Fall 2010

Biodiesel production using supercritical methanol

Dhaval Nitin Modi

Recommended Citation

Modi, Dhaval Nitin, "Biodiesel production using supercritical methanol" (2010). *Masters Theses*. 5004.
https://scholarsmine.mst.edu/masters_theses/5004

BIODIESEL PRODUCTION USING SUPERCRITICAL METHANOL

by

DHAVAL MODI

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

2010

Approved

Douglas Ludlow, Academic Advisor
Paul Nam, Research Advisor
Neil Book

PUBLICATION THESIS OPTION

This thesis has been prepared in the style utilized by the journal FUEL Pages 27-40 and 41 – 61 will be submitted for publication in that journal. An appendix has been added as is normal in thesis/dissertation writing.

ABSTRACT

The catalyst-free transesterification of oil (triglycerides) in supercritical methanol at a temperature and pressure above 239^{o}C and 8.1MPa, respectively, provides a new way of producing biodiesel. High reaction temperature and pressure help to accelerate the transesterification because the supercritical methanol becomes non-polar and has enhanced contact with oil.

The supercritical transesterification of soybean oil was carried out in a 170 ml volume high-pressure batch reactor. The pressure within the batch reactor was self-generated from heating the contents since no pumps were used. Transesterification of soybean oil with supercritical methanol readily produced biodiesel. Since the supercritical transesterification is carried out without a traditional acid/base catalyst and does not produce any saponified byproducts, the recovery of pure biodiesel product becomes much simpler. After the reaction, the products readily separated into two phases of biodiesel (fatty acid methyl esters) and glycerol. Process variables such as pressure, volume, and temperature were studied. Also, the effect of supercritical CO_2 as a potential co-solvent was investigated.

Several 7 ml volume mini-reactors were fabricated and used to evaluate the supercritical transesterification reaction and develop an analytical method for lipid composition determination. Reaction temperature, reaction time, and the methanol-to-oil molar ratio were studied. The effect of water, free fatty acids, hexane, co-solvents, and reaction with different alcohols (n-propanol, isopropanol, allyl alcohol) were also studied. A sequential analytical process was developed by extracting lipids directly from oil seeds using hexanes and converting them to fatty acid esters, using supercritical alcohol.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Douglas Ludlow for his guidance and support during my masters' study at Missouri S&T. I would like to express my heartfelt gratitude to my research advisor, Dr. Paul Nam. He has been a great source of inspiration and encouragement throughout my research and study at Missouri S&T. I sincerely thank Dr. Neil Book for serving as my committee member and for his guidance. Dr. Honglan Shi at the Environmental Research Laboratory is acknowledged for her help with GC analysis. I would also like to acknowledge Dr. Kee-soo Lee at Lincoln University, Jefferson City, Missouri. The help and support from the Chemical Engineering department faculty and staff is greatly appreciated.

I thank my family for always being there and loving me unconditionally. They have been a source of encouragement and strength. I thank my friends who have motivated and supported me through the years.

I acknowledge the Missouri Life Sciences Research Board and USDA – CSREES Evans Allen Grant for funding the project.

TABLE OF CONTENTS

SECTION

PAPER

LIST OF ILLUSTRATIONS

Figure

Paper I

Paper II

LIST OF TABLES

1. INTRODUCTION

1.1 GLOBAL ENERGY SCENARIO

Energy has played a vital role towards human development. In the 21st century, nations consume even more power for industrial expansion, transportation, and domestic purposes than ever before. Given the growing demand for energy, our dependency on its limited sources has become one of the most crucial problems for humanity in the coming century.

Worldwide energy consumption has increased 18-fold in the last century. In the early 1900s, global energy consumption was 22 exajoules (or 20 quadrillion Btu). The global energy consumption has increased from 355 exajoules in 2000 to was 495 quadrillion Btu, or 12,029 million tons of oil equivalent (Mtoe) in 2007 [1]. It is expected to increase to 739 quadrillion Btu by 2035 as seen from Fig.1.1. More than 80% of the world's energy requirements are met largely by fossil fuels; coal, crude oil, and natural gas (Fig. 1.2). However, such fuel sources are limited, and the demand for energy is increasing so rapidly that future demands cannot be sustained by relying on these conventional sources. The *Oil & Gas Journal* estimated that the worldwide reserves (proven and recoverable) of oil and gas, at today's rate of consumption, would last for only 40 years and 64 years, respectively [2].

The growing human population and increased industrialization are accelerating the demand for energy, and driving the exploration of alternative options for energy resources. Experts predict that there will be a decrease in dependence on liquids, as crude oil reserves are being rapidly depleted, and coal may well become the preferred fuel source. In the years to come, renewables will assume greater import as replacement for fossil fuels.

The environmental impact, depletion of fossil fuel resources, and the monopoly of oil importing nations are key reasons for interest in biomass energy. Since a fifth of the total carbon dioxide emissions are contributed by the transportation sector, an alternative "green" fuel is being sought [3]. A renewable fuel is essential for energy security since 94% of the global transport needs are currently being met by crude oil derivatives [3].

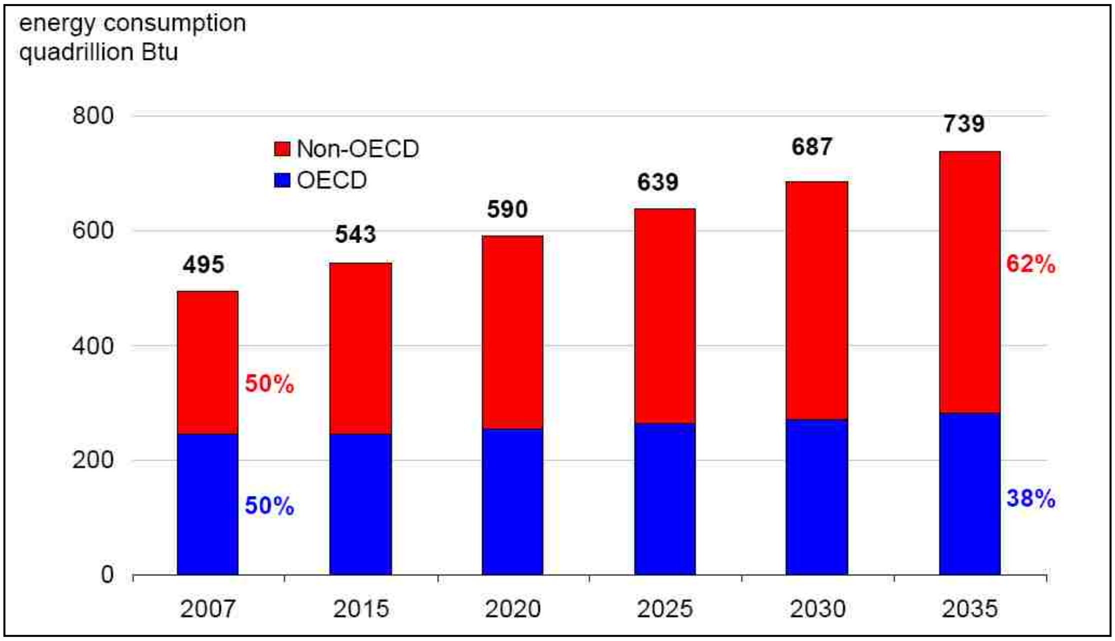


Fig. 1.1: World Energy Consumption in Quadrillion Btu from 2007 to 2035 [8]. OECD and Non-OECD are member states and non-member states of *Organisation for Economic Co-orporation and Development*.

Biofuels refer to liquid or gaseous fuels used by the transport sector that are predominantly produced from biomass. Since a large percentage of energy consumption is for transport needs, it is essential that more sustainable alternative fuel options be explored. Great promise has been shown by biodiesel as a biofuel. According to the American Society for Testing and Materials (ASTM), biodiesel is defined as monoalkyl esters of long chain fatty acids.

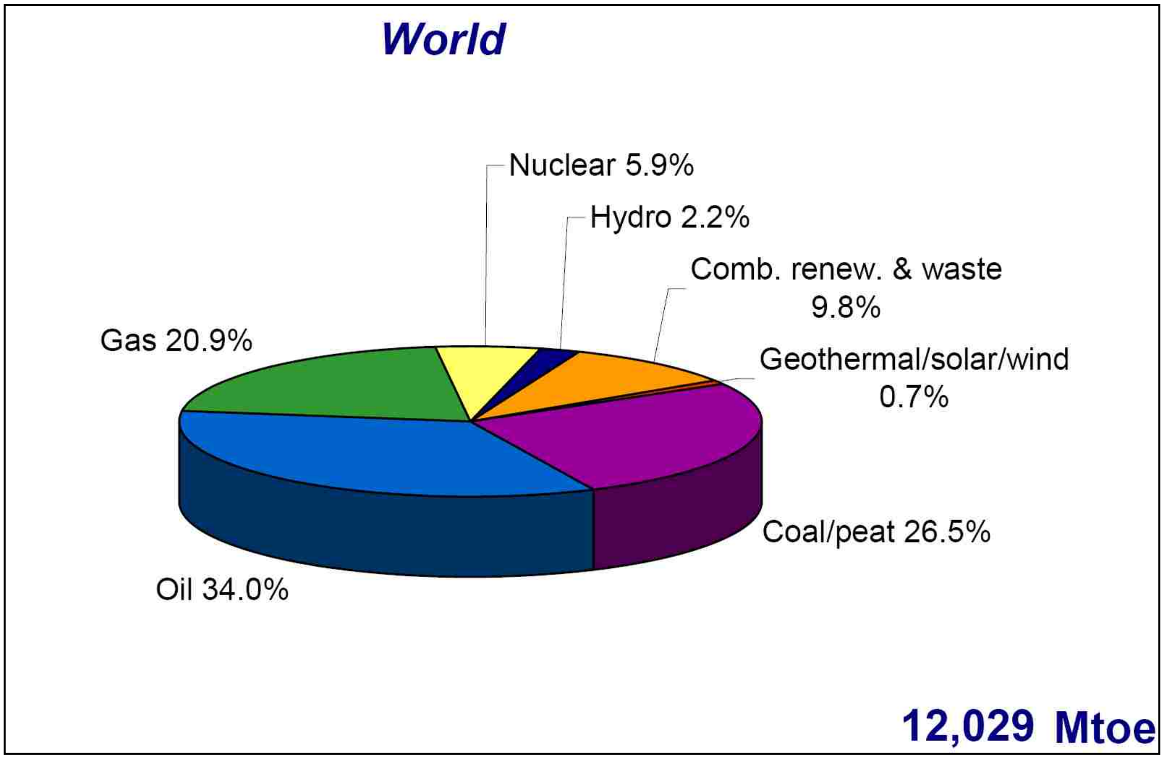


Fig. 1.2: Contribution of Different Energy Sources Towards the Supply of Global Energy [9].

Biodiesel is mixed with diesel in different ratios and can be used in conventional unmodified diesel engines. Currently, a 20% biodiesel/80% diesel combination, known as B20, is used. A 93% reduction in total unburnt hydrocarbons and an 80% reduction in polycyclic aromatic hydrocarbons are seen with combustion of neat (100%) biodiesel [EPA, 2002]. Sulphur content in diesel is 20-50 times that in biodiesel, plus biodiesel is easy to handle and store since it is non-toxic and is as biodegradable as sugar [4].

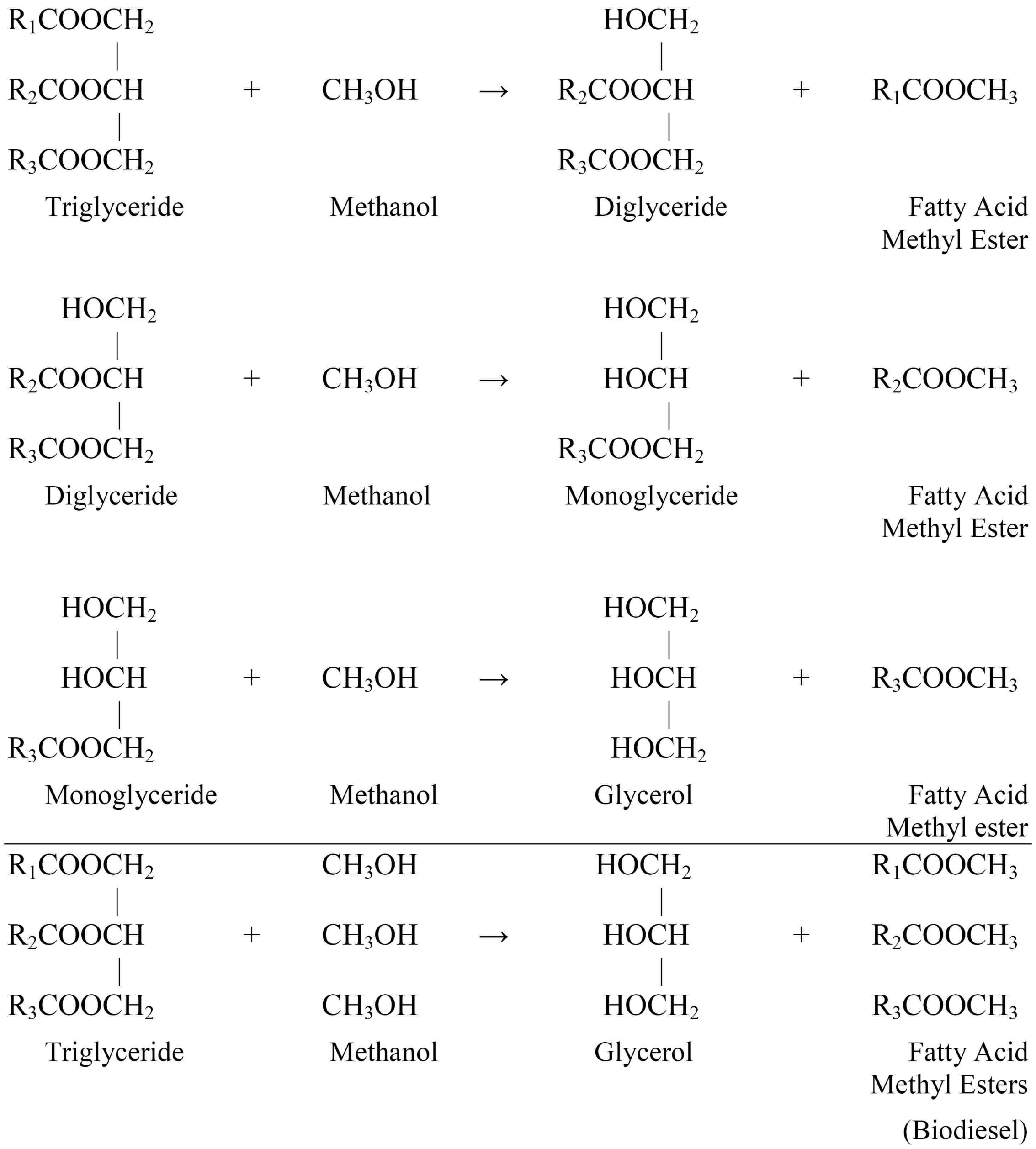
Biofuels are hailed as being environmentally benign carbon neutral fuels, i.e. the CO_2 absorbed during a plant's life cycle is the CO_2 formed when combustion occurs. Hence, there is no net CO_2 pollution.

Annually, 11.1 million tons of biodiesel are produced to meet global energy requirements [5]. Germany ranks first in its usage of biodiesel with 2.8 million tons of biodiesel produced in 2008 [6]. In that same year, 0.3 million gallons was consumed in the United States [7]. Industrially, biodiesel is prepared using a catalytic process. Myriads of catalysts have been investigated, including basic, acidic, and heterogeneous solid catalysts. Alternative processes, such as the enzymatic process, have been suggested as potential economical process.

1.2 TRANSESTERIFICATION PROCESSES FOR BIODIESEL PRODUCTION

1.2.1 Homogeneous Base Catalyst Process. Biodiesel is conventionally produced using alkaline catalysts. High reaction rate and low reaction times make homogeneous base catalysts preferred industrially. The base catalyst process has been shown to require a low alcohol/oil ratio and a low reaction temperature. Catalysts commonly used are NaOH, KOH, and $NaOCH_3$ [10-16].

A triglyceride (TG) molecule sequentially reacts with three short chain alcohol molecules, releasing an ester molecule each time, as it converts to diglyceride (DG), then monoglyceride (MG), and finally to glycerol (Gly). This three-step reaction is reduced to a shunt reaction, as shown in Fig. 1.3.



$$\begin{array}{ccccccc} R_1COOCH_2 & & & & HOCH_2 & & \\ | & & & & | & & \\ R_2COOCH & + & CH_3OH & \rightarrow & R_2COOCH & + & R_1COOCH_3 \\ | & & & & | & & \\ R_3COOCH_2 & & & & R_3COOCH_2 & & \\ \text{Triglyceride} & & \text{Methanol} & & \text{Diglyceride} & & \text{Fatty Acid Methyl Ester} \end{array}$$

$$\begin{array}{ccccccc} HOCH_2 & & & & HOCH_2 & & \\ | & & & & | & & \\ R_2COOCH & + & CH_3OH & \rightarrow & HOCH & + & R_2COOCH_3 \\ | & & & & | & & \\ R_3COOCH_2 & & & & R_3COOCH_2 & & \\ \text{Diglyceride} & & \text{Methanol} & & \text{Monoglyceride} & & \text{Fatty Acid Methyl Ester} \end{array}$$

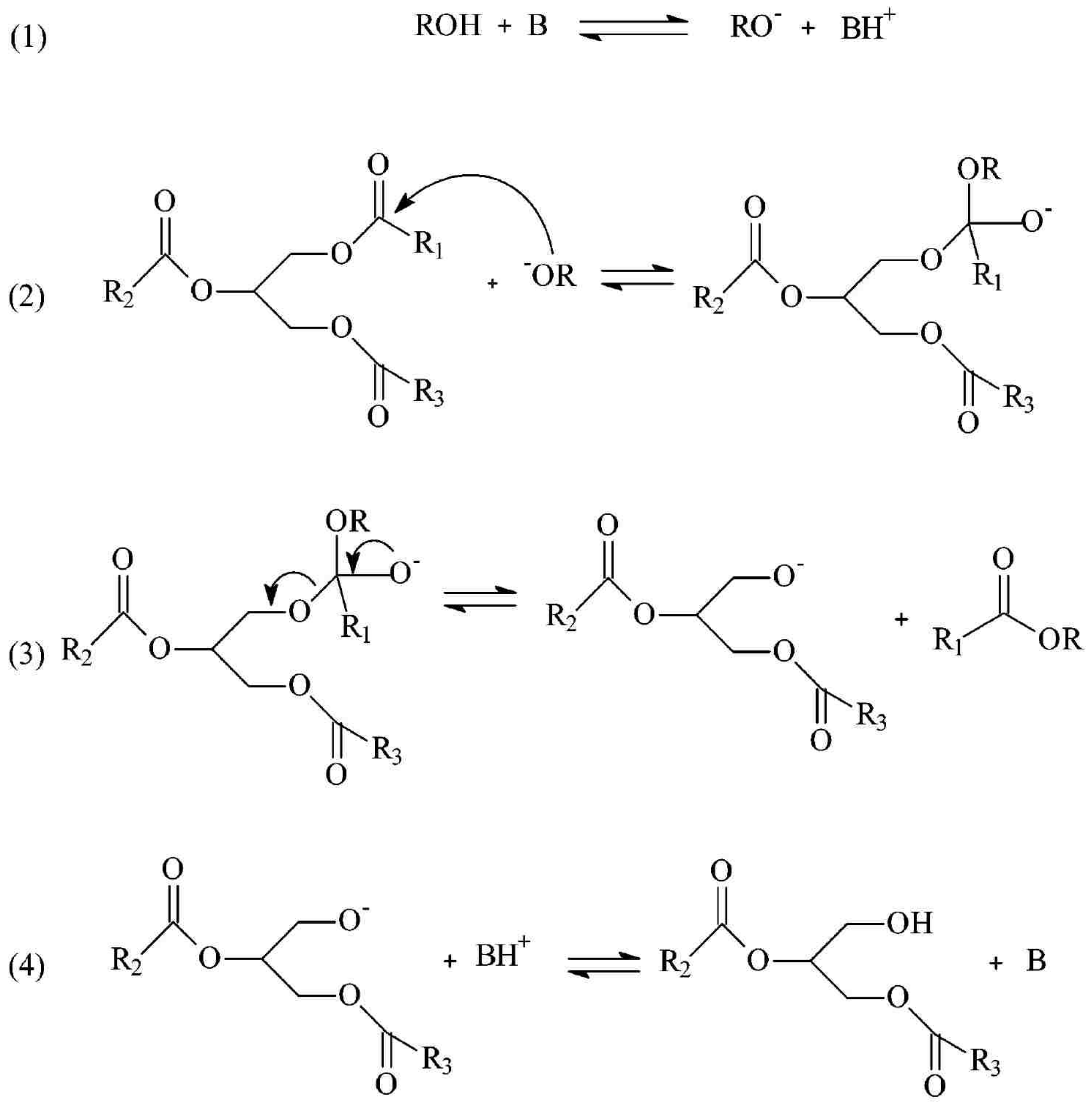
$$\begin{array}{ccccccc} HOCH_2 & & & & HOCH_2 & & \\ | & & & & | & & \\ HOCH & + & CH_3OH & \rightarrow & HOCH & + & R_3COOCH_3 \\ | & & & & | & & \\ R_3COOCH_2 & & & & HOCH_2 & & \\ \text{Monoglyceride} & & \text{Methanol} & & \text{Glycerol} & & \text{Fatty Acid Methyl ester} \end{array}$$

$$\begin{array}{ccccccc} R_1COOCH_2 & & CH_3OH & & HOCH_2 & & R_1COOCH_3 \\ | & & & & | & & \\ R_2COOCH & + & CH_3OH & \rightarrow & HOCH & + & R_2COOCH_3 \\ | & & & & | & & \\ R_3COOCH_2 & & CH_3OH & & HOCH_2 & & R_3COOCH_3 \\ \text{Triglyceride} & & \text{Methanol} & & \text{Glycerol} & & \text{Fatty Acid Methyl Esters (Biodiesel)} \end{array}$$

Fig. 1.3: Transesterification Reaction of Triglycerides with Alcohol (Methanol). R_1, R_2, R_3 are carbon chains of fatty acids

At room temperature, the triglycerides and alcohol are immiscible. Mixing between the reactants is considered essential [10, 13]. Noureddini and Zhu, in 1997 [10], and Darnoko and Cheryan, in 2000 [13], described the base catalyzed reaction system as a second order system. A sigmoidal curve is generated when concentration of ester formed is plotted against reaction time. The system is initially diffusion controlled since it is a two-phase system. The reaction rate depends on mixing the reactants and the catalyst. The system soon becomes uniphase, with a sharp increase in reaction yield. This phase is kinetically controlled and is dependent on the reaction temperature. An increase in the temperature allows better mixing between the two liquid phases. The activation energies for the reaction are, $E_{aMG} < E_{aDG} < E_{aTG}$; therefore, the first reaction for conversion of triglyceride to diglyceride is the rate-determining step.

An alkaline catalyst such as NaOH dissociates to form charged ionic species such as Na^+ and OH^-, which react with the alcohol to form an active alkoxide species. As a strong nucleophile this alkoxide, immediately attacks the carbonyl atom of the triglyceride, and the intermediate formed is unstable (step 2 in Fig. 1.4). The oxygen atom donates an electron pair to the carbonyl atom forming a double bond. The alkyl ester molecule dissociates from the tetrahedral intermediate. The sequence is repeated twice more with diglyceride and monoglyceride, eventually producing a glycerol molecule.



B: base catalyst
R_1,R_2,R_3: carbon chain of the fatty acids
R: alkyl group of the alcohol

Fig. 1.4: Homogeneous Base Catalyzed Reaction Mechanism [17].

The appropriate choice of base catalyst and the amount required are often debated. Umer Rashid and Farook Anwar, 2008 [16], studied anhydrous NaOH, KOH, $NaOCH_3$, and $KOCH_3$ and determined that $NaOCH_3$ was the best catalyst for alcoholysis of safflower oil. Methoxide catalysts are preferred since they are already dissolved in methanol, thereby providing faster mass transfer and reaction rate. Hydroxide ions are known to produce water and soap; therefore, they are not ideal [11,16]. The efficiency of a catalyst is attributed to its ability to dissociate; hence, sodium and potassium based catalysts were chosen. Sodium based catalysts have shown to produce better yield [11,16]; and contributed to a lower molecular mass of Na^+ than K^+, thereby producing more ions [11]. The amount of catalyst used is dependent on the fatty acid content of the oil, which generally varies from 0.5 to 1.5%. Excess catalyst loading increases the viscosity and produces an emulsion or gel [15]. The rate of stirring or mixing is also very important because it enhances the mass transfer and reaction rates [10].

Reaction time and temperature are known to affect reaction conversion. Reaction kinetics suggests high temperatures are favorable because the high reaction constants reduce the reaction time [10, 13]. The reaction temperature is chosen at 60-65^oC [10, 12, 13, 15, 16, 18]. Guan and cowokers, 2009 [18], showed that in a microtube reactor, for a residence time of 200 seconds, the sunflower oil ester yield increased from 70% to 100%, with an increase in temperature from 20^oC to 40^oC. The residence time for complete conversion decreased further from 200 sec to 75 sec when the temperature was elevated from 40^oC to 60^oC.

Most researchers maintain a molar ratio of alcohol to oil of 6 [12, 14, 16] to allow greater conversion and ester yield. Although the typical conditions for the base catalyst reaction are temperatures of 60-65^{o}C, alcohol/oil ratio 6, a catalyst 0.5%-1.5% (by weight of oil), and reaction time of 1 to 3 hrs; the base catalyst process has its shortcomings. The base catalyst is very sensitive to the presence of free fatty acids (FFA) and water.

Free fatty acids in feed react with an alkaline catalyst to produce alkaline salts of fatty acids, or soap, as seen in Fig. 1.5. This soap not only decreases the alkyl ester yield but also forms an emulsion between the esters, alcohol, and glycerol. The post-reaction separation of the catalyst and soap from the products is very tedious and uneconomical. Repeated washing of the product with water to separate the catalyst and soap resulted in large volumes of wastewater. Also, the water is separated using an energy intensive distillation process [19, 20]. Fatty acids naturally occur in oils in concentration ranging from 0.5% in virgin soybean oil to over 10% in waste frying oil [21]. However, according to Ma et al., [22], the free fatty acid content should not exceed 0.6% in feed oil. Often, weak lye is used to neutralize fatty acids before the alcoholysis reaction [21].

$$\underset{\text{Free Fatty Acids}}{\mathrm{R{-}COOH}} + \underset{\text{Base Catalyst}}{\mathrm{Na{-}OH}} \rightarrow \underset{\text{Soap}}{\mathrm{R{-}COO{-}Na}} + \mathrm{H_2O}$$

Fig. 1.5: Saponification of Free Fatty Acids in Presence of a Base Catalyst.

Furthermore, the base catalyst is sensitive to the presence of water in the feedstock. Water content should be maintained below 0.05% for a high ester yield [22].

As indicated in Fig. 1.6, water hydrolyzes the alkyl ester product to free fatty acids that, in turn, consume the catalyst [20]. Also, water is known to hydrolyze triglycerides to produce free fatty acids and glycerol [23], inactivating the base catalyst and inhibiting any further reaction.

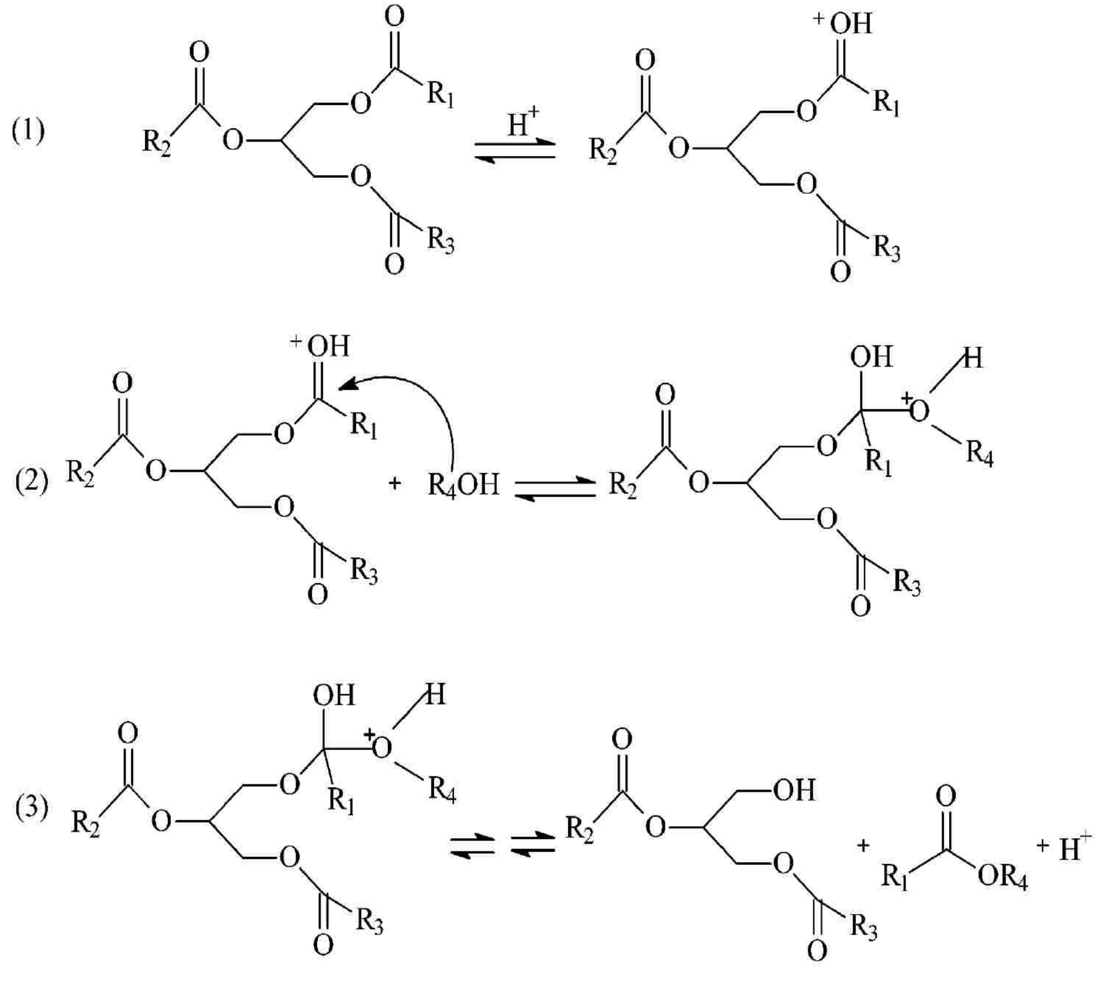
$$\underbrace{R—CO—OCH_3}_{\text{Fatty Acid Methyl Esters}} + H—OH \rightarrow \underbrace{R—COOH}_{\text{Free Fatty Acid}} + CH_3—OH$$

Fig. 1.6: Hydrolysis of Fatty Acid Methyl Esters (FAME) to Free Fatty Acids.

Under these circumstances, only virgin oil can be used for biodiesel production without expensive pretreatment of the feed. Therefore, 80% of the cost of the biodiesel can be attributed to the use of virgin oil [80,81].

1.2.2 Homogeneous Acid Catalyst Process. Many researchers have proposed acid catalyst process as an alternative because of the base catalyst’s sensitivity to free fatty acids. Unlike alkaline catalysts, acid catalysts can handle acid oils. The most commonly used catalysts include H_2SO_4, HCl, H_3PO_4, and BF_3. An acid catalyst is capable of alkyl esterification of free fatty acids, as well as simultaneous transesterification of triglycerides.

Acid dissociates to generate hydrogen protons that catalyze the transesterification reaction. The proton forms a covalent coordinate bond with the oxygen atom, and the adjoining carbonyl atom becomes a strong electrophile. The nucleophilic methanol molecule bonds with the carbonium ion, generating a tetrahedral intermediate, as shown in Fig. 1.7. With the migration of the hydrogen proton from the methanol molecule, the intermediate dissociates to form alkyl ester and diglyceride. The sequence is repeated twice until glycerol and three alkyl ester molecules are formed.



R_1,R_2,R_3: carbon chain of the fatty acids
R_4 : alkyl group of the alcohol

Fig. 1.7: Homogeneous Acid Catalyzed Transesterification Reaction Mechanism [17].

However, the acid catalyst process is 4,000 times slower than the base catalyst process [24, 17]. A typical acid catalyst reaction can take from 3 to 24 hr to complete [20]. In order to hasten the reaction, Freedmann et al., 1984 [25], and also Canakci and coworkers, 1999 [26], have recommended the use of a higher alcohol-to-oil molar ratio. For a high alkyl ester yield, they increased the ratio to 30:1. Therefore, for high ratios, forward reactions are believed to be pseudo first-order reactions, whereas the backward reactions are second-order reactions [27]. Zheng et al., 2006, suggested the use of a molar ratio of up to 100 for waste frying oil [28]. However, these high molar ratios of alcohol to oil not only increase the costs of alcohol recovery, but also increase product separation costs. For the acid catalyzed transesterification process, high temperatures are preferred to improve the reaction rates. Freedman et al., 1986, demonstrated that, at 117^{o}C, the reaction had neared completion in 3 hours, whereas at 77^{o}C it required 20 hr [27]. Although acid catalysts are resilient in the presence free fatty acids, they are very sensitive to the presence of water. The slow reaction rate, demand for a high temperature and molar ratio, and the corrosive nature of the acid catalyst make it industrially less favorable.

However, the ability of acid catalysts to handle oils high in free fatty acid is very useful, even though reaction rates and yields are low. Hence, a two-step process is used industrially. Feed oil with high fatty acid content is first pre-esterified using an acid catalyst. Esterification of fatty acids to methyl esters is stopped using a base. The presence of a base allows quick alkaline transesterification of triglycerides to esters at low temperatures and alcohol/oil ratios. Consequently, by combining acid and base catalysts, even acid oils can be used.

Chongkhong et al., 2009 [29], studied esterification of palm fatty acid distillate (PFAD) using the 2-step process. The temperature was maintained at 75°C for the acid catalyst process (using H_2SO_4) and 80°C for the base catalyst purification process (using 3M NaOH). The molar ratio of PFAD/Methanol/H_2SO_4 was maintained at 1/8.8/0.05. After acid catalysis converted 93% FFA content palm fatty acid distillate into 97% FAME content, it was neutralized using alkali. The final FAME content was 99.7% after base esterification.

However, this process still requires complicated and lengthy product separation. The salts formed from neutralization of the acid must also be separated from the glycerol. Finally, because this process cannot handle the presence of water in feed, pre-treatment for water is necessary.

1.2.3 Heterogeneous Solid Catalyst Process. Using a homogeneous catalyst requires expensive steps for product purification. Therefore, heterogeneous catalysts, (basic and acidic) are investigated. Georgogianni et al., 2009 [30], investigated the use of Mg/MCM-41, Mg-Al hydrotalcite, and potassium ions impregnated ZrO_2 as heterogeneous catalysts. The yield of FAME was directly proportional to the concentration of the cations. Mg-Al hydrotalcite showed a 97% yield with a very long 24 hr reaction time required compared to a 96% yield in 1 hr using NaOH (1.5% wt.) at 60°C. The time for a heterogeneous catalyst was reduced to 5 hr using ultrasonication for mixing, although, a homogeneous catalyst required only 10 min for an equivalent conversion of esters.

Vicente et al., in 1998 [31], compared the use of NaOH, anion and cation exchange resins, zirconium hydroxide (sulphate doped), titanium silicate, $SnCl_2$, MgO, USY-292 zeolite, and Novozyme® 435. They concluded that, at 60°C after 8 hr, there was complete conversion for NaOH, whereas MgO and $SnCl_2$ showed 11% and 3% conversion, respectively. A zirconium based catalyst and Novozyme 435 showed no ester formation. None of the other catalysts produced alkyl esters over 1%. Gryglewicz; 1999 [32], reported that, when CaO is used as a solid base catalyst, it dissolves slightly in methanol, requiring an extra separation step such as use of an ion exchange resin during product separation and purification. Often, active sites of CaO are poisoned by the reaction of CaO with water and atmospheric CO_2 [33].

Alkaline, and acidic zeolites, can be prepared and used as solid catalysts. Since a zeolite pore size is 1-2 nm, a large triglyceride molecule experiences mass transfer resistance resulting in a low reaction rate and a weak catalytic performance by zeolites.

In pursuit of inexpensive and renewable catalysts, researchers have also studied sulphonation of amorphous organic carbon. Organic carbon sources, like glucose and starch, have been pyrolyzed at low temperatures to form rigid carbon rings, which provide sites for sulphonation. [34]. Takagaki et al., 2006 [35], reported using d-glucose for incomplete carbonization to form a polycyclic aromatic carbon matrix. The carbon solids were ground and mixed with sulphuric acid and to allow HSO_3 groups to attach to the carbon atoms. Although the catalyst's characteristics are excellent, the reaction rate for ethyl oleate formation was half of that when using H_2SO_4 directly. The complicated separation process can be avoided and the catalyst can easily be regenerated and reused, but the reaction time would be double that of acid esterification.

Although heterogeneous catalysts do not require sophisticated downstream processes for purification and separation, they have very low reaction rates that result in long reaction times. On the other hand, they can easily be regenerated and reused, making them economically viable.

1.2.4 Enzymatic Process. The possibility of a biochemical route that used enzymes for biodiesel production has intrigued researchers. Biodiesel production, using intracellular or extracellular lipase, requires low energy inputs because ambient temperatures and atmospheric pressures are preferred. The enzymes are divided into three categories, according to regioselectivity or the positions of the scissile (breakable) ester bonds. An sn-1,3-specific lipase, like *Mucor Mehei*, hydrolyzes the R_1 and R_3 positioned ester links of triglyceride, theoretically providing a maximum yield of only 66%. Conversion has been observed to be 90% because of the migration of the acyl group to terminal positions. An sn-2-specific lipase, like *Geotrichum Candidum*, hydrolyzes only the R_2 esters of triglycerides. Non-specific enzymes do not distinguish between the positions of ester bonds to be cleaved. Intracellular and extracellular enzymes, known as lipase, are either immobilized on a substrate or dispersed free in the system. Microorganisms like *Candida Antartica*, *Pseudomonas Fluorescens, Pseudomonas Cepacia,* and *Candida Rugosa* are commonly used to extract these lipases.

These enzymes are known to handle feedstock high in both free fatty acids content and water. Immobilized enzymes can be used repeatedly, and there is no need for complicated, expensive separation and purification processes. Also, various lipases have exhibited different biological pathways to produce alkyl esters, thereby making them resilient to impurities and open to process modification [36].

In 1996, Nelson et al., [37], experimented with *Mucor Mehei*, *Candida Antartica*, *Pseudomonas Cepacia*, and others to study the transesterification of triglycerides. They reported an increase in conversion, from 19% to 94%, when hexane was added as a solvent during methanolysis using *Mucor Mehei*. Although *Mucor Mehei* performed better for transesterification with the primary alcohols, *C.Antarica* and *P.Cepacia* were better with the secondary alcohols. Also, a higher yield was obtained with secondary alcohol in the absence of any solvent. Kaieda et al., 2001 [38], studied the effects of methanol and water. When enzymes were introduced in a dry form (as powder), only *P.Cepacia* showed some esterification reaction. The low activity was attributed to the low surface area exposed by the powder. *Pseudomonas fluoroscens* and *Candida Rugosa* were activated when introduced as enzyme solutions. The presence of water protected the lipase from becoming denatured by methanol and also enhanced the reaction rate.

High concentration of methanol is known to denature enzymes [38]. Step-wise introduction of methanol has been reported to increase the yield without inhibiting the lipase [2, 37]. An inhibition effect due to glycerol formation has been observed. Solvents, like hexane, or alternative acyl acceptors, like methyl acetate [39], are suggested to overcome this problem. High yields of 91% have been reported by Modi et al., 2007 [40], using ethyl acetate as an acyl acceptor. Abigor et al., 2000 [41], reported that ethanol is the preferred alcohol for enzymatic reactions. Iso et al., 2001 [42], claimed that methanol performed well, only when 1,4-dioxane was used, whereas the reaction was not homogeneous when ethanol was used. They suggested 1-propanol and 1-butanol as viable alcohols in the absence of any solvent for the enzymatic esterification process.

The greatest of disadvantage of a biochemical route is the high cost associated with enzymes. Biodiesel production via enzymatic action is more expensive than any other process. Although there is a possibility of reusing the enzymes, they often get deactivated at the end of the reaction. Also, the reaction time is very long in the absence of any solvent. Fukuda et al., 2000 [36], reported a reaction time of 90 hrs for an 80% yield of methyl esters. Abigor et al., in 2000 [41] reported a 42% ester yield after 8 hrs of reaction with propanol and butanol.

1.2.5 Supercritical Process. Saka and Kusdiana proposed a non-catalytic supercritical process that can handle high water and free fatty acid content [43]. Since both the enzymatic process and the heterogeneous catalyst process showed slow reaction rates and low ester yield, it has been suggested that supercritical conditions of high temperature and pressure be used to catalyze the transesterification reaction. Figure 1.8 illustrates the liquid, and the gaseous states of methanol, as temperature and pressure are varied. At a high temperature and pressure, methanol enters a supercritical region. In the supercritical region, it behaves like a compressible fluid having density intermediate between that of a gas and that of a liquid. Viscosity and surface tension of supercritical methanol is low, allowing excellent mass transfer characteristics. An increase in temperature decreases the ionic product of various polar solvents such as CO_2, alcohols, and water, converting them into non-polar solvents. Table 1.1 lists the critical conditions for different solvents, beyond which they become supercritical fluids.

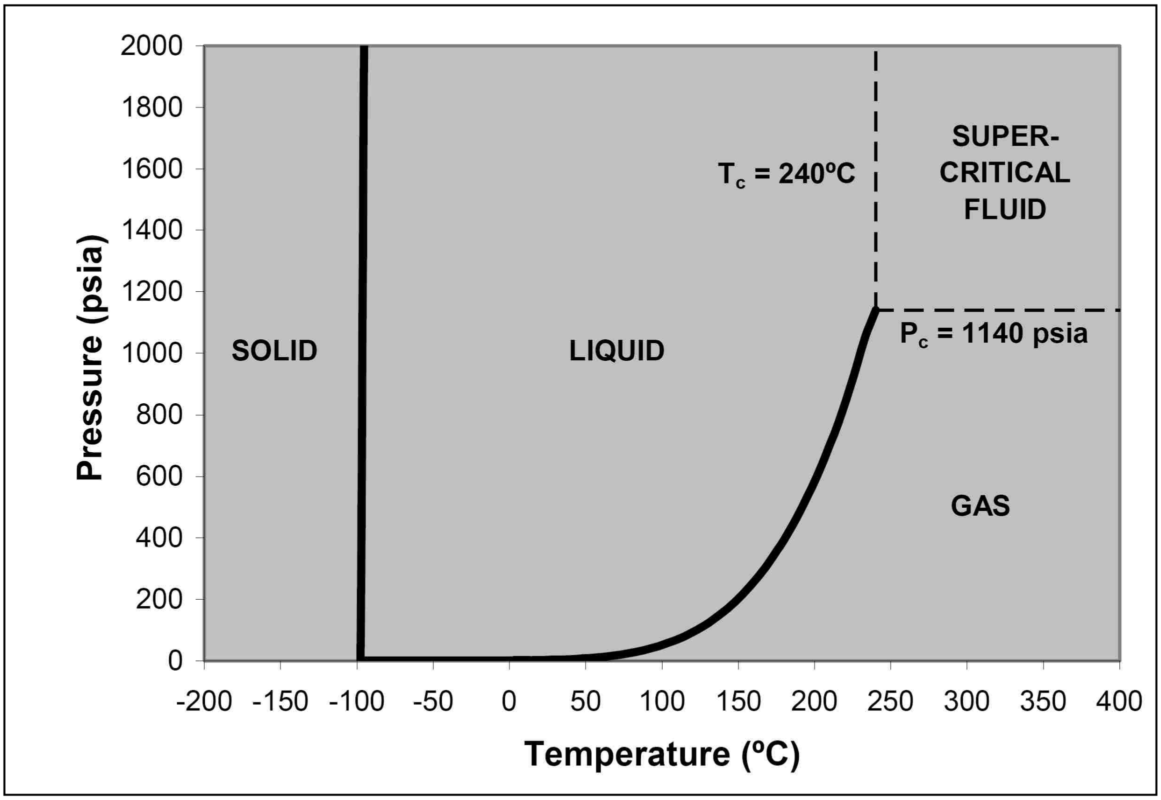


Fig. 1.8: Methanol Critical Diagram [44].

Table 1.1: Critical Temperature and Pressure for Common Solvents

Chemical	T_c (°C)	P_c (MPa)	Reference
Water	374	22.05	Freitag et al., 2006 [45]
CO_2	31	7.38	Gil et al., 2008 [46]
Methanol	240	8.09	Gil et al., 2008 [46]
Ethanol	241	6.3	Gil et al., 2008 [46]
1-Propanol	264	5.06	Warabi et al., 2004 [47]
2-Propanol	235	4.76	Freitag et al., 2006 [45]
Allyl Alcohol	267	5.62	Joback’s Method
Acetone	235	4.7	Sue et al., 2004 [48]
Hexane	234	3.02	Gil et al., 2008 [46]
CH_2Cl_2	235	6.35	Marsh et al., 2004 [49]
Toluene	320	4.22	Abdulagatov et al., 2008 [50]

The transesterification reaction between triglycerides and supercritical alcohol takes place without any catalyst present. The hydrogen bonding between the alcohol molecules decreases dramatically in the supercritical region [51], allowing alcohol molecules to act as an acid catalyst. At high pressure, the alcohol monomer directly attacks the triglyceride carbonyl atom (as seen in Fig. 1.9) and imparts a positive charge. The methoxide is transferred and the intermediate dissociates forming a fatty acid alkyl ester molecule and a diglyceride molecule. This sequence is repeated twice more until glycerol is formed as an end product.

The apparent activation energy for the transesterification reaction in the supercritical state is 56kJ/mol, whereas it is only 11.2kJ/mol in the subcritical region (below 240^{o}C) [52]. Several researchers [51-53], have suggested that the reaction system needs to cross an energy barrier, beyond which there is a distinct increase in the reaction rate constant. The reaction rate constant was increased by a factor of 85, when the temperature was increased from the subcritical range at 239^{o}C to 350^{o}C [53]. Hence high temperatures are required to overcome this energy barrier. It is further observed that the change in the reaction rates in the Arrhenius plots was the result of increase in activation energy, E_a, and also the pre-exponential factor [51]. D'ippolito et al., 2007, suggested that a decrease in hydrogen bonding and variation in physical properties of methanol are responsible for changes in the pre-exponential factor. All reactions below the critical point are insignificant because the reaction rates are low; the subcritical reaction rates are two orders of magnitude slower [51].

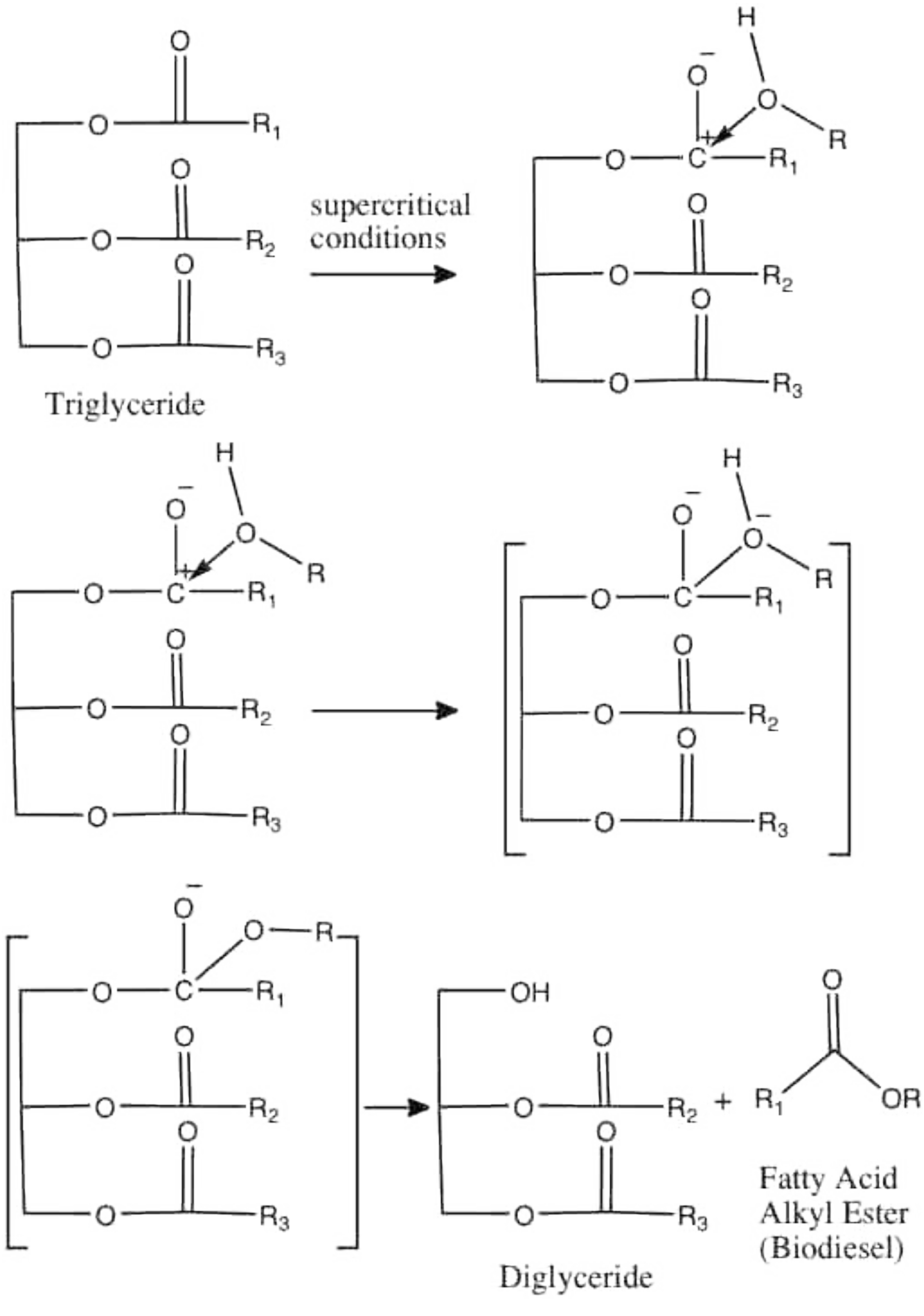


Fig. 1.9: Reaction Mechanism for Supercritical Process.

Dadan Kusdiana and Shiro Saka [21] reported that high temperatures are preferable for saturated fatty acids and that they show faster and more complete conversion when the temperatures are high. However, when temperatures increase, unsaturated fatty acids tended to degrade. Hence, temperatures should be kept below 350°C. He et al. [54] showed an increase in FAME yield from 50% at 240°C to 75% at 280°C; however, a further increase in temperature to 340°C resulted in product degradation and a decrease in FAME yield to 50% .

In the first few minutes after methanol entered the supercritical region, Saka et al. [55] observed close to 80% conversion. They reported a complete conversion occurred in 4 min at 400°C. Yin et al., 2008 [56], reported a 95% conversion in 10 min at 350°C, whereas there was only a 30% conversion after 60 min at 260°C. Silva et al., 2007 [57], reported an increase in fatty acid ethyl ester (FAEE) yield from 10% at 300°C to 60% at 350°C. At 375°C, the FAEE degraded, and 45% was the total product yield. No reaction was observed at the subcritical condition of 200°C.

Various molar ratios have been studied to optimize methanol-oil contact. A high methanol/oil molar ratio in the reaction mixture is desirable because when oil is dissolved in methanol there is a better contact. At 300°C for 450 seconds, the molar ratio of methanol to oil has been shown to vary from 12 to 24 to 42, with a FAME yield increase from 50% to 75% to 90%, respectively [58]. Further increases in the molar ratio have no apparent effect on the yield [54]. Gui et al., 2009 [59], studied the interaction of temperature and the ethanol/oil molar ratio and reported that, at a molar ratio of 16 the yield of FAEE was very low at 320°C, but increased with an increase in temperature. For a molar ratio of 40, the FAEE yield at 320^{o}C was 45%, but decreased as the temperature increased to 360^{o}C.

Pressure is known to affect the physical properties of supercritical alcohol. At high pressure, fluid density is also high, allowing more collisions between methanol molecules and oil. The collisions create better contact and increase reaction rates. Alkyl ester yield is known to increase with an increase in pressure. Hawash et al., 2008 [60], observed an increase in FAME yield from 20% ester yield to 95% ester yield when the pressure was increased from 6 MPa to 9 MPa. The minimum pressure of the reaction system should be greater than that of the critical pressure to allow the alcohol to enter the supercritical region. The reaction yield increased from 55% to 95% when pressure increased from 10 MPa to 25 MPa. After 25 MPa the change in ester conversion with an increase in reaction pressure is not significant [54, 61].

Various alcohols have different critical conditions. Further, the addition of carbon atoms changes the polarity and hydrogen bonding, among other physico-chemical properties. Warabi et al., 2004 [47], reported an increase in reaction time with increase in number of carbon atoms. 1-propanol required twice the reaction time as that required by methanol. The longer molecular structures of the alcohols offer steric hindrance, thus slowing down the reaction rate and requiring longer reaction time. The temperature requirements were also higher because the critical temperature was higher for longer alcohols. Also with the easy availability of methanol and ethanol, most of research is conducted using these alcohols. Ayhan Demirbas [62], reported using ethanol and methanol with linseed oil to produce alkyl esters. Although the yield of ethyl esters was close to the methyl ester yield, it was still lower by 10% [62]. Saka et al., 2009 [63], suggested using methyl acetate instead of methanol to produce triacetin and FAME as biofuel. When methyl acetate is used triacetin is produced instead of glycerol as a byproduct, which can also be used as a biofuel. In addition, supercritical acetic acid and methanol have been used in a two-step process to produce triacetin and FAME [64].

Europe produces biodiesel mainly from rapeseed oil, whereas the United States uses soybean oil. Middle East countries prefer palm oil, and tropical countries produce biodiesel from coconut oil. Assorted oils have been used to study the non-catalytic processes because all oils consist largely of triglycerides (over 90%) and fatty acids. They vary in terms of the number of carbon atoms they have and their degree of saturation, which result in adjustments in reaction conditions and minor variations in ester properties. Demirbas, 2002 [65], compared diesel to the properties of the methyl esters formed from various vegetable oils, like hazelnut oil, poppy seed oil, sunflower oil, safflower oil, rapeseed oil, and cottonseed oil. He also studied the properties of linseed oil esters formed with methanol and ethanol. Bunyakiat et al., 2006 [58], found that coconut oil reacted at a lower temperature than palm kernel oil during the non-catalytic transesterification process using a continuous reaction system. Dippolito et al., 2006 [51], used refined soybean oil, and suggested using a two-step supercritical reaction process. Because the use of virgin oil as feedstock is responsible for 80% of biodiesel’s total cost, various cheaper oil feedstocks are being investigated [80, 81]. Demirbas, 2009 [66], used waste sunflower seed oil to produce FAME and reported esterification of FFA that result in a greater ester yield from supercritical methanol than from the base catalyst process. Patil et al., 2009 studied waste vegetable oil as a potential biodiesel feedstock. They tested supercritical methanol as an alternative method to the two-step catalyst process, using ferric sulphate as an acid catalyst, followed by KOH to deal with high FFA content [67]. Marulanda et al., 2010 [68], have investigated the use of chicken fat as a potential feedstock for biodiesel. Although animal fats and waste oils are impure, because of their high water and FFA content, they are a cheap source of oil. A wide variety of crops is currently being genetically modified in order to have greater lipid content that will enhance the yield.

Yin et al., 2008 [56], experimented with hexane and carbon dioxide as co-solvents to enhance the homogeneity of the mixture and thus to increase the ester yield. They reported an increased yield in the presence of hexane at 300^{o}C in 30 min, and observed a maximum ester yield of 85% when 2.5% (by weight) hexane was added. They also reported a 0.2 molar ratio of CO_2-to-methanol as a critical amount that resulted in increased ester yield, from 60% to 90% at 300^{o}C. Han et al., 2005 [69], and Cao et al., 2005 [70], suggested that the energy barrier for the transesterification reaction could be overcome by using catalysts or co-solvents. Han et al. [69] reported using CO_2 as a co-solvent at a 0.1 molar ratio, and observed a complete ester conversion at a lowered reaction temperature of 280^{o}C. Similarly, Cao et al., 2005, suggested using propane as a co-solvent because its critical temperature is 96^{o}C and its critical pressure is 4.2 MPa. They reported that the presence of a 0.05 molar ratio of propane-to-methanol enhanced the homogeneity of the mixture resulting in a complete ester yield at a decreased reaction temperature of 275^{o}C. Wang et al., 2007 [71], reported use of organic amines as a co-solvent. They reported that ethylenediamine gave the highest ester yield since it had the maximum basic catalytic activity compared to diethylamine and triethylamine. Wang et al. also suggested using propylene oxide as a co-catalyst with triethylamine to enhance the biodiesel yield. Imahara et al., 2009 [72], however, claimed that use of any co-solvent diluted the reactants and decreased the ester yield. The presence of nitrogen or carbon dioxide as co-solvents increased the pressure of the reaction system, resulting in an enhanced yield.

2. OBJECTIVE

The overall objective of this research was to investigate the transesterification of soybean oil to fatty acid alkyl esters as biodiesel, using supercritical alcohol.

Specifically, reaction parameters were evaluated for a pump-less batch reactor system, and the effect of carbon dioxide, as a co-solvent on the ester yield was determined.

The effects of reaction conditions such as temperature, pressure, time, and methanol-to-oil molar ratio were studied in relation to biodiesel yield using a small-scale reactor system. The effects of free fatty acids and water content on ester yield were also evaluated. To enhance the mutual solubility between the reactants, and improve the fatty acid ester yield, co-solvents were investigated. Fatty acid alkyl esters were produced using other alcohols such as 1-propanol, 2-propanol and allyl alcohol.

In addition, an analytical technique was developed using supercritical alcohol for qualitative as well as quantitative analysis of the lipids in oil seeds.

PAPER

I. EFFECT OF CARBON DIOXIDE ON BIODIESEL PRODUCTION USING SUPERCRITICAL METHANOL IN A PUMP-LESS BATCH REACTOR

1. Introduction

Supercritical fluids are substances above their critical temperature and pressure and exhibit properties of liquids as well as gases. They become compressible fluids with adjustable densities close to a liquid while having diffusivity like that of a gas. Small changes in the temperature or pressure above a critical point can greatly influence their density dependent properties like solubility parameter, diffusivity, viscosity, and dielectric constant. The ability to fine-tune these properties has made supercritical fluid (SCF) the preferred solvent in various industries for extraction, reaction medium and separation.

Kusdiana et al. proposed using supercritical methanol as a medium for non-catalytic transesterification of triglycerides for biodiesel production [53]. Unlike the conventional transesterification reaction processes, this requires no catalyst and can handle many feedstocks including used cooking oil. At high temperature and pressure supercritical methanol acts as a solvent, acid catalyst, and a reactant [23]. The excellent mass transfer characteristics of the SCF result in quick reaction rates and high product yields. Saka et al. reported the conversion of rapeseed oil to fatty acid methyl esters (FAME) within 4 min when supercritical methanol was used in a 5ml reaction vessel at 400^oC [55]. Imahara et al. studied the effect of CO_2 and N_2 as co-solvents on the supercritical transesterification process using a 5.3ml Inconel 625 reactor, at 300^{o}C to generate the required conditions [72]. A 95% ester yield was achieved in a pump-less 100ml autoclave at 250^{o}C, using hazelnut kernel oil for non-catalytic transesterification by Demirbas [65]. Hawash et al. varied the volume occupied by the reactants in a 3.7 liter batch reactor from 16% to 36% and converted jatropha oil to biodiesel using supercritical methanol at 340^{o}C and 4 min reaction time [60]. Tan et al. used a pump-less batch type tube reactor for their study of heptane as co-solvent on supercritical transesterification [85]. He et al. worked with soybean oil using a tube reactor with high pressure pumps to provide additional reaction pressure and produced 96% esters by gradually raising the temperature from 100^{o}C to 320^{o}C in 25 min [54]. Bunyakiat et al. tested reaction conditions for palm kernel oil and coconut oil using a two-step process [58].

Higher reaction conditions were used to overcome the high-energy barrier for the transesterification reaction. It has been suggested that the presence of a catalyst/co-solvent could possibly lower the requirement for high temperature and pressure [69, 70]. Carbon dioxide, alkanes, and even amines have been studied as possible co-solvents [56, 69, 70-72]. Han et al. used carbon dioxide as a co-solvent and proposed an optimum CO_2/methanol molar ratio of 0.1 for maximum ester conversion [69]. They claimed that the presence of CO_2 would overcome the energy barrier at a lower temperature and reduced methanol/oil molar ratio. Yin et al. used carbon dioxide as a co-solvent and reported a steady increase in ester yield from 50% to 90%, with an increase in the molar ratio of CO_2/methanol until it reached 0.2 [56]. Imahara et al. studied the effect of CO_2 on the ester yield and suggested that the dilution effect decreased the ester yield [72].

Transesterification of refined soybean oil, using supercritical methanol, was performed in a batch reactor without the use of any high pressure pump in order to study the reaction conditions like reaction time and pressure and also to determine the possible effect from a co-solvent like supercritical CO_2.

2. Experimental

2.1 Materials

Refined soybean oil (Crisco®) was obtained from local grocer and directly used for this study. Methanol used was of ACS grade of 99.99% purity and purchased from Aldrich Chemicals Co., Inc. Welding-grade CO_2 cylinder was used for CO_2. Ethyl ether, hexane and acetic acid used for thin layer chromatography analysis were of ACS grade and purchased from Fischer Scientific Ltd..

2.2 Supercritical Reactor

The transesterification reaction was carried out in a laboratory fabricated high-pressure batch reactor shown in Fig.1 consisted of a 172 ml stainless steel body, pressure gauge, and a thermocouple sensor. The reactor was heated using a thermostated aluminum block jacket, and maintained at a specified temperature and time. The reaction mixture was constantly stirred using a magnetic stirring bar. Due to the mechanical limitations of the reactor the pressure was maintained below 25 MPa by venting the contents through a shut off valve into collection vessel.

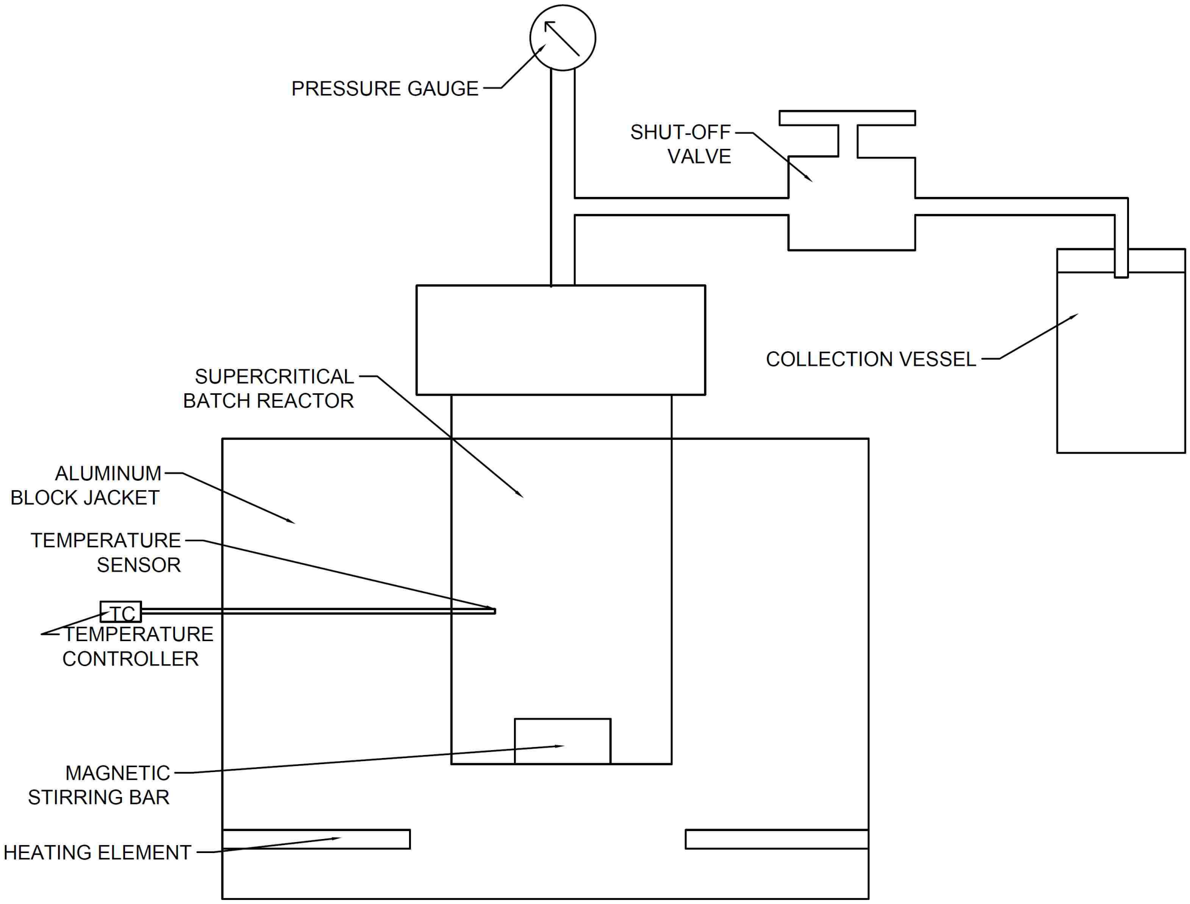


Fig 1: A Schematic Diagram of Supercritical Batch Reactor System.

2.3 Supercritical Transesterification

Initially, the soybean oil and methanol mixture of methanol/oil molar ratio of 42 was charged into the batch reactor. The volume of the reactant filled reactor varied from 47% to 95% of the 172ml vessel volume, the rest being occupied by air. The reactor was then placed into the heating jacket that had been preheated to the desired temperature. The temperature and the pressure inside the vessel were monitored, and the pressure was kept below 25 MPa. The temperature was maintained above the critical temperature of

240^{o}C, and the reaction time was varied from 30 min to 5 hr. After the specified reaction time, the reaction vessel was removed from the heating jacket and cooled in a water basin.

For reactions with CO_2, the volume of oil-methanol mixture was halved to leave room in the vessel for the CO_2. The masses used were approximately 42g of methanol and 25 g oil. During the experiment to determine the effect of co-solvent on the reaction rate, CO_2 was added by connecting a valve to a welding-grade CO_2 cylinder fitted with a siphon tube. The pressure was 6.2 MPa after adding CO_2.

2.4 Product Separation and Analysis

The product mixture was poured into a separatory funnel and allowed to separate into non-polar (fatty acid methyl esters) and polar (glycerol) phases. The top layer containing methyl esters was collected and rotary evaporated at 50^{o}C, to remove methanol, until steady weight was reached. The esters were weighed to determine the transesterification yield.

The purity of the esters was checked via thin layer chromatography (TLC) with a silica gel plate (5 x 10 cm) and a 90:10:1 (by volume) mixture of hexane/ethyl ether/acetic acid and TLC plates stained using iodine vapors.

A Hewlett Packard 5890 Series II Gas Chromatography-flame ionization detector (GC-FID) with a cyanopropyl stationary phase-coated capillary column (30 m x 0.25 mm i.d.) was used to determine the fatty acid methyl ester composition and determine the ester conversion.

3. Results and Discussion

3.1 Behavior Characteristics of the Reactor

The internal temperature and the pressure of the supercritical batch reactor were studied. The variation in the internal temperature of the reactor as it was introduced in the preheated block was examined. The pressure generated in the batch reactor was directly from the heating of the reactants, and no additional pressure was introduced by pumping. Therefore, the pressure profile of the reactor was established by changing the volume of the reactants.

3.1.1 Temperature Profile for the Reaction System

Temperature is an important factor in the supercritical process. The rate of heating for 65% reactor volume filled is described in Fig. 2. A heating jacket was preheated to a predetermined temperature before the reactor was placed in the heating block. As shown in Fig. 2, the heating block was heated to 340^{o}C, and then the reactor was placed in it. The reactor gradually heated up to 260^{o}C and reached a steady state. Below the critical condition of methanol there was no transesterification reaction.

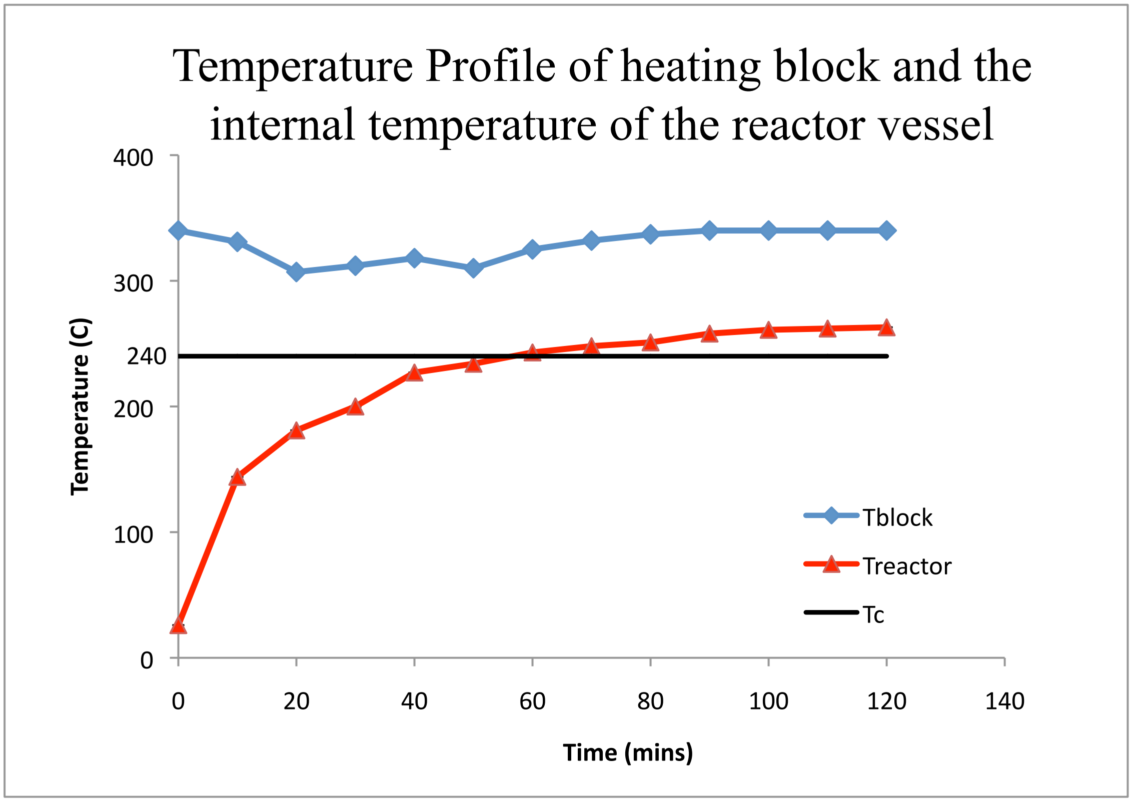


Fig 2: Temperature Profile of Heating Block and the Internal Temperature of the Reactor Vessel.

3.1.2 Pressure Profile of the Reactor as the Reaction Volume Varied

The amount of methanol in the reactor was largely responsible for the pressure generated during the reaction. The methanol/oil molar ratio was kept constant at 42, and the total volume of the reactor filled by the reactants was changed. This had a major impact upon the yield since the pressure generated and the reaction time both varied. The experiments were performed at 47%, 65%, 75%, 82%, and 95% volume filled with oil/methanol mixture. At high volume percentages like 95% and 82%, there was a significant amount of venting to maintain the pressure below 25 MPa. Therefore, resulting in over 9g loss of reactants. The steady state pressures generated by 95% and 82% filled were determined to be 75 MPa and 40 MPa, respectively.

The minimum volume filled was 47%, since the pressure generated below this volume was below the critical pressure of 8 MPa. Fig. 3 shows the pressure generated by different volume percentages of the filled reactor. When the pressure exceeds 25 MPa the reactor contents were vented to reduce the pressure.

He et al. reported an increase in the FAME yield, from 55% to 95%, with increased reaction pressure from 10 MPa until it reached 25 MPa [52]. Further increases in pressure, however, did not enhance the ester conversion [52]. Accordingly, the constraint of maintaining the pressures below 25 MPa should not have an inhibiting effect on FAME yield. Pressure was over 29 MPa in the first 15 min for 95% of the volume filled, requiring venting of the reactants. From the graph (Fig. 3), the volume filled was optimized at 65-80%, since sufficient pressure was generated and there was no need to vent the contents to prevent product loss.

3.2 Effect of Pressure on FAME Yield

When the volume of the filled reactor varied, there was a direct effect on the pressure generated. When the reactor was half filled with oil-methanol mixture (remaining being air), the pressure generated was 9 MPa, allowing methanol to become supercritical. From Fig. 3, it can be seen that the pressure generated in the reactor is a function of the volume occupied by the reactants. As shown in Figs. 3 and 4, increased volume resulted in an increase in pressure and complete reaction.

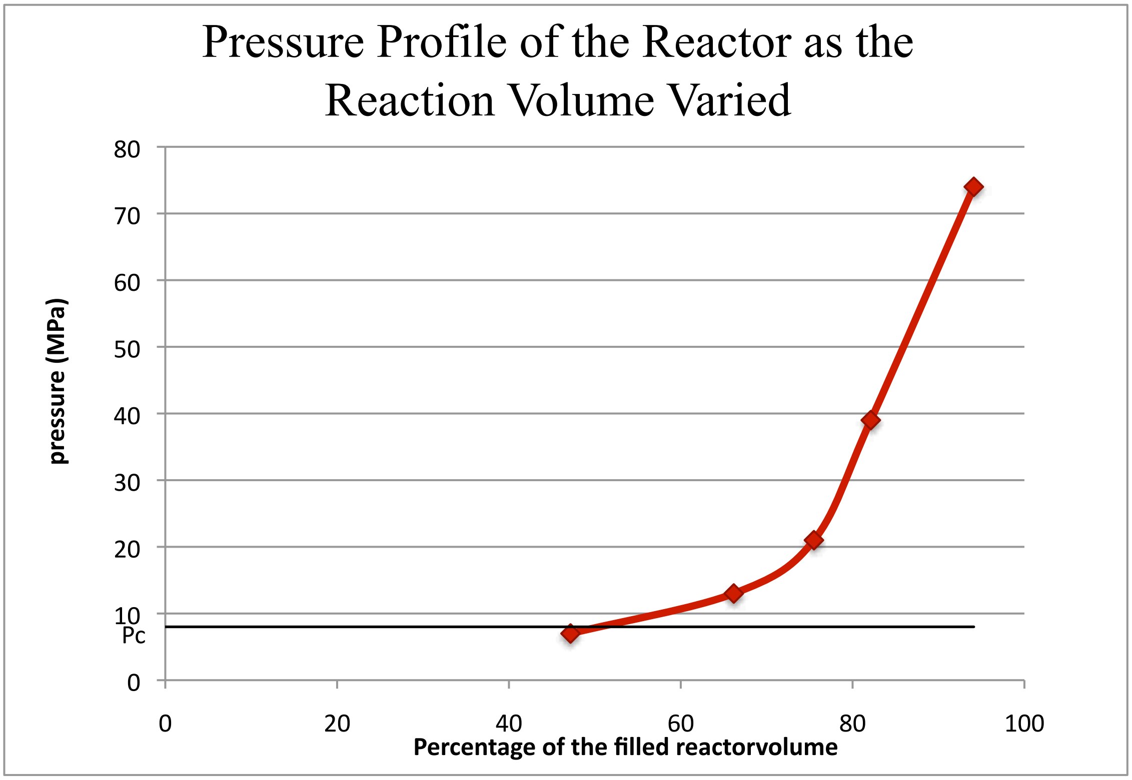


Fig 3: Pressure Profile of the Reactor as the Reaction Volume Varied.

A complete conversion to esters was observed at all of the different volumes since critical conditions were maintained for 2 hr of reaction time. However, when 95% of the reactor volume was filled the total ester yield was observed to be low. Although, there was complete conversion of the reactants to esters, the vented contents do not experience the reaction conditions to convert completely, which resulted in loss of the product. The pressure can be more efficiently controlled in a closed loop continuous reaction system where the vented product can be captured and recycled. At high pressure, more collisions between the methanol molecules and oil resulted in better contact and an increased reaction rate.

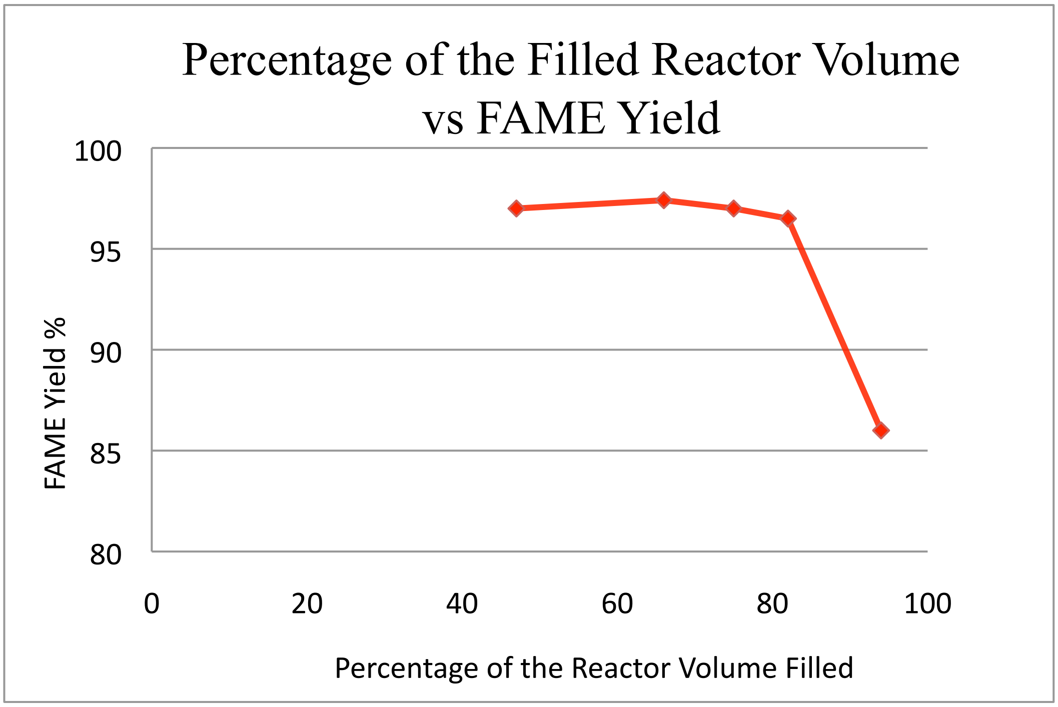


Fig 4: Effect of Pressure Generated by the Filled Reactor Volume on the FAME Yield.

3.3 Effect of Carbon Dioxide on FAME Yield

The amount of oil (45 g) and methanol (75 g) charged in the reactor was constant at a methanol/oil molar ratio of 42. Fig. 5 shows that, at the end of 1 hr, the conversion was less than 15%. This is attributed to methanol being in subcritical state for the greater part of the initial hour. Once the system reached the supercritical state the reaction rates were high and nearly complete conversion was observed at the end of the 2 hr. When the reaction mixture was maintained for periods of 4 and 5 hr, the yield of FAME decreased. This reduction in yield is attributed to the thermal degradation of fatty unsaturated acids like linoleic acid and linolenic acid. The degradation was not very high even after 4hrs of reaction time, with or without CO_2 since the reaction temperatures were below 300°C. Imahara et al. report that significant product oxidation occurs only at temperatures above 300°C [73]. The transesterification reaction is conducted at 280°C, 320°C, and 360°C to confirm the effect of reaction temperature on the product degradation. As seen in Fig. 6, there is a gradual decrease in unsaturated fatty acid concentration. The linoleic esters, $C_{18:2}$ and linolenic esters, $C_{18:3}$ decrease in concentration as they get oxidized as the reaction temperature is increased from 280°C to 360°C.

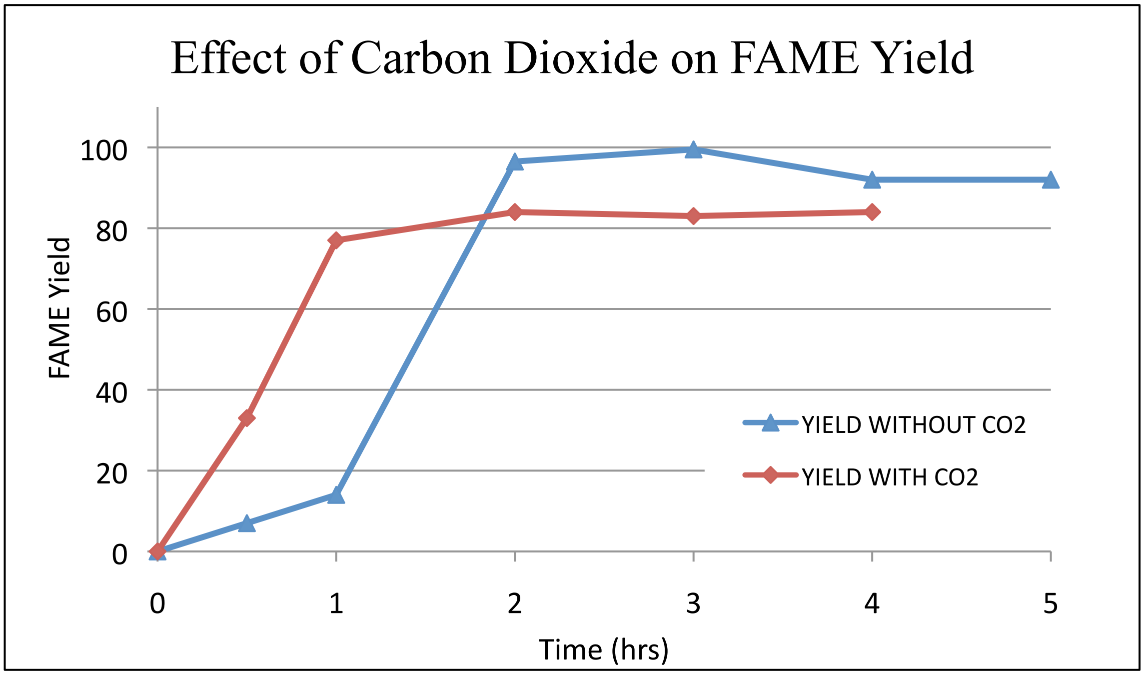


Fig. 5: Progress of the Supercritical Transesterification Reaction with and without Carbon Dioxide.

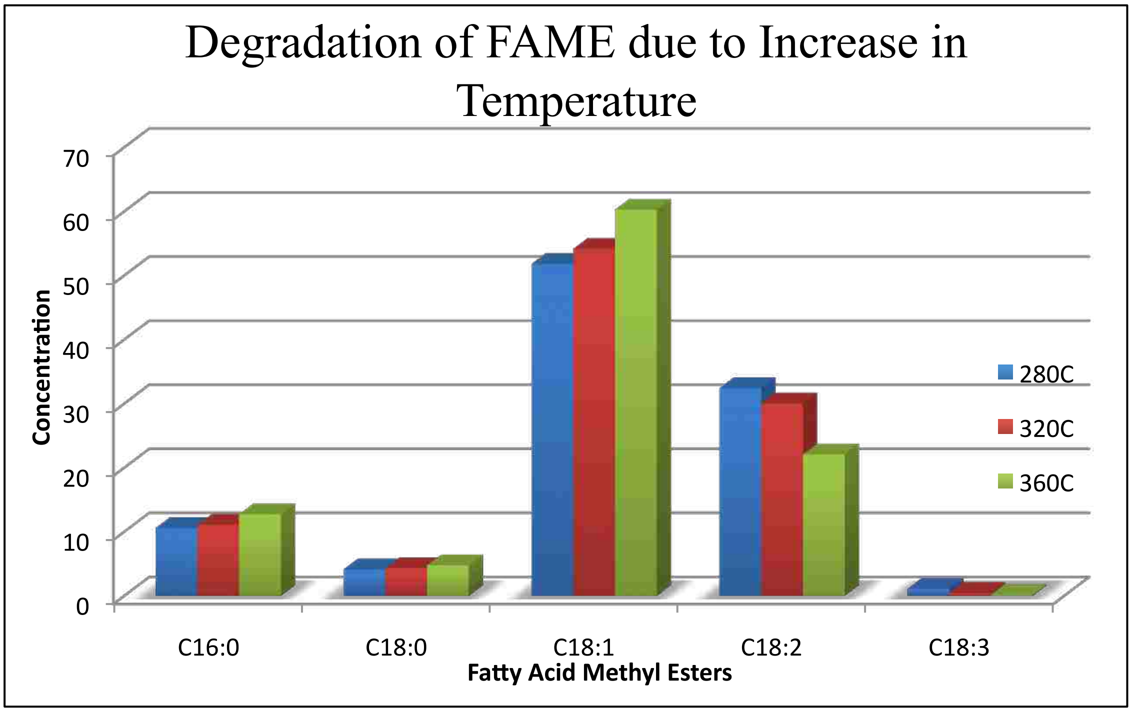


Fig. 6: Thermal Degradation of Linoleic and Linolenic Esters. The temperatures studied are 280°C, 320°C, and 360°C for 30mins with CO_2.

Commonly used supercritical CO_2 (having relatively low critical conditions) has encouraged investigation of CO_2 for use as a co-solvent. The possible increase in solubility of oil in methanol and its effect on the transesterification reaction was investigated using supercritical CO_2. It was hoped that with enhanced mutual solubility there would be an increased reaction rate at lower critical conditions of the reaction mixture. Oil and methanol amounts were decreased to 25 g and 42 g, respectively, to accommodate CO_2 in the reactor. The methanol-to-oil molar ratio was maintained at 42 and the CO_2/methanol molar ratio was maintained at 0.22. The conversion for the system, at the end of 30 min, was 33% in the presence of CO_2 and over 75% at the end of 1 hr, as seen in Fig. 5. This is attributed to possibility that the system reached the supercritical state sooner. The presence of CO_2 increased the reaction pressure of the system, resulting in better contact between the reactants. The increased collisions between the reactant molecules allow efficient heat transfer, resulting in faster increase in temperature and thus attaining the supercritical state faster. Therefore, a better reaction yield and conversion are seen at the end of the first hour. The increased reaction rate is not attributed to a co-solvent effect, but to the higher pressure generated by CO_2. However, the overall yield for the system, with CO_2 was below 85%. Pressure limitations of the reactor prohibited reaction pressures above 25 MPa. Therefore, the reaction contents were vented and resulted in product loss.

According to Han et al., the presence of supercritical CO_2 resulted in better mixing between oil and methanol, therefore requiring a lower methanol/oil molar ratio [69]. It has also been speculated that the high-energy barrier in the supercritical process can be overcome with a lower reaction conditions by using co-solvents [51].

Since pure CO_2 has a critical point ($T_c = 31^{o}C$; $P_c = 7.38$ MPa) that is below that of methanol, it was expected to lower the critical point of the mixture. H. Han et al. suggested a decrease in the critical point of the mixture since the presence of $CO_{2,}$ as a co-solvent would overcome the energy barrier [69]. Yin et al. increased the ester yield from 50% to 90% in the presence of a 0.2 CO_2/methanol molar ratio [56].

Imahara et al. reported an increased ester yield at a 0.11 CO_2/methanol molar ratio but a decrease in ester conversion with further increases in the ratio [72]. However, when a quasi-pressure of 10.8 MPa was maintained, the ester yield was greater in the absence of CO_2, and showed a steady decrease in ester yield as CO_2 was added. The increased yield of esters was due to the increase in reaction pressure resulting in enhanced contact between methanol and oil. However, a further increase in the CO_2 concentration resulted in dilution of the reactants.

4. Conclusion

The batch reactor system produced the required reaction pressure in absence of any external pump. The change in the volume of the reactor filled allowed us to vary the generated reaction pressures. The presence of CO_2 resulted in an increase in internal reactor pressure and therefore enhancing the contact between the oil and methanol molecules. Although there is no lowering of the critical conditions of the reaction mixture, there is better heat transfer between the reactants resulting in methanol reaching the supercritical state sooner. Therefore the presence of CO_2 reduced the required reaction time. High temperatures and long reaction time resulted in thermal degradation of the unsaturated fatty acids, thus decreasing the final product yield.

II. BIODIESEL PRODUCTION AND LIPID QUANTIFICATION USING SUPERCRITICAL ALCOHOL

1. Introduction

The production of fuels from biomass is gaining importance with the growing demand for energy and the need to decrease environmental degradation. Fuels like bio-ethanol are produced from large sugar content crops and biodiesel is produced from large lipid content crops. Various oleaginous resources with dissimilar cultivation demands are researched as potential feedstocks for countries with different climatic and geographical limitations. Also, since a minimal environmental footprint is desired by burning these eco-fuels, utilization of waste oils and lipids extracted from commercial crops are also considered as potential raw materials. Although various oil sources have been studied, they are all largely constituted of triglycerides (over 90%) and fatty acids. These vary on the number of carbon atoms and degree of saturation. Biodiesel is chemically a mixture of fatty acid alkyl esters, and even when produced from these diverse sources can meet the required ASTM standards. Also, this ability of biofuels to be produced from disparate sources makes it a practical option as a substitute for fossil fuels.

Vegetable oil crops that are commonly cultivated include soybeans, corn, rapeseed, sesame seed, groundnut, palm oil, safflower, olives and sunflower seeds. Different genetic hybrids for rapeseed, corn, and soybean among others are being studied to enhance their oil content or vary their fatty acid profile.

These lipids could not be directly analyzed using gas chromatography, because for many acylglycerides and fatty acids, the boiling point temperatures are very high and often close to their decomposition temperatures. Also, it was observed that of the mixture of various acylglycerides and fatty acids, there was an incomplete separation resulting in tailing and overlapping [75]. Hence, these lipids are commonly converted to their equivalent esters to increase volatility and enhance separation between fatty acids peaks and diglyceride and monoglyceride peaks [76].

Conventional transesterification of lipids to esters was carried out using base catalysts (NaOH, KOH, $NaOCH_3$) or acid catalysts (H_2SO_4, HCl, BF_3), in the presence of alcohol (methanol being most commonly used). Base catalysts are known to need less reaction time for complete conversion. However, the sample needs to be dehydrated before the reaction. The free fatty acids cannot be analyzed, since, they are converted to soaps that form an emulsion and require difficult separation. Acid catalysts converted the fatty acids into alkyl esters. Acid catalysts show very slow reaction rates and require long reaction time for complete conversion of the sample to esters. Also water cannot be present in the sample since this adversely affects the acid catalyzed transesterification process.

BF_3 is known to be an excellent methylation agent due to its high reactivity, but it cannot be stored for long periods and the process cannot be automated [76]. The common BF_3 treatment preferred includes sample dehydration and base catalyzed transesterification before alkyl esterification by 14% BF_3 to convert the FFA and achieve complete conversion.

A supercritical process for production of fatty acid methyl esters (FAME) as biodiesel has been recommended by Shiro Saka et al., 2001[21]. This paper investigated the use of supercritical technology as an analytical technique to quantitatively and qualitatively analyze various lipid-bearing crops. Different process parameters were studied to optimize the technique for biodiesel production and to transesterify the lipids extracted from various oil seeds to esters for chromatography analysis.

2. Experimental

2.1 Materials

Crisco® refined soybean oil and ACS grade 99.99% methanol purchased from Aldrich Chemicals Co., Inc. were used in this study. Hexane, stearic acid, acetone, toluene and n-propanol and isopropanol were all purchased from Fischer Scientific. Allyl alcohol was purchased from Alfa Aeser.

For thin layer chromatography analysis, the ethyl ether and glacial acetic acid were ACS grade, and were purchased from Aldrich Chemicals Co., Inc.

2.2 Supercritical Transesterification

2.2.1 Supercritical Reactor and Transesterification Reaction

The transesterification reaction was carried out using a 7ml volume stainless steel reactor (Fig. 1) comprised of ½ inch O.D. tube and Swagelok fittings. Specific amounts of soybean oil and methanol were charged into the batch reactor and placed in an oven that had been preheated to the desired temperature (200-320°C). The reaction time was varied from 30 min to 4.5 hr to study the progress of the transesterification reaction. The methanol-to-oil molar ratio was varied from 6 to 63, to study its effect on the reaction. After the reaction, the reactor was placed in an ice-water bath to arrest any further reaction.

Fig. 1: Mini Reactors used for Supercritical Transesterification Reaction.

2.2.2 Oil Extraction from Seeds

Soybeans and black sesame seeds (*Sesamum Indicum L.*) were used to determine the lipid profile of oil seeds. Soybeans were ground into soy flour. For the extraction process, 1 g of soy flour and 5 ml of hexane were placed in a tube and sonicated for 30 min. The mixture was then centrifuged to settle the soy flour. Black sesame seeds (*Sesamum Indicum L.*) were crushed using a mortar and pestle. Similarly, 1 g of crushed sesame seeds and 5 ml of hexane were sonicated and centrifuged.

A 2 ml portion of the supernatant hexane-oil mixture, and 4 ml of alcohol were charged into the reactor and sealed. The transesterification reaction was carried out at 290^{o}C for 1.5 hr in an oven. The weight ratio of oil/methanol/hexane was approximately 1:50:21. After reaction, the reactor was cooled in an ice-water bath to arrest any further reaction.

1-propanol was tested as a lipid extraction solvent using 1 g of soybean flour with 8 ml of 1-propanol. The mixture was sonicated for 30 min, centrifuged and 5 ml of the supernatant oil-propanol mixture were charged into the reactor. The transesterification reaction was conducted at 290^{o}C for 2 hr in order to achieve conversion of lipids to propyl esters.

2.2.3 Product Separation and Analysis

The reaction mixture was emptied into a glass vial, and the reactor was rinsed with a small volume of methanol to transfer the remaining residues. The vial was placed on a hot plate to evaporate the methanol. The product was washed with water to remove polar compounds including glycerol. Hexane was added to dissolve the esters and extract biodiesel. The hexane was evaporated and, when steady state weight was reached.

The purity of the esters was checked using thin layer chromatography (TLC). Biodiesel product was spotted on silica gel plate (5 x 10 cm) and developed using a 90:10:1 mixture of hexane/ethyl ether/acetic acid. TLC plates were stained using iodine vapors. A Hewlett Packard Model 5890 Series II Gas chromatography-flame ionization detector (GC-FID) with a cyanopropyl stationary phase coated capillary column (30 m x 0.25 mm I.D.) was also used to investigate the fatty acid alkyl ester composition.

3. Results and Discussion

The transesterification reaction between oil and methanol can only occur when methanol surpasses its critical conditions of $T_c = 239^oC$ and $P_c = 8$ MPa. From the study of the large-scale batch reactor, it was concluded that the optimum volume required for ester conversion was 60-80%, since methanol could then generate relatively high pressures. A filled reactor volume below 80% was not sufficient to generate the required reaction conditions for ester conversion, since the small scale reactor was heated differently. High pressures are known to contribute towards greater conversion and faster reaction, therefore, reactor volume filled was maintained above 80%.

3.1 Evaluation of Supercritical Transesterification Reaction Conditions

3.1.1. Effect of Reaction Temperature on FAME Yield

According to Saka and Kusdiana, reaction temperature has considerable effect on fatty acid ester conversion [77]. At subcritical temperatures the ester conversion is negligible. In our experiments, a conversion at $200^{o}C$ was 10% after 2 hr of reaction time. However, once methanol entered the supercritical state there is a steep increase in the conversion. Thus, the change in the thermo-physical properties of methanol, as a supercritical fluid, was responsible for the transesterification reaction.

The pressure of the reaction system also increased as the reaction temperature increased. Hence, the change in ester conversion contributed to the collective effects of temperature and pressure. At a temperature above $300^{o}C$, there was a slight decrease in the yield. The yield decreased from 99% at $275^{o}C$ to 92% at $320^{o}C$, as seen in Fig. 2. In the literature, this has been attributed to the unsaturated fatty acids linoleic esters, $C_{18:2}$ and linolenic esters, $C_{18:3}$, participating in side reactions involving dehydrogenation and thermal decomposition at higher temperatures [21, 54, 55]. The isomerizaton of the *cis* type C=C double bond to *trans* type C=C double bond leads to degradation of the unsaturated fatty acids [60, 73]. Hence, the reaction temperature was maintained between $240^{o}C$ and $300^{o}C$. It is reported that high temperatures are favored by $C_{16:0}$ and $C_{18:0}$ since the saturated fatty acid methyl esters were seen to be more stable at higher temperatures [21, 54].

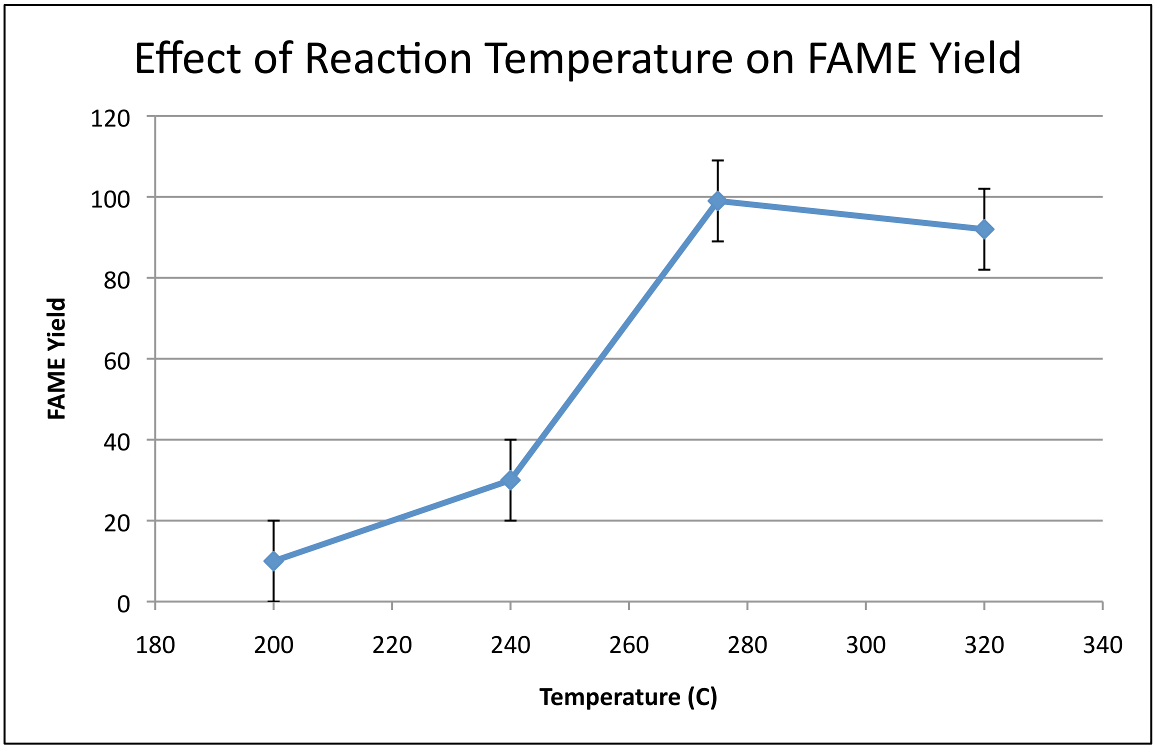


Fig. 2: Effect of Reaction Temperature on FAME Yield.
(Methanol/oil molar ratio = 42 and reaction time = 2hr)

The progress of the reaction was studied by monitoring the reaction time. Temperature for the reaction was maintained at 275°C and the molar ratio of oil: methanol was maintained at 42 to study the variation in methyl ester yield with the reaction time (Fig. 3). At 30 min the conversion is only 17% while at 90 min the conversion was 55% complete. Since there is over 99.5% conversion at 120 mins, it's the minimum time required for complete conversion.

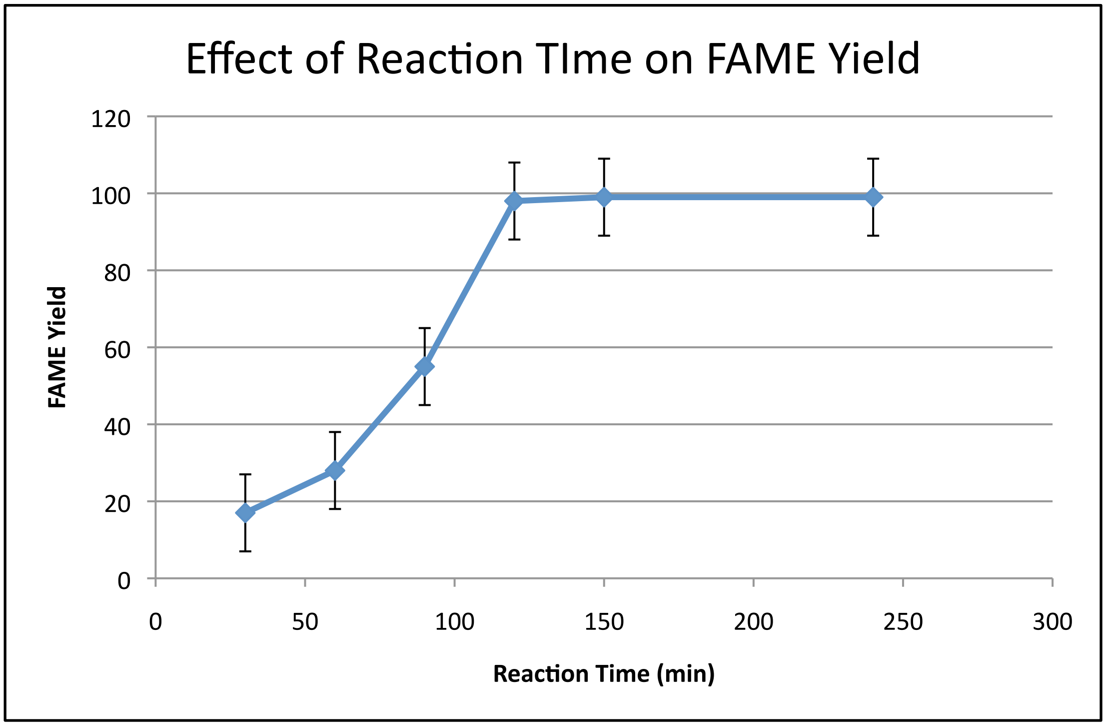


Fig. 3: Effect of Reaction Time on FAME Yield.
(Temperature = 275°C and methanol/oil molar ratio = 42)

3.1.2 Effect of Methanol-to-Oil Molar Ratio on FAME Yield

At room temperature, methanol and oil are a two-phase mixture. However, when methanol surpasses the critical conditions, its dielectric constant decreased and it becomes non-polar. Therefore, at a high methanol to oil molar ratio, supercritical methanol acted as a solvent to dissolve the non-polar oil, creating a homogeneous uni-phase reaction system.

Since methanol is a reactant, the high molar ratio causes the reaction equilibrium to shift towards the product side, resulting in an increased conversion [78, 54].

Supercritical methanol acts as a solvent, reactant and also an acid catalyst [20, 23]. Hence, the molar ratio of methanol /oil is kept high.

At supercritical conditions, there was a decrease in the hydrogen bond strength. The average number of hydrogen bonds per molecule, was 1.93 at the subcritical temperature, but decreased to 0.7 in the supercritical region [79]. This broke the chain-like structure present in alcohol, due to hydrogen bonding, and allowed the methanol to be a free monomer. Reaction mechanism, according to Kusdiana et al. is a nucleophilic attack by the methanol monomer on the sp2 carbonyl atom [23]. The high molar ratio ensured better contact with more molecules of alcohol surrounding the oil molecule [58].

The increase in methanol content was also responsible for decreasing critical conditions for the reaction mixture [58]. In the conventional acid catalyst reaction system, the methanol/oil molar ratio was maintained at 30 for better conversion [20]. This was close to the molar ratio range for the non-catalytic reaction system. Also, high molar ratio generates greater pressures in the reactor due to greater amount of methanol present.

Excess methanol was required to dissolve the oil and convert a heterogeneous reaction system to homogeneous. The yield doubled from 38% to 79% when the methanol-to-oil molar ratio was increased from 6 to 25. There is an increase in FAME yield with the increase in molar ratio, as seen in Fig. 4. He et al. reported decrease in ester yield to 77% with increase in molar ratio of methanol/oil to 65. Once the system became homogenous, further addition of methanol did not improve the FAME yield, and the ester yield decreases [54]. Hence, the molar ratio was chosen as 42 in the region of high ester yield.

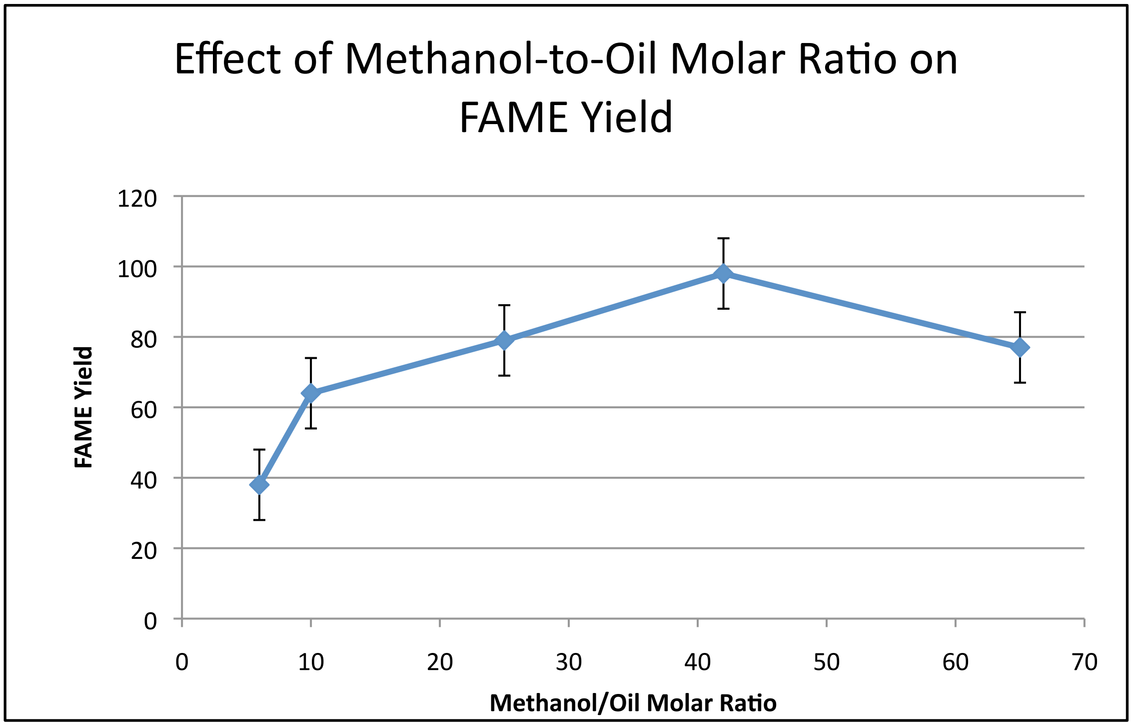


Fig 4: Effect of Methanol-to-Oil Molar Ratio on FAME Yield.
(Temperature = 275^{o}C time = 2 hr.)

3.1.3 Effect of Water on FAME Yield

The presence of water in the feedstock is extremely harmful to the catalyst reaction system. According to Ma et al. the water content should be below 0.06% [22]. In the base catalyst process, the presence of water resulted in fats splitting to produce free fatty acids, which consumed the alkaline catalyst. Presence of water in the feedstock requires expensive feed pre-treatment. Even the acid catalyst process that is immune to the presence of fatty acids is sensitive to the presence of water. Approximately, 80% of the total operating cost required to produce biodiesel is currently attributed to the virgin oil that has to be used as the feedstock [80,81].

Additional water was added externally to the oil to see its effect on the supercritical reaction. Cheap feedstocks, like waste oils, animal fats, and tallow could be used if the reaction system were resistant to presence of water.

There was no significant decrease in FAME yield, as compared to the conventional catalytic process, since; even when the water content was as high as 20% by weight in oil the yield was 82% (Fig 5). Kusdiana and Saka, reported that FAME yield for acid catalyst reaction system decreased to 6% in the presence of 5% water content in the feed, and the FAME yield decreased close to 70% for the base catalyst process [23]. Tan et al. mentioned that the FAME yield decreased to 13% when the water content was increased to 15% for the heterogeneous montmorillonite KSF catalyst at 190^{o}C and 3 hr [84].

The presence of subcritical water can be beneficial for the supercritical transesterification reaction system since it has co-solvent properties and can also protect unsaturated acids from degradation [82, 83]. It has been reported that lower molar ratios of methanol/oil are required in the presence of water since free fatty acids and subcritical water both act as acid catalysts like methanol [78, 23].

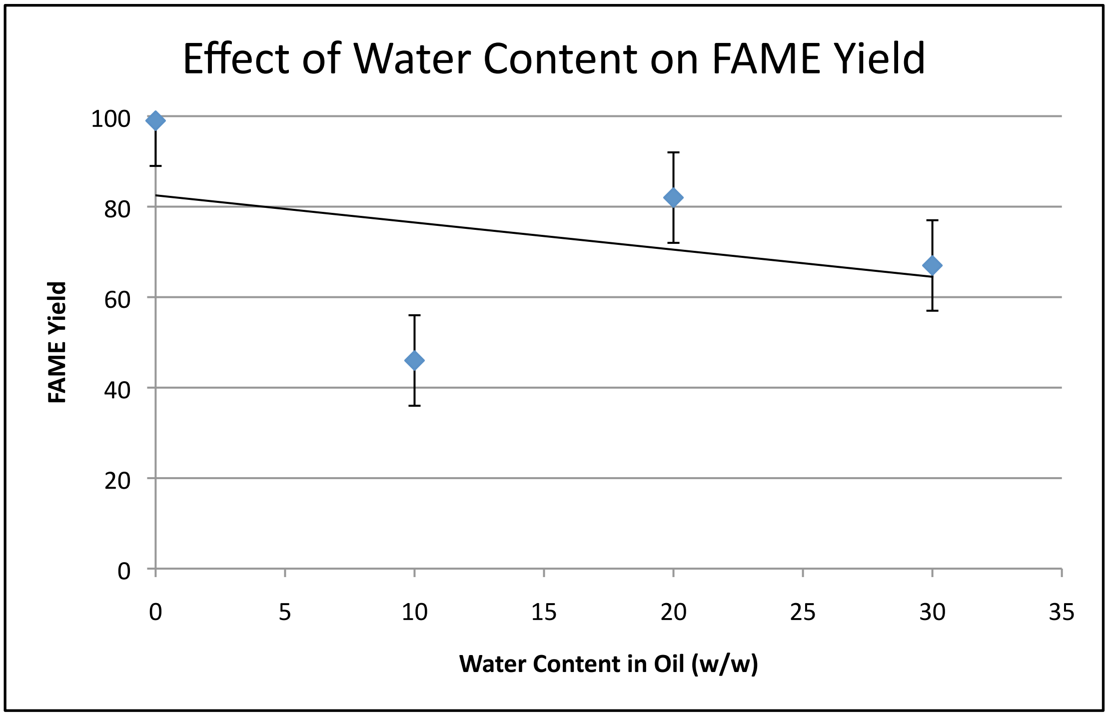


Fig. 5: Effect of Water Content on FAME Yield.
(Temperature = 275^{o}C; time = 2 hr and molar ratio =42)

3.1.4 Methyl Esterification of Free Fatty Acids

The presence of free fatty acids in oil inactivated the base catalyst by reacting with it to form soap. In soybean oil, 3-4% of stearic acid, a saturated fatty acid is commonly present. Stearic acid 1 g and 5.8 ml of methanol was charged in the reactor and were heated to 275^{o}C for 2 hr of esterification reaction. After reaction, the methyl stearate was collected. The TLC showed complete conversion of the free stearic acid to stearic ester. Ranging from 0.5% to11%, free fatty acids are always present in oilseeds [84]. Unlike the conventional base catalyst process where the fatty acids were unfavorable and converted to soap, supercritical methanol converted the fatty acids present in oil to alkyl esters [21]. This indicates the versatility of the non-catalytic process. Also, the fatty acid converted to esters accounted for greater overall yield, making the process favored [21, 43]. Warabi et al. suggested that alkyl esterification of fatty acids was indeed, a faster reaction that required shorter time periods [47]. They contend that fatty acids, being more soluble in alcohol, will have a better mass transfer and better reaction rates. Further since alkyl esterification is a single-step reaction so that it results in a shorter reaction time as compared to the three-step transesterification process [47].

3.1.5 Effect of Co-solvents on FAME Yield

The effects of co-solvents were studied using acetone and toluene in the presence of supercritical methanol. Acetone had intermediate polarity and dissolved methanol and oil to form a homogeneous mixture. Co-solvents were added at 10% weight of oil, and the methanol/oil molar ratio was maintained at 42. The reaction time was 1.5 hr and reaction temperature was 275^{o}C to evaluate any increase in ester yield. The ester yield in the presence of acetone and toluene was 99% and 87%, respectively. In the absence of any co-solvent, the yield of methyl esters formed, was 55%. Although toluene did increase the yield, acetone having intermediate polarity showed a better conversion. Saka et al. suggested the use of methyl acetate and acetic acid as reactants to produce triacetin by transesterification reaction as a commercial byproduct biofuel instead of glycerol [63, 64].

3.1.6 Effect of Different Alcohols on Ester Yield

Methanol and ethanol are generally preferred because of their ready availability and their similar behavior due to proximity of their critical points. With further increases in number of carbon atoms, the polarity and critical properties of alcohols vary. Propyl esters have better cloud point characteristics allowing the use of biodiesel at even a lower temperature. Hence, our studies were focused on the use of propanols as compared with methanol.

As seen in Fig. 6, there was almost complete conversion at 96% of soybean oil to propyl esters at 300^{o}C from 79% at 275^{o}C when 1-propanol was used. The transesterification reaction for n-propanol was conducted at a higher temperature because n-propanol has critical temperature, T_c = 264^{o}C and, critical pressure, P_c = 5.06 MPa [47].

Isopropyl alcohol has a critical temperature of 235^{o}C and a critical pressure of 4.76 MPa. This is much lower than the critical conditions of n-propanol. When allowed to react at 275^{o}C for 2 hr, 43% conversion was observed. With increase in temperature to 300^{o}C the ester conversion increased to 92% and decreased to 81% when temperature was 320^{o}C. No increase was observed in the ester formation, however, when the reaction time was increased to 2.5 hr for temperatures 275^{o}C, 300^{o}C and 320^{o}C.

Allyl alcohol was also used to study alkylation of triglycerides. The critical temperature and pressure were calculated using Joback's Method and Lydersen's Method. The critical temperature was calculated to be 267^{o}C and the critical pressure was 5.7 MPa. As with n-propanol, the critical conditions for allyl alcohol were greater than those of methanol or iso-propanol, however complete conversion was observed at 300°C and 320°C and 2 hr reaction time using TLC. Allyl alcohol (like n-propanol) has a high boiling point and evaporated at 120°C until steady weight was achieved. Fatty acid allyl esters reacted with atmospheric oxygen and were oxidized to probably form epoxy compounds. This can be avoided in an inert environment or when they are vacuum heated. These epoxy compounds can potentially be used to synthesize bioresins and biopolymers.

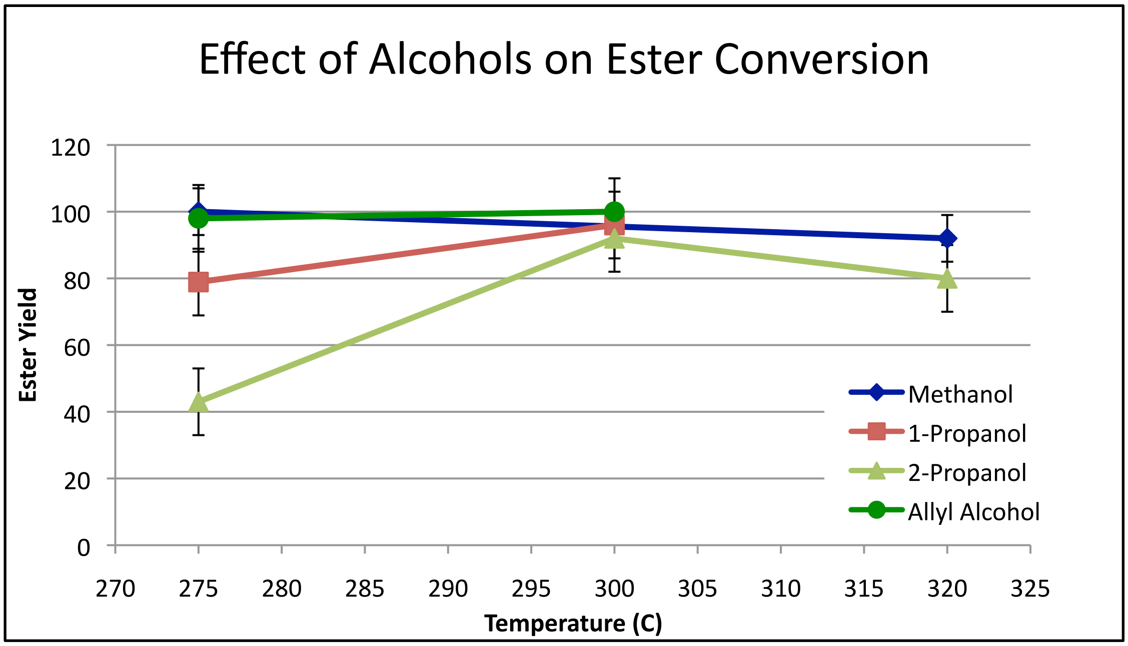


Fig. 6: Comparing the Yield of Fatty Acid Esters when Different Alcohols were Used.

Isopropanol (2-propanol) showed the lowest reaction rate among the alcohols tested. The need for high temperatures with isopropanol can only be explained by the position of the –OH bond, as a secondary alcohol. The –OH bond positioned on the second carbon atom, offers steric resistance. Hydrogen bonding in a supercritical alcohol plays a vital role in their reactivity. Supercritical methanol is also more acidic than supercritical propanols, therefore, acts as a better acid catalyst and also a superior alkylation agent. The high temperature requirement, however, increased risk of degradation of unsaturated fatty acids.

3.1.7 Effect of Hexane on FAME Yield

It has been reported that hexane, being non-polar, acts as a solvent for oil, thereby, enhancing mass transfer [56]. Hexane is also a common solvent for oil extraction from oil seeds. In order to develop a sequential process of lipid extraction and transesterification, the resilience of the reaction system to the presence of hexane was studied. Its effect on the reaction system was evaluated at 275°C with a methanol-to-oil molar ratio at 42 for reaction time of 2 hr. Hexane/methanol molar ratios ranged from 0.03 up to 0.18 as seen in Fig. 7. At high hexane to methanol molar ratios of 0.074 and 0.11, the ester yield was seen to be high at 98% having no significant negative effect on the ester yield. The reaction system was resilient to the presence of hexane. Many researchers have considered adding a third component as co-solvents and catalysts to decrease the reaction conditions. Yin et al. studied the effect of hexane as a co-solvent and reported an increase in the yield when 2.5% weight hexane was used [56]. Imahara et al. reported a minor increase in FAME yield with a hexane/methanol molar ratio of 0.05. A further increase in hexane resulted in decreased FAME yield [72].

It was also speculated that an increase in hexane would form a mixture, and lower critical conditions for supercritical state. However, Imahara et al. and Yin et al. reported that increasing the hexane ratio beyond the optimum did not enhance the FAME yield but actually decreased it [56, 72]. Imahara et al. reported that addition of hexane to a reaction mixture diluted the oil, thereby hindering oil molecules from methanol contact. Tan et al., studied the effect of heptane as a co-solvent and reported an increase in FAME yield with an optimum heptane/methanol ratio of 0.15 [85].

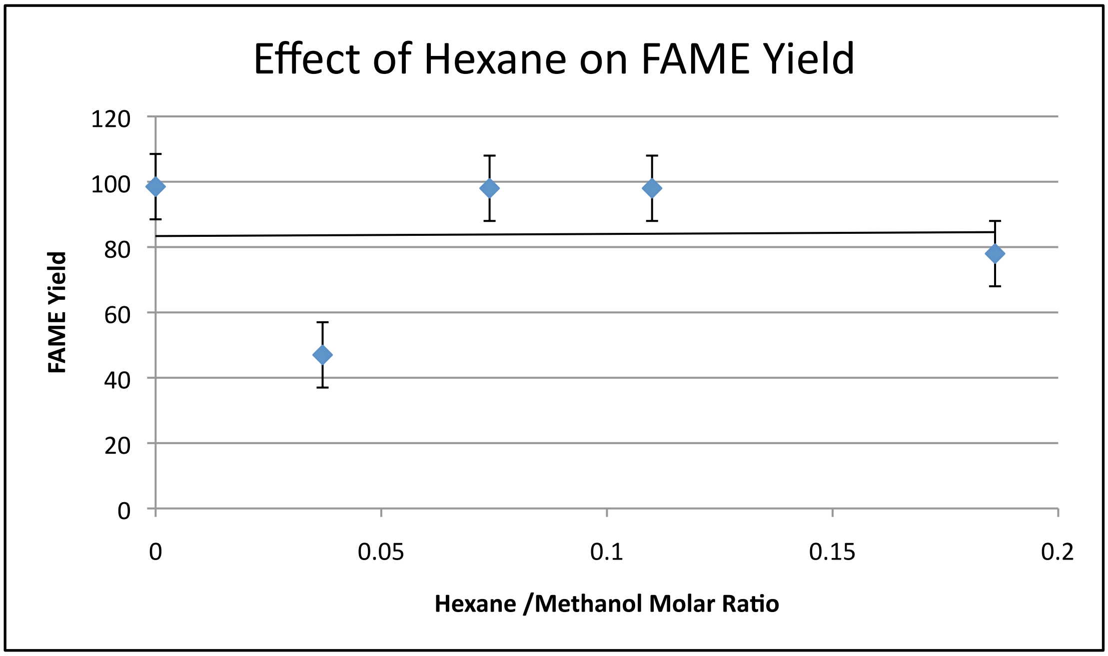


Fig 7: Effect of Hexane on FAME Yield.
(Methanol/oil molar ratio = 42; time = 2hr; temperature = 275°C)

3.2 Direct Analysis of Lipid Containing Samples using Supercritical Alcohols

Lipids are difficult to analyze directly using gas chromatography, since their high boiling point is very close to their decomposition temperature. Also, using the high temperature to vaporize them can harm the capillary column. Commonly, lipids are derivitized to esters that have lower boiling points, and distinct separate peaks. Commonly, lipid samples are converted to esters using a two-step catalytic process, using base catalyst and BF_3. The samples undergo tedious pretreatment to remove moisture and other impurities due to sensitivity of the catalysts. The supercritical transesterification process is proposed for one-step direct derivitization, since it is resilient to moisture, fatty acids, and other impurities. Lipid analyzes from different oil seeds were studied using sequential processes of hexane extraction and supercritical transesterification. From the study of reaction parameters, the supercritical reaction conditions are determined at $290^{o}C$ and 1.5 hr.

The lipid content in the flour was 16% and the conversion to esters was 96%. Lipids that can be extracted from oleaginous samples, and be converted to biodiesel were determined through this method.

Sesame seeds (*Sesamum Indicum L.*) are known for their high lipid content of up to 45%. The oil content of sesame seeds was determined to be 33% and the conversion was 92%. The ester conversion can be increased, by modifying the reaction conditions. Also sesame seeds had polyunsaturated fatty acids, which are stable at room temperature due to the presence of the antioxidants such as sesamin and sesamolin. Thus, the low ester conversion could be because of the possible product degradation.

To avoid the presence of hexane during a transesterification reaction, 1-propanol was substituted for hexane as the extraction solvent for lipids from soy flour. Since 1-propanol has greater critical conditions than methanol, it required a longer reaction time, at the same temperature. The TLC showed a conversion of 93% at 290°C, when the reaction time was increased to 2 hr. Hence, an alternative analytical technique is developed that can be used to study potential oil crops for biodiesel production. Lipids from various oil seeds can be quantified, for their potential to be converted to biodiesel.

4. Conclusion

The reaction conditions for transesterification of triglycerides to methyl esters were evaluated and optimized to 2 hr of reaction time at a 275°C, with the methanol to oil molar ratio maintained at 42. It has been established that the supercritical process was resilient to the presence of water and free fatty acids. Organic solvents like acetone, and toluene showed co-solvent effects and increased the yield by to 99% and 87% respectively for a reaction time of 1.5hr. Various alcohols were also tested and it was observed that the increase in number of carbon atoms slowed the reaction rate. The secondary alcohols showed slower reaction rates due to steric hindrance, as compared to primary alcohols.

An analytical process was developed for the quantification of lipids from oil crops using supercritical alcohol as an alkylation agent. A conversion of over 96% of lipids from soybean flour was attained. For sesame seeds, a 92% lipid transesterification using supercritical methanol was achieved. Accordingly, this technique can be used as a quick analytical method for lipid profiling of oilseeds. It can be used for one step lipid derivitization of samples with high moisture content like waste cooking oil, algae, and animal fats, without any pretreatment. Also, the lipid profile of genetically modified crops can be studied since it is resilient to the presence of other compounds extracted from the oil seeds.

APPENDIX

PICTURES

Fig. 1: (L-R) Soybean oil (left), biodiesel from catalyst process, biodiesel (2nd from right) formed using supercritical methanol, glycerol (right) formed using supercritical methanol

Fig. 2: Supercritical batch reactor is used to produce biodiesel. The pressure gauge and thermocouple are used to determine the reaction conditions. Supercritical methanol and oil are added and heated above 240C and 8.1 MPa using a heating block. The valve is opened to vent the contents if the reaction pressure exceeds 25 MPa

Fig. 3: Soybean oil and methanol (top layer) mixture forming a two-phase system at room temperature before the supercritical transesterification reaction.

Fig. 4: Fatty acid methyl esters (top layer) and glycerol in methanol immediately after the supercritical transesterification reaction.

Fig. 5: Non-polar methyl esters (top layer) and polar glycerol separating into two distinct phases, 45 min after the reaction.

Fig 6: Fatty acid methyl esters (top layer) and glycerol separated into two layers in a vial for the small scale reactor after supercritical transesterification.

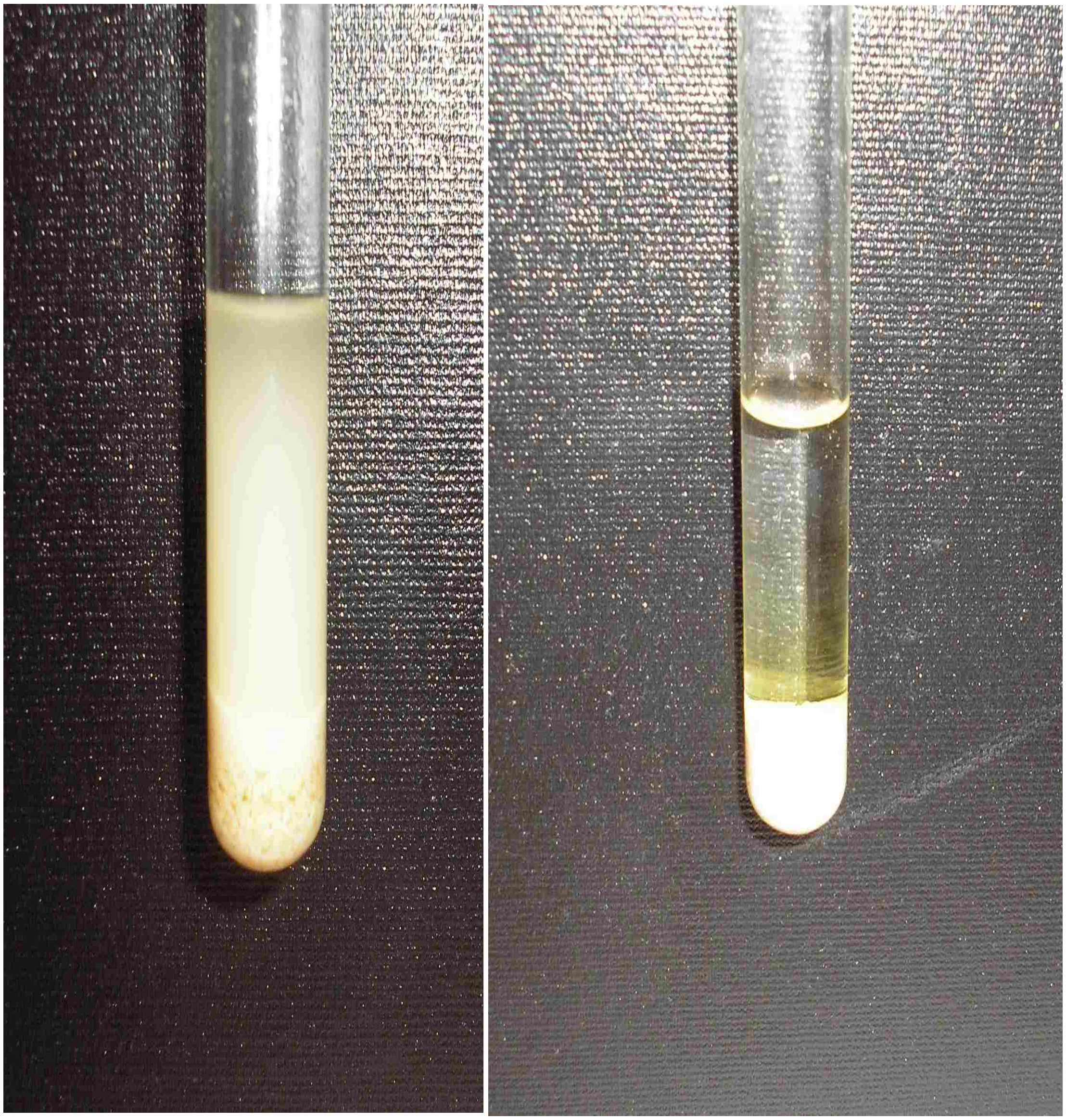


Fig 7: (L-R) Soybean flour and hexane after sonication (left) and after centrifuging (right). The hexane-oil supernatant is esterified and used for lipid analysis.

Fig 8: Sesame seeds roughly crushed using mortar and pestle. Crushing the sesame seeds exposes the oil to hexane for easy extraction.

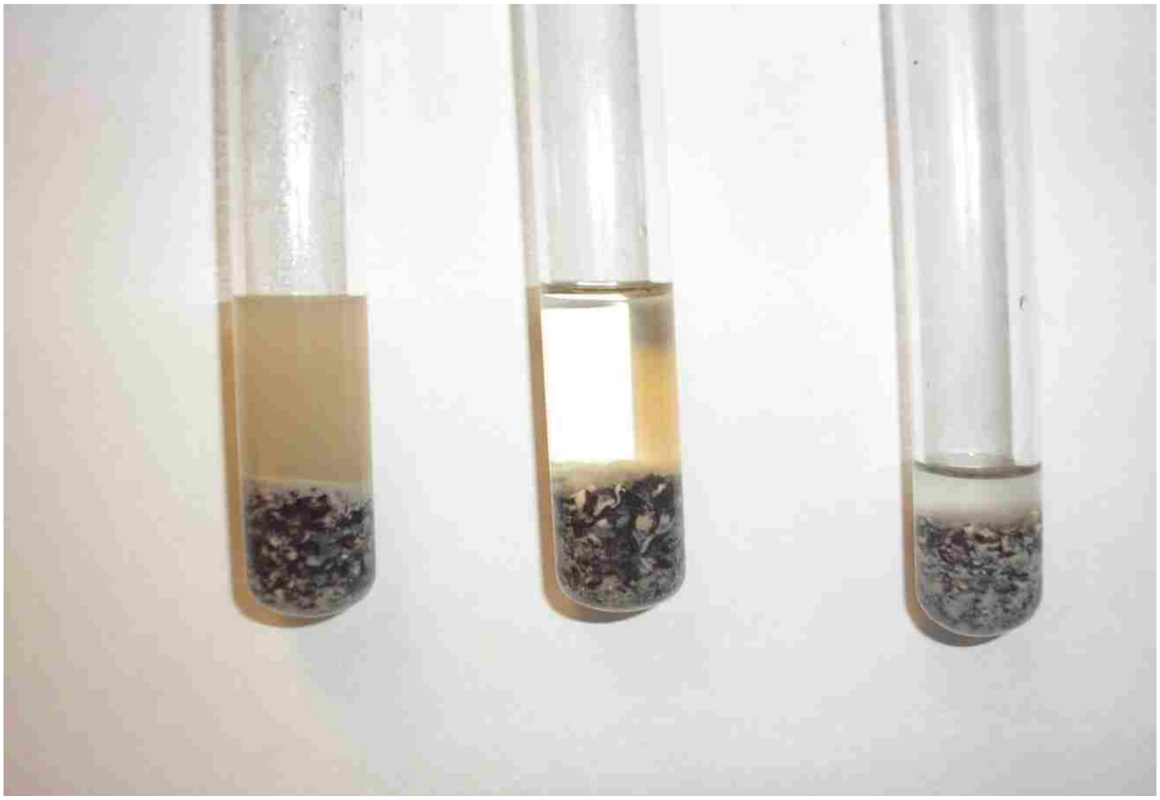


Fig 9: (L-R) Crushed Sesame seeds and Hexane sonicated (left) and centrifuged (center). followed by removal of 2 ml of supernatent hexane-oil mixture.

BIBLOGRAPHY

1. Vaclav Smil. 2000. Energy in the twentieth century: resources, conversions, costs, uses, and consequences. Annu. Rev. Energy Environ. 25: 21-51

2. Vasudevan, P., Briggs, M. 2008. Biodiesel production- Current state of the art and challenges. Journal of Ind Microbiol Biotechnol. 35: 421-430

3. IEA statistic's CO_2 emissions from fuel combustion: 2009 edition

4. Demirbas, A. 2007. Importance of biodiesel as transportation fuel. Energy Policy. 35: 4661-4670

5. Biodiesel 2020: A global market survey, 2nd Edition

6. http://www.ebb-eu.org/stats.php
   June 2010

7. http://www.afdc.energy.gov/afdc/data/fuels.html
   June 2010

8. http://www.eia.doe.gov/oiaf/ieo/
   June 2010

9. http://www.iea.org/stats/pdf_graphs/29TPESPI.pdf
   June 2010

10. Noureddini, H., and Zhu, D. 1997. Kinetics of transesterification of soybean oil. Biocatalysis Articles. 74: 1457-1463

11. Pena, R., Romero, R., Martinez, S., Ramos, M., Martinez, A., Natividad, R. 2009. Tranesterification of castor oil: effect of catalysts and cosolvent. Industrial & Engineering Chemistry Research. 48: 1186-1189

12. Meka, P.K., Tripathi, V., Singh, R.P. 2007. Synthesis of biodiesel fuel from safflower oil using various reaction parameters. Journal of Oleo Science. 56: 9-12

13. Darnoko, D., and Cheryan, M. 2000. Kinetics of palm oil transesterification in a batch reactor. J Am Oil Chem Soc. 77:1263-1267

14. Colucci, J., Borrero, E., Alape, F. 2005. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. Journal of the American Oil Chemists' Society. 82: 525-530

15. Patil, P., and Deng, S. 2009. Optimization of biodiesel production from edible and non-edible vegetable oils. Fuel. 88, 1302-1306

16. Rashid, U., and Anwar, F. 2008; Production of biodiesel through base catalyzed transesterification of safflower oil using an optimized protocol. Energy & Fuels. 22, 1306-1312

17. Lotero, E., Liu, Y., Lopez, D., Suwannakarn, K., Bruce, D., Goodwin, J. 2005; Synthesis of biodiesel via acid catalysis; Ind. Eng. Chem. res.44, 5353-5363

18. Guan, G., Kusakabe, K., Moriyama, K., Sakurai, N. 2009. Transesterification of sunflower oil in methanol with a microtube reactor. Industrial & Engineering Chemistry Research. 48: 1357-1363

19. Diasakou, M., Louloudi, A., Papayannakos, N. 1998. Kinetics of the noncatalytic transesterification of soybean oil. Fuel. 77, 1297-1302

20. Pinnarat, T., and Savage, P. 2008. Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions. Ind. Eng. Chem. Res. 47: 6801-6808

21. Kusdiana, D. and Saka, S. 2001. Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol. Journal of Chem. Eng. of Japan. 34, 383-387

22. Ma, F., Clements, L., Hanna, M. 1998. Biodiesel fuel from animal fat. Ancillary studies on transesterification of beef tallow. Ind. Eng. Che. Res. 37: 3768-3771

23. Kusdiana, D., and Saka, S. 2004. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresource Technology. 91: 289–295

24. Vyas, A., Verma, J., Subrahmanyam, N. 2010. A review on FAME production processes. Fuel. 89: 1-9

25. Freedman, B., Pryde, E., Mounts, T. 1984; Variables affecting the yield of fatty esters from transesterified vegetable oils. Journal of the American Oil Chemists' Society. 61: 1638-1643

26. Canacki, M., J. Van Gerpen. 1999. Biodiesel production via acid catalysis. Transactions of ASAE. 42:1203-1212

27. Freedman, B., Butterfield, R., Pryde, E. 1986; Transesterification kinetics of soybean oil. Journal of the American Oil Chemists' Society. 63, 1375-1380

28. Zheng, S., Kates, M., Dube, M., McLean, D. 2006. Acid catalyzed production of biodiesel from waste frying oil; Biomass & Bioenergy. 30, 267-272

29. Chongkhong, S., Tongurai, C., Chetpattananondh, P. 2009. Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. Renewable Energy. 34: 1059-1063

30. Georgogianni, K., Katsoulidis, A., Pomonis,P., Manos, G., Kontominas, M. 2009 Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. Fuel Processing Technology. 90. 1016-1022

31. Vicente, G., Cotoron, A., Martinez, M., Aracil, J. 1998. Application of factorial design of experiments and response surface methodology to optimize biodiesel production. International Crops and Products. 8: 29-35

32. Gryglewicz, S. 1999**.** Rapeseed oil methyl esters preparation using heterogeneous catalysts. Bioresource Technology. 70: 249-253

33. Lam, M., Lee,K., Mohamed, A. 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid (waste cooking oil) to biodiesel: A review. Biotechnology Advances. 28: 500-518

34. Toda, M., Takagaki, A., Okamura, M., Kondo, J., Hayashi, S., Domen, K., Hara, M. 2005. Green chemistry: Biodiesel made with sugar catalyst. Nature 438, 178

35. Takagaki, A., Toda, M., Okamura, M., Kondo, J., Hayashi, S., Domen, K., Hara, M. 2006. Esterification of higher fatty acids by a novel strong solid acid. Catalysis Today. 116: 157–167

36. Fukuda, H., Kondo, A., Noda,H. 2000. Biodiesel fuel production by transesterification of oils. Journal of Bioscience and Bioengineering. 92: 405-416

37. Nelson,L., Foglia, T., Marmer, W. 1996. Lipase-catalyzed production of biodiesel. Journal of the American Oil Chemists' Society. 73: 1191- 1195

38. Kaieda, M., Samukawa, T., Kondo, A., Fukuda, H. 2000. Effect of methanol and water contents on production of biodiesel fuel from plant oil catalyzed by various lipases in a solvent-free system. Journal of Bioscience and Bioengineering. 91: 12-15

39. Du, W., Xu, Y., Liu, D. and Zeng, J. 2004. Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. Journal of Molecular Catalysis B: Enzymatic**.** 30: 125–129

40. Modi, M., Reddy,J., Rao,B., Prasad, B. 2007. Lipase-mediated conversion of vegetable oil into biodiesel using ethyl acetate as acyl acceptor. Bioresource Technology. 98: 1260-1264

41. Abigor, R., Uadia, P., Foglia, T., Hass, M., Jones, K., Okpefa, E., Obibuzor, J., Bafor, M. 2000. Lipase catalysed production of biodiesel fuel from some Nigerian lauric oils. Biotechnological Aspects: Complex Lipids. 28: 979-981

42. Iso, M., Chen, B., Eguchi, M., Kudo, T., Shrestha, S. 2001. Production of biodiesel fuel from triglycerides and alcohol using immobilized lipase. Journal of Moleculer Catalysis B: enzymatic. 16: 53-58

43. Kusdiana, D. and Saka, S. 2002. Biodiesel fuel for diesel fuel substitute prepared by catalyst-free supercritical methanol. Fuel. 186-187

44. Babcock, R., Clausen, E., Popp, M., Schulte, B. 2007. Yield characteristics of biodiesel produced from chicken fat-tall oil blended feedstocks. Project Number MBTC-2092

45. Freitag, J., Tuma, D., Ulanova, T., and Maurer, G. 2006. High-pressure multiphase behavior of the ternary systems (ethene + water + 1-propanol) and (ethene + water + 2-propanol): Part II: Modeling. 39: 174-186

46. Gil, L., Otín, S., Embid, J., Gallardo, M., Blanco, S., Artal, M., Velasco, I. 2008. Experimental setup to measure critical properties of pure and binary mixtures and their densities at different pressures and temperatures: Determination of the precision and uncertainty in the results. The Journal of Supercritical Fluids. 44: 123-138

47. Warabi, Y., Kusdiana, D., Saka, S. 2004. Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols. Bioresource Technology. 91: 283-287

48. Sue, K., Mizutani, T., Usami, T., Arai, K., Kasai, H., Nakanishi, H. 2004. Titanyl phthalocyanine solubility in supercritical acetone. Journal of Supercritical Fluids. 30: 281-285

49. Kenneth N. Marsh, K., Abramson, A., Ambrose, D., Morton, D., Nikitin, E., Tsonopoulos, C., Young, C. 2007. Vapor−liquid critical properties of elements and compounds: 10 organic compounds containing halogens. J. Chem. Eng. Data. 52:1509–1538

50. Abdulagatov, I., Polikhronidi, N., Bruno, T., Batyrova, R., Stepanov, G. 2008. Measurements of the isochoric heat capacity, the critical point (T_C, ρ_C) and vapor−liquid coexistence curve (T_S, ρ_S) of high-purity toluene near the critical point. Fluid Phase Equilibrium. 263: 71– 84

51. D'Iipolito, S., Yori, J.C., Ituria, M.E., Pieck, C.L., Vera, C.R. 2007. Analysis of a two step, non-catalytic, supercritical biodiesel production process with heat recovery. Energy & Fuels. 21: 339-346

52. He, H., Sun, S., Wang, T., Zhu, S. 2007. Transesterification kinetics of soybean oil for production of biodiesel in supercritical methanol. Journal of the American Oil Chemists' Society. 84, 399-404

53. Kusdiana and Saka. 2001. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol; Fuel. 80, 693-698

54. He, H., Wang, T., Zhu S. 2007. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. Fuel. 86: 442-447

55. Saka, S. and Kusdiana,D. 2001. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel. 80: 225-231

56. Yin, J., Xiao, M. and Song, J. 2008. Biodiesel from soybean oil in supercritical methanol with co-solvent. Energy Conversion & Management. 49: 908-912

57. Silva, C., Weschenfelder, T., Rovani, S., Corraza, F., Corraza, M., Dariva, C., Oliveira, J. 2007. Continuous production of fatty acid ethyl esters from soybean oil in compressed ethanol. Ind. Eng. Chem. Res.46: 5304- 5309

58. Bunyakiat, K., Makmee, S., Sawangkeaw, R., Ngamprasertsith, S. 2006. Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol. Energy & Fuels. 20: 812-817

59. Gui, M., Lee, K., Bhatia, S. 2009. Supercritical ethanol technology for the production of biodiesel: Process optimization studies. Journal of Supercritical Fluids. 49: 286-292

60. Hawash, S., Kamal, N., Zaher, F., Kenawi,O., Diwani, G. 2009. Biodiesel fuel from jathropa oil via noncatalytic supercritical methanol transesterification. Fuel. 88: 579-582

61. He, H., Sun, S., Wang, T., Zhu, S. 2007. Transesterification kinetics of soybean oil for production of biodiesel in supercritical methanol. Journal of American Oil Chem. Soc. 84: 399-404

62. Demirbas, A. 2009. Production of biodiesel fuels from linseed oil using methanol and ethanol in noncatalytic supercritical conditions. Biomass and Bioenergy. 33: 113-118

63. Saka, S. and Isayama,Y. 2009. A new process for catalyst free production of biodiesel using supercritical methyl acetate. Fuel. 88: 1307-1314

64. Saka, S., Isayama, Y., Ilham, Z., Jiayu, X. 2009. New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol. Fuel

65. Demirbas, A. 2002. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Conversion & Management. 43: 2349-2356

66. Demirbas, A. 2009. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. Energy Conversion and Management. 50: 923-927

67. Patil, P., Deng, S., Rhodes, J., Lammers, P. 2010. Conversion of waste cooking oil to biodiesel using ferric sulphate and supercritical methanol processes; Fuel. 89: 360-364

68. Marulanda, V., Anitescu, G., Tavlarides, L. 2010. Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks. Journal of Supercritical Fluids. 54: 53-60

69. Han, H., Cao, W., Zhang, J. 2005. Preparation of biodiesel from soybean oil using supercritical methanol and CO_2 as cosolvent. Process Biochemistry. 40: 3148-3151

70. Cao, W., Han, H., Zhang, J. 2005. Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent. Fuel. 84: 347-351

71. Wang, L., Tang, Z., Xu, W., Yang, J. 2007. Catalytic transesterification of crude rapeseed oil by liquid organic amine and co-catalyst in supercritical methanol. Catalysis Communication. 8: 1511-1515

72. Imahara, H., Xin, J., Saka, S. 2009. Effect of CO_2/N_2 addition to supercritical methanol on reactivities and fuel qualities in biodiesel production. Fuel. 88: 1329-1332

73. Imahara, H., Minami, E., Hari, S., Saka, S. 2008. Thermal stability of biodiesel in supercritical methanol. Fuel. 87: 1-6

74. Singh, S., Singh, D. 2010. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review; Renewable and Sustainable Energy Reviews. 14:200-216

75. Marcato, B., Cecchin, G. 1996. Analysis of mixtures containing free fatty acids and mono-, di- and triglycerides by high-performance liquid chromatography coupled with evaporative light-scattering detection. Journal of Chromatography A. 730: 83-90

76. Brondz, I. 2002. Development of fatty acid analysis by high performance liquid chromatography, gas chromatography and related techniques. Analytica Chimica Acta. 465: 1-37

77. Kusdiana, D. and Saka, S. 2003. Catalytical effect of metal reactor in transesterification of vegetable oil; Journal of the American Oil Chemists' Society. 81: 103-104

78. Minami, E., and Saka, S. 2006. Kinetics of hydrolysis and methyl esterification for biodiesel production in two step supercritical methanol process. Fuel. 85: 2479-2483

79. Wu X., Chen Y., Yamaguchi T. 2007. Hydrogen bonding in methanol studied by infrared spectroscopy. Journal of Molecular Spectroscopy. 246: 187-191

80. Marchetti, J.M., Miguel, V., Errazu, A. 2008. Techno economic study of different alternatives for biodiesel production. Fuel Processing Technology. 89: 740-748

81. Marchetti, J.M. and Errazu, A.F. 2008. Techno economic study of supercritical biodiesel production plant. Energy Conversion and Management. 49: 2160-2164

82. Vieitez, I., Silva, C., Alckmin, I., Borges, G., Corazza, F., Oliveira, J., Grompone, M., and Jachmanin, I. 2009; Effect of temperature on the continuous synthesis of soybean esters under supercritical ethanol. Energy & Fuels. 23, 558-563

83. Vieitez, I., Silva, C., Alckmin, I., Borges, G., Corazza, F., Oliveira, J., Grompone, M., and Jachmanin, I. 2008. Continuous production of soybean biodiesel in supercritical ethanol-water mixtures. Energy & Fuels. 22, 2805- 2809

84. Satyarthi, S. and Ratnasamy. 2009. Estimation of free fatty acid content in oils, fats and biodiesel by H NMR spectroscopy. Energy &Fuels. 23, 2273-2277

85. Tan, K. Lee, K. Mohamed, A. 2010. Effects of free fatty acids, water content and co-solvent on biodiesel production by supercritical methanol reaction. Journal of Supercritical Fluids. 53: 88-91

VITA

Dhaval Nitin Modi was born in Mumbai, India on December 4th, 1986. He pursued his Bachelor's Degree in Chemical Engineering at D.J.Sanghvi College of Engineering (affiliated with the University of Mumbai). In 2007, he won the 3rd prize at the International Seminar on "Coal Gasification: Challenges and Opportunities for India" by Indian Institute of Chemical Engineers (IIChE). He also won the prestigious Carbo-blast Award for "Underground Coal Gasification" at IIChE's Outstanding Young Chemical Engineers Conference in 2008. He received his Bachelor's Degree in Chemical Engineering from Mumbai University in 2008.

For further studies, he enrolled at the Missouri University of Science and Technology in Rolla, 2008. He joined Dr. Nam's research group as a graduate student in September 2008 and worked in the field of biodiesel production. He presented his research work "Transesterification in Supercritical Methanol for Biodiesel Production and Analysis" at Pittcon, 2010. He graduated from Missouri University of Science and Technology in Spring, 2011 with Master's Degree in Chemical Engineering.