, 2nd generation heterogeneous-catalysis can be run in either batch or continuous mode, giving the flexibility to continue with current batch manufacturing or retrofit processes with a continuous flow reactor operation (Yan *et al.*, 2010). Therefore, the problem associated with the 1st generation homogeneous-catalyzed has been addressed by using a 2nd generation heterogeneous-catalyzed process for the production of biodiesel from oil containing FFA (Baig and Ng, 2010).

A higher degree of unsaturation can result in the oxidation of biodiesel affecting its stability during storage. Due to these problems, biodiesel quality standards such as EN 14103 have restricted the amount of linolenic ester (C18:3) to the maximum value of 12%. However, this limit has been set to accommodate the use of rapeseed oil (high linolenic C18:3 content) which is one of the major crops produced in European Union as a feedstock for biodiesel production. Therefore, a decrease in C18:3 is highly desirable to enhance the stability of biodiesel. This problem can be addressed by using a feedstock such as *jatropha* oil that already possess a fatty acid profile suitable to produce biodiesel with enhanced stability to meet quality standard requirements for industrial- scale production of biodiesel (Knothe, 2008).

According to the best of our knowledge, a systematic in-depth study on single-step heterogeneous-catalysis for biodiesel production from industrial-scale untreated real waste feedstocks such as crude *jatropha* oil has not been explored in depth. The production of biodiesel from soybean oil with added FFA in a single-step solid acid-catalyzed process has already been demonstrated in Chapter 4 (Baig and Ng, 2010). In this chapter, as the third phase of process development, the application of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) is evaluated using a real non-edible feedstock (crude *jatropha* oil). A novel 2nd generation technology for the production of biodiesel using a simple and environmentally green direct single-step heterogeneous-catalyzed process has been developed to produce high quality biodiesel from crude *jatropha* oil as shown schematically in Figure 6.3.

In contrast to conventional homogeneous-catalysis, this approach does not require complex downstream washing and separation processes, while the heterogeneous catalyst can be recycled and is environmentally benign. This technology provides a direct route for the synthesis of biodiesel from crude *jatropha* oil. Furthermore, the heterogeneous catalysts are also potentially inexpensive. Heterogeneous catalysts can be customized and tuned to acquire desired catalytic properties so that the presence of FFA or water does not adversely affect the catalytic activity during and after the biodiesel production process.

As part of process development, the effects of the amount of catalyst, calcination temperature of catalyst, rate of mixing and use of co-solvent (THF) on FAME content and FFA conversion have been studied and optimized.

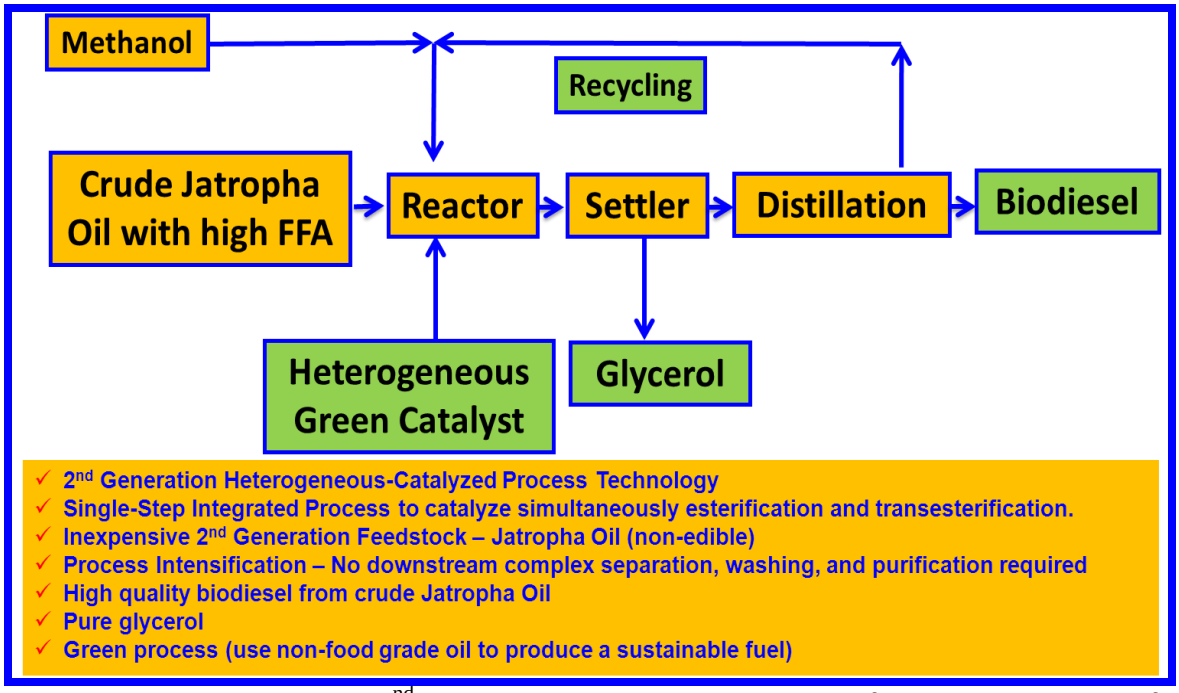


Figure 6.3. Novel green 2nd generation catalytic technology for the production of biodiesel from crude *jatropha* oil.

6.2 Experimental procedures

6.2.1 Materials

The crude *jatropha* oil with 29% FFA was obtained from Indonesia (Yogyakarta). The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): 2-propanol (anhydrous, 99.5%), toluene (anhydrous, 99.8%), *p*-naphtholbenzein (indicator grade), 0.1 N KOH (volumetric standard, in isopropanol), methyl heptadecanoate, n-heptanes and rapeseed FAME standard mixture.

6.2.2 Catalyst preparation

The catalyst (12-tungstophosphoric acid, $H_3PW_{12}O_{40}{\cdot}nH_2O$ supported onto neutral alumina) was prepared as discussed earlier in section 4.2.2. For more details, please refer to Appendix-G.

6.2.3 Equipment

Esterification and transesterification with the solid acid catalyst was carried out in a fully automated high-pressure high-temperature batch reactor (PARR Instrument, 4843, Moline, Illinois, USA). The equipment consisted of a high pressure cylindrical chamber, heater, water line (in order to control the temperature), sampling outlet and stirrer.

6.2.4 Procedures

Simultaneous Esterification and Transesterification.

The crude *jatropha* oil with 29% FFA was used as feedstock for simultaneous transesterification and esterification. The reaction was carried out in a 300 cc Parr reactor (Parr Instrument Co.) equipped with a temperature controller as shown in Figure 6.4. Initially, the reactor was charged with crude *jatropha* oil and methanol. The solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) was added to the reaction vessel. The reactor was pressurized (depending on the reaction temperature) to ensure that the reactants were in the liquid phase at the desired reaction temperature.

A temperature of 200°C and a pressure of 600 psi were selected for experiments (or otherwise as stated). Once the reaction mixture reached the desired reaction temperature, then the mixing of the reaction was started and this point was taken as time zero for the reaction. All the reactionswere carried out or a total reaction time of 10 h unless otherwise stated. Samples were taken at regular time intervals. Methanol was evaporated under reduced pressure using a rotary evaporator.Then, introduced into a centrifuge to remove the solid catalyst. The reason for the absence of glycerol phase in earlier samples may be due to the production of small amount of glycerol at earlier stage of the reaction or/and glycerol was not able to separate into a different phase. Samples from the ester-rich phase of crude biodiesel were analyzed without any post experiment treatment such as water washing to remove impurities and purify FAME. Hence, results are based on crude biodiesel which more accurately represents the progress of esterification and transesterification reactions, reactant conversion and product formation. Acid number and FAME content were chosen as indicators for esterification and transesterification reactions, respectively.

GC Analysis

Samples from the ester-rich phase were analyzed for ME formation at pre-determined time intervals by using an Agilent 7980A GC system equipped with a 7683 auto injector, flame ionization detector and capillary column for injecting the sample to determine the ester content with HP-INNOWax column (30 m x 320 mm x 0.25 µm) using a split/splitless inlet as per EN 14103(as validated in Chapter 3; section 3.1). Helium was used as the carrier gas.

Quantitative analysis of % ME was done using European standard EN 14103 for the determination of ester and linolenic acid methyl ester content (EN 14103, 2003). The % ME yield was calculated using Equation (**6.1**). Free fatty acids in the samples were determined using stock solution (methyl heptadecanoate and n-heptane).

$$\%\ of\ ME = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad \textbf{(6.1)}$$

where,

$\sum A$ = Total peak area of methyl ester from C_{14} to $C_{24:1}$

A_{EI} = Peak area corresponding to methyl heptadecanoate (C_{17})

C_{EI} = Concentration of metyl heptadecanoate (C_{17}) solution (mg/mL)

V_{EI} = Volume of metyl heptadecanoate (C_{17}) solution (mL)

m = Mass of the sample (mg)

Acid Number Analysis

The acid number was determined and calculated by using equation (**6.2**) as per ASTM D 974 (Baig and Ng, 2011):

$$Acid\ \ Number, mg\ \ of\ \ KOH\ \ / g = \left[\frac{(A-B) \times M \times 56.1}{W} \right] \qquad \textbf{(6.2)}$$

where,

A = KOH solution volume required for titration of the sample (mL)

B = KOH solution volume required for titration of the blank (mL)

M = molarity of the KOH solution

W = mass of the sample used (g)

The FFA content was determined as per ASTM D974 (Baig and Ng, 2011). The conversion of free fatty acid was calculated using the following equation (6.3).

$$\text{FFA conversion}(\%) = \left(\frac{a_i - a_t}{a_i} \right) \times 100 \qquad \textbf{(6.3)}$$

where a_i is the initial acid number of the mixture and a_t is the acid number at time t as specified in ASTM D 6751.

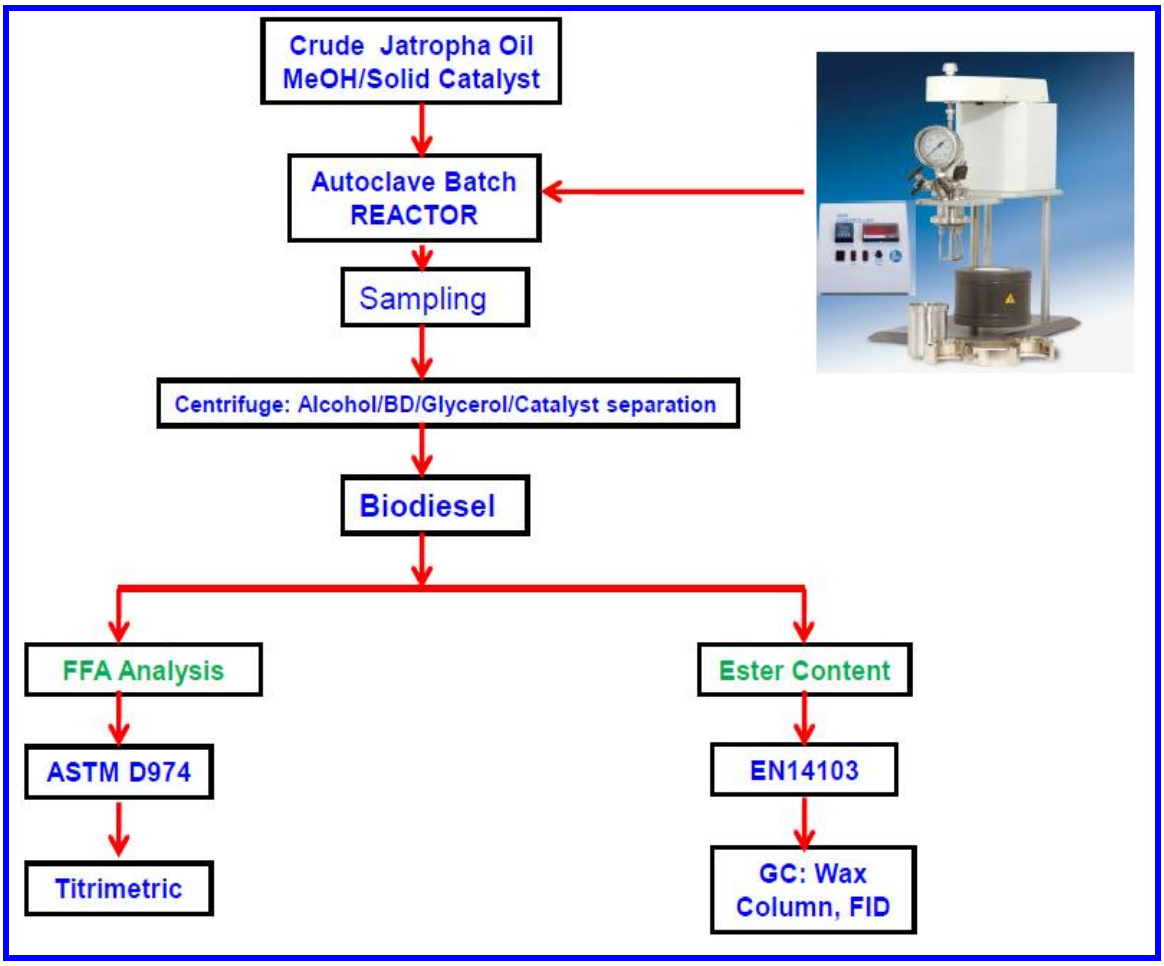


Figure 6.4 Process flow chart for experimental work.

6.3 Results and discussion

6.3.1 Effect of amount of catalyst

Generally, a high amount of catalyst can produce a high product yield. On the other hand, from industrial perspective, the use of a high amount of catalyst raises production cost. Therefore, it is essential to determine the optimum amount of catalyst required for high biodiesel yield.

The effect of the catalyst amount (3% and 10%) at a molar ratio of oil-to-methanol 1:27 was investigated at reaction temperature 200 ± 2^{o}C and stirring speed of 600 rpm over the period

of 10 h. The relationship between the catalyst amount and the FFA conversion and the methyl ester content are presented in Figures 6.5 and 6.6, respectively. These results show that the methyl ester content (mass %) and FFA conversion are dependent on the amount of catalyst. Initially, the ME yield was higher with 10 wt.% catalyst amount as compared to 3 wt.% catalyst. However, at the end of 10 h, there was no significant difference in the ME yield in both cases. Therefore, the optimal amount of catalyst was determined to be 3 wt.%.

6.3.2 Effect of rate of mixing

One of the major challenges for biodiesel process chemistry is the reaction between two reactants tryglyceride (non-polar) and alcohol (polar), which are immiscible in each other. The existence of a two-phase reaction causes the progress of reaction to be slow. In the case of the heterogeneous-catalyzed process, this system involves three-phases (solid-liquid-liquid) which is even more challenging. Hence, to establish the effect of external mass-transfer limitations during the simultaneous esterification and transesterification, experiments were performed at different rates of mixing. The stirrer speed, beyond which the rates of esterification and transesterification are no longer affected was considered to be the minimum speed of agitation required to eliminate external transport effects (Srilatha *et al.*, 2010). The effects of rate of mixing on the FFA conversion and the methyl ester content are presented in Figures 6.7 and 6.8, respectively. The results showed that the mixing speed has no significant effect on FFA conversion since esterification involves the reaction of FFA (small molecules with the methanol and external mass transfer may be less significant. Although triglycerides are large molecules, but there was still no significant effect of rate of mixing observed on tranesterification and ME content at 600 rpm and 700 rpm remains the same. As shown in Figures 6.7 and 6.8, the external transport control was negligible for stirrer speeds greater than 600 rpm. Hence, the optimal rate of mixing selected was 600 rpm.

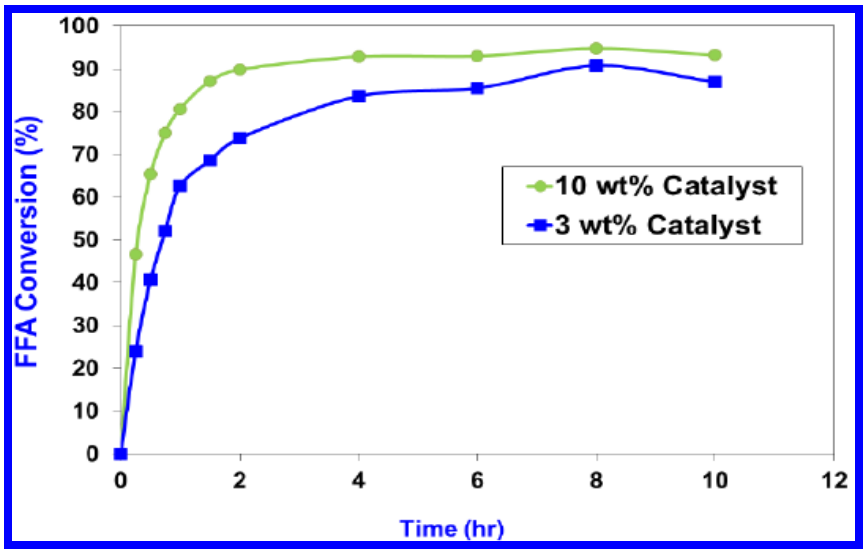


Figure 6.5 Effect of amount of catalyst on FFA conversion as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst (3 wt.% and 10 wt.%).

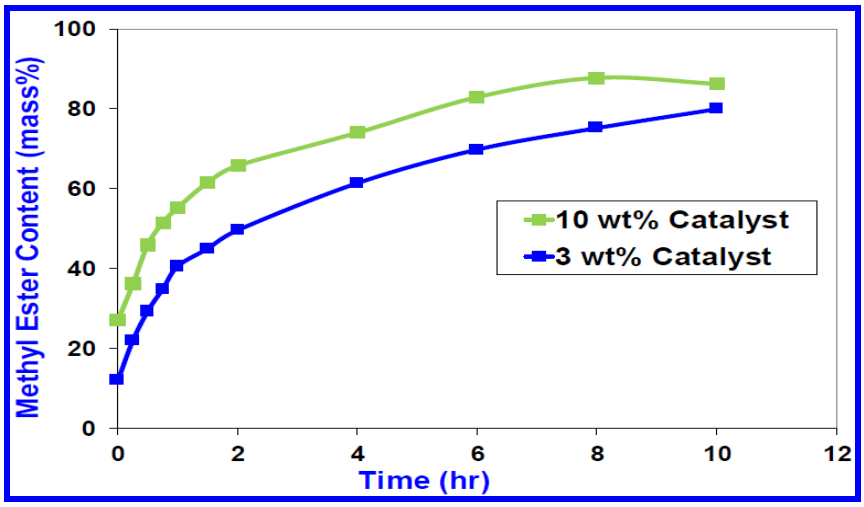


Figure 6.6 Effect of amount of catalyst on ME (mass %) content as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% and 10 wt.%).

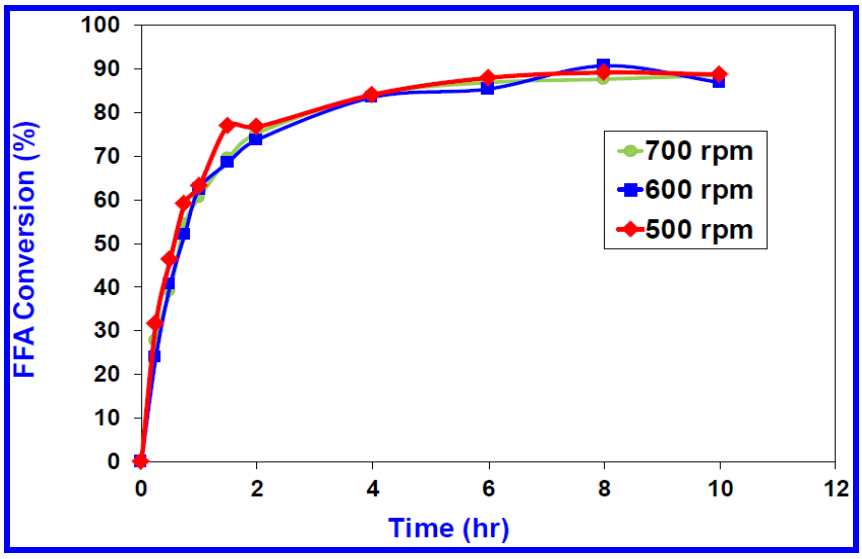


Figure 6.7 Effect of rate of mixing on FFA conversion (%) as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, catalyst 3 wt.%, stirring speed (500, 600 and 700 rpm)

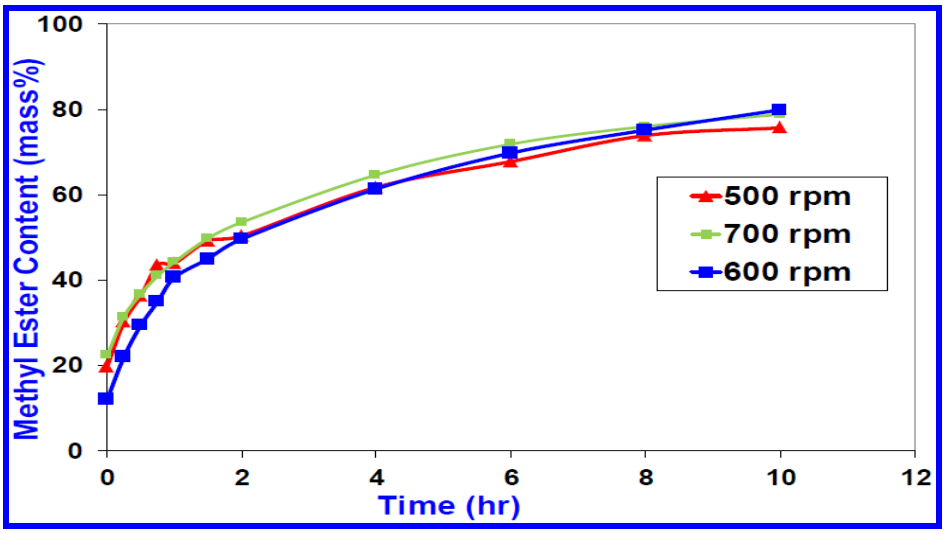


Figure 6.8 Effect of rate of mixing on ME (mass %) content as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, catalyst 3 wt.%, stirring speed (500, 600 and 700 rpm).

6.3.3 Effect of co-solvent

To enhance mass transfer, tetrahydrofuran (THF) has been selected as a co-solvent to

study its effect on mass transfer of transesterification. The effect of THF as co-solvent for the production of biodiesel from crude *jatropha* oil using a solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) is shown in Figures 6.9 and 6.10. It can be seen that the presence of THF results in a decrease in the ester yield. In 10 h, without and with THF as co-solvent, the ester yields of 79.97% and 67.88% were obtained, respectively. As discussed in Chapter 2, the reason for the use of co-solvent is to convert a three-phase system (oil-alcohol-solid catalyst) into a two-phase system (oil/alcohol and solid catalyst), which would help in reducing the mass transfer limitation of mixing non-polar oil (triglycerides) with polar alcohol. Also, this could help to reduce the rate of mixing which ultimately results in low energy consumption and will improve the economical feasibility of the process. However, it appeared at high mixing rate (i.e. 600 rpm) external mass transfer has been overcome (as reported in the literature) and and the use of THF causes the rate of ester formation to slow down. This may be attributed to the deactivation of the catalyst due to the absorption of THF on catalyst surface.

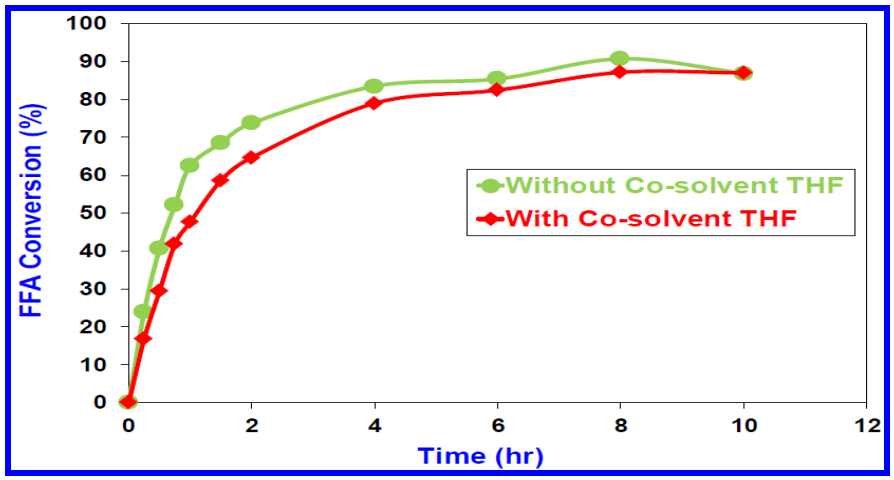


Figure 6.9 Effect of co-solvent THF on FFA conversion (%) as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%, alcohol-to-THF 1:1.

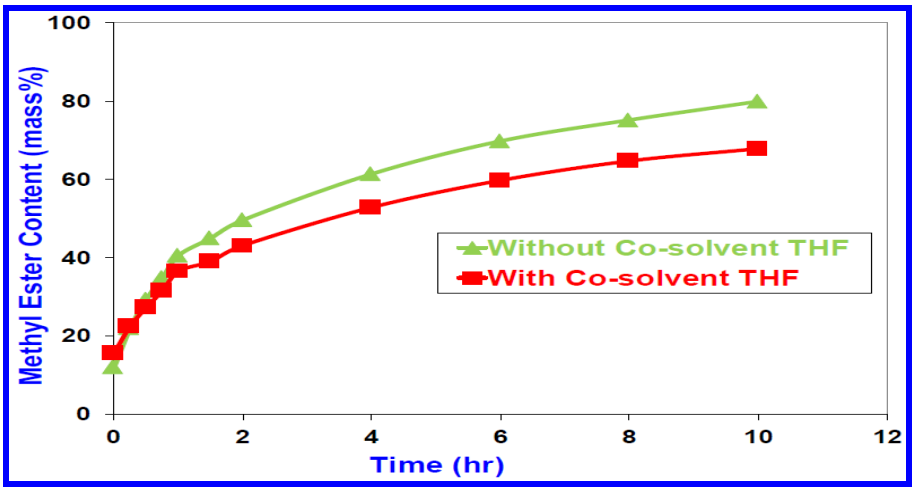


Figure 6.10 Effect of co-solvent THF on ME (mass %) content as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%, alcohol-to-THF 1:1.

6.3.4 Effect of calcination temperature.

Calcination temperature is an important parameter that affects catalytic activity. The calcination temperature was varied between 200 and 400°C to investigate its relation to catalytic activity. The relationship between calcination temperatures and the FFA conversion and the methyl ester content are presented in Figures 6.11 and 6.12, respectively. The results showed that the FFA conversion was not strongly dependent on the temperature whereas the ester yield was more strongly affected. The optimal calcination temperature for the catalyst determined was 300°C.

6.3.5 Optimum conditions for simultaneous esterification and transesterification of crude *jatropha* oil

The productions of biodiesel from CJO using the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) under optimum condition are shown in Figure 6.13. This solid acid catalyst showed promising activity towards simultaneous esterification and transesterification of CJO with 29% FFA.

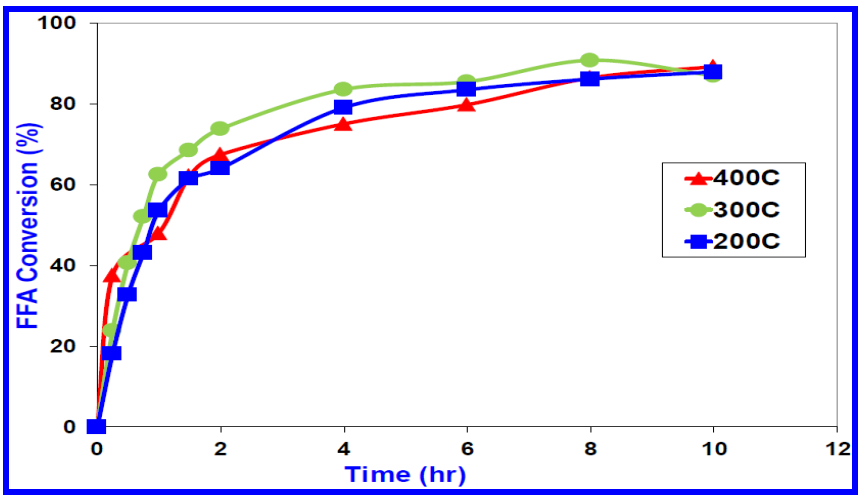


Figure 6.11 Effect of calcination temperature for the catalyst on FFA conversion (%) as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%, calcination temp (200°C, 300°C and 400°C).

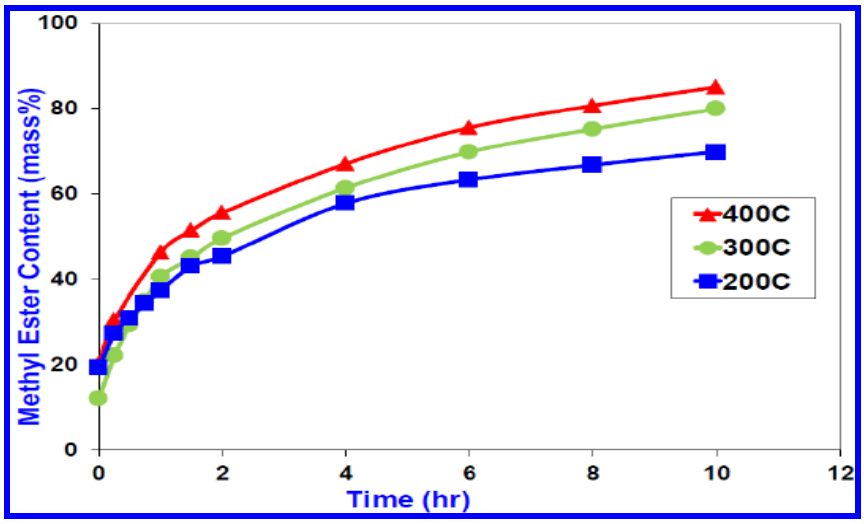


Figure 6.12 Effect of calcination temperature for the catalyst on ME (mass %) content as a function of time for simultaneous esterification and transesterification of crude *jatropha* oil as 2nd generation feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%, calcination temp (200°C, 300°C and 400°C).

A conversion of 94% for FFA present in CJO was obtained using the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina) which is similar to the FFA conversion of ~ 95% using sulfuric acid as a homogeneous catalyst (as shown in Chapter 3, section 3.2.3). Furthermore, after 24 h reaction time, CJO was successfully transesterified with ester content of 91 mass % in the ester-rich phase of crude biodiesel without any purification and refining step.

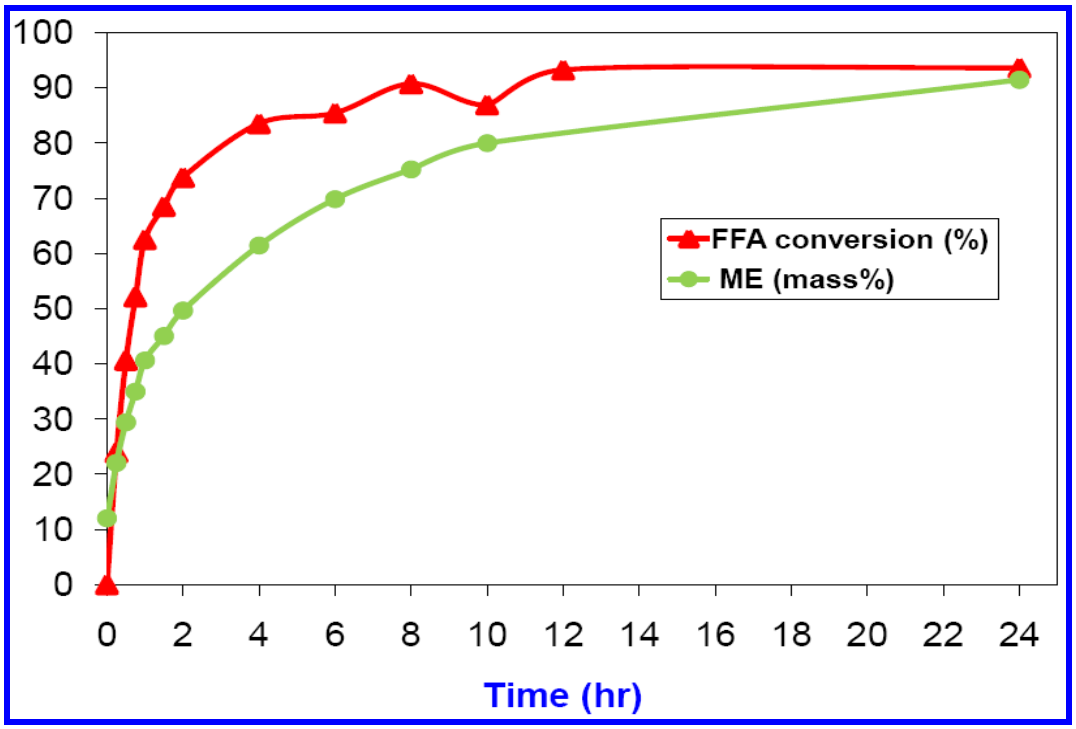


Figure 6.13 FFA conversion (%) and ME (mass %) content as a function of time for simultaneous esterification and transesterification of *jatropha* oil as feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%.

This catalyst is suitable to catalyze not only the esterification reaction but also the transesterification reaction. Biodiesel analysis based on the ASTM D974, and EN 14103 standards confirmed the production of high-purity biodiesel from crude *jatropha* oil.

6.3.6 Composition of biodiesel produced from crude *jatropha* oil

Crude *jatropha* oil (feedstock) and the biodiesel produced from crude *jatropha* oil using a direct single-step solid acid catalyzed process are shown in Figure 6.14 and 6.15, respectively. Typical chromatographs obtained for samples of *jatropha*-based biodiesel as per EN 14103 (as validated in Chapter 3; section 3.1) is shown in Figure 6.16. The large peaks observed in the chromatograph are the FAMEs present in the samples (C16 and C18). Also, it shows the regions of the crude Jatropha based biodiesel chromatograph based on retention times, where different FAME (from C14 to C24 carbon chains including saturated and unsaturated) elute.

Figure 6.14 Crude *jatropha* oil (feedstock).

Figure 6.15 Biodiesel produced from crude *jatropha* oil.

Furthermore, a high amount of unsaturation in FAME remains a major challenge for the stability of biodiesel. Higher degree of unsaturation leads to oxidation of biodiesel which affect its stability during storage.

Due to these problems, biodiesel quality standards such as EN 14103 restrict the amount of linolenic ester (C18:3) to the maximum value of 12%. This limit has been set to accommodate the use of rapeseed oil (high linolenic C18:3 content), which is one of the

major crops produced in European Union as a feedstock for biodiesel production. A decrease in C18:3 is highly desirable to enhance the stability.

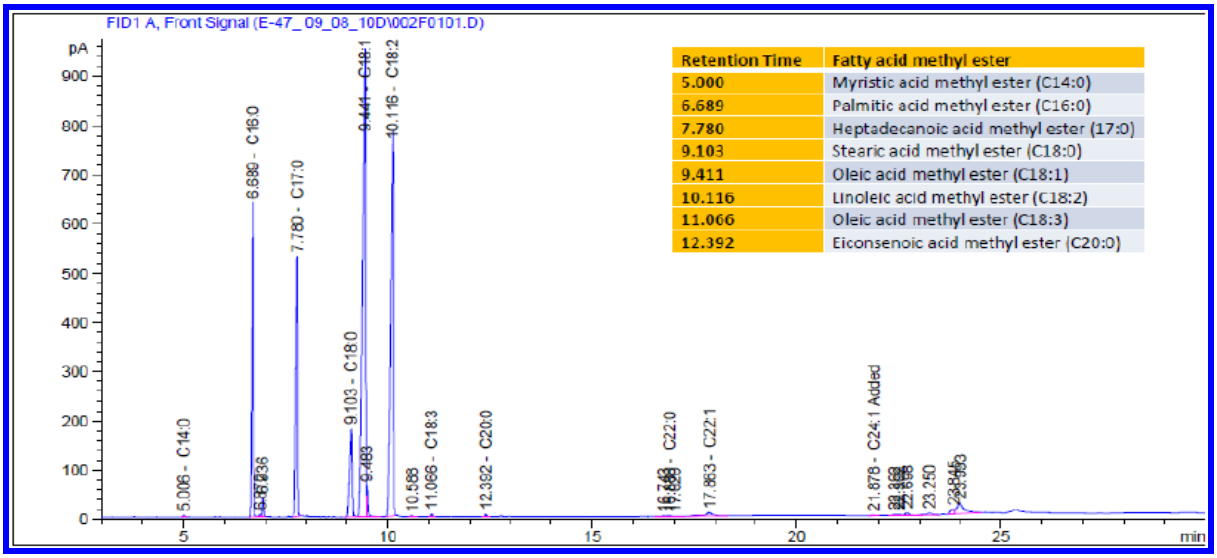


Figure 6.16 GC chromatogram showing typical analysis of ester content in the *jatropha* based methyl ester (biodiesel) sample as per EN 14103.

Table 6.3 Fatty acid composition of *jatropha curcas L.*

Fatty Acid	***jatropha***	***Jatropha Curcas L*** **(Sarin *et al.*,2007)**
Myristic acid (C14:0)	0.06	Not detected
Palmitic Acid (C16:0)	13.92	14.2
Stearic Acid (C18:0)	7.26	6.9
Oleic Acid (C18:1)	44.72	43.1
Linoleic Acid (C18:2)	32.39	34.4
Linolenic Acid (C18:3)	0.18	-
Arachidice Acid (C20:0)	0.22	-

The FFA composition in our *jatropha* oil shown in Table 6.3 is in accordance with the feedstock compositions (*jatropha*) reported in the literature (Table 6.2). The compositions of FAME produced from soybean oil, yellow grease and crude oil are shown in Tables 6.4, 6.5 and 6.6 and their comparative FAME profiles are presented in Figure 6.17. The biodiesel produced from soybean oil and yellow grease contains higher amounts of C18:3 than *jatropha* oil. On the other hand, FAME produced from crude *jatropha* oil contains only 0.17% C18:3 Therefore, crude *jatropha* oil could be used as an economical feedstock to produce biodiesel with enhanced stability to meet quality standards requirements for industrial scale production of biodiesel.

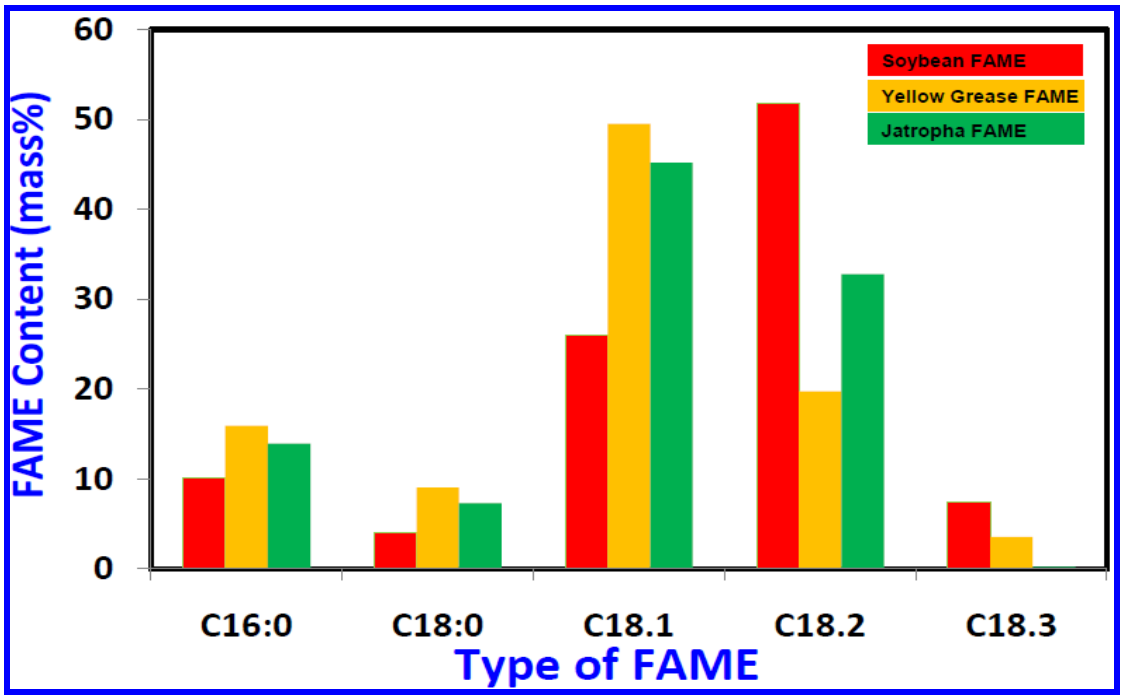


Figure 6.17 Comparative FAME profile of biodiesel produced from soybean oil, yellow grease and crude *jatropha* oil.

6.4 Conclusion

Jatropha oil is a future renewable source of non-edible oil for biodiesel production. Biodiesel production from JCO requires both esterification and transesterification processes due to its

high FFA content. Single-step esterification and transesterificaton using a heterogeneous acid-catalyst would simplify the biodiesel production process and decrease the cost of production. We have developed a novel 2nd generation technology for the production of biodiesel using a simple and environmentally green direct single-step heterogeneous-catalyzed process to produce high quality biodiesel from crude *jatropha* oil. It was found that 93.6% FFA present in crude *jatropha* oil was converted. Furthermore, crude *jatropha* oil was successfully transesterified with ester content of 91.44 mass % after 24 h reaction time. This process is suitable to catalyze not only the esterification reaction but also the transesterification reaction.

	FAME (wt%)									
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
0.5	0.00	10.72	4.10	26.90	51.58	6.41	0	0.00	0.30	0.00
1.0	0.03	10.52	4.20	26.76	51.39	6.83	0	0.00	0.28	0.00
2.0	0.03	10.41	4.15	26.70	51.40	7.05	0	0.00	0.26	0.00
3.0	0.04	10.28	4.02	26.13	51.65	7.35	0.24	0.00	0.25	0.00
4.0	0.04	10.12	4.01	25.95	51.74	7.38	0.24	0.19	0.24	0.00

Table 6.4 Composition of FAME produced using soybean oil as feedstock using solid-acid catalyzed process as a function of time. Reaction conditions: reaction temperature 200°C, molar ratio of oil-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).

Biodiesel analysis based on the ASTM D974 and EN 14103 standards confirmed the production of high-purity biodiesel from crude *jatropha* oil with only 0.17 % linolenic ester which is far below the limit of EN 14103.In contrast to conventional homogeneous-catalysis, this approach does not require complex downstream washing and separation processes, and the heterogeneous catalyst can be recycled and is environmentally benign. This technology provides a direct route for the synthesis of biodiesel from crude *jatropha* oil.

Furthermore, the heterogeneous catalysts are also inexpensive. Heterogeneous catalysts can be customized and tuned to acquire desired catalytic properties so that the presence of FFA or water does not adversely affect the catalytic activity during and after the biodiesel production process. This novel 2nd generation catalytic technology could be used to produce biodiesel from crude *jatropha* oil on an industrial scale.

FAME (wt %)										
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
0	0.00	18.42	10.78	49.58	21.21	0.00	0	0.00	0.00	0.00
0.25	0.00	17.25	9.94	50.82	20.31	3.05	0	0.00	0.00	0.00
0.5	1.01	16.78	9.63	49.66	19.85	3.07	0	0.00	0.00	0.00
0.75	1.00	16.49	9.47	49.62	19.76	3.02	0	0.00	0.65	0.00
1	0.99	16.35	9.40	49.46	19.70	3.01	0	0.56	0.53	0.00
1.5	1.01	16.41	9.42	49.76	19.81	3.04	0	0.55	0.00	0.00
2	1.01	16.36	9.38	49.81	19.84	3.04	0	0.55	0.00	0.00
4	1.02	16.21	9.27	49.79	19.85	3.02	0	0.84	0.00	0.00
6	1.03	16.07	9.17	49.65	19.87	2.99	0.38	0.84	0.00	0.00
8	1.03	16.04	9.14	55.41	23.34	2.97	0.38	0.84	0.00	0.00
10	1.02	15.86	9.03	49.31	19.75	3.58	0.37	0.83	0.24	0.00
24	1.03	15.90	9.04	49.60	19.79	3.41	0.37	0.85	0.00	0.00
24.5	1.03	15.92	9.03	49.52	19.74	3.54	0.37	0.85	0.00	0.00

Table 6.5 Composition of FAME produced using yellow grease as feedstock using solid-acid catalyzed process as a function of time. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 800 rpm, catalyst 3 wt.%.

FAME (wt %)												
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1	C24:0	C24:1
0	0.00	11.42	5.93	35.53	25.54	0.00	0	0.00	1.58	19.33	0.00	0.67
0.25	0.00	13.03	6.71	40.64	29.65	0.00	0	0.00	1.22	7.98	0.00	0.79
0.5	0.00	13.48	6.95	42.20	30.83	0.19	0	0.00	0.69	5.43	0.00	0.23
0.75	0.00	13.69	7.06	42.98	31.41	0.19	0.21	0.00	0.56	3.61	0.00	0.28
1	0.00	13.79	7.13	43.44	31.76	0.19	0.22	0.00	0.54	2.66	0.00	0.28
1.5	0.00	13.91	7.20	43.90	32.08	0.19	0.22	0.00	0.48	1.78	0.00	0.25
2	0.00	13.91	7.21	44.04	32.19	0.19	0.22	0.00	0.43	1.74	0.00	0.08
4	0.00	13.99	7.26	44.48	32.53	0.19	0.28	0.00	0.22	1.07	0.00	0.08
6	0.06	13.92	7.26	44.63	32.65	0.19	0.22	0.00	0.17	0.84	0.00	0.07
8	0.06	13.96	7.28	44.83	32.42	0.19	0.22	0.00	0.15	0.84	0.00	0.06
10	0.06	13.92	7.26	44.72	32.39	0.18	0.22	0.00	0.11	1.07	0.00	0.07
24	0.06	13.92	7.29	45.15	32.80	0.17	0.22	0.00	0.00	0.33	0.00	0.05
24.5	0.06	13.94	7.31	45.19	32.80	0.17	0.22	0.00	0.00	0.25	0.00	0.06

Table 6.6 FAME profile of *jatropha* based biodiesel produced from simultaneous esterification and transesterification of *jatropha oil* as feedstock. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.%.

CHAPTER 7

DETERMINATION OF ACID NUMBER OF BIODIESEL AND BIODIESEL BLENDS.[2]

Overview

Due to an increase in the commercial use of biodiesel and biodiesel blends, both ASTM D6751 and EN 14214 include the acid number (AN) as an important quality parameter. It was found that determination of AN of biodiesel and biodiesel blend using the ASTM D974 results in large values of repeatability (up to 73.41%) and larger % error (up to 42.88%). Therefore, ASTM D974 has been modified using a lower concentration of base (0.02 M KOH instead of 0.1 M KOH) as well as reducing the amount of toxic titration solvent from 100 mL to only 10 mL. This makes the modified ASTM D974 a green analytical method by using a reduced amount of toxic solvent. This modified method significantly reduced the maximum percentage error from 42.88 to 5.92%. The application of this modified ASTM D974 for the determination of AN of biodiesel and biodiesel blends was studied. The accuracy of this modified ASTM D974 for biodiesel (B100) was measured to be within 3.51% over the AN range of 0.313 – 0.525 mg KOH/g and maximum repeatability was decreased from 8.37 to 2.75% within this AN range which is far below the ASTM D 974 stated repeatability specifications. For B20, B10, B5, B2, and B1, the most accurate values were measured at AN values of 0.177, 0.067, 0.072, 0.126, and 0.096 mg KOH/g, respectively. Excellent linearity values of R^2 for calculated and experimentally determined AN were obtained. The difference between the experimental and the calculated AN for all

[2] Adapted from Aijaz Baig and Flora T.T. Ng. "Determination of Acid Number of Biodiesel and Biodiesel Blends",J Am Oil Chem Soc (2011) 88:243-253.

biodiesel and biodiesel blend samples was within ± 0.018 mg KOH/g. This extensive study has demonstrated that this modified ASTM D974 is a reliable method for the determination of AN and could be used for establishing the specifications of AN for biodiesel and biodiesel blends ranging from B1 to B20 in quality standards.

Keywords Acid Number, Biodiesel, ASTM D974, Biodiesel Blends, Biodiesel Standards

7.1 Introduction

Biodiesel is defined by the American Society for Testing and Materials (ASTM) as mono alkyl esters of long chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat (Baig and Ng, 2010). Due to increasing interest and use of biodiesel around the world, the assurance of biodiesel quality has become of paramount interest for its successful commercialization and market acceptance. Therefore, various biodiesel standards have been established around the world, including the United States (ASTM D6751) and Europe (EN 14214) (Knothe, 2006).

ASTM standard D6751 and European Committee for Standardization (CEN) standard EN 14214 set similar specifications for biodiesel as motor fuel (ASTM D6751-09a, 2009; DIN EN 14214, 2003). In both standards, one important quality parameter for biodiesel is the acid number (AN). AN is measured as the mg of KOH required to neutralize the acids in 1 gram of the sample (ASTM D974-08, 2008). AN is a measure of the degree of oxidation and hydrolysis in the biodiesel (Wang *et al*., 2008). AN measurement detects both weak organic acids and strong inorganic acids. Both ASTM D6751 and EN 14214 have restricted the maximum value of AN to be 0.50 mg KOH/g for biodiesel (B100).

This is due to the fact that free fatty acids (FFA), which can be generated during the production process (Mahajan *et al*., 2006), can cause severe operational problems (e.g. engine deposit) and are considered as a safety risk during storage due to the possibility of corrosion by the FFA (Wang *et al*., 2008).

As the biodiesel ages, it becomes more acidic due to the hydrolytic cleavage of the ester bond and/or the oxidation degradation of double bonds (Mahajan *et al*., 2006). A high AN makes the fuel prone to polymerization as well as hydrolysis (Mahajan *et al*., 2006). The AN of biodiesel depends on the type of feedstock and how well the biodiesel was processed during and after the production. Production of biodiesel from high FFA content feedstock is gaining momentum around the world due to its economical, commercial and environmental benefits (Baig and Ng, 2010). This requires an accurate determination of AN to monitor the progress of the biodiesel production process.

AN determination, like kinematic viscosity, is a facile method for monitoring fuel quality (Knothe, 2006). Analytical methods for AN determination can be divided into two titration categories: potentiometric or colorimetric. Two major ASTM test methods, ASTM D664 and ASTM D974 can be used for AN determination. Determination of AN is described in ASTM D6751 using ASTM D664, a potentiometric method. However, ASTM D664 suffers from mediocre reproducibility, a problem mentioned in the method itself (ASTM Designated D664-09a, 2009). The problem is likely due to the variability of electrodes which introduce an additional level of uncertainty (Mahajan *et al*., 2006). Recently, it has been confirmed that better accuracy and repeatability can be obtained only if the ASTM D664 method is modified by using a tedious electrode cleaning process, which requires almost double the analysis time (Wang *et al*., 2008). This becomes critical for current commercial production where fast analytical methods are essential for controlling the quality of biodiesel.

This problem can be addressed by using ASTM D974 which is another nonaqueous colorimetric-titration based method which uses KOH in isopropanol with *p*-naphtholbenzein as an indicator and is suitable even for colored samples (Knothe, 2006; Mahajan *et al*., 2006). ASTM D974 permits the AN of petroleum oils (ASTM D974-08, 2008) to be determined. Furthermore, ASTM D974 is a versatile method which is easy to perform and duplicate in laboratories as it involves only glassware, solution, and an indicator (Mahajan *et al*., 2006). Recently, ASTM D974 has been successfully used for the determination of AN to monitor

the biodiesel production from high FFA feedstocks (Baig and Ng, 2010). Analytical results were more consistent using ASTM D974 than with ASTM D664 (Mahajan *et al*., 2006).

In the literature, ASTM D974 has been used to determine the AN of biodiesel (Mahajan *et al*., 2006). However, in that study, standards were made by adding palmitic acid to soybean oil instead of biodiesel. Furthermore, over 50% of the standards were in the AN range which exceeds the specification for AN in the ASTM standards (0.50 mg KOH/g) (Mahajan *et al*., 2006). ASTM D974 has not yet been evaluated for the determination of AN of biodiesel blends. This study measures the accuracy and repeatability of ASTM D974 for refurbished waste oil and fat based biodiesel (B100) and its blends (B20, B10, B5, B2, and B1). The European biodiesel fuel standard EN 14214 uses EN 14104 as the standard method for the determination of AN and is also a colorimetric acid-base titration method; however, it uses a dilute ethanolic KOH solution with phenolphthalein as an indicator (Knothe, 2006).

Biodiesel can be used alone (B100) or blended with petroleum diesel in any proportion. It is usually blended with ultra-low sulfur diesel (ULSD) at various levels for lubricity improvement and emissions control (Clean cities fact sheet, 2010). Furthermore, when biodiesel is used at low levels (< 5%) such as B1 and B2, the user may not experience any significant decrease in power, torque and fuel economy as compared to high level blends such as B20 (Clean cities fact sheet, 2010). Recently, a quality survey of biodiesel blends sold commercially emphasize the need for ASTM standards for the biodiesel blends and monitoring of the quality of the biodiesel blends sold at retailers (Tang *et al*., 2008). This requires an easy-to-use, fast and economical method to analyze AN in the field or a retailer location. As a result, field test kits have been developed for cost-effective on-site analysis, which were also based on acid-base colorimetric titration, not on potentiometric method.
Recently, in the USA and Canada, the commercial use of biodiesel as a mo tor fuel has involved using its blends such as B1, B2, B5, B10, and B20. At present, in the USA, ASTM has set the specifications for biodiesel blends with more than 5% B100 (B6-B20) in standard ASTM D 7467-09 which allows for a maximum AN of 0.3 mg KOH/g. However, no

specifications for AN have been set yet for lower biodiesel blends such as B1, B2 and B5. On the other hand, the Canadian General Standards Board (CGSB) has developed the specifications for biodiesel blends (from B1 to B5) in CAN/CGSB-3.520. This standard set the maximum AN limit to 0.10 mg KOH/g and uses ASTM D974 as the reference standard method. However, specifications for blends with high levels of biodiesel (B6-B20) have not been developed. Recently, the accuracy and repeatability of ASTM D664 has been evaluated for biodiesel blends but ASTM D974 was not tested for comparison (Wang *et al*., 2008). Also, the study was limited to only B20 (Wang *et al*., 2008). No study has been reported in the literature for the application of ASTM D 974 for the determination of the AN of lower level biodiesel blends such as B10, B5, B2 and B1. To the best of our knowledge, this study is the first report on the evaluation of ASTM D974 for the determination of the AN of biodiesel blends (B1, B2, B5, B10, and B20) where accuracy and repeatability were determined.

7.2 Experimental

7.2.1 Materials

The waste oil and fat based biodiesel (B100) was obtained from Rothsay (Quebec, Canada). Ultra low sulfur diesel (USLD) was obtained from Boucher & Jones Fuels (Petro Canada, Waterloo, Ontario). Biodiesel blends B20, B10, B5, B2 and B1 were prepared by mixing B100 and ULSD at a volume ratio of 1:4, 1:9, 1:19, 1:49 and 1:99, respectively.

The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): palmitic acid (99%), 2-propanol (anhydrous, 99.5%), toluene (anhydrous, 99.8%), *p*-naphtholbenzein (indicator grade). The titrant solution, 0.1 M KOH (volumetric standard, in isopropanol), was supplied by Fisher Scientific (Ottawa, ON, Canada) and used to prepare 0.02 M KOH in isopropanol.

7.2.2 Methods

The titration solvent and indicator solution were prepared as detailed in ASTM D 974. Blends of B100 and ULSD were prepared to obtain weight percentages ranging from 0 to 90% as shown in Tables 7.1, 7.2, and 7.3. Also, biodiesel blends with a range of known AN levels ranging from 0.05 to 0.55 mg KOH/g were prepared by adding palmitic acid to the solutions of B1, B2, B5, B10, B20, and B100. As shown in Table 7.4, 7.5, 7.6, 7.7, 7.8 and 7.9, Bxx-1 represents unspiked samples and Bxx-2 represents samples spiked with palmitic acid. For example B20-1 is not spiked and B20-2 is spiked. Mixtures are derived by blending different wt. % of Bxx-1 and Bxx-2. The analyst did not know the exact calculated value of AN. The range of AN values of biodiesel and biodiesel blends was restricted to the AN as per the specifications in standards for biodiesel and biodiesel blends. For B100 and B20 each sample was titrated in triplicate (in order to compare with the literature reported results of ASTM D664). For B1 to B10, each sample was titrated six times.

To determine the AN of biodiesel and biodiesel blends, 2 g (measured to four decimal places) of a sample was collected in an Erlenmeyer flask (125 mL). Ten milliliters of titration solvent (a mixture of toluene, isopropanol and water in the volume ratio of 100:99) using a 10 mL pipette and eight drops of the *p*-naphtholbenzein indicator solution were added to each sample. The sample was then titrated against a 0.02 M KOH solution using a 10 mL burette. The titration was deemed complete when a color change from orange to green was observed in the titration mixture that persists for at least 15 s.

The experimental acid number was determined using Equation **7.1** as per ASTM D974 (ASTM D 974-08, 2008):

$$Acid\ \ Value, mg\ \ of\ \ KOH\ \ / g = \left[\frac{(A-B) \times M \times 56.1}{W} \right] \qquad (\mathbf{7.1})$$

where
A = KOH solution volume required for titration of the sample (mL)
B = KOH solution volume required for titration of the blank (mL)
M = molarity of the KOH solution
W = sample mass (g)

TABLE 7.1
Calculated and Experimental AN of the B100 and ULSD mixtures as per ASTM D 974 (using 0.1N KOH and 100mL Titrating Solvent) (unit: mg KOH/g)

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.313, 0.315, 0.302	0.310	-	0.0056	0.00	-	-
89.95	0.263, 0.255, 0.301	0.273	0.280	0.0094	9.53	-2.41	0.007
79.02	0.284, 0.264, 0.248	0.266	0.247	0.0077	8.04	7.50	-0.019
70.04	0.201, 0.236, 0.220	0.219	0.220	0.0080	10.12	-0.50	0.001
60.41	0.177, 0.173, 0.175	0.175	0.192	0.0055	8.71	-8.71	0.017
49.97	0.148, 0.173, 0.244	0.188	0.162	0.0055	8.11	16.12	-0.026
40.08	0.146, 0.144, 0.144	0.144	0.131	0.0078	14.90	10.28	-0.013
30.21	0.141, 0.144, 0.148	0.144	0.101	0.0078	14.91	42.88	-0.043
20.03	0.089, 0.039, 0.092	0.073	0.071	0.0078	29.36	3.25	-0.002
10.07	0.037, 0.038, 0.038	0.038	0.041	0.0078	57.21	-8.24	0.003
0.00	0.011, 0.011, 0.011	0.011	-	0.0327	0.08	-	-

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B100-1) x wt% component of (B100-1) in the mixture} + {AN of (B100-2) x wt% component of (B100-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of ASTM D 974 (using 0.1N KOH and 100mL Titrating Solvent) to B100 and ULSD mixtures resulted in large repeatability and errors as indicated in tabulated data.

TABLE 7.2
Calculated and Experimental AN of the B100 and ULSD mixtures as per modified ASTM D 974 (using 0.02N KOH and 100mL Titrating Solvent) (unit: mg KOH/g)

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.304, 0.309, 0.326	0.313	-	0.0056	0.00	-	-
89.95	0.286, 0.290, 0.286	0.287	0.284	0.0094	9.06	1.18	-0.003
79.02	0.278, 0.263, 0.253	0.265	0.253	0.0077	8.07	4.57	-0.012
70.04	0.225, 0.217, 0.227	0.223	0.227	0.0080	9.94	-1.78	0.004
60.41	0.206, 0.204, 0.206	0.205	0.199	0.0055	7.44	3.08	-0.006
49.97	0.182, 0.161, 0.180	0.175	0.169	0.0055	8.74	3.37	-0.006
40.08	0.143, 0.18, 0.140	0.144	0.140	0.0078	14.99	2.55	-0.004
30.21	0.108, 0.114, 0.101	0.108	0.112	0.0078	19.97	-3.78	0.004
20.03	0.073, 0.076, 0.073	0.074	0.083	0.0078	29.09	-10.87	0.009
10.07	0.054, 0.056, 0.048	0.053	0.054	0.0078	40.73	-2.14	0.001
0.00	0.039, 0.018, 0.18	0.025	-	0.033	0.04	-	-

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B100-1) x wt% component of (B100-1) in the mixture} + {AN of (B100-2) x wt% component of (B100-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 (using 0.02N KOH and 100mL Titrating Solvent) to B100 and ULSD mixtures resulted in good accuracy and repeatability as indicated in tabulated data.

7.3 Results and discussion

According to ASTM, the repeatability of a method is defined as "the difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed only in one case in twenty" (ASTM D974-08, 2008).

In this study, a single operator, using the same apparatus carried out the analysis within a short time between tests. These conditions are in accordance with the requirements of ASTM for repeatability.

Therefore, the repeatability values were calculated using the following Equation **7.2**:

$$repeatability\ (\%) = \left[\frac{2.77 \times SD}{Experimental\ Mean \times n} \right] \times 100\% \qquad (\mathbf{7.2})$$

where

n = number of operators involved in the analysis = 1

In this study, the errors were calculated using the following Equation **7.3** (Wang *et al.*, 2008):

$$Error(\%) = \left[\frac{Experimental\ AN\ Mean - Calculated\ AN}{Calculated\ AN} \right] \times 100\% \qquad (\mathbf{7.3})$$

In the above equation, the calculated AN was based on the sum of the wt% composition of low AN and high AN samples of biodiesel and biodiesel blend mixtures as shown in Equation **7.4**. The calculated AN is derived from the experimentally determined values of Bxx-1 and Bxx-2. For example, the calculated AN for B100 samples, will be as follows:

Calculated AN = [{AN of (B100-1) x wt % component of (B100-1) in the mixture} +
{AN of (B100-2) x wt % component of (B100-2) in the mixture}/100] (**7.4**)

Therefore, as an example, for Mixture-1 in Table 7.4, calculated AN will be determined using Equation 7.4 as follows:

Calculated AN = [{(0.275 x 89.45) + (0.633 x 10.45)}/100] = 0.313

ASTM D974 was applied to blends of B100 and ULSD, to yield the results shown in Table 7.1. It was found that application of ASTM D974 which used 0.1 M KOH and 100 mL of titration solvent, results in high values of repeatability (up to 57.2%) and very large percentage error (up to 42.9%). This error was anticipated since relatively little amount of base was consumed. Therefore, to investigate further, a lower concentration of base was used (0.02 M KOH). It was confirmed that the use of 0.02 M KOH reduced the maximum repeatability value of 40.7% and percentage error to 10.9% as compared to the maximum repeatability value of 57.2% and percentage error of 42.9% when higher concentration of base (0.1 M KOH) was used as per ASTM D974 as shown in Table 7.2.

Furthermore, it would be preferable to reduce the amount of toxic chemicals used in analytical methods. ASTM D974 required 100 mL of titration solvent which is a mixture consisting of toluene, isopropanol and water in the volume ratio of 100:99:1. Therefore, to reduce the amount of toxic chemicals used in ASTM D974, a lower volume of titration solvent (10 mL) was used with modified ASTM D974 (0.02 M KOH). This was found to reduce the maximum percentage error value to 5.92% compared to the value of 10.87% obtained when higher amounts of titration solvent (100 mL) were used as per modified ASTM D974 (0.02 M KOH) (Table 7.3). At the same time, the values of repeatability obtained were similar to those when modified ASTM D974 (0.02 M KOH) was used with the higher amount of titration solvent (100 mL). The linearity between the experimentally determined AN obtained according to ASTM D974 (0.1 M KOH and 100 mL titration solvent), modified ASTM D974 (0.02 M KOH and 100 mL titration solvent) and modified ASTM D974 (0.02 M KOH and 10 mL titration solvent) and the calculated AN of the biodiesel and ULSD mixtures are shown in Figure 7.1 Correlation coefficient (R^2) values of 0.9474, 0.9960 and 0.9968, respectively were obtained.

This demonstrates that this modified ASTM D974 method has better linearity. Therefore, this modified ASTM D974 method, using 0.02 M KOH and 10 mL of titration solvent, was used for the determination of AN values for biodiesel and biodiesel blends.

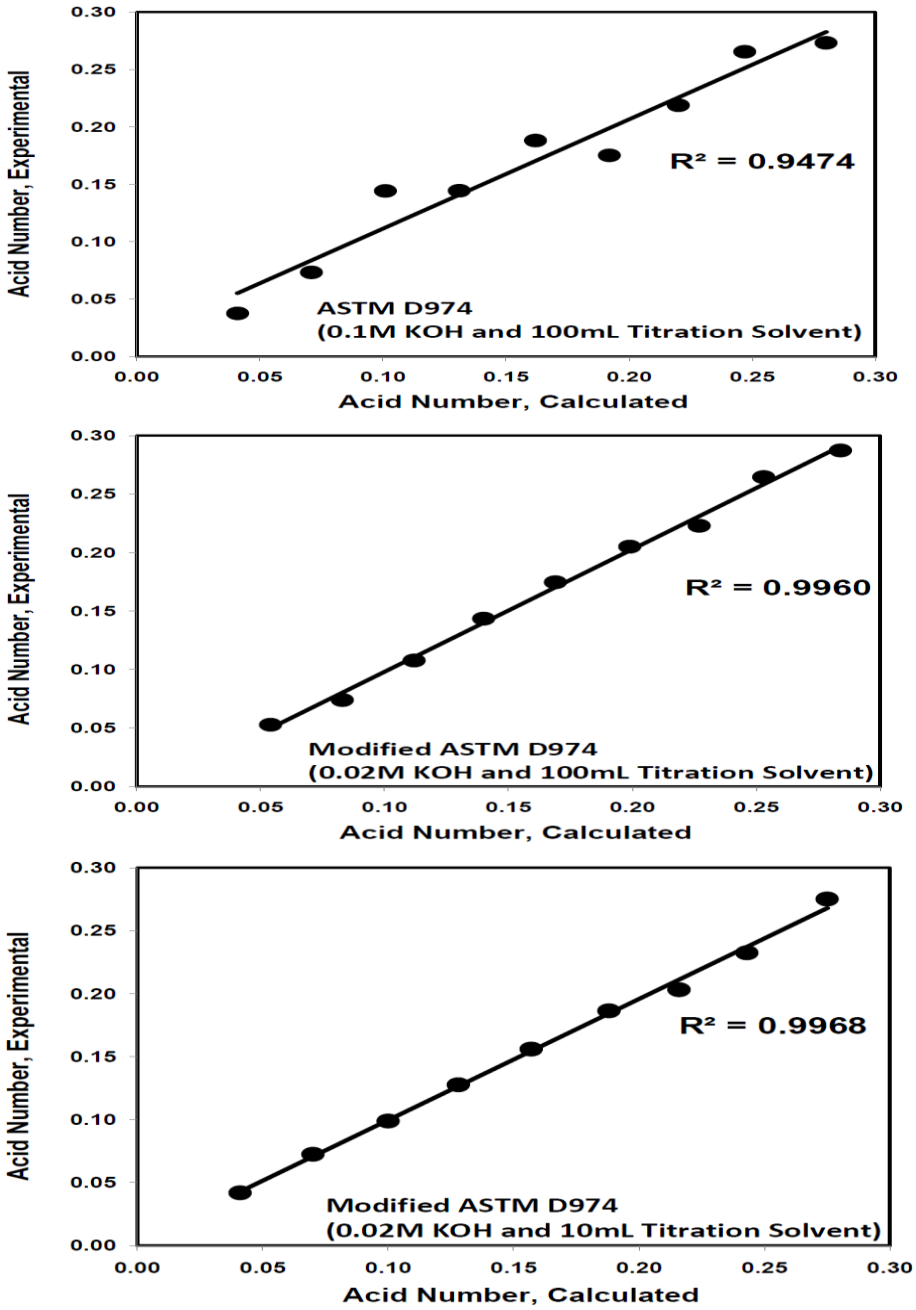


Figure 7.1 Experimental AN *vs* calculated AN of the B100 and ULSD mixtures as per: (1). ASTM D974 (using 0.1 M KOH and 100 mL titration solvent), (2). Modified ASTM D974 (using 0.02 M KOH and 100 mL titration Solvent). (3). Modified ASTM D974 (using 0.02 M KOH and 10 mL titration solvent) (unit: mg KOH/g).

TABLE 7.3
Calculated and Experimental AN of the B100 and ULSD mixtures as per modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) (unit: mg KOH/g)

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.309, 0.299, 0.305	0.304	-	0.0056	0.00	-	-
89.95	0.267, 0.278, 0.280	0.275	0.275	0.0094	9.46	0.08	0.00
79.02	0.233, 0.226, 0.239	0.232	0.243	0.0077	9.19	-4.32	0.011
70.04	0.188, 0.205, 0.216	0.203	0.216	0.008	10.90	-5.92	0.013
60.41	0.187, 0.183, 0.189	0.186	0.188	0.0055	8.19	-0.86	0.002
49.97	0.155, 0.164, 0.148	0.156	0.157	0.0055	9.78	-0.64	0.001
40.08	0.123, 0.135, 0.125	0.128	0.128	0.0078	16.85	-0.23	0.000
30.21	0.099, 0.096, 0.102	0.099	0.100	0.00078	21.77	-1.14	0.001
20.03	0.062, 0.077, 0.078	0.073	0.070	0.0078	29.68	3.59	-0.003
10.07	0.047, 0.037, 0.041	0.042	0.041	0.0078	51.37	2.19	-0.001
0.00	0.009, 0.014, 0.009	0.011	-	0.0327	0.09	-	-

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B100-1) x wt% component of (B100-1) in the mixture} + {AN of (B100-2) x wt% component of (B100-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) to B100 and ULSD mixtures resulted in l good accuracy and repeatability as indicated in tabulated data.

Results for the determination of the AN for the biodiesel (B100) are shown in Table 7.4. B100-1 in Table 7.4 is the original sample with low AN, whereas, B100-2 is the high AN sample prepared by adding a calculated amount of palmitic acid to B100-1. Mixtures 1-7 in Table 7.4 were obtained by mixing B100-1 and B100-2 at different wt% ratios to produce biodiesel with different AN in the range of 0.313 – 0.525 mg KOH/g. Each sample was titrated three times; the mean, standard deviation (SD), repeatability, percentage error (less error, higher accuracy), and the difference between experimental and calculated AN are also shown in Table 7.4.

ASTM D974 cites that a repeatability of 0.05 mg KOH/g in the AN range of 0.1 to 0.5 mg KOH/g should be obtained for 20.0 g samples of petroleum oil. This corresponds to 50 and 10% for AN values of 0.1 and 0.5 mg KOH/g, respectively. ASTM recommends a sample size of 20 g when the AN lies between 0.0 and 3.0 mg KOH/g. In this study, the repeatability

TABLE 7.4
Calculated and Experimental AN of the B100 samples as per modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) (unit: mg KOH/g)

Samples	Composition (wt %) B100-1	B100-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
B100-1	100	0	0.268, 0.276, 0.281	0.275	-	0.0066	0.00	-	-
B100-2	0	100	0.624, 0.631, 0.644	0.633	-	0.0102	0.00	-	-
Mixture 1	89.45	10.45	0.310, 0.303, 0.321	0.311	0.313	0.0094	8.36	-0.41	-0.001
Mixture 2	79.47	11.82	0.359, 0.362, 0.347	0.356	0.349	0.0077	6.00	2.05	0.007
Mixture 3	69.70	30.21	0.394, 0.386, 0.402	0.394	0.383	0.0080	5.62	2.76	0.011
Mixture 4	59.44	40.56	0.428, 0.423, 0.434	0.428	0.421	0.0055	3.56	1.87	0.008
Mixture 5	48.90	51.10	0.474, 0.478, 0.463	0.472	0.458	0.0078	4.56	2.97	0.014
Mixture 6	40.18	59.82	0.519, 0.49, 0.504	0.507	0.489	0.0112	6.15	3.51	0.017
Mixture 7	30.19	69.81	0.533, 0.539, 0.529	0.534	0.525	0.0050	2.61	1.62	0.009

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B100-1) x wt% component of (B100-1) in the mixture} + {AN of (B100-2) x wt% component of (B100-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 to B100 resulted in good accuracy and repeatability as indicated in tabulated data.

of the B100 ranged from 8.37 to 2.75% within the AN range of 0.313-0.525 mg KOH/g as shown in Table 7.4. These repeatability values are within the stated limits specified in ASTM D974 although the sample sizes were one-tenth as large and also far below the recently reported maximum and minimum repeatability values of 27.64 and 5.45%, determined using the ASTM D664 method without any modification (Wang *et al*., 2008). In addition, percentage error of modified ASTM D974 for all B100 samples was measured to be within 3.51% over the AN range of 0.313–0.525 mg KOH/g. At an AN value of 0.525 mg KOH/g, the error was only 1.62% as compared to the value of 3.30% at an AN value of 0.595 mg KOH/g reported in the literature (Mahajan *et al*., 2006).

From Table 7.4, the maximum absolute experimental error among all seven samples was 3.51%. For B100, an AN of 0.313 mg KOH/g was measured with best accuracy (least error). For B100, these data show this modified ASTM D974 can be used even when AN values are low.

The results for the determination of the AN of biodiesel blends, B20, B10, B5, B2 and B1 are shown in Tables 7.5, 7.6, 7.7, 7.8 and 7.9, respectively, using modified ASTM D974. The range of AN values of biodiesel blends was restricted as per the specifications in standards for biodiesel blends. For example, for B1-B5, the AN specification is 0.10 mg KOH/g and hence the range of AN selected was 0.035-0.127 mg KOH/g. For blends with high levels of biodiesel such as B10 and B20, the range of AN was 0.067-0.313 mg KOH/g as the standard limit is 0.3 mg KOH/g. For B20, the modified ASTM D974 can measure AN values at levels as low as 0.073 mg KOH/g with a small error of -6.60% which is much better compared to not only ASTM D664, but even the modified ASTM D664 method, which obtained the lowest reported AN value of 0.123 mg KOH/g with an error of 4.13% (Wang *et al*., 2008).

TABLE 7.5
Calculated and Experimental AN of B20 samples as per modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) (unit: mg KOH/g)

Samples	Composition (wt %) B20-1	B20-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
B20-1	100	0	0.060, 0.052, 0.058	0.057	-	0.0042	20.30	-	-
B20-2	0	100	0.411, 0.430, 0.424	0.421	-	0.0097	6.38	-	-
Mixture 1	94.27	5.73	0.077, 0.072, 0.078	0.073	0.078	0.0094	35.91	-6.60	-0.005
Mixture 2	88.18	11.82	0.104, 0.109, 0.110	0.112	0.100	0.0077	19.13	11.76	0.012
Mixture 3	79.53	20.47	0.141, 0.138, 0.139	0.139	0.131	0.0080	15.91	6.02	0.008
Mixture 4	67.78	32.22	0.191, 0.185, 0.156	0.177	0.174	0.0055	8.61	1.78	0.003
Mixture 5	60.69	39.31	0.194,0.213,0.208	0.205	0.200	0.0055	7.44	2.53	0.005
Mixture 6	49.78	50.22	0.260, 0.251, 0.251	0.254	0.240	0.0078	8.48	5.84	0.014
Mixture 7	39.65	60.35	0.290, 0.288, 0.292	0.290	0.277	0.0112	10.73	4.83	0.013
Mixture 8	29.61	70.39	0.327, 0.322, 0.338	0.329	0.313	0.0050	4.23	5.02	0.016

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B20-1) x wt% component of (B20-1) in the mixture} + {AN of (B20-2) x wt% component of (B20-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 to B20 resulted in good accuracy and repeatability as indicated in tabulated data.

TABLE 7.6
Calculated and Experimental AN of the B10 samples as per modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) (unit: mg KOH/g)

Samples	Composition (wt %) B10-1	B10-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
B10-1	100	0	0.051,0.031, 0.038, 0.027, 0.028,0.036	0.035	-	0.0089	0.01	-	-
B10-2	0	100	0.305, 0.340, 0.320, 0.323, 0.344, 0.321	0.326	-	0.0144	0.00	-	-
Mixture 1	88.94	11.06	0.069, 0.082, 0.068, 0.074, 0.047, 0.064	0.067	0.067	0.0094	38.67	0.09	0.000
Mixture 2	80.19	19.81	0.085, 0.084, 0.095, 0.097, 0.105, 0.095	0.094	0.093	0.0077	22.82	0.95	0.001
Mixture 3	68.91	31.09	0.125, 0.125,0.130, 0.111, 0.122, 0.119	0.122	0.126	0.0080	18.17	-2.87	-0.004
Mixture 4	59.08	40.92	0.144, 0.166, 0.164, 0.159, 0.147, 0.156	0.156	0.154	0.0055	9.79	1.11	0.002
Mixture 5	40.46	59.54	0.204, 0.201, 0.184, 0.200, 0.190, 0.202	0.196	0.208	0.0055	7.77	-5.69	-0.012
Mixture 6	30.23	69.77	0.242, 0.232, 0.235, 0.225, 0.204, 0.205	0.237	0.238	0.0078	9.10	-0.64	-0.002

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B10-1) x wt% component of (B10-1) in the mixture} + {AN of (B10-2) x wt% component of (B10-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 to B10 resulted in good accuracy and repeatability as indicated in tabulated data.

TABLE 7.7
Calculated and Experimental AN of the B5 samples as per modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) (unit: mg KOH/g)

Samples	Composition (wt %) B5-1	B5-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
B5-1	100	0	0.010, 0.009, .005, 0.010, 0.011, .006	0.008	-	0.0024	0.01	-	-
B5-2	0	100	0.293, 0.280, .291, 0.299, 0.293, 0.292	0.291	-	0.0062	0.00	-	-
Mixture 1	90.42	9.58	0.028, 0.037, 0.039, 0.057, 0.044, 0.035	0.040	0.035	0.0094	65.06	14.35	0.005
Mixture 2	84.16	15.84	0.054, 0.056, 0.054, 0.075, 0.068, 0.060	0.061	0.053	0.0077	34.79	15.83	0.008
Mixture 3	79.99	20.01	0.071, 0.072, 0.080, 0.077, 0.064, 0.067	0.072	0.065	0.0080	30.88	9.67	0.006
Mixture 4	74.96	25.04	0.098, 0.100, 0.085, 0.100, 0.088, 0.101	0.095	0.079	0.0055	16.00	25.75	0.016
Mixture 5	69.97	30.03	0.101, 0.096, 0.110, 0.111, 0.132, 0.113	0.102	0.093	0.0055	14.90	10.14	0.009
Mixture 6	59.53	40.47	0.143, 0.133, 0.127, 0.121, 0.152, 0.414	0.134	0.123	0.0078	16.05	8.93	0.011

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B5-1) x wt% component of (B5-1) in the mixture} + {AN of (B5-2) x wt% component of (B5-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 to B5 resulted in good accuracy and repeatability as indicated in tabulated data.

TABLE 7.8
Calculated and Experimental AN of the B2 samples as per modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) (unit: mg KOH/g)

Samples	Composition (wt %) B2-1	B2-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN Difference (Exp. - Cal.)
B2-1	100	0	0.018, 0.009, 0.018, 0.009, 0.014, 0.004	0.012	-	0.0056	0.01	-	-
B2-2	0	100	0.373, 0.372, 0.361, 0.449, 0.374, 0.367	0.383	-	0.0327	0.00	-	-
Mixture 1	90.42	9.58	0.061, 0.064, 0.063, 0.053, 0.052, 0.065	0.060	0.050	0.0094	43.52	19.67	0.010
Mixture 2	84.16	15.84	0.080, 0.075, 0.080, 0.076, 0.083, 0.095	0.082	0.071	0.0077	26.20	14.82	0.011
Mixture 3	79.99	20.01	0.102, 0.096, 0.101, 0.104, 0.095, 0.113,	0.102	0.091	0.008	21.74	12.03	0.011
Mixture 4	74.96	25.04	0.108, 0.115, 0.123, 0.119, 0.110, 0.104	0.113	0.097	0.0055	13.48	16.69	0.016
Mixture 5	69.97	30.03	0.112, 0.120, 0.106, 0.104, 0.106, 0.117	0.113	0.107	0.0055	13.51	5.57	0.006
Mixture 6	59.53	40.47	0.110, 0.113, 0.142, 0.128, 0.141, 0.126	0.121	0.127	0.0078	17.74	-4.45	-0.006

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B2-1) x wt% component of (B2-1) in the mixture} + {AN of (B2-2) x wt% component of (B2-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 to B2 resulted in good accuracy and repeatability as indicated in tabulated data.

TABLE 7.9
Calculated and Experimental AN of the B1 samples as per modified ASTM D 974 (using 0.02N KOH and 10mL Titrating Solvent) (unit: mg KOH/g)

Samples	Composition (wt %) B1-1	B1-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN Difference (Exp. - Cal.)
B1-1	100	0	0.017, 0.019, 0.004, 0.019, 0.019, 0.008	0.013	-	0.0068	0.01	-	-
B1-2	0	100	0.225, 0.238, 0.226, 0.210, 0.209, 0.230	0.223	-	0.0114	0.00	-	-
Mixture 1	81.03	18.97	0.065, 0.056, 0.050, 0.054, 0.051, 0.057	0.056	0.053	0.0094	46.80	5.25	0.003
Mixture 2	74.32	25.68	0.087, 0.085, 0.077, 0.082, 0.074, 0.073	0.080	0.067	0.0077	26.80	19.05	0.013
Mixture 3	67.05	32.95	0.104, 0.090, 0.083, 0.095, 0.096, 0.086	0.092	0.082	0.0080	23.96	12.45	0.010
Mixture 4	64.68	35.32	0.099, 0.113, 0.091, 0.099, 0.096, 0.082	0.097	0.087	0.0055	15.78	10.92	0.010
Mixture 5	60.22	39.78	0.092, 0.101, 0.104, 0.085, 0.107, 0.085,	0.099	0.097	0.0055	15.41	2.53	0.002
Mixture 6	48.78	51.22	0.112, 0.116, 0.110, 0.100, 0.131, 0.104	0.112	0.120	0.0078	19.14	-6.76	-0.008

[a]Experimentally determined as per ASTM D 974.
[b]Calculated AN = [{AN of (B1-1) x wt% component of (B1-1) in the mixture} + {AN of (B1-2) x wt% component of (B1-2) in the mixture}/100]
[c] Standard Deviation (SD)
Application of modified ASTM D 974 to B1 resulted in good accuracy and repeatability as indicated in tabulated data.

For B20, B10, B5, B2, and B1, the most accurate values were measured at AN values of 0.177, 0.067, 0.072, 0.126, and 0.096 mg KOH/g, respectively. For all biodiesel blend samples, better repeatability was obtained as the AN values increase.

The linearity between experimentally determined AN by modified ASTM D974 and the calculated AN of the biodiesel and biodiesel blends are shown in Figure 7.2. The correlation coefficient (R^2) values obtained for B100, B20, B10, B5, B2, and B1 were 0.9974, 0.9969, 0.9968, 0.9882, 0.9599 and 0.8988, respectively. The difference between the experimental AN determined as per modified ASTM D974 and the calculated AN for all biodiesel and biodiesel blend samples was within ± 0.018 mg KOH/g as shown in Tables 7.4, 7.5, 7.6, 7.7, 7.8, and 7.9 demonstrating the reliability of the modified ASTM D974 method.

A major limitation for the application of ASTM D974 was that the color changes during the titration and at the end point in dark- colored samples could not be observed. However, in this study, distilled biodiesel (B100) was colorless and the distilled biodiesel blends samples (from B1 to B20) were very light in color (due to the color of ULSD), which enabled color changes during the titration to be easily observed.

In this study, a low concentration of base (KOH) (0.02 M) was used instead of 0.1 M. It is recommended that an even lower concentration of base, e.g. 0.01 M KOH be used for low AN biodiesel blends such as B1 and B2. This will increase the volume of KOH required to reach the equivalence point which should enhance the volume of titrant consumed to be more precisely measured. In this study, a 10 mL burette with 0.05 mL subdivision was used as per ASTM D974 recommendation. However, it is recommended to use a burette of 5 mL with divisions of 0.02 mL (also recommended by ASTM D974).

7.4 Conclusion

The ASTM reference standard method D664, a potentiometric method, has major problems such as mediocre reproducibility, tedious process for cleaning electrodes and longer analysis

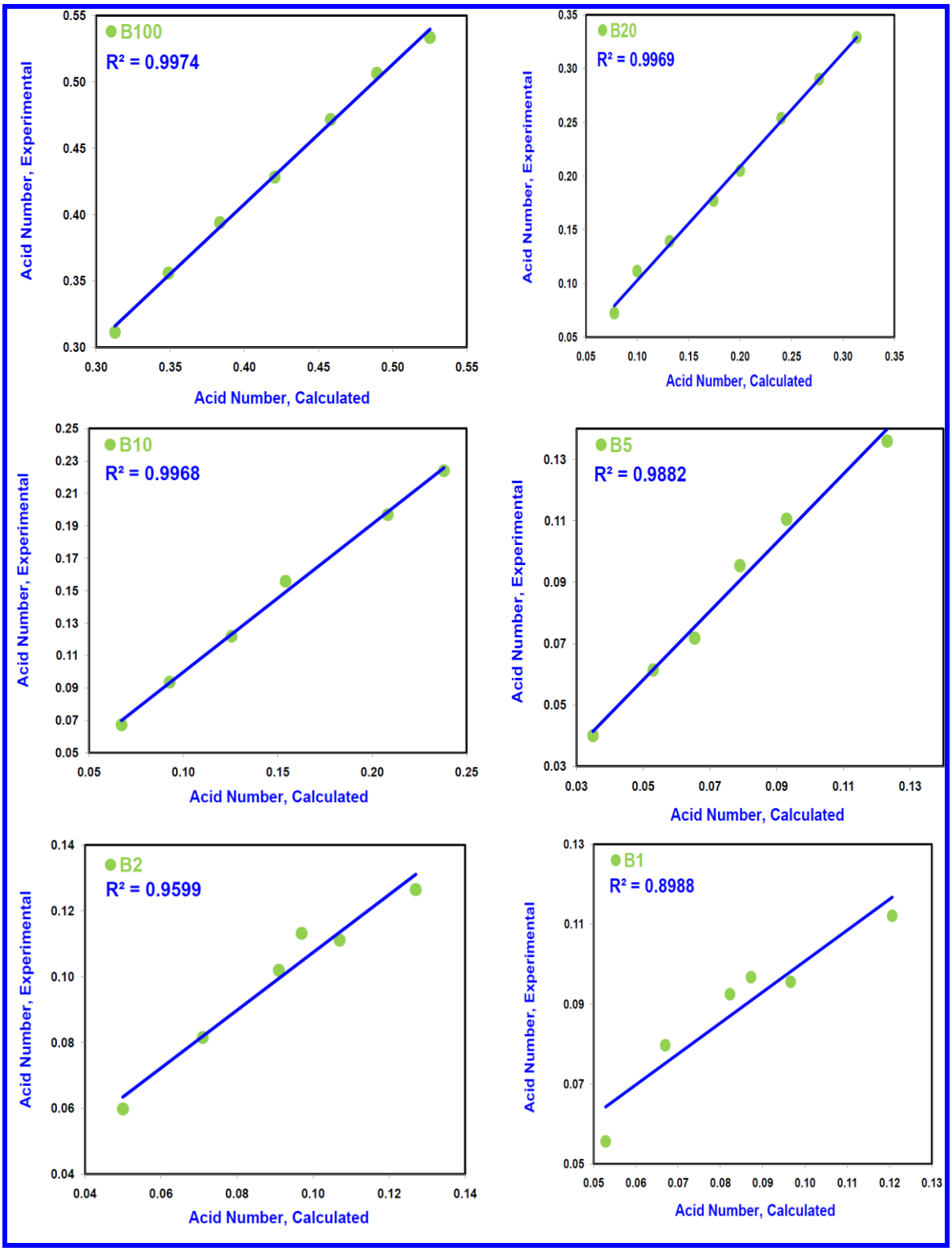


Figure 7.2 Experimental AN (as per ASTM D974) *vs* calculated AN for Biodiesel (B100) and Biodiesel Blends (B20, B10, B5, B2 and B1) (unit: mg KOH/g).

time. On the other hand, ASTM D974 is a non-aqueous colorimetric titration-based method which offers various advantages such as ease, reproducibility, cost-effectiveness and time-

efficiency. However, it was found that determination of AN of biodiesel and biodiesel blend using the current ASTM D 974 results in large values of repeatability (up to 73.41%) and larger percentage error (up to 42.9%). Therefore, ASTM D974 has been modified using a lower concentration of base (0.02 M KOH instead of 0.1 M KOH) as well as reducing the amount of toxic titration solvent from 100 mL to only 10 mL. This makes reduced the amount of toxic solvent used. This modified method significantly reduces the maximum percentage error from 42.88 to 5.92%. The application of this modified ASTM D974 for the determination of AN of biodiesel and biodiesel blends was studied. Application of the modified ASTM D974 to biodiesel and biodiesel blend was tested with good accuracy and repeatability. Good accuracy and repeatability were also obtained within ASTM D6751-09a specifications for the AN, which is 0.50 mg KOH/g. For B20, B10, B5, B2, and B1, the most accurate values were measured at AN values of 0.177, 0.067, 0.072, 0.126, and 0.096 mg KOH/g, respectively. The difference between the experimental AN determined as per modified ASTM D974 and the calculated AN for all biodiesel and biodiesel blend samples was within ± 0.018 mg KOH/g. All distilled biodiesel and biodiesel blend samples were found to be very light in color, which eliminates the major obstacle for the application of ASTM D974. Also, this study confirms the detection limit of this modified ASTM D974 up to 0.05 mg KOH/g which shows that a specification of 0.1 mg KOH/g for AN can be set for B1-B5. Furthermore, due to simplicity and cost-effectiveness this modified ASTM D974, it can be used in field biodiesel analytical kits to determine AN on site or at a retailer location. Therefore, this modified ASTM D974 is recommended as a reference method for AN determination of biodiesel and biodiesel blends. This extensive study has demonstrated that this modified ASTM D974 method is a reliable method for the determination of AN and could be used for establishing the specifications of AN for biodiesel and biodiesel blends ranging from B1 to B20 in quality standards.

CHAPTER 8

A SIMPLE AND GREEN ANALYTICAL METHOD FOR ACID NUMBER ANALYSIS OF BIODIESEL AND BIODIESEL BLENDS BASED ON POTENTIOMETRIC TECHNIQUE[3]

Overview

Acid number is an important quality parameter for biodiesel and biodiesel blends and has been included in various standards including ASTM D6751 and EN 14214. In this paper, a new simple and potentiometric method based on green chemistry approaches has been developed to determine the acid number of biodiesel and biodiesel blends. This new method uses a reduced amount of titration solvent and a smaller sample size than currently recommended in the ASTM reference method D664. A time-efficient electrode cleaning procedure has been developed which completely eliminates the use of toxic solvents. This proposed method significantly reduced the maximum % error from 101% to only -18% and the repeatability from 290% to 100% when compared to ASTM D664 method using the sample size of 2 g.

This analytical procedure could be used as a simple time-efficient, cost effective and environmentally friendly method for the determination of acid number of biodiesel and biodiesel blends in R&D as well as in industrial quality control laboratories.

Keywords Acid number, Free fatty acid, Biodiesel, Green chemistry, Potentiometry, Green analytical method.

[3] Adapted from Aijaz Baig, Michael Pastzi, and Flora T.T. Ng. "A Simple and Green Analytical Method for Acid Number Analysis of Biodiesel and Biodiesel Blends based on Potentiometric Technique". Fuel 2013,104, 426–432.

8.1 Introduction

Biodiesel is defined by the American Society for Testing and Materials (ASTM) as the mono alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat (Baig and Ng, 2010). Recently, due to increasing interest and use of biodiesel around the world, the assurance of biodiesel quality has become a critical factor that could play a vital role in its successful commercialization and market acceptance.

Therefore, various biodiesel standards have been developed around the world, including the United States (ASTM D6751) and Europe (EN 14214) (Knothe, 2006). Quality standards for biodiesel as motor fuel have been established in ASTM standard D6751 and European Committee for Standardization (CEN) standard EN 14214 (ASTM D6751-09a, 2009; DIN EN 14214-2003, 2003). In both standards, one important quality parameter for biodiesel is the acid number (AN).

According to ASTM D664, AN is measured as the mg of KOH required to neutralize the acids in 1 gram of the sample (ASTM D6751-09a, 2009). AN is a measure of the degree of oxidation and hydrolysis in the biodiesel (Wang *et al*., 2008). Hydrolysis during biodiesel production can result in the formation of FFA. FA can be formed by the hydrolysis of ester linkages in both the TG feedstock and the biodiesel during its manufacture (Mahajan *et al*., 2006). Furthermore, the presence of FFAs can cause severe operational problems and is considered as a safety risk during storage due to the possibility of corrosion by the FFA (Wang *et al*., 2008). Therefore, both ASTM D6751 and EN 14214 have restricted the maximum value of AN to be 0.50 mg KOH/g for biodiesel (B100). AN of biodiesel depends on the type of feedstock and how well the biodiesel was processed during and after production.

Due to the high cost of refined vegetable oils, alternative inexpensive feedstocks with high FFA content are gaining interest around the world for the production of biodiesel due to their economical, commercial and environmental benefits (Baig and Ng, 2010).

This requires the development of time-efficient, reliable, and low cost analytical methods for an accurate determination of AN to monitor the acid number of biodiesel and biodiesel blends (Wang *et al.*, 2008; Mittelbach, 1996; Baig and Ng, 2011).

Biodiesel can be used alone (B100) or blended with petroleum diesel in any proportion. Generally, it is blended with ultra-low sulfur diesel (ULSD) at various levels in order to improve the lubricity and emissions control (Clean Cities Fact Sheet: Biodiesel Blends, 2008). In the past few years, the commercial use of biodiesel has increased as a motor fuel in blends such as B2, B5, and B20 in the USA and Canada.

At present, ASTM has set the specifications for biodiesel blends in the USA with more than 5% B100 (B6-B20) in the standard D7467-09 which allows for a maximum AN of 0.3 mg KOH/g. On the other hand, the Canadian General Standards Board (CGSB) has not developed the specifications for biodiesel blends with high levels of biodiesel such as B20 (Baig and Ng, 2011).

Currently, ASTM D664 is a reference method for measuring the AN of biodiesel and biodiesel blends in ASTM D6751 that is based on potentiometric titration in a non- aqueous medium and is suitable even for colored samples (ASTM D664-09a,2009; Wang *et al.*, 2008). ASTM D664 has been applied even to heavy oils and bitumens for acid number analysis (Fuhr *et. al.*, 2007). Despite several studies, the detection limit of ASTM D664 remains debatable (Wang *et al.*, 2008). Furthermore, due to an increase in research on new processes for the production of biodiesel from alternative inexpensive feedstocks which contain a high amount of FFA, kinetics studies are required for process development. In order to study the kinetics in small lab scale batches (varying from a few grams to hundreds of grams), collection of large samples such as 20 g (as required by ASTM D664 to determine the AN within the ASTM D6751 specified range of 0.5 mg KOH/g) from the reactor for analysis makes it nearly impossible to obtain accurate kinetic data. However, this could be achieved by using a small sample size for AN determination. Recently, a modified ASTM

D664 has been used to determine the AN of biodiesel and biodiesel blends (Wang *et al.*, 2008). However, this method requires largesample sizes, large amounts of toxic titration solvent, and complex electrode cleaning procedure using toxic solvents similar to those specified in ASTM D664. It also recommends a longer time for soaking the electrode with water which almost doubles the analysis time (ASTM D664-09a, 2009; Wang *et al.*, 2008; Baig and Ng, 2011). Furthermore, these analytical methods generate large amount of hazardous waste which is highly undesirable. Recently, potentiometric and visual titration-based methods were developed in an attempt to reduce the use of toxic solvents. However, such methods still employed large sample sizes and large amounts of organic solvent (1:1 mixture of ethanol and water) (Tubino *et al*., 2011; Aricetti *et al*., 2012). Even, if low toxic calibration fluids are used, problems still remain a challenge for green analytical chemistry (GAC) (Hamblin *et al.,* 2004). This becomes critical for current commercial production processes where time-efficient, cost-effective and environmentally green analytical methods are essential for meeting the quality standards for biodiesel and biodiesel blends.

These problems can be addressed by using green chemistry approaches to minimize toxic chemical consumption and waste generation which should reduce operating costs, including those spent on waste treatment and disposal (Armenta *et al.,* 2008). "Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc. that are hazardous to human health or the environment" (Anastas, 1999). As a result of the emergence of green chemistry in the late 1990s, in the past few years, a paradoxical situation has developed whereby most of the analytical methods generate a large amount of hazardous chemical waste, which has significant impact on the environment (Kruanetr *et al.,* 2007). This becomes more critical in some cases, where the chemicals used for analysis are even more toxic than the species being analyzed. As a result, GAC emphasized the use of smaller sample sizes, lower consumption of toxic chemicals and reduction hazardous waste. To the best of our knowledge, this study is the first report using green chemistry approaches, (e.g smaller sample sizes, reduction in the use of toxic chemicals, less hazardous waste and elimination of the use of toxic chemicals in

the electrode cleaning process) to develop a green potentiometric method to determine the AN of biodiesel (B100) and biodiesel blends (B20). Also, a single-step green aqueous-based electrode cleaning procedure has been developed.

8.2 Experimental procedures

8.2.1 Materials

Biodiesel (B100) produced from waste oils and fats was obtained from Rothsay (Quebec, Canada). Ultra-low sulfur diesel (USLD) was obtained from Boucher & Jones Fuels (Petro Canada, Waterloo, Ontario). The biodiesel blend B20 was prepared by mixing B100 and ULSD at a volume ratio of 1:4. The following chemicals were supplied by VWR Canada: 2-propanol (anhydrous, 99.9%), toluene (anhydrous, 99.5%), ASTM Type-II water, and 0.1M KOH (volumetric standard, in isopropanol). Palmitic acid (99%) was supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI). Benzoic acid (certified ACS) was supplied by Fisher Scientific (Ottawa, ON, Canada), while the electrode storage solution was supplied by Metrohm Ltd (Switzerland).

8.2.2 Electrodes and instrumentation

A Metrohm 808 Titrando auto-titrator equipped with a stirrer from Metrohm (Switzerland), data acquisition software and a solvotrode non-aqueous glass electrode with LiCl saturated solution in ethanol electrolyte was used to detect the endpoint potentiometrically.

8.2.3 Methods

The titration solvent was prepared as detailed in ASTM D664 (ASTM D664-09a, 2009). Blends of B100 and ULSD were prepared to obtain weight percentages of biodiesel ranging from 20% to 80% as shown in Tables 8.1 and 8.2. Also, biodiesel blends with a range of known AN levels ranging from 0.127 to 0.567 mg KOH/g were prepared by adding palmitic acid to the solutions of B20 and B100.

As shown in Table 8.3 and 8.4, Bxx-1 represents unspiked samples and Bxx-2 represents samples spiked with palmitic acid. For example B20-1 is not spiked and B20-2 is spiked. Mixtures are derived by blending different wt. % of pure Bxx-1 and pure Bxx-2. The analyst did not know the exact calculated value of AN. The range of AN values of biodiesel and biodiesel blends was restricted according to the standards for biodiesel and biodiesel blends. Each B100 and B20 sample was titrated in triplicate.

TABLE 8.1 Calculated and experimental AN of the B100 and ULSD mixtures as per ASTM D 664 (using 0.1 M KOH, 125 mL titration solvent, and 2 g sample size) (unit: mg KOH/g).

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.159, 0.115, 0.187	0.154	-	0.03630	0.01	-	-
79.07	0.215, 0.058, 0.125	0.133	0.124	0.07878	164.49	6.99	0.009
59.92	0.106, 0.034, 0.018	0.053	0.097	0.04688	246.54	-45.70	-0.044
40.18	0.010, 0.134, 0.041	0.062	0.070	0.06453	289.87	-11.90	-0.008
20.56	0.036, 0.114, 0.010	0.084	0.042	0.05412	177.77	100.79	-0.042
0.00	0.015, 0.007, 0.018	0.013[d]	-	0.005686	0.01	-	-

Application of ASTM D 664 to B100 and ULSD mixtures resulted in high values of repeatability and % error as indicated in tabulated data.

[a] Experimentally determined as per ASTM D 664

[b] Calculated AN = [{AN of (B100) x wt% component of (B100) in the mixture} + {AN of (ULSD) x wt% component of (ULSD) in the mixture}/100]

[c] Standard Deviation (SD)

[d] Determined as per the proposed green method (using 0.1 M KOH, 10 mL titration solvent, and 2 g sample size)

The AN of biodiesel and biodiesel blends was determined by collecting 2 g (measured to four decimal places) of a sample in a glass vial (40 mL). Ten milliliters (otherwise as stated) of titration solvent (a mixture of toluene, isopropanol and water in the volume ratio of 100:99:1)

using a 10 mL pipette was added to each sample. The sample was then titrated against a 0.1 M KOH solution using a Metrohom 808 Titrando auto-titrator to detect the endpoint potentiometrically. Experimental procedures were performed as per ASTM D 664 (otherwise as stated). Between each titration, the electrode was strongly rinsed with spray of water for about 1 min and then gently dried with a tissue (otherwise as stated).

TABLE 8.2 Calculated and experimental AN of the B100 and ULSD mixtures as per the proposed green method (using 0.1 M KOH, 10 mL titration solvent, and 2 g sample size) (unit: mg KOH/g).

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.259, 0.260, 0.242	0.254		0.01012	0.00	-	-
79.07	0.207, 0.189, 0.193	0.196	0.203	0.009452	13.33	-3.28	-0.007
59.92	0.160, 0.195, 0.136	0.164	0.157	0.02967	50.22	4.25	0.007
40.18	0.072, 0.095,0.103	0.090	0.110	0.01609	49.53	-18.18	-0.020
20.56	0.074, 0.044, 0.039	0.052	0.063	0.01893	100.19	-16.93	-0.011
0.00	0.015, 0.007, 0.018	0.013[d]	-	0.005686	0.01	-	-

Application of the proposed green method to B100 and ULSD mixtures resulted in lower values of repeatability and % error as indicated in tabulated data

[a] Experimentally determined as per the proposed green method

[b] Calculated AN = [{AN of (B100) x wt % component of (B100) in the mixture} + {AN of (ULSD) x wt% component of (ULSD) in the mixture}/100]

[c] Standard Deviation (SD)

[d] Determined as per the proposed green method (using 0.1 M KOH, 10 mL titration solvent, and 2 g sample size).

TABLE 8.3 Calculated and experimental AN of the B100 samples as per the proposed green method (using 0.1 M KOH, 10 mL titration solvent, and 2 g sample size) (unit: mg KOH/g)

Samples	Composition (wt %) B100-1	B100-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
B100-1	100	0	0.422, 0.498, 0.284	0.401	-	0.1085	0.00	-	-
B100-2	0	100	0.574, 0.601, 0.618	0.598	-	0.02219	0.00	-	-
Mixture 1	93.13	6.87	0.388, 0.456, 0.359	0.401	0.415	0.04979	34.39	-3.37	-0.014
Mixture 2	75.83	24.17	0.447, 0.391, 0.424	0.421	0.449	0.02813	18.53	-6.33	-0.028
Mixture 3	35.73	64.27	0.486, 0.488, 0.488	0.487	0.527	0.001155	0.66	-7.53	0.040
Mixture 4	15.78	84.22	0.501, 0.549, 0.495	0.515	0.567	0.029603	15.92	-9.17	-0.052

Application of the proposed green method to B100 resulted in lower values of repeatability and % error as indicated in tabulated data

[a] Experimentally determined as per the proposed green method

[b] Calculated AN = [{AN of (B100-1) x wt % component of (B100-1) in the mixture} + {AN of (B100-2) x wt% component of (B100-2) in the mixture}/100]

[c] Standard Deviation (SD)

TABLE 8.4 Calculated and experimental AN of the B20 samples as per the proposed green method (using 0.1 M KOH, 10 mL titration solvent, and 2 g sample size) (unit: mg KOH/g)

Samples	Composition (wt %) B20-1	B20-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
B20-1	100	0	0.045, 0.028, 0.045	0.039	-	0.009815	0.00	-	-
B20-2	0	100	0.612, 0.534, 0.535	0.560	-	0.04475	0.00	-	-
Mixture 1	83.23	16.77	0.127, 0.142, 0.159	0.143	0.127	0.01601	31.09	12.34	0.016
Mixture 2	69.93	30.07	0.179, 0.220, 0.140	0.180	0.196	0.040004	61.68	-8.33	-0.016
Mixture 3	56.38	43.62	0.281, 0.243, 0.280	0.268	0.267	0.02166	22.38	0.37	0.001
Mixture 4	48.24	51.76	0.269, 0.322, 0.356	0.316	0.309	0.04384	38.47	2.16	0.007

Application of the proposed green method to B20 resulted in lower values of repeatability and % error as indicated in tabulated data

[a] Experimentally determined as per the proposed green method

[b] Calculated AN = [{AN of (B20-1) x wt % component of (B20-1) in the mixture} + {AN of (B20-2) x wt% component of (B20-2) in the mixture}/100]

[c] Standard Deviation (SD)

The experimental acid number was determined by Metrohm software using equation **8.1** as per ASTM D 664 (ASTM D664-09a, 2009):

$$Acid\ \ Number, mg\ \ of\ \ KOH\ \ / g = \left[\frac{(A-B) \times M \times 56.1}{W} \right] \qquad (\mathbf{8.1})$$

where

A = KOH solution volume required for titration of the sample (mL)

B = KOH solution volume required for titration of the blank (mL)

M = molarity of the KOH solution

W = sample mass (g)

8.3 Results and discussion

According to ASTM, the repeatability of a method is defined as "the difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed only in one case in twenty" (ASTM D664-09a, 2009).

Fresh oils = 0.044 (X+1) (**8.2**)

Used oils buffer end point = 0.117 X (**8.3**)

where X = the average of the two test results.

In this study, a single operator in the same laboratory using the same apparatus carried out analysis within a short time between tests. These conditions are in accordance with the ASTM requirements for repeatability.

Therefore, the repeatability values were calculated using the following equation **8.4** (Baig and Ng, 2011):

$$repeatability(\%) = \left[\frac{2.77 \ \times \ SD}{Experimental\ \ Mean \ \ \times \ \ n} \right] \times 100\,\% \qquad (\mathbf{8.4})$$

where

n = number of operators involved in the analysis = 1

In this study, the errors were calculated using the following equation **8.5** (Baig and Ng, 2011):

$$Error(\%) = \left[\frac{Experimental\ \ AN\ \ Mean - Calculated\ \ AN}{Calculated\ \ AN} \right] \times 100\% \qquad (\mathbf{8.5})$$

In the above equation, the calculated AN was based on the sum of the wt% composition of low AN and high AN samples of biodiesel and biodiesel blend mixtures as shown in Equation **8.6**. The calculated AN is derived from the experimentally determined values of pure Bxx-1 and pure Bxx-2. For example, the calculated AN for B100 samples, is as follows (Baig and Ng, 2011):

Calculated AN = [{AN of (B100-1) x wt % component of (B100-1) in the mixture} +
{AN of (B100-2) x wt % component of (B100-2) in the mixture}/100] …..(**8.6**)

Therefore, as an example, for Mixture-1 in Table 8.3, the calculated AN is determined as follows:

Calculated AN = [{(0.401 x 93.13) + (0.598 x 6.87)}/100] = 0.415

ASTM D664, using a small sample size of 2 g instead of 20 g, was applied to blends of B100 and ULSD to yield the results shown in Table 8.1.

It was found that application of this method which used 125 mL of titration solvent, resulted in high values of repeatability (up to 290%) and very large % error (up to 101%) when the sample size was reduced from 20 g to only 2 g. This error could be mainly due to the small sample size (2 g) as well as the low accuracy of the method for low AN values. The small sample size could reduce the accuracy of measurement due to a decrease in the limit of

detection. On the other hand, the use of large amount of solvent could also contribute to the significant error due to high solvent/sample ratio (dilution effect). Furthermore, ASTM D664 required the use of excess amount of organic solvent for cleaning the electrode with longer soaking time in water in order to regenerate the electrodes which were dehydrated by the use of organic solvents. This dehydration could decrease the sensitivity of the electrode (ASTM D664-09a, 2009; Wang *et al*., 2008).

According to ASTM D664, the electrode should be rinsed in the following liquids between each measurement, titration solvent, then 2-propanol, then 5 min rinse with water, then 2-propanol and finally again with titration solvent (ASTM D664-09a, 2009). A recently modified ASTM D664 required 10 min of soaking the electrodes in water, in addition to the rinsing with toxic solvents as required by ASTM D664 (Wang *et al*., 2008). With the objective of overcoming the problem of electrode dehydration caused by the use of organic solvent, a water-based cleaning procedure was developed. This method not only eliminates the dehydration of electrode but also reduces hazardous waste. Furthermore, instead of a long soaking time in water (10 min), only 1 min of a strong water spray wash is sufficient to clean the electrode. The schematic showing a comparison of this new cleaning procedure with ASTM D664 and modified ASTM D 664 is shown in Figure 8.1.

Furthermore, an emphasis exists to make chemical processes and analytical methods greener by reducing the reliance on toxic chemicals. ASTM D664 required 125 mL of titration solvent which is a mixture of toluene, isopropanol and water in the volume ratio of 100:99:1. In an attempt to develop a green analytical method, a lower volume of titration solvent (10 mL) was used with the proposed method. It was found that the use of 10 mL of titration solvent in the new proposed method (Table 8.2) reduced the maximum % error value to 18% compared to the maximum of 101% when higher amounts of titration solvent (125 mL) were used (Table 8.1). Also, the maximum repeatability was reduced to 100% compared to the 290% when higher amounts of titration solvent (125 mL) were used based on ASTM D664 method (Table 8.1). Furthermore, the linearity curves relating the AN determined

experimentally by ASTM D664 (125 mL titration solvent, and 2 g sample size), and the proposed method (10 mL titration solvent, and 2 g sample size), to the calculated AN of the biodiesel and ULSD mixtures were obtained with the coefficient of determination (R^2) values of 0.235 and 0.978, respectively, as shown in Figure 8.2. This demonstrates that this proposed method has better linearity as compared to current ASTM D664. Therefore this proposed method, using 2 g of sample size and 10 mL of titration solvent, was used for the determination of AN values for biodiesel and biodiesel blends.

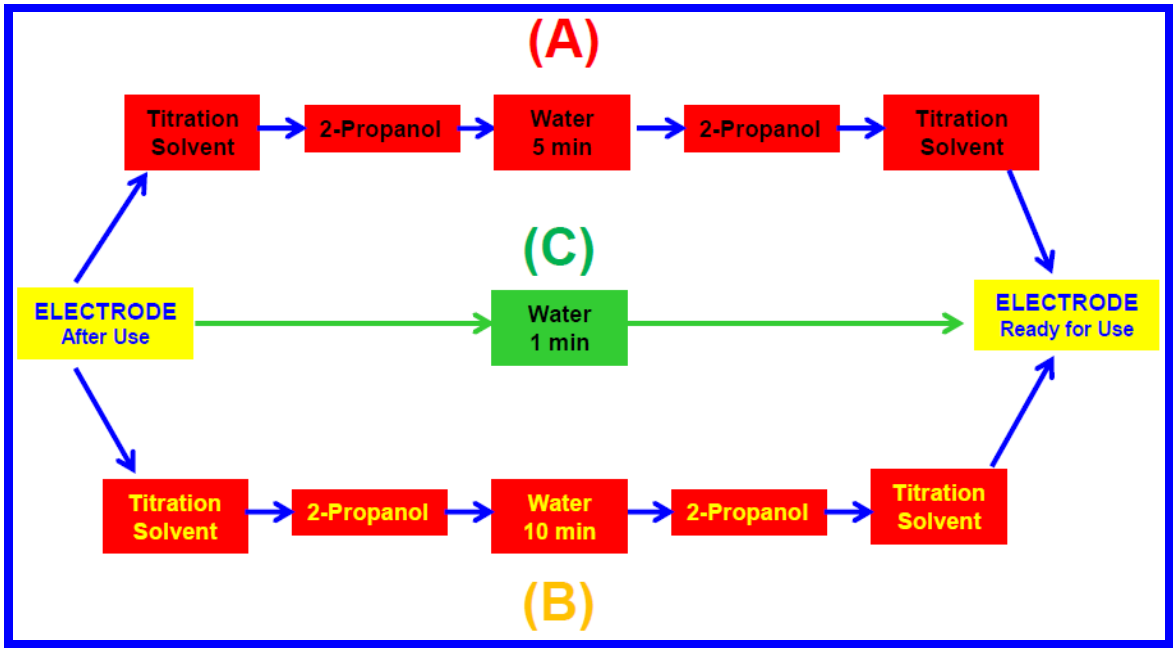


Figure 8.1 Comparison of cleaning procedure for electrode using (A) ASTM D664*(ASTM D664-09a, 2009) (B) modified ASTM D664 (Wang *et al.*, 2008) (C) proposed green method.

* ASTM D664 was used with the reduced sample size of 2.00 g instead of 20.0 g.

The results for the determination of the AN for the biodiesel (B100) are shown in Table 8.3. B100-1 in Table 8.3 is the original sample with low AN, whereas, B100-2 is the high AN sample prepared by adding a calculated amount of palmitic acid to B100-1. Mixtures 1-4 in Table 8.3 were obtained by mixing B100-1 and B100-2 at different wt% ratios to produce

biodiesel with different AN samples in the range of 0.415 – 0.567 mg KOH/g. Each sample was titrated three times; the mean, standard deviation (SD), repeatability, % error and the difference between experimental and calculated AN are also shown in Table 8.3.

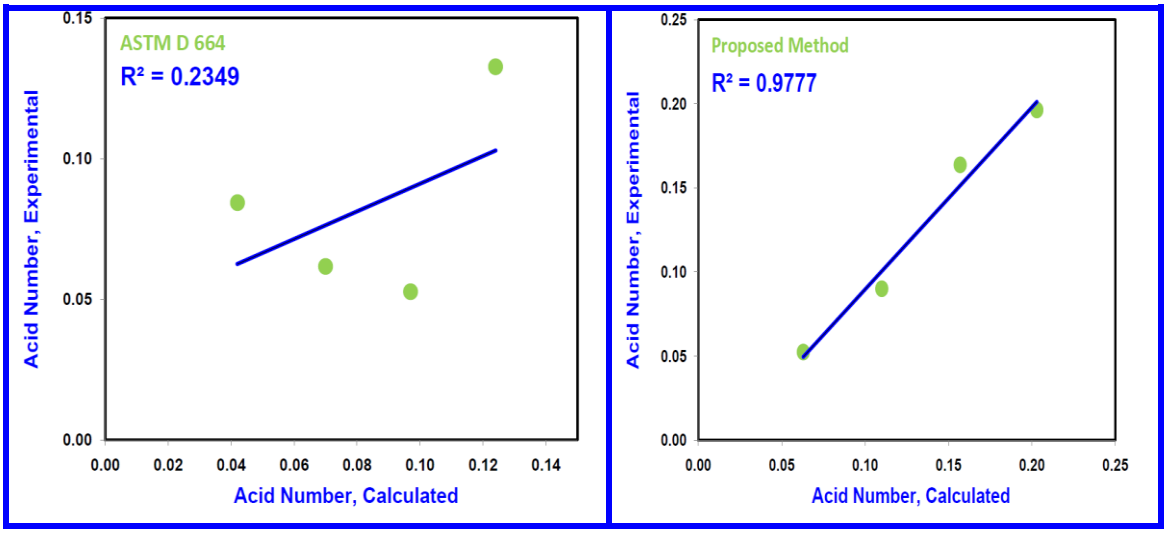


Figure 8.2 Experimental AN *vs*. calculated AN of the B100 and ULSD mixtures as per: 1) ASTM D664* (using 125 mL titration solvent, and 2 g sample size) 2) Proposed green method (using 10 mL titration solvent, and 2 g sample size) (unit: mg KOH/g).
*ASTM D664 was used with the reduced sample size of 2.00 g instead of 20.0 g

ASTM recommends a sample size of 20 g when the AN lies between 0.0 and 3.0 mg KOH/g. In this study, an AN measurement for 0.415 mg KOH/g for B100 was found to have the best accuracy (least error). In general, the accuracy values are good, which shows that even at small AN, the proposed method using a small sample size of 2 g is effective.

The results for the AN of B20 biodiesel blends are shown in Table 8.4 using the proposed method. The range of AN values of biodiesel blends was restricted to the standards for biodiesel blends. For example, the range of AN for B20 was 0.127 - 0.309 mg KOH/g as the standard limit is 0.3 mg KOH/g. It was found that the proposed method can measure AN values at levels as low as 0.127 mg KOH/g with a small error of 12% even when the sample

sizes were one-tenth as large. For B20, the most accurate AN value of 0.267 mg KOH/g was measured with a small error of only 0.4%.

The linearity curves relating the experimental AN by the proposed method to the calculated AN of the biodiesel and biodiesel blends were obtained as shown in Fig 8.3. The coefficient of determination (R^2) values obtained for B100 and B20 were 0.99**7** and 0.924, respectively, as shown in Figure 8.3. This demonstrates good linearity. The difference between the experimental AN determined as per the proposed method and the calculated AN for all biodiesel and biodiesel blend samples was within ± 0.05 mg KOH/g and ± 0.01 mg KOH/g, respectively, as shown in Tables 8.3 and 8.4, demonstrating the reliability of the proposed method.

TABLE 8.4 Calculated and experimental AN of the B20 samples as per the proposed green method (using 0.1 M KOH, 10 mL titration solvent, and 2 g sample size) (unit: mg KOH/g)

Samples	Composition (wt %) B20-1	B20-2	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
B20-1	100	0	0.045, 0.028, 0.045	0.039	-	0.009815	0.00	-	-
B20-2	0	100	0.612, 0.534, 0.535	0.560	-	0.04475	0.00	-	-
Mixture 1	83.23	16.77	0.127, 0.142, 0.159	0.143	0.127	0.01601	31.09	12.34	0.016
Mixture 2	69.93	30.07	0.179, 0.220, 0.140	0.180	0.196	0.040004	61.68	-8.33	-0.016
Mixture 3	56.38	43.62	0.281, 0.243, 0.280	0.268	0.267	0.02166	22.38	0.37	0.001
Mixture 4	48.24	51.76	0.269, 0.322, 0.356	0.316	0.309	0.04384	38.47	2.16	0.007

Application of the proposed green method to B20 resulted in lower values of repeatability and % error as indicated in tabulated data

[a] Experimentally determined as per the proposed green method

[b] Calculated AN = [{AN of (B20-1) x wt % component of (B20-1) in the mixture} + {AN of (B20-2) x wt % component of (B20-2) in the mixture}/100]

[c] Standard Deviation (SD).

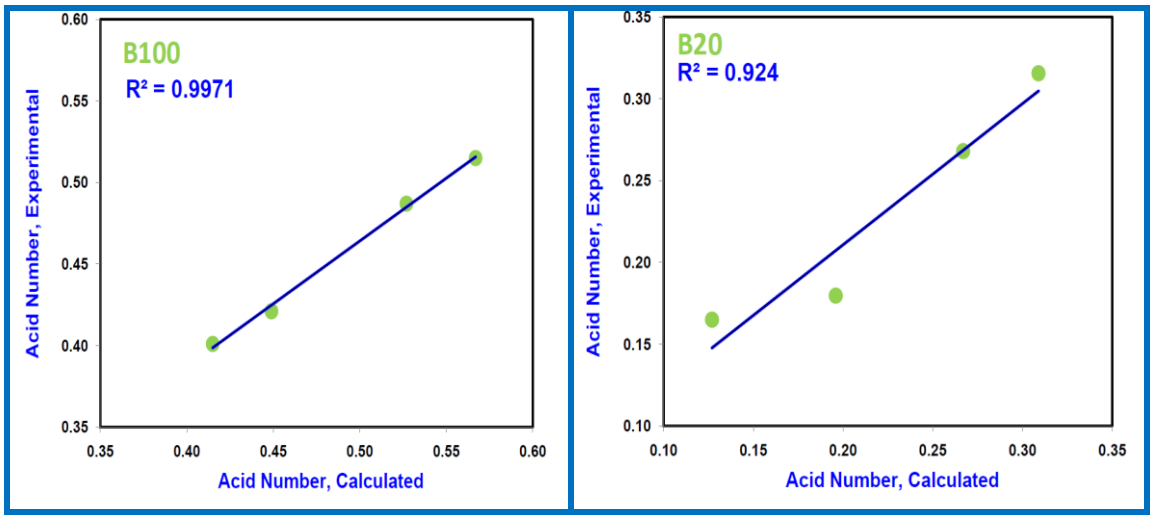


Figure 8.3 Experimental AN (as per proposed green method) *vs* calculated AN for biodiesel (B100) and biodiesel blend (B20) (unit: mg KOH/g).

This proposed new method has many economical and environmental advantages compared to the current ASTM D664 and modified ASTM D664 methods as shown in Table 8.5 (ASTM D664-09a, 2009; Wang *et al*., 2008). The proposed method reduced the consumption of toxic solvents and hazardous waste by over 90%. Furthermore, the proposed method completely eliminates the use of toxic chemicals during electrode cleaning by using only 100% water. Finally, sample size and electrode washing time were reduced by over 90% and 80%, respectively.

8.4 Conclusion

The ASTM reference standard method D664, a potentiometric method, has major problems such as use of toxic solvents, large sample size, mediocre reproducibility, tedious process for cleaning electrodes and relatively long analysis time. The AN of biodiesel and biodiesel blends using the current ASTM D664 results in large values of repeatability (up to 290%) and % error (up to 101%) when the sample size was reduced from 20 g to 2 g. This error could be mainly due to the small sample size (2 g) as well as the low accuracy of the method for low AN values.

TABLE 8.5 Comparison of advantages of using proposed method vs ASTM D664* (ASTM D664-09a, 2009) and modified ASTM D 664 (Wang *et al*., 2008)

* ASTM D664 was used with the reduced sample size of 2.00 g instead of 20.0 g.

Characteristics	ASTM D664 [5]	Modified ASTM D664* [6]	Proposed Method
Sample Size (g)	20.0	20.0	**2.00**
Volume of Toxic Titration Solvent (mL)	125	125	**10.0**
Time for Cleaning Electrode using water (min)	5	10	**1**
Reduction in use of Toxic Titration Solvent	0	0	**> 90%**
Reduction in Toxic Waste	0	0	**> 90%**
Reduction in sample size	0	0	**90%**
Elimination of toxic solvents in electrode cleaning process	0	0	**100%**
Reduction in electrode cleaning process time	0	0	**> 80%**

Therefore, the proposed new method based on green chemistry approaches, has been developed to determine acid number of biodiesel and biodiesel blends using a small sample size (2 g instead of 20 g), reduced toxic solvent (from 125 mL to only 10 mL) and fast cleaning of electrodes (1 min as compared to over 10 min) that does involve the use of toxic solvents. This makes the proposed method a green analytical method which is technically feasible, economically reasonable, and environmentally friendly. Application of the proposed

method to biodiesel and biodiesel blend was tested and found to have good accuracy and repeatability.

This proposed method significantly reduces the maximum % error from 101% (using ASTM D664 with the sample size of 2 g) to only -18% and the maximum repeatability from 290 to 100 % when compared to ASTM D 664 using the sample size of 2 g. Good accuracy and repeatability were also obtained using ASTM D6751-09a and ASTM D7467-09 specifications for the AN, which are 0.50 mg KOH/g and 0.30 mg KOH/g, respectively.

The proposed method can measure AN values as low as 0.127 mg KOH/g with a small error of only 12% when the sample sizes were one-tenth as large. For B20, the most accurate AN value was 0.267 mg KOH/g with a small error of only 0.4%. The differences between the experimental AN determined by the proposed method and the calculated AN for all biodiesel and biodiesel blend samples were within ± 0.05 mg KOH/g and ± 0.01 mg KOH/g, respectively, demonstrating the reliability of the proposed method. The coefficient of determination (R^2) values obtained for B100 and B20 were 0.997 and 0.924, respectively.

This proposed new analytical method provides accurate, precise and reliable results for acid number analysis of biodiesel and biodiesel blends and could be used in R&D as well as in industrial laboratories as a simple, time-efficient, cost effective and environmentally friendly method. This method offers various advantages such as time-efficiency, simplicity, small sample size, reduced amount of toxic titration solvent. Therefore, this proposed new method can be recommended as a reference method for acid number determination of biodiesel and biodiesel blends.

CHAPTER 9

DETERMINATION OF ACID NUMBER OF BIODIESEL AND BIODIESEL FEEDSTOCK FOR MONITORING BIODIESEL PRODUCTION PROCESS AS A QUALITY CONTROL TOOL.

Overview

Due to the growing concerns over the high cost of vegetable oil as feedstock for biodiesel and food *vs* fuel concerns, the use of inexpensive non-edible feedstock has been significantly increased globally. The quality of biodiesel depends on the quality of feedstock, processing technology, post-production refining steps and effectiveness of quality control tools used to control and monitor the chemical processes. Acid number (AN) has been considered a critical process and quality parameter to measure the FFA content in the biodiesel feedstock and the biodiesel and is included in both ASTM D 6751 and EN 14214. Using green chemistry approaches, ASTM D 974 has been modified using a lower concentration of base (0.02 M KOH instead of 0.1 M KOH) and the amount of toxic titration solvent reduction from 100 mL to 10 mL. The application of this modified method for the determination of AN of biodiesel bio-feedstock was studied. The proposed method can measure AN values at levels as low as 0.154 mg KOH/g with a small error of only 17% and repeatability of 12% even when the sample sizes were one-tenth as large. The difference between the experimental AN determined by the proposed method and the calculated AN for all the biodiesel feedstock were within ± 0.09 mg KOH/g, demonstrating the reliability of the proposed method. The coefficient of determination (R^2) value obtained for biodiesel feedstock was 0.999. The range of AN of the feedstock samples was restricted to values commonly found in refined vegetable oil (low FFA feedstock), used cooking oils (high FFA feedstock) and biodiesel (the final product). Hence, this method could also be used as a quality control tool for monitoring biodiesel production process.

9.1 Introduction

Globally, increasing concerns over the depletion of fossil fuels and increasing pollution, have directed research towards the development of "renewable" fuels. Biodiesel has attracted worldwide attention as an alternative "green" fuel due to its environmental benefits (Kiss *et. al.*, 2006; Gui *et. al*, 2008; Baig and Ng, 2010; Wang *et. al.*, 2012).

More than 95% of the biodiesel around the world are produced from expensive refined vegetable oil (Gui *et. al.*, 2008). The major cost of biodiesel product is attributed to feedstock. For example, 95% of the production cost of biodiesel is due to the use of expensive refined vegetable oils (Gui *et. al.*, 2008). This is due to the ease of processing refined vegetable oils (contains < 1.0% FFA) using conventional first generation base-catalyzed technologies.

Currently, most biodiesel is produced by traditional alkali-catalyzed transesterification of triglycerides of refined/edible vegetable oils using methanol and an alkaline catalyst (NaOH, NaOMe), which gives biodiesel and byproduct glycerol as shown in Figure 9.1 (Bournay *et al.*, 2005)

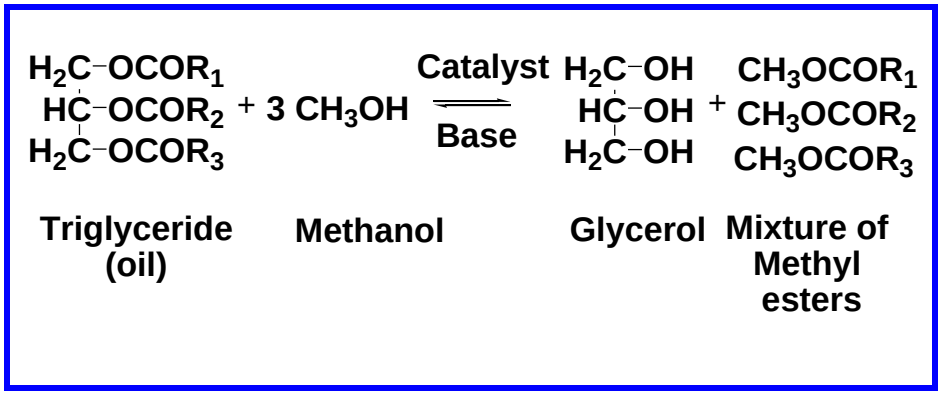


Figure 9.1 Overall transesterification reaction for the conversion of vegetable oils to methyl esters using conventional base-catalyzed process.

The problem of expensive feedstock has been addressed by evaluating various alternative feedstocks as possible substitutes such as used vegetable oil, animal fats and refurbished oils and fats in which the amount of free fatty acids (FFA) varies from 3% to 40% (Ma *et al.*, 1999; Srivastava *et al.*, 2007). Innovative feedstocks will be required for economicallfeasible industrial-scale production of biodiesel (Haas, 2005; Parawira, 2009). Furthermore, due to the growing concerns of food *vs* oil, the use of non-edible oils is gaining momentum around the world (Ramadhas *et al.*, 2005; Acthten *et al.*, 2008; Leung *et al.*, 2010; Baig *et al.*, 2011; Juan *et al.*, 2011). However, these non-edible, 2nd generation feedstocks also contain high amounts of FFA. These alternative feedstocks cannot be processed using conventional base-catalysis since the catalyst and raw material will be consumed by saponification reaction between FFA and base as shown in Equation **9.1** (Baig and Ng, 2010):

$$\text{R-COOH} + \text{NaOH} \rightarrow \text{R-COONa} + \text{H}_2\text{O} \qquad (\mathbf{9.1})$$

The soap causes downstream processing problems in product separation because of emulsion formation (Ma *et al.*, 1999). The selection of biodiesel production technology depends directly on the quality of the feedstock. The feedstocks with high FFA content require different process technologies for the production of biodiesel than the feedstocks with lower FFA content (Jain *et al.*, 2010). Hence, two-step process technologies have been developed in which FFAs present in the feedstock are converted to biodiesel by esterification followed by base-catalysis. Esterification involves the reaction of fatty acid with methanol in the presence of an acid catalyst to produce FAME and water:

$$\text{R-COOH} + \text{R'-OH} \leftrightarrow \text{R-COO-R'} + \text{H}_2\text{O} \qquad (\mathbf{9.2})$$

where R and R' are the alkyl groups of FFA and alcohol, respectively.

Esterification is the main reaction to reduce the amount of FFA present in the feedstock by converting FFAs to biodiesel and thus making the esterified feedstock suitable for conventional base-catalyzed transesterification. This requires an accurate determination of AN to monitor the progress of the biodiesel production process. Therefore, it is essential to

determine the amount of FFA present in the feedstock in order to fine tune the esterification process parameters. Due to rapid increase in the production and the use of biodiesel, the assurance of fuel properties and quality has become of paramount interest for the successful commercialization and market acceptance of biodiesel. Accordingly, biodiesel standards have been established or are being developed in various countries and regions around the world, including the United States (ASTM D6751), Europe (EN 14214), Brazil, South Africa, Australia and elsewhere (Knothe, 2006). ASTM standard D6751 and European Committee of Standardization (CEN) standard EN 14214 set similar specifications for biodiesel blending and motor fuels (ASTM International D6751, 2006, European committee for Standardization EN 14214, 2003).

According to ASTM D6751, AN is measured as the mass of KOH in mg required to neutralize the acids in 1 gram of the sample (ASTM D6751-09a, 2009). AN is a measure of the degree of oxidation and hydrolysis in the biodiesel (Wang *et al*., 2008). Hydrolysis during biodiesel production process can result in the formation of FFA by the hydrolysis of ester linkages in both the TG feedstock and the biodiesel during its manufacture (Mahajan *et al*., 2006). Furthermore, FFA can result in severe operational problems and is considered as a safety risk during its storage due to the possibility of corrosion by the FFA (Wang *et al*., 2008). Therefore, both ASTM D6751 and EN 14214 have restricted the maximum value of AN to be 0.50 mg KOH/g for biodiesel (B100).

ASTM D974 is a non-aqueous colorimetric-titration based method which uses KOH in isopropanol with *p*-naphtholbenzein as an indicator and is suitable even for colored samples (Knothe, 2006; Mahajan *et al.*, 2006). ASTM D974 is a method for measuring the AN of petroleum oils (ASTM D974-08, 2008). We successfully developed a modified ASTM D 974 using green chemistry approaches for the determination of acid number of biodiesel and biodiesel blends (Baig and Ng, 2011).

The quality of biodiesel depends on the quality of feedstock, processing technology, post production refining steps and effectiveness of tools used to control and monitor the chemical processes. Acid number has been considered a critical parameter to measure the FFA present in the biodiesel (Mahajan *et al*., 2006; Wang *et al.*, 2008; Tubino *et al*., 2011; Baig and Ng, 2011; Baig *et al.*, 2012; Aricetti *et al*., 2012). However, all these studies focused on determination of acid number of biodiesel only. It is important to develope analytical method to determine the acid number of feedstocks used for biodiesel, in-process control of FFA conversion and the biodiesel product.

To the best of our knowledge, this study is the first report using green chemistry approaches, such as reduction of sample size, reduction of the use of toxic chemicals and decrease in hazardous waste to determine the AN of biodiesel feedstock. This method could also be used as in-process quality control tool for monitoring biodiesel production processes.

9.2 Experimental procedures

9.2.1 Materials

The soybean oil used as the solvent was a food-grade President's Choice product, purchased from Zehrs Super Market (Waterloo, ON, Canada). The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): palmitic acid (99%), 2-propanol (anhydrous, 99.5%), toluene (anhydrous, 99.8%), *p*-naphtholbenzein (indicator grade). The titrant solution, 0.1 M KOH (volumetric standard, in isopropanol), was supplied by Fisher Scientific (Ottawa, ON, Canada) and used to prepare 0.02 M KOH in isopropanol.

9.2.2 Methods

The titration solvent and indicator solution were prepared as detailed in ASTM D974. Twelve synthetic standards with a range of known AN levels ranging from 0.154 to 8.265 mg KOH/g were prepared by blending palmitic acid and refined soybean oil as shown in Table 9.1. The range of the standards was restricted to acid number commonly found in refined

vegetable oil (low FFA feedstock), used cooking oils (high FFA feedstock) and biodiesel (final product). The range of the standards includes the AN ~ 0.5 mg KOH/g as per the AN specifications in quality standards (e.g. ASTM D6751) for biodiesel. Each sample was titrated six times. To determine the AN of biodiesel and biodiesel blends, 2 g (measured to four decimal places) of a sample was collected in an Erlenmeyer flask (125 mL). Ten milliliters of titration solvent (a mixture of toluene, isopropanol and water in the volume ratio of 100:99:1) and eight drops of the *p*-naphtholbenzein indicator solution were added to each sample. The sample was then titrated against a 0.02 M KOH solution using a 10 mL burette. The titration was deemed complete when a color change from orange to green that persisted for at least 15 seconds was observed in the titration mixture.

The experimental acid number was determined using Equation 9**.1** as per ASTM D974 (ASTM D 974-08, 2008):

$$Acid\ \ Value, mg\ \ of\ \ KOH\ \ / g = \left[\frac{(A-B) \times M \times 56.1}{W} \right] \qquad (\mathbf{9.1})$$

where

A = KOH solution volume required for titration of the sample (mL)

B = KOH solution volume required for titration of the blank (mL)

M = molarity of the KOH solution

W = sample mass (g)

Each standard was titrated at least six times by the operator.

9.3 Results and discussion

Any suitable method can be used to measure the acid number of the solvent when the value is significantly lower than that of the standards. Therefore, we also used ASTM D 974 for the refined soybean oil (SBO). From Table 9.1, one can see that the mean acid number of the solvent was 0.233 with a SD of 0.0098. This uncertainty is incorporated in the calculated values of the standards and was deemed acceptable, as confirmed by the final results of this

study. The contribution to the uncertainty from the solvent measurement is obviously greater for the lower acid number standards. According to ASTM, the repeatability of a method is defined as the difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed only in one case in twenty" (ASTM D974-08, 2008).

In this study, the same operator, the same laboratory, and the same apparatus were used with a short time between tests. These conditions are in accordance with the ASTM requirements for repeatability. Therefore, the repeatability values were calculated using the following Equation **9.2** (Baig and Ng, 2011):

$$repeatability(\%) = \left[\frac{2.77 \times SD}{Experimental\ \ Mean \times n} \right] \times 100\,\% \qquad (\mathbf{9.2})$$

where

n = number of operators involved in the analysis = 1

In this study, the errors were calculated using the following Equation **9.3** (Baig and Ng, 2011):

$$Error(\%) = \left[\frac{Experimental\ \ AN\ \ Mean - Calculated\ \ AN}{Calculated\ \ AN} \right] \times 100\% \qquad (\mathbf{9.3})$$

The results for the determination of the AN of standards samples are shown in Table 9.1 using modified ASTM D974. The range of the standards was restricted to the acid number commonly found in refined vegetable oil (low FFA feedstock), used cooking oils (high FFA feedstock) and biodiesel (final product). The range of the standards includes AN ~ 0.5 mg KOH/g as per AN specifications in quality standards (e.g. ASTM D6751) for biodiesel. Generally, refined vegetable oils have AN values of 0.2 -1.0 mg KOH/g, whereas, used cooking oils have higher acid values (e.g. 1.0 mg KOH/g to 8.0 mg KOH/g or more).

TABLE 9.1 Calculated and experimental acid numbers of feedstock standards by modified ASTM D 974.

Standard No.	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability[d] (%)	Accuracy[e]	Error (%)	AN difference (Exp. - Cal.)
SBO	0.250, 0.222, 0.233, 0.231, 0.223, 0.241, 0.233	0.233	-	0.0098	-	-		-
1	0.404, 0.407, 0.435, 0.412, 0.406,0.421	0.414	0.492	0.0118	7.91	84.19	-15.85	-0.078
2	0.170, 0.190, 0.179, 0.172, 0.188, 0.183	0.180	0.154	0.0079	12.20	117.06	16.88	0.026
3	1.814, 1.824, 1.813, 1.835, 1.778, 1.854	1.691	1.789	0.0254	4.16	94.50	-5.14	-0.098
4	0.916, 0.977, 0.962, 0.949, 0.978, 0.996	0.963	0.908	0.0278	8.01	106.09	6.05	0.055
5	2.503, 2.624, 2.583, 2.569, 2.525, 2.547	2.558	2.468	0.0430	4.65	103.66	3.64	0.090
6	2.724, 2.778, 2.763, 2.746, 2.771, 2.727	2.752	2.725	0.0225	2.27	100.98	0.99	0.027
7	3.587, 3.564, 3.603, 3.612, 3.562, 3.594	3.587	3.600	0.0205	1.58	99.64	-0.36	- 0.013
8	4.893, 5.033, 4.999, 4.919, 4.809, 4.804	4.909	4.898	0.0944	5.33	100.23	0.22	0.011
9	5.661, 5.710, 5.728, 5.751, 5.759, 5.677	5.714	5.798	0.0395	1.92	98.56	1.44	-0.084
10	6.473, 6.578, 6.533. 6.522, 6.465, 6.494	6.511	6.489	0.0423	1.80	100.33	0.33	0.022
11	7.184, 7.290, 7.208, 7.312, 7.337, 7.303	7.259	7.334	0.0656	2.50	98.97	-1.02	-0.075
12	8.069, 8.214, 8.273, 8.222, 8.196, 8.177	8.192	8.265	0.0682	2.31	99.11	-0.88	-0.073

Application of the proposed green method to synthetic biodiesel feedstock mixtures resulted in good repeatability and errors as indicated in tabulated data

[a]Experimentally determined as per the proposed method (using 0.1M KOH, 10 mL titration solvent, and 2 g sample size)

[b]Calculated acid numbers are based on the weight% of palmitic acid (FFA) in the soybean oil (SBO; triglyceride) in the standards

[c] Standard Deviation (SD)

[d] Repeatability expressed as a percentage of the experimental mean.

[e] Accuracy = (experimental mean/calculated acid number) x 100.

During this study, we demonstrated that this modified method can measure AN values as low as 0.154 mg KOH/g with % error of -16% and as high as 8.265 mg KOH/g with a % error of only – 0.88%. AN values of all the samples were determined with repeatability ranging from 1.58% to only 12.20% over the entire AN range of 0.154 mg KOH/g -8.265 mg KOH/g.

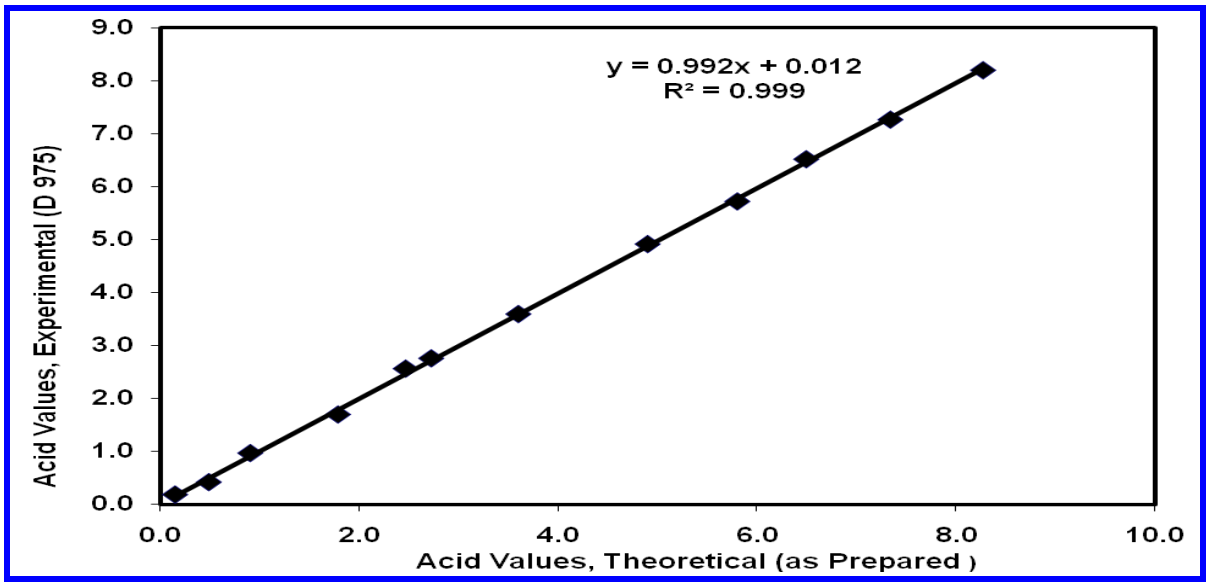


Figure 9.2 Calibration curve relating the concentration of FFA determined experimentally by modified ASTM D974 to the nominal content of FFA (palmitic acid) present in the mixtures**.** (unit: mg KOH/g).

The linearity curves relating the concentration of AN determined experimentally by modified ASTM D974 to the calculated AN of the standard mixtures (nominal content of palmitic acid) were obtained as shown in Figure **9.1**. The coefficient of determination (R^2) exceeded the specification of 0.99 set forth in the ASTM method. This demonstrates excellent linearity. The differences between the experimental AN determined as per modified ASTM D974 and the theoretical values for all samples was as low as ± 0.01 mg KOH/g and never exceeded ± 0.09 mg KOH/g as shown in Table 9.1, Figure 9.1, and Figure 9.2.

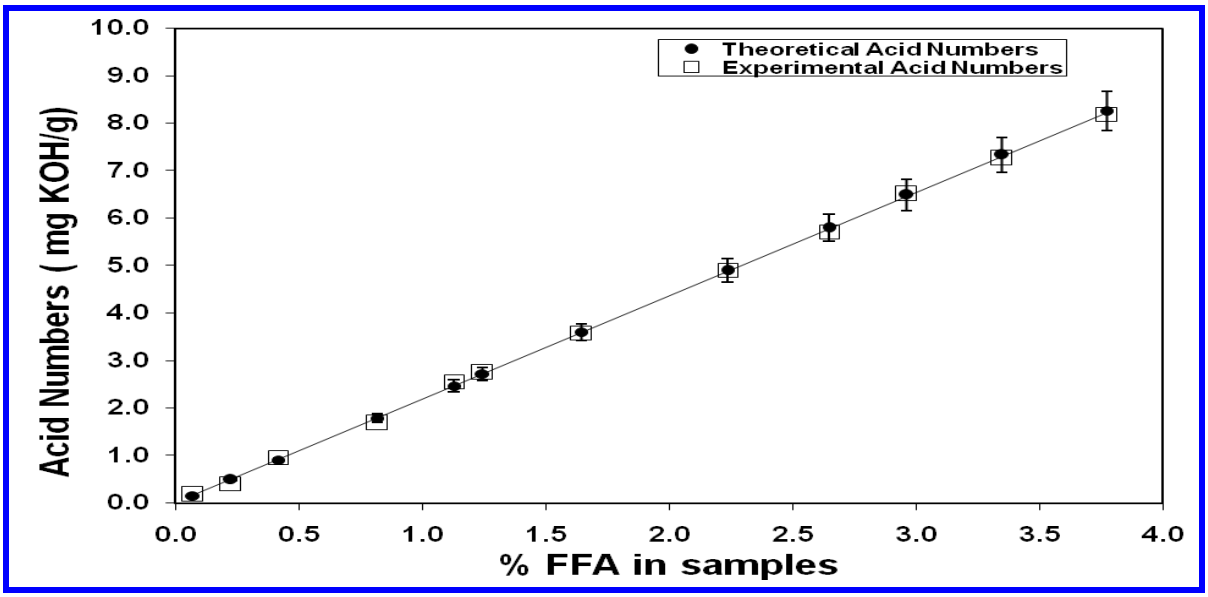


Figure 9.3 Experimental AN (as per modified ASTM D974) *vs.* calculated AN for FFA (palmitic acid) present in the mixtures (unit: mg KOH/g).

9.4 Conclusion

The quality of biodiesel depends on the quality of feedstock, processing technology, post-production refining steps, and effectiveness of the tools used to control and monitor the chemical processes. Acid number has been considered a critical parameter to measure the FFA present in the biodiesel. However, all the studies reported in the literature focused only on the determination of acid number of the product, biodiesel and biodiesel blends. It is also important to develope analytical method to determine the acid number of feedstocks used for biodiesel, in-process control of FFA conversion and the final biodiesel product. Therefore, the proposed new method based on green chemistry approaches, has been developed to determine the acid number of biodiesel feedstock using a small sample size (2 g instead of 20 g) and reduced toxic solvents (from 125 mL to only 10 mL). The application of this modified ASTM D974 for the determination of AN of biodiesel feedstock was studied. The proposed method can measure AN values even as low as 0.154 mg KOH/g with a small error of only 17% and repeatability of 12% even when the sample sizes were one-tenth as large. The differences between the experimental AN determined by the proposed method and the

calculated AN for all the biodiesel feedstock were always within ± 0.09 mg KOH/g, demonstrating the reliability of the proposed method. The coefficient of determination (R^2) value obtained for biodiesel feedstock was 0.999. The range of AN of the feedstock samples was restricted to the acid number commonly found in refined vegetable oil (low FFA feedstock), used cooking oils (high FFA feedstock) and biodiesel (final product). Hence, this method could also be used as in-process quality control tool for monitoring biodiesel production processes.

CHAPTER 10

CONCLUSION AND RECOMMENDATIONS

10.1 Conclusion

This research has three main objectives. The first is to develop a second generation single-step heterogeneous solid acid-catalyzed process for the production of biodiesel from multi-feedstock including first generation (edible vegetable oils) and second generation sources (non-edible *jatropha* oil as well as waste oils and fats). The second aim is to develop a solid acid-catalyst which can simultaneously catalyze both the esterification and transesterification reactions. The final objective is to develop green analytical methods for the acid number of biodiesel and bio-feedstock for biodiesel production to ensure the use of appropriate process technology and improve quality control.

These objectives had been achieved through the following research approaches:

[1] exploration of different alternative bio-feedstocks (edible and non-edible) for biodiesel production.

[2] process optimization for individual feedstocks.

[3] determination of suitable solid acid catalyst for simultaneous esterification and transesterification reactions for biodiesel production.

[4] synthesis, catalytic activity and recycling studies of the developed catalyst.

[5] kinetics studies of heterogeneous catalyst.

[6] hydrolysis studies of the catalyst to control the process chemistry of biodiesel production from multi-feedstocks.

[7] development of green and simple analytical method for determination of acid number of biodiesel and biodiesel blends.

[8] determination of acid number of feedstocks for biodiesel production process.

The conclusions obtained from this research study are as follow:

1) ***A single-step solid acid catalyzed process for the production of biodiesel from high free fatty acid feedstocks has been developed*** and applied to model feedstock. A novel solid acid catalyst (tungstophosphoric acid; TPA; $H_3PW_{12}O_{40}$ supported on neutral alumina) has been developed and evaluated. It was demonstrated that this heterogeneous solid acid catalyzed esterification and transesterification simultaneously. The total glycerin, ester content and acid numbers were determined according to ASTM D6584, EN 14103 and ASTM D974, respectively. It was found that at 200°C, 1:27 oil-to-alcohol molar ratio and 3 wt % of catalyst, a high quality biodiesel with an ester content of 93.95 mass % was produced from a model synthetic feedstock (soybean oil containing 10% PA) in 10 h. The effect of process parameters such as catalyst amount, oil to alcohol molar ratio, and FFA content in the feedstock has been investigated. This single-step catalysis process has the potential for industrial scale production of biodiesel from high free fatty acid feedstocks (Baig and Ng, 2010).

2) ***A novel second-generation green technology for the production of biodiesel from multi-feedstocks for global applications has been developed*** using yellow grease (as a representative multi-feedstock). In this study, catalytic activity, catalyst recycling and feedstock flexibility were investigated for the production of biodiesel using a 2^{nd} generation heterogeneous-catalyzed technology for processing multi-feedstocks. Also, as a part of process development, the effects of parameters including catalyst loading, feed to alcohol molar ratio, reaction temperature, rate of mixing, nature of support, water content and use of co-solvent were investigated. Results showed that the FFAs present in yellow grease were converted into biodiesel with 95% conversion using the solid acid catalyst.

Furthermore, yellow grease was successfully transesterified with ester content of 87.3 mass % in the ester-rich phase.

Analysis based on the ASTM D974 and EN 14103 standards confirmed the production of high-purity biodiesel from yellow grease. Also, recycling, hydrolysis and kinetic studies were performed and kinetic parameters such as rate constants, activation energy and Arrhenius constant were determined. These results are very promising and suggest the feasibility of using low cost feedstock with high FFA content for the industrial production of biodiesel using this green single-step process as compared to current multi-step industrial processes. This technology can be used for multi-feedstocks whether 1st generation or 2nd generation, with unlimited FFA content. Due to the high catalytic activity, reusability and low cost, this process has potential for industrial scale production of biodiesel from multi-feedstocks (Baig and Ng, 2011).

3) ***A direct method for the synthesis of fatty acid methyl ester (FAME) from crude jatropha oil as second generation feedstock has been developed.***

Crude *jatropha* oil was with FFA content of 29% was successfully transesterified to yield ester content of 91.4 mass%. Furthermore, 93.6% conversion of FFA was achieved. Biodiesel analysis based on the ASTM D974 and EN 14103 standards confirmed the production of high-purity biodiesel from crude *jatropha* oil with only 0.17% linolenic ester which is far below the EN 14103 limit. As part ofprocess development, the effects of the amount of catalyst, calcination temperature of catalyst, rate of mixing and the use of co-solvent (THF) on FAME content and FFA conversion have been studied and optimized. Overall, crude *jatropha* oil (CJO) as a potential non-edible feedstock for biodiesel production was explored and investigated. Due to the high catalytic activity and low cost, this green 2nd generation technology has potential for industrial-scale production of biodiesel from crude *jatropha* oil as a 2nd generation non-edible feedstock. To the best of the author's knowledge, this is the first report on the development of a direct single-step solid acid-catalyzed process for the production of biodiesel from untreated crude *jatropha* oil (Baig and Ng, 2012).

4) ***A colorimetric titration based analytical method for the determination of acid number of biodiesel and biodiesel blends has been developed.*** This modified ASTM D974 offers various advantages such as ease of reproducibility, cost-effectiveness, and time-efficiency. It was found that determination of acid number (AN) of biodiesel and biodiesel blend using the current ASTM D 974 results in large values of repeatability (up to 73.41%) and larger percentage error (up to 42.88%). Therefore, ASTM D974 has been modified to significantly reduce the maximum percentage error from 42.88 to 5.92%. Application of the modified ASTM D974 to biodiesel and biodiesel blends was tested with good accuracy and repeatability. Excellent linearity values of R^2 were obtained for biodiesel and biodiesel blends. The differences between the experimental AN determined by modified ASTM D974 and the calculated AN for all biodiesel and biodiesel blend samples were within ± 0.018 mg KOH/g. All distilled biodiesel and biodiesel blend samples were found to be very light in color, which eliminated the major obstacle for the application of ASTM D974. Also, this study confirmed a detection limit of 0.05 mg KOH/g for this modified ASTM D974. Thus, a specification of 0.1 mg KOH/g for AN can be set for B1-B5. Furthermore, due to the advantages of this modified ASTM D974, it can be used in field biodiesel analytical kits to determine AN on-site or at a retailer location. Therefore, this modified method is recommended as a reference method for AN determination of biodiesel and biodiesel blends. To the best of our knowledge, this study is the first report on the evaluation of ASTM D974 for the determination of the AN of biodiesel blends (B1, B2, B5, B10, and B20) where accuracy and repeatability were determined (Baig and Ng, 2011).

5) ***A simple and green analytical method for acid number analysis of biodiesel and biodiesel blends based on potentiometric technique has been developed.*** Acid number is an important quality parameter for biodiesel and biodiesel blends and has been included in various quality standards including ASTM D6751 and EN 14214. This new method uses a reduced amount of titration solvent and a small sample size instead of large sample size as stated in the ASTM reference method D664. A time-efficient electrode cleaning procedure has been developed which completely eliminates the use of toxic solvents.

This proposed green method significantly reduced the maximum % error from 101% to only -18% and repeatability from 290% to 100% when compared to ASTM D664 method using the sample size of 2 g. This proposed procedure could be used for the determination of acid number of biodiesel and biodiesel blends in R&D as well as in industrial quality control laboratories as a simple, time-efficient, cost effective, and environmentally friendly method for acid number determination. To the best of the author's knowledge, this study is the first report using green chemistry approaches, such as reduction of sample size, reduction in the use of toxic chemicals, decrease in hazardous waste and elimination of the use of toxic chemicals for electrode cleaning, to develop a potentiometric analytical method for the determination of the AN of biodiesel (B100) and biodiesel blends (B20). Also, a single-step aqueous-based electrode cleaning procedure has been developed (Baig and Ng, 2012).

6) ***Determination of acid number of biodiesel and biodiesel feedstock for monitoring biodiesel production process as a quality control tool has been developed.*** The quality of biodiesel depends on the quality of feedstock, processing technology, post-production refining steps and effectiveness of tools used to control and monitor the chemical processes. Acid number is considered a critical parameter to measure the FFA present in the biodiesel. However, all the studies reported in the literature focused only on the determination of acid number of the product, biodiesel and biodiesel blends. It would be important to develope an analytical method for acid number determination of feedstocks used for biodiesel, in-process control of FFA conversion and the final biodiesel product. Therefore, the proposed new method based on green chemistry approaches, has been developed to determine acid number of biodiesel feedstock using small sample size (2 g instead of 20 g) and less toxic solvent (from 125 mL to only 10 mL). The application of this modified ASTM D 974 for the determination of AN of biodiesel bio-feedstock was studied. The proposed method can measure AN values as low as 0.154 mg KOH/g, with a small error of only 17% and repeatability of 12% even when the sample sizes were one-tenth as large.

The differences between the experimental AN determined using the proposed method and the calculated AN for all the biodiesel feedstock were within ± 0.09 mg KOH/g y, demonstrating the reliability of the proposed method. The range of AN of the feedstock samples was restricted to values commonly found in refined vegetable oil (low FFA feedstock), used cooking oils (high FFA feedstock) and biodiesel (the final product). Hence, this method could also be used as in-process quality control tool for monitoring biodiesel production processes.

10.2 Recommendations

The following studies are important recommendations stemming from this research study to further build up our current knowledge of heterogeneous acid catalysis, process chemistry, and quality control for biodiesel production process from multi-feedstocks (edibile and non-edible).

1) A scaled-up pilot reactor is the next step to design an industrial-scale commercial production system.

2) To increase the efficiency of this solid acid-catalyzed process, it is important to evaluate the performance of this novel neutral alumina supported tungstophospharic acid catalyst in different reactor configurations such as continuous reactor. This would help in designing a commercial scale production system for biodiesel.

3) For a multi-feedstock process, the effect of the impurities present in inexpensive low cost biodiesel feedstocks on catalytic activity of the solid acid catalyst should be investigated in order to assess the robustness of the multi-feedstock process.

4) Economic and environmental assessment should be performed to compare this 2nd generation heterogeneous solid acid-catalyzed process to conventional homogeneous base-catalyzed processes. This will assess the economic and environmental feasibility for potential commercialization of this solid acid-catalyzed technology.

5) It is essential to develop an on-line green and simple analytical method for monitoring biodiesel acid number in real time. This will provide effective quality control tools to monitor biodiesel production processes at industrial-scale and will ensure that the biodiesel product meets the quality standards.

Most of the essential studies of this novel 2nd generation heterogeneous solid acid-catalyzed process have already been performed for producing high quality biodiesel from multi-feedstocks through the lab-scale reactor. However, the remaining studies should involve a scaled-up pilot reactor.

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APPENDICES

Appendix – A: ASTM D6751 Specification

North American biodiesel-standard ASTM D6751-06 (ASTM, 2006)

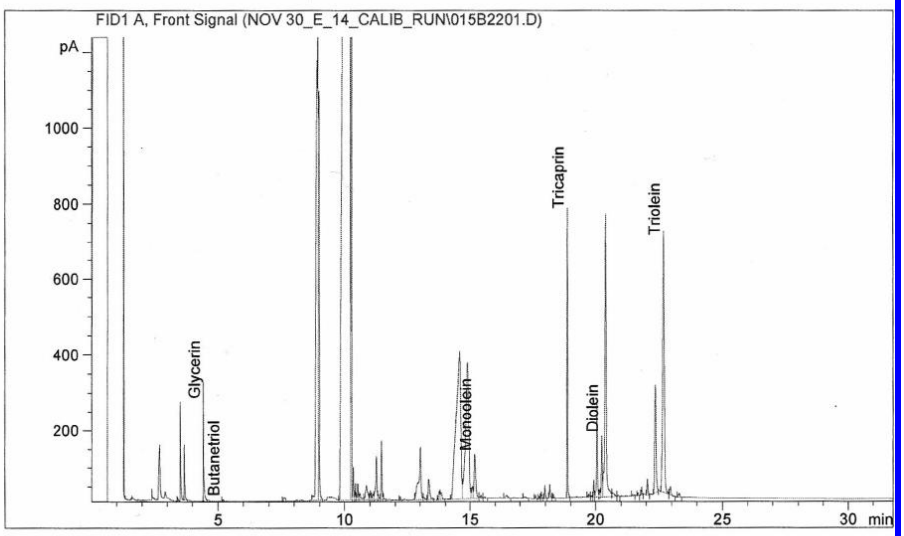
Property	**Test Method**	**Limits**	**Units**
Flash point (closed cup)	D93	130.0 min	°C
Water and sediment	D2709	0.05 max	% volume
Kinematic viscosity, 40C	D 445	1.9-6.0	mm^2/s
Sulfated ash	D 874	0.02 max	% mass
Sulfur	D 5453	0.0015max(S15) 0.05 max(S500)	% mass (ppm)
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.05 max	% mass
Acid number	D 664	0.50 max	mg KOH/g
Free Glycerin	D 6584	0.240	% mass
Total Glycerin	D 6584	0.240	% mass
Phosphorus content	D 4951	0.001 max	% mass
Sodium/potassium	UOP 391	5 max. combined	ppm
Distillation T, 90% recovery	D 1160	360 max	°C

Appendix B: Biodiesel Sample Analytical Reports

B.1: Biodiesel Produced from Soybean Oil; ASTM D 6584 Report

ASTM D 6584 Determination of Free and Total Glycerin in Biodiesel

Injection Date	: Sat, 29. Nov. 2008	Seq Line	: 22
Sample Name	: E - 14 @ 4.5hr B	Location	: Vial 15
Acq Operator	: Aijaz	Inj. No.	: 1
Multiplier	: 1.00	Dilution	: 1.00
Acq. Method	: C:\CHEM32\1\METHODS\6584NOV302008.M		
Analysis Method	: C:\CHEM32\1\METHODS\6584NOV302008.M		
Data File	: C:\CHEM32\1\DATA\NOV 30_E_14_CALIB_RUN\015B2201.D		



ASTM D 6584 Determination of Free and Total Glycerine in Biodiesel

Analyte	RT	<range>	Area	Mass%
Free Glycerine :	4.432	- -	499.86771	4.959
Monoglycerides :	15.095	- 15.495	738.88221	0.356
Diglycerides :	19.819	- 20.613	4015.43894	2.143
Triglycerides :	21.713	- 24.722	4499.40285	3.450
Bound Glycerine:	-	- -	-	0.771
Total Glycerine:	-	- -	-	5.731

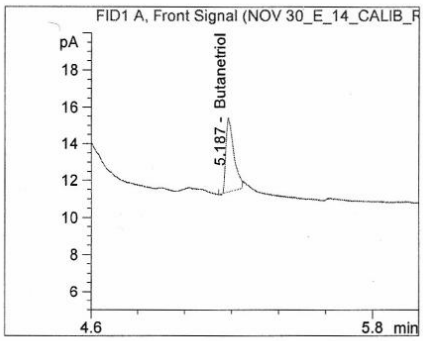
Calibrator	Meas. RT	Slope*	Intercept*
Glycerin :	4.432	0.87554	0.00912
Monoolein :	15.175	0.72385	0.02315
Diolein :	20.233	0.84361	0.01243
Triolein :	22.682	1.21221	0.01899

ISTD	Meas. RT	Area	Weight
Butanetriol:	5.187	9.29098	0.1000
Tricaprin :	18.870	1337.54163	0.8000

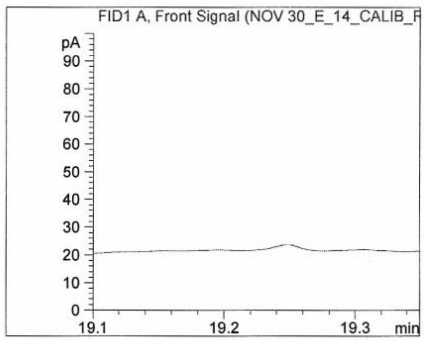
Sample Weight: 95.000

*ASTM D6584 Calibration Function

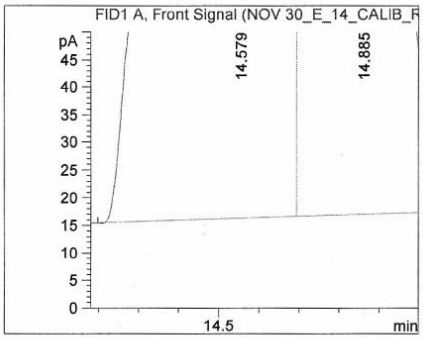
ASTM D 6584 Determination of Free and Total Glycerin in Biodiesel



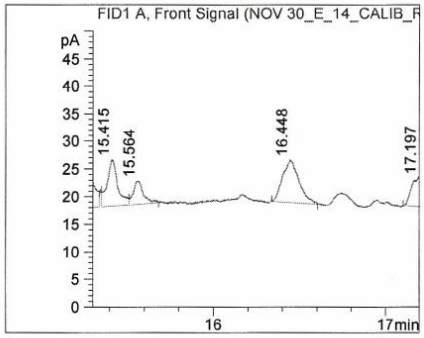
Triols:



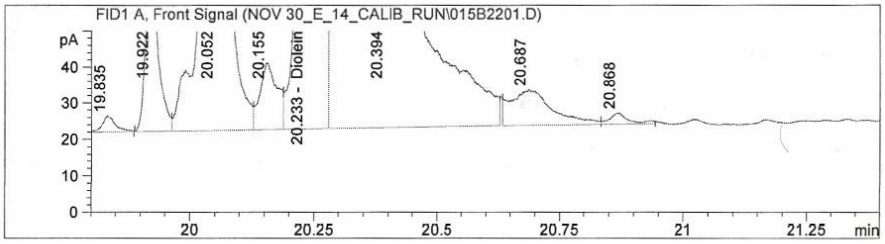
Tricaprin:



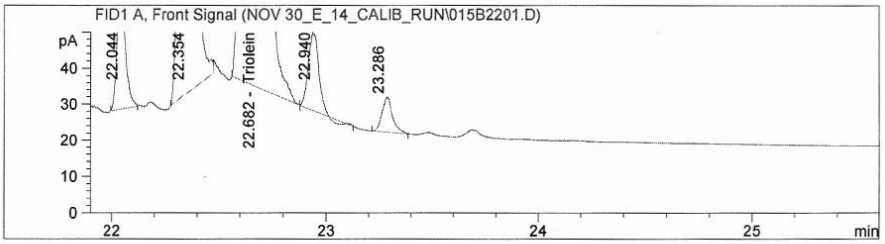
Monopalmitin: 13.696 - 13.895



Monoglycerides: 15.095 - 15.495



Diglycerides: 19.819 - 20.613



Triglycerides: 21.713 - 24.722

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Summed Peaks Report

iodiesel GC Sat, 29. Nov. 2008 02:41:50 pm ==Page ==2 of 3======

ASTM D 6584 Determination of Free and Total Glycerin in Biodiesel

Name	Start Time [min]	End Time [min]	Total Area [pA*s]	Area %
C16	8.597	9.247	9525.68481	8.7535
C18	9.697	10.357	8.32560e4	76.5065
C20:0;C20:1	11.216	11.546	796.32579	0.7318
C22:0;C22:1	12.896	13.186	884.84378	0.8131
Monopalmitin	13.695	13.895	164.80575	0.1514
Monoglycerides	15.095	15.495	36.55437	0.0336
C24:0;C24:1	17.744	17.944	64.20758	0.0590
Diglycerides	19.818	20.613	3602.17432	3.7369
Triglycerides	21.713	24.722	1290.30154	1.8478
Totals :				92.6335

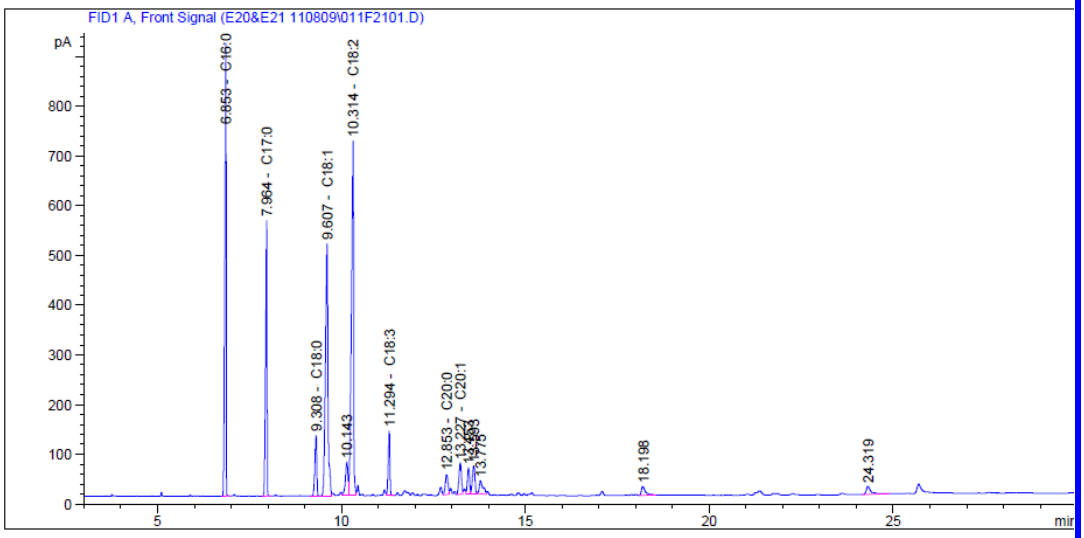
Final Summed Peaks Report

Name	Total Area [pA*s]	Area %
C16	9525.68481	8.7535
C18	8.32560e4	76.5065
C20:0;C20:1	796.32579	0.7318
C22:0;C22:1	884.84378	0.8131
Monopalmitin	164.80575	0.1514
Monoglycerides	36.55437	0.0336
C24:0;C24:1	64.20758	0.0590
Diglycerides	3602.17432	3.7369
Triglycerides	1290.30154	1.8478
Glycerin	499.86771	0.2596
Butanetriol	9.29098	5.509e-3
Monoolein	537.52209	0.4939
Tricaprin	1337.54163	1.5831
Diolein	413.26462	0.4287
Triolein	3209.10132	4.5956
Totals :		100.0000

B.2: Biodiesel Produced from Soybean Oil; EN 14103 Report

Data File C:\CHEM32\1\DATA\E20&E21 110809\011F2101.D
Sample Name: E-21 @ 10 hr Bot

Acq. Operator	: Aijaz	Seq. Line	: 21
Acq. Instrument	: Instrument 1	Location	: Vial 11
Injection Date	: 8/12/2009 4:28:20 PM	Inj	: 1
		Inj Volume	: 1 µl
Acq. Method	: C:\CHEM32\1\METHODS\14103N080809.M		
Last changed	: 8/8/2009 3:21:24 PM by Aijaz		
Analysis Method	: C:\CHEM32\1\METHODS\14103N080809.M		
Last changed	: 8/17/2009 6:36:59 PM by Aijaz		
Method Info	: 14103		



Area Percent Report

Sorted By : Signal
Calib. Data Modified : 8/17/2009 6:24:41 PM
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	5.020		0.0000	0.00000	0.00000	C14:0
2	6.853	BB	0.0369	2313.94336	19.37272	C16:0
3	7.964	BB I	0.0397	1502.41406	12.57846	C17:0

Data File C:\CHEM32\1\DATA\E20&E21 110809\011F2101.D
Sample Name: E-21 @ 10 hr Bot

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
4	9.308	BB	0.0501	434.23743	3.63551	C18:0
5	9.607	BV	0.0685	2454.28247	20.54766	C18:1
6	10.314	VV	0.0558	3022.79834	25.30737	C18:2
7	11.294	VB	0.0490	414.40829	3.46949	C18:3
8	12.853	VV	0.0803	208.95233	1.74938	C20:0
9	13.227	BV	0.0772	301.66043	2.52555	C20:1
10	17.361		0.0000	0.00000	0.00000	C22:0
11	17.616		0.0000	0.00000	0.00000	C22:1
12	22.011		0.0000	0.00000	0.00000	C24:0
13	22.911		0.0000	0.00000	0.00000	C24:1 Added

Totals : 1.06527e4 89.1861

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	10.143	VV	0.0665	323.93915	2.71207	?
2	13.453	VV	0.0646	212.77777	1.78141	?
3	13.593	VB	0.0786	267.41681	2.23886	?
4	13.775	BV	0.1046	193.77309	1.62230	?
5	18.198	BV	0.1130	142.08717	1.18958	?
6	24.319	BB	0.1336	151.65100	1.26965	?

Uncalib. totals : 1291.64499 10.8139

2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found

*** End of Report ***

B.3: Biodiesel Produced from Yellow Grease; EN 14103 Report

Data File C:\CHEM32\1\DATA\E34_ 21_05_10\002F0101.D
Sample Name: E-34 @ 24 h FP

```
==================================================================
Acq. Operator   : Aijaz                          Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 2
Injection Date  : 5/21/2010 10:29:24 AM               Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\14103A.M
Last changed    : 5/13/2010 9:23:48 AM by Aijaz
Analysis Method : C:\CHEM32\1\METHODS\14103A.M
Last changed    : 5/31/2010 2:58:41 PM by Aijaz
Method Info     :  14103
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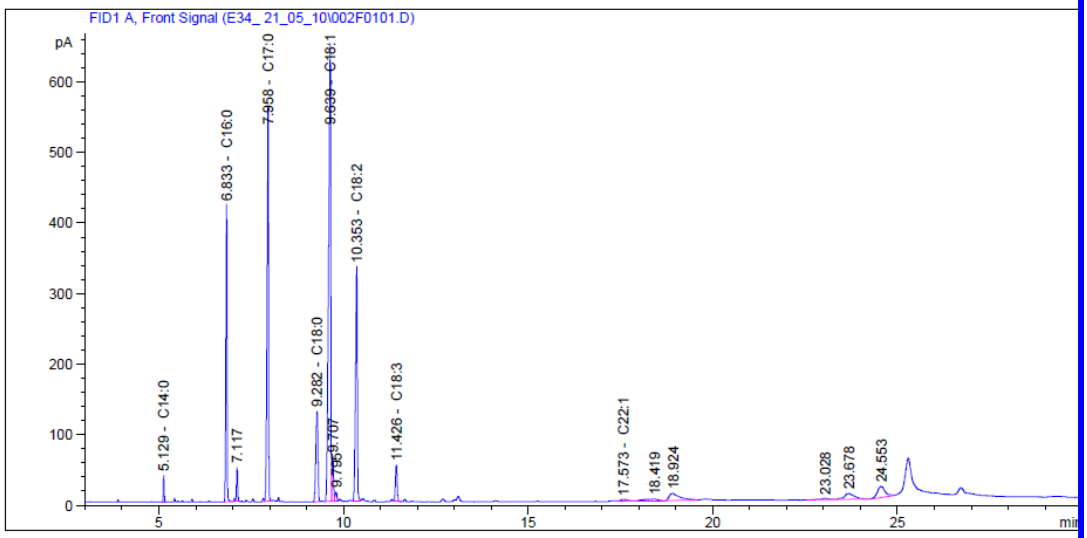


```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Calib. Data Modified  :      5/31/2010 2:48:09 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime  Type   Width     Area      Area    Name
  #   [min]          [min]   [pA*s]        %
----|-------|------|-------|----------|--------|--------------------
   1   5.129 BB      0.0238   59.50288  0.73729 C14:0
   2   6.833 BB      0.0348  938.81549 11.63272 C16:0
   3   7.958 VB   I  0.0416 1578.12598 19.55432 C17:0
```

Data File C:\CHEM32\1\DATA\E34_ 21_05_10\002F0101.D
Sample Name: E-34 @ 24 h FP

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
4	9.282	BB	0.0639	518.81030	6.42850	C18:0
5	9.639	BV	0.0579	2623.88965	32.51221	C18:1
6	10.353	BV	0.0530	1150.27588	14.25289	C18:2
7	11.426	VB	0.0542	177.46913	2.19899	C18:3
8	12.600		0.0000	0.00000	0.00000	C20:0
9	12.950		0.0000	0.00000	0.00000	C20:1
10	17.000		0.0000	0.00000	0.00000	C22:0
11	17.573	VB	0.1613	34.11412	0.42270	C22:1
12	21.436		0.0000	0.00000	0.00000	C24:0
13	22.011		0.0000	0.00000	0.00000	C24:1 Added

Totals : 7081.00343 87.7396

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	7.117	VB	0.0338	107.59749	1.33322	?
2	9.707	VV	0.0427	178.32700	2.20962	?
3	9.795	VB	0.0483	39.01266	0.48340	?
4	18.419	BB	0.3150	61.93162	0.76739	?
5	18.924	BB	0.2302	189.87892	2.35276	?
6	23.028	BB	0.1889	31.04172	0.38463	?
7	23.678	BB	0.2259	160.68152	1.99098	?
8	24.553	BB	0.1707	220.99915	2.73837	?

Uncalib. totals : 989.47007 12.2604

1 Warnings or Errors :

Warning : Calibrated compound(s) not found

==========

*** End of Report ***

B.4: Biodiesel Produced from crude Jatropha Oil; EN 14103 Report

Data File C:\CHEM32\1\DATA\E-47_ 09_08_10D\002F0101.D
Sample Name: E-47 @ 10 h

```
==========================================================================
Acq. Operator    : Aijaz                          Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 2
Injection Date  : 8/11/2010 7:49:01 PM                Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\14103B.M
Last changed    : 7/21/2010 3:33:01 PM by Aijaz
Analysis Method : C:\CHEM32\1\METHODS\14103C.M
Last changed    : 8/11/2010 12:14:35 PM by Aijaz
Method Info     :  14103
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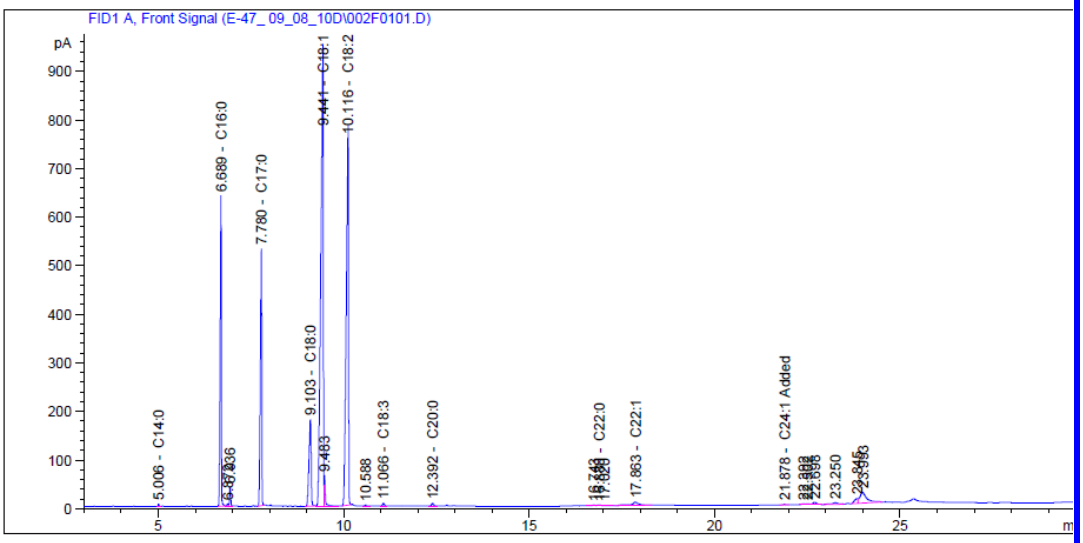


```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      8/11/2010 12:14:31 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime  Type   Width     Area      Area    Name
  #   [min]          [min]   [pA*s]        %
----|-------|------|-------|----------|--------|--------------------
   1   5.006 BB      0.0224    5.70447  0.04674 C14:0
   2   6.689 BB      0.0331 1417.18701 11.61214 C16:0
   3   7.780 BB   I  0.0400 1448.79553 11.87113 C17:0
```

Instrument 1 8/13/2010 12:46:07 PM Aijaz Page 1 of 2

Data File C:\CHEM32\1\DATA\E-47_ 09_08_10D\002F0101.D
Sample Name: E-47 @ 10 h

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
4	9.103	BV	0.0595	739.22449	6.05705	C18:0
5	9.441	VV	0.0604	4410.54443	36.13909	C18:1
6	10.116	BB	0.0556	3298.09375	27.02390	C18:2
7	11.066	BB	0.0484	18.66543	0.15294	C18:3
8	12.392	BB	0.0570	22.17998	0.18174	C20:0
9	12.950		0.0000	0.00000	0.00000	C20:1
10	16.880	VV	0.0959	10.90438	0.08935	C22:0
11	17.863	BB	0.1890	109.44001	0.89673	C22:1
12	21.336		0.0000	0.00000	0.00000	C24:0
13	21.878	BB	0.0841	7.29246	0.05975	C24:1 Added
Totals :				1.14880e4	94.1306	

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	6.872	BV	0.0338	9.62652	0.07888	?
2	6.936	VB	0.0313	77.83633	0.63777	?
3	9.483	VB	0.0336	143.68654	1.17734	?
4	10.588	BB	0.0484	7.62925	0.06251	?
5	16.743	BV	0.0774	7.14407	0.05854	?
6	17.020	VB	0.0792	5.07799	0.04161	?
7	22.392	BV	0.0743	9.36066	0.07670	?
8	22.502	VV	0.0905	15.51552	0.12713	?
9	22.698	VB	0.0934	35.46714	0.29061	?
10	23.250	BB	0.1500	39.45952	0.32332	?
11	23.845	BV	0.0797	63.44166	0.51983	?
12	23.993	VV	0.1609	302.08188	2.47520	?
Uncalib. totals :				716.32708	5.8694	

2 Warnings or Errors :

Warning : Calibrated compound(s) not found
Warning : Invalid calibration curve, (C24:1 Added)

==========

*** End of Report ***

Appendix C: Representative FAME Composition Sample Data

C.1: Biodiesel Produced from Soybean Oil; EN 14103 Report

	FAME (wt%)									
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
0.5	0.00	10.72	4.10	26.90	51.58	6.41	0	0.00	0.30	0.00
1.0	0.03	10.52	4.20	26.76	51.39	6.83	0	0.00	0.28	0.00
2.0	0.03	10.41	4.15	26.70	51.40	7.05	0	0.00	0.26	0.00
3.0	0.04	10.28	4.02	26.13	51.65	7.35	0.24	0.00	0.25	0.00
4.0	0.04	10.12	4.01	25.95	51.74	7.38	0.24	0.19	0.24	0.00

Composition of FAME produced using soybean oil as feedstock using solid-acid catalyzed process as a function of time. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

C.2: Biodiesel Produced from Yellow Grease; EN 14103 Report

FAME (wt %)										
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
0	0.00	18.42	10.78	49.58	21.21	0.00	0	0.00	0.00	0.00
0.25	0.00	17.25	9.94	50.82	20.31	3.05	0	0.00	0.00	0.00
0.5	1.01	16.78	9.63	49.66	19.85	3.07	0	0.00	0.00	0.00
0.75	1.00	16.49	9.47	49.62	19.76	3.02	0	0.00	0.65	0.00
1	0.99	16.35	9.40	49.46	19.70	3.01	0	0.56	0.53	0.00
1.5	1.01	16.41	9.42	49.76	19.81	3.04	0	0.55	0.00	0.00
2	1.01	16.36	9.38	49.81	19.84	3.04	0	0.55	0.00	0.00
4	1.02	16.21	9.27	49.79	19.85	3.02	0	0.84	0.00	0.00
6	1.03	16.07	9.17	49.65	19.87	2.99	0.38	0.84	0.00	0.00
8	1.03	16.04	9.14	55.41	23.34	2.97	0.38	0.84	0.00	0.00
10	1.02	15.86	9.03	49.31	19.75	3.58	0.37	0.83	0.24	0.00
24	1.03	15.90	9.04	49.60	19.79	3.41	0.37	0.85	0.00	0.00
24.5	1.03	15.92	9.03	49.52	19.74	3.54	0.37	0.85	0.00	0.00

Composition of FAME produced using yellow grease as feedstock using solid-acid catalyzed process as a function of time. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 800 rpm, 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

C.3: Biodiesel Produced from crude Jatropha Oil; EN 14103 Report

FAME (wt %)												
Time (h)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1	C24:0	C24:1
0	0.00	11.42	5.93	35.53	25.54	0.00	0	0.00	1.58	19.33	0.00	0.67
0.25	0.00	13.03	6.71	40.64	29.65	0.00	0	0.00	1.22	7.98	0.00	0.79
0.5	0.00	13.48	6.95	42.20	30.83	0.19	0	0.00	0.69	5.43	0.00	0.23
0.75	0.00	13.69	7.06	42.98	31.41	0.19	0.21	0.00	0.56	3.61	0.00	0.28
1	0.00	13.79	7.13	43.44	31.76	0.19	0.22	0.00	0.54	2.66	0.00	0.28
1.5	0.00	13.91	7.20	43.90	32.08	0.19	0.22	0.00	0.48	1.78	0.00	0.25
2	0.00	13.91	7.21	44.04	32.19	0.19	0.22	0.00	0.43	1.74	0.00	0.08
4	0.00	13.99	7.26	44.48	32.53	0.19	0.28	0.00	0.22	1.07	0.00	0.08
6	0.06	13.92	7.26	44.63	32.65	0.19	0.22	0.00	0.17	0.84	0.00	0.07
8	0.06	13.96	7.28	44.83	32.42	0.19	0.22	0.00	0.15	0.84	0.00	0.06
10	0.06	13.92	7.26	44.72	32.39	0.18	0.22	0.00	0.11	1.07	0.00	0.07
24	0.06	13.92	7.29	45.15	32.80	0.17	0.22	0.00	0.00	0.33	0.00	0.05
24.5	0.06	13.94	7.31	45.19	32.80	0.17	0.22	0.00	0.00	0.25	0.00	0.06

FAME profile of Jatropha based biodiesel produced from simultaneous esterification and transesterification of Jatropha oil as feedstock. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, 3 wt.% of the solid acid catalyst (tungstophosphoric acid with 30% loading supported on neutral alumina).

Appendix D: List of Important Formula used for Calculations

Free Fatty Acid Conversion:

$$\text{FFA conversion}(\%) = \left(\frac{a_i - a_t}{a_i} \right) \times 100$$

where a_i is the initial acid number of the mixture and a_t is the acid number at time t as specified in ASTM D6751.

Determination of methyl ester content:

$$\%\ of\ ME = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100$$

where,

$\sum A$ = Total peak area of methyl ester from C_{14} to $C_{24:1}$

A_{EI} = Peak area corresponding to methyl heptadecanoate (C_{17})

C_{EI} = Concentration of the to metyl heptadecanoate (C_{17}) solution (mg/mL)

V_{EI} = Volume of the methyl heptadecanoate (C_{17}) solution (mL)

m = Mass of the sample (mg)

Determination of Acid Number:

$$Acid\ \ Number, mg\ \ of\ \ KOH\ \ / g = \left[\frac{(A-B) \times M \times 56.1}{W} \right]$$

where,

A = KOH solution volume required for titration of the sample (mL)

B = KOH solution volume required for titration of the blank (mL)

M = molarity of the KOH solution

W = mass of the sample used (g)

Appendix E: Sample Calculations

Experimental Data of Jatropha's Run# 13

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.2476	0	8.85	8.85	8.74	39.61	19.90	0.00
2	0.25	0.5175	0	13.9	13.9	13.79	29.90	15.02	24.51

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL**,** **M =** Molarity of the KOH solution = 0.02 M

Determination of Acid Number for Sample #2 @ 0.25 hr:

$$Acid\ \ Number, mg\ \ of\ \ KOH\ \ / g = \left[\frac{(A-B) \times M \times 56.1}{W} \right]$$

where,

A = KOH solution volume required for titration of the sample (mL) = V = 13.9 mL

B = KOH solution volume required for titration of the blank (mL) = Vb = 0.11 mL

M = molarity of the KOH solution = 0.02 M

W = mass of the sample used (g) = 0.5175 g

$$Acid\ \ Number = \left[\frac{(13.9-0.11) \times 0.02 \times 56.1}{0.5175} \right] = 29.90$$

Free Fatty Acid Conversion:

$$\text{FFA conversion}(\%) = \left(\frac{a_i - a_t}{a_i} \right) \times 100$$

where a_i is the initial acid number of the mixture and a_t is the acid number at time t as specified in ASTM D6751.

$$FFA\ conversion\ (\%) = \left(\frac{19.90 - 15.02}{19.90} \right) \times 100 = 24.51\ \%$$

Experimental Data of Jatropha's Run# 13

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.083	265.4	3234.69	1434.61	0	12.02	0
0.25	5.083	214.8	4076.92	1425.38	0	22.01	0
0.5	5.083	214.1	4976.39	1431.69	6.61	29.39	0.19

MEC (%) = Total Ester Content (mass %)
EC (%) = Ester Content (mass %)
FP = Final Product
V_{EI} = Volume of the methyl heptadecanoate solution (mL) = 5 mL

Determination of methyl ester content:

$$\%\ of\ ME = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100$$

where,

$\sum A$ = Total peak area of methyl ester from C_{14} to $C_{24:1}$= 4976.39

A_{EI} = Peak area corresponding to methyl heptadecanoate (C_{17}) = 1431.69

C_{EI} = Concentration of the to metyl heptadecanoate (C_{17}) solution (mg/mL) = 5.083

V_{EI} = Volume of the methyl heptadecanoate (C_{17}) solution (mL) = 5 mL

m = Mass of the sample (mg) = 214.1 mg

$$\%\ of\ ME = \frac{4976.39 - 1431.69}{1431.69} \times \frac{5.083 \times 5}{214.1} \times 100 = 29.39\,\%$$

Appendix F: Representative Experimental Sample Data

F.1: Biodiesel Produced from Yellow Grease

F.1.1: Effect of Oil to Alcohol Molar Ratio

(1:6 and 1:18)

Run # 12: Simultaneous esterification and transesterification of yellow grease with 9.1% FFA as a non-edible feedstock using 12-tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:18, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.026	131.1	2263.6	1498.32	0	3.92	0.00
0.25	5.026	101.3	3502.15	1481.74	57.244	13.53	2.83
0.5	5.026	123.2	4766.75	1492.24	94.197	17.90	2.88
0.75	5.026	117.3	5418.13	1510.78	111.784	22.16	2.86
1	5.026	109.2	5802.42	1511.12	123.653	26.14	2.88
1.5	5.026	104.3	7063.41	1534.85	160.655	34.71	2.91
2	5.026	103.9	7343.82	1547.14	167.692	36.25	2.89
4	5.026	109.1	8371.24	1543.91	197.805	40.74	2.90
6	5.026	119.2	11116.4	1527.3	272.335	52.94	2.84
8	5.026	143.3	13820.1	1511.69	348.215	57.11	2.83
10	5.026	132.4	13076.1	1496.14	325.049	58.76	2.81
24	5.026	106.9	12391.3	1515.24	352.867	67.49	3.24
FP	5.026	116.8	15101.5	1533.59	57.777	76.14	0.43

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.335	2.9	7.64	4.74	4.63	15.51	7.79	0.00
2	0.25	0.3335	7.64	10.9	3.26	3.15	10.60	5.33	31.66
3	0.5	0.4184	0.9	4	3.1	2.99	8.02	4.03	48.29
4	0.75	0.3975	4.05	6.45	2.4	2.29	6.46	3.25	58.32
5	1	0.1416	6.45	7.23	0.78	0.67	5.31	2.67	65.76
6	1.5	0.2389	7.25	8.11	0.86	0.75	3.52	1.77	77.29
7	2	0.2266	8.15	8.98	0.83	0.72	3.57	1.79	77.01
8	4	0.2129	0	0.7	0.7	0.59	3.11	1.56	79.95
9	6	0.19	0.75	1.35	0.6	0.49	2.89	1.45	81.34
10	8	0.1519	1.4	1.88	0.48	0.37	2.73	1.37	82.38
11	10	0.1324	1.9	2.32	0.42	0.31	2.63	1.32	83.06
12	24	0.1062	2.35	2.91	0.56	0.45	4.75	2.39	69.34
13	FP	1.881	2.95	7.26	4.31	4.2	2.51	1.26	83.84

Vi = Initial Volume; **Vf** = Final Volume; **V**=Vf-Vi; **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL, **M** = Molarity of the KOH solution = 0.02 M

Run # 13: Simultaneous esterification and transesterification of yellow grease with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:6, stirring speed 600 rpm, amount of catalyst 3 wt.%, and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.968	113.1	2117.19	1407.43	0	4.43	0.00
0.25	4.968	114.5	4013.16	1415.18	75.4228	15.93	2.90
0.5	4.968	109	4899.38	1398.67	104.02	22.82	2.97
0.75	4.968	113.3	5931.99	1442.05	132.786	27.31	2.96
1	4.968	121.5	7355.59	1559.31	171.279	30.40	2.95
1.5	5.026	118.7	8091.69	1553.87	192.6	35.63	2.95
2	5.026	105	8161.96	1548.75	195.524	40.88	2.96
4	5.026	115.6	10250.5	1521.17	260.126	49.90	2.98
6	5.026	109.9	12716.9	1532.86	328.25	66.73	2.93
8	5.026	106.2	13091.1	1534.6	338.17	71.27	2.93
10	5.026	97.1	12196.7	1529.46	309.356	72.20	2.90
FP	5.026	123.8	16067.3	1539.03	516.284	76.64	3.55

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.2898	0	4.21	4.21	4.1	15.87	7.98	0.00
2	0.25	0.2845	4.25	6.7	2.45	2.34	9.23	4.64	41.86
3	0.5	0.3657	6.7	8.83	2.13	2.02	6.20	3.11	60.96
4	0.75	0.3569	0	1.58	1.58	1.47	4.62	2.32	70.89
5	1	0.2838	1.6	2.62	1.02	0.91	3.60	1.81	77.34
6	1.5	0.2971	2.65	3.46	0.81	0.7	2.64	1.33	83.35
7	2	0.3665	3.5	4.32	0.82	0.71	2.17	1.09	86.31
8	4	0.3942	4.35	5.1	0.75	0.64	1.82	0.92	88.52
9	6	0.4014	5.11	5.84	0.73	0.62	1.73	0.87	89.08
10	8	0.5064	5.86	6.7	0.84	0.73	1.62	0.81	89.81
11	10	0.4731	0	0.8	0.8	0.69	1.64	0.82	89.69
12	FP	1.4626	0.85	2.88	2.03	1.92	1.47	0.74	90.72

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL**,** **M =** Molarity of the KOH solution = 0.02 M

F.1.2: Effect of Nature of Support

(acidic and basic)

Run # 18: Simultaneous esterification and transesterification of yellow grease with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on acidic alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. conc.	Sample Weight (	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.996	269.8	2616	1393.46	32.356	8.12	2.65
0.25	4.996	250.7	3382.02	1395.74	54.664	14.18	2.75
0.5	4.996	227	3930.42	1426.04	69.9	19.33	2.79
0.75	4.996	250.9	4850.96	1427.41	107.581	23.88	3.14
1	4.996	212.1	4788.85	1432.35	107.137	27.60	3.19
1.5	4.996	232.9	5865.57	1431.9	150.815	33.21	3.40
2	4.996	234.1	6446.97	1415.18	172.244	37.94	3.42
4	4.996	219.4	8070.2	1432.43	229.209	52.76	3.45
6	4.996	227.3	9355.75	1426.28	282.483	61.10	3.56
9.25	4.996	212.6	10037.9	1441.68	797.388	70.06	9.28
10	4.996	206.2	9838.19	1437.89	299.78	70.77	3.57
24	4.996	249	13108	1442.91	412.874	81.10	3.54
FP	4.996	233	12386.6	1446.92	386.366	81.06	3.53

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.3112	0	4.2	4.2	4.09	14.75	7.41	0.00
2	0.25	0.5285	4.25	9.39	5.14	5.03	10.68	5.37	27.58
3	0.5	0.3801	0	2.95	2.95	2.84	8.38	4.21	43.15
4	0.75	0.4612	3	5.8	2.8	2.69	6.54	3.29	55.62
5	1	0.4363	5.8	7.85	2.05	1.94	4.99	2.51	66.17
6	1.5	0.4577	7.9	9.55	1.65	1.54	3.78	1.90	74.40
7	2	0.4821	0	1.32	1.32	1.21	2.82	1.42	80.90
8	4	0.4003	1.35	2.15	0.8	0.69	1.93	0.97	86.88
9	6	0.5822	2.2	3.11	0.91	0.8	1.54	0.77	89.54
10	9.25	0.617	3.15	4.09	0.94	0.83	1.51	0.76	89.76
11	10	0.7939	4.1	5.21	1.11	1	1.41	0.71	90.42
12	24	0.9812	5.25	6.55	1.3	1.19	1.36	0.68	90.77
13	FP	2.1148	6.55	9.06	2.51	2.4	1.27	0.64	91.37

Vi = Initial Volume; **Vf** = Final Volume; **V**=Vf-Vi; **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL, **M** = Molarity of the KOH solution = 0.02 M

Run # 19: Simultaneous esterification and transesterification of yellow grease with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on basic alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.%, and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.044	235.3	2089.09	1432.18	16.024	4.92	2.44
0.25	5.044	248	3232.14	1410.15	48.984	13.14	2.69
0.5	5.044	270.2	3860.73	1452.21	65.393	15.48	2.72
0.75	5.044	255.8	4568.09	1437.09	86.026	21.48	2.75
1	5.044	244.5	4543.59	1456.86	85.247	26.22	2.76
1.5	5.044	240.4	5624.79	1439.4	140.057	30.50	3.35
2	5.044	239.9	6332.78	1457.55	163.175	35.16	3.35
4	5.044	248.1	7816.61	1439.02	215.01	45.05	3.37
6	5.044	272.8	9824.48	1458.17	289.96	53.04	3.47
8	5.044	256.2	10878.3	1463.32	326.006	63.33	3.46
10	5.044	202.4	7836.37	1419.28	214.091	56.33	3.34
FP	5.044	258.4	13270	1449.46	408.561	79.59	3.46

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.306	0	4.55	4.55	4.44	16.28	8.18	0.00
2	0.25	0.5193	4.6	9.77	5.17	5.06	10.93	5.49	32.85
3	0.5	0.329	0.01	3.03	3.02	2.91	9.92	4.99	39.04
4	0.75	0.4835	3.05	6.3	3.25	3.14	7.29	3.66	55.24
5	1	0.5752	6.3	9.25	2.95	2.84	5.54	2.78	65.97
6	1.5	0.3586	0	1.55	1.55	1.44	4.51	2.26	72.32
7	2	0.4442	1.55	3.02	1.47	1.36	3.44	1.73	78.90
8	4	0.4695	3.05	4.1	1.05	0.94	2.25	1.13	86.20
9	6	0.6714	4.2	5.42	1.22	1.11	1.85	0.93	88.61
10	8	0.9	5.45	6.95	1.5	1.39	1.73	0.87	89.36
11	10	0.197	6.95	7.34	0.39	0.28	1.59	0.80	90.20
12	FP	2.0298	7.34	10.05	2.71	2.6	1.44	0.72	91.17

Vi = Initial Volume; **Vf** = Final Volume; **V**=Vf-Vi; **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL, **M** = Molarity of the KOH solution = 0.02 M

F.1.3: Effect of Tetrahydrofuran as Co-solvent

(with cosolvent)

Run # 15: Simultaneous esterification and transesterification of yellow grease with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.%, tetrahydrofuran as co-solvent (volume ratio alcohol-to-THF, 1:1) and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.026	213	1748.49	1330.44	10.877	3.71	2.60
0.25	5.026	243.2	2413.02	1334.6	29.424	8.35	2.73
0.5	5.026	257.9	3561.55	1350.85	61.566	15.95	2.78
0.75	5.026	272.6	3097.48	1346.06	48.592	11.99	2.77
1	5.026	228.9	3522.09	1301.9	62.361	18.72	2.81
1.5	5.026	247.7	4553.96	1328.22	92.875	24.64	2.88
2	5.026	250.5	5253.58	1353.14	112.7	28.92	2.89
4	4.947	205.8	5978.62	1356.17	134.194	40.97	2.90
6	4.947	206.6	7324.78	1411.25	173.001	50.17	2.93
8	4.947	233	8861.71	1409.38	217.067	56.13	2.91
10	4.947	205.8	8668.98	1399.61	209.416	62.43	2.88
24	4.947	228.5	11926.9	1444.02	284.526	78.59	2.71
FP	4.947	227.6	11940.8	1454.58	284.413	78.35	2.71

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.1888	0	2.95	2.95	2.84	16.88	8.48	0.00
2	0.25	0.2441	3	6.05	3.05	2.94	13.51	6.79	19.93
3	0.5	0.1946	6.05	7.81	1.76	1.65	9.51	4.78	43.63
4	0.75	0.1567	0.05	1.75	1.7	1.59	11.38	5.72	32.55
5	1	0.1792	1.8	3.2	1.4	1.29	8.08	4.06	52.14
6	1.5	0.2057	3.25	4.44	1.19	1.08	5.89	2.96	65.10
7	2	0.2297	4.45	5.5	1.05	0.94	4.59	2.31	72.79
8	4	0.2405	5.5	6.18	0.68	0.57	2.66	1.34	84.24
9	6	0.2443	6.2	6.77	0.57	0.46	2.11	1.06	87.48
10	8	0.3246	6.8	7.48	0.68	0.57	1.97	0.99	88.33
11	10	1.4505	7.5	9.75	2.25	2.14	1.66	0.83	90.19
12	24	0.7248	0	1.1	1.1	0.99	1.53	0.77	90.92
13	FP	2.0345	1.15	3.93	2.78	2.67	1.47	0.74	91.28

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL**,** **M =** Molarity of the KOH solution = 0.02 M

F.2.1:Biodiesel Produced from crude Jatropha oil

F.2.1.1: Effect of Amount of Catalyst

(1 wt %, 3 wt % and 10 wt %)

Run # 1: Simultaneous esterification and transesterification of crude *jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 10 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.954	169.7	4074.05	1428.35	7.81	27.04	0.30
0.25	4.954	202.4	5622.98	1421.89	7.77	36.16	0.18
0.5	4.952	170.8	6014.53	1440.40	7.69	46.04	0.17
0.75	4.952	174.1	6624.36	1433.21	7.51	51.51	0.14
1	4.952	177.2	7084.00	1429.05	7.47	55.30	0.13
1.5	4.952	166.2	7322.32	1426.11	7.66	61.60	0.13
2	4.952	163.5	7602.61	1422.49	7.36	65.80	0.12
4	4.952	196.6	9775.04	1420.74	7.37	74.06	0.09
6	4.952	239	12801.58	1421.25	20.75	82.96	0.18
8	4.952	240	13585.65	1428.51	22.07	87.80	0.18
10	4.952	252.6	14282.63	1456.74	22.99	86.31	0.20
FP	4.952	275.7	15973.04	1427.97	25.73	91.48	0.18

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.3672	0	10.42	10.42	10.28	31.41	15.78	0.00
2	0.25	0.6382	0.45	10	9.55	9.41	16.54	8.31	47.33
3	0.5	0.7415	0	7.2	7.2	7.06	10.68	5.37	65.99
4	0.75	0.7761	0	5.42	5.42	5.28	7.63	3.84	75.70
5	1	0.6113	2.65	5.98	3.33	3.19	5.86	2.94	81.36
6	1.5	0.8315	6	9	3	2.86	3.86	1.94	87.71
7	2	0.932	0	2.65	2.65	2.51	3.02	1.52	90.38
8	4	0.9567	2.65	4.57	1.92	1.78	2.09	1.05	93.35
9	6	1.0172	4.6	6.6	2	1.86	2.05	1.03	93.47
10	8	0.6618	6.6	7.58	0.98	0.84	1.42	0.72	95.47
11	10	0.996	8	9.9	1.9	1.76	1.98	1.00	93.69
12	FP	2.2322	0	4.18	4.18	4.04	2.03	1.02	93.54

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.14 mL**,** **M =** Molarity of the KOH solution = 0.02 M

Run # 2: Simultaneous esterification and transesterification of crude *Jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 1 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.952	249.9	4738.22	1406.21	0	23.48	0.00
0.25	4.952	219.9	5462.47	1419.01	0	32.09	0.00
0.5	4.952	201.4	5739.36	1408.49	5.926	37.80	0.14
0.75	4.952	171.9	5649.32	1433.85	6.327	42.35	0.15
1	4.952	205.9	6811.29	1421.01	8.477	45.62	0.16
1.5	4.952	189.9	7265.25	1424.28	9.968	53.47	0.17
2	4.952	184.1	7710.97	1431.84	10.619	58.98	0.17
4	4.952	208.4	9992.87	1429.42	15.465	71.18	0.18
6	4.952	262.7	13288	1404.97	21.629	79.72	0.18
8	4.952	222.9	12403.9	1408.63	20.471	86.71	0.19
10	4.952	237.5	13846.8	1423.5	22.275	90.99	0.18
FP	4.952	252.3	14822.8	1436.61	23.777	91.45	0.18

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.5813	0	21	21	20.86	40.26	20.23	0.00
2	0.25	0.4228	0	11.65	11.65	11.51	30.54	15.35	24.14
3	0.5	0.4465	0	10	10	9.86	24.78	12.45	38.46
4	0.75	0.5947	0	11.48	11.48	11.34	21.39	10.75	46.86
5	1	0.5701	0	9.6	9.6	9.46	18.62	9.36	53.76
6	1.5	0.5717	0	7.55	7.55	7.41	14.54	7.31	63.88
7	2	0.7019	0	7.9	7.9	7.76	12.40	6.23	69.19
8	4	0.7472	0	5.83	5.83	5.69	8.54	4.29	78.78
9	6	0.8187	0	4.8	4.8	4.66	6.39	3.21	84.14
10	8	0.7165	4.85	8.13	3.28	3.14	4.92	2.47	87.79
11	10	1.1816	0	4.05	4.05	3.91	3.71	1.87	90.78
12	FP	2.139	0	7	7	6.86	3.60	1.81	91.06

Vi = Initial Volume; **Vf** = Final Volume; **V**=Vf-Vi; **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.14 mL, **M** = Molarity of the KOH solution = 0.02 M

Run # 13: Simultaneous esterification and transesterification of crude *Jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.083	265.4	3234.69	1434.61	0	12.02	0
0.25	5.083	214.8	4076.92	1425.38	0	22.01	0
0.5	5.083	214.1	4976.39	1431.69	6.61	29.39	0.19
0.75	5.083	264.5	6583.9	1419.86	9.76	34.95	0.19
1	5.083	199.8	6069.69	1447.78	8.76	40.61	0.19
1.5	5.083	226.3	7211.62	1439.88	11.05	45.02	0.19
2	5.083	259.9	8882.93	1462	14.22	49.64	0.19
4	5.083	238.5	9774.1	1445.07	15.86	61.43	0.19
6	5.083	270.1	11989.5	1423.89	19.82	69.83	0.19
8	5.083	213.6	10483.5	1432.04	16.88	75.21	0.19
10	5.083	223.4	11631.7	1448.8	18.67	79.97	0.18
24	5.083	221.8	12978.7	1445.43	19.65	91.44	0.17
FP	5.083	225.2	13136.9	1445.48	19.87	91.29	0.17

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.2476	0	8.85	8.85	8.74	39.61	19.90	0.00
2	0.25	0.5175	0	13.9	13.9	13.79	29.90	15.02	24.51
3	0.5	0.6085	0	12.8	12.75	12.64	23.31	11.71	41.15
4	0.75	0.4202	0	7.1	7.1	6.99	18.66	9.38	52.87
5	1	0.9226	0	12.2	12.2	12.09	14.70	7.39	62.88
6	1.5	0.6006	2.25	8.92	6.67	6.56	12.25	6.16	69.06
7	2	0.4246	0	3.93	3.93	3.82	10.09	5.07	74.51
8	4	0.7863	3.95	8.52	4.57	4.46	6.36	3.20	83.93
9	6	0.335	0	1.72	1.72	1.61	5.39	2.71	86.38
10	8	0.4993	4.6	6.23	1.63	1.52	3.42	1.72	91.38
11	10	0.6617	6.3	9.35	3.05	2.94	4.99	2.51	87.41
12	24	0.6735	0	1.6	1.6	1.49	2.48	1.25	93.73
13	FP	2.2627	1.61	6.7	5.09	4.98	2.47	1.24	93.76

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V – Vb
Vb = Volume used for blank (solvent) = 0.11 mL**,** **M =** Molarity of the KOH solution = 0.02 M

F.2.2: Effect of Rate of Mixing

(500 rpm, 600 rpm, and 700 rpm)

Run # 3: Simultaneous esterification and transesterification of crude *jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:27, stirring speed 500 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.952	219.2	3865.66	1406.2	7.8513	19.76	0.32
0.25	4.952	238.9	5490.12	1402.8	5.176	30.20	0.13
0.5	4.952	237.1	6245.19	1395.09	7.4	36.31	0.15
0.75	4.952	219.5	6825.25	1405.24	8.749	43.51	0.16
1	4.952	248.7	7565.15	1396.37	10.503	43.98	0.17
1.5	4.952	238.2	8083.42	1407.68	11.922	49.30	0.18
2	4.952	252.9	8573.75	1394.98	14.004	50.39	0.20
4	4.952	217.4	9054.05	1409.1	14.395	61.79	0.19
6	4.952	294.3	12598.9	1390.14	20.893	67.84	0.19
8	4.952	279	12910.5	1383.58	21.964	73.94	0.19
10	4.952	267.3	12817.7	1396.73	20.959	75.75	0.18
FP	4.952	223	11551.7	1426.68	19.3	78.80	0.19

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.4615	0	17.65	17.65	17.51	42.57	21.39	0.00
2	0.25	0.5394	0	14	14	13.86	28.83	14.49	32.28
3	0.5	0.5995	0	12.2	12.2	12.06	22.57	11.34	46.98
4	0.75	0.6298	0	9.75	9.75	9.61	17.12	8.60	59.78
5	1	0.6555	0	9.15	9.15	9.01	15.42	7.75	63.77
6	1.5	0.6551	1.35	7.05	5.7	5.56	9.52	4.79	77.63
7	2	0.6434	0	5.68	5.68	5.54	9.66	4.85	77.31
8	4	0.2044	5.75	6.98	1.23	1.09	5.98	3.01	85.94
9	6	0.3619	7	8.65	1.65	1.51	4.68	2.35	89.00
10	8	0.293	0	1.2	1.2	1.06	4.06	2.04	90.46
11	10	0.1826	1.25	2.03	0.78	0.64	3.93	1.98	90.76
12	FP	2.0499	2.05	9.25	7.2	7.06	3.86	1.94	90.92

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.14 mL**,** **M =** Molarity of the KOH solution = 0.02 M

Run # 4: Simultaneous esterification and transesterification of crude *jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 700 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.952	182.2	3761.01	1421.3	0	22.37	0.00
0.25	4.952	200.8	5023.34	1414.27	0	31.47	0.00
0.5	4.952	226.5	6142.6	1407.32	6.508	36.78	0.14
0.75	4.952	246	7105.11	1402.12	8.57	40.94	0.15
1	4.952	276.5	8281.14	1393.42	11.307	44.27	0.16
1.5	4.952	273.3	9073.41	1395.95	13.277	49.83	0.17
2	4.952	268.5	9495.58	1394.56	13.948	53.57	0.17
4	4.952	254.4	10679.1	1396.43	16.433	64.70	0.18
6	4.952	220.2	10396.5	1405.81	15.967	71.92	0.18
8	4.952	248.2	12138.9	1407.36	19.015	76.07	0.18
10	4.952	297.9	14646.3	1395.97	23.471	78.90	0.18
FP	4.952	283.6	14048.4	1406.6	22.9	78.47	0.18

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.2982	0	10.8	10.8	10.66	40.11	20.16	0.00
2	0.25	0.4199	0	10.85	10.85	10.71	28.62	14.38	28.65
3	0.5	0.4641	0	10.1	10.1	9.96	24.08	12.10	39.97
4	0.75	0.4449	2	9.25	7.25	7.11	17.93	9.01	55.29
5	1	0.3951	0	5.57	5.57	5.43	15.42	7.75	61.55
6	1.5	0.546	0	5.95	5.95	5.81	11.94	6.00	70.23
7	2	0.651	0	5.75	5.75	5.61	9.67	4.86	75.89
8	4	0.5746	0	3.25	3.25	3.11	6.07	3.05	84.86
9	6	0.7159	3.3	6.65	3.35	3.21	5.03	2.53	87.46
10	8	0.6312	6.7	9.48	2.78	2.64	4.69	2.36	88.30
11	10	0.1934	0	0.79	0.79	0.65	3.77	1.89	90.60
12	FP	2.1141	1	8.65	7.65	7.51	3.99	2.00	90.06

Vi = Initial Volume; **Vf** = Final Volume; **V**=Vf-Vi; **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.14 mL, **M** = Molarity of the KOH solution = 0.02 M

Run # 13: Simultaneous esterification and transesterification of crude *jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.083	265.4	3234.69	1434.61	0	12.02	0
0.25	5.083	214.8	4076.92	1425.38	0	22.01	0
0.5	5.083	214.1	4976.39	1431.69	6.61	29.39	0.19
0.75	5.083	264.5	6583.9	1419.86	9.76	34.95	0.19
1	5.083	199.8	6069.69	1447.78	8.76	40.61	0.19
1.5	5.083	226.3	7211.62	1439.88	11.05	45.02	0.19
2	5.083	259.9	8882.93	1462	14.22	49.64	0.19
4	5.083	238.5	9774.1	1445.07	15.86	61.43	0.19
6	5.083	270.1	11989.5	1423.89	19.82	69.83	0.19
8	5.083	213.6	10483.5	1432.04	16.88	75.21	0.19
10	5.083	223.4	11631.7	1448.8	18.67	79.97	0.18
24	5.083	221.8	12978.7	1445.43	19.65	91.44	0.17
FP	5.083	225.2	13136.9	1445.48	19.87	91.29	0.17

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.2476	0	8.85	8.85	8.74	39.61	19.90	0.00
2	0.25	0.5175	0	13.9	13.9	13.79	29.90	15.02	24.51
3	0.5	0.6085	0	12.8	12.75	12.64	23.31	11.71	41.15
4	0.75	0.4202	0	7.1	7.1	6.99	18.66	9.38	52.87
5	1	0.9226	0	12.2	12.2	12.09	14.70	7.39	62.88
6	1.5	0.6006	2.25	8.92	6.67	6.56	12.25	6.16	69.06
7	2	0.4246	0	3.93	3.93	3.82	10.09	5.07	74.51
8	4	0.7863	3.95	8.52	4.57	4.46	6.36	3.20	83.93
9	6	0.335	0	1.72	1.72	1.61	5.39	2.71	86.38
10	8	0.4993	4.6	6.23	1.63	1.52	3.42	1.72	91.38
11	10	0.6617	6.3	9.35	3.05	2.94	4.99	2.51	87.41
12	24	0.6735	0	1.6	1.6	1.49	2.48	1.25	93.73
13	FP	2.2627	1.61	6.7	5.09	4.98	2.47	1.24	93.76

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL**,** **M =** Molarity of the KOH solution = 0.02 M

F.2.3: Effect of Calcination Temperature of the Catalyst

(200 °C, 300 °C, and 400 °C)

Run # 6: Simultaneous esterification and transesterification of crude *Jatropha* oil with 9.1%FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 400°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.954	213.4	3901.98	1437.24	0	19.91	0.00
0.25	4.954	177.2	4594.83	1449.61	0	30.33	0.00
0.5	4.954	169	7528.19	1436.48	9.987	62.16	0.16
0.75	4.954	250.3	5235.79	1463.96	5.723	25.50	0.15
1	4.954	239.6	7891.98	1439.9	10.828	46.33	0.17
1.5	4.954	218.1	8039.79	1453.96	11.524	51.45	0.17
2	4.954	186.8	7653.71	1474.44	10.892	55.58	0.18
4	4.954	254.3	11336	1437.04	17.92	67.10	0.18
6	4.954	227.3	11402	1437.51	17.983	75.54	0.18
8	4.954	247.6	13053.8	1439.64	20.935	80.71	0.18
10	4.954	228.1	12976.3	1469.21	20.488	85.06	0.18
FP	4.954	198.9	11710.2	1471.67	18.031	86.65	0.18

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.4796	0	17.3	17.3	17.16	40.14	20.17	0.00
2	0.25	0.524	0	11.7	11.7	11.56	24.75	12.44	38.34
3	0.5	0.6637	11.7	24.05	12.35	12.21	20.64	10.37	48.58
4	0.75	0.671	0	9.08	9.08	8.94	14.95	7.51	62.76
5	1	0.6876	9.2	17.22	8.02	7.88	12.86	6.46	67.97
6	1.5	0.7738	17.3	24.22	6.92	6.78	9.83	4.94	75.51
7	2	0.442	0	3.2	3.2	3.06	7.77	3.90	80.65
8	4	0.6778	3.2	6.5	3.3	3.16	5.23	2.63	86.97
9	6	0.6794	6.6	9.23	2.63	2.49	4.11	2.07	89.76
10	8	0.6366	9.3	11.5	2.2	2.06	3.63	1.82	90.96
11	10	0.1624	11.7	12.2	0.5	0.36	2.49	1.25	93.80
12	FP	2.0624	12.5	18.7	6.2	6.06	3.30	1.66	91.79

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.14 mL**,** **M =** Molarity of the KOH solution = 0.02 M

Run # 7: Simultaneous esterification and transesterification of crude *Jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 200°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.955	152.2	3183.55	1456.09	0	19.31	0.00
0.25	4.955	222.5	5023.87	1457.66	0	27.24	0.00
0.5	4.955	219.8	5368.54	1434.03	5.178	30.92	0.13
0.75	4.955	244.1	6310.63	1439.89	7.106	34.33	0.15
1	4.955	236.3	6816.39	1496.8	8.152	37.26	0.15
1.5	4.955	163.6	5602.38	1454.63	6.548	43.18	0.16
2	4.955	236.8	7644.12	1432.4	10.36	45.37	0.17
4	4.955	191.7	7946.13	1451.94	11.037	57.80	0.17
6	4.955	204.5	8938.82	1435.41	13.12	63.33	0.17
8	4.955	237.1	10506.3	1420.97	16.066	66.81	0.18
10	4.955	189.1	9174.04	1448.14	13.374	69.89	0.17
FP	4.955	235.6	11371.6	1471.37	17.352	70.75	0.18

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.6173	0	23.8	23.8	23.66	43.00	21.61	0.00
2	0.25	0.6365	0	19.95	19.95	19.81	34.92	17.55	18.80
3	0.5	0.6125	0	15.8	15.8	15.66	28.69	14.42	33.29
4	0.75	0.6953	0	15.15	15.15	15.01	24.22	12.17	43.68
5	1	0.6633	0	11.8	11.8	11.66	19.72	9.91	54.14
6	1.5	0.5673	11.82	20.2	8.38	8.24	16.30	8.19	62.10
7	2	0.5361	0	7.4	7.4	7.26	15.19	7.64	64.67
8	4	0.5292	7.4	11.65	4.25	4.11	8.71	4.38	79.74
9	6	0.6624	11.7	15.9	4.2	4.06	6.88	3.46	84.01
10	8	0.7924	15.9	20.12	4.22	4.08	5.78	2.90	86.57
11	10	0.8508	0	3.95	3.95	3.81	5.02	2.52	88.32
12	FP	2.2242	4	14.45	10.45	10.31	5.20	2.61	87.91

Vi = Initial Volume; **Vf** = Final Volume; **V**=Vf-Vi; **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.14 mL, **M** = Molarity of the KOH solution = 0.02 M

Run # 13: Simultaneous esterification and transesterification of crude *jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed to alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.083	265.4	3234.69	1434.61	0	12.02	0
0.25	5.083	214.8	4076.92	1425.38	0	22.01	0
0.5	5.083	214.1	4976.39	1431.69	6.61	29.39	0.19
0.75	5.083	264.5	6583.9	1419.86	9.76	34.95	0.19
1	5.083	199.8	6069.69	1447.78	8.76	40.61	0.19
1.5	5.083	226.3	7211.62	1439.88	11.05	45.02	0.19
2	5.083	259.9	8882.93	1462	14.22	49.64	0.19
4	5.083	238.5	9774.1	1445.07	15.86	61.43	0.19
6	5.083	270.1	11989.5	1423.89	19.82	69.83	0.19
8	5.083	213.6	10483.5	1432.04	16.88	75.21	0.19
10	5.083	223.4	11631.7	1448.8	18.67	79.97	0.18
24	5.083	221.8	12978.7	1445.43	19.65	91.44	0.17
FP	5.083	225.2	13136.9	1445.48	19.87	91.29	0.17

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.2476	0	8.85	8.85	8.74	39.61	19.90	0.00
2	0.25	0.5175	0	13.9	13.9	13.79	29.90	15.02	24.51
3	0.5	0.6085	0	12.8	12.75	12.64	23.31	11.71	41.15
4	0.75	0.4202	0	7.1	7.1	6.99	18.66	9.38	52.87
5	1	0.9226	0	12.2	12.2	12.09	14.70	7.39	62.88
6	1.5	0.6006	2.25	8.92	6.67	6.56	12.25	6.16	69.06
7	2	0.4246	0	3.93	3.93	3.82	10.09	5.07	74.51
8	4	0.7863	3.95	8.52	4.57	4.46	6.36	3.20	83.93
9	6	0.335	0	1.72	1.72	1.61	5.39	2.71	86.38
10	8	0.4993	4.6	6.23	1.63	1.52	3.42	1.72	91.38
11	10	0.6617	6.3	9.35	3.05	2.94	4.99	2.51	87.41
12	24	0.6735	0	1.6	1.6	1.49	2.48	1.25	93.73
13	FP	2.2627	1.61	6.7	5.09	4.98	2.47	1.24	93.76

Vi = Initial Volume; **Vf =** Final Volume**;** **V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL**,** **M =** Molarity of the KOH solution = 0.02 M

F.2.4: Effect of Tetrahydrofuran as Co-solvent

(with or without cosolvent)

Run # 9: Simultaneous esterification and transesterification of crude *jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200^{o}C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.%, tetrahydrofuran as co-solvent (volume ratio alcohol to THF, 1:1) and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	4.955	188.2	3206.39	1462.5	0	15.70	0.00
0.25	4.955	148.2	3420.78	1457.1	0	22.53	0.00
0.5	4.955	199.9	4642.86	1448.84	0	27.32	0.00
0.75	4.955	205.3	5294.85	1463.62	5.48	31.59	0.14
1	4.955	203.4	5844.41	1460.01	6.35	36.58	0.14
1.5	4.955	217.4	6365.53	1437.59	7.9	39.06	0.16
2	4.955	199.1	6496.21	1454.33	8.368	43.14	0.17
4	4.955	242	8994.26	1458.6	13.242	52.89	0.18
6	4.955	176.3	7750.8	1475.07	10.937	59.78	0.17
8	4.955	209.9	9509.73	1466.36	14.192	64.74	0.18
10	4.955	269.2	12019	1434.98	18.628	67.88	0.20
24	4.955	194.6	10692.7	1458.68	15.532	80.59	0.17
FP	4.955	254.8	13925.8	1480.19	20.61	81.75	0.17

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight (gram)	Vi (mL)	Vf (mL)	V (mL)	Vnet (mL)	Acid Number mg KOH/g	FFA (%)	FFA Conversion (%)
-	-								
1	0	0.3366	0	13.1	13.1	12.96	43.20	21.71	0.00
2	0.25	0.2856	0	9.15	9.15	9.01	35.40	17.79	18.06
3	0.5	0.2502	0	6.8	6.8	6.66	29.87	15.01	30.87
4	0.75	0.4464	0	10	10	9.86	24.78	12.45	42.63
5	1	0.4309	0	8.68	8.68	8.54	22.24	11.17	48.53
6	1.5	0.3546	0	5.65	5.65	5.51	17.43	8.76	59.64
7	2	0.3383	0	4.6	4.6	4.46	14.79	7.43	65.76
8	4	0.2118	0.35	2.06	1.71	1.57	8.32	4.18	80.75
9	6	0.2268	2.1	3.63	1.53	1.39	6.88	3.46	84.08
10	8	0.371	3.65	5.48	1.83	1.69	5.11	2.57	88.17
11	10	0.2345	5.5	6.67	1.17	1.03	4.93	2.48	88.59
12	24	1.5251	0	4.55	4.55	4.41	3.24	1.63	92.49
13	FP	2.0471	0	6.13	6.13	5.99	3.28	1.65	92.40

Vi = Initial Volume; **Vf =** Final Volume**; V**=Vf-Vi**;** **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.14 mL**, M =** Molarity of the KOH solution = 0.02 M

Run # 13: Simultaneous esterification and transesterification of crude *jatropha* oil with 9.1% FFA as a non-edible feedstock using tungstophosphoric acid (TPA) with 30% loading supported on neutral alumina as solid acid catalyst. Reaction conditions: reaction temperature 200°C, molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, amount of catalyst 3 wt.% and calcination temperature of catalyst 300°C.

Methyl Ester Analysis (GC):

Time (hr)	Std. Conc. (mg/mL)	Sample Weight (mg)	Total Area	C17 Area	18:3 Area	MEC (%)	C18:3 EC (%)
0	5.083	265.4	3234.69	1434.61	0	12.02	0
0.25	5.083	214.8	4076.92	1425.38	0	22.01	0
0.5	5.083	214.1	4976.39	1431.69	6.61	29.39	0.19
0.75	5.083	264.5	6583.9	1419.86	9.76	34.95	0.19
1	5.083	199.8	6069.69	1447.78	8.76	40.61	0.19
1.5	5.083	226.3	7211.62	1439.88	11.05	45.02	0.19
2	5.083	259.9	8882.93	1462	14.22	49.64	0.19
4	5.083	238.5	9774.1	1445.07	15.86	61.43	0.19
6	5.083	270.1	11989.5	1423.89	19.82	69.83	0.19
8	5.083	213.6	10483.5	1432.04	16.88	75.21	0.19
10	5.083	223.4	11631.7	1448.8	18.67	79.97	0.18
24	5.083	221.8	12978.7	1445.43	19.65	91.44	0.17
FP	5.083	225.2	13136.9	1445.48	19.87	91.29	0.17

MEC (%) = Total Ester Content (mass %); **EC (%)**= Ester Content (mass %); **FP**= Final Product

Acid Number Analysis (Titrimetric):

S.No.	Time (hr)	Sample Weight	Vi	Vf	V	Vnet	Acid Number	FFA	FFA Conversion
-	-	(gram)	(mL)	(mL)	(mL)	(mL)	mg KOH/g	(%)	(%)
1	0	0.2476	0	8.85	8.85	8.74	39.61	19.90	0.00
2	0.25	0.5175	0	13.9	13.9	13.79	29.90	15.02	24.51
3	0.5	0.6085	0	12.8	12.75	12.64	23.31	11.71	41.15
4	0.75	0.4202	0	7.1	7.1	6.99	18.66	9.38	52.87
5	1	0.9226	0	12.2	12.2	12.09	14.70	7.39	62.88
6	1.5	0.6006	2.25	8.92	6.67	6.56	12.25	6.16	69.06
7	2	0.4246	0	3.93	3.93	3.82	10.09	5.07	74.51
8	4	0.7863	3.95	8.52	4.57	4.46	6.36	3.20	83.93
9	6	0.335	0	1.72	1.72	1.61	5.39	2.71	86.38
10	8	0.4993	4.6	6.23	1.63	1.52	3.42	1.72	91.38
11	10	0.6617	6.3	9.35	3.05	2.94	4.99	2.51	87.41
12	24	0.6735	0	1.6	1.6	1.49	2.48	1.25	93.73
13	FP	2.2627	1.61	6.7	5.09	4.98	2.47	1.24	93.76

Vi = Initial Volume; **Vf** = Final Volume; **V**=Vf-Vi; **Vnet** = V - Vb
Vb = Volume used for blank (solvent) = 0.11 mL, **M** = Molarity of the KOH solution = 0.02 M

Appendix G: Catalyst Preparation and Characterization

Catalyst Preparation:

The catalyst ($H_3PW_{12}O_{40}\cdot nH_2O$ supported on neutral alumina) was synthesized by wetness impregnation method. A series of catalysts containing 10–40% 12-tungstophosphoric acid (TPA) supported on neutral alumina were synthesized by an impregnation method. Required amounts of TPA dissolved in 100 mL of deionized water. The resultant solution was added slowly drop wise to the support (n-Al_2O_3). The mixture is stirred for 35 h using a magnetic stirrer. After this, the water was evaporated and the resultant catalyst powder was dried at 100^0C for 10 h. The final catalyst was calcined at 300^0C for 5 h in the air.

Catalyst Characterization

Powder X-Ray diffraction (XRD) patterns of the catalysts were recorded on a Siemens D-5000 diffractometer using nickel-filtered Cu Kα radiation, with a scan speed of 2° min^{-1} and a scan range of 2 - 80°. Brunauer-Emmett-Teller (BET) surface area of the catalysts were determined using Gemini 2375 adsorption equipment at liquid nitrogen temperature. Scanning electron microscopy (SEM) of the catalysts was obtained in a LEO 1530 electron microscope at an accelerated voltage of 10 kV. Sampes were mounted on aluminum stubs using double-adhesive tape and were gold coated in a Denton sputter coater DESK II.

Results and Discussion

TPA (10-40 wt %)/n-Al_2O_3 catalysts were characterized by BET, XRD, and SEM. The BET results of 10-40 wt % TPA/n-Al_2O_3 catalysts along with support n-Al_2O_3 are shown in Table 1 and Figure 1 shows the values of BET specific area (S_{BET}), external surface area (S_{ext}), miroporous volume (V_{micro}), average pore diameter (D_{ave}), and pore volume (V_{pore}). The specific surface area, average pore diameter was determined using the BET method, while microporous volume and external surface area were determined by the t-method. It was observed that the specific surface area and the pore volume decrease continuously with the increase of heteropolyacid loading on alumina; this can be due to the pore blockage of the surface with TPA.

Table 1. Textural Properties of the Catalyst Physicochemical characterization of the catalyst (tungstophosphoricacid supported on neutral alumina).

	TPA load (%)	Surface Area [a] (m^2/g)	External surface area[b] (m^2/g)	Microporous volume[b] (cm^3/g)	Average Pore Diameter [c] (°A)	Pore Volume [d] (cm^3/g)
PSAW00ABC	0	131.5337	135.2936	-0.003229	19.7539	0.064958
PSAW00ABUC	0	116.0121	123.2140	-0.004996	19.7217	0.057199
PSAW10ABUC	10	114.5003	122.5656	-0.005459	19.7027	0.056399
PSAW10ABC	10	128.9839	129.7549	-0.001486	19.8130	0.063889
PSAW20ABUC	20	97.9177	97.9182	-0.000854	19.7986	0.048466
PSAW20ABC	20	115.0572	111.8867	0.000791	19.8223	0.057017
PSAW25ABUC	25	90.7037	85.2418	0.002186	19.8852	0.045091
PSAW25ABC	25	105.8078	94.6221	0.005236	19.9083	0.052661
PSAW30ABUC	30	77.5836	72.6385	0.002043	19.8565	0.038513
PSAW30ABC	30	107.4232	98.6782	0.003917	19.8588	0.053332
PSAW40ABUC	40	33.8807	30.8946	0.001337	19.9096	0.016864
PSAW40ABC	40	89.9795	64.7631	0.012888	20.0691	0.045145

[a] BET; [b] t-Method; [c] Average BET pore diameter
[d] Single point total pore volume. C= Calcined; UC= Uncalcined

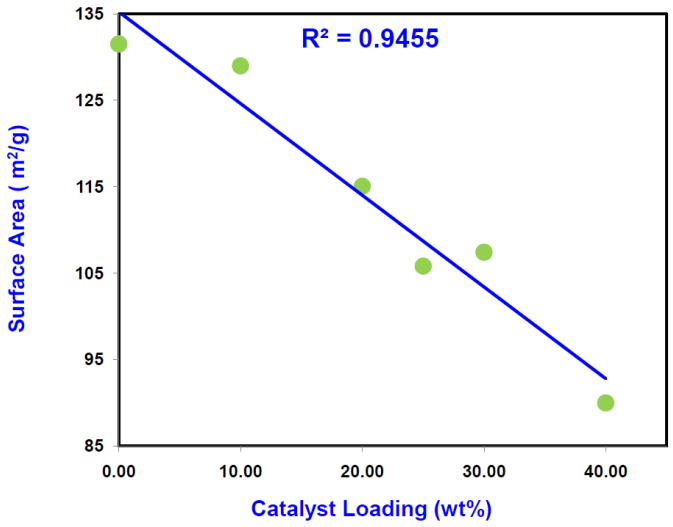

Figure 1. Effect of catalyst loading on surface area.

The XRD patterns of pure TPA and supported TPA catalysts are as shown in Figure 2. The XRD spectrum of pure TPA exhibited characteristic crystalline peaks of TPA (intense peak at 2θ = 10°). In the case of supported TPA only the XRD patterns of alumina supported TPA displayed no indication of any crystalline phases related to TPA indicating that the particles are too small or well dispersed to be detected by XRD technique. These results are indicative of a stronger interaction between TPA and alumina. The XRD data reveal that the well dispersion of TPA keggin ions upto 40 wt %.

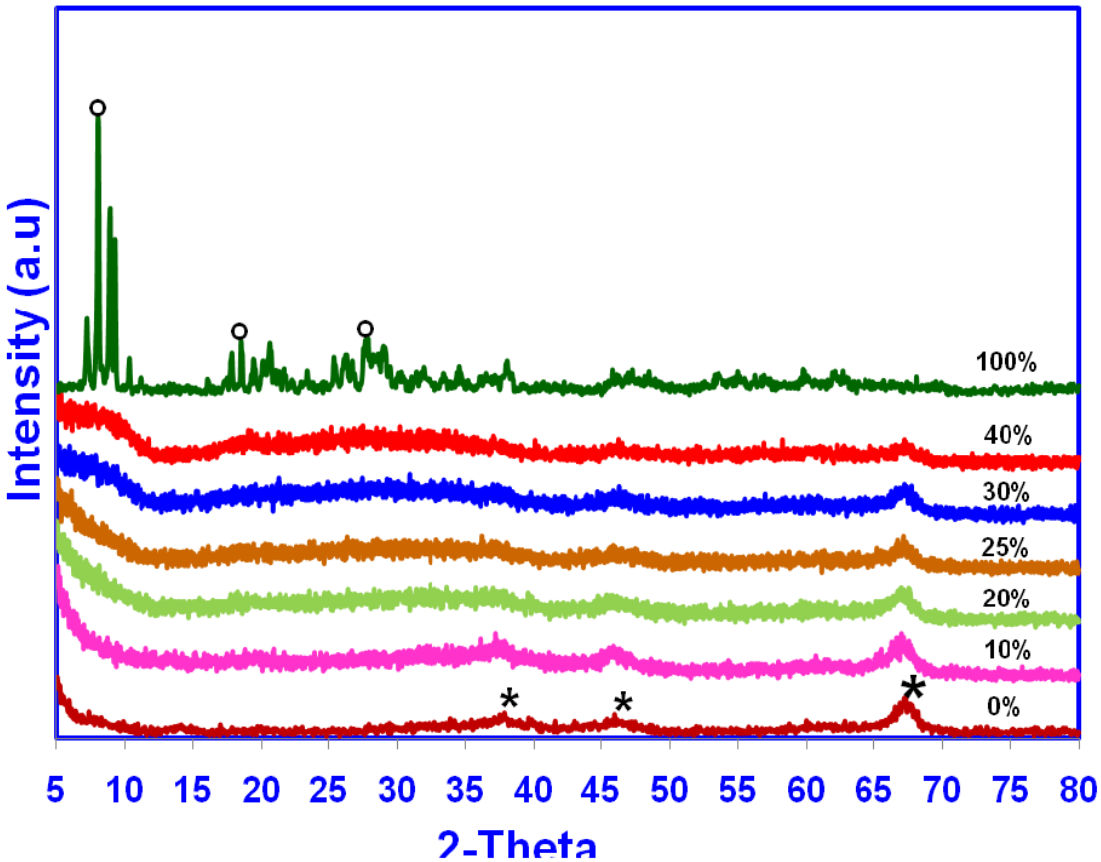

Figure 2. XRD patterns of a) Al_2O_3, (b) 10 wt % TPA/n-Al_2O_3, (c) 20 wt % TPA/n-Al_2O_3, (d) 25 wt % TPA/n-Al_2O_3, (e) 30 wt % TPA/n-Al_2O_3, (f) 40 wt % TPA/n-Al_2O_3. (g) 100 wt % TPA.

SEM pictures of 0-40 wt % TPA/n-Al_2O_3 catalysts calcined at 300°C for 5 h are shown in Figure 3. It clearly indicates an increase in the size of the catalysts with respect to the high

amount of TPA. SEM images are a visible reconfirmation of the aforementioned phenomenon of agglomeration of particles. Thus, SEM observations further support the attainment of the bulk nature of catalysts at higher TPA loading.

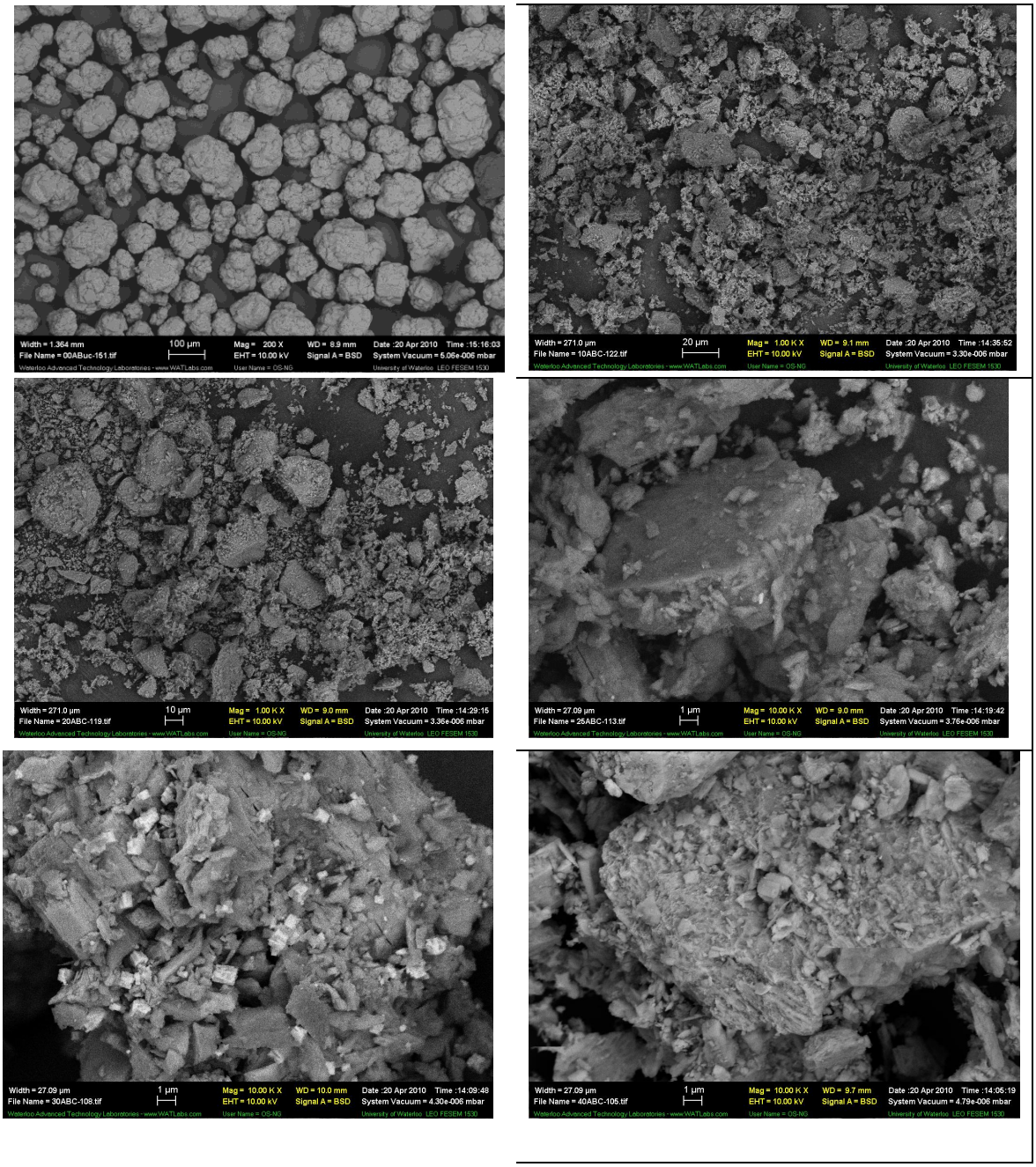

Figure 3. Scanning electron micrographs of (a) Al_2O_3, (b) 10 wt % TPA/n-Al_2O_3, (c) 20 wt % TPA/n-Al_2O_3, (d) 25 wt % TPA/n-Al_2O_3, (e) 30 wt % TPA/n-Al_2O_3, and (f) 40 wt % TPA/n-Al_2O_3.

Figure 4 shows the SEM images of physically mixed TPA with the support, n-Al_2O_3 and the impregnated 30 wt % TPA/n-Al_2O_3

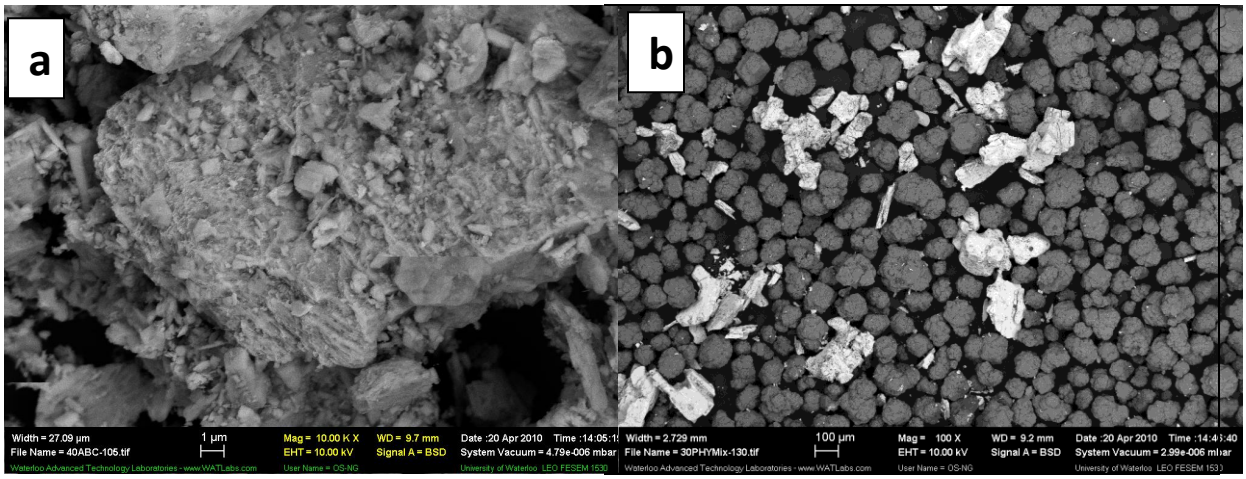

Figure 4. Scanning electron micrographs of (a) impregnated 30 wt % TPA/n-Al_2O_3, and (b) 30 wt % Physically mixed TAP and n-Al_2O_3.

Appendix H: BET Analysis Report Summary For Recycled Catalyst After Run#4 (Table 5.6)

StarDriver V2.03 Gemini 2375 V5.01 Serial # 3243 Page 8

File Name: C:/DOCUME~1/ADMIN/MYDOCU~1/BEN/E50RUN4.MGD
Sample ID: E50RUN4
Setup Group:

Started: 9/3/3810 10:14:02AM
Completed: 9/3/3810 11:13:37AM
Report Time: 9/3/2010 2:23:40PM
Evac. Rate: 300.0 mmHg/min
Analysis Mode: Equilibration
Sat. Pressure: 740.08 mmHg
Meas. Freespace: -0.2248 cm³
Sample Weight: 0.1314 g
Evac. Time: 6.000000 minutes
Equil. Interval: 5 secs

Summary Report

Area

Single Point Surface Area at P/Po 0.29996756 :	71.7126	m²/g
BET Surface Area:	74.4562	m²/g
Langmuir Surface Area:	119.3219	m²/g
Micropore Area:	-6.1417	m²/g
External Surface Area:	80.5980	m²/g
BJH Adsorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 A Diameter:	72.7002	m²/g

Volume

Single Point Adsorption Total Pore Volume of pores less than 27.2040 A Diameter at P/Po 0.29996756:	0.036400	cm³/g
Micropore Volume:	-0.004078	cm³/g
BJH Adsorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 A Diameter:	0.038860	cm³/g

Pore Size

Adsorption Average Pore Diameter (4V/A by BET):	19.5552	A
BJH Adsorption Average Pore Diameter (4V/A):	21.3808	A

Figure 5.14 Effect of temperature on the conversion of FFA as a function of time during simultaneous esterification and transesterification using yellow grease with 9.1% FFA as feedstock. Reaction conditions: reaction temperature (175, 200 and 225°C), molar ratio of feed-to-alcohol 1:27, stirring speed 600 rpm, catalyst 3 wt.% (tungstophosphoric acid with 30% loading supported on neutral alumina).