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Evaluating One-Step Catalytic Free Method Including Hydrolysis, Esterification, Transesterification, and Degradation Reactions to Produce Biodiesel from Soybean Oil

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Evaluating One-Step Catalytic Free Method Including Hydrolysis, Esterification, Transesterification, and Degradation Reactions to Produce Biodiesel from Soybean Oil

A thesis submitted in partial fulfillment
of the requirements for the degree of
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by

Mahmood Gheni Jebur
Tikrit University
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Abstract

Due to the environmental and economic impacts of diesel fuel based on petroleum, several studies have been done to find an alternative source of energy. Biodiesel is considered one of these alternative sources. It is a renewable source of energy produced from vegetable oils and animal fats. There are two main reaction routes used to produce biodiesel (fatty acid methyl esters). Transesterification reaction is the first route used to convert triglycerides to fatty acid methyl esters (FAMEs), while hydrolysis followed by esterification reactions are the second route employed to convert triglycerides to free fatty acids (FFA) and then further converted to FAMEs. The traditional method used to produce FAMEs is the catalytic method, such as acid and alkali-catalyzed. However, a common drawback of these two methods is they are very sensitive to the presence of water. The free-catalytic method (supercritical methanol method) was, also, developed to generate FAMEs. The major drawback in this method is the severe conditions, of temperature and pressure used to produce FAMEs.

The objective of this study was to evaluate the one-step catalytic free method at subcritical conditions using soybean oil (SBO), methanol (MeOH), and water (H_2O) as reactants. Two system configurations were investigated, continuous and batch systems. A variety of conditions were tested, such as reaction time, temperature, and molar ratio (SBO:MeOH:H_2O). Furthermore, a kinetic model described by four reactions (transesterification, hydrolysis, esterification, and degradation) was developed depending on current and previous studies done to produce FAMEs. Theoretical results of this model showed a sufficient agreement with experimental results due to obtaining an accepted standard error of estimate (3.86 and 6), which can indicate how much experimental and theoretical results are different, in both batch and continuous systems, respectively. This model showed that the optimum biodiesel yield values are

((83% and 55%) in batch and continuous systems, respectively, which occurred under sub-critical conditions and 1:39:22 molar ratio of SBO:MeOH:H_2O. Also, the effects of degradation reactions were explained in this work. In general, the results in this study establish a strong understanding about all the reactions which happened in a one-step sub-critical method.

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I would like to thank my supervisor Dr. Jamie for supporting me during my research. Also, I would like to thank my family, especially my parents and my wife for their support and encouragement. Thanks go to my country, especially, the Higher Committee for Education Development in Iraq, for funding my study and giving me the opportunity to come here and get the master’s degree. Thanks also for my group for helping me conduct my experiments. Finally, thanks to the faculty and staff of both the Ralph E. Martin Department of Chemical Engineering at the University of Arkansas, and the Department of Chemical Engineering at Tikrit University for helping me during my research and study as a chemical engineer.

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CHAPTER 1: INTRODUCTION

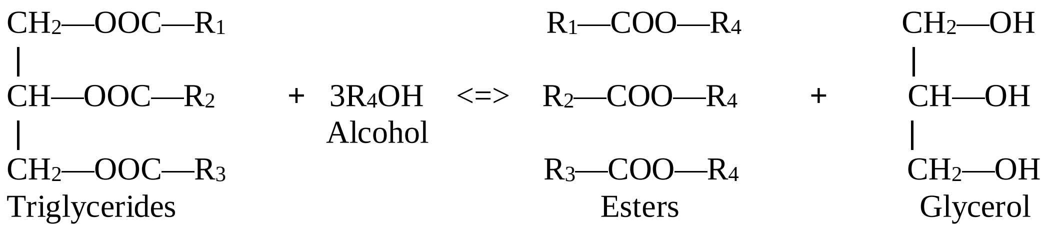
According to the International Energy Outlook 2016 (IEO2016), the world energy use is going to rise 36% between 2017 and 2040. This increase in demand is due to both economic and population growth. In addition, the energy produced from fossil fuels, such as coal, natural gas, and oil, covers over 75% of the whole worldwide energy production [1]. As energy consumption increases, development of alternative energy sources will become important. One such alternative is biodiesel. It is a renewable source of energy prepared from vegetable oils and animal fats. Biodiesel is non-toxic and degrades very fast. Also, biodiesel does not generate greenhouse gases and does not contain any sulfur or sulfur dioxide that affect the environment [2,3]. Furthermore, the worldwide CO_2 emissions are reduced from 2.2583 to 1.395 Kg CO_2/L (38%) when using biodiesel, especially palm biodiesel, over petroleum diesel [4].

There are a variety of biodiesel sources such as edible vegetable oils (canola, coconut, corn, palm, soybean, sunflower etc.), non-edible vegetable oils (jatropha, neem, castor etc.), waste cooking oils, and animal fats (tallow, lard, yellow grease etc.) [5–8]. Using edible vegetable oils as biodiesel sources can raise another problem, which is the competition with food resources [9,10]. In order to solve the food shortage problems, waste cooking oils can be used as feedstocks for producing biodiesel. Furthermore, using waste cooking oils to produce biodiesel solves another issue caused by pouring waste cooking oils down the drain, which is considered as an environmental hazard [5,8,11].

According to the Energy Information Administration, the United States (US) may generate around 100 million gallons of waste cooking oils each day, which is equal to 9 pounds per capita [12]. Soybean oil is the most commonly used edible oil with a consumption rate of

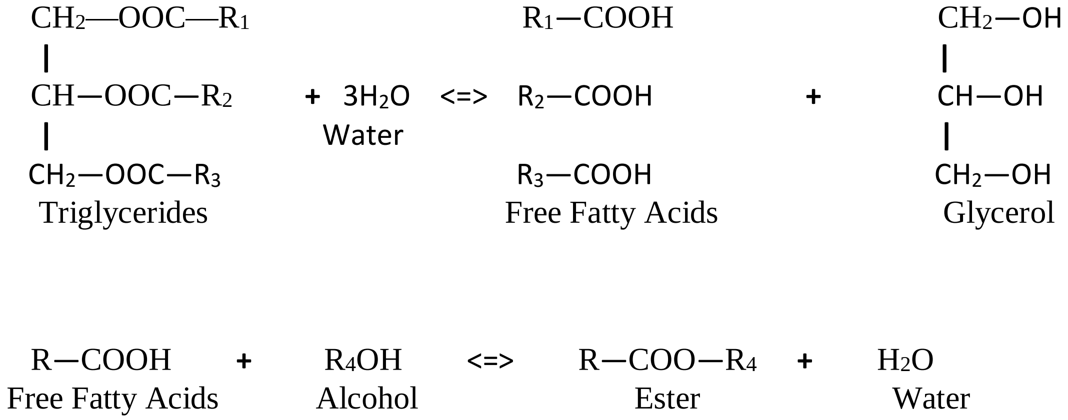
9275 thousand metric tons per year with in the US. As a result, soybean waste cooking oil is an essential feedstock for producing biodiesel in the US [13]. Even though there are several methods that can be used to produce biodiesel, using waste cooking oils as feedstock can address several challenges faced by each method. For example, the alkali-catalyzed transesterification method is very sensitive to feedstock containing more than 0.5% free fatty acids [14–17]. Also, the acid-catalyzed transesterification method can't handle feedstocks with a high presence of water [18]. The supercritical methanol method is reported as promising because this method can successfully tolerate the high water and free fatty acid content in feedstocks [18–20]. On the other hand, the supercritical methanol method, especially the one-step method, needs harsh reaction conditions, e.g. high temperature and pressure [20].

The objective of this study was to evaluate the efficacy of the one-step method to produce biodiesel from soybean oil reacted with methanol mixed with water at subcritical conditions. Numerous experiments were conducted in batch and continuous systems in order to understand the effects of a variety of parameters on the yield of fatty acid methyl esters (biodiesel). The impacts of four reactions (transesterification, hydrolysis, esterification, and degradation) depicted in Fig. 1, 2, and 3 were observed in this work. Additionally, a kinetic model was developed to describe the effects of these four reactions, especially the degradation reaction.



$$\begin{array}{lcccccc} CH_2\text{—}OOC\text{—}R_1 & & & & R_1\text{—}COO\text{—}R_4 & & CH_2\text{—}OH \\ | & & & & & & | \\ CH\text{—}OOC\text{—}R_2 & + & 3R_4OH & \Leftrightarrow & R_2\text{—}COO\text{—}R_4 & + & CH\text{—}OH \\ | & & \text{Alcohol} & & & & | \\ CH_2\text{—}OOC\text{—}R_3 & & & & R_3\text{—}COO\text{—}R_4 & & CH_2\text{—}OH \\ \text{Triglycerides} & & & & \text{Esters} & & \text{Glycerol} \end{array}$$

Fig. 1. Transesterification Reaction of Triglycerides (route one).



$$\begin{array}{lcccccc} CH_2\text{—}OOC\text{—}R_1 & & & & R_1\text{—}COOH & & CH_2\text{—}OH \\ | & & & & & & | \\ CH\text{—}OOC\text{—}R_2 & + & 3H_2O & \Leftrightarrow & R_2\text{—}COOH & + & CH\text{—}OH \\ | & & \text{Water} & & & & | \\ CH_2\text{—}OOC\text{—}R_3 & & & & R_3\text{—}COOH & & CH_2\text{—}OH \\ \text{Triglycerides} & & & & \text{Free Fatty Acids} & & \text{Glycerol} \end{array}$$

$$\begin{array}{ccccccc} R\text{—}COOH & + & R_4OH & \Leftrightarrow & R\text{—}COO\text{—}R_4 & + & H_2O \\ \text{Free Fatty Acids} & & \text{Alcohol} & & \text{Ester} & & \text{Water} \end{array}$$

Fig. 2. Hydrolysis and Subsequent Methyl Esterification Reactions (route two).

$R\text{—}COO\text{—}R_4 \Longrightarrow$ by products

Fig. 3. Degradation reaction of fatty acids methyl esters.

CHAPTER 2: LITERATURE REVIEW

2.1. Converting Vegetable Oils to Diesel Fuels

In order to use vegetable oil as diesel fuels, the properties of vegetable oil should be improved by reducing the viscosity, increasing volatilities, and changing the cold flow properties [21]. Viscosity is the main property that can affect using vegetable oil as fuels. Microemulsification, dilution with hydrocarbons (blending), pyrolysis (thermal cracking), and transesterification (alcoholysis) are the main methods used to reduce the viscosity of vegetable oil. The most used method among these four methods is transesterification, which generates monoalkyl esters known as biodiesel [21–23].

2.1.1. Microemulsification

In microemulsification, several components, such as oil, water, surfactant, and sometimes a small amphiphilic molecule (co-surfactant), disperse together to make isotropic, transparent, thermodynamically stable microemulsion fluid [23–25]. Vegetable oils with an ester and dispersant (cosolvent), or an alcohol and a surfactant can be used to make microemulsions. Using an alcohol in microemulsification can produce an alternative diesel fuel with low volumetric heating values compared to petroleum diesel fuels. However, the alternative diesel fuel produced from alcohol in microemulsification can have latent heat of vaporization higher than that in petroleum based fuels. Using this alternative diesel fuel can reduce the heat of the combustion chamber and decrease the nozzle coking in diesel engines [25].

Several ionic and non-ionic microemulsion fuels, with differing performance, were prepared and reported in the literature. For example, a non-ionic emulsion of 33.4% (v/v) 1-

butanol, 13.3% (v/v) 190-proof ethanol and 53% (v/v) alkali-refined and winterized sunflower oil, which had a viscosity of 6.31 cSt at 40°C, was prepared by Ziejewski et al. [26]. Furthermore, in the Engine Manufacturers Association (EMA), the 200 hrs EMA screening test was performed to test the quality of the ship non-ionic (SNI) fuel, which consists of 20% 1-butanol, 50% No. 2 Diesel fuel, 5% 190-proof ethanol and 25% degummed and alkali-refined soybean oil. The SNI fuel successfully passed the 200 hrs test. However, at the end of the test, several issues were apparent, such as coating the injector tips, tops of the cylinder linear and tulips of the intake valves by carbon and lacquer accumulations [27,28].

2.1.2. Dilution

In the dilution method, vegetable oil is blended with diesel fuels, a solvent or ethanol to produce an alternative diesel fuel [29]. For example, sunflower oil was diluted with diesel with a volume ratio of 1:3 (sunflower oil to diesel) to prepare a diesel fuel [30]. The viscosity of this blend is (4.88 cSt at 40 °C), which is higher than the maximum ASTM viscosity value (4.0 cSt at 38 °C). The long-term use of this blend as direct injection diesel engines was not successfully performed due to the severe coking and sticking in the injector nozzle [18,21,31]. Table 1 shows several examples of alternative diesel fuels prepared by using the dilution technique.

Table 1

Several alternative diesel fuels produced by dilution technique

Blend	Ratio (v/v%)	Viscosity (cSt)	Comments
Sunflower oil to diesel	25:75	4.88 at 40 ºC	Not good for long term use [21]
High-oleic safflower oil to diesel	25:75	4.92 at 40 ºC	Passing the 200 hr EMA test [23].
Winter rapeseed oil to No.1 diesel fuel	30:70	-------	Working for 850 hr with no problems [27].
Winter rapeseed oil to No.2 diesel fuel	15:85	-------	--------------------------------------[27].
Safflower oil to No.2 diesel fuel	20:80	-------	Reducing CO and hydrocarbon emissions [32].
Crude sunflower oil to diesel fuel	25:75	-------	Generating high solids contamination in the lubricating oil [33]
Canola oil to diesel fuel	75:25 50:50	40 at 10 ºC 19 at 10 ºC	-------------------------------------[34]
Canola oil to pure ethanol	90:10	21.15 at 37 ºC	--------------------------------------[34]
Soybean oil to Stoddard solvent	50:50	5.12 at 38 ºC	Passing the 200 hr EMA test [35].
Unrefined soybean oil to diesel fuel	75:25	--------	Not good for working more than 159 hr [36].

2.1.3. Pyrolysis

In pyrolysis (thermal cracking), alkanes, alkenes, alkadienes, carboxylic acids, and aromatics are produced by thermal degradation of vegetable oils, which includes heating in the absence of oxygen [37]. Alkane and alkenes are the dominant products with 60% of the total weight, while carboxylic acids are generated with a weight fraction of 9.6-16.1% [7,38]. There are three types of pyrolysis: conventional, fast, and flash, which are classified according to the operation conditions [31]. Fig. 4 shows the thermal cracking mechanism of triglycerides [21]. Several studies have been done on the pyrolysis of vegetable oils to produce fuels, especially during world wars I and II. For instance, tung oils were converted to hydrocarbons, which were used as feedstocks to produce gasoline and diesel in China during world war II [39]. Animal fats, natural fatty acids, and methyl esters can be used as feedstocks for the pyrolysis process [40]. Also, several types of vegetable oils were converted to fuels by using the pyrolysis process, such as soybean [37,39,41], rapeseed [42], olive husk [43], castor [39], palm tree [39,44], tung [45], and safflower [42].

Pyrolysis of soybean oil was performed to produce a fuel with a cetane number of 43, which is higher than that of soybean oil (37.9) and the minimum value of ASTM (40) [37]. The pyrolyzed soybean oil had a viscosity of (10.2 cSt) at 38°C, which passed the viscosity of No.2 diesel fuel (1.9-4.1 cSt) according to the ASTM specification, but was still lower than the viscosity of soybean oil (32.6 cSt) [46]. Cottonseed oils produced from the frying process were also pyrolyzed by using a catalyst of Na_2CO_3 at 450°C to generate a product with 70% alkanes, especially C8 to C20. The properties of pyrolyzed cottonseed oils were lower than those of diesel fuel, such as cetane number, flash point, and viscosity [47]. Furthermore, pyrolyzate of rapeseed oil methyl esters were prepared in nitrogen dilution methyl esters at 550 to 850°C to give mainly linear 1-alkenes, straight-chain alkenes, unsaturated methyl esters, and a small amount of CO, CO_2, and H_2 [42]. Vegetable oils and fats can react with NaOH to produce Na soaps as shown in Fig. 5 (a). Then Na soaps were pyrolyzed to generate hydrocarbon rich products as depicted in Fig. 5 (b) [43,48]. Reaction temperature is a significant parameter in pyrolysis of vegetable oil soaps. Increasing the reaction temperature leads to an increase in the yield of decarboxylation products. For instance, the yields of pyrolyzed soybean oil soaps were 2.9 and 97.8 (w/w%) at 127 °C and 337° C, respectively [31].

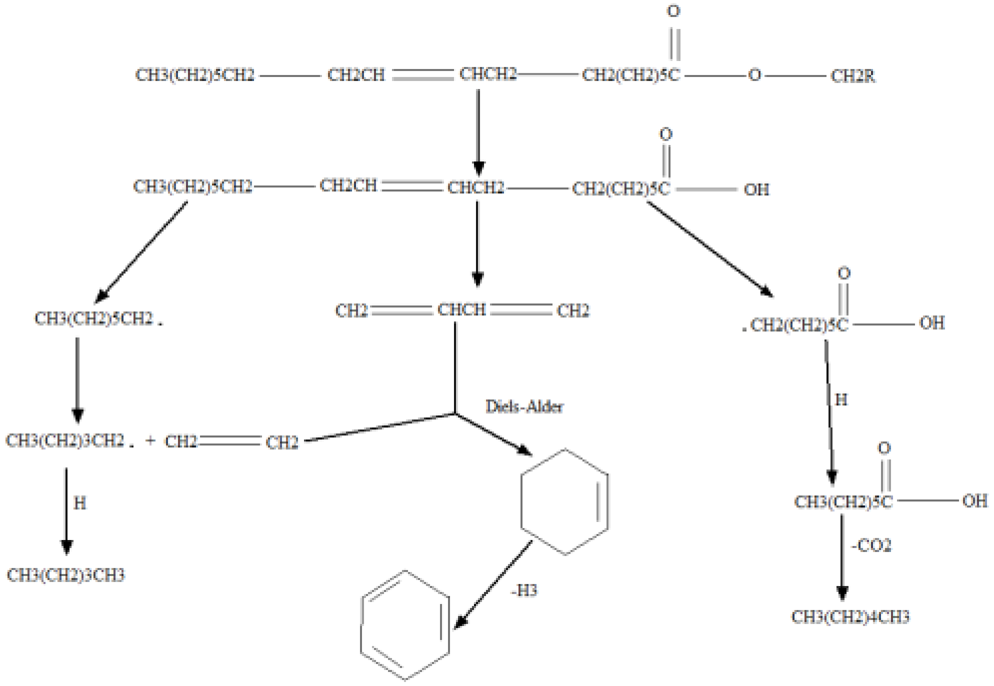


Fig. 4. Mechanism of triglyceride pyrolysis (thermal cracking) [37].

Vegetable oils or fats + NaOH ===> RCOONa + Glycerin (a)

2RCOONa + ½ O_2 ===> R–R + Na_2CO_3 + CO_2 (b)

Fig. 5. (a) saponification reaction, (b) pyrolysis of sodium soap reaction [31].

2.1.4. Transesterification (alcoholysis)

Transesterification is described as a reaction that mainly occurs between triglycerides and low molecular weight alcohols (methanol, ethanol, or propanol) to produce fatty acid methyl esters and glycerol [18,27,49]. This reaction was invented by Rochieder to prepare glycerol from castor oil in 1846 [50]. After that, several studies have been carried out to produce biodiesel from vegetable oils and animal fats by using transesterification reactions [19,51–55]. The transesterification reaction can occur in the presence of a catalyst in order to push the reaction to the desired product at high yields. This catalyst can be an acid, or a base, and either homogeneous or heterogeneous. Furthermore, it can be an enzyme [56–76]. The transesterification of triglycerides or fats can also be performed using non-catalytic methods (supercritical methanol), which employ high temperatures and pressures [49,77–79]. In some cases, a two-step process can be used [80–82]. In the two-step process, the transesterification reaction was replaced by a hydrolysis reaction followed by an esterification reaction.

2.1.4.1. Catalytic transesterification

Catalytic transesterification, which consists of acid or alkali catalyzed transesterification, is the most commonly used method for producing biodiesel in industry due to the use of catalysts that are low in cost and more efficient [61,83]. In the alkali-catalyzed method, sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (CH_3ONa), or potassium methoxide (CH_3OK) are employed as homogeneous catalysts [84]. The activity of sodium or potassium methoxide is more than that of sodium or potassium hydroxide, but the latter group of catalysts is less expensive [84,85]. The main obstacle of using the alkali-catalyzed method is the presence of free fatty acids and water (more than 0.1%), which form soap that require complicated and expensive separation methods [15,17,56,86]. Odin et al. [87] used the alkali-catalyzed method at 60^oC and 4 hrs with a 1:9 molar ratio of oil to methanol and 2.5% (w/w) (CH_3ONa) catalyst to produce biodiesel with a yield of 98.6%.

To minimize separation problems and increase catalyst recovery, heterogeneous base catalysts have been used to produce biodiesel, such as basic zeolites [88], hydrotalcites [71,72,89,90], alkaline earth oxide base catalysts [91], and alkaline metal salts on porous support [16,88,92]. In heterogeneous base catalysts, soybean oil has been converted to fatty acid methyl esters with a conversion of 95% using CaO, SrO as a catalyst at 65^{o}C and 0.5-3 hr residence time with 12:1 methanol to oil molar ratio [93,94]. Also, a conversion of 94.6% was observed in transesterification of soybean oil in the presence of ETS-10 as a catalyst under conditions of 120^{o}C, 24 hr residence time, and 6:1 methanol to oil molar ratio [76,88]. Mg-Al HT catalyst was employed to generate biodiesel from rapeseed oil with a conversion of 90.5% at 65^{o}C, 4 hr residence time, and 6:1 molar ratio of methanol to oil [76,95].

In acid-catalyzed transesterification, sulfuric (H_2SO_4) [96], hydrochloric (HCL) [96,97], or sulfonic acid (RSO_2OH) [76] is utilized as a homogeneous catalyst for biodiesel production. The acid-catalyzed method requires a high molar ratio of alcohol to oil (20:1 – 40:1) and large amounts of catalyst (5-25%) [98,99]. Furthermore, this method needs a very long reaction time, unlike the alkali-catalyzed method [15]. However, acid catalysis can be used directly to convert feedstocks with high free fatty acids, which is considered a main disadvantage in alkaline catalysts [15,99]. Soybean oil was reacted with methanol in the presence of 1% H_2SO_4 (mole/mole) to give a 99% conversion efficiency under conditions of 65^{o}C, 30:1 molar ratio of methanol to oil, and 50 hr reaction time [100]. Using heterogeneous acid catalysts is the key to reduce corrosion and separation problems incurred in homogeneous acid catalysts, but synthesizing a solid acid catalyst with high activity toward the desired product is not easy [76]. Zeolites [64], heteropoly acids [65], and functionalized zirconia and silica [101] are the major kinds of heterogeneous acid catalysts. To achieve 99% biodiesel yield, 0.185% (w/w) $Cs_{2.5}PW$

(heteropoly acid catalyst) was employed at 65^{o}C, 40 min, and 5.3:1 methanol to oil molar ratio. This catalyst was found to be highly active and suitable to use for feedstock with high content of free fatty acids and water [65].

The enzyme catalyzed transesterification method was also used to produce biodiesel using several enzymes, such as *Candida rugasa* [102], immobilized lipase (Lipozyme RMIM) [75,103], *Rhizomucar miehei* [104], *Candida antarctica* [105], or *Pseudomonas* spp. [104]. Each kind of enzyme can provide a different yield. For example, Bernardes et al. [75] reported that 60% biodiesel yield was achieved in 1 hr at 50^{o}C, and 3:1 molar ratio of ethanol to oil by using immobilized lipase (Lipozyme RMIM) with a concentration of 7% (w/w). Furthermore, in another study, P. *cepacia* was utilized to produce biodiesel with a yield of 98% at 50^{o}C and 8 hr reaction time with 4-5% (w/w) water content [106]. Enzyme catalyzed transesterification can generally perform at moderate temperature (30-40^{o}C) to produce a high biodiesel yield. Also, this technique can tolerate feedstocks with high water and free fatty acid content, which can affect the yield of biodiesel in other methods [24,107]. The main drawbacks for the enzyme catalyzed transesterification method are the long reaction time and the enzyme high cost and sensitivity to impurities [73].

2.1.4.2. Non-catalytic transesterification

Non-catalytic transesterification at supercritical methanol temperature is another method used to convert triglycerides and free fatty acids simultaneously into biodiesel. A one-step catalyst-free method was conducted at temperatures and pressures above the critical temperature and pressure for methanol (240 ^{o}C and 8.1 MPa) [14,19,108]. In a study by Saka et al. [109], it was found that biodiesel can be generated with a yield of 97% at 350 ^{o}C, 43 MPa, and 42:1 molar ratio of methanol to rapeseed oil in 4 min. reaction time. In addition, Demirbas [79] reported that 250^{o}C and 41:1 molar ratio of methanol to hazelnut kernel oil are the optimum conditions to produce biodiesel with a yield of 95% in 5 min. Vegetable oils with high free fatty acid and water content can directly convert to biodiesel with high yields in this process. Also, diffusion and separation problems are reduced due to using the free catalyst method [77,110]. On the other hand, the free catalyst method requires consuming a huge amount of energy for recovering unreacted methanol and reaching the high reaction conditions (temperature and pressure) [7].

The non–catalytic transesterification method can also be employed in two-steps (hydrolysis followed by esterification) [82,111]. Vegetable oils are hydrolyzed to free fatty acids as a first step in free catalyst sub- and supercritical water at 260-280^{o}C and 15-20 min reaction time [112]. In the second step, free fatty acids react with methanol to produce fatty acid methyl esters with a complete conversion at 300 ^{o}C and 12 min reaction time [111]. Several studies showed that alkyl esterification requires a lower reaction temperature than that of transesterification [113,114]. Thus, hydrolysis followed by esterification is a promising method due to its ability to decrease the reaction temperature, eliminate the diffusion and separation problems, and tolerate feedstocks with high water and free fatty acid content.

CHAPTER 3: HYDROLYSIS, ESTERIFICATION, AND TRANSESTERIFICATION REACTIONS IN ONE STEP TO PRODUCE BIODIESEL AT SUBCRITICAL CONDITIONS

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Abstract

In this study, a one-step method at subcritical methanol conditions was conducted in both tubular and batch reactors using methanol (MeOH), soybean oil (SBO), and water (H_2O) to produce biodiesel. This method was evaluated studying a variety of variables in order to determine the optimum conditions used to produce biodiesel, including the reaction temperature (230-330 ^oC), the oil to methanol molar ratio (1:28-1:48), pressure (6.9 MPa), and reaction time (20-480 min). The water to oil molar ratio in the reacted materials also varied from 11 to 42. The results showed that the oil to methanol to water molar ratio (1:39:22), and 120 min reaction time at 6.9 MPa and 265^{o}C were the optimum subcritical conditions for producing biodiesel with a yield of 79 %. In addition, supercritical conditions were performed in the batch reactor by changing the pressure from 6.9 to 10.9 MPa, which increased the yield to 90.15% mainly due to putting all the components in a single phase, which was determined by a ASPEN simulation of the process. The reaction kinetics were modeled using existing models for hydrolysis, esterification, and transesterification. It was found that the model fit well if degradation by – products were considered. Overall, this is one of the first studies on subcritical biodiesel productions using a mixture of triglycerides and free fatty acids.

Keywords: Biodiesel, subcritical conditions, one-step, soybean oil

3.1. Introduction

Biodiesel, which mostly consists of fatty acid methyl esters (FAMEs), is a renewable source of energy. Using biodiesel can therefore minimize environmental effects and our dependence on fossil fuels because petroleum diesel fuel contributes to global warming and an unstable economy. FAMEs can be produced in several ways that depend on a general reaction called transesterification (alcoholysis). This reaction occurs between plant oils or animal fats and alcohol, such as methanol or ethanol. This reaction can be implemented by one of two procedures: catalytic transesterification or non-catalytic supercritical methanol transesterification [1–3]. Several studies investigated supercritical reaction processes but few, if any, have considered one reactor conversion of triglycerides to FAMEs in a subcritical environment. The subcritical reaction of these products allow for a lower pressure operation and thus lower capital and operating costs [4]. Thus, the objective of this study was to investigate the viability of a one-step method including hydrolysis, methyl esterification, transesterification, and degradation reactions to produce biodiesel fuel at moderate conditions (temperature and pressure). In this work, a model was developed to describe these four reactions.

Catalytic transesterification is the most common process for producing biodiesel fuel [3]. It can be divided into alkali, acid, and enzyme-catalyzed transesterifications [1,3]. However, in alkali-catalyzed transesterification, using oil containing a high percentage of free fatty acids can lead to an increase in the by-product reaction, which happens between free fatty acids and an alkaline catalyst. As a result, this reaction generates soaps that demand a complicated expensive procedure to purify the final products [5,6]. In contrast, the acid-catalyzed transesterification process is suitable to use with oils that have high concentrations of free fatty acids, but has a very long reaction time [7]. In general, the catalytic transesterification method is also very sensitive to water presence due to the soap formation [8]. A one-step subcritical reaction has the potential to be inexpensive, rapid, and have low capital costs.

Non-catalytic supercritical methanol transesterification is considered another method for producing biodiesel. Transesterification of triglycerides and methyl esterification of free fatty acids are processed simultaneously in non-catalytic supercritical methanol to produce a high yield of FAMEs [9–11]. In addition, the non-catalytic method can handle high water contents to produce FAMEs of high quality, unlike acid and alkali-catalyzed transesterifications [12]. This method was performed at 350 ^{o}C, 43 MPa, 42:1 molar ratio of methanol to triglyceride, with 4 min reaction time in order to produce biodiesel at high yield of 97% [13]. Some studies, however, showed that a high ratio of alcohol to oil and harsh temperature and pressure conditions are the main economic obstacles for producing biodiesel, especially in a one-step supercritical methanol method [1]. The primary reason for this is high costs and safety concerns.

Hydrolysis and subsequent methyl esterification reactions are considered another path to produce biodiesel instead of transesterification. Hydrolysis of vegetable oil (fat splitting) is performed by lipase-catalyzed, acid/alkaline-catalyzed, or a non-catalytic method [14–16]. An alkaline-catalyzed vegetable oil hydrolysis (basic process) was employed for 6-10 hr reaction time at 180 ^{o}C and 1 MPa to achieve a yield of 95% [17]. On the other hand, the acid-catalyzed method (acid splitting) was processed for 20 to 48 hr reaction time at water boiling point temperature in an open stream (atmospheric pressure) to give 85% yield in one-step [15]. The catalyst-free method at sub- and supercritical water was also used to hydrolyze vegetable oil at temperatures of 260-280 ^{o}C with a reaction time of 15-20 min reaction time to produce free fatty acids with a yield of more than 97% [18].

In methyl esterification, free fatty acids generally react with methanol by using the acid-catalyzed method at the boiling point of methanol. Methyl esterification could also be processed in non-catalytic supercritical methanol method at a temperature of 350 ^{o}C although the reaction pressure will be high [4,9]. Furthermore, alkyl esterification of fatty acids and transesterification of vegetable oil were studied in a batch reactor at 300 ^{o}C by using supercritical alcohol method [19]. This study showed that the reaction rates of alkyl esterification was faster than those of transesterification. In addition, the reaction temperature of alkyl esterification was lower than that of transesterification suggesting that a single step hydrolysis followed by esterification might be a desirable method for producing biodiesel.

3.2. Material and Method

3.2.1. Materials

Refined vegetable oil (soybean oil; Wesson, OMAHA, NE) was purchased from a neighborhood market. Methanol, isopropyl alcohol, acetone and hexane (all HPLC grade 99%) were purchased from VWR International. Two standards: Marine Oil FAME MIX (20 components) and methyl heptadecanoate (C17) were obtained from Restek Corporation. Marine Oil FAME MIX was used as an external standard to determine the retention time for methyl esters in the samples, while methyl heptadecanoate was used as an internal standard to maintain analysis performance and calculate the FAME concentration. Potassium hydroxide pellets and phenolphthalein powder were also purchased from VWR international to use in Free Fatty Acids (FFA) analysis.

3.2.2. Apparatus and Procedure

Two systems were used to produce biodiesel fuel in this study. In the first system (see Fig. 6), a 207 ml tubular reactor (seventeen 3/8’’ outside diameter by 12” (eight) and 4” (nine) long, 316 SS tubes, connected in series in a harp arrangement) was employed. Each of the straight section of tubing had a segmented twisted tape (L/D = 1/5) mixer inside it to provide radial mixing. The mixer units were connected with Swagelok elbows and fittings to form a rectangular coil. The tubular reactor was mounted inside a stainless-steel tank (6” x 6” x 18”) filled with sand (sand bath). At the wall of the tank, four electrical strips heaters were affixed to two Variac variable voltage autotransformers for power. To insulate the sand bath, a DUROCK cement board (1/2” thick) box (15” x 15” x 23”) filled with vermiculite was used to hold the stainless-steel sand bath tank. Two HPLC pumps (Water 501), one in use and one standby, were utilized to feed the reactor with a mixture of methanol and water. Each HPLC pump was connected to a 500 ml graduated feed reservoir. The HPLC pump provided flow rates ranging from 0.1 to 9.9 ml/min. Soybean oil was also pumped to the reactor by using two syringe pumps (ISCO 100D), one in use (265ml) and one standby (125ml), with flow rate capabilities ranging from 0.3 to 7 and 0.5 to 15 ml/min, respectively. Methanol and soybean oil flowed through 1/8” (diameter) 316 stainless-steel tubing after leaving their individual pumps.

Before entering the reactor, methanol water mixture and soybean oil were mixed together in a T-joint. The mixture of reactant materials then entered the tubular reactor. The reactor temperature was increased to the desired temperature by controlling the Varics. Nine Omega K-type thermocouples were hose clamped to the mixer outlets and were used to control the reactor temperature. Eight sheathed thermocouples were placed at different positions inside the sand bath. The ninth thermocouple was located at the exit of the reactor and was considered the reaction temperature. All the temperature data were recorded using DAQami Data Acquisition Companion Software, and USB DAQ Data Acquisition purchased from MEASUREMENT COMPUTING.

The product from the reactor continued flowing into a double pipe heat exchanger cooler to quench and stop further reactions. Two product reservoirs (247 ml and 458 ml) were affixed to the end of the system to collect the final product after leaving the heat exchanger (cooler). These two reservoirs provided sufficient operating time by switching between them until steady state was obtained. A nitrogen cylinder was used to pressurize the system to 6.9 MPa. The system pressure was controlled by using a vent valve placed between the product reservoirs with several pressure gauges. Product samples were always collected from a 247 ml product reservoir after depressurizing the whole system.

A variety of reaction temperatures (265-330 ^{o}C) was investigated. Also, the molar ratio of oil to methanol and oil to water ranged from 1:28 to 1:48 and 1:11 to 1:42, respectively. Pressure was maintained at 6.9 MPa. Finally, the reaction time varied between 20 and 60 min. Each experiment was conducted with a total elapsed time of 12 hours. The first 6 hours were the preheated time to reach steady state condition. During the preheated time, the reactor was filled with a mixture of methanol and water until the desired temperature was reached. The system was then pressurized using a nitrogen cylinder up to 6.9 MPa. The flow ratio of reactants was adjusted to ~~get~~ obtain the desired value. The mass and thermal steady states were reached after one residence time. In order to make sure that a kinetic steady state was also reached, all the samples were collected after five reactor volumes had flowed after reaching steady state.

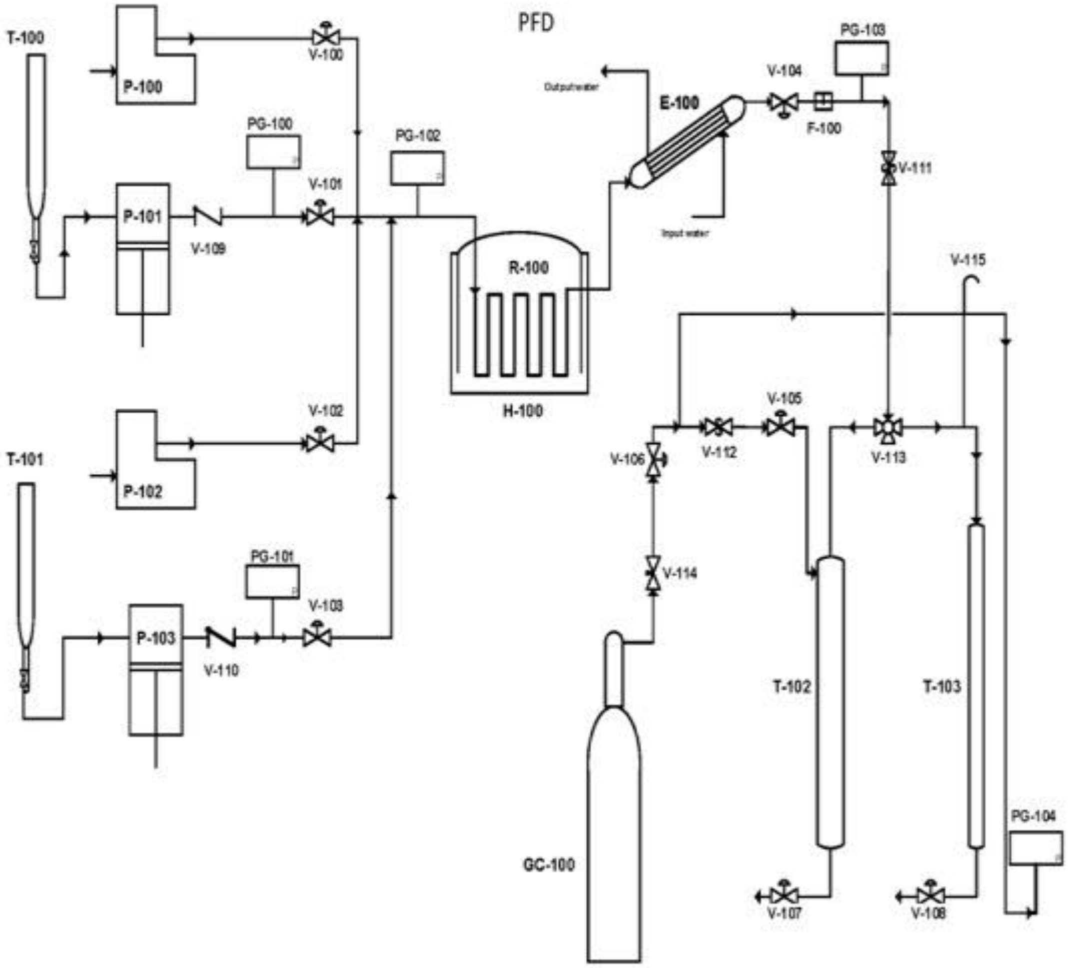

Fig. 6. Biodiesel production system using tubular reactor (continuous system). *T-100 and T-101, methanol water mixture feed reservoirs; P-100, Syringe oil pump; P-101, HPLC methanol pump; P-102, Syringe oil pump stand by; P-103, HPLC methanol pump stand by; H-100, sand bath; R-100, tubular reactor; E-100, cooler; T-102 and T-103, product reservoirs; GC-100, nitrogen cylinder; V-100 to V-108, valve; PG-100 to PG-104, pressure gage; V-109 and V-110, check valve; V-111 and V-112, relief valve; F-100, filters; V-113, 3-way plug valve; V-114, needle valve and V-115, vent valve.*

In the second system, a Parr Instruments 4520 series, 2-L reactor was used to produce biodiesel. This 316 stainless steel reactor can handle a maximum temperature and pressure of 350 ^{o}C and 1900 psia, respectively. The reactor was charged with a desired molar ratio of soybean oil to methanol to water and heated to reach thermal steady state using a 1500 watt Calrod-type sheathed element heater. The temperature and pressure of the reactor were measured using a type-J, sheathed thermocouple connected to a reader (Omega HH82A thermocouple) and a pressure gage ranged from 0-13.78 MPa. The reaction temperature was maintained using a temperature controller (MYPIN® TA4) with an accuracy of ± 3 ^{o}C. A magnetic stirrer was placed inside the reactor to provide a sufficient agitation to improve mixing. Also, a spiral cooling-water coil was employed inside the reactor in order to quench and stop further reactions.

In the batch system, the reaction temperature and pressure were varied from 230 to 301 ^{o}C, and 5.1 to 17.5 MPa, respectively. The reaction time was tested in the range of 60 to 480 min. The molar ratio of soybean oil to methanol to water was held constant at 1 to 39 to 22. After each experiment, the reactor was allowed to cool for at least 6 hours. Afterwards, the mixture inside the reactor was placed in a 1000 mL container for analyses.

3.2.3. Analysis

Two immiscible layers were observed in each sample collected from the previous two systems. These two layers were separated overnight by using a separatory funnel. Methanol, water and glycerin were the main components in the top layer, while biodiesel and unreacted oil mixture saturated with methanol was the main component in the bottom layer. Methanol was removed from each layer by using a Graham Condenser at 90 ^{o}C in order to prepare each layer for analysis. Gas Chromatograph (GC-2014; Shimadzu) with an auto injector (AOC-20i), auto sampler (AOC-20s), and a flame ionization detector (FID) was used to analyze the final biodiesel product and standards. The column employed in this set up for the separation was Zebron ZB-WAX (30 m × 0.25 mm I.D. × 0.25 μm film thickness) supplied from Phenomenex Inc. The carrier gas used was Helium at 1:30 split ratio and 1.02 ml/min column flow rate. The injector and detector temperatures were 220 ^{o}C and 250 ^{o}C, respectively. The oven temperature was started at 160 ^{o}C for 0 min holding time, then ramped up 5^{o}C/min to 200 ^{o}C with a holding time of 25 min [20].

The samples were prepared prior to analyzing by weighing 0.1 gm of biodiesel and diluting it in 1.5 ml of standard solution (1 mg/ml methyl heptadecanoate). The standard solution was made by adding methyl heptadecanoate, the internal standard, to hexane. After preparing samples, 0.5 µL of each sample was injected into the column. To identify the peak area for the compounds in each sample, the retention times of the external standard compound were compared to that in the samples. The FAMEs' concentration was calculated by using the internal standard according to the EN standard method.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) purchased from PerkinElmer Inc. was performed to analyze FAME samples as a qualitative method. A Zinc Selenide (ZnSe) crystal was employed in the ATR sampling accessory in the horizontal position. In these experiments, 1 ml of the FAME was utilized to achieve a sufficient contact with the crystal. Before analyzing any sample, the background spectrum was measured by using a clean sampling accessory, especially for air. All spectra were performed with a resolution of 4 cm^{-1} and a wavenumber range from 650 to 4000 cm $^{-1}$. The ATR-FTIR spectra were also used to explain the thermal degradation effects that occurred in the FAME samples. The water content was calculated as well by using a DL31 Volumetric Karl Fischer (KF) Titrator supplied from Mettler-Toledo International Inc. In addition, a titration method was used to measure % FFA in biodiesel. KOH (1 N) was utilized as a titrant into a mixture of 1-4 gm sample, 50 mL of 50/50 isopropyl alcohol and acetone, and a few drops of phenolphthalein. The

KOH was added one drop at a time while sufficiently mixing until getting a pink color. The titration method of each sample was performed in triplicate to get accurate results. In each titration, the volume of KOH was recorded and applied in Eq. (1) to calculate the % FFA [21].

$$\% \, FFA = \frac{\text{Titrant(mL)} * KOH \ normality * 28.25}{\text{Sample Weight (gm)}} \tag{1}$$

3.3. Results and Discussion

In this research, two system configurations (continuous and batch) were used to produce FAMEs from SBO. This allowed for the simulation of large time differences in experimentation. All the experiments were processed in triplicate and the results were depicted as a mean value with a very small error (shown on the graph with small error bars). This study showed the effect of four reactions (transesterification, hydrolysis, esterification, and degradation) on the yield of FAMEs. Fig. 7 and 8 show the effect of reaction time on the yield of FAMEs in continuous and batch systems, respectively, at different temperatures. Overall, reaction time influenced maximum FAME yields in Fig. 7 and 8. In Fig. 7 at 265 ^{o}C, an increase in reaction time from 20 min to 60 min produced a 26.49% increase in yield. On the other hand, 50.6% and 38.7% yield increases were observed from 20 min to 40 min at 301 ^{o}C and from 20 min to 30 min at 330 ^{o}C, respectively. At 301 ^{o}C, the maximum yield of the reaction was reached in 40 min, while it was 30 min at 330 ^{o}C. Increasing the reaction time further can lead to reduce the FAME yield as depicted in Fig. 7. This is thought to be the result of a degradation of the biodiesel due to long times at high temperature. In a study by He [22] (1:40 molar ratio of SBO to MeOH and 32 MPa), the same phenomena were observed, but at lower reaction times. These differences can be due to the differences in the experimental conditions between these experiments, especially pressure. Fig. 8 demonstrates that the optimum conditions for generating a maximum FAME yield (79.5%) in a batch system were 265 °C, and 120 min reaction time at 6.9 MPa. In Fig. 8, it is apparent that the optimum reaction time at both 265 °C and 301 °C was 120 min.

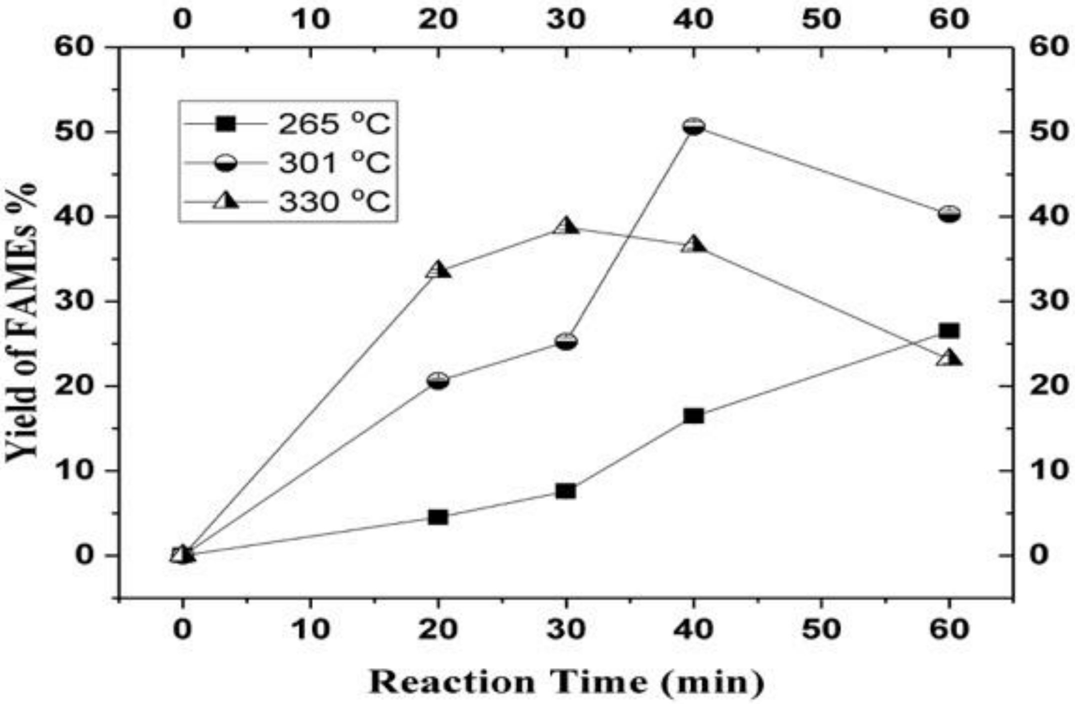

Fig. 7. Effect of reaction time on yield of fatty acid methyl esters (FAMEs) at various temperatures in continuous system (P = 6.9 MPa, SBO:MeOH:H2O = 1:39:22).

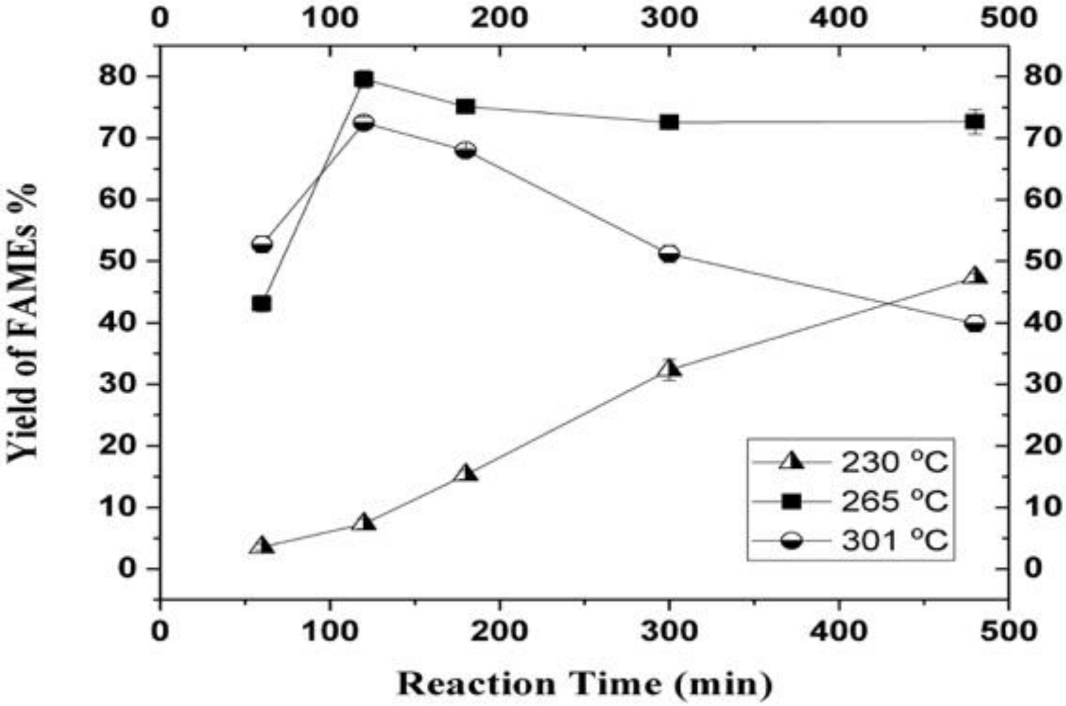

Fig. 8. Effect of reaction time on yield of fatty acid methyl esters (FAMEs) at various temperatures in batch system (P = 6.9 MPa, SBO:MeOH:H2O = 1:39:22).

The degradation reactions (thermal decomposition, dehydrogenation, and cis-trans isomerization) of poly unsaturated FAMEs, especially Methyl linoleate (C18:02) and Methyl linolenate (C18:3), were the main reason for the decrease of FAMEs after passing the critical point of reaction time. Imahara [23] reported that saturated fatty acid methyl esters were stable at temperatures below 300 °C, while the unsaturated fatty acid methyl esters, especially poly unsaturated fatty acid methyl esters, were stable at 270 °C and thermal decomposition became more obvious at 300 °C or more.

To test the hypothesis of He and Imahara in this single phase subcritical reaction conditions, a GC analysis was made of the degradation by-products. Fig. 9 and 10 present the effect of degradation reactions on the yield of FAME at different temperatures in batch and continuous systems, respectively. The FAME chromatograms show that the peaks of poly unsaturated fatty acid methyl esters split off to several peaks by increasing the temperature from 230 ^{o}C to 330 ^{o}C. A similar degradation effect was reported from Kusdiana et al., Saka et al., and He et al. but at different reaction times and temperatures [9,11,22,24].

Furthermore, the types of bonds attacked in the degradation was investigated using ATR-FTIR. Fig. 11 shows the ATR-FTIR spectra at different reaction times in batch and continuous systems. The absorbance of $C=C_{(cis)}$ peak at wavenumber of 665 (cm^{-1}) decreased by increasing the reaction time from 120 to 480 min and 30 to 60 min in batch and continuous systems, respectively, whereas the formation of the absorption peak of $C=C_{(trans)}$ (965 cm^{-1}) was observed clearly by increasing the reaction time from 120 to 480 min and 30 to 60 min. The change from $C=C_{(cis)}$ to $C=C_{(trans)}$ was a main effect seen in biodiesel degradation. This change can occur due to the formation of a C-11 free radical (autoxidation). The C-11 free radical can simply convert to two conjugated forms (C-9 and C-13), which are more stable forms than C-11 [25]. In addition, the same ATR-FTIR spectra behavior was noticed in Fig. 12 at different temperatures showing that regardless of temperature the degradation by-products are likely the same.

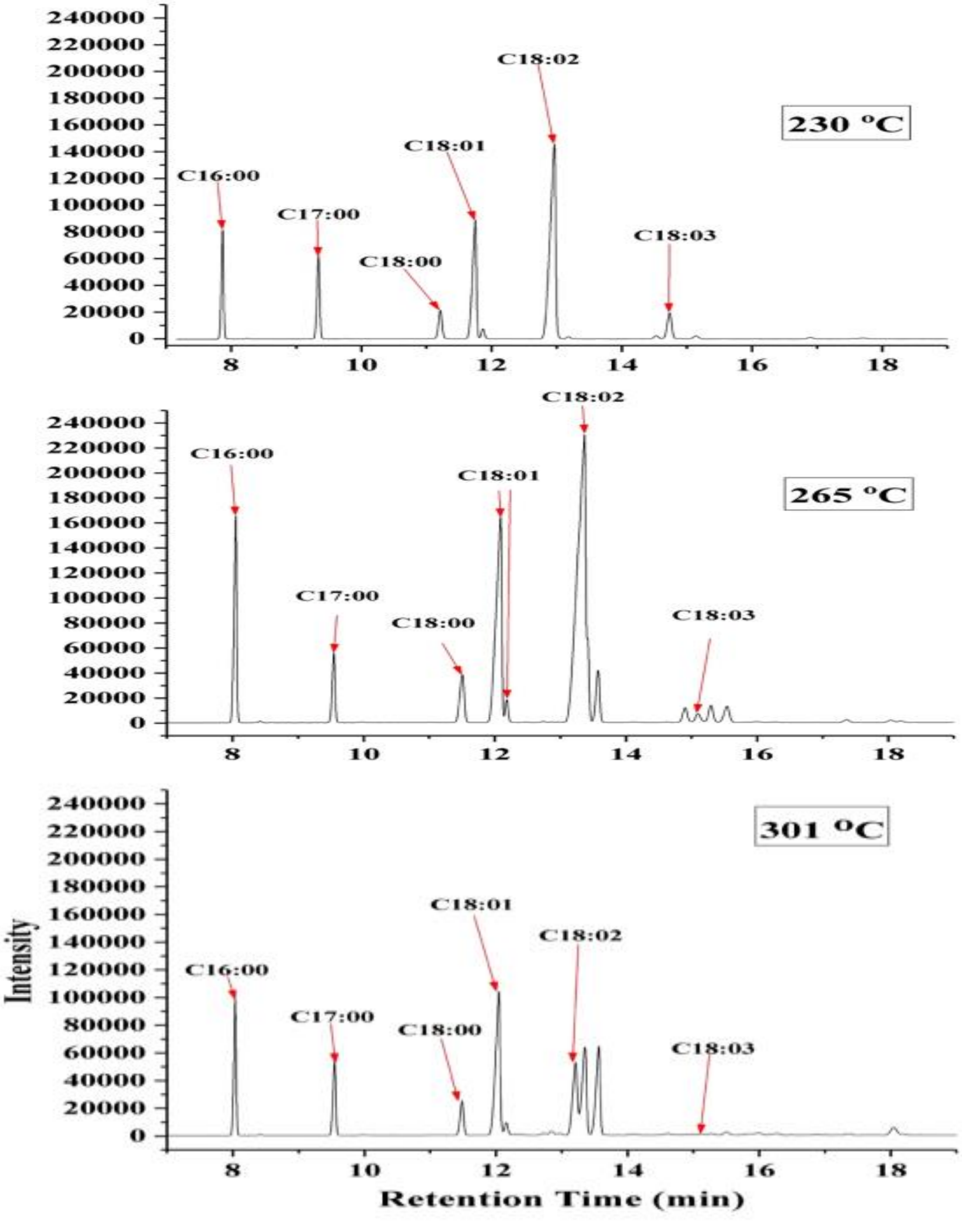

Fig. 9. FAME chromatograms (GC) at different reaction temperatures (P = 6.9 MPa, 480 min reaction time, SBO:MeOH:H2O = 1:39:22) batch system.

From Fig. 13 and 14, it can be seen that the optimum molar ratio of SBO:MeOH:H_2O in a continuous system is 1:39:22. However, the optimum molar ratio of vegetable oil to methanol was 1:40 and 1:42 in Demirbas and Saka et al., respectively [8,11]. Fig. 15 depicts the effect of pressure on the yield of FAMEs. It was found that increasing pressure can lead to high yield of FAME (91%), primarily due to the effect of phase behavior. Aspen HYSYS V8.8 was used to simulate the phase behavior of the reactants showing that most of the methanol leaves the reactor in vapor phase at sub-critical conditions (low pressure) while triglycerides form a stable liquid phase. Because the FAME reactions occurred in the liquid phase [26], increasing the pressure was important to keep all the reactants in the liquid phase. Table 2 shows Aspen phase behavior results for all the reactants at different conditions. This was a different phenomena than was seen with subcritical free fatty acids [4] clearly showing that the phase behavior is the principle reason why the supercritical conditions may be desirable when working with triglycerides. Also, Aspen was employed to estimate the pressure in the batch reactor by calculating the amount of each reactant needed to be fed in the reactor. This simulation showed a good agreement between the pressure and the liquid phase needed for the reaction.

Table 2
Aspen HYSYS results for phase behavior simulation.

		Vol. Ratio	SBO		MeOH		H2O		Total	Total
Temp. (^{o}C)	Pressure (Mpa)	SBO:MeOH:H2O	Liq. %	Vap. %	Liq. %	Vap. %	Liq. %	Vap. %	Liq. %	Vap. %
265	6.9	1:1.66:0.43	23.6	0	32.6	64.6	43.8	35.4	35.3	64.7
301	6.9	1:1.66:0.43	53	0	20.5	64	26.5	36	33	67
330	6.9	1:1.66:0.43	66.8	0	14.7	63.6	18.5	36.4	32.7	67.3
301	10.9	1:1.66:0.43	27	0	32	64.5	41	35.5	34.5	65.5
301	15.5	1:1.66:0.43	34	0	52	71	14	29	60	40

Where:
Vap. %:- Vapor percent (v/v)
Liq. %:- Liquid percent (v/v)

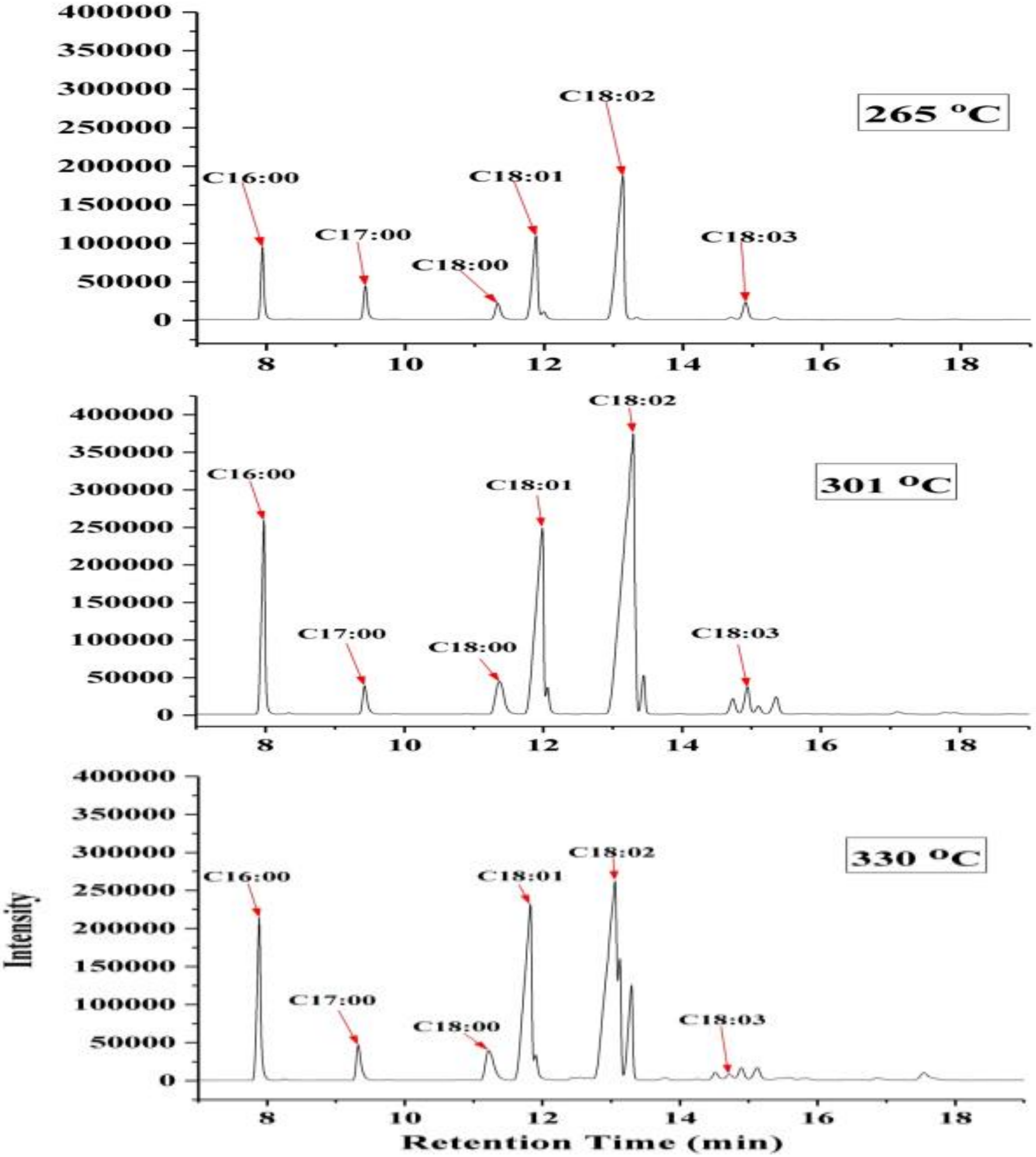

Fig. 10. FAME chromatograms (GC) at different reaction temperatures (P = 6.9 MPa, 40 min reaction time, SBO:MeOH:H2O = 1:39:22) continuous system.

Since there was no study showing hydrolysis, esterification, transesterification, and degradation modeled in a single reactor, a model was developed above. Literature reaction coefficients were used when possible, however, reaction coefficients were modified to fit the degradation. Table 3 presents all the coefficients used in this study. The degradation and transesterification were modeled as a first order reaction Eq. (2) and (3), while hydrolysis and esterification were modeled as a second order reactions Eq. (4) and (5). Arrhenius conditions were obtained for the degradation reaction using the same procedure as White [4]. Matlab was used to solve all the ordinary deferential equations (Eq. (2), (3), (4), and (5)), simultaneously. To obtain the model rate constant coefficients, a non-linear least squares regression analysis was performed. Fig. 16 shows the comparison between the experimental and theoretical yields. The experimental results are depicted as solid line, while the theoretical results are plotted as dashed line. Theoretical results of the reaction kinetic model and the experimental results of this study showed a good agreement by giving a small value of standard error of estimate (3.86 and 6) in continuous and batch systems, respectively. This model explained by these four reactions can be used to give a good prediction for biodiesel yield. Based on this model it is predicted that optimum yield in a sub-critical reaction is 83 % and 55% at sub-critical conditions and 1:39:22 molar ratio of SBO:MeOH:H_2O in batch and continuous systems, respectively.

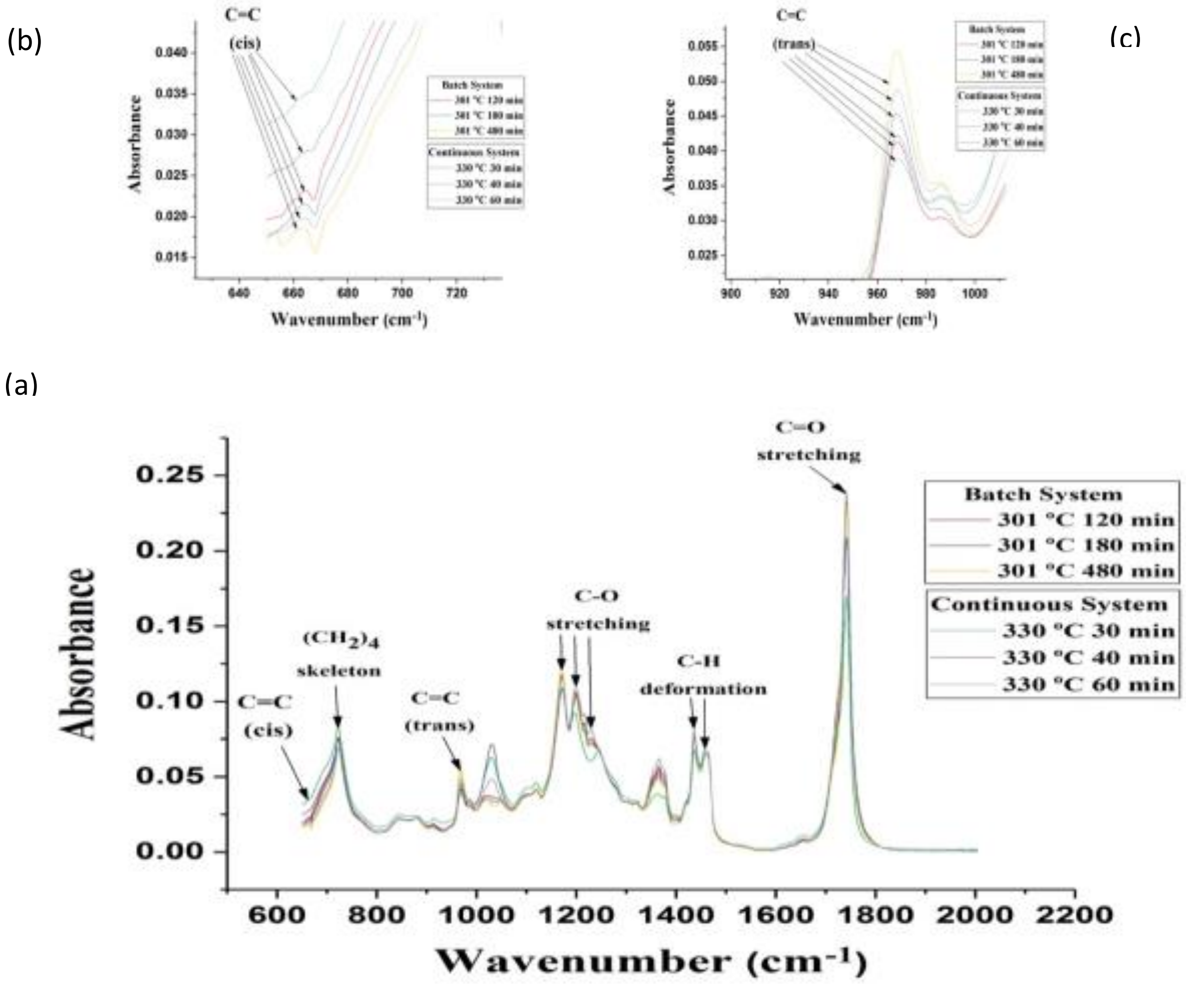

Fig. 11. ATR-FTIR spectra of FAME samples at different reaction times (P = 6.9 MPa, SBO:MeOH:H2O = 1:39:22): (a) whole spectra; (b) C=C (cis); (c) C=C (trans).

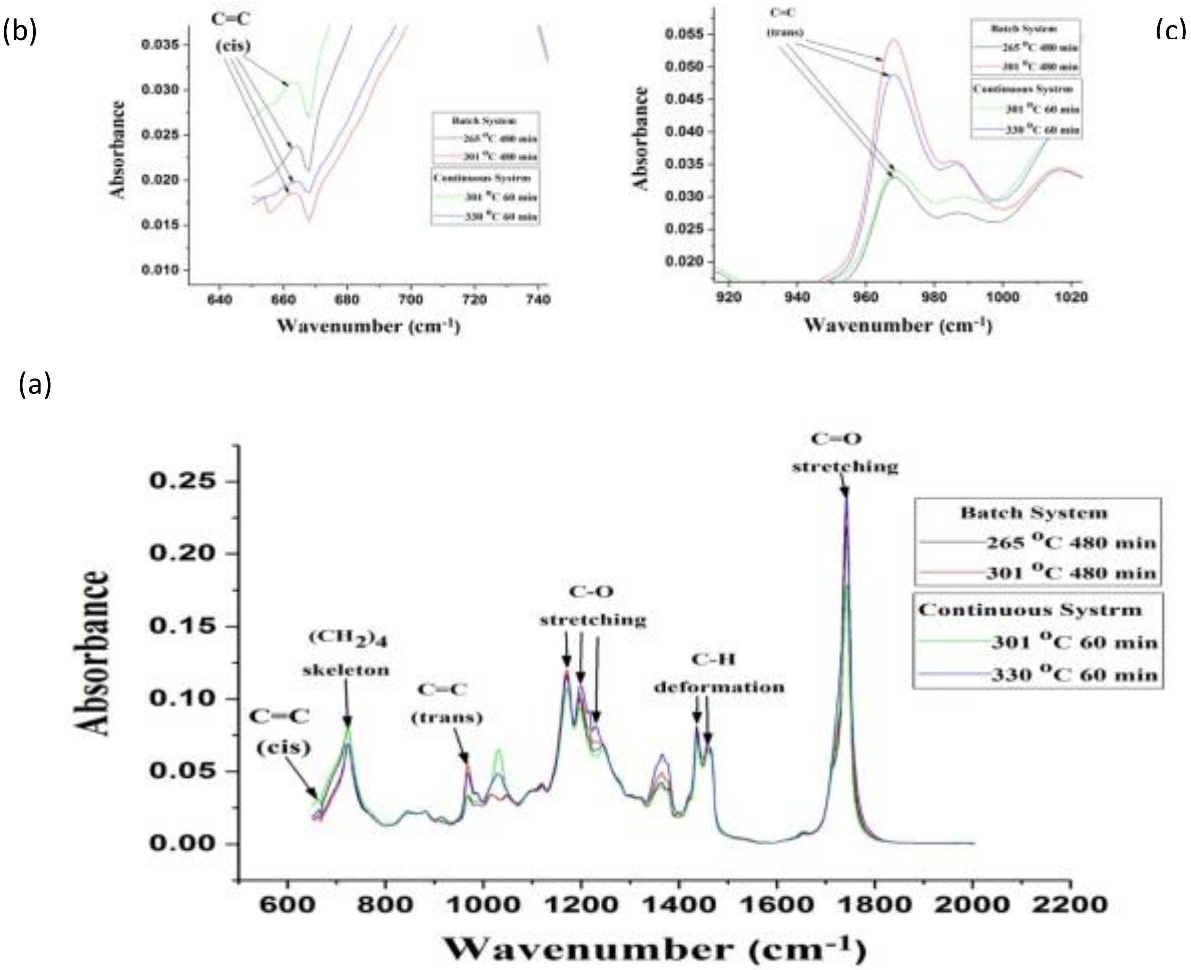

Fig. 12. ATR-FTIR spectra of FAME samples at different reaction temperatures (P = 6.9 MPa, SBO:MeOH:H2O = 1:39:22): (a) whole spectra; (b) C=C (cis); (c) C=C (trans).

$$\frac{dC(Dp)}{dt} = K1\ C(FAME) \tag{2}$$

$$\frac{dC(FAME)}{dt} = K2\ C(TG) \tag{3}$$

$$\frac{dC(FFA)}{dt} = K3\ C(TG)\ C(H2O) \tag{4}$$

$$\frac{dC(FAME)}{dt} = K4\ C(FFA)\ C(MeOH) \tag{5}$$

Where:

Dp :- Degradation by-product; FFA :- Free fatty acids; TG :- Triglycerides

The batch reactor showed better yield than the tubular reactor at the same experimental conditions. In the tubular reactor, MeOH was leaving the reactor faster than the SBO, so the reaction time was difficult to determine accurately for all the reactants. In contrast, in the batch reactor, all the reactants were placed inside the batch reactor (constant volume) with the same reaction time so the determination of reaction time was more consist in the batch system than in the continuous system. Eq. (6) and (7) present the design equations for the batch and tubular reactors, respectively.

Table 3
Reaction rate constant coefficients used in this model.

reaction Rate Constant (K)				
	Degradation	**Transesterification**	**Hydrolysis**	**Esterification**
	(1/min)	(1/min)	(L/mol*min)	(L/mol*min)
Batch	0.0024	0.0426	1.1192	0.001515
Continuous	0.031	0.00526	1.1192	0.0029

$$t = \mathrm{NAo} \int_0^x \frac{dx}{-rA * V} \qquad (6)$$

$$V = \mathrm{FAo} \int_0^x \frac{dx}{-rA} \qquad (7)$$

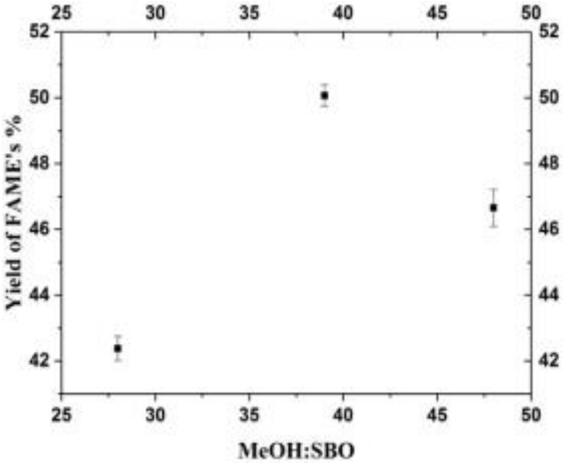

Fig. 13. Effects of methanol to soybean oil molar ratio (MeOH:SBO) on yield of fatty acids methyl esters (FAMEs) at (T = 301 °C, 40 min reaction time, P = 6.9 MPa, H2O:SBO = 22:1 continuous system.

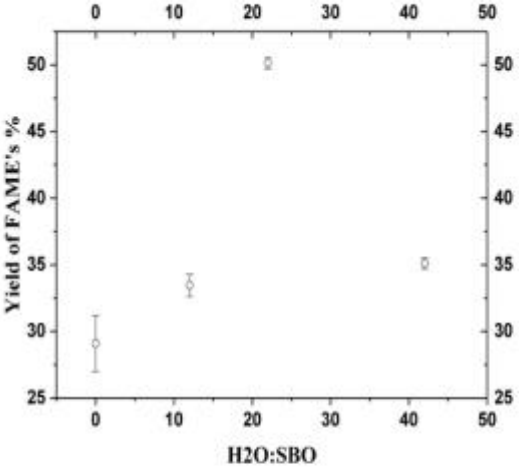

Fig. 14. Effect of water to soybean oil molar ratio on yield of fatty acids methyl esters (FAMEs) at (T = 301 °C, 40 min reaction time, MeOH:SBO = 39:1, P = 6.9 MPa) continuous system.

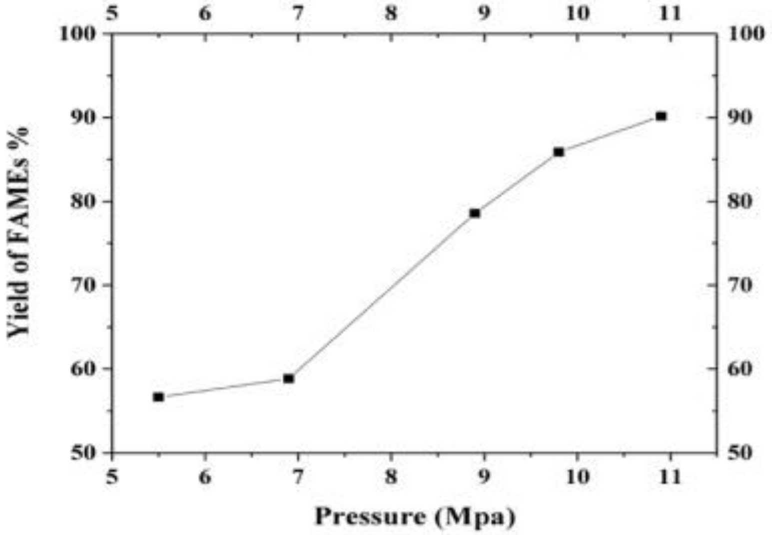

Fig. 15. Effect of pressure on yield of fatty acid methyl esters (FAMEs) at (2 hours reaction time, T = 301°C, and SBO:MeOH:H2O=1:39:22) batch system.

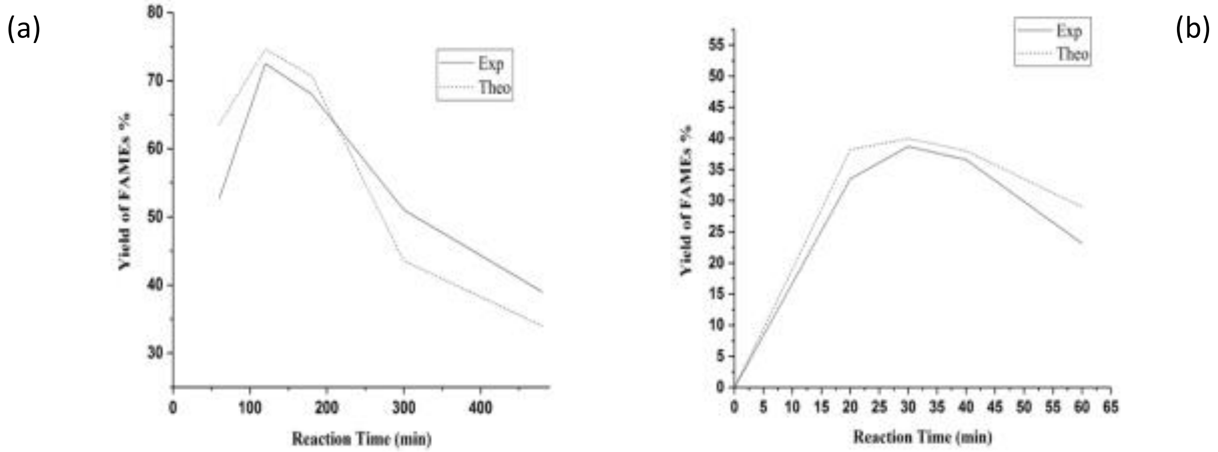

Fig. 16. Yields determined by experiment compared with yields estimated by kinetic model in a) batch system (301°C and 6.9 MPa); b) continuous system (330°C and 6.9 MPa). (solid line: experiment results (Exp), dashed line: theoretical results (Theo)).

3.4. Conclusion

The yield of FAMEs in the batch reactor was higher than in the tubular reactor. This behavior was due to the differences in determining the reaction time between these two reactors. Several critical reaction times were observed at different temperatures. In the batch system at the critical point of reaction time (120 min), the maximum yield of 79% was observed at 265 °C, while the maximum yield was 50.6% in the continuous system at the critical point of reaction time (40 min) and temperature (301°C). The decrease of FAME yields after passing the critical point was due to the degradation reactions of the poly unsaturated fatty acids methyl esters. This kind of degradation was caused by forming free radicals converted from $C{=}C_{(cis)}$ to $C{=}C_{(trans)}$. In the future, to avoid degradation, an antioxidant such as butylated hydroxytoluene (BHT) should be added to stabilize the poly unsaturated FAMEs. The effects of phase behavior were also observed in this study. Increasing pressure led to an increase in the reactant liquid phase, which further increased the FAME yield.

The kinetic model of this study illustrates the effects of four reactions, especially the degradation effect on FAME yield. Matlab was used to solve the ordinary differential equations of these kinetic reactions. The theoretical results, which calculated by the kinetic model, and experimental results show a sufficient fit with each other. Also, this model predicts the optimum biodiesel yields (83% and 55%) under sub-critical conditions and 1:39:22 molar ratio of SBO:MeOH:H_2O in both batch and continuous systems, respectively. Thus, these results indicate that although subcritical processing allow for lower costs, it may be desirable to use supercritical processing because of more complete reactions and less degradation by-products.

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CHAPTER 5: SUMMARY

Even though there are several methods used to produce biodiesel, each method has advantages and disadvantages toward generating high biodiesel yields. A one-step method was evaluated to produce biodiesel at sub-critical conditions. Two system configurations were tested under a variety of conditions using this method. There were a clear variety in biodiesel yields between batch and continuous systems. The batch reactor showed higher yield than that of the continuous reactor due to the differences in accurately determined reaction times for each component inside the reactor. In general, increasing reaction time and temperature affected biodiesel yields. In the batch reactor, a maximum yield (79%) was observed at 265 ^oC and 120 min reaction time. However, a yield of 50.6% was calculated in continuous reactor at 301 ^oC and 40 min. The effects of degradation reactions clearly appeared after passing 120 min and 40 min in batch and continuous reactors, respectively. These degradation reactions occurred due to autoxidation effects, which led to the formation of free radicals of polyunsaturated fatty acid methyl esters (C18:02 and C18:03) that can easily converted from $C{=}C_{(cis)}$ to $C{=}C_{(trans)}$.

A significant increase in biodiesel yield was observed after increasing the pressure to reach supercritical conditions. This increase was due to the influences of phase behaviors for reacted material. Aspen HYSYS V8.8 was used to describe the effects of reacted phase behaviors. In this work, it was found that maintaining the reacted material in liquid phase at high temperature is favorable to achieve high biodiesel yield. Thus, working at supercritical conditions was important to get a liquid phase at sufficient molar ratio of reacted components. A kinetic model was developed to describe four reactions (transesterification, hydrolysis, esterification, and degradation). Matlab was utilized to solve all the ordinary differential equations in this model. The reaction rate constant coefficients were obtained in this work to fit the degradation effects. Experimental and theoretical results showed appropriate fit with each other by giving a small value of standard error of estimate (3.86 and 6) in batch and continuous systems, respectively. This model was also used to predict the maximum biodiesel yield value (83% and 55%) at sub-critical conditions and 1:39:22 molar ratio of SBO:MeOH:H_2O in batch and continuous systems, respectively. Using the one step method at subcritical conditions might be promising for cost reduction. However, the effects of degradation reactions, which was observed in this method, can lead to significant loss in biodiesel before reaching a complete conversion.

It is recommended to add butylated hydroxytoluene (BHT) as an antioxidant to stabilize the polyunsaturated fatty acid methyl esters and avoid the autoxidation impacts. Also, it is favorable to work at supercritical conditions rather than subcritical conditions to make sure all the reactants in liquid phase. All the calculations for the residence time were performed for accounting the liquid, so in order to get more accurate residence time, the effects of gas and liquid phases should be included in these calculations.

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APPENDIX A: STANDARD OPERATING PROCEDURE (SOP) for USING BATTCH REACTOR IN PRODUCING BIODIESEL

This experiment is conducted to produce biodiesel at high pressure and temperature (subcritical conditions). All the chemicals and equipment should place inside the hood. The PPE used in this experiment is safety glasses and appropriate gloves. In addition, a polycarbonate shield will place in front of the pressurized system during the runs.

Methanol, water and soybean oil are used in this experiment as reacted materials. Also, Fatty acid methyl esters, free fatty acids, and glycerol are produced as final products in this experiment. No side-products that could increase the hazards are known.

Table A1

Material CAS number and their hazards. Adapted from SDS.

Material Name, CAS#	**Hazards**
Methanol, 67-56-1	Highly flammable material. Toxic
Glycerol, 56-81-5	Skin and serious eye irritation
Free fatty acids, 61790-12-3	Toxic
Nitrogen, 7727-37-9	Gas under pressure, if heated may explode
Fatty acid methyl esters, 67762-38-3	N/A

Note:

1. Before using the batch reactor, you should calculate the proper amount of reactants at different temperatures and pressures to make sure that you are going to work at safe conditions.

2. You have to test the reactor with water before using your feedstock to make sure everything is ok.
3. An analysis in Aspen was run to simulate the reaction conditions prior to use. The simulation looks at density and mass fraction of vapor, density and mass fraction of liquid for the mixture at specific conditions.
4. Specific conditions: 150-325C, 1000 psia, and less than 250 ml of feed mixture.
5. The unit is A Parr Instruments 4520 series, 2 liters with max. reaction volume of 1 L.
6. The water used for cooling is from sink.

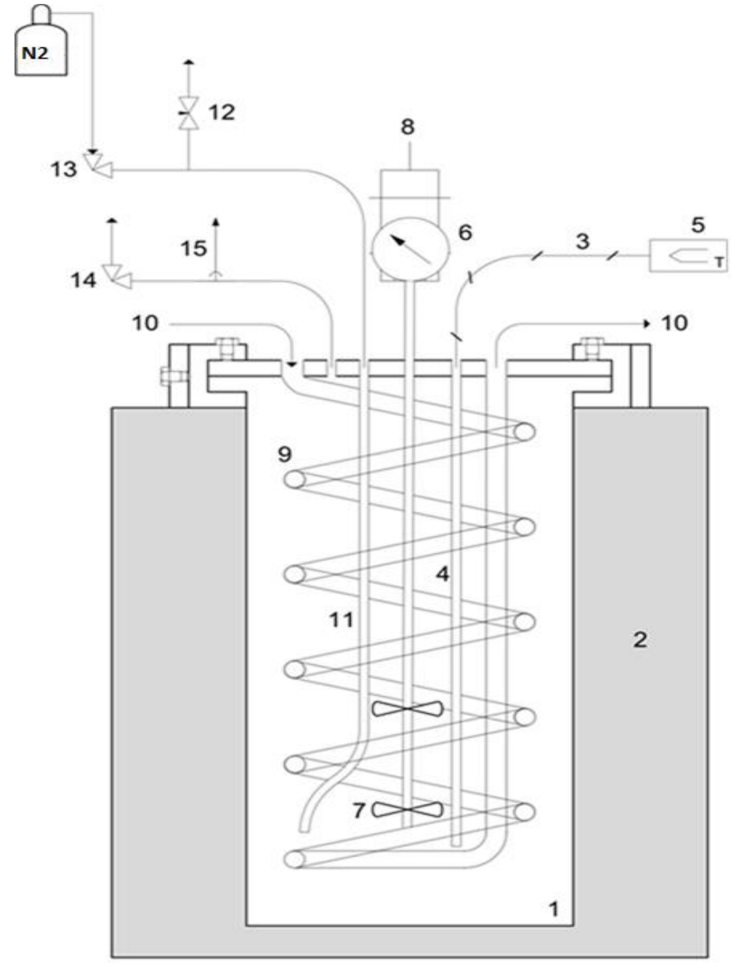

Fig. A1. The batch reactor schematic. Adopted from William Brent Schulte Thesis (2007)

Table A2

Equipment numbers, names, and structure properties

Part Number	**Name**	**Max. Working Pressure**	**Material**
1	Parr Instruments 4520 series	2000 psig	316-stainless steel
2	1,500-watt, Calrod-type shelled element heater	2000 psig	
3	type-J, sheathed thermocouple		
4	Thermowell	2000 psig	316-stainless steel
5	Omega HH82A thermocouple reader		
6	pressure gauge (0-2000 psi)		
7	2.25"diameter, 6-blade, 45°-pitched impellers	2000 psig	
8	magnetic drive shaft	2000 psig	
9	spiral cooling-coil	2000 psig	316-stainless steel
10	supply of cooling water		
11	dip tube		316-stainless steel
12	Valve	2000 psig	
13	gas inlet angle valve	2000 psig	
14	angle valve	2000 psig	
15	burst disc (526HCPF)	2000 psig	

Start Up

7. Remove the drop band, followed by the split ring and the head assembly.

8. Put the calculated proper amount of reactants into the reactor vessel.

9. Return the head assembly, split ring and the drop band.

10. Place the reactor vessel inside the heater.

11. Use a Nitrogen cylinder with a regulator valve in order to purge the reactor vessel.

12. Connect the Nitrogen line to the reactor's gas inlet.

13. Purge the system for 5 minutes by opening the gas inlet valve and the gas release valve.

14. After purging the reactor, close all the valves and disconnect the Nitrogen line

15. Make sure that a cooling water is supplied to the cooling coil inlet.

16. To prevent the supply water line from damage, you need to use three kinds of tubing arranged in proper way (stainless steel, thermal resistant, and PVC tubing).

17. To prevent the magnetic drive's, you need to use another cooling water supply circulating through it.

18. Install the motor above the magnetic stirrer.

19. Turn on the heater and start heating gradually to reach the desire conditions.

20. Turn on the magnetic stirrer motor to provide agitation above 600 rpm.

21. During the heating, you have to monitor the pressure and record its values with time at different temperatures in order to compare it with the calculated values of vapor pressure.

Shut down

1. After a specific residence time, the reactor is cooled down by turning off the heater and opening the cooling water valve
2. Make sure that the temperature and pressure of the reactor are reached the safe conditions (bellow 60 C and 5 Psia) before handling it.
3. If there is any excess pressure after cooling the reactor, you have to open the gas release valve to decrease it.
4. Disconnect the cooling water lines and removing the motor magnetic stirrer.
5. Remove the drop band, the split ring, and the head assembly.
6. Pour the reactor contents into 1000 ml container to get samples.
7. Clean the reactor vessel after finishing each experiment with methanol.

Waste

Collect all chemicals and material in a sealed compatible container, either HDPP or glass, label with waste label, and request a pickup. Store in waste accumulation site until picked up by EH&S.

Emergency Shut down

In general case, you have to follow this procedure for emergency.

1. Turn off heater.
2. Unplug all electrical equipment.
3. Open cooling water valves.
4. Pull down hood sash if not already in position

5. Evacuate the lab
6. Put DO NOT ENTER sign on door which is found in spill kit
7. Call your supervisor, EH&S, or other appropriate personnel
8. Do not re-enter the lab until it is deemed safe by EH&S, your advisor, or safety personnel.

Leaks in system

In this case, follow Emergency Shutdown procedures.

Over pressurize

We have installed a burst disc (@ 1900 psi) to relieve pressure in case of an emergency situation. Follow all emergency shut-down procedures if burst disc is engaged or system pressure increases beyond desired experimental conditions.

Spills Inside hood or on equipment

Due to flammability hazards, you should also turn off the whole system, especially, the electrical equipment and try to contain the spill to inside the hood. Wear appropriate PPE and clean spills immediately if not dangerous. If dangerous, flammable chemicals may be left to evaporate in hood before attempting cleaning or until the danger has been eliminated. Use absorbent pads or absorbent granules around the spill to contain it. Follow with absorbing rest of spill. Collect all cleanup material in a sealed compatible container, label with waste label, and request a pickup.

Spills Outside Hood

Clean spills immediately. Wear appropriate PPE and clean spills immediately if not dangerous. Use absorbent pads or absorbent granules around the spill to contain it. Follow with absorbing rest of spill. Sweep up material with a broom from spill kit. Collect all cleanup material in a sealed compatible container, label with waste label, and request a pickup. If there is a large spill greater than 4L, evacuate the area immediately and alert others nearby. Follow Emergency shut-down procedures.

Table A3

Emergency Response. Adapted from SDS

Skin Contact	Rinse affected skin with large amounts of water for 15 min. after removing contaminated clothing.
Eye Contact	Rinse the affected eye(s) thoroughly using the eye wash for 15 min., and lift eyelids and roll eyeballs occasionally. Go seek medical attention.
Inhalation	Move into fresh air as soon as possible.
Ingestion	Rinse the mouth with water.
	Always seek medical help after first aid is performed in the cases above