Biodiesel Synthesis via Transesterification Reaction in Supercritical Methanol: a) A Kinetic Study, b) Biodiesel Synthesis Using Microalgae Oil

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Abstract

The transesterification reaction in supercritical methanol between various oil feedstocks and alcohols is proposed as an alternative cost effective method to produce biofuels. Two studies were conducted related to this process in order to (a) supplement a previous kinetics study to better understand the reaction mechanism and (b) assess basic reaction conditions for effective conversion of microalgae oil to biofuels in supercritical methanol.

A one-step transesterification reaction has been used in some supercritical batch experiments to explain the kinetic results (He, Sun, Wang, & Zhu, 2007; Kusdiana & Saka, 2001). However, one-step kinetic models ignore the detailed multi-step reaction mechanism and cannot be used to predict the concentration of the intermediates. In this study, reactions were conducted in a continuous flow reactor of supercritical methanol with a model triglyceride compound, triolein (C_{57}H_{104}O_{6}), under various reaction conditions to study the consecutive reactions of this compound and to better understand the reaction kinetics of this transesterification reaction. Triolein is a major triglyceride component in many types of feedstock, such as 40 wt. % in palm oil, 40 wt. % in olive oil, 64 wt. % in rapeseed oil, and 41 wt. % in chicken fat. The effects of process variables (residence time and temperature) on triglycerides conversion and formation of intermediates were assessed. A three-step kinetic model for biodiesel production in supercritical methanol is proposed based on experimental data obtained earlier (Cong & Tavlarides, 2010) and augmented with the experiments and analysis conducted during this work.

The second objective of this study was to determine suitable conditions for the transesterification of microalgae oil with supercritical methanol. Experiments were conducted using microalgae oil at different methanol-to-oil molar ratios (6:1 to 12:1), temperatures (350 to 400 °C), pressures (150 to 300 bar), and residence times (3 to 12 min) in order to find an
appropriate reaction condition. The effects of temperature, pressure, molar ratio of the reactants, and residence time on conversion and free glycerol content were assessed. In particular, the kinetic model proposed above for triolein was applied to this system to predict reaction conversion at 385 °C, 200 bar, molar ratio of 9:1, and residence time from 4 to 10 min. These results demonstrate the potential for use of transesterification reactions in supercritical methanol to produce biodiesel fuels from microalgae oils.
BIODIESEL SYNTHESIS VIA TRANSESTERIFICATION REACTION IN
SUPERCRITICAL METHANOL: a) A KINETIC STUDY, b) BIODIESEL
SYNTHESIS USING MICROALGAE OIL

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THESIS

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Chapter 1: Introduction
Commercial biodiesel production has been facing two big problems. First, current industrial biodiesel production uses alkaline as catalyst, and biodiesel fuel is synthesized at low temperatures (i.e., ~ 60 °C) and ambient pressure (Alcantara et al., 2000). The production process normally takes hours, and needs to separate biodiesel from catalyst, which is complex and enhances cost. Biodiesel synthesis in supercritical methanol was proposed years ago to optimize production process (Bunyakiat, Makmee, Sawangkeaw, & Ngamprasertsith, 2006). Reaction time was reduced from hours to minutes to improve efficiency. Because no catalyst is required in the non-catalytic method, separation steps are reduced and production costs decrease. An economic analysis of biodiesel production with supercritical methanol process has been performed. It was found that the cost through the non-catalytic technology could be half of that of the actual conventional methods (Deshpande, Anitescu, Rice, & Tavlarides, 2010).

With years of study on non-catalytic biodiesel technology (D'Ippolito, Yori, Iturria, Pieck, & Vera, 2007b; A. Demirbas, 2002; Gui, Lee, & Bhatia, 2009; Madras, Kolluru, & Kumar, 2004), much lower molar ratio (i.e., 9:1 instead of 42:1) and shorter residence time (i.e., 10 min instead of 30 min) shows the potential to make high quality biodiesel, and saves cost in terms of less heating and reactant-transporting energy. Besides economical advantages, other benefits from non-catalytic technology include improved biodiesel viscosity, cold flow properties, cetane number, and much less glycerol as byproduct (Marulanda, Anitescu, & Tavlarides, 2010b). Regardless which technology will be used in the future, conventional alkaline method or non-catalytic technology, all improvement of biodiesel production technology is based on understanding the synthesis reaction mechanism and reaction kinetics. Because of the complex chemical composition of biodiesel feedstocks, only a few kinetics studies were published (Al-Zuhair, 2005; Diasakou, Louloudi, & Papayannakos, 1998; He et al., 2007).
Biodiesel feedstocks have different types and amount of fatty acid profiles, which makes it difficult to predict the reaction kinetics and, as such, the reactor design. This lack of understanding will hinder the development of biodiesel production processes. To better understand the reaction mechanism, in this study, transesterification of triolein, a model triglyceride compound, was investigated at 385 °C and 15 MPa in supercritical methanol, residence time from 0.5 to 2 min, and methanol-to-triolein molar ratio of 9. These data augment the previous results (Cong & Tavlarides, 2010). The conversion of triolein and the composition of the reaction intermediates were determined by chromatographic analysis for these reaction conditions. A three-step kinetic model is proposed to predict content of triolein, diolein, monoolein, methyl oleate, and methanol during reactions. The step-reactions from diolein to monoolein and from monoolein to glycerol are assumed to be reversible. Reaction rate constants have been determined. Compared with the simple one-step model, the three-step model better represents intermediate reaction product evolutions that are related to bound glycerol fractions in the biodiesel.

Second, commercial biofuel is primarily produced from vegetable oil and animal fat. Use of more land for biofuel feedstock cultivation now is in competition with resources for human food production. It is important to develop biofuel produced from non-food feedstocks such as microalgae, which potentially offers greatest opportunities in a longer term. Biodiesel synthesis under supercritical methanol conditions provides both energy and economic benefits over the conventional base catalyzed biodiesel production process. In this study, transesterification of microalgal oil with supercritical methanol was investigated at different temperatures (350, 385, and 400 °C), pressures (150, 200, and 300 bar), methanol-to-oil molar ratios (from 6:1 to 12:1), and residence times (3-12 min). Compared with amount of methanol used in other supercritical
transesterification process (up to 42:1), in this work the methanol-to-oil ratio is much lower. This reduction of methanol use is helpful to greatly reduce the pumping, preheating costs and recovery of the excess methanol in commercial applications. In these studies, the composition of the reaction intermediates were evaluated by GC-FID, free glycerol and bound glycerol fractions in the methyl ester phase were determined by the ASTM method, and the components of microalgae oil and biodiesel made in this study were analyzed by GC-FID according to the peak report of a FAME standards (methyl linoleate 20 wt%, methyl linolenate 20 wt%, methyl oleate 20 wt%, methyl palmitate 20 wt%, and methyl stearate 20 wt%). In this study, the reaction conversion reached above 99% in seven minutes at 400 °C, which shows microalgae oil has a great potential to be a feedstock of non-catalytic biodiesel production, and the reaction conditions are very efficient. Lower temperatures (350 and 385 °C) require longer residence time to complete reaction.
Chapter 2: Literature review
2.1 Biodiesel synthesis under supercritical methanol conditions

Recent increases in liquid fossil fuel prices and uncertainties in its availability have stimulated interest in renewable liquid fuels. One of these attractive fuels is biodiesel, which can be made from triglycerides of various biomass sources such as plant oils (e.g., corn, palm) (Rathore & Madras, 2007), animal fats (Marulanda, Anitescu, & Tavlarides, 2010b), rapeseed oil (Bajaj, Lohan, Jha, & Mehrotra, 2010; Saka & Kusdiana, 2001), soybean oil (He et al., 2007; He, Wang, & Zhu, 2007; Silva et al., 2007), and microalgae oil (M. F. Demirbas, 2010). The chemical process to produce biodiesel is called transesterification in which triglycerides are reacted with methanol or ethanol to give methyl or ethyl esters of fatty acids and glycerol.

Commercial biodiesel is currently produced through transesterification reactions using acid or alkali solutions as catalysts. However, these conventional processes require a high purity of feedstock with very low free fatty acid and water content. Furthermore, the complexity of separation steps to remove catalyst, glycerol and excess alcohol from biodiesel drives up biodiesel cost (Warabi, Kusdiana, & Saka, 2004). Another enzyme-catalyzed process is more tolerant of impurities and has simple post reaction separations, but is relatively expensive to implement (Bajaj et al., 2010).

A catalyst-free method for the transesterification of plant oils and animal fats at supercritical alcohol conditions has been proposed (A. Demirbas, 2002; A. Demirbas, 2007; Kusdiana & Saka, 2001; Marulanda, Anitescu, & Tavlarides, 2010a; Saka & Kusdiana, 2001). The non-catalytic process has significant advantages over conventional catalytic methods to treat various low-quality feedstocks. Transesterification of nonpolar triglycerides with a polar alcohol is usually a heterogeneous, two liquid phase reaction at conventional processing conditions (Madras et al., 2004). This process characteristic is due to incomplete miscibility of the nonpolar and polar reactants. According to mixing ratio, at appropriate temperatures and pressures, the
methanol and triglycerides binary system can mix and form a homogeneous phase which will accelerate the transesterification reactions due to removal of the oil-alcohol interphase that limits mass transfer and hence reaction rates (Srivastava & Prasad, 2000). Furthermore, separating biodiesel product from glycerol byproduct is simple, because the products are immiscible at ambient temperature and no soap or other side products need to be removed (Pinnarat & Savage, 2008).

There have been several studies of transesterification under supercritical methanol conditions. Table 2-1 summarizes some of recent studies using different feedstocks. Reaction temperatures of 300 to 350 °C and alcohol-to-oil molar ratio of 42 were often suggested to be the best set of conditions for non-catalytic biodiesel production (Hawash, Kamal, Zaher, Kenawi, & El Diwani, 2009). It was considered that large excess of alcohol is required to shift the reaction equilibrium toward biodiesel product. However, a major drawback that hampers the industrial application of this method is the extremely high alcohol-to-oil molar ratio (i.e., 42:1) which will cause additional preheating, pumping, and separation costs (Marulanda, Anitescu, & Tavlarides, 2010a). Some recent work shows that non-catalytic biodiesel synthesis can be performed at much lower molar ratios (e.g. 9:1 and 12:1) and higher temperatures (e.g. 385 °C) (Anitescu, Deshpande, & Tavlarides, 2008; Marulanda, Anitescu, & Tavlarides, 2010a).
Table 2-1 Summarization of recent studies of non-catalytic transesterification.

<table>
<thead>
<tr>
<th>oil/fat</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>alcohol:oil molar ratio</th>
<th>τ (min)</th>
<th>reactor</th>
<th>reaction type</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapeseed</td>
<td>350</td>
<td>45</td>
<td>42:1</td>
<td>4</td>
<td>5 mL Inconel-625</td>
<td>batch</td>
<td>(Kusdiana &amp; Saka, 2001)</td>
</tr>
<tr>
<td>Chicken fat</td>
<td>400</td>
<td>30</td>
<td>12:1</td>
<td>8</td>
<td>8 m tubular; 316SS 8 mL SS</td>
<td>continuous</td>
<td>(Marulanda et al., 2010)</td>
</tr>
<tr>
<td>Sunflower</td>
<td>350</td>
<td>20</td>
<td>40:1</td>
<td>40</td>
<td>8 mL SS</td>
<td>batch</td>
<td>(Madras et al., 2004)</td>
</tr>
<tr>
<td>Soybean &amp; sunflower</td>
<td>425</td>
<td>30</td>
<td>24:1</td>
<td>8.2</td>
<td>8 m tubular; 316SS 100 mL</td>
<td>continuous</td>
<td>(Anitescu et al., 2008)</td>
</tr>
<tr>
<td>Hazelnut kernel</td>
<td>250</td>
<td>N/A</td>
<td>41:1</td>
<td>5</td>
<td>100 mL cylindrical autoclave; 316SS 100 mL</td>
<td>batch</td>
<td>(Demirba 2002)</td>
</tr>
<tr>
<td>Sunflower</td>
<td>250</td>
<td>N/A</td>
<td>41:1</td>
<td>6</td>
<td>100 mL cylindrical autoclave; 316SS 100 mL</td>
<td>batch</td>
<td>(Demirbas, 2007)</td>
</tr>
<tr>
<td>Soybean</td>
<td>310</td>
<td>25</td>
<td>40:1</td>
<td>25</td>
<td>75 mL tubular; 316SS 11 mL</td>
<td>continuous</td>
<td>(He et al., 2007b)</td>
</tr>
<tr>
<td>Soybean</td>
<td>280</td>
<td>28</td>
<td>42:1</td>
<td>25</td>
<td>200 mL</td>
<td>continuous</td>
<td>(He et al., 2007a)</td>
</tr>
<tr>
<td>Soybean</td>
<td>350</td>
<td>20</td>
<td>40:1</td>
<td>15</td>
<td>24 and 42 mL; tubular</td>
<td>continuous</td>
<td>(Silva et al., 2007)</td>
</tr>
<tr>
<td>Coconut &amp; palm</td>
<td>350</td>
<td>19</td>
<td>42:1</td>
<td>7</td>
<td>5.5 m tubular; SS316 cylindrical autoclave; 316SS 100 mL</td>
<td>continuous</td>
<td>(Bunyakiat et al., 2006)</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>250</td>
<td>N/A</td>
<td>41:1</td>
<td>8</td>
<td>100 mL cylindrical autoclave; 316SS 11 mL</td>
<td>batch</td>
<td>(Demirbas, 2008)</td>
</tr>
<tr>
<td>Palm &amp; ground nut</td>
<td>400</td>
<td>20</td>
<td>50:1</td>
<td>10</td>
<td>11 mL; 316SS</td>
<td>batch</td>
<td>(Rathore &amp; Madras, 2007)</td>
</tr>
<tr>
<td>Castor &amp; linseed</td>
<td>350</td>
<td>20</td>
<td>40:1</td>
<td>40</td>
<td>11 mL; 316SS</td>
<td>batch</td>
<td>(Varma &amp; Madras, 2007)</td>
</tr>
<tr>
<td>Vegetable</td>
<td>330</td>
<td>16</td>
<td>40:1</td>
<td>N/A</td>
<td>7 m tubular; 316SS</td>
<td>continuous</td>
<td>(Chen et al., 2009)</td>
</tr>
<tr>
<td>Jatropha</td>
<td>340</td>
<td>8.6</td>
<td>43:1</td>
<td>4</td>
<td>3.7 L; 316SS</td>
<td>batch</td>
<td>(Hawash et al., 2009)</td>
</tr>
<tr>
<td>Palm</td>
<td>300-</td>
<td>N/A</td>
<td>5-50</td>
<td>2-30</td>
<td>11ml, 316SS</td>
<td>batch</td>
<td>(Gui et al., 2009)</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soybean</td>
<td>260-</td>
<td>N/A</td>
<td>42:1</td>
<td>0-30</td>
<td>250ml cylindrical autoclave</td>
<td>batch</td>
<td>(Yin, Xiao, &amp; Song, 2008)</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Vieitez et al., 2008)</td>
</tr>
<tr>
<td>Soybean</td>
<td>350</td>
<td>20</td>
<td>40:1</td>
<td>N/A</td>
<td>42ml; 316SS</td>
<td>continuous</td>
<td>(Song, Lim, Lee, &amp; Lee, 2008)</td>
</tr>
<tr>
<td>Palm</td>
<td>200-</td>
<td>N/A</td>
<td>3-80:1</td>
<td>0.5-20</td>
<td>4.7 ml; 316SS</td>
<td>batch</td>
<td>(Varma, Deshpande, &amp; Madras, 2010)</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Song, Lim, Lee, &amp; Lee, 2008)</td>
</tr>
<tr>
<td>Sesame &amp; mustard</td>
<td>275-</td>
<td>20</td>
<td>30-80:1</td>
<td>5-70</td>
<td>10ml; 316SS</td>
<td>batch</td>
<td>(Song, Lim, Lee, &amp; Lee, 2008)</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Varma, Deshpande, &amp; Madras, 2010)</td>
</tr>
<tr>
<td>Palm oil</td>
<td>300-</td>
<td>15-25</td>
<td>20-60:1</td>
<td>5-25</td>
<td>12ml; 316SS</td>
<td>batch</td>
<td>(Tan, Gui, Lee, &amp; Mohamed, 2010)</td>
</tr>
<tr>
<td>420</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Bertoldi et al., 2009)</td>
</tr>
<tr>
<td>Soybean</td>
<td>300-</td>
<td>7.5-20</td>
<td>10-40:1</td>
<td>N/A</td>
<td>88ml, 13.5ml; 316SS</td>
<td>continuous</td>
<td>(Bertoldi et al., 2009)</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Bertoldi et al., 2009)</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>200-</td>
<td>10.5</td>
<td>10-60:1</td>
<td>5-30</td>
<td>23ml; 316SS</td>
<td>batch</td>
<td>(Yoo et al., 2010)</td>
</tr>
<tr>
<td>270</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In order to achieve a homogeneous reaction phase to avoid other issues such as interphase mixing and mass transfer, the pressure-temperature relationships of triglyceride-alcohol mixtures were studied by using Peng Robinson equation of state. It was found that higher alcohol-to-oil ratios actually reduce the critical temperature of the reactant mixture.

One major concern about transesterification in supercritical methanol is the extent to which biodiesel components decompose at the high reaction temperatures. The decomposition of methyl esters was assumed to occur at temperatures above 350 °C. From the recent study, decomposed products such as smaller molecular compounds from unsaturated and saturated FAMEs, and glycerol will improve some biodiesel qualities such as volatility, cold flow properties and viscosity (Marulanda, Anitescu, & Tavlarides et al., 2010b).

2.2 Kinetic studies of transesterification reactions

Due to complex composition of feedstocks, only a few non-catalytic transesterification kinetics studies have been published. Kinetics of transesterification reactions with either acid or alkali as catalyst has been reported by some researchers. Back to early 1970s, Dufek and coworkers (Schwab, Frankel, Dufek, & Cowan, 1972) studied esterification and transesterification using an acid as catalyst of methyl carboxystearate and its mono- and dimethyl esters, and reported unequal chemical reactivity for different carboxymethyl and carboxyl groups. A review summarized by Sridharan and Mathai (Sridhara.R & Mathai, 1974) on the transesterification reactions involves studies of alcoholysis, acidolysis, vinyl interchange, and ester-ester interchange earlier than 1974. Kinetics of transesterification of C18 unsaturated fatty acids in tall oil with methanol (Solovev, Bychkov, Koshel, & Rodivilova, 1989), acidolysis of castor oil with oleic acid (Erciyes, Dandik, & Kabasakal, 1991), and methanolysis of sunflower
oil catalyzed with KOH (Mittelbach & Trathnigg, 1990) were investigated at the end of the last century.

Freedman et al. (Freedman, 1986) reported the transesterification reaction of soybean oil and other vegetable oils with butanol and alcohols (Freedman, Butterfield, & Pryde, 1986), and examined what were the effects of the type of alcohol, molar ratio, type and amount of catalyst and reaction temperature on rate constants and kinetic order. The reaction rate constants were determined, and the effect of other reaction parameters was investigated such as molar ratio of alcohol to soybean oil, temperature, catalyst type and concentration. A completely reversible three-step second-order reaction model was proposed to describe the mechanism. In particular at a molar ratio of 6:1, a second-order mechanism with a fourth-order shunt mechanism (the reaction began with a second order then turned to a fourth order) best described the kinetics.

Noureddini and Zhu (Noureddini & Zhu, 1997) studied the kinetics of the transesterification of soybean oil with methanol in which they particular investigated the effect of mixing (Noureddini & Zhu, 1997). Darnoko (Darnoko & Cheryan, 2000) also studied the effect of mixing of reactants, and at the same time the alcohol type, the molar ratio of alcohol to oil, the reaction temperature, and the type and amount of catalyst for the conventional transesterification of the vegetable oil.

Bikou et al. (Bikou, Louloudi, & Papayannakos, 1999) described the effect of water on the kinetics of cotton oil ethanolysis catalyzed by KOH. In their study the kinetics of the non-catalytic methanolysis of soybean oil at 220 and 230 °C were discussed. Diasakov et al. reported kinetics on non-catalytic transesterification reaction of soybean oil processed at 220–235 °C (Diasakou et al., 1998).
Kinetics of the transesterification reaction under non-catalytic conditions is another important part of biodiesel synthesis kinetic study. Kusdiana and Saka (Kusdiana & Saka, 2001) studied the kinetics of transesterification of rapeseed oil to biodiesel fuel without the application of a catalyst in supercritical methanol. The effect of the molar ratio, pressure, and reaction temperature on FAME formation, reaction rate and apparent activation energy was investigated, and a simple model for the kinetics of the transesterification reaction was proposed. In the work done by He et al. (He et al., 2007), the kinetics study of transesterification reaction of soybean oil in supercritical methanol without any catalyst was investigated. Table 2-2 summarizes kinetic models proposed in different studies.
Table 2-2 Summarization of different kinetic models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Reactions</th>
<th>Order</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three steps, reversible, alkaline as catalyst</td>
<td>$TG + MeOH \xrightleftharpoons[k_1]{k_{-1}} DG + ME$</td>
<td>Second order</td>
<td>(Darnoko &amp; Cheryan, 2000, Noureddini &amp; Zhu, 1997, Wenzel et al., 2006, Shahbazi, M.R. et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>$DG + MeOH \xrightarrow[k_2]{k_{-2}} MG + ME$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$MG + MeOH \xrightleftharpoons[k_3]{k_{-3}} GL + ME$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$TG + MeOH \xrightarrow[k_1]{k_{-1}} DG + ME$</td>
<td>First order</td>
<td>(Diasakou et al., 1998)</td>
</tr>
<tr>
<td></td>
<td>$DG + MeOH \xrightarrow[k_2]{k_{-2}} MG + ME$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$MG + MeOH \xrightarrow[k_3]{k_{-3}} GL + ME$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three steps, irreversible, no catalyst</td>
<td>$TG + MeOH \xrightarrow[k_1]{k_{-1}} DG + ME$</td>
<td>First order</td>
<td>(Kusdiana &amp; Saka, 2001, He et al., 2007)</td>
</tr>
<tr>
<td></td>
<td>$DG + MeOH \xrightarrow[k_2]{k_{-2}} MG + ME$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$MG + MeOH \xrightarrow[k_3]{k_{-3}} GL + ME$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>One step, reversible, non catalyst</td>
<td>$TG + 3MeOH \xrightleftharpoons[k_1]{k_{-1}} GL + 3ME$</td>
<td>First order</td>
<td>(Singh &amp; Fernando, 2007)</td>
</tr>
<tr>
<td>One step reversible, different base catalyst</td>
<td>$TG + 3MeOH \xrightleftharpoons[k_1]{k_{-1}} GL + 3ME$</td>
<td>First order, or third order, depends on catalyst type</td>
<td></td>
</tr>
</tbody>
</table>

2.3 Microalgae oil as a feedstock for biodiesel production

It is inevitable to largely use non-conventional fuel such as biodiesel rather than conventional petroleum-based diesel in the future in order to decrease the pollution (Anitescu et al., 2008; Canoira et al., 2008; D'Ippolito, Yori, Iturria, Pieck, & Vera, 2007a; Pinnarat & Savage, 2008). Biodiesel, a common term for long chain alkyl esters, is a renewable, biodegradable, and non-toxic biofuel that shows great promise to environment and human daily life (Krohn, McNeff, Yan, & Nowlan, 2011). It can be produced from esterification and transesterification reactions of free fatty acids and triglycerides which are derived from plants, animals, or microbes (McNeff et al., 2008; Williams & Laurens, 2010). Compared to petroleum diesel, biodiesel emits lower levels of environmental pollutants such as particulate matter, volatile organic compounds, and sulfur-compounds during combustion (Graboski & McCormick, 1998; Swanson, Madden, & Ghio, 2007).

Biodiesel production is mostly produced from refined vegetable oils which are expensive, and which makes commercial biodiesel’s cost prohibitively high without government subsidies. Furthermore, biodiesel plants must also compete with food, cosmetics, industrial, and livestock feed demands for the feedstock oil (McNeff et al., 2008). Although countries that use biodiesel are not expected to take full responsibility, international concerns about the upward pressure on global food prices and intensified competition for cropland currently make the use of crop-based biodiesel a somewhat politically embarrassing situation (Xu & Mi, 2011).

To decrease competition with food stock and production costs to make biodiesel profitable in comparison with petroleum fuels, it is inevitable for production processes to use inexpensive triglyceride sources, such as unrefined waste cooking oils, vegetable oils, animal fats, or microalgae oils (Marulanda, Anitescu, & Tavlarides, 2010a).
Microalgae oil, which offers many potential advantages as a non-food feedstock for biodiesel production (Chisti, 2007), has been recognized as a promising alternative source for oil production. Microalgae can accumulate substantial amounts of lipids – up to 50% of dry cell weight in certain species (Chisti, 2007), which is as much as 40 times more oil per acre than other plants used for biofuels (Schenk et al., 2008). There are several microalgae species which have high lipid content, such as Chlorella protothecoides heterotrophic (38 – 51% lipid content), Botryococcus braunii (68% - 74% lipid content), Dunaliella tertiolecta (37 – 40% lipid content), Nitzschia (49 – 51% lipid content), and Nannochloropsis sp. (39 – 42% lipid content).

Microalgae growth technology has been researched and developed in various design options for more efficient productions since the last century. The cultivating systems mainly include 1) Open Pond Systems, 2) Closed Pond Systems, 3) Plastic Bag Systems, 4) Tubular Systems, and 5) Pyramid Photobioreactor Systems which produced the microalgae oil used in this work, as shown in Fig. 2-1.

Soley Institute in Turkey studied and compared the five systems with each other in terms of daily productivity, energy requirement, area requirement, maintenance requirement, and other factors. The results are listed in Table 2-3. We can see that based on 100 tons water as media, Pyramid Photobioreactor Systems exhibit the best efficiency, and provide impressive advantages over other systems in terms of productivity, energy efficiency, and other factors studied.
Table 2-3 Comparison of different microalgae cultivating systems. From the study done by Soley Institute in Turkey (Kizililsoley & Helvacioglu, 2008).

<table>
<thead>
<tr>
<th></th>
<th>Open Pond</th>
<th>Closed Pond</th>
<th>Plastic Bag</th>
<th>Tubular</th>
<th>Pyramid Photobioreactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Media (tons)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Area Requirement (m²)</td>
<td>250</td>
<td>250</td>
<td>1200</td>
<td>1200</td>
<td>60</td>
</tr>
<tr>
<td>Daily Productivity (kg dry wt.)</td>
<td>35</td>
<td>35</td>
<td>60</td>
<td>80</td>
<td>145</td>
</tr>
<tr>
<td>Areal Productivity (kg/m²/day)</td>
<td>0.14</td>
<td>0.14</td>
<td>0.05</td>
<td>0.07</td>
<td>2.42</td>
</tr>
<tr>
<td>Contamination Risk</td>
<td>++++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Energy Requirement</td>
<td>+++</td>
<td>++</td>
<td>+++</td>
<td>++++</td>
<td>+</td>
</tr>
<tr>
<td>Staff Requirement</td>
<td>++++</td>
<td>+++</td>
<td>++</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Microbiological Safety</td>
<td>+</td>
<td>++</td>
<td>+++</td>
<td>++++</td>
<td>+</td>
</tr>
<tr>
<td>Periodic Maintenance Requirement</td>
<td>+++++</td>
<td>+++++</td>
<td>+++</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Productivity Stability (temp., sunlight, etc)</td>
<td>+</td>
<td>++</td>
<td>+++</td>
<td>++++</td>
<td>++++</td>
</tr>
</tbody>
</table>

“+” represents the value of the objects, the more “+”, the higher value of the objects.
To extract oil from microalgae cell, in lab scale work, people often either directly use supercritical carbon dioxide (Aresta, Dibenedetto, Carone, Colonna, & Fragale, 2005; Halim, Gladman, Danquah, & Webley, 2011), or use microwaves to break cell wall, and then add organic solvent (i.e. chloroform) to extract oil from microalgae biomass (Mata, Martins, & Caetano, 2010; Wahlen, Willis, & Seefeldt, 2011). In industrial scale production, complicated production methods have been applied. Fig. 2-2 illustrates the method applied by Soley Institute in Turkey (Kızılılsoley & Helvacioglu, 2008) to extract oil from microalgae.

In photobioreactor systems, microalgae crops can be produced 3–4 times more than in open ponds in a day. Microalgae harvest filters are used to collect microalgae biomass. After collecting microalgal sludge from water media, the collected biomass is treated for 4 hours by extractor bacteria which can crack microalgae cell walls. Then the biomass undergoes 2 hours ultrasonic extraction, 2 hours microwave extraction, and 2 hours water extraction after which a cold press process is applied to totally separate the biomass from the oil-water mixture. Then oil and water are separated. The final step is to use oil filtration and UV sterilization to clean the final product, microalgae oil. With improved microalgae-growth technology and oil-extraction technology, cost of microalgae oil is getting lower (e.g. $0.5/liter) (Microalgae oil trade. Retrieved June 26, 2012, from http://www.soleybio.com/oil-trade.html).
Fig. 2-2. Microalgae oil production process applied by Soley Institute in Turkey. (Kizilsoley & Helvacioglu, 2008).
However, because high amounts of free fatty acids (FFAs) and sometimes a little water which react with the catalyst exist in feedstocks, conventional catalytic production processes cannot efficiently make use of such feedstocks mentioned above without additional pretreatment steps. Studies show that the transesterification reaction of biodiesel production with supercritical methanol successfully solves these problems. As shown in Table 2-4, there have been only a few studies of transesterification in supercritical methanol conditions using microalgae oil as feedstock. Nannochloropsis and Chlorella were chosen as the oil provider. Only one continuous reaction study was published (Krohn et al., 2011), other work (Levine, Pinnarat, & Savage, 2010; Patil et al., 2011) studied non-catalytic transesterification using microalgae oil in batch reactors. In the study done by Krohn et al., they claimed high conversion can be achieved at a residence time of 0.5 min. But as shown in their flow diagram, oil and methanol mixed together before going into the reactor at high temperature and pressure, and biodiesel was not separated with the rest of reactants until reaching the separation system, which means oil and methanol started to react before the reactor and did not stop reacting after leaving the reactor. Considering this problem, it is not appropriate to calculate residence time just considering the reactor volume as they did. In summary, the calculation of residence time and flow rate are not correct, so it can be concluded that there is no study clearly showing continuous transesterification reaction under supercritical methanol conditions with microalgae oil as feedstock. Accordingly, another purpose of this work is to systemically study the transesterification reaction under supercritical methanol conditions in a continuous flow reactor with microalgae oil as feedstock.
Table 2-4 Micoalgae species oils applied in non-catalytic biodiesel synthesis studies.

<table>
<thead>
<tr>
<th>Microalgae Type</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>alcohol:oil ratio</th>
<th>τ (min)</th>
<th>reactor</th>
<th>reaction type</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nannochloropsis oculata; Dunaliella tertiolecta</td>
<td>300 - 450°C</td>
<td>15</td>
<td>32:1 (molar)</td>
<td>0.5</td>
<td>Blank stainless steel 1cm i.d.*15cm long</td>
<td>continuous</td>
<td>(Krohn et al., 2011)</td>
</tr>
<tr>
<td>Chlorella vulgaris</td>
<td>275°C, 325°C</td>
<td>N/A</td>
<td>36:1(molar)</td>
<td>60</td>
<td>120</td>
<td>1.6 mL 316 stainless steel</td>
<td>batch</td>
</tr>
<tr>
<td>Nannochloropsis sp.</td>
<td>240-260°C</td>
<td>1200psi</td>
<td>1:4 - 1:12 (wt./vol.)</td>
<td>10-30</td>
<td>100 mL PARR micro-reactor</td>
<td>batch</td>
<td>(Patil et al., 2011)</td>
</tr>
<tr>
<td>Chlorella protothecoides</td>
<td>350°C, 385°C, 400°C</td>
<td>15, 20, 30</td>
<td>6:1, 9:1, 12:1 (molar)</td>
<td>3-12</td>
<td>1.753 i.d.*4m 316 SS high-pressure tubing</td>
<td>continuous</td>
<td>This work</td>
</tr>
</tbody>
</table>
Chapter 3: Kinetics of triolein transesterification as model compound for biodiesel synthesis in supercritical methanol
3.1 Materials and Methods

3.1.1 Materials

Triolein (C\textsubscript{57}H\textsubscript{104}O\textsubscript{6}) with a purity of 99.9 wt\%, gas chromatography (GC) standard solutions, N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), and internal standards to analyze total and free glycerol (according to the ASTM method D-6584) were purchased from Sigma Aldrich. N-heptane and methanol were purchased from Thermo Fisher Scientific and used without further purification.

3.1.2 Laboratory setup

A schematic diagram of the experimental setup is illustrated in Fig. 3-1. It mainly consists of two syringe pumps (Teledyne ISCO) for methanol and triolein delivery at high pressure, two electrical heating tapes twining round the pipes to preheat oil and methanol, a stainless steel coiled tubular reactor (3.175 mm outer diameter × 0.711 mm wall thickness (1.753 mm inner diameter); 4-m long for runs at 385 °C and residence time from 0.5-2 min; 6-m long for other runs), an electrical furnace (Briskheat) to heat the reactor, a micrometering valve (Autoclave Engineers) at the reactor outlet to control the system pressure, and thermocouples to measure temperatures at the inlet (T3), middle (T4), and outlet (T5) of the reactor and at the exits of the two preheated pipes (T1, T2). Temperatures were monitored and recorded by a National Instruments data acquisition system (model TBX-68T), and system pressure was measured by an Ashcroft test gauge (model 1082, 0-10000 psig). The reaction products were collected in a vial cooled by an ice bath. Because of the low flow rate of each feedstock and relative large heat transfer area between the pipe and air, products were cooled down soon after leaving the reactor.
Fig.3-1 Experimental flow diagram. P1 and P2 are syringe pumps; $P$ – pressure indicator, $T1$-$T5$ – thermocouples.
3.1.3. Experimental Conditions

Transesterification experiments of triolein in supercritical methanol were originally designed to be performed in a temperature range of 355-400 °C, pressure of 15 MPa, residence time range of 0.5-10 min, and constant methanol-to-triolein molar ratio of 9:1. The experiments conducted for this thesis were at 0.5-2 minutes, the experiments at the other reaction times were executed by Cong (Cong & Tavlarides, 2010). Previous experimental results show that under selected parameters, a homogenous reaction phase could be achieved and led to an almost-complete conversion of triglyceride to biodiesel. Further, at longer residence times, glycerol decomposition occurs, and the products are included in the fuel (Anitescu et al., 2008). A Table of flow rates of oil and MeOH at reaction conditions for each run is listed in Appendix A.

In a specific run, the reactor was preheated to reaction temperature, and methanol was pumped into the reactor to keep the system pressure at 15 MPa. Flow rates were set according to the residence time, volume of the reactor, and the molar volume of reactants calculated by Peng – Robinson equation of state (See Appendix A). After achieving steady state, effluent stream samples were collected. To test reversibility of transesterification reaction, a batch reaction done by Tao Cong (Cong & Tavlarides, 2010) was conducted using methyl oleate (C_{19}H_{36}O_{2}) and excess amount of glycerol at 400 °C. Methyl oleate (0.2 ml) and glycerol (0.2 ml) were mixed in a 2ml batch reactor. The batch reactor was heated in an oven from room temperature to 400 °C at a rate of 50 °C / min. After stabilized at 400 °C for 10 min, the reactor was cooled down to room temperature in 5 min. The sample was collected and then analyzed without any pretreatment.
Note: The experiments in this kinetics work were done by Mr. Tao Cong (runs 5 – 11 in Table 3-1) and the author (runs 1 – 4 in Table 3-1). The batch experiment to test the reversibility of reaction was done by Mr. Tao Cong.

3.1.4. Analytical Methods

Free and total glycerol quantification were performed by a GC (HP 5890 series II) equipped with a Restek Rtx-Biodiesel triglyceride column (10 m × 0.32 mm I.D. × 0.1 μm film thickness) and a flame ionization detector (FID). Helium was used as a carrier gas. The temperature program was from 60 °C hold for 2 min, to 180 °C at 15 °C/min, and then to 380 °C at 7 °C/min. The injection and detection temperatures were 360 and 380 °C, respectively.

3.2 Results and Discussion

3.2.1. Conversion and Yields of the Reaction Components

The triglycerides are converted to diglycerides which in turn are converted to monoglycerides, and then to glycerol. One FAME molecule (methyl oleate) is produced at each step. If the reaction is incomplete, then there will be triglycerides, diglycerides, and monoglycerides left in the product. Each of these compounds still contains a glycerol molecule skeleton that has not been released. The glycerol portion of these compounds is referred to as bound glycerol, and affects the quality of biodiesel. According to ASTM D-6584, samples from each run were analyzed to determine the component concentration. Table 3-1 summarizes the experimental reaction conditions and analysis results for each run in this study. All samples were diluted before injecting into the GC column to fit within the standard curve range. One should notice that in Table 3-1, the measured weight percentage of each compound is the weight
percentage in collected samples, rather than the weight percentage in the homogeneous reaction system.

The transesterification conversion (conversion) was defined as the ratio of weight percent of methyl esters (i.e. oleic and stearic) and their smaller molecular decomposition product in a known mass of sample to the weight percent of initial triolein, which is 99.9%:

$$conversion = 100 \left(1 - \frac{C_{TO} + C_{DO} + C_{MO}}{C_0}\right)$$  (3-1)

Here $C_{TO}$, $C_{DO}$, $C_{MO}$ are weight percentage of triolein, diolein and monoolein after reaction, respectively, in weight %. $C_0$ is the initial weight percentage of triolein before the reaction, which equals to 99.9 wt%. The conversion increased from 50.93% to 97.66% for residence time increase from 0.5 min to 10 min at 385 °C. Also almost complete conversion was achieved at 400 °C for 6 min of residence time. GC-FID chromatograms are shown in Fig. 3-2, and the calculation of mass fraction of each compound is shown in Appendix B.
Table 3-1: Species content in collected samples determined by GC-FID. The data from runs 5 to run 11 were from Tao Cong’s report (Cong & Tavlarides, 2010).

<table>
<thead>
<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>T^a (min)</th>
<th>GL^b (wt%)</th>
<th>MO^c (wt%)</th>
<th>DO^d (wt%)</th>
<th>TO^e (wt%)</th>
<th>conversion (%)</th>
<th>BG^f (wt%)</th>
<th>TG^g (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>385</td>
<td>15</td>
<td>0.5</td>
<td>0.007</td>
<td>1.12</td>
<td>16.15</td>
<td>31.55</td>
<td>50.9</td>
<td>5.98</td>
<td>5.98</td>
</tr>
<tr>
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<td>385</td>
<td>15</td>
<td>1.0</td>
<td>0.026</td>
<td>2.85</td>
<td>14.23</td>
<td>12.17</td>
<td>70.6</td>
<td>4.12</td>
<td>4.20</td>
</tr>
<tr>
<td>3</td>
<td>385</td>
<td>15</td>
<td>1.5</td>
<td>0.265</td>
<td>3.20</td>
<td>6.55</td>
<td>8.05</td>
<td>82.2</td>
<td>2.64</td>
<td>2.90</td>
</tr>
<tr>
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<td>15</td>
<td>2.0</td>
<td>0.54</td>
<td>3.45</td>
<td>4.07</td>
<td>3.46</td>
<td>89.0</td>
<td>1.25</td>
<td>1.79</td>
</tr>
<tr>
<td>5</td>
<td>385</td>
<td>15</td>
<td>4.0</td>
<td>0.50</td>
<td>2.69</td>
<td>0.98</td>
<td>0.15</td>
<td>96.2</td>
<td>0.86</td>
<td>1.36</td>
</tr>
<tr>
<td>6</td>
<td>385</td>
<td>15</td>
<td>6.0</td>
<td>0.44</td>
<td>2.30</td>
<td>0.90</td>
<td>0.07</td>
<td>96.7</td>
<td>0.74</td>
<td>1.18</td>
</tr>
<tr>
<td>7</td>
<td>385</td>
<td>15</td>
<td>8.0</td>
<td>0.38</td>
<td>2.12</td>
<td>0.69</td>
<td>0.06</td>
<td>97.1</td>
<td>0.66</td>
<td>1.04</td>
</tr>
<tr>
<td>8</td>
<td>385</td>
<td>15</td>
<td>10.0</td>
<td>0.36</td>
<td>1.76</td>
<td>0.54</td>
<td>0.04</td>
<td>97.7</td>
<td>0.54</td>
<td>0.90</td>
</tr>
<tr>
<td>9</td>
<td>355</td>
<td>15</td>
<td>6.0</td>
<td>0.44</td>
<td>3.58</td>
<td>0.87</td>
<td>1.17</td>
<td>94.4</td>
<td>1.18</td>
<td>1.62</td>
</tr>
<tr>
<td>10</td>
<td>370</td>
<td>15</td>
<td>6.0</td>
<td>0.51</td>
<td>3.83</td>
<td>0.89</td>
<td>0.57</td>
<td>94.7</td>
<td>1.19</td>
<td>1.70</td>
</tr>
<tr>
<td>11</td>
<td>400</td>
<td>15</td>
<td>6.0</td>
<td>0.18</td>
<td>1.18</td>
<td>0.36</td>
<td>0.03</td>
<td>98.4</td>
<td>0.36</td>
<td>0.54</td>
</tr>
</tbody>
</table>

a- the residence time; b- free glycerol; c- monoolein; d- diolein; e- triolein; f- bound glycerol; and g- total glycerol (GL+BG).
Fig. 3-2 FID chromatograms for the reaction products of triolein-MeOH transesterification at 385 °C, 15 MPa, and methanol-to-triolein molar ratio of 9. Peak Identification in first chromatograph: 1 – Glycerol, 2 – Internal Standard (butanetriol), 3 – Fatty acid methyl esters, 4 – Monoolein, 5 – Internal Standard (tricaprin), 6 – Diolein, and 7 – Triolein.
Based on Mr. Tao Cong’s work (Cong & Tavlarides, 2010), the content variation of triolein and the consequent reaction products (diolein, monoolein and glycerol), in the ester phase, with temperature are shown in Fig. 3-3. The weight profiles of triolein, diolein, monoolein, and glycerol were determined from their relative calibration curves according to ASTM D-6584. The triolein content decreased as reaction temperature is increased from 355 to 400 °C. The monoolein weight percent decreased significantly with reaction temperature greater than 370 °C as shown in Fig. 3-3. No coke or dark brown color products were observed in any of the runs.

Glycerol appeared under all reaction conditions but the amount decreased with reaction residence times and temperature. Without any purification, in collected samples, free glycerol contents in all runs are above the ASTM standards maximum limit of 0.024 wt%. Also bound glycerol which represents the presence of monoglycerides, diglycerides, and triglyceride affects the quality of biodiesel. As shown in Eq.3-2 according to ASTM method D-6584, content of bound glycerol is calculated by

\[ \text{bound glycerol (wt %)} = 0.2591 \times MO + 0.1488 \times DO + 0.1044 \times TO \] (3-2)

where MO, DO, and TO refer to the weight percent of monoolein, diolein, and triolein, respectively. These constants 0.2591, 0.1488, and 0.1044 are the mass fractions of monoolein, diolein and triolein in glyceride molecules to the bound glycerol content. In Fig. 3-3, both free and bound glycerol amounts decreased significantly as temperature increased from 355 to 400 °C.
**Fig. 3-3** Species content profile in collected samples at a residence time of 6 min. Data were from Tao Cong’s work (Cong & Tavlarides, 2010).
Mass Balance on Reactor. The data presented in Table 3-1 provides the biodiesel product composition for each set of reaction conditions, after steady state operation was achieved. In order to evaluate kinetic models to describe the reaction system it is necessary to have a material balance over the reactor to describe the reaction product composition for each set of reaction conditions. It is noted that the product is composed of two phases, the biodiesel or ester phase consisting of triolein, diolein, monolein, free glycerol and methyl oleate, and the second phase of unreacted methanol and glycerol. This two phase structure assumes no other degradation products or ethers are formed. As only the mass composition of the product in the biodiesel phase was measured for each set of flow conditions in the reactor, after steady state and stabilized reaction conditions were achieved, a mass balance over the reactor is employed to obtain the weight fraction of each compound in the product. The calculation procedure is shown in Appendix C.

Table 3-2 shows the weight percentage of each compound when in the homogeneous reaction system. Data from Table 3-2 was chosen to do the kinetics simulation.
Table 3-2 Species content in the reaction system.

<table>
<thead>
<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>τ&lt;sup&gt;a&lt;/sup&gt; (min)</th>
<th>GL and others&lt;sup&gt;b&lt;/sup&gt; (wt%)</th>
<th>MO&lt;sup&gt;c&lt;/sup&gt; (wt%)</th>
<th>DO&lt;sup&gt;d&lt;/sup&gt; (wt%)</th>
<th>TO&lt;sup&gt;e&lt;/sup&gt; (wt%)</th>
<th>ME&lt;sup&gt;f&lt;/sup&gt; (wt%)</th>
<th>MeOH&lt;sup&gt;g&lt;/sup&gt; (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>385</td>
<td>15</td>
<td>0.5</td>
<td>9.63</td>
<td>0.78</td>
<td>11.28</td>
<td>22.04</td>
<td>35.55</td>
<td>20.72</td>
</tr>
<tr>
<td>2</td>
<td>385</td>
<td>15</td>
<td>1.0</td>
<td>12</td>
<td>1.96</td>
<td>9.78</td>
<td>8.36</td>
<td>48.51</td>
<td>19.32</td>
</tr>
<tr>
<td>3</td>
<td>385</td>
<td>15</td>
<td>1.5</td>
<td>11.47</td>
<td>2.25</td>
<td>4.61</td>
<td>5.67</td>
<td>57.87</td>
<td>18.3</td>
</tr>
<tr>
<td>4</td>
<td>385</td>
<td>15</td>
<td>2.0</td>
<td>11.75</td>
<td>2.44</td>
<td>2.88</td>
<td>2.45</td>
<td>63.1</td>
<td>17.74</td>
</tr>
<tr>
<td>5</td>
<td>385</td>
<td>15</td>
<td>4.0</td>
<td>10.79</td>
<td>1.95</td>
<td>0.71</td>
<td>0.11</td>
<td>69.8</td>
<td>17.02</td>
</tr>
<tr>
<td>6</td>
<td>385</td>
<td>15</td>
<td>6.0</td>
<td>10.37</td>
<td>1.68</td>
<td>0.66</td>
<td>0.05</td>
<td>70.61</td>
<td>16.93</td>
</tr>
<tr>
<td>7</td>
<td>385</td>
<td>15</td>
<td>8.0</td>
<td>10.13</td>
<td>1.55</td>
<td>0.51</td>
<td>0.04</td>
<td>71.15</td>
<td>16.87</td>
</tr>
<tr>
<td>8</td>
<td>385</td>
<td>15</td>
<td>10.0</td>
<td>9.82</td>
<td>1.3</td>
<td>0.4</td>
<td>0.03</td>
<td>71.96</td>
<td>16.78</td>
</tr>
<tr>
<td>9</td>
<td>355</td>
<td>15</td>
<td>6.0</td>
<td>11.39</td>
<td>2.56</td>
<td>0.62</td>
<td>0.84</td>
<td>67.66</td>
<td>17.25</td>
</tr>
<tr>
<td>10</td>
<td>370</td>
<td>15</td>
<td>6.0</td>
<td>11.68</td>
<td>2.74</td>
<td>0.64</td>
<td>0.41</td>
<td>67.65</td>
<td>17.25</td>
</tr>
<tr>
<td>11</td>
<td>400</td>
<td>15</td>
<td>6.0</td>
<td>9.09</td>
<td>0.88</td>
<td>0.27</td>
<td>0.02</td>
<td>73.2</td>
<td>16.65</td>
</tr>
</tbody>
</table>

<sup>a</sup> - the residence time; <sup>b</sup> - free glycerol and decomposition products; <sup>c</sup> - monoolein; <sup>d</sup> - diolein; <sup>e</sup> - triolein; <sup>f</sup> - methyl oleate; and <sup>g</sup> - methanol.
3.2.2. Critical Properties of Triolein-Methanol Mixtures

Kinetics investigations of castor oil and linseed oil systems revealed an unusual behavior of the reaction constant with increasing temperature and pressure (Varma & Madras, 2007): a significant increase occurs between sub- and supercritical state. In order to explain this phenomenon, a study of the phase behavior in triglyceride-methanol mixtures is needed. The experimental values of critical constants of triolein are not available because it is chemically unstable and decomposes at high temperatures. For this reason the Gani Method (Glisic, Montoya, Orlovic, & Skala, 2007), a method to estimate properties of high molecular weight compounds (Araujo & Meireles, 2000), was used to estimate the critical properties of triolein. The critical properties and other parameters of the pure components are listed in Table 3-3.

In this work, considering that: a) supercritical methanol rushed into liquid triolein at high pressure and high temperature, b) short residence time, and c) extremely high ratio of the reactor-length (4 meter) and reactor diameter (1.75 mm), it was assumed that triolein and methanol was mixed well in a short period. This assumption was also proved in Appendix D.
Table 3-3 Physical properties of triolein and methanol used in this study (Glisic & Skala, 2010).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M (g/mol)</th>
<th>T_c (°C)</th>
<th>P_c (MPa)</th>
<th>ω^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>32</td>
<td>239</td>
<td>8.00</td>
<td>0.565</td>
</tr>
<tr>
<td>Triolein</td>
<td>885</td>
<td>705</td>
<td>0.334</td>
<td>1.987</td>
</tr>
</tbody>
</table>

a- acentric factor
In the study done by Ngamprasertsith et al. (Bunyakiat et al., 2006), the critical temperatures and pressures of triolein-methanol mixtures were estimated by Lorentz-Berthelot type mixing rules as follows:

\[
T_{ci,j} = \sqrt{T_{ci}T_{cj}} \tag{3-3}
\]

\[
P_{ci,j} = \frac{1}{V_{ci,j}} \sqrt{P_{ci}P_{cj}V_{ci}V_{cj}} \tag{3-4}
\]

\[
z_{ci,j} = 0.5(z_{ci} + z_{cj}) \tag{3-5}
\]

\[
V_{ci,j}^{1/3} = 0.5 \left( V_{ci}^{1/3} + V_{cj}^{1/3} \right) \tag{3-6}
\]

\[
V_{cm} = \sum_i \sum_j x_i x_j V_{ij} = x_i^2 V_{ci} + 2x_i x_j V_{ci,j} + x_j^2 V_{cj} \tag{3-7}
\]

\[
T_{cm}V_{cm} = \sum_i \sum_j x_i x_j T_{ci,j}V_{ij} = x_i^2 T_{ci}V_{ci} + 2x_i x_j T_{ci,j}V_{ci,j} + x_j^2 T_{cj}V_{cj} \tag{3-8}
\]

\[
z_{cm} = \sum_i \sum_j x_i x_j z_{ci,j} = x_i^2 z_{ci} + 2x_i x_j z_{ci,j} + x_j^2 z_{cj} \tag{3-9}
\]

\[
T_{cm} = \frac{T_{cm}V_{cm}}{V_{cm}} \tag{3-10}
\]

\[
P_{cm} = \frac{z_{cm}RT_{cm}}{V_{cm}} \tag{3-11}
\]

where \(i, j\) are subscripts for triolein and methanol, respectively; \(cm\) is subscript for triolein-methanol mixture, \(x\) is mole fraction, \(T_c\) is critical temperature, \(V_c\) is critical molar volume, \(z_c\) is compressibility factor and \(P_c\) is critical pressure.

But the critical properties calculated by Lorentz-Berthelot type mixing rules are actually the pseudocritical properties rather than the true critical properties. These pseudocritical properties usually differ quite markedly from the true values. In fact, the true critical properties of mixtures often can be evaluated with equations of state (Walas & Knovel, 1990; 1988). Peng-Robinson EOS (PR EOS) is a popular equation of state applied in industry and theoretical work. PR EOS is a modification of the Redlich-Kwong equation of state and was published by Peng and Robinson in 1976 (Peng, D.Y., Robinson, D.B, 1976). It is similar to the Soave-Redlich-
Kwong equation in many respects and was designed to improve the poor liquid density predictions over the SRK method.

Tang et al. (Tang et al., 2006) proves that PR EOS can be applied to predict the true critical properties of mixture of triolein and methanol. Their work shows that PR EOS can describe the Pressure-Temperature relationship of triolein-methanol mixture well. The equation can be expressed as follows (Peng, D.Y., Robinson, D.B., 1976):

\[
P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)}
\]

(3-12)

\[
a = a_c \times \alpha
\]

(3-13)

\[
\alpha^{0.5} = 1 + (0.37646 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})
\]

(3-14)

\[
a_c = 0.457235 \frac{(RT_c)^2}{P_c}
\]

(3-15)

\[
b = 0.077796 \frac{RT_c}{P_c}
\]

(3-16)

\[
T_r = \frac{T}{T_c}
\]

(3-17)

Where \(\omega\) is the acentric factor, R is the universal gas constant. For a mixture of two pure components i and j, the mixing rule applied here is (Prausnitz, Lichtenhaler, & de Azevedo, 1999):

\[
a = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{a,i,j})
\]

(3-18)

\[
b = \sum \sum x_i x_j \frac{b_i + b_j}{2} (1 - k_{b,i,j})
\]

(3-19)

The critical temperatures of triolein-methanol mixtures as a function of methanol-to-triolein molar ratio, predicted by PR EOS and Lorentz-Berthelot type mixing rules, are plotted in
**Fig. 3-4.** In Fig. 3-4, we can see the values predicted by LB mixing rules are quite different from the values calculated by PR EOS. For example, at stoichiometric molar ratio of 3, the pseudocritical temperature is near 440 °C, while the real critical temperature calculated by EOS is around 660 °C. LB mixing rules shows that at the reaction condition in this study, a supercritical state will be reached, while the reaction system is at a homogeneous liquid state based on the result calculated by PR EOS.

In this study, methanol-to-triolein molar ratio was kept at 9, and temperature was above 355 °C (from 355 to 400 °C). It is necessary to calculate the phase envelope of the triolein-methanol system in order to determine the physical state of the mixture in the reactor. PR EOS was applied to do the calculation. **Fig.3-5** illustrates the phase envelope of methanol-triolein mixture with a molar ratio of 9:1. The critical temperature is 557.6 °C, and critical pressure is 99.4 bar. The temperature and pressure at cricondenbar point is 428.9 °C and 126.4 bar, respectively. The temperature and pressure at cricondentherm point is 631.96 °C and 34.7 bar, respectively. Because all reaction conditions in this study are at a temperature range from 350 to 400 °C and a pressure of 150 bar, from **Fig. 3-5** we can see in the runs of this study, assuming that triolein and methanol were mixed well, a homogeneous liquid phase was reached with 9:1 methanol-to-triolein molar ratio.

As shown in **Table 3-2**, the weight fraction of each compound in the reactor changes with residence time. In other words, the critical properties of the reaction system change with residence time. Using PR EOS, the critical properties of the mixtures (triolein, diolein, monoolein, glycerol, methanol, and methyl oleate) at different residence time in the reactor were calculated, and the values are listed in **Table 3-4. Fig. 3-6** illustrates the P-T relationship of the mixtures at different residence time in the reactor.
Fig. 3-4 Critical temperature of triolein-methanol mixture at different methanol to triolein molar ratios calculated by Lorentz-Berthelot type mixing rules, and Peng-Robinson equation of state.
**Fig. 3-5** Phase envelope of triolein- methanol mixture. Methanol-to-triolein molar ratio is 9. Critical temperature is 557.6 °C, and critical pressure is 99.4 bar.
Fig. 3-6 Pressure-temperature relationship curves of reaction mixtures at different residence time in the reactor.
From Fig. 3-6, with the consumption of triolein and methanol and the appearance of methyl oleate, the enclosed area under P-T curve shrinks quickly till four minutes when the reaction is reaching equilibrium. This transaction helps mixtures in the reactor reach a homogeneous state. From Table 3-4, we can see the critical temperature drops from 557°C to 467°C in 0.5 min since the appearance of methyl oleate help decrease the critical temperature. The critical pressure also decreases from 99 bar to 64 bar in ten minutes. Considering the reaction conditions were kept as constant at temperature of 385 °C and 150 bar, the reaction did not occur at supercritical state. These results show that throughout the entire region of reaction conditions the reaction mixture was in a homogeneous liquid state which was getting closer to a supercritical state with reaction.
Table 3-4 Critical temperature and pressure of the reaction mixtures at different residence time in the reactor.

<table>
<thead>
<tr>
<th>$\tau$ (min)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$P_c$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>557.62</td>
<td>99.46</td>
</tr>
<tr>
<td>0.5</td>
<td>466.97</td>
<td>88.11</td>
</tr>
<tr>
<td>1.0</td>
<td>444.79</td>
<td>82.51</td>
</tr>
<tr>
<td>1.5</td>
<td>436.42</td>
<td>74.14</td>
</tr>
<tr>
<td>2.0</td>
<td>430.71</td>
<td>70.65</td>
</tr>
<tr>
<td>4.0</td>
<td>425.49</td>
<td>65.44</td>
</tr>
<tr>
<td>6.0</td>
<td>425.36</td>
<td>64.98</td>
</tr>
<tr>
<td>8.0</td>
<td>425.15</td>
<td>64.51</td>
</tr>
<tr>
<td>10.0</td>
<td>425.04</td>
<td>63.95</td>
</tr>
</tbody>
</table>
3.2.3 Kinetic Model

In most kinetic studies which focused on biodiesel synthesis in supercritical methanol (D'Ippolito, Yori, Iturria, Pieck, & Vera, 2007a; Dasari, Goff, & Suppes, 2003; Diasakou et al., 1998; He et al., 2007; Kusdiana & Saka, 2001) and even some work done under conventional conditions (Darnoko & Cheryan, 2000), weight percentage has been used as the unit of each compound in transesterification reaction, because concentration of each compound in reactors under non-catalytic conditions cannot be measured or calculated accurately. Mole per liter sometimes has been chosen as the unit in the biodiesel-synthesis kinetics work done under conventional conditions (Al-Zuhair, 2005; Noureddini & Zhu, 1997). In this study, weight percentage was applied first in the kinetic model, then the mole fraction was chosen for the kinetic analysis, in order to demonstrate both units can be used in non-catalytic biodiesel kinetic study.

In this study, four temperature values were chosen (355, 370, 385, and 400 °C). At 385 °C, runs of different residence time were performed. But only one run was performed for each of the other rest three temperature values. Because a three – step kinetic model will be proposed in this study, it is difficult to calculate the reaction constants for the three – step reactions with only one set of data. The kinetic model in this work only focuses on the runs at 385 °C.

Three-step Kinetic Model. Transesterification reactions are in principle assumed to be equilibrium reactions under supercritical methanol conditions. However, the consecutive transesterification reaction, which is a completely reversible three-step model, is in part adapted here. Based on the experimental results, we propose that triolein (TO) reacts irreversibly with methanol to produce diolein (DO), which further reacts reversibly with methanol to generate
monoolein (MO), and finally, monoolein reacts reversibly with methanol to give glycerol. To test this hypothesis, a batch reaction was conducted by Mr. Tao Cong using methyl oleate (95% purity) and excess amount of glycerol at 400 °C. The analytic results show small amounts of monoglyceride and diglyceride were generated after 10 min reaction time. However, no triglyceride was detected by GC-FID as shown in Fig. 3-7. Only small amounts of monoolein and traces of diolein were detected. Accordingly, the following reactions are proposed to describe this mechanism:

\[
TO + MeOH \xrightarrow{k_1} DO + ME
\]  
(3-20)

\[
DO + MeOH \xrightleftharpoons[k_2]{k^{-2}} MO + ME
\]  
(3-21)

\[
MO + MeOH \xrightleftharpoons[k_3]{k^{-3}} GL + ME
\]  
(3-22)

Hence, only Eqs. 3-21 and 3-22 were assumed to be reversible reactions. The best reaction constants and reaction order were determined by minimizing the averaged absolute relative deviation (AARD).
Fig. 3-7 GC-FID chromatographs of methyl oleate before (bottom) and after reaction (top) with glycerol at 400 °C and 10MPa for 10 min. Peak identification: 1 – Glycerol, 2 – Internal Standard (butanetriol), 3 – Monoolein, 4 – Internal Standard (tricaprin), and 5 – Diolein. Done by Tao Cong (Cong & Tavlarides, 2010).
Accordingly, the kinetics of the transesterification process can be described by the following differential equations (Diasakou et al., 1998). Data in Table 3-2 were analyzed using this model. The results are shown in Fig. 3-8.

\[
\frac{dX_{TO}}{d\tau} = -\frac{1}{M_{WMeOH}} k_1^* X_{TO} X_{MeOH}
\]

(3-23)

\[
\frac{dX_{DO}}{d\tau} = \frac{M_{WDO}}{M_{WTO} \times M_{WMeOH}} k_1^* X_{TO} X_{MeOH} - \frac{1}{M_{WMeOH}} k_2^* X_{DO} X_{MeOH} + \frac{M_{WDO}}{M_{WMO} \times M_{WMe}} k_{-2}^* X_{MO} X_{Me}
\]

(3-24)

\[
\frac{dX_{MO}}{d\tau} = \frac{M_{WMO}}{M_{WDO} \times M_{WMeOH}} k_2^* X_{DO} X_{MeOH} - \frac{1}{M_{WME}} k_{-2}^* X_{MO} X_{Me}
\]

(3-25)

\[
\frac{dX_{MeOH}}{dt} = -\frac{1}{M_{WTO}} k_1^* X_{TO} X_{MeOH} - \frac{1}{M_{WDO}} k_2^* X_{DO} X_{MeOH} - \frac{1}{M_{WMO}} k_3^* X_{MO} X_{MeOH}
\]

(3-26)

\[
+ \frac{M_{WMeOH}}{M_{WMO} \times M_{WME}} k_{-2}^* X_{MO} X_{Me} + \frac{M_{WMeOH}}{M_{WGL} \times M_{WME}} k_{-3}^* X_{GL} X_{Me}
\]

\[
\frac{dX_{ME}}{d\tau} = \frac{M_{WME}}{M_{WTO} \times M_{WMeOH}} k_1^* X_{TO} X_{MeOH} + \frac{M_{WME}}{M_{WDO} \times M_{WMeOH}} k_2^* X_{DO} X_{MeOH}
\]

(3-27)

\[
+ \frac{M_{WME}}{M_{WMO} \times M_{WMeOH}} k_3^* X_{MO} X_{MeOH} - \frac{1}{M_{WMO}} k_{-2}^* X_{MO} X_{ME} - \frac{1}{M_{WGL}} k_{-3}^* X_{GL} X_{ME}
\]
Fig. 3-8 Three-step kinetic model simulation results. Data of residence time 4 – 10 min was from Mr. Tao Cong’s work (Cong & Tavlarides, 2010), as shown in Table 3-2.
In these equations, \( k_1^* \), \( k_2^* \), \( k_2^- \), \( k_3^* \), and \( k_3^- \) have the following relationship with the reaction rate constants \( k_1 \), \( k_2 \), \( k_2^- \), \( k_3 \), and \( k_3^- \):

\[
k^* = k \frac{m}{V_{\text{reactor}}}
\]  

(3-28)

where \( m \) is the total mass of compounds in the reactor which can be calculated according to methanol and triolein flow rates listed in Appendix A, \( V_{\text{reactor}} \) is the volume of reactor, and \( X \) the weight percent of components as shown in Table 3-2. \( M_w \) represents molecular weight of components and are 885 g/mol, 621 g/mol, 356 g/mol, 296.5 g/mol, 92 g/mol and 32 g/mol for \( TO \), \( DO \), \( ME \), \( MO \), \( GL \) and methanol (MeOH), respectively. The best fit coefficients are shown in Table 3-5, and the corresponding simulated results are plotted in Fig. 3-8. Scientist 3.0 from Micromath was used to fit the experimental data. Initial guesses for the rate constants were determined manually by a trial-and-error method. Polymath 6.10 was used for the model simulations after rate constants were determined.

The unit applied in the above kinetic differential equations is weight percentage which has been normally used in biodiesel synthesis kinetics. If mole concentration fraction is applied in this model, the differential equations become:

\[
\frac{dC_{TO}}{d\tau} = -k_1^C_{TO}C_{MeOH}
\]  

(3-29)

\[
\frac{dC_{DO}}{d\tau} = k_1^C_{TO}C_{MeOH} - k_2^C_{DO}C_{MeOH} + k_2^-C_{MO}C_{ME}
\]  

(3-30)

\[
\frac{dC_{MO}}{d\tau} = k_2^C_{DO}C_{MeOH} - k_2^-C_{MO}C_{ME} - k_3^C_{MO}C_{ME} + k_3^-C_{GL}C_{ME}
\]  

(3-31)

\[
\frac{dC_{MeOH}}{d\tau} = -k_1^C_{TO}C_{MeOH} - k_2^C_{DO}C_{MeOH} + k_2^-C_{MO}C_{ME} - k_3^C_{MO}C_{MeOH}
\]  

(3-32)
\[
\frac{dC_{ME}}{d\tau} = -\frac{dC_{MeOH}}{d\tau}
\]  
(3-33)

Where C represents mole concentration fraction of each compound, and \( k' \) is the constant in the above equations where

\[
k' = C_{\text{total}}k
\]  
(3-34)

According to mass fraction of each compound shown in Table 3-2 and the flow rate of triolein and methanol shown in Appendix A, mole concentration and mole concentration fraction of each compound can be calculated and plotted, as shown in Fig. 3-9. The best fit coefficients are shown in Table 3-6.
**Table 3-5** Constants for the proposed mechanism, wt% as unit.

<table>
<thead>
<tr>
<th>k</th>
<th>k₁</th>
<th>k₂</th>
<th>k₂'</th>
<th>k₃</th>
<th>k₃'</th>
</tr>
</thead>
<tbody>
<tr>
<td>g · mol⁻¹ min⁻¹</td>
<td>2.88</td>
<td>4.40</td>
<td>1.06</td>
<td>12.75</td>
<td>1.59</td>
</tr>
</tbody>
</table>

**Table 3-6.** Constants for the proposed mechanism, mol% as unit.

<table>
<thead>
<tr>
<th>k</th>
<th>k₁</th>
<th>k₂</th>
<th>k₂'</th>
<th>k₃</th>
<th>k₃'</th>
</tr>
</thead>
<tbody>
<tr>
<td>min⁻¹</td>
<td>2.88</td>
<td>4.40</td>
<td>1.06</td>
<td>12.75</td>
<td>1.59</td>
</tr>
</tbody>
</table>
Fig. 3-9. Three-step kinetic model simulation results, mol% as unit.
Fig. 3-10 illustrates the reaction conversion changing with residence time. The averaged absolute relative deviation (AARD) of reaction conversion is defined here as:

$$AARD_{\text{conversion}} = \frac{1}{n} \times \sum_{j=1}^{n} \left| \frac{X_{\text{cal}} - X_{\text{exp}}}{X_{\text{exp}}} \right|$$

(3-34)

Where $X_{\text{cal}}$ is conversions calculated from the model, and $X_{\text{exp}}$ is the ones from experimental data. The conversion AARD in this work is 0.03. A good agreement between the experimental and the calculated values is observed in Fig. 3-8, 3-9, and 3-10. The bound glycerol and triglyceride conversion is well predicted: triolein concentration decreased sharply with residence time, while monoolein and diolein mass concentration increased to a maximum before further decreasing towards relatively small concentrations. These results imply that the three-step kinetic model proposed in this work can be used for design calculations when considering possible applications.
Fig. 3-10. Reaction conversion vs. residence time.
3.3. Conclusions

Transesterification of triolein with methanol was carried out at 355 – 400 °C, 150 bar, methanol-to-triolein molar ratio of nine, and residence time of 0.5 – 10 min. The 0.5 – 2.0 min experiments were the focus of this project. The concentrations of intermediate components were determined by GC-FID. The free glycerol and bound glycerol fractions were calculated according to ASTM D-6584. Critical properties and phase behavior of reaction mixture were studied using PR EOS. At such a lower methanol to triolein molar ratio (9:1), the reactions occur in a homogeneous liquid phase. The kinetics of the transesterification was studied, since there has been no published works on biodiesel kinetics study under similar reaction conditions (high temperature and low molar ratio). A totally reversible three-step kinetic model was revised to a partially reversible model where the first step reaction is assumed to be irreversible. A consecutive second order reaction mechanism was employed. The corresponding constants in the kinetic model at temperature of 385 °C were evaluated. The evolution of concentration of each component in the homogenous reaction system in this experiment can be well predicted by the kinetic model derived from the proposed consecutive reaction mechanism.
Chapter 4: Transesterification of microalgae oil in supercritical methanol for biodiesel production
4.1 Materials and methods

4.1.1 Materials

Microalgae oil was provided by Soley Institute in Turkey. N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), reference FAME standards (methyl linoleate 20 wt%, methyl linolenate 20 wt%, methyl oleate 20 wt%, methyl palmitate 20 wt%, and methyl stearate 20 wt%) for gas chromatography, a kit with gas chromatography (GC) standard solutions and internal standards to analyze total and free glycerol were purchased from Sigma Aldrich. N-heptane and HPLC-grade methanol were purchased from Thermo Fisher Scientific.

4.1.2 Laboratory setup

A schematic diagram of the experimental setup is illustrated in Fig. 3-1. It mainly consists of two syringe pumps (Teledyne ISCO) for methanol and microalgae oil delivery at high pressure, two electrical heating tapes twining round the pipes to preheat microalgae oil and methanol to 350 and 385 °C respectively, a stainless steel coiled tubular reactor (3.175 mm outer diameter × 0.711 mm wall thickness, 4-m long), an electrical furnace (Briskheat) to heat the reactor, a micrometering valve (Autoclave Engineers) at the reactor outlet to control the system pressure, and thermocouples to measure temperatures at the inlet (T3), middle (T4), and outlet (T5) of the reactor and at the exits of the two preheated pipes (T1, T2). Temperatures were monitored and recorded by a National Instruments data acquisition system (model TBX-68T), and system pressure was measured by an Ashcroft test gauge (model 1082, 0-10000 psig). The reaction products were collected in a vial cooled by an ice bath.
4.1.3 Experimental Conditions

Transesterification experiments of microalgae oil in supercritical methanol were conducted in a temperature range of 350-400 ºC, pressure of 15-30 MPa, residence time range of 3-12 min, and methanol-to-oil molar ratio from 6:1 to 12:1. Previous experimental results show that with similar reaction conditions, a homogenous reaction phase was achieved and led to an almost-complete conversion of triglyceride to biodiesel fuel (Marulanda, Anitescu, & Tavlarides, 2010a).

In a specific run, the reactor was preheated by the furnace to a given reaction temperature, and methanol was preheated and pumped into the reactor to pressurize the system to the desired pressure. As soon as the temperature and pressure condition reached the given set points, the oil pump and preheater were turned on and the flow rates of oil and methanol were set for the specified reaction conditions to give the desired residence time. Methanol and microalgae oil were preheated to 385 and 350 ºC, respectively. After steady-state conditions were achieved, effluent stream samples were collected. All the samples were directly analyzed without further purification.

4.1.4 Analytical Methods

To determine the fatty acid profile of microalgae oil and FAME produced in this work, an HP 5890 series II GC was used with a flame ionization detector (FID) and a Restek Rtx-Biodiesel triglyceride column with dimensions of 10 m × 0.32 mm I.D. × 0.1 μm film thickness. Helium was used as carrier gas. The temperature program started at 60 ºC (for two min) and continued with a ramp of 6 ºC/min to 150 ºC (for 10 min), and then with a ramp of 10 ºC/min to 350 ºC (for 2 min).
Free and total glycerol quantification were performed by a GC (HP 5890 series II) equipped with a Restek Rtx-Biodiesel triglyceride column (10 m × 0.32 mm I.D. × 0.1 μm film thickness) and a flame ionization detector (FID). Helium was used as a carrier gas. The temperature program was from 60 °C held for 2 min, to 180 °C at 15 °C/min, and then to 360 °C at 7 °C/min. The injection and detection temperatures were 360 and 380 °C, respectively.

4.2 Results and discussions

4.2.1 Microalgae oil characterization

To establish the microalgae oil fatty acid profile, a transesterification reaction of microalgae oil using conventional method (acid-catalyzed method) was performed at 65 °C for 24h at 30:1 methanol-to-oil molar ratio or 1.32:1 methanol-to-oil volume ratio. The volume ratio of microalgae oil to sulfuric acid (98%) is 1:0.148. The reaction product consisted of two layers which were separated by gravity settling: an upper biodiesel layer consisted of biodiesel, and a lower layer consisted of catalyst - methanol. The FAMEs layer was then washed three times using deionized water in order to remove methanol, glycerol, and acid catalyst. A 98.7% FAME yield was achieved. According to FAMEs standards, the experimental fatty acid profile of the methyl ester generated in this work was reported as shown in Fig. 4-1, this also shows the composition of microalgae oil. A comparison with other microalgae oil used in other biodiesel studies is shown in Table 4-1. According to the peak sequence of FAME standards, it is clear that the fatty acid of microalgae oil mainly consists of palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. In Ms. Yiying Zhu’s work (Zhu & Tavlarides, 2012), she demonstrated that the amount of each fatty acid is in direct proportion to its peak area. So the
weight percentage of each fatty acid was calculated according to their peak area, as listed in Table 4-1.
Fig. 4-1 GC-FID chromatography of fatty acid profile of microalgae oil used in this work (bottom) and FAME standards as reference material (top).
Table 4-1 Fatty acid profiles of microalgae oils used in this work and other biodiesel syntheses studies.

<table>
<thead>
<tr>
<th>Fatty Acid Profile (wt%)</th>
<th>Chlorella protothecoides (this work)</th>
<th>Chlorella (Ehimen, Sun, &amp; Carrington, 2010)</th>
<th>Nannochloropsis (Koberg, Cohen, Ben-Amotz, &amp; Gedanken, 2011)</th>
<th>C. vulgaris (Levine et al., 2010)</th>
<th>D. tertiolecta (Krohn et al., 2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 12:0</td>
<td>ND</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 14:0</td>
<td>ND</td>
<td>0</td>
<td>6.6</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>C 15:0</td>
<td>ND</td>
<td>0</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 16:0</td>
<td>5.5</td>
<td>4.4</td>
<td>42.8</td>
<td>27.8</td>
<td>44.3</td>
</tr>
<tr>
<td>C 16:1</td>
<td>ND</td>
<td>0.4</td>
<td>27.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 17:0</td>
<td>ND</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 18:0</td>
<td>2.0</td>
<td>0</td>
<td>1.0</td>
<td>2.1</td>
<td>7.8</td>
</tr>
<tr>
<td>C 18:1</td>
<td>61.8</td>
<td>9.1</td>
<td>45.5</td>
<td>47.9</td>
<td></td>
</tr>
<tr>
<td>C 18:2</td>
<td>19.9</td>
<td>1.3</td>
<td>9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 18:3</td>
<td>12.2</td>
<td>0.4</td>
<td>12.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>other</td>
<td>1.0</td>
<td>1.3</td>
<td>2.0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Microalgae oil molecular weight was calculated as the sum of the molecular weight of the individual methyl esters multiplied by their mass fraction and then multiplied by three to approximately measure its molecular weight, which was 879 g/mol. At room temperature, the density of microalgae oil is 0.94 g/ml.

Based on a previous study (Marulanda, Anitescu, & Tavlarides, 2010a), oil was assumed to decompose when the reaction temperature is higher than 350 °C. Accordingly, in each run microalgae oil was preheated only up to 350 °C.

4.2.2 Screening experiments

The purpose of the screening experiments was to find an appropriate range of temperature, pressure, molar ratio, and residence time at which a nearly complete conversion can be achieved, and concentration of glycerol left in biodiesel fuel can satisfy the limitation set by ASTM. A temperature range from 350 to 400 °C, a pressure range from 150 to 300 bar, a molar ratio range from 6:1 to 12:1, and a residence time range from 6 to 12 min were chosen as reaction conditions. Samples made at these reaction conditions were collected.

Fig. 4-2 shows that the higher the temperature, the darker the biodiesel color is observed in the samples, which means FAMEs decompose more at higher temperatures. According to ASTM D-6584, these samples were analyzed by GC-FID without further purification. The results are reported in Table 4-2.
Fig. 4-2 Biodiesel samples made at different conditions. The sequence of vials from left to right is the same with the sequence of runs in Table 4-2.
Table 4-2 Glycerol content and reaction conversions in screening experiments.

<table>
<thead>
<tr>
<th>run</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>molar ratio</th>
<th>τ (min)</th>
<th>GL (wt%)</th>
<th>conversion (%)</th>
<th>Observation of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>350</td>
<td>150</td>
<td>6:1</td>
<td>6</td>
<td>0.61</td>
<td>88.1</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>150</td>
<td>9:1</td>
<td>8</td>
<td>0.85</td>
<td>93.1</td>
<td>a</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>200</td>
<td>9:1</td>
<td>8</td>
<td>0.93</td>
<td>91.4</td>
<td>b</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>150</td>
<td>9:1</td>
<td>10</td>
<td>0.79</td>
<td>93.6</td>
<td>b</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>200</td>
<td>9:1</td>
<td>12</td>
<td>0.60</td>
<td>95.7</td>
<td>b</td>
</tr>
<tr>
<td>6</td>
<td>350</td>
<td>300</td>
<td>12:1</td>
<td>10</td>
<td>0.63</td>
<td>96.9</td>
<td>b</td>
</tr>
<tr>
<td>7</td>
<td>385</td>
<td>150</td>
<td>6:1</td>
<td>6</td>
<td>0.41</td>
<td>95.5</td>
<td>b</td>
</tr>
<tr>
<td>8</td>
<td>385</td>
<td>150</td>
<td>9:1</td>
<td>6</td>
<td>0.22</td>
<td>96.4</td>
<td>a</td>
</tr>
<tr>
<td>9</td>
<td>385</td>
<td>150</td>
<td>9:1</td>
<td>8</td>
<td>0.28</td>
<td>97.4</td>
<td>a</td>
</tr>
<tr>
<td>10</td>
<td>385</td>
<td>200</td>
<td>9:1</td>
<td>8</td>
<td>0.20</td>
<td>98.4</td>
<td>b</td>
</tr>
<tr>
<td>11</td>
<td>385</td>
<td>150</td>
<td>9:1</td>
<td>10</td>
<td>0.25</td>
<td>97.6</td>
<td>b</td>
</tr>
<tr>
<td>12</td>
<td>385</td>
<td>150</td>
<td>9:1</td>
<td>12</td>
<td>0.21</td>
<td>97.9</td>
<td>b</td>
</tr>
<tr>
<td>13</td>
<td>385</td>
<td>200</td>
<td>12:1</td>
<td>10</td>
<td>0.25</td>
<td>98.5</td>
<td>b</td>
</tr>
<tr>
<td>14</td>
<td>400</td>
<td>200</td>
<td>6:1</td>
<td>6</td>
<td>0.11</td>
<td>99.1</td>
<td>b</td>
</tr>
<tr>
<td>15</td>
<td>400</td>
<td>200</td>
<td>9:1</td>
<td>6</td>
<td>0.06</td>
<td>99.3</td>
<td>b</td>
</tr>
<tr>
<td>16</td>
<td>400</td>
<td>200</td>
<td>9:1</td>
<td>8</td>
<td>0.02</td>
<td>99.6</td>
<td>b</td>
</tr>
<tr>
<td>17</td>
<td>400</td>
<td>200</td>
<td>12:1</td>
<td>6</td>
<td>0.12</td>
<td>98.7</td>
<td>c</td>
</tr>
</tbody>
</table>

a- One clear FAMEs phase with insoluble droplets on bottom
b- Two phases: upper FAMEs phase and lower glycerol-methanol film
c- Two phases: upper clear phase and lower FAMEs phase
Table 4-2 shows the experimental reaction conditions, reaction conversion, glycerol content and observation of product samples in screening experiment. Reaction conversion increases with residence time and temperature. Transesterification runs performed at a molar ratio of 9:1 produced an upper layer which is biodiesel, and a lower layer which was considered to be water, methanol, and glycerol solution. With a molar ratio of 12:1, biodiesel phase is present as a lower phase. At this time, the upper phase was thought to be aqueous solution of some of the glycerol reaction products and unreacted methanol (Marulanda, Anitescu, & Tavlarides, 2010a). The transesterification conversion was defined as the ratio of mass fraction of the reacted triglyceride to the mass fraction of initial triglyceride (assumed to be 99.9% purity), as the same in Eq. 3-1.

Free glycerol concentration was calculated according to ASTM D-6584. From Table 4-2, we can see at 350 °C, free glycerol concentration exceeds largely 0.024wt% which is the limitation of ASTM. At temperatures of 385 and 400 °C, it appears that there is potential to lower the free glycerol concentration to the required level through longer residence times.

4.2.3 Yields of reaction products and conversion

To systematically study how different variables (i.e., molar ratio, temperature, residence time) affect the biodiesel synthesis process under non-catalytic reaction conditions, an appropriate range of variables should be selected. Molar ratios higher than 3:1 are acceptable, to complete reaction of the triglycerides and FFAs at the same time providing excess methanol to prevent other side reactions. Results also show that at a molar ratio of 6:1 and 400 °C, the biodiesel product was coked. So a higher molar ratio of 9:1 or 12:1 should be used in subsequent experiments to avoid serious biodiesel decomposition. Based on the data in Table 4-2, a medium
high pressure 200 bar was proposed to be used in further experiments to improve conversion without costing too much energy. A wide residence time range of 3-12 min was considered since under selected conditions the reaction conversions were nearly complete. **Table 4-3** summarizes experimental reaction conditions and concentration profiles of different component in biodiesel product samples. Runs 1-9 were performed at 385°C, 200 bar, molar ratio of 9:1, and residence time from 3 to 12 min. Runs 10-18 were performed at 400°C, 200 bar, molar ratio of 9:1, and residence time from 3 to 12 min. Runs 19-26 were performed at 400°C, 200 bar, molar ratio of 12:1, and residence time from 3 to 12 min.
Table 4-3 Conversion of each run, and content of glycerol, monoglyceride, diglycerides, triglyceride, bound glycerol, and total glycerol in collected samples.

<table>
<thead>
<tr>
<th>Run</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Molar ratio</th>
<th>τ (min)</th>
<th>GL (wt%)</th>
<th>MG (wt%)</th>
<th>DG (wt%)</th>
<th>TG (wt%)</th>
<th>X (%)</th>
<th>BG (wt%)</th>
<th>TG (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>3</td>
<td>0.96</td>
<td>4.26</td>
<td>5.76</td>
<td>3.09</td>
<td>86.87</td>
<td>2.28</td>
<td>3.24</td>
</tr>
<tr>
<td>2</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>4</td>
<td>0.79</td>
<td>3.08</td>
<td>1.61</td>
<td>0.23</td>
<td>95.07</td>
<td>1.06</td>
<td>1.85</td>
</tr>
<tr>
<td>3</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>5</td>
<td>0.56</td>
<td>2.89</td>
<td>1.16</td>
<td>0.13</td>
<td>95.82</td>
<td>0.93</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>6</td>
<td>0.37</td>
<td>1.8</td>
<td>0.42</td>
<td>0.06</td>
<td>97.72</td>
<td>0.54</td>
<td>0.91</td>
</tr>
<tr>
<td>5</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>7</td>
<td>0.25</td>
<td>1.54</td>
<td>0.25</td>
<td>0.03</td>
<td>98.18</td>
<td>0.44</td>
<td>0.69</td>
</tr>
<tr>
<td>6</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>8</td>
<td>0.23</td>
<td>1.3</td>
<td>0.19</td>
<td>0.02</td>
<td>98.49</td>
<td>0.37</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>9</td>
<td>0.22</td>
<td>1.23</td>
<td>0.16</td>
<td>0.01</td>
<td>98.59</td>
<td>0.35</td>
<td>0.56</td>
</tr>
<tr>
<td>8</td>
<td>385</td>
<td>20</td>
<td>9:1</td>
<td>10</td>
<td>0.22</td>
<td>1.32</td>
<td>0.16</td>
<td>0.01</td>
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<td>0.03</td>
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</tr>
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<td>24</td>
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<td>0.08</td>
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<td>99.31</td>
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</tr>
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<td>12:1</td>
<td>12</td>
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<td>0.38</td>
<td>0.04</td>
<td>0.02</td>
<td>99.56</td>
<td>0.11</td>
<td>0.16</td>
</tr>
</tbody>
</table>

a- the residence time; b- free glycerol; c- monoglyceride; d- diglyceride; e- triglyceride; f- reaction conversion; g- bound glycerol; and h- total glycerol (GL+BG).
Concentration of free glycerol, monoglyceride, diglycerides, triglyceride, bound glycerol, and total glycerol was measured from their relative calibration curves according to ASTM D-6584. According to ASTM D-6584 method, bound glycerol is estimated by multiplying the mass fractions of monoglyceride, diglyceride, and triglyceride which are 0.2591, 0.1488, and 0.1044, respectively. Total glycerol is calculated as the sum of free glycerol and bound glycerol.

As expected, reaction conversion increases with temperature and residence time, while glycerol content decreases with temperature and residence time. The reaction conversion was almost complete at 400 °C and residence time longer than five minutes. For 400 °C, 200 bar, molar ratio of 9, residence time longer than 6 min, both free glycerol concentration and total glycerol concentration satisfy the limitation of ASTM standards which is 0.024% and 0.24%, respectively.

4.2.4 Temperature effect

Temperature is an important factor which affects the biodiesel synthesis process. The reaction conversion and concentration variation of triglyceride and the consequent reaction products (diglyceride, monoglyceride and glycerol) with temperature at 200 bar, molar ratio of 9, residence time 8 min are shown in Fig. 4-3.
Fig. 4-3 Temperature effect (350, 385, 400 °C) at 200 bar, molar ratio of 9:1, residence time of 8 min on conversion and concentration of each component.
The triglyceride concentration decreased as reaction temperature is increased from 350 to 400 °C. The monoglyceride weight percent decreased significantly with reaction temperature as shown in Fig. 4-3. At 400°C, the content of free glycerol and unreacted glycerides decreases to meet the ASTM standards. The reaction conversion increased from 91.39% to 99.58% with temperature increasing from 350 to 400°C.

The decomposition of methyl esters was assumed to occur at temperatures above 350 °C (Imahara, Minami, Hari, & Saka, 2008). Fig. 4-4 shows GC-FID chromatography of biodiesel samples made at acid-catalyst conditions and non-catalytic conditions (200 bar, molar ratio of 9:1, residence time of 8 min, and different temperatures of 350, 385, and 400 °C). Fig. 4-4 clearly shows that with increasing temperature, the areas of the peaks of FAMEs shrink comparing to FAMEs from acid method, which means FAME partially decomposed into smaller molecules, which is thought to improve some biodiesel-properties such as viscosity and cloud point (Marulanda, Anitescu, & Tavlarides et al., 2010b). The FAMEs decomposition products mainly consist of smaller molecules of methyl esters in the range of C₈ - C₁₄, saturated and unsaturated (Marulanda, Anitescu, & Tavlarides, 2010a), or C₆-C₁₅ FAMEs and C₁₀-C₁₇ hydrocarbons (Anitescu, G., Bruno, T. J. 2012). The content of glycerol and unreacted glycerides decreased with increasing temperature. No coke or dark brown color products were observed in any of the runs.
**Fig. 4-4** GC-FID chromatography of biodiesel sample made at different temperature. Peak identification: (1) Glycerol, (2) Internal Standard, Butanetriol, (3) Monoglyceride, (4) Internal Standard, Tricaprin, (5) Diglyceride, (6) Triglyceride.
4.2.5 Residence time effect

As important as temperature, residence time affects biodiesel synthesis conversion and quality. Fig. 4-5 illustrates how residence time influences conversion and concentration of components in biodiesel samples made at 400 °C, 200 bar, and molar ratio of 9:1. Monoglyceride decreased significantly from 3 to 5 min, then decreased slightly with residence time. Free glycerol content decreased with residence time, and when residence time is longer than 6 min, free glycerol concentration is lower than 0.024 wt%, which satisfies ASTM standards limit. The reaction conversion increased with residence time, and achieved very high values after 6 min (> 99%). Longer residence time means lower flow rate of reactants, which causes reactants and biodiesel product to remain for a longer time in the reactor. So it is obvious that the longer residence time, the more significant biodiesel decomposition occurs. Increasing temperature and residence time in an appropriate range is a way to get high conversion and low glycerol content. From Fig. 4-5, residence times from 5 min to ~ 8 min are recommended in order to reach a nearly complete conversion and less decomposition at the same time. A systematic study of how these decomposition products affect biodiesel quality would permit determination of the optimal residence time.
Fig. 4-5. Residence time effect (3-12 min) at 400 °C, 200 bar, molar ratio of 9:1.
4.2.6 Molar ratio effect

In earlier works, a very high methanol-to-oil molar ratio (i.e., up to 42) and temperature around 250 °C have been used to achieve homogenous reaction conditions. This not only increases additional cost of preheating, pumping, and separating, but also was proved not necessary, because a homogeneous state will also be achieved at lower molar ratio (i.e., 9:1) and higher temperatures. So in this study, three values of methanol to microalgae oil molar ratio are discussed here, 6:1, 9:1, and 12:1. From Fig. 4-2 we can see that at molar ratio of 6:1, 400 °C, the color of the sample is dark, which means biodiesel decomposed, coked, or polymerized significantly. Molar ratio in the range from 6:1 to 12:1 does not affect reaction conversion much according to Fig. 4-6. From the observation of samples, non-catalytic reaction runs performed at a molar ratio of 9:1 produced an upper biodiesel phase, and a lower film layer which was considered to be glycerol, water, and some unreacted methanol. With a higher molar ratio of 12:1, the biodiesel phase is present as a lower phase. Without analysis, the upper phase was thought to be an aqueous solution of some of the glycerol decomposition products and unreacted methanol.
Fig. 4-6. Molar ratio effect (6:1, 9:1, and 12:1) at 400 °C, 200 bar, residence time of 6 min.
4.2.7. Kinetic model application

In Chapter 3, a kinetic study of biodiesel synthesis under supercritical methanol conditions (385 °C, 150 bar, molar ratio of 9:1, residence time from 0.5 to 10 min) using pure triolein was reported. A three-step kinetic model was proposed to predict concentrations of triolein, diolein and monoolein during reactions. The step-reactions from diolein to monoolein and from monoolein to glycerol are assumed to be reversible. It is useful to apply this model to other experiments performed with microalgae oil. In Chapter 4, similar conditions of reaction temperature 385 °C (same temperature with the one applied in the kinetic model study in Chapter 3), pressure of 200 bar, and residence time range of 3 to 10 min were employed in a set of the biodiesel synthesis experiments. The results were listed in Table 4-3. Using the same mass balance method, the data of first nine runs in Table 4-3 was transferred to show the amount of each compound changing in the reactor, weight percentage as unit, as listed in Table 4-4.
Table 4-4 Species mass fraction in the reaction system, at 385 °C, 20 MPa, 9:1 methanol to oil molar ratio, and residence time from 3 to 12 min.

<table>
<thead>
<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>P (Mpa)</th>
<th>τ (min)</th>
<th>Others⁰</th>
<th>MG¹</th>
<th>DG²</th>
<th>TG³</th>
<th>ME⁴</th>
<th>MeOH⁵</th>
</tr>
</thead>
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<tr>
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<td>3</td>
<td>12.17</td>
<td>2.86</td>
<td>3.86</td>
<td>2.07</td>
<td>61.07</td>
<td>17.96</td>
</tr>
<tr>
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<td>4</td>
<td>10.83</td>
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</tr>
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<td>0.84</td>
<td>0.09</td>
<td>69.32</td>
<td>17.07</td>
</tr>
<tr>
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<td>9.519</td>
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<td>0.02</td>
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</tr>
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<td>0.12</td>
<td>0.007</td>
<td>73.37</td>
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<tr>
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<td>9.04</td>
<td>0.98</td>
<td>0.12</td>
<td>0.007</td>
<td>73.2</td>
<td>16.65</td>
</tr>
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<td>0.02</td>
<td>0.006</td>
<td>74.55</td>
<td>16.5</td>
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</tbody>
</table>

a- free glycerol and decomposition products; b- monoglyceride; c- diglyceride; d- triglyceride; e- methyl ester; and f- methanol
Based on data file of triglycerides, diglycerides, monoglycerides, and conversion, the three-step kinetic model proposed in Chapter 3 (from Eq. 3-23 to 3-27, wt% as unit) is applied here to model the reactant conversion and product distributions of the runs at 385 °C. The AARD of reaction conversion in this work is 0.05, which means the kinetic model in proposed in Chapter 3 successfully predicts the experimental data in the work described in Chapter 4. The AARD was mainly caused by temperature-control variation between the kinetics work in Chapter 3 and the work in Chapter 4. In Fig. 4-7, we can see that the content of methyl ester did not match the theoretical value well at residence time of 3 min. More repeated runs will be performed to minimize the experimental deviation. Also runs at short residence times (0.5, 1, 1.5, and 2 min) will be performed to examine if the model can work well on all residence time range.
Fig. 4-7. Application of the kinetic model in Chapter 3 to predict compounds mass fraction and reaction conversion.
4.3 Conclusions

The non-catalytic transesterification of microalgae oil was conducted at temperatures of 350, 385, and 400 °C, pressures of 150, 200, 300 bar, with methanol to oil molar ratios of 6:1, 9:1, and 12:1, and residence times of 3 – 12 min. According to experimental data, biodiesel produced at temperature of 400 °C, pressure of 200 bar, a molar ratio of 9:1, and residence time of 7 – 12 min will satisfy some ASTM standards. Unreacted glycerides decrease with temperature and residence time. Free glycerol decomposed into smaller molecules with temperature and residence time. Free glycerol content satisfies ASTM standards limitation after residence time 6 min at temperature of 400 °C, pressure of 200 bar. Because of the high temperature, biodiesel molecules will decompose into smaller molecules, which are thought to improve viscosity and cold flow properties of biodiesel.

Also an application of the three-step kinetic model proposed in Chapter 3 to biodiesel synthesis using microalgae oil was performed, and shows that the kinetic model can predict concentration profiles of components in biodiesel and reaction conversion, which means it has further potential to be applied to industrial production.
Chapter 5: Conclusions and Future work

5.1 Conclusions

First, in kinetics of biodiesel synthesis work, pure triolein (C_{57}H_{104}O_{6}) was chosen as triglyceride feedstock considering its symmetrical chemical structure and the relative biodiesel product’s properties between saturated and unsaturated methyl esters. This is the first study where a near pure triglyceride was used to study the transesterification reaction in order to avoid complications caused by different components of triglycerides. In other biodiesel synthesis kinetic studies, completely reversible one-step and three-step model are often proposed without proving reversibility of reactions. In this work, a three-step first order kinetic model was proposed to predict biodiesel synthesis reactions. The corresponding reaction rate coefficients at temperature of 385 °C were evaluated. In particular, the reversibility of each reaction step was discussed and evaluated. It is shown that partially reversible three-step second order transesterification reaction describes the kinetics well. The evolution of content of each component in this experiment can be well predicted by the kinetic model derived from the proposed consecutive reaction mechanism. These results imply that the three-step kinetic model proposed in this work can be used for design calculations when considering possible applications.

Second, biodiesel synthesis using microalgae oil under supercritical methanol conditions was studied. Microalgae oil has been accepted to have a great potential of being a feedstock for biodiesel synthesis. As summarized in Chapter 2, lab scale of microalgal biodiesel mainly focuses on extracting oil from microalgae biomass followed by transesterification reaction in a batch reactor. There is no systematic study of microalgal biodiesel synthesis in a continuous flow reactor under supercritical condition. With more mature oil-extracting technology and cheaper microalgae oil price, it is possible and necessary to study microalgal biodiesel synthesis in a
continuous flow reactor considering higher conversion and efficiency. In this study, the fatty acid profile of the microalgae oil used in this work was determined, and effects of temperature, pressure, residence time, and molar ratio were discussed. Experiments were performed at different temperatures (350 – 400 °C), pressures (150 - 300 bar), molar ratios (6:1 – 12:1), and residence times (3 – 12 min). Glycerol content did not satisfy the limitation set by ASTM until the temperature reached 400 °C, and residence time longer than 6 min. According to the experimental data, a molar ratio of 9:1 is thought to be the best option. The impact of pressure is not as much as temperature and molar ratio. Biodiesel starts to decompose at 350 °C. From a previous study, it was suggested that the decomposition products will improve the cold flow property, viscosity, and cetane number of biodiesel. Also an application of the three-step kinetic model proposed in Chapter 3 to biodiesel synthesis using microalgae oil was performed, and shows that the kinetic model can predict mass profiles of components in biodiesel and conversion, and indicates that the model can be applied to industrial production.

5.2 Future work

Future biodiesel synthesis studies can be pursued in the following three directions:

1. **The effect of biodiesel decomposition under different non-catalytic conditions**

   There is evidence that decomposition products will improve some biodiesel physical properties, for example cold flow property and viscosity. But there is not a systematic study which provides enough data to show exactly how biodiesel decomposition effects the quality of biodiesel fuel. It would be valuable to pursue studies in this direction.

2. **How the component of gas product change with reaction conditions**
Under non-catalytic condition, there will be gas biodiesel decomposition products produced with liquid products. There is little study which describes how the gas product components change with reaction conditions. It is necessary to understand the decomposition products formed in order to optimize reaction conditions at which there will be a maximum yield and less decomposition.

3. **The effect of water in methanol/ethanol**

One big problem biodiesel industrial production faces now is the high cost of feedstocks which are of good quality triglycerides and the use of dry alcohol. Microalgae shows great potential to provide cheap and good quality oil. To further lower the cost, it is necessary to avoid using expensive dry alcohol. Considering that biodiesel synthesis under supercritical conditions is tolerant to water content, it would be valuable to study how different water content effects biodiesel product quality and the synthesis process under supercritical conditions.
Appendix A: Flow rates of methanol and triolein in Chapter 3

The flow rates of methanol and triolein were calculated according to the molar volume of reactants mixture, the volume the reactor, and residence time. The molar volume was calculated using Peng-Robinson equation of state.

\[
P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)}
\]

(A1)

\[a = a_c \times \alpha\]

(A2)

\[\alpha^{0.5} = 1 + (0.37646 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})\]

(A3)

\[a_c = 0.457235\left(\frac{RT_c}{P_c}\right)^2\]

(A4)

\[b = 0.077796\left(\frac{RT_c}{P_c}\right)\]

(A5)

\[T_r = \frac{T}{T_c}\]

(A6)

Where \(\omega\) is the acentric factor, R is the universal gas constant. For a mixture of two pure components i and j, the mixing rule applied here is (Prausnitz, Lichtenthaler, & de Azevedo, 1999):

\[a = \sum x_i x_j \sqrt{a_i a_j} (1 - k_{a,ij})\]

(A7)

\[b = \sum x_i x_j \frac{b_i + b_j}{2} (1 - k_{b,ij})\]

(A8)

Using the equation above, we can calculate the value of V, the molar volume of the mixture under 150bar, 385°C. The value is:
\[ V = 0.432 \frac{m^3}{kmol} \]

Because the volume of the reactor is 9.65 ml, according to each residence value, the mole flow rate and volume flow rate of methanol and triolein were calculated and listed in the following table. **Table A1** describes the flow rates of methanol and triolein at each specific reaction condition.

**Table A1** Flow rates of methanol and triolein at different residence time.

<table>
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<tr>
<th>Run #</th>
<th>T  (°C)</th>
<th>P  (MPa)</th>
<th>( \tau ) (min)</th>
<th>Mo(TO) mol/min</th>
<th>Mo(MeOH) mol/min</th>
<th>( F_{TO} ) (mL/min)</th>
<th>( F_{MeOH} ) (mL/min)</th>
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<td>0.04019</td>
<td>4.345</td>
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<td>0.00219</td>
<td>0.237</td>
<td>0.089</td>
</tr>
<tr>
<td>8</td>
<td>385</td>
<td>15</td>
<td>10</td>
<td>0.00019</td>
<td>0.00175</td>
<td>0.189</td>
<td>0.071</td>
</tr>
</tbody>
</table>
Appendix B: Calibration functions in Chapter 3

ASTM D-6584 was applied to determine the concentration of glycerol, monoolein, diolein, and triolein in samples. First, it is necessary to construct calibration curves for each component. The standards solution component concentrations and corresponding peak areas from gas chromatography are shown in Table B1. For each reference substance, response ratio (\( \text{rsp}_i \)) and amount ratio (\( \text{amt}_i \)) are calculated using Eq. B1 and Eq. B2:

\[
\text{rsp}_i = \frac{A_i}{A_{is}}
\]

(B1)

Where:

\( A_i \) = area of reference substance, and

\( A_{is} \) = area of internal standard

\[
\text{amt}_i = \frac{W_i}{W_{is}}
\]

(B2)

Where:

\( W_i \) = mass of reference substance, and

\( W_{is} \) = mass of internal standard

The calibration curves for each component were prepared by plotting the response ratio (\( \text{rsp}_i \)), as the y-axis, versus the amount ratios (\( \text{amt}_i \)), as the x-axis. The linear equations are in the form:

\[
\frac{W_i}{W_{is}} = a_x \times \left( \frac{A_i}{A_{is}} \right) + b_x
\]

(B3)

Where \( a_x \) and \( b_x \) are slope and intercept of the calibration function, respectively.

**Fig. B1** shows calibration curves of each component according to data in Table B1.
Table B1 Peak report of standard solutions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Glycerol mass (µg)</th>
<th>Area (µg)</th>
<th>Monoolein mass (µg)</th>
<th>Area (µg)</th>
<th>Diolein mass (µg)</th>
<th>Area (µg)</th>
<th>Tiolein mass (µg)</th>
<th>Area (µg)</th>
<th>I.S. 1 mass (µg)</th>
<th>Area (µg)</th>
<th>I.S. 2 mass (µg)</th>
<th>Area (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std 1</td>
<td>0.00054</td>
<td>60548.77</td>
<td>0.0108</td>
<td>456476.8</td>
<td>0.00538</td>
<td>107519</td>
<td>0.00538</td>
<td>57109</td>
<td>476753.9</td>
<td>1710987</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std 2</td>
<td>0.0016</td>
<td>105504.1</td>
<td>0.0329</td>
<td>863551.9</td>
<td>0.0108</td>
<td>203387</td>
<td>0.0108</td>
<td>134665</td>
<td>508972.9</td>
<td>179996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std 3</td>
<td>0.00269</td>
<td>129932.1</td>
<td>0.0538</td>
<td>1251684</td>
<td>0.0215</td>
<td>460987</td>
<td>0.0215</td>
<td>289337</td>
<td>485716.7</td>
<td>1834354</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std 4</td>
<td>0.00322</td>
<td>158236.6</td>
<td>0.0806</td>
<td>1673876</td>
<td>0.0376</td>
<td>810677</td>
<td>0.0376</td>
<td>550216</td>
<td>515559.2</td>
<td>1851226</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std 5</td>
<td>0.00538</td>
<td>205406.9</td>
<td>0.108</td>
<td>2202772</td>
<td>0.0538</td>
<td>1230542</td>
<td>0.0538</td>
<td>829508</td>
<td>474723.1</td>
<td>1977658</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. B1. Calibration curves of glycerol, monoolein, diolein, and triolein.
Table B2 shows peak areas of each component in samples made from run 1 to run 4. The data of run 1, run 2, run 3, and run 4 in Table 3-1 in Chapter 3 was calculated by the calibration equations shown in Fig. B1 according to the data provided by Table B2. The peak report of Mr. Tao Cong’s (Cong & Tavlarides, 2010) work is not shown here.

Table B2 Peak reports of biodiesel samples.

<table>
<thead>
<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>τ^b (min)</th>
<th>GL^c</th>
<th>MO^d</th>
<th>DO^e</th>
<th>TO^f</th>
<th>I.S.1</th>
<th>I.S.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>385</td>
<td>15</td>
<td>0.5</td>
<td>23732</td>
<td>1897</td>
<td>3439665</td>
<td>368140</td>
<td>475992</td>
<td>168765</td>
</tr>
<tr>
<td>2</td>
<td>385</td>
<td>15</td>
<td>1.0</td>
<td>128758</td>
<td>4905</td>
<td>3081620</td>
<td>171407</td>
<td>475523</td>
<td>165914</td>
</tr>
<tr>
<td>3</td>
<td>385</td>
<td>15</td>
<td>1.5</td>
<td>907758</td>
<td>5372</td>
<td>1342130</td>
<td>107310</td>
<td>494871</td>
<td>165852</td>
</tr>
<tr>
<td>4</td>
<td>385</td>
<td>15</td>
<td>2.0</td>
<td>173357</td>
<td>7557</td>
<td>1164688</td>
<td>505224</td>
<td>483669</td>
<td>173361</td>
</tr>
</tbody>
</table>
Appendix C: Calculation of mass balance over the reactor in Chapter 3

The example provided below is based on the first set of data in Table 3-1.

According to residence time and the molar ratio of 9:1, feed flow rate of triolein and methanol was determined. Assume the feed flow rate of methanol and triolein is $\frac{m}{t}$ g/min and $3.073\frac{m}{t}$ g/min, respectively. In $t$ min, there will be $m$ g methanol and $3.073m$ g triolein flowing into the reactor. Say these amounts of feedstock generate $n$ g ester phase product. Take the residence time of 0.5 min as an example (weight percentage data from Table 3-1).

![Diagram](image)

**Fig. C1.** Mass balance diagram. The example provided is based on the first set of data in Table 3-1.
In the diagram above, each molecule of triolein will either be unreacted or reacted with methanol to produce either one molecule of diolein and an ester molecule, one molecule of monoolein and two ester molecules, or one molecule of glycerol and three ester molecules. So the mass balance of triolein is:

Initial triolein = unreacted triolein + triolein to produce monoolein + triolein to produce diolein + triolein to produce three ester or one glycerol, which is further described as:

\[ 3.073m = 0.3155n + \left( \frac{0.0112n}{356.54} + \frac{0.1615n}{621} + \frac{0.509n}{3 \times 296.49} \right) \times 885.4 \]  

(C1)

Also one molecule generated methyl oleate means one molecule methanol was consumed. So the mass of consumed methanol is: \((0.509n/296.49) \times 32 \) g. So the mass of unreacted methanol is: \(m - (0.509n/296.49) \times 32 \) g.

From Eqn. C1, \(m/n = 0.3515\).

So the weight fraction of each compound is calculated from the following equations:

\[
\frac{0.3155n}{m + 3.073m} = 0.2204 \\
\text{Triolein:}
\]

\[
\frac{0.1615n}{m + 3.073m} = 0.1128 \\
\text{Diolein:}
\]

\[
\frac{0.0112n}{m + 3.073m} = 0.0078 \\
\text{Monoolein:}
\]

\[
\frac{0.509n}{m + 3.073m} = 0.3555 \\
\text{Methyl Oleate:}
\]

\[
\frac{m - \frac{0.509n}{296.49} \times 32}{m + 3.073m} = 0.2072 \\
\text{Methanol:}
\]
Glycerol and others: $1 - (0.2204 + 0.1128 + 0.0078 + 0.2555 + 0.2072) = 0.0963$

Weight profiles of other runs were calculated by the same procedure shown above.
Appendix D: Diffusion behavior from methanol to triolein

Methanol and triolein were mixed at a T-shaped joint before entering the microtube reactor. The following calculation estimates how long it takes to change from a slug flow to a homogeneous flow. Because it is only an estimation without experimental data, and there is not a published study about mixing issues in non-catalytic biodiesel synthesis being published, several assumptions were made:

1. The length of slugs are 1.6 mm. This is based on the slugs length in a previous study (Guan, G. et al., 2009).

2. Since there is no equation to accurately calculate the diffusion coefficient for this case, the Wilke-Chang correlation was chosen to estimate the diffusion coefficient roughly.

\[
D_{AB} = \frac{7.4 \times 10^{-8} \times (\phi \times M_B)^{0.5} \times T}{\mu \times V_A^{0.6}}
\]  

(D1)

Where \(D_{AB}\) is the diffusion coefficient of solute \(A\) in solvent \(B\), in cm\(^2\)/sec; \(M_B\) is the molecular weight of solvent \(B\); \(T\) is the temperature in K; \(\mu\) is the viscosity in centipoises; \(V_A\) is the molar volume of solute \(A\) at its normal boiling temperature. So in this study, \(A\) is methanol as solute, \(B\) is triolein as solvent. \(T\) is 658.15 K. \(\mu\) is 1.67 cp (Rowley et al., 2004). \(M_B\) is 885 g/mol. \(V_A = 40.5\) cm\(^3\)/mol. \(\phi = 1\).

So \(D_{AB} = 9.4 \times 10^{-5}\) cm\(^2\)/s.

At 385 °C and 150 bar, the density of methanol is 0.1 g/cm\(^3\). So the concentration of pure methanol slugs before mixing is 3.125 mol/l. From Appendix A, the molar volume of methanol-triolein mixture is 0.432 m\(^3\)/kmol which means the concentration of the mixture is 2.3 mol/l.

Because the molar ratio of methanol to triolein is 9:1, it is assumed that when methanol is totally
mixed with triolein, the concentration of methanol is 2.08 mol/l, and the initial concentration of triolein is 0.23 mol/l. **Fig. D1** also describes this problem.

**Fig. D1.** Methanol diffusion into triolein slug.

The diffusion was assumed to match the following differential equation:

\[
\frac{\partial C}{\partial t} = D_{AB} \times \frac{\partial^2 C}{\partial x^2}
\]  

**(D2)**

The boundary conditions are: \(C(0,t)=3.125\) mol/l, and when \(x=L\) which is the middle point of diffusion distance, \(\frac{\partial C(x,t)}{\partial x} = 0\).

The initial condition is: when \(t=0\), \(C(0,0)=0\).

The solution is

\[
C = 3.125 + \sum_{n=0}^{\infty} \frac{12.5}{(2n+1)\pi} \times \sin\left(\frac{(2n+1)\pi}{2L}\right) \times x \times e^{\frac{(2n+1)^2\pi^2 t}{4L^2}}
\]  

**(D3)**

The result when \(t=5\), 10, and 20s were plotted as shown in **Figure D2** from which we can see it would take about 15 seconds for methanol to diffuse into triolein to reach a final average methanol concentration as 2.08 mol/L (when methanol to triolein molar ratio of 9:1). The above calculation does not consider chemical reaction which occurs with diffusion, which actually contributing establishing a homogeneous phase quickly.
**Figure D2.** Methanol Concentration vs. diffusion distance. Triolein slug lengths are assumed to be equal to the reactor diameter.
Appendix E: Calibration functions in Chapter 4

The method to construct calibration curves is exactly the same as the one in Appendix B. In Chapter 4, Table 4-3 describes the concentration of glycerol, monoglyceride, diglyceride, and triglyceride in each sample according to ASTM D-6584 where monoolein, diolein, and triolein are used as reference standard for monoglyceride, diglyceride, and triglyceride.

Table E1 shows the standard solution peak report of the work done in Chapter 4. Because of slightly different gas flow rate and deviation of preparing solution, peak area of each component is different from the relative ones in Table B1.
**Table E1** Peak report of standard solutions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Glycerol</th>
<th>Monoolein</th>
<th>DIOlein</th>
<th>Tiolein</th>
<th>I.S. 1</th>
<th>I.S. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mass (ug)</td>
<td>Area</td>
<td>mass (ug)</td>
<td>Area</td>
<td>mass (ug)</td>
<td>Area</td>
</tr>
<tr>
<td>Std 1</td>
<td>0.00054</td>
<td>24170.21</td>
<td>0.0108</td>
<td>249496.4</td>
<td>0.0054</td>
<td>104956</td>
</tr>
<tr>
<td>Std 2</td>
<td>0.0016</td>
<td>63979.47</td>
<td>0.0269</td>
<td>651057.9</td>
<td>0.0108</td>
<td>217738</td>
</tr>
<tr>
<td>Std 3</td>
<td>0.00269</td>
<td>111407.19</td>
<td>0.0538</td>
<td>1287900</td>
<td>0.0215</td>
<td>437748</td>
</tr>
<tr>
<td>Std 4</td>
<td>0.00376</td>
<td>154045.56</td>
<td>0.0806</td>
<td>1923978</td>
<td>0.0376</td>
<td>764020</td>
</tr>
<tr>
<td>Std 5</td>
<td>0.00538</td>
<td>217574.99</td>
<td>0.108</td>
<td>2553647</td>
<td>0.0538</td>
<td>1083968</td>
</tr>
</tbody>
</table>
According to the data shown above in Table E1, calibration curves of glycerol, monoglyceride, diglyceride, and triglyceride were constructed as shown in Fig.E1.

**Fig.** E1 Calibration curves of glycerol, monoglyceride, dioglyceride, and triglyceride using glycerol, monoolein, diolein, and triolein as reference standards, respectively.

*Table E2* reports the peak area of glycerol, monoglyceride, diglyceride, triglyceride, internal standard 1, and internal standard 2, which was used to generate *Table 4-3* in *Chapter 4*. 
Table E2 Peak area from chromatograms of biodiesel samples in Chapter 4.

<table>
<thead>
<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>Molar ratio</th>
<th>$\tau$ (min)</th>
<th>GL$^a$</th>
<th>MO$^b$</th>
<th>DO$^c$</th>
<th>TO$^d$</th>
<th>I.S.1$^e$</th>
<th>I.S.2$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>385</td>
<td>9:1</td>
<td>3</td>
<td>4442252</td>
<td>11103606</td>
<td>127695534</td>
<td>4817757</td>
<td>388905</td>
<td>1355035</td>
</tr>
<tr>
<td>2</td>
<td>385</td>
<td>9:1</td>
<td>4</td>
<td>3578953</td>
<td>8058423</td>
<td>3577599</td>
<td>356756</td>
<td>383075</td>
<td>1358591</td>
</tr>
<tr>
<td>3</td>
<td>385</td>
<td>9:1</td>
<td>5</td>
<td>2577263</td>
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<td>385984</td>
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</tr>
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<td>9:1</td>
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<td>1711766</td>
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<td>388624</td>
<td>1321829</td>
</tr>
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<td>380097</td>
<td>518564</td>
<td>32735</td>
<td>376656</td>
<td>1277608</td>
</tr>
<tr>
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<td>385</td>
<td>9:1</td>
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<td>1065818</td>
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<td>381599</td>
<td>1327541</td>
</tr>
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<td>385</td>
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</tr>
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</tr>
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<td>391631</td>
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</tr>
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</tr>
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<td>370378</td>
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</tr>
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<td>10</td>
<td>80180</td>
<td>825190</td>
<td>40234</td>
<td>4458</td>
<td>393751</td>
<td>1311546</td>
</tr>
<tr>
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<td>400</td>
<td>9:1</td>
<td>12</td>
<td>68180</td>
<td>531975</td>
<td>36201</td>
<td>2957</td>
<td>395072</td>
<td>1332483</td>
</tr>
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<td>1700813</td>
<td>789986</td>
<td>380111</td>
<td>1371766</td>
</tr>
<tr>
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<td>400</td>
<td>12:1</td>
<td>4</td>
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<td>4154492</td>
<td>1166218</td>
<td>561215</td>
<td>375170</td>
<td>1394117</td>
</tr>
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<td>385705</td>
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</tr>
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<td>21184622</td>
<td>240718</td>
<td>87918</td>
<td>399167</td>
<td>1377647</td>
</tr>
<tr>
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<td>400</td>
<td>12:1</td>
<td>7</td>
<td>520653</td>
<td>1925440</td>
<td>296809</td>
<td>53524</td>
<td>385127</td>
<td>1444265</td>
</tr>
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<td>400</td>
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<td>444728</td>
<td>1486375</td>
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<td>400</td>
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<td>523991</td>
<td>1401065</td>
<td>209651</td>
<td>60225</td>
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</tr>
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<td>270621</td>
<td>1043144</td>
<td>95379</td>
<td>24662</td>
<td>410638</td>
<td>1424212</td>
</tr>
</tbody>
</table>

a- Glycerol. b- monoolein. c- diolein. d- triolein. e- internal standard 1. f- internal standard 2.
Appendix F: GC-FID chromatography of the screening experiments (Table 4-2) in Chapter 4

Runs 1-6, 7-13, and 14-17 are performed at 350, 385, and 400 °C, and different residence times, pressure, and molar ratio. Figure F1 through F9 are the chromatograms of the biodiesel samples from the screening experiments.

**Fig. F1.** Chromatography of biodiesel samples made at 350 °C, 150 bar, molar ratio of 6:1 and 9:1, residence time of 6 and 8 minutes.
Fig. F2. Chromatography of biodiesel samples made at 350 °C, 200 and 150 bar, molar ratio of 9:1, residence time of 8 and 10 minutes.
Fig. F3. Chromatography of biodiesel samples made at 350 °C, 200 and 300 bar, molar ratio of 9:1 and 12:1, residence time of 12 and 10 minutes.
Fig. F4. Chromatography of biodiesel samples made at 385 °C, 150 bar, molar ratio of 6:1 and 9:1, residence time of 6 minutes.
Fig. F5. Chromatography of biodiesel samples made at 385 °C, 150 and 200 bar, molar ratio of 9:1, residence time of 8 minutes.
Fig. F6. Chromatography of biodiesel samples made at 385 °C, 150 bar, molar ratio of 9:1, residence time of 10 and 12 minutes.
Fig. F7. Chromatography of biodiesel samples made at 385 °C, 400 °C, 200 bar, molar ratio of 12:1 and 6:1, residence time of 10 and 6 minutes.
Fig. F8. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 9:1, residence time of 6 and 10 minutes.
Fig. F9. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 12:1, residence time of 6.
Appendix G: GC-FID chromatography for runs listed in Table 4-3 in Chapter 4.

Figure G1 through G13 are chromatograms of runs listed in Table 4-3 at different reaction conditions (385 and 400 °C, 200 bar, methanol to oil molar ratio of 9 and 12, and residence times from 3 to 12 min).

**Fig. G1.** Chromatography of biodiesel samples made at 385 °C, 200 bar, molar ratio of 9:1, residence time of 3 and 4 minutes.
Fig. G2. Chromatography of biodiesel samples made at 385 °C, 200 bar, molar ratio of 9:1, residence time of 5 and 6 minutes.
Fig. G3. Chromatography of biodiesel samples made at 385 °C, 200 bar, molar ratio of 9:1, residence time of 7 and 8 minutes.
Fig. G4. Chromatography of biodiesel samples made at 385 °C, 200 bar, molar ratio of 9:1, residence time of 9 and 10 minutes.
Fig. G5. Chromatography of biodiesel samples made at 385 and 400 °C, 200 bar, molar ratio of 9:1, residence time of 12 and 3 minutes.
Fig. G6. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 9:1, residence time of 4 and 5 minutes.
Fig. G7. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 9:1, residence time of 6 and 7 minutes.
Fig. G8. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 9:1, residence time of 8 and 9 minutes.
Fig. G9. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 9:1, residence time of 10 and 12 minutes.
Fig. G10. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 12:1, residence time of 3 and 4 minutes.
Fig. G11. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 12:1, residence time of 5 and 6 minutes.
Fig. G12. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 12:1, residence time of 7 and 9 minutes.
Fig. G13. Chromatography of biodiesel samples made at 400 °C, 200 bar, molar ratio of 12:1, residence time of 10 and 12 minutes.
References


carboxystearate by catalytic-oxidation of hydroformylated oleate. *Journal of the American
Oil Chemists Society, 49*(1), 75-8.

(2007). Continuous production of fatty acid ethyl esters from soybean oil in compressed

heterogeneous metal oxide catalysts. *Chemical Engineering & Technology, 30*(12), 1716-
1720.

esterification of C18 unsaturated fatty acis by methyl-alcohol. *Journal of Applied Chemistry


Energy Reviews, 4*(2), 111-133.

Swanson, K. J., Madden, M. C., & Ghio, A. J. (2007). Biodiesel exhaust: The need for health


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