Noncatalytic Esterification for Biodiesel Production

by

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DEDICATION

This dissertation is dedicated to my family

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ABSTRACT

Noncatalytic esterfication of fatty acids is an alternative process for biodiesel production. This thesis showed the possibility of conducting the esterification of oleic acid under subcritical ethanol conditions with an acceptable yield. A yield of around 75% was obtained at 230 $^{\circ}$C, 5.5 MPa with an hour of reaction. The molar ratio of ethanol to oleic acid was found to have an optimal point, which is 3:1 within the range studied of 1:1 to 10:1. Water was shown to inhibit the reaction. The stainless steel reactor walls do not have a significant catalytic effect on the reaction. This thesis also demonstrates the possibility of biodiesel production from micro-algae without drying and extraction by using the concept of a two-step noncatalytic process involving hydrolysis followed by esterification.

This thesis also examined the esterification kinetics at both phenomenological and mechanistic levels. The phenomenological models (simple power-law kinetics and fatty acid catalyzed kinetics) provide a reasonable prediction of conversion with a small number of parameters. The simple power-law kinetics model with few parameters was able to fit experimental data from esterification. The model provides an acceptable conversion prediction within the parameter studied. The fatty acid catalyzed kinetics model used experimental data from both esterification and hydrolysis (reverse path of esterification) to estimate the values of its 6 parameters. This model gives a reasonable prediction for a wider range. The mechanistic model was developed to study how the reaction proceeds. The study showed that esterification is mainly catalyzed by protons, which came from the dissociation of oleic acid.

CHAPTER 1

Introduction

Alternative fuels are a subject of significant research interest in response to increasing liquid fuel demand. World demand for oil has been predicted to surpass supply by 2015 [1]. A large part of this demand comes from the transportation sector. The supply of liquid fuel for transportation is largely based on petroleum sources, which take a long time to accumulate and generate. Therefore, we cannot rely mainly on petroleum sources for fuel. There is a need to find other supply sources that can produce fuel with equivalent properties.

Besides the problem of the depletion of petroleum sources, increasing concerns over the environment have prompted research on alternative liquid fuels. The use of fuel from petroleum sources generates pollution that might be reduced through the use of more environmentally friendly fuels such as bio oil, bio alcohol, and biodiesel.

Biodiesel has been shown to be a viable alternative to petroleum diesel. This fuel has properties that are similar to those of diesel oil [2] and can be used directly in diesel engines without modification [3] to achieve similar performance [4]. Biodiesel also has distinct advantages over petroleum-based diesel: it is environmentally friendly, renewable and biodegradable. In addition, when used in engines, biodiesel emits less CO, SO_x, and unburned hydrocarbons [5, 6]. Some studies show that biodiesel increases the amount of NO_x. This excess NO_x can be easily eliminated through addition of an additive [7]. Overall, the potential benefits over those of petroleum fuel have

encouraged research in this area.

Despite the potential of biodiesel as an alternative fuel, a drawback is that it is more expensive than petroleum diesel fuel. Most of the production cost is related to acquiring the triglyceride feedstock in biomass by drying and solvent extraction. In early work on biodiesel production, the feedstock used came from crop oil such as that from soybeans, rapeseed, and palm, which are also food sources [8-12]. This raised the issue of food chain interruption. To address this concern, inedible crops such as Jatropha, Pongami pinnata, and Mahua [13, 14] have been introduced to replace edible ones. Recently, a very promising source has been proposed, aquatic plants such as algae, which can yield more oil per acre of growth than any other crop plant [15].

In the early development of the diesel engine, vegetable oil was directly used as a fuel. Problems with using unmodified vegetable oil as fuel became apparent; the high viscosity of vegetable oil (10-20 times that of modern diesel fuel) causes compression ignition problems in the engine. Vegetable oil also has low volatility, which leads to incomplete burning and formation of deposits in the fuel injectors. To improve the properties of these vegetable oils for use in diesel engines, several refinement methods have been proposed, including dilution, microemulsions, pyrolysis, catalytic cracking, and transesterification. Of these, transesterification appears to be a promising approach [16]. This reaction replaces the glycerol structure in triglycerides with a short-chain alcohol to produce fatty acid esters (biodiesel) and glycerol as a byproduct (see Figure 1.1).
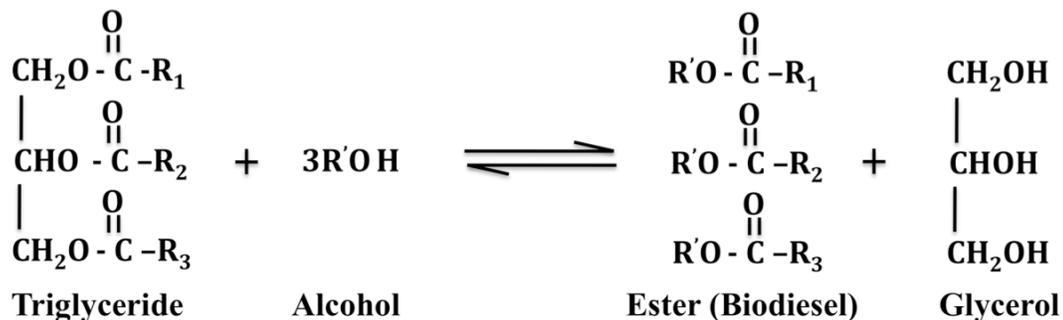
Figure 1.1: Transesterification reaction of triglyceride

In commercial processes, a catalyst is used to accelerate transesterification. After the reaction, the catalyst will be separated and the crude biodiesel needs a post-processing for further purification in order to meet the ASTM biodiesel standards. This separation/purification adds operating and capital cost to biodiesel production.

The type of catalysts used depends on the nature of the feedstock. For example, homogeneous base catalysts such as KOH, NaOH, $NaOCH_3$, and $KOCH_3$ are usually used to accelerate the reaction for purified feedstock. The reaction occurs at moderate temperatures around 60 ^{o}C and at atmospheric pressure with a short reaction time of around an hour [17]. This produces high biodiesel yield but requires a refined feedstock.

For cheaper feedstocks with impurities, which mainly consist of water and free fatty acids (FFAs), homogeneous base catalysts will react with impurities resulting in undesired products, which will lower conversion and reduce biodiesel product yield. An acid catalyst can handle feedstock that has high levels of FFAs. However, if both water and FFAs are present in the feed, water will inhibit the acid catalyst, again resulting in lower biodiesel yield.

To deal with the problems posed by impurities and post-process separation, many alternative processes have been suggested. These include pre-treatment with an esterification reaction with an acid catalyst to lower FFAs [18], direct reactions with a heterogeneous catalyst for easier separation [19], reactions with enzymes [20] and reactions in supercritical alcohol [21]. This last process is very interesting since the reaction is done without a catalyst and is less sensitive to water and free fatty acid than conventional homogeneous catalyst. Moreover, supercritical alcohol reactions reach complete conversion within a very short time, around 4 minutes [21], and the product yield remains high. The process does, however have one major drawback, it must occur under very severe conditions consisting of high temperature and pressure, which might lead to high energy consumption. The details of each alternative processes and also advantages and disadvantages of the processes will be presented in the next chapter, literature review.

One approach to reduce the high operating cost is to use a two-step production process in which hydrolysis of the triglyceride is followed by esterification of the hydrolyzed product in supercritical alcohol [22]. This two-step noncatalytic biodiesel production has advantages similar to those of the direct supercritical alcohol transesterification process, but uses a lower temperature and pressure. However, supercritical conditions are still required in the second step so high temperatures and pressures are needed, pointing to the need to determine the feasibility of performing the reactions at milder conditions and thereby creating an opportunity to reduce the production cost.

When initiating this thesis research, there was very little information in the literature on biodiesel production without a catalyst at non-supercritical conditions. Because of the potential in two-step noncatalytic biodiesel production, this study will focus on this method (mainly on the second step, esterification). No previous reports had focused on using ethanol in the two-step noncatalytic process (methanol has been used in most previous work). We chose to use ethanol in this investigation because it can be produced from biomass, it is less toxic than methanol, and some properties of biodiesel, such as its cloud point, can be improved by using longer chain alcohols [23, 24]. Therefore, biodiesel produced using this method will be 100% renewable. Gui et al. [25] recently articulated the motivation for using ethanol to produce biodiesel and reviewed the limited work that had been done with this alcohol.

In this dissertation, we will first highlight key aspects of conventional catalyzed biodiesel production and the problems that need to be solved to reduce the processing cost. A review of the literature on alternative processes of biodiesel production will also be presented in chapter 2. This thesis will focus mainly on esterification as an alternative reaction for biodiesel production. We then introduce the experimental materials and methods in our work in chapter 3 and then present and discuss our findings in the following three chapters. In chapter 4, we will study the feasibility of esterification under subcritical conditions. Then important parameters that affect the reaction will be investigated. Next in chapter 5, the concept of two-step noncatalytic synthesis will be applied to show the feasibility of making biodiesel directly from wet algae without drying

and extraction. Another important portion of this work will focus on the kinetics of the esterification. There are only a few studies on the kinetics of noncatalytic esterification [26, 27]. In addition, the previous work used a simplified kinetics model. This work will investigate the kinetics more thoroughly on both a phenomenological level and a mechanistic level in chapter 6. Moreover, a combination of kinetics and thermodynamics in the mathematical model will be used to capture the reaction behavior under subcritical conditions where both vapor and liquid phases are present. We will summarize our work in chapter 7 and offer at the end, directions for future work in this area in chapter 8.

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CHAPTER 2

Literature Review

Biodiesel can be produced by either catalyzed or uncatalyzed transesterification. The former process is currently used in commercial biodiesel production while the latter method, which typically involves supercritical conditions, was developed to facilitate processing of lower quality, and hence lower cost feedstocks. This section reviews these existing methods of producing biodiesel, beginning with information on current catalyzed production processes. We highlight key aspects of conventional catalyzed production and the problems that need to be solved to reduce the processing cost, especially for low-cost feedstocks such as waste cooking oil. We then present a comprehensive review of catalyst-free biodiesel synthesis, both via transesterification and alternative esterification reactions. We illustrate the current state of knowledge in the field and identify key areas for additional research.

2.1 Catalytic Biodiesel Production

Commercial biodiesel is currently produced by transesterification using either an alkali or acid catalyst solution. In either case, the processes require both high purity raw materials (triglyceride from biomass) and an additional step for catalyst separation from the product at the end of the process. Both of these requirements drive up the cost of biodiesel. For example, high purity fats and refined oils tend to cost more than alternative, less pure feedstocks. The main impurities in the triglyceride feed, if it is not virgin plant oil, are typically free fatty acids (FFAs) and water. Waste cooking oil, for example, usually contains up to 3 wt% water and more than 6 wt% FFAs [1]. Because water and FFAs must be present in only limited amounts in the catalyzed transesterification reactor, feed pretreatment is required. Pretreatment adds to the cost of

employing catalyzed transesterification methods, which make low cost materials less attractive.

The other main difficulty with the catalyzed process is the post reaction separation of catalyst, byproduct, and product. At the end of the reaction, two liquid phases exist, a biodiesel layer and a glycerol layer. The glycerol layer contains most of the catalyst, which must be removed if pure glycerol is to be produced as a byproduct. The trace amount of the catalyst in the ester layer needs to be removed by washing, which is increasingly being done in a closed loop process to avoid generating large volumes of wastewater. Even so, the water reuse cycle relies on evaporation, which of course, requires additional energy.

Transesterification with an alkali catalyst offers a fast reaction along with a low alcohol to oil ratio. Because of these features base catalyzed transesterification is the preferred commercial route. The most commonly used alkali catalysts are KOH, NaOH, NaOCH$_3$, and KOCH$_3$. Typical operating conditions for the alkali-catalyzed process are a temperature around 60 ^{o}C, a catalyst concentration around 1 wt%, a molar ratio of alcohol to oil of around 6:1, and about an hour of reaction time [2]. The alkali catalyst is very sensitive to water and FFAs in the feedstock [3, 4]. No more than 0.06 wt% water and 0.5 wt% FFAs [5] are allowed in the reaction to ensure the high yield. If water is present in the feed, the alkyl ester product will be hydrolyzed. The hydrolysis will in turn produce FFAs, which then react with the base catalyst to form soap during the production, thus making separation of these component more difficult. To prevent soap formation, feedstock pretreatment is required to limit the impurities entering the reactor. In addition, the end product, which comprises the desired esters along with glycerol, FFAs, unreacted triglyceride, diglyceride, monoglyceride, soap, alcohol and catalyst, must be refined to meet fuel standards. This refining process increases production cost and time. It is also technically difficult, potentially leading to a loss in the yield of the biodiesel product [6].

Transesterification with an acid catalyst is the preferred process method for a triglyceride feedstock containing high levels of FFAs because the acid catalyst can simultaneously transesterify the triglyceride and alkyl esterify the FFAs to produce the

desired alkyl esters (biodiesel). Sulfuric acid is typically used in transesterification of triglyceride and alkyl esterification of the FFAs to produce the alkyl esters. Although sulfuric acid is typically used in transesterification, other acids such as HCl, BF_3, H_3PO_4, and organic sulfonic acid have also been used. When sulfuric acid is used, the catalyst concentration is typically 1-5 wt%. This reaction gives a high product yield when using a high alcohol to oil molar ratio (around 30:1), and the time needed to complete the reaction is long (3-20 hours). Processing time can be reduced by increasing the reaction temperature. For example, in the butanolysis of soybean oil with 1 wt% sulfuric acid, 3 hours is required to complete the reaction at 117 ^{o}C whereas 20 hours is needed at 77 ^{o}C [1]. Another option to reduce reaction time and deal with high FFA content in the reactant is a two-step catalyzed process. In this process, the FFAs in the feed are first esterified with acid catalysis to produce alkyl ester. This step prevents soap formation during the second step, the transesterification of the unreacted triglyceride with an alkali catalyst to obtain alkyl esters. This approach was used by Wang et al. [7] to produce 97% biodiesel. In their work, the first step involved esterification of FFAs at 95 ^{o}C for 4 hours using 2 wt% ferric sulfate with a methanol to oil molar ratio of 10:1. The subsequent step was transesterification of the triglycerides with an alkali catalyst, 1% potassium hydroxide, using a 6:1 molar ratio of methanol to oil at 65 ^{o}C for 1 hour.

Although acid-catalyzed transesterification can handle feeds with a high FFA content, the reaction is very sensitive to the water content in the feedstock. Even 0.1% of water in the feed causes a reduction in the yield of methyl esters [8]. In addition, the separation of product and catalyst is required, which again costs time and money.

To avoid the separation required in a homogeneous catalytic system, researchers have explored the use of heterogeneous catalysts. DiSerio et al. [9] studied transesterification of soybean oil with both basic and acidic heterogeneous catalysts. Their experiment were performed at 180 ^{o}C with 2 g soybean oil, 0.88 g methanol and 0.1g catalyst for both basic and acidic catalyst. For basic catalysts, hydrotalcites (CHT) and MgO were used. Yields of 92% and 75% were obtained for CHT and MgO, respectively. The yield slightly decreased when the catalyst was reused. However, soap formation occurred when the feedstock contained FFAs. The presence of water also

promoted hydrolysis of triglycerides to FFAs, resulting in the same problem of soap formation. Although the separation of the heterogeneous catalyst is easier than that of homogeneous catalyst, the problem associated with impurities in the feedstock still persists. For acidic catalysts, titanium oxide supported on silica TiO_2/SiO_2 (TS) and vanadyl phosphate $VOPO_4.2H_2O$ (VOP) were used. A yield of around 70% was obtained for VOP, but strong deactivation occurred when the catalyst was reused. Therefore, the catalyst needs to be regenerated in this process. TS catalyst is more stable when reused, but only 40% yield was observed. FFAs slightly affect the reaction, and water has a strong deactivating effect on the TS catalyst. Therefore, at present, alkaline/acidic heterogeneous catalysis is a good choice only for refined oil. It does not appear to be suitable for lower cost feedstocks, which contain impurities.

A number of studies have focused on using lipase catalysis for biodiesel production. As reviewed by Fukada et al., [10] this enzyme-catalyzed biodiesel synthesis has overcome the problems with impurities that plague the alkali/acid catalytic method, i.e, FFAs in the raw materials can be converted to esters, and water has no influence on the reaction. In lipase catalysis, the recovery of glycerol is easy, and a relatively high yield of ester is produced. However, lipase catalysts are very expensive compared to the alkali/acid catalyst. This high catalyst cost is the main obstacle to the use of enzyme catalysts in the commercial production of biodiesel.

2.2 Noncatalytic Biodiesel Production

As outlined above, the use of homogeneous acid or base catalysts creates processing problems for biodiesel synthesis. Specifically, the use of these catalysts limits feedstocks to those with low water and FFA content and requires difficult separation steps at the end of the process. Heterogeneous catalysts solve the separation problem, but still require purified feedstock. An enzyme-catalyzed process is more tolerant of impurities and has simple post reaction separations, but it is very expensive to implement. These limitations of catalytic transesterification processes have led to the exploration and development of noncatalytic processes.

Transesterification under supercritical reaction conditions has been used for catalyst-free biodiesel synthesis. Transesterification of triglycerides (nonpolar molecules) with an alcohol (polar molecule) is usually a heterogeneous (two liquid phases) reaction at conventional processing temperatures because of the incomplete miscibility of the nonpolar and polar components. Under supercritical conditions, however, the mixture becomes a single homogeneous phase, which will accelerate the reaction because there is no interphase mass transfer to limit the reaction rate. The alcohol under supercritical condition has lower dielectric constant and becomes hydrophobic resulting in higher solubility of triglyceride in alcohol [8]. In addition, the noncatalytic supercritical process potentially has environmental advantages because no waste is generated from catalyst treatment and separation from the final product.

The separation of the noncatalytic biodiesel product and glycerol occur at ambient temperature and there is no catalyst in the mixture to remove. Furthermore, this noncatalytic method requires no pretreatment of the feedstock because impurities in the feed do not significantly affect the reaction. Transesterification with an alcohol to oil molar ratio of 42:1 at 350 ^{o}C and 45 MPa gives a very high product yield (over 95%) with a short reaction time of only 4 minutes [11]. When water and FFAs are present in the feed, three types of reactions (transesterification, hydrolysis of triglycerides, and alkyl esterification of fatty acids) occur simultaneously as shown in Figure 2.1 [8]. Of these, alkyl esterification is faster than transesterification and ensures that all FFAs in the feed, whether present originally or products of triglyceride hydrolysis, are completely transformed into alkyl ester [12]. For example, at 270 °C, esterification was nearly complete (98% yield) in 20 minutes, whereas the transesterification yield was only 76% even after 40 minutes.
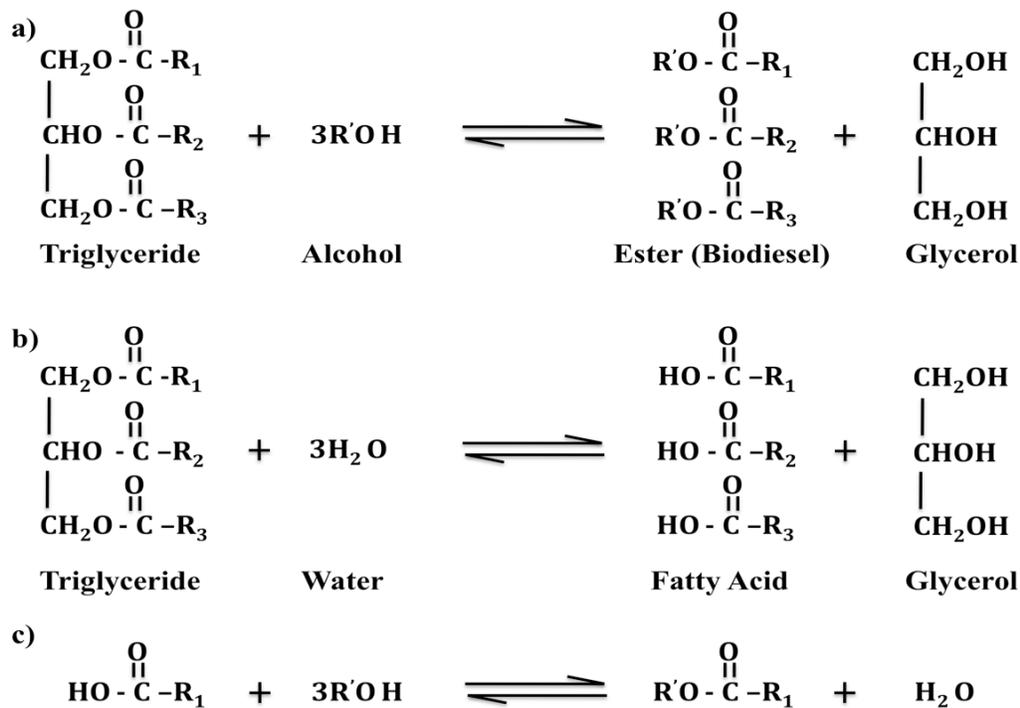
Figure 2.1: Reactions with supercritical alcohol (a) Transesterification of triglycerides, (b) Hydrolysis of triglycerides, (c) Esterification of fatty acids.

A drawback of employing supercritical conditions is the higher pressure and temperature, which require high energy and/or a process well engineered for energy recovery, and perhaps higher capital costs for the reactor. An economic study, however, showed that the total investment and operation costs under supercritical conditions [13] are less than those of the conventional method with alkali and acid catalysts [14]. In these biodiesel production processes that were studied with and without catalyst, waste cooking oil was used as a feedstock. For synthesis without catalyst, propane was used as a co-solvent to reduce the critical point of mixture. The literature also indicates that process modifications can reduce energy requirements and operating cost. D'Ippolito et al. [15] showed that a two-reactor process comprising a perfectly mixed reactor in the first stage followed by a plug flow reactor with recovery of heat in the second stage can reduce the total pressure and be operated at a low methanol to oil molar ratio of 10-15. Finally, West et al. [16] report that the economics for noncatalytic supercritical transesterification are superior to those from homogeneous acid- or base-catalyzed processes for waste cooking oil. The homogeneously catalyzed processes generated

financial losses, whereas the supercritical process generated a profit (though it was too small to be economically attractive). West et al. concluded that a process employing a solid acid catalyst, if technically feasible, would be preferred on economic grounds. All of this evidence supports the technological and economic feasibility of biodiesel production under supercritical conditions without catalyst. It shows the possibility of economical advantage if the process is a well-designed energy integrated system.

Another disadvantage is the high alcohol to oil ratio used in the experiments (more than 40:1). If used commercially, such a high ratio would create difficulties in separating the biodiesel from the excess methanol for recovery and reuse. It would also required large reactor sizes to accommodate the large fluid volume.

There have been several studies of transesterification at supercritical reaction conditions. Different plant oils have been tested. Doing so is important because the conversion and properties of biodiesel depend on the type of feedstock used. Different types of fats and oils contain different types of triglycerides, which process differently in the reaction.

Many of the studies reported in the literature examined the effects of different process variables and identified the best reaction conditions within the region of the parameter space explored. Table 2.1 summarizes these most favorable reaction conditions identified for different feedstocks. High temperature, pressure, and alcohol-to-oil ratios are generally needed to get high conversion.

Table 2.1: Reaction conditions for high yields from noncatalytic transesterification

Authors	Oil Type	T, P	Alcohol:oil molar ratio	Reaction time (min)	Reactor Type	Conversion
Saka and Kusdiana [11]	Rapeseed oil	350°C, 4.5 MPa	42:1	4	5 mL Inconel-625	95%
Demirbas [17]	Hazelnut kernael oil	350°C	41:1	5	100 mL cylindrical autoclave 316SS	95%
Madras et al. [18]	Sunflower oil	350°C, 20.0 MPa	40:1	40	8 mL SS reactor	96%
He et al. [19]	Soybean oil	280°C, 25.0 MPa	42:1	30	200 mL reactor	90%
He et al. [20]	Soybean oil	310°C, 35.0 MPa	40:1	25	75 mL tube reactor	77%

Table 2.1: Reaction conditions for high yields from noncatalytic transesterification (continued)

Authors	Oil Type	T, P	Alcohol:oil molar ratio	Reaction time (min)	Reactor Type	Conversion
He et al. [20]	Soybean oil	100-320°C	40:1	25	75 mL tube reactor	96%
Silva et al. [21]	Soybean oil (ethanol)	350°C, 20.0 MPa	40:1	15	24 and 42 mL tubular 316 SS	80%
Buyakiat et al. [22]	Coconut oil, palm kernel oil	350°C, 19.0 MPa	42:1	7	316SS tubular flow reactor	95%
Demirbas [23]	Cottonseed oil (methanol)	230°C	41:1	8	Cylindrical autoclave of SS	98%
	Cottonseed oil (ethanol)	230°C	41:1	8	Cylindrical autoclave of SS	75%
Vieitez et al. [24]	Soybean oil (ethanol)	350°C, 20.0 MPa	40:1	28	42 mL tubular reactor	78%
Varma and Madras [25]	Castor and linseed oil (both methanol and ethanol)	350°C, 20.0 MPa	40:1	40	11 mL SS316	100%
Hawash et al. [26]	Jatropha oil	320°C, 8.4 MPa	43:1	4	3.7 L SS 316	100%
Rathore and Madras [27]	Palm oil, Groundnut oil, Pongamia pinnata, Jatropha curcas (both methanol and ethanol)	350°C, 20.0 MPa	50:1	40	11 mL SS316	90%
Song et al. [28]	Refined, bleached and deodorized palm oil	350°C, 40.0 MPa	45:1	5	7 mL SUS316	95%
Cao et al. [29]	Soybean oil	330°C	33:1	10	250mL cylindrical SS Autoclave reactor	100%
		280°C with Propane: MeOH =0.04	33:1	10		100%
Han et al. [30]	Soybean oil	280°C with CO_2: MeOH =0.04	24:1	10	250mL cylindrical SS Autoclave reactor	98%

The influence of each of these variables will be discussed more fully in the following sections. Note also that all of the results in Table 2.1 are from experiments in metal reactors. Thus there is the distinct possibility that unintentional metal-catalyzed reactions may have occurred in these studies. This topic is also examined more fully in a subsequent section.

2.2.1 Effect of Temperature and Pressure.

Temperature and pressure are important parameters for supercritical phase reactions because they allow the solvent properties to be adjusted. Many studies have shown that an increase in temperature accelerates the reaction, especially at conditions beyond the critical point. For instance, Madras et al. [18] showed that the transesterification conversion of sunflower oil increased from 78% to 96% as the temperature increased from 200 ^{o}C to 400 ^{o}C. In this process, the methanol to oil molar ratio was 40, the pressure was 20 MPa, and a 40 minute reaction time was used. Similar results were also reported by Demirbas [17], whose study showed that conversion at 5 minutes can nearly double from 50% at 177°C to over 95% at 250°C with a 41:1 molar ratio of methanol to hazelnut kernel oil. Bunyakiat et al. [22] also found that the conversion of coconut oil almost doubled (from 50% to 95%) when the transesterification temperature increased from 270 ^{o}C to 350 ^{o}C. The conversion nearly tripled in the case of palm kernel oil (from 38% to 96%) over the same temperature range with a molar ratio of methanol to oil of 42 and a reaction time of 7 minutes. In yet another study, the yield was increased around 20% when the temperature was changed from subcritical to supercritical for transesterification of cottonseed oil with both methanol and ethanol at a molar ratio of alcohol to oil of 41 [23]. Varma and Madras [25] reported complete conversion in less than 40 minutes for tranesterification of castor oil and linseed oil with both methanol and ethanol at 350 ^{o}C and a molar ratio of alcohol to oil of 40. (Note here that the critical temperature of methanol and ethanol are 240 ^{o}C and 243 ^{o}C, and their critical pressures are 8.0 and 6.3 MPa, respectively.) . The increase in ester yield with increasing temperature was also observed by other researchers [26-28].

Other results consistent with this finding are from Kusdiana and Saka [31]. Their study shows that low conversion of rapeseed oil was obtained from transesterification at

subcritical temperatures. The conversion was 70% at 230 ^{o}C for 1 hour of reaction. However, at supercritical conditions, high conversion was achieved at very short time. For example, in just 4 minutes, 80% conversion was obtained at 300 ^{o}C and 95% conversion at 350 ^{o}C. At an even higher temperature of 400 ^{o}C, the reaction was complete within 2 minutes, but there existed the potential for an undesired thermal decomposition reaction taking place [31]. Indeed, Imahara et al. [32] showed that the thermal stability of biodiesel can be compromised at synthesis temperatures above 300 ^{o}C. Vieitez et al. [24] also observed decomposition and trans-isomerization of unsaturated fatty acid, which increases with an increasing reaction time, 350 ^{o}C, 20 MPa. He et al. [33] also reported higher conversions at higher temperatures, but their conversions were lower than those of other authors. A conversion of 72% was obtained at 280 ^{o}C with a 50 minutes reaction time and 82% conversion was obtained at temperatures higher than 300 ^{o}C with 25-30 minutes of reaction for the transesterification of soybean oil.

As indicated in the above studies, high transesterification conversions can be obtained at supercritical conditions in the absence of an added catalyst.

The influence of reaction pressure on noncatalytic transesterification has also been investigated. In one interesting study, He et al. [19] found that pressure can have a significant influence on the yield. Their results at a constant temperature of 280 ^{o}C, molar ratio of methanol to oil of 42, and reaction time of 30 minutes show that, at a pressure less than 15.5 MPa, this variable had a considerable impact on the product yield. At 8.7 MPa, the product yield was 56% and this amount increased to 82% at 15.5 MPa. However, increasing the pressure further to 25 MPa led to only a 9% increase in yield. Additional pressure increases had negligible effects on the yield. Results from Warabi et al. [34] and Bunyakiat et al. [22] were similar in that pressure did not significantly increase the reaction rate when starting with high pressure. Their results differed from those of He et al. [19], however, in that this pressure-independent yield was encountered at a lower pressure around 10 MPa. It is likely that the pressure effects observed are due to the higher molar density in these systems. The higher concentration would promote faster reaction rates. Other studies starting with low pressure reported the same trend of

increasing ester yield with increasing pressure up to a point, and then no significant change was observed beyond that point [8, 26, 28].

2.2.2 Effect of Water and FFAs in Feedstock

As described earlier, water and FFAs cause many problems in catalyzed transesterification systems. However, these impurities pose no problem when present in feedstock that undergoes noncatalytic supercritical transesterification. In fact, the conversion tended to increase slightly as the FFA content increased in rapeseed oil [8]. The presence of water does not slow down this kind of reaction as is typical in catalyzed synthesis. In fact, there is a work showing that water content as high as water to triglyceride molar ratio of 26 did not greatly affect the yield of methyl ester [8]. This outcome is likely due to the ability of water at elevated temperatures to dissolve both non-polar and polar solutes. Water at temperatures above 250 ^{o}C can solubilize most non-polar organic compounds, including hydrocarbons. When water and methanol are mixed at high temperature, the mixture will have both strong hydrophilic and hydrophobic properties [8].

Vieitez et al.[24] claimed that water has a positive effect on the ester product from continuous conversion of soybean oil under supercritical ethanol at the low flow rates, (0.8 and 1.0 mL/min, long reaction time) but not at high flow rates, (2.0 and 2.5 mL/min). However, this work did not report the uncertainty of their data. By observing their results, there are only slight increases in the amount of ester formed with increasing water in the low flow rate experiments. The difference might be within the experimental error.

Water in the feedstock can hydrolyze the oil and form FFAs, posing no problem in noncatalytic supercritical processes because esterification of the FFAs will occur at a rate faster than transesterification. Therefore, all FFAs will be converted to their corresponding esters [12]. Finally, water contributes to an easier separation at the end of the supercritical process because the biodiesel product is not miscible in water at room temperature.

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2.2.3 Effect of Alcohol to Oil Molar Ratio

One of the most important variables affecting transesterification reactions is the molar ratio of alcohol to oil. Stoichiometrically, three moles of alcohol are required to react with one mole of triglyceride (see Figure 2.1). In practice, an excess amount of alcohol is usually used to drive the reversible reaction to the right side to produce more ester. Higher alcohol to oil ratios also reduce the critical temperature of the mixture, which allows homogeneous reaction conditions at milder temperatures for supercritical processing. Therefore, as more alcohol is used, higher conversions can be obtained, but eventually a point is reached where more alcohol does not help accelerate the reaction [11, 20, 22, 25, 26, 28]. This phenomenon was examined by He et al. [20], who found that the optimal alcohol to oil molar ratio to be 40:1. Similarly, Saka and Kusdiana [11] obtained high product yields (over 95%) with a methanol to rapeseed oil ratio of 42:1 at 350 ^{o}C and 45 MPa for only 4 minutes of reaction time. Bunyakiat et al. [22] found that the conversion nearly doubled when the methanol to oil molar ratio was increased from 6 to 42 for transesterification of coconut oil and palm kernel oil. Varma and Madras [25] found increases in conversion with increases in the molar ratio of methanol/ethanol to oil up to 40:1 for transesterification of castor oil and linseed oil. These results are all in good agreement and suggest that an alcohol to oil molar ratio of about 40:1 facilitates the batch and plug-flow supercritical transesterification of triglycerides.

2.2.4 Effect of Alcohol Identity

The most commonly used alcohols in transesterification for biodiesel synthesis are short chain alcohols such as methanol and ethanol. Of these, methanol is more widely used because it is inexpensive. However, ethanol is also an interesting reactant because it can be produced from renewable sources and, is less environmentally harmful. In addition, some properties of biodiesel, such as its cloud point, can be improved by using longer chain alcohols. For instance, the cloud point of an ethyl ester was 3 ^{o}C lower than that of the analogous methyl ester [34], which ensures that it can be used more easily in cold weather without clogging the engine.

The research on the effects of different alcohols has yielded conflicting results. Madras et al. [18] showed that higher conversions were obtained from ethanol compared

to methanol under the same reaction conditions (200 ^{o}C, 250 ^{o}C, 300 ^{o}C, 350 ^{o}C, 400 ^{o}C). However, Warabi et al. [12] found that shorter alkyl chain alcohols gave faster reaction rates. At 300°C, only 15 minutes is required to complete the transesterification of rapeseed oil with methanol, whereas 45 minutes is needed with ethanol and 1-propanol. Warabi et al. [34] gave two reasons why longer chains were less reactive. The first reason is that the acidity of the alcohol decreases with alkyl chain length. The alcohol can act as an acid catalyst under supercritical conditions. At high temperature and pressure, the ion product of alcohol increases and provides a system with a more acidic environment [34]. The reactivity would be lower for a long alkyl chain alcohol. The second reason is steric effects in which the smaller alcohols can attack the chains in the triglyceride more easily than the longer chain alcohol. Other studies have also reported a lower yield with ethanol than with methanol in transesterification of castor oil, linseed oil, and cottonseed oil at the same conditions [23, 25].

Geuens et al. [35] performed transesterification of rapeseed oil with 1-butanol and no added catalyst via microwave heating. They obtained a 91% yield of butyl esters after four hours of reaction at 310°C. Butanol is attractive because it is less volatile than lower alcohols, so a lower processing pressure is required at a given temperature.

2.2.5. Effect of Different Oil type

Not only does the oil reactant choice affect the properties of biodiesel end product, it also influences the reaction rate. To explore this influence, Varma, Rathore and Madras [25, 27] compared the kinetics for different types of oil and found that the reaction rate constant for a triglyceride comprising saturated fatty acids is higher than that for a triglyceride with unsaturated acids. Also the reaction became slower with an increase in the number of double bonds in the unsaturated acids. Warabi et al. [12], in contrast, found that saturated fatty acids had slightly lower reactivity than did unsaturated fatty acids. He et al. [20] observed that the yield of saturated fatty acid methyl ester (FAME) increases with reaction time while the unsaturated FAME participates more readily in side reactions that reduce its yield at longer times. Losses of unsaturated FAME in side reaction become severe for unsaturated FAME with multiple double

bonds. The authors showed that these could be reduced by gradually heating the reactor from 100 to 320 $^{\circ}$C, which improved the yield to 96%.

2.2.6 Catalytic Effect of Metal Reactor

Metal reactors have been used in all prior supercritical transesterification research, which likely induces a catalytic effect in the reaction. Dasari et al. [36] studied the effects of a metal surface on transesterification of soybean oil. Transesterification in a 316 stainless steel (316SS) reactor was compared with the reaction in a glass capillary tube (but not at supercritical conditions). The results showed that the conversion obtained from the 316SS reactor (10%) was higher than that in the glass tube (2%) under the same conditions (180 $^{\circ}$C, alcohol: oil molar ratio of 6:1 for 4 hours). Moreover, when fine mesh 316SS and nickel shavings were placed into the glass capillary tube reactor, reaction rates were accelerated 30 and 400 fold, respectively. These results clearly demonstrate that the metal walls in laboratory reactors can catalyze transesterification. Therefore, it is quite likely that all supercritical transesterification results reported to date were influenced by both homogeneous and heterogeneous metal-catalyzed reactions.

Kusdiana and Saka [37] offer another perspective, arguing that the catalytic effect of the metal surface in the reactor is less important than other factors (molar ratio of alcohol to oil, temperature for supercritical condition). Their study showed that no nickel, chromium, or molybdenum, and only a trace of iron was found in the reaction mixture during transesterification in an Inconel 625 reactor. Of course, these results address only potential homogeneous catalysis by dissolved metals. Heterogeneous catalysis by the reactor wall could still be very important.

2.2.7 Kinetics of Noncatalytic Transesterification

Some attempts have been made to model the kinetics of noncatalytic transesterification. These have generally used relatively simple models with assumed reaction orders. Moreover, these models are based on data from metal reactors, which means that the kinetics were likely influenced from both homogeneous and metal-catalyzed routes.

Diasakou et al. [38] modeled the kinetics of noncatalytic transesterification using three consecutive steps as follows.

$$Triglyceride + Methanol \xrightarrow{k1} Diglyceride + FAME \qquad (2.1)$$

$$Diglyceride + Methanol \xrightarrow{k2} Monoglyceride + FAME \qquad (2.2)$$

$$Monoglyceride + Methanol \xrightarrow{k_3} Glycerol + FAME \qquad (2.3)$$
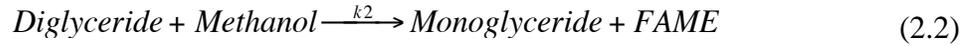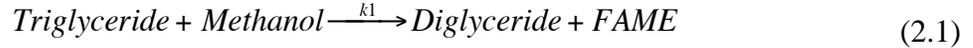
The reaction was assumed to be first order with respect to each reacting component and irreversible because a large excess of methanol was used. The concentrations of methyl esters and triglyceride calculated from the model showed good agreement with their experimental data. The calculation of kinetics parameters for soybean oil transesterification with methanol was done to obtain data at 220 $^{\circ}$C and 235 $^{\circ}$C. The results showed that the rate constants for the first and second reactions (equation (2.1) and (2.2)) were comparable, and both were temperature dependent. However, the rate constant for the last step (equation (2.3)), monoglyceride conversion to glycerol, was much lower than those for the first two steps, and it was independent of temperature.

Varma and Madras [25] used the simplified single step model (equation (2.4)) of the above three steps by ignoring the intermediates. Using the model over a temperature range of 200 to 350 $^{\circ}$C, they obtained activation energies of 35 and 55 kJ/mol for castor oil methyl ester and ethyl ester, respectively, and activation energies of 47 and 70 kJ/mol for linseed oil methyl ester and ethyl ester, respectively.

$$Triglyceride + 3Methanol \xrightarrow{k} Glycerol + 3FAME \qquad (2.4)$$

Kusdiana and Saka [31] also used the simplified single overall step as in equation (2.4). The reaction was assumed to be first order in triglyceride. The influence of methanol concentration was ignored because methanol was present in large excess amounts. The rate constants for transesterification of rapeseed oil were reported at

different temperatures in the range of 200 to 487 ^{o}C and found to increase with temperature. This same approach was used by He et al. [19] for determining the kinetics of transesterification of soybean oil and produced similar results. Both studies reported comparable values for rate constants in the temperature range of 210 to 280 ^{o}C. For example, the rate constant from He et al. [19] is 7.91x 10^{-4} s^{-1} at 270 ^{o}C, and at the same temperature Kusdiana and Saka [39] found the rate constant to be 7 x 10^{-4} s^{-1}. The two studies also revealed similar trends for the Arrhenius plot. A non-linear trend was observed over the temperature range 210 to 280 ^{o}C, which crosses the critical temperature of methanol. There were separate linear trends, however, within the subcritical region (T < 239 ^{o}C) and within the supercritical region (T > 239 ^{o}C). He et al. [19] reported an activation energy of 56 kJ/mol at supercritical conditions (T = 240-280 ^{o}C) and 11.2 kJ/mol at subcritical conditions (T = 210-230 ^{o}C). The existence of these two regions could be tied to the phase behavior. At subcritical conditions, two liquid phases might exist and the rate of inter-phase mass transfer could be limiting the observed rate. Indeed, Dasari et al. [36] suggested that the reaction rates are limited by methanol solubility at subcritical conditions. Specifically, the reaction rate increases as the reaction proceeds because the intermediates and products that form increase methanol solubility with oil.

In contrast, Rathmore and Madras [27] observed no obvious discontinuity near the critical temperature. They reported activation energies between 9–15 kJ/mol for transesterification of four other oils with either methanol or ethanol at temperatures between 200– 400 °C. These values for the activation energy are much lower than those in their earlier study [25].

In another study, Wang and Yang [40] reported an activation energy of 92 kJ/mol for transesterification of soybean oil with methanol at temperatures between 200 – 260 °C. Again, there was no discontinuity around the critical temperature. Interestingly, Wang et al. [41] report an activation energy for subcritical temperatures of 85.4 kJ/mol for transesterification of rapeseed oil in methanol with added NaOH. In general, one expects the activation energy for a catalyzed reaction to be lower than that of its noncatalytic analog. This result, along with the wide range of activation energies

reported in the literature, points to the difficulty of doing transesterification kinetics studies and separating out all potentially intrusive transport, mixing, and phase behavior effects.

Silva et al. [21] also used the pseudo-first-order kinetic model, which provided satisfactory agreement with their experimental data. A rate constant of 0.1 min^{-1} was obtained at 350 $^{\circ}$C for transesterification of soybean oil with ethanol. For comparison, the rate constant was 1.07 min^{-1} at similar conditions for transesterification of rapeseed oil in supercritical methanol [39]. Thus it appears that the kinetics are sensitive to the specific alcohol and oil used in the transesterification reaction.

To summarize, kinetics analyses to date have used global reaction models with assumed reaction orders and typically a single overall reaction. The experimental data used to determine rate constants and activation energies have all been potentially influenced by unintended metal-catalyzed reactions. Furthermore, activation energies in some studies (but not all) differ in the subcritical and supercritical regions (based on the critical temperature of the alcohol). There is clearly a need for more work on the kinetics of noncatalytic transesterification so that the reaction orders, intrinsic rate constants (rather than pseudo-first-order global rate constants), and intrinsic activation energies can be determined.

2.2.8 Phase behavior

The transesterification rate is low at subcritical (multiphase) conditions, but significantly accelerated at supercritical (single phase) conditions. One portion of this acceleration is due to temperature effects, and another portion is also due to the presence of a single supercritical phase at supercritical conditions. Therefore, the phase behavior of the mixture in the system is an important consideration in biodiesel production.

The phase behavior and critical points for some binary mixtures in supercritical transesterification have been studied. Shimoyama et al. [42] examined methanol-methyl ester systems, which reflect the final products from transesterification. They provide experimental measurements for the compositions of the co-existing liquid and vapor phases, and they correlated the results using the Peng-Robinson equation of state. Glisic

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et al. [43] examined systems that reflect the reactants. They measured the phase equilibria for methanol-sunflower oil mixtures. The best correlation of the experimental results was by the Redlich-Kwong-ASPEN equation of state with van der Waals mixing rules. It must be noted, however, that the system examined is a reactive one and that sunflower oil is a mixture but it was treated thermodynamically as a single pseudo component. The effect of these items on determining the best equation of state to use remains unclear. The conditions examined by these authors always resulted in only a single liquid phase being present. They provide no data for liquid-liquid-vapor equilibrium, which would exist when there are separate oil-rich and methanol-rich liquid phases. Despite these limitations, this article is significant because it explored the use of different equations of state and began to address key issues in supercritical synthesis of biodiesel. In a more recent study, Glisic and Skala [44] developed phase diagrams for triglyceride transesterification using the Redlich-Kwong-ASPEN equation of state and experimental data. At low temperature (150 ^{o}C) and pressure (1.1 MPa), two liquid phases (oil and methanol) mainly exist at the beginning and a third phase was formed after glycerol was produced. At conditions below the critical point of methanol (210 ^{o}C, 4.5 MPa), the phase change is similar to the previous case, but as the reaction progress, the oil phase disappears and becomes two liquid phases with mainly methanol and ester and finally a single liquid phase of methanol-ester. Two conditions were studied at 240 ^{o}C and 270 ^{o}C both at 20 MPa. For lower temperature of 240 ^{o}C, two liquid phases exist at the beginning and then became a single supercritical phase when conversion of triglyceride is beyond 95 mass%. At 270°C 20 MPa, the reaction took place in the supercritical phase throughout the course of reaction.

Hegel et al. [45] examined mixtures of soybean oil, methanol, and propane. They showed visually how the system evolves from three phases (LLV) to two (LV) to one (supercritical) as the mixture is heated and reacts. A single liquid phase was observed to exist for several mixtures at temperatures as low as 160 °C. Supercritical temperatures are not required to have a single homogeneous fluid phase containing the reactants.

Another way to obtain a single-phase system for noncatalytic transesterification, but at potentially lower temperatures and pressures than the values for supercritical alcohol, is to use a co-solvent. To explore this approach, Cao et al. [29] used propane as a co-solvent for biodiesel production from soybean oil with methanol. In their study, the critical point of the mixture is reduced with increasing amounts of propane, which is a good solvent for vegetable oil, allowing a single phase to be formed in the mixture. This use of propane reduces the amount of methanol required and results in a significant reduction in the system pressure. The reaction conditions that gave the best results (98% yield in 10 minutes) in their study were a temperature of 280 $^{\circ}$C, propane to methanol molar ratio of 0.05, methanol to oil ratio of 24, and a system pressure of 12.8 MPa. This same research group also used CO_2 as a co-solvent [30]. The results with CO_2 were similar to those with propane. Milder conditions could be used. A 98.5% yield in 10 minutes was obtained at 280 $^{\circ}$C, a CO_2 to methanol ratio of 0.1, a methanol to oil ratio of 24, and a system pressure of 14.3 MPa.

In another study, Sawangkeaw et al. [46] used tetrahydrofuran (THF) and hexane as co-solvents to reduce the viscosity of vegetable oil. These solvents did help the flow properties in the continuous reaction system, but they did not lead to the reaction being completed under milder conditions. The alkyl ester product, which is continuously produced throughout the course of the reaction, could also be viewed as a cosolvent. For instance, Busto et al. [47] showed that a single liquid phase can exist even at 40 °C if methyl esters are added to the oil and methanol mixture. At a methanol to soybean oil molar ratio of 6, adding enough methyl ester to reach a 36% (by volume) solution created a single homogeneous liquid phase.

Large excess amounts of alcohol have been used in previous supercritical transesterification research because this practice reduces the critical temperature of the mixture. Given that the critical properties of triglyceride-alcohol mixtures have not been a topic of much research, the precise amount of alcohol needed to achieve supercritical conditions at a given temperature is not readily available. To address this issue, Bunyakiat et al. [22] used Lydersen's method of group contributions to estimate the critical temperature and pressure of vegetable oil. They then used Lorentz-Berthelot type

mixing rules to calculate what they took to be the critical values for mixtures of oil and alcohol. The properties they calculated, though, are actually pseudo-critical properties, not true critical points. Therefore, the results from their thermodynamic calculations have no bearing on the actual phase behavior. Pseudo-critical properties have been used to parameterize equations of state for mixtures, but these values are not the same as the true thermodynamic critical point of a mixture. The two are often quite different. To determine the actual critical point of a mixture an appropriate equation of state can be used.

It is important to recognize, as well, that the critical temperature of the mixture will change as the transesterification reaction progresses, because the reaction changes the identities of species present in the mixture and their mole fractions. Thus, if one intends to examine or use supercritical conditions for transesterification, it is not adequate to simply choose a reaction temperature that exceeds the critical temperature of the alcohol being used. Rather, the critical temperature of the mixture as the reaction progresses must be known to ensure that the reaction temperature remains above these values throughout.

2.3 Two-step Noncatalytic Biodiesel Production.

To address limitations with catalyzed biodiesel synthesis, another alternative two-step process for synthesizing biodiesel without a catalyst has been explored [48]. This process involves hydrolysis of triglyceride in subcritical water to produce FFAs as the first step. The second step is the subsequent alkyl esterification of the FFAs in supercritical alcohol to produce the alkyl ester (biodiesel). This two-step process, which was suggested by Kusdiana and Saka [48], has the same advantages as direct transesterification in supercritical alcohol. The impurities (water and FFAs) do not interfere with the system. The impurities are reactants for this production path since in the first step, hydrolysis, water is used to react with triglyceride and produce fatty acids and glycerol. In the second step, the FFAs from the original feedstock and the hydrolyzed product from the first step undergo esterification. In addition, this process can be accomplished at lower temperatures and pressures compared to the supercritical transesterification, potentially leading to a reduction in production cost. Another

advantage of the two-step process is that a lower ratio of alcohol to oil is required. Only a 5:1 methanol to oil molar ratio is needed to get more than 90% yield of methyl ester in methyl esterification at 270 ^{o}C and 20 MPa [49].

The biodiesel produced from this alternate two-step method is cleaner than that from the transesterification of triglyceride alone. No mono- or diglycerides or glycerol appear as by products from the ester formation step since these compounds will have been removed after the first reaction stage [50]. The amount of glycerol in biodiesel phase can be reduced dramatically. The glycerol content has a significant effect on fuel properties such as viscosity, pour point, and amount of carbon residue, which causes problems with deposition on the injector and combustion chamber. The total glycerol content of biodiesel prepared by one-step and two-step supercritical processes were 0.39 and 0.15 wt%, respectively [50]. The U.S. biodiesel specification standard, ASTM for total glycerol content is less than 0.24 wt% [51].

The first step, hydrolysis of triglyceride, is a well-known process. The reaction has been extensively explored in term of the important parameters that affect the reaction [48, 52-55]. Both catalyzed and uncatalyzed kinetics have been studied [49, 53].

On the other hand, the second step, esterification, most of the study was done using an acid catalyzed route [56-63]. Only a few studies use catalyst-free reaction. In addition, only a handful of researchers have reported on the noncatalytic kinetics of fatty acid esterification [49, 64], pointing out the need for research in this area. Therefore, the focus of this work will be on the second step, esterification of fatty acid. We will first briefly talk about the first step, hydrolysis, and then move on in detail for the second step, esterification. We give here a review of the variables (T, molar ratio of alcohol to fatty acid, alcohol type, FFA type) that have an effect on the reaction and give details on the kinetics available to date for the noncatalytic fatty acid esterification.

Hydrolysis Reaction

Hydrolysis has been an important reaction to process oils and fats for the oleochemical industry for many years. Hydrolysis of triglyceride is a stepwise reaction from triglyceride to diglyceride to monoglyceride, which then produces glycerol and fatty

acids. The pathway is shown in equation (2.5) [52].

$$C_3H_5(OCOR)_3 \xleftrightarrow{HOH} C_3H_5(OH)(OCOR)_2 + RCOOH \xleftrightarrow{HOH} C_3H_5(OH)_2(OCOR) + RCOOH \xleftrightarrow{HOH} C_3H_5(OH)_3 + RCOOH$$

$$(2.5)$$
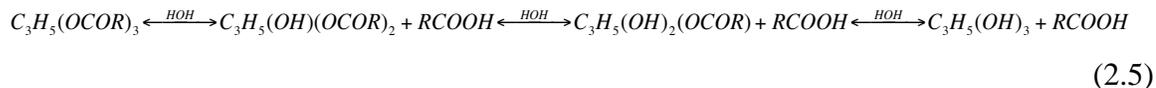
where RCOOH represents any fatty acid and $C_3H_5(OH)_3$ is glycerol

The reaction is usually carried out under 100-260 ^{o}C and 0.1-7 MPa using 0.4-1.5 w/w initial water to oil with or without catalyst [53]. In early production of fatty acids, sulfuric acid was used in the hydrolysis reaction. Later, the Twitchell process was developed to lower the corrosion, which occurred in strong sulfuric acid. The operation of the Twitchell process is at atmospheric pressure and temperature of 100 ^{o}C using 0.75-1.25 %w/w water [53, 54]. A batch autoclave process is also used under pressure (0.1-0.3 MPa) and 180-230 ^{o}C [53]. The reaction rate is increased approximately 33% for each 10 ^{o}C increase [54].

At low temperature, two phases occur (oil and water phase). The study indicated that homogeneous reaction occurred in the oil phase and minor reaction occurs at the oil-water interface [52, 55, 65]. The immiscibility of an oil/water system causes an increase in the reaction time at low temperatures. For example, shorter times are used to reach equilibrium with increased temperature, only half an hour for 280 ^{o}C, but longer times of 35 hours for 150 ^{o}C [52]. If the feed oil used contains higher amounts of FFAs, the times required will be shorter because FFAs are more soluble in the water phase [65]. In high temperature hydrolysis, water and oil become miscible. Therefore, shorter reaction times are required. Water can solubilize most nonpolar organic compounds starting at 200-250 ^{o}C (Note here that the critical condition of water is T_c=374 ^{o}C, P_c=22.1 MPa) [55].

Hydrolysis of vegetable oil in subcritical water (260-280 ^{o}C) without use of catalyst gave high conversions of 97% with short reaction times of 15-20 minutes [55]. Conversion doubled when the water to oil molar ratio increased from 3:1 to 10:1. However, further increases in the amount of water to more than 33:1 have no effect on conversion (maximum 90%) in the study of hydrolysis of beef tallow at 260 ^{o}C [52]. Kusdiana and Saka [48] reported the similar tend of increasing yield with increasing

molar ratio of water to rapeseed oil. Yield of 60% was obtained at a molar ratio of 13:1 while 85% yield was obtained at 54:1 and more water added does not have a significant effect on yield. A kinetics study of hydrolysis of vegetable oil and animal fat was reported by Patil et al. [53]. The kinetics under subcritical water without catalyst through autocatalysis by FFAs was proposed by Minami and Saka [49]. However, no rate constants were reported in their study.

Esterification Reaction

The esterification of carboxylic acids with alcohols is a reaction that produces organic esters, which have many practical industrial applications, especially as for lubricants, cosmetics, and fuels [66-68]. The esters produced from the long-alkyl chain fatty acid (C16-C18) are suitable as a liquid fuel known as biodiesel.

In biodiesel production, esterification can be used as a pretreatment for feedstock with high FFAs or as a direct reaction to produce biodiesel. Commercial esterification of fatty acids with alcohols uses homogeneous acid catalysts, such as sulfuric acid [58, 59, 69, 70, 71, 72]. The homogeneously catalyzed process is effective in the production of esters. However, this production path poses two main obstacles: catalyst waste production and the corrosion of equipment. In the first obstacle, the acid catalyst must be neutralized at the end of the process. It requires energy for this purification process. This adds operational cost to the system. In the second drawback, the corrosion caused by the use of a strong acid in the production process might require more expensive reactor material, which also adds to the capital cost.

To address these issues, several types of heterogeneous catalysts have been introduced. These heterogeneous acids help ease the separation process. However, limitations persist with this type of catalyst. These include low thermal stability (Amberlyst-15) [73], mass transfer resistance (zeolites) [74], loss of active acid sites in the presence of a polar medium (HPA/silica) [75], and decreased conversion after reuse (supported resin catalyst Nafion/silica nanocomposite: SAC-13) [76]. Another alternative means of ester production is esterification without catalyst with supercritical alcohol [48]. This process eliminates corrosive acid catalysts that result in hazardous

waste. In addition, the end process separation is easier compared to the traditional method, because biodiesel and water byproduct are not miscible and separate into two phases at room temperature. However, the rates are slow compared to the reaction with acid catalysts. Aranda et al. [77] obtained 35% conversion of palmitic acid residue with methanol at 130 ^{o}C in an hour whereas 98% conversion was reached with methane sulfonic acid with the same conditions. To accelerate the esterification reaction, a higher supercritical temperature (270 ^{o}C) was applied. Complete conversion was reached within 20 minutes according to the work of Kusdiana and Saka [48].

In the following subsection, the effect of important parameters such as temperature, alcohol type and amount used, and FFA type will be reviewed.

2.3.1 Effect of Temperature

Esterification is a reversible and endothermic reaction [57, 63]. Increasing the temperature of the system will increase the yield of the product at equilibrium. This phenomena is true when using a reactant of pure FFAs [49, 64] or using oil with some FFA impurities [57, 59-61, 71].

Many researchers observed that the reaction rate is fast at the beginning of the reaction and then slow [49, 57, 58, 60, 78, 79]. Minami and Saka [49] hypothesized that this is because the fatty acid acts as a catalyst in the reaction because fatty acid is a weak acid and can dissociate to give a proton, which catalyzed the reaction. A high amount of FFAs at the beginning makes the rate spike quickly, but as the reaction proceeds, fewer FFAs are in the system and the rate slows.

2.3.2 Effect of Alcohol to FFAs Molar Ratio and Alcohol Identity

Amount of alcohol is one of the important parameters in esterification since the reaction is reversible. The molar ratio of alcohol to FFAs affects the esterification reaction. Researchers observed different trends when changing the amount of alcohol in the system. The difference depends on the starting material used.

In the study of esterification, two main type of feedstock are used: pure FFAs and a blend of FFAs in triglyceride (FFA-oil mixture). For the studies using pure FFAs, an

increase in the alcohol molar ratio will increase the product yield until it reaches the optimum point and a lower yield was obtained after more alcohol is added. Alenezi et al. [64] observed that the yield increases with increasing molar ratio up to 3 (0.7, 1, 1.6, 3) and then decreases from molar ratio of 3 to 7 in a noncatalytic esterification of FFAs with supercritical methanol. The FFA used in their study is mainly oleic acid (88%) in the temperature range of 250-320 ^{o}C and pressure of 10 MPa.

In another study, Minami and Saka [49] obtained higher yield of FAME with a smaller amount of methanol in esterification of oleic acid at 270 ^{o}C and 20 MPa. The amount of methanol used in their study is in between 0.9 to 5.4 (v/v) or equivalent to 5 to 29 in molar basis. They explain that this is because of the autocatalytic phenomena. The system will give higher yield if there is a higher concentration of FFAs. When using a high excess of alcohol, the system will be diluted resulting in a lower yield.

In the Minami and Saka work, they only observed the decrease in yield with increasing amount of alcohol. This may be because they started with a high amount of alcohol (0.9 v/v or equivalent to 5:1 in the molar basis). These studies suggested that there is an optimum amount of alcohol to add to the system, beyond the stoichiometric requirement of one mole of alcohol to react with one mole of FFAs. More alcohol added to the system will help shift the reaction more to the right side and produce more product. However, too much alcohol will dilute the system resulting in decreases in the yield.

On the other hand, an increase in the molar ratio of alcohol to oil will give a positive effect on the system for a reactant of oil mixed with FFA impurities. This might be due to the fact that not only does esterification take place but also transesterification. If in transesterification higher molar ratio of alcohol gives higher yield, then the reaction with both transesterification and esterification might follow a similar trend [59, 60, 61, 71]. However, the study of Marchetti and Errazu [57] on oleic acid mixed with refined sunflower oil reacting with ethanol and catalyzed by sulfuric acid at 45 ^{o}C, showed that reaction was faster when the molar ratio was low but reached a lower final conversion.

The different types of alcohol also have an effect on the reaction. Shorter chain alcohols tend to give a faster reaction rate. Aranda et al [77] got faster reaction rates

from methanol compared to ethanol. They explained that this is because of the shorter chain of methanol and its higher polarity. Steric hindrance inherent to both the carboxylic acid and the alcohol species, which seems to be important in the step of the nucleophilic attack of the alcohol, made reaction with methanol proceed faster. Warabi et al. [34] also observed the similar trend of faster reaction rate with shorter chain alcohol. Their study was conducted with methanol, ethanol, 1-propanol, 1-butanol and 1-octanol at 300 ^{o}C with alcohol to rapeseed oil molar ratio of 42 without added catalyst.

2.3.3 Effect of Different FFAs Feed Type

The feedstock for biodiesel is usually a mix of different type of FFAs. Therefore, the knowledge of how different FFAs affect the reaction is important. This might also have an effect on the properties of fuel produced.

Liu et al. [76] studied the effect of chain length in short chain carboxylic acids (acetic, propionic, butyric, hexanoic and caprylic acid) with methanol. The carboxylic acid reactivity decreased with increasing alkyl chain length. Their study is at temperature of 60 ^{o}C and uses a commercial Nafion/silica composite solid acid catalyst (SAC-13) with initial concentration of carboxylic acid at 3M and 6M of methanol. They suspected that this trend was caused by 2 effects: an inductive effect and a steric effect [19]. The inductive effect is that electron-releasing ability increases with alkyl chain length, which helps the protonation of the carbonyl oxygen. At the same time the electrophilicity of the carbonyl carbon decreases, resulting in more difficulty for nucleophillic attack by alcohol. The steric effect is that smaller carboxylic acids are easier for alcohol to attack. These two effects support the lower conversion obtained with higher number of alkyl chain length of carboxylic acid [76]. In the case of H_2SO_4, the effect of chain length on reactivity was insignificant for carboxylic acids larger than butyric acid.

Aranda et al. [77] calculated protonation energies of acids by using Mulliken charge distributions. Similar values were obtained for oleic acid (C18:1) and palmitic acid (C16:0). The reactivity is related to the carboxyl moiety and not the alkyl chain. This should result in similar reaction rate for oleic acid and palmitic acid. However, their study of activation energy by semi-empirical methods reveals that the activation energy

33

of oleic acid (176 kJ/mol) is lower than that of palmitic acid (272 kJ/mol). This might be assigned to the polarity of the double bond of oleic acid, which increases the reactivity of the carboxylic moiety. Warabi et al., [12] confirmed that saturated fatty acids (palmitic and stearic acid) have slightly lower reactivity than unsaturated ones (oleic, linoleic, linolenic) especially with ones containing more than one double bond. Their result also shows a slight difference between palmitic acid (C16:0) and stearic acid (C18:0), with the reaction being faster with shorter chain length.

2.3.4 Effect of Water

The amount of water might be an important parameter in esterification that uses cheap feedstocks, which contain some amount of water. The study of the water effect will determine maximum water allowance to maintain high yield.

Liu et al. [72] found that the presence of water promotes the reverse reaction and the effect of water on catalyst activity is critical for both homogeneous catalyst (H_2SO_4) and heterogeneous catalyst (SAC-13) in esterification of acetic acid. The hydrophobicity of the reacting carboxylic acid increases with increasing carbon chain length. Large carboxylic acids had little effect on water deactivation of Bronsted acid sites for solid catalysts, despite the increased hydrophobicity. The weak effect of water on large carboxylic acids was also obtained from the study of Camera and Aranda [80]. They suspect that this is due to lower pKa of longer chain FA. The dissociation constant of carboxylic acids is associated with the stabilization of the carboxylic anion by water. Water influences reaction more significantly by stabilizing the conjugate base A^- of FA, which shifts the equilibrium to the right. This was observed from an insignificant change in conversion of stearic acid using anhydrous and dehydrated ethanol (4%w/w) compared to a decrease in conversion for the reaction with palmitic acid and lauric acid. Aranda et al. [77] showed that the inhibition effect of water on the reaction is stronger in ethanol than in methanol. This might be related to phase miscibility and emulsion formation. Yucel and Turkay [79] observed higher yield using 99.1% ethanol compared to 96% ethanol, which showed an inhibition by water.

2.3.5 Kinetics of Noncatalytic Esterification

This section will focus mainly on the kinetics of esterification without catalyst and related kinetics model. The kinetics have been studied in two levels: phenomenological and mechanistic.

Phenomenological Kinetics:

Berrios et al. [59] studied the kinetics of FFA esterification in sunflower oil with methanol in the presence of sulfuric acid. Esterification was a reversible heterogeneous reaction and chemical reaction occurs in the oil phase. The noncatalytic rate was negligible compared to the catalyzed reaction, and the methanol to oleic acid ratio was high enough to assume a constant concentration of methanol throughout the reaction. They proposed a pseudo homogeneous model that was first order in the forward path and second order in the reverse path. The kinetics equation was shown in equation (2.6) with $C_{R\text{-}OH}$ constant.

$$\frac{dC_{FAAE}}{dt} = k_f C_{FA} C_{R-OH} - k_r C_{FAAE} C_W \tag{2.6}$$

C_{FA}, $C_{R\text{-}OH}$, C_{FAAE}, and C_W are the concentrations of fatty acids, alcohol, alkyl ester, and water, respectively. k_f and k_r are the kinetics constant for the forward and reverse path, respectively.

Berrios et al. [59] found that the kinetics constant of the forward reaction increased with increasing molar ratio of methanol to oleic acid. This observation contradicts the fact that kinetics constant depends mainly on temperature but does not depend on the change in alcohol amount used in the system. This finding might be due to the assumption of constant methanol concentration. Therefore, the initial amount of alcohol should be incorporated into the model so that the kinetics constant is independent of molar ratio of alcohol. Also note here that their work used sunflower oil, which mainly consists of linoleic acid, but they used oleic acid as the fatty acid basis in the molar ratio. They also observe that rate constant of the forward path depends on the catalyst concentration. Similarly, this parameter might be able to built into the model as

one of the variables. The rate constant for the reverse reaction is negligible. The activation energy of 50.7 kJ/mol at 5% sulfuric acid was obtained in a temperature range of 30-60 ^{o}C.

Thiruvengadaravi et al (Pongamia pinnata oil) and Satriana and Supardan (low grade crude palm oil) [58, 71] used the same kinetics model as Berrios et al. and found similar results of irreversible behavior with an insignificant value of the reverse rate constant. Both studies used methanol as alcohol and sulfuric acid as a catalyst. The forward rate increases with increasing methanol to oil ratio and catalyst quantity. Satriana and Supardan found that the equilibrium constant changed with the molar ratio of methanol to oil. However, this equilibrium constant value should be the same at the same temperature. By observing their data, it seems that the reported forward rate constant is the same with some variation at different levels of alcohol. The differences in the equilibrium constant in their study might be caused by inaccurate data obtained for the reverse kinetics constant. In the study of Thiruvengadaravi et al. and Satriana and Supardan, the activation energy of the forward reaction is low with the value of 0.28 kJ/mol and 30.4 kJ/mol, respectively. This might be the result of diffusion effects in the system with FFA-oil mixture because alcohol and oil are not soluble.

Camera and Aranda [80], and Alenezi et al. [64] used a similar kinetics model as above, but set the concentration of alcohol as a variable in their model as in equation (2.6). Camera and Aranda [80] studied the esterification of fatty acids (stearic, palmitic and lauric) with anhydrous and hydrated ethanol using niobium oxide catalyst. Their study was at subcritical temperature of 150 ^{o}C and 200 ^{o}C with a molar ratio of ethanol to FA of 3. The kinetics constants obtained from anhydrous and hydrated ethanol at the same temperature showed different values. However, this kinetics constant should not be a function of the water content in an alcohol because the amount of water is already built into the model and has to be provided as an initial value in the model. Similarly, the equilibrium constant at the same temperature in reaction with anhydrous and hydrated ethanol should be the same, but their results showed otherwise. A more significant difference in equilibrium constant was observed at higher temperature. This might be because water might play an important role at higher temperature perhaps making the

components more miscible. If the concentration of water was not included in the initial value, it will make a big difference in the rate constant value. Alenezi et al. [64] also use the same model of equation (2.6), but the study was done without catalyst in esterification of fatty acid with supercritical methanol at 250 ^{o}C to 320 ^{o}C using methanol to FFAs molar ratio of 7. They found the forward activation energy to be 72 kJ/mol, which is in agreement with the work of Tesser et al (66 kJ/mol). The activation energy in the forward direction is three times higher than the activation energy of the reverse reaction, which shows endothermic behavior of the esterification reaction.

Aranda et al. [77] ignored the reversibility of the reaction but assumed the reaction order with respect to fatty acid to be α and the order with respect to alcohol to be β. They found first order with respect to fatty acid and zero order with respect to alcohol at 130 °C. However, they did not vary the alcohol concentration enough to determine the reaction order with respect to alcohol because they used a constant alcohol to fatty acid ratio of 3. Moreover, their noncatalytic experiments were all at 130 °C, and it is not clear that a single fluid phase was present throughout the reaction. The activation energy in their work was calculated as 176 kJ/mol and 272 kJ/mol for oleic acid and palmitic acid, respectively.

Minami and Saka [49] included reversibility and used an autocatalytic reaction scheme wherein the fatty acid reactant also served as an acid catalyst for the reaction. Note that this scheme is not a classical autocatalytic reaction, which involves catalysis by an intermediate or product from the reaction and not the reactant itself. They did not report any of the kinetics parameters. Their kinetics model is shown in equation (2.7).

$$\frac{dC_C}{dt} = k_f C_{FA}^2 C_{R-OH} - k_r C_C C_W C_A \qquad (2.7)$$

Tessser et al. [81] used the same kinetics model as Minami and Saka (equation (2.7)). Their study in the low temperature of 100-120 ^{o}C with methanol to oleic acid molar ratio of 8 used heterogeneous ionic exchange sulphonic acid resin and assumed a pseudo homogeneous single liquid phase existed. The liquid-liquid phase behavior and

amount of volatile methanol and water was neglected. Their activation energy for the forward reaction is 66 kJ/mol. They also used Eley-Rideal type kinetics to model their system, which led to less error than the pseudo-homogeneous reversible model.

Popken et al. [82] used a simple power law model in the study of acetic acid esterification with methanol as in equation (2.8).

$$Rate = a_{FA}^{\alpha}(k_1 a_{FA} a_{MeOH} - k_{-1} a_{FAME} a_{H_2O})$$ (2.8)

The use of activities in the kinetics model instead of mole fraction in their study resulted in a smaller error. They found that the order α is equal to one in the noncatalytic case, which became the same model as that proposed by Minami and Saka.

Liu et al used a combination of 2 catalytic routes: homogeneous acid catalyzed and autocatlyzed as shown in equation (2.9) and (2.10).

$$FA + MeOH + H_2SO_4 \xleftrightarrow{k_c} FAME + H_2O$$ (2.9)

$$FA + FA + MeOH \xleftrightarrow{k_{Auto}} FAME + H_2O + FA$$ (2.10)
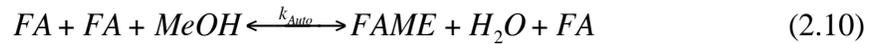
The rate equation derived from these reaction paths follows third order kinetics (equation (2.11)).

$$-\frac{dC_{FA}}{dt} = k_C C_{cat} C_{FA} C_{MeOH} + k_{Auto} C_{FA}^2 C_{MeOH}$$ (2.11)

They neglected the reverse path and obtained a good fit with their experimental data at 60 ^{o}C with methanol to acetic acid ratio of 2 in the presence of sulfuric acid.

Mechanistic kinetics:

According to the mechanistic classification, acid-catalyzed esterification is usually $A_{AC}2$ [83]. $A_{AC}2$ refers to acid catalyzed (A), acyl cleavage (AC) and rate

limiting step is bimolecular (2). Esterification is reversible and symmetrical with hydrolysis. Therefore, the mechanisms for both esterification and hydrolysis are the same. The evidence for the $A_{AC}2$ mechanism for acid catalysis is; 1) Isotope labeling of oxygen in H_2O (with ^{18}O) confirmed that ^{18}O appears in the acid as in equation (2.12) not in the alcohol as equation (2.13); 2) esters having R' with chiral center were found to give alcohols with the same configuration as R'; 3) no rearrangement occurs when R' is allylic; and 4) R' having a neopentyl group did not give rearrangement. All these facts indicate that the O-R' bond in the ester is not broken [83].

$$
\begin{array}{cccc}
\overset{O}{\underset{|}{R\text{-}C\text{-}OR'}} + \overset{18}{H\text{-}O\text{-}H} & \rightleftharpoons & \overset{O}{\underset{}{R\text{-}C\text{-}OH}}^{18} + & H\text{-}O\text{-}R' \\
\end{array}
\qquad (2.12)
$$

$$
\begin{array}{cccc}
\overset{O}{\underset{|}{R\text{-}C\text{-}OR'}} + \overset{18}{H\text{-}O\text{-}H} & \rightleftharpoons & \overset{O}{\underset{}{R\text{-}C\text{-}OH}} + & R'\text{-}\overset{18}{O}H \\
\end{array}
\qquad (2.13)
$$
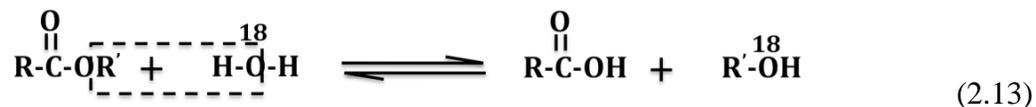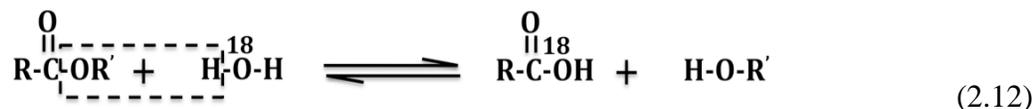
In the reverse $A_{AC}2$ mechanism, the first step is the protonation of the fatty acid to generate a carbocation (i.e. catalyzed by proton). The carbocation is subsequently attacked by an alcohol molecule and then forms the corresponding ester and water. The mechanism is shown in Figure 2.2

$$R-\overset{\overset{O}{\|}}{C}-OH \;+\; H^+ \;\rightleftharpoons\; R-\overset{\overset{OH}{|}}{\underset{+}{C}}-OH$$

$$R-\overset{\overset{OH}{|}}{\underset{+}{C}}-OH \;+\; R'OH \;\overset{slow}{\rightleftharpoons}\; R-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{+}{\underset{H}{O}}R'$$

$$R-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{+}{\underset{H}{O}}R' \;\rightleftharpoons\; R-\overset{\overset{+OH_2}{|}}{\underset{\underset{OH}{|}}{C}}-OR'$$

$$R-\overset{\overset{+OH_2}{|}}{\underset{\underset{OH}{|}}{C}}-OR' \;\overset{slow}{\rightleftharpoons}\; R-\overset{\overset{OH}{|}}{\underset{+}{C}}-OR' \;+\; H_2O$$

$$R-\overset{\overset{OH}{|}}{\underset{+}{C}}-OR' \;\rightleftharpoons\; R-\overset{\overset{O}{\|}}{C}-OR' \;+\; H^+$$
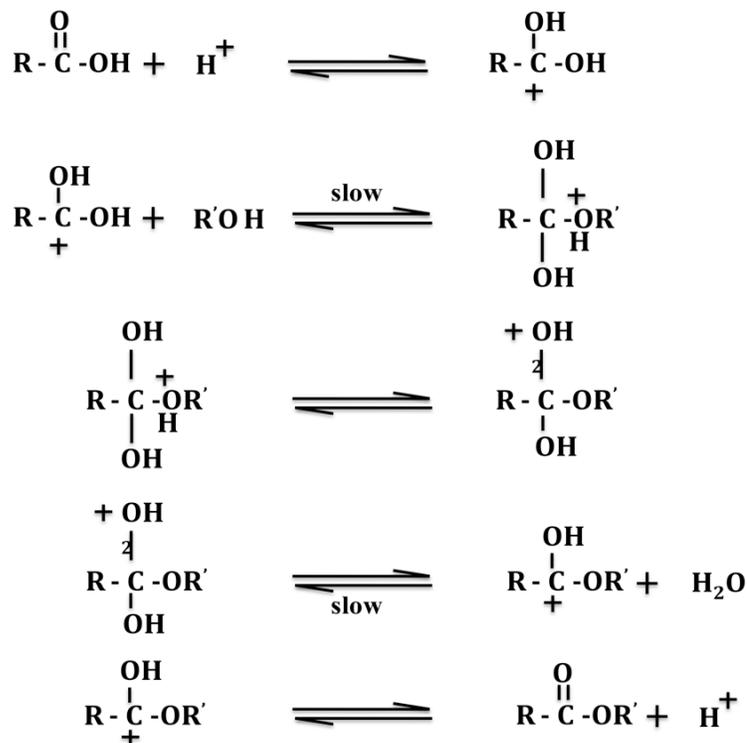
Figure 2.2: The acid-catalyzed esterification by $A_{AC}2$ mechanism

Minami and Saka [49] proposed a mechanism of esterification similar to the $A_{AC}2$ mechanism. The fatty acid is catalyzed by the proton from the dissociation of the fatty acid. Then this cabocation reacts with methanol to form intermediate and water. This intermediate releases a proton and produces ester in the final step. However, in their kinetic model they did not include the concentration of proton, which is an important parameter. The proton can come from the dissociation of fatty acid or water, for systems with some amount of water initially present.

Goto et al. [84] also used a mechanism similar to $A_{AC}2$ to fit their experimental data of palmitic acid esterification with isobutyl alcohol using sulfuric acid. They suggested that sulfuric acid reacts with isobutyl alcohol to produce isobutyl sulfuric acid, which acts as a catalyst in the system.

Ronnback et al. [62] studied esterification of acetic acid with methanol using hydrogen iodine as acid catalyst. They proposed that hydrogen iodine and acetic acid act as proton donors through protolysis with water. The nucleophilic attack of methanol to

the carbonium ion formed through proton donation to acetic acid was the rate determining step. They also included a side reaction that occurs by catalyst and methanol in their model. The concentration-based rate equation as well as activity-based using UNIFAC activity coefficient estimations were used. The results from both models did not show a significant difference in their results in the temperature range of 30-60 ^{o}C for low catalyst concentration. But the activity-based model showed a better result with high concentration of catalyst.

Liu et al. [72] have proposed a modified mechanism for sulfuric acid catalyzed esterification of acetic acid with methanol at 60 °C, wherein the alcohol gets protonated by the catalyst in the presence of water. The protonated alcohol then protonates the acetic acid. The protonated acid attacks another alcohol molecule, in a rate–limiting step, to generate ester and water as shown in Figure 2.3. They also derived the kinetics model based on this mechanism for acid-catalyzed esterification. However, they did not use this mechanistic-kinetics model to fit their experimental data.

$$2H_2SO_4 + CH_3OH + H_2O \xrightarrow{\;fast\;} CH_3OH_2^+ + H_3O^+ + 2HSO_4^-$$

$$CH_3OH_2^+ + CH_3COOH \xleftrightarrow{\;k_{MeOH}\;} CH_3OH + CH_3COOH_2^+$$

$$H_3O^+ + CH_3COOH \xleftrightarrow{\;k_W\;} H_2O + CH_3COOH_2^+$$

$$CH_3OH + CH_3COOH_2^+ \xleftrightarrow{\;slow\;} CH_3COOCH_3H^+ + H_2O \quad (RDS)$$

$$CH_3COOCH_3H^+ + CH_3OH \longleftrightarrow CH_3OH_2^+ + CH_3COOCH_3$$

$$CH_3COOCH_3H^+ + H_2O \longleftrightarrow H_3O^+ + CH_3COOCH_3$$
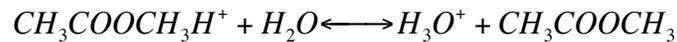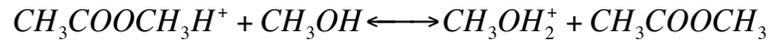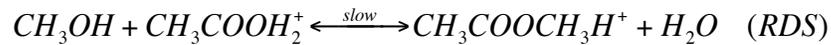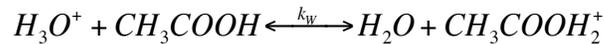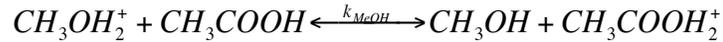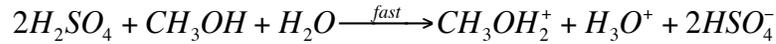
Figure 2.3: The acid-catalyzed esterification by Liu et al. [72]

Bart et al. [63] studied the kinetics of esterification of levulinic acid with n-butanol using sulfuric acid in the temperature range of 25-118 ^{o}C, with a molar ratio of alcohol to fatty acid of 0.02-1. They proposed the mechanism wherein sulfuric acid directly protonates levulinic acid and gives an intermediate that cannot be isolated. Then the protonated acid reacts with n-butanol to produce ester and water as shown in equation (2.12) and (2.13). The kinetics model derived from the proposed mechanism fit well with their data.

$$FA + H_2SO_4 \leftrightarrow FA^+.HSO_4^- \tag{2.12}$$

$$FA^+.HSO_4^- + BuOH \leftrightarrow FABE + H_2O + H_2SO_4 \tag{2.13}$$
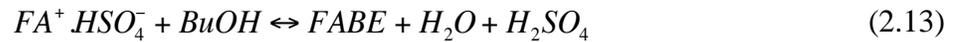
Au-Chin and Kuo-Sui [85] proposed a different mechanism of esterification as in Figure 2.4. In their mechanism, H^+ protonates the fatty acid and alcohol to give carbocations. These carbocations react with fatty acid to form intermediates, which then were attacked by alcohol and produced ester and water and give back the H^+.
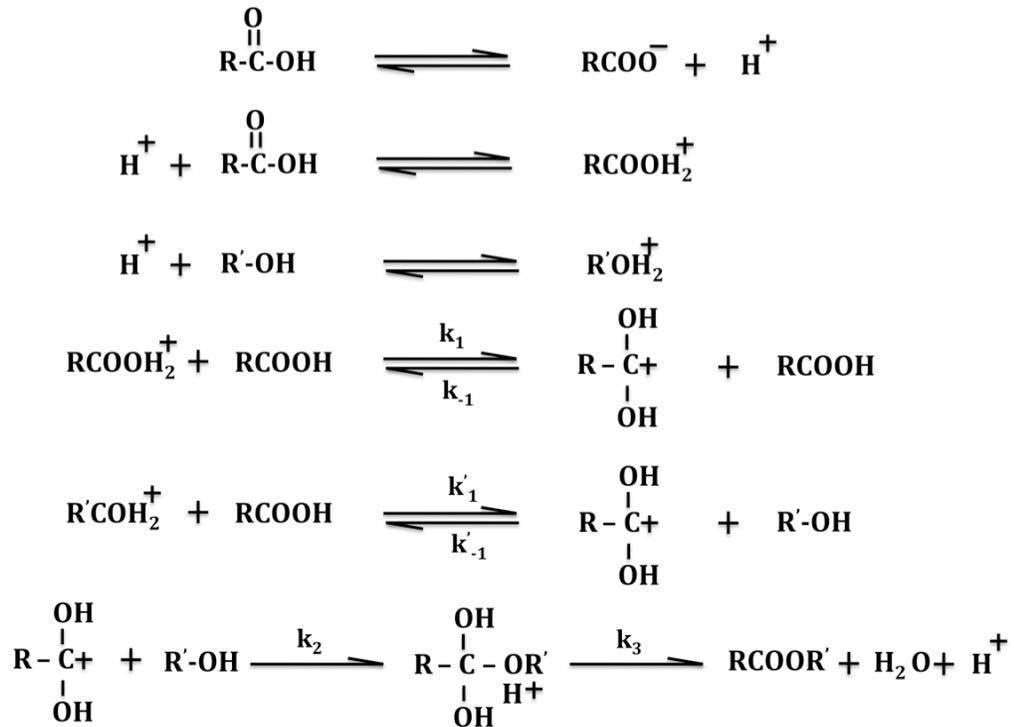
Figure 2.4: The acid-catalyzed esterification by Au-Chin and Kuo-Sui [85]

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CHAPTER 3

Experimental and Modeling

3.1 Experimental

3.1.1 Feasibility Study

Oleic acid was chosen as a model fatty acid because it is commonly found in the feedstocks for biodiesel production. Ethanol was used as a reactant, which might help improve the quality of biodiesel. All chemicals were obtained in high purity from Sigma Aldrich and Fisher Scientific and used as received. Two different constant-volume batch reactors were used. The one we used initially was made from a quartz tube to avoid potential catalytic effects from a metal reactor wall. The reactor is 2 mm i.d., 6 mm o.d., and either 18.1 cm or 13.8 cm in length. We also did experiments in 316 stainless steel reactors fashioned from ¼-inch Swagelok caps and a port connector (0.6 mL total volume) to test for the possibility of metal-catalyzed reactions by the reactor wall.

We explored reaction conditions ranging from 150 to 320 °C and times between 0 and 1440 minutes. The ethanol to oleic acid molar ratio ranged from 1:1 to 35:1. The batch reactor volumetric filling fraction, f, was varied from 0.04 to 0.80. This variable is the fraction of the reactor volume loaded with reactant solution at room temperature. This variable sets the fluid density at reaction conditions. Hence, it controls the phase(s) that exist at reaction conditions. Low values of f lead to mostly gas phase systems at the reaction temperatures we investigated. Likewise, high values of f lead to liquid phase reactions when below the critical temperature of the mixture. For reference, the critical point of ethanol is $T_c = 243$ °C, $P_c = 6.3$ MPa [1].

Standard solutions with various molar ratios of ethanol to oleic acid (1:1, 3:1, 5:1, 7:1, 10:1 and 35:1) were used as reactor feedstock. The solutions were well mixed before

being loaded into the batch reactor with a syringe. The loaded reactor was then sealed and immersed in a preheated isothermal fluidized sand bath at the desired temperature. After reacting for a period of time, the reactor was removed from the sand bath, cooled by air (for quartz reactor) or water (for metal reactor), and then opened. Methanol was added into the reactor at least once to ensure that all products were recovered. This solution was then diluted to 25 mL total volume and subsequently analyzed.

We followed a published procedure [2] to analyze the product solution using reverse-phase High Performance Liquid Chromatography (HPLC) with UV detector at 205 nm. The HPLC column contained a Waters Symmetry® C18 (4.6 mm id x 75 mm length) stationary phase with a 3.5μm particle size. A 30 μL sample injection was eluted with gradient operation. The mobile phase flowed at 1 mL/min and its composition shifted from 85% aqueous methanol (0.05% acetic acid) to 100% methanol over 20 minutes. The only compounds detected were oleic acid and ethyl oleate, and the amounts present were determined from calibration curves prepared from analysis of authentic standards. Multiple reactors were used for each reaction condition. The conversions reported are mean values based on the amount of oleic acid remaining and ethyl oleate formed. The uncertainties reported for the conversions are the experimentally determined 95% confidence intervals.

3.1.2 Application: Biodiesel from Algae

Lipid-rich *Chlorella vulgaris* was used as a biodiesel feedstock. The algae was grown and processed in house by Robert Levine. Biomass dry weight was measured gravimetrically following centrifugation of the culture media (2000 RCF, 15 minutes) and drying of the wet algal pellet (65 °C for 24 hours). The cells collected by centrifugation were dried, ground briefly (<15 seconds) with mortar and pestle to obtain a homogenous powder, and stored at 4 °C prior to use. The algae to biodiesel study was conducted jointly with Robert Levine.

In-situ lipid hydrolysis and supercritical in-situ (trans)esterification (SC-IST/E).

All high temperature reactions with wet algal biomass were carried out in 316 stainless steel (SS) reactors fashioned from Swagelok parts (2 caps and 1 port connector).

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Once loaded, reactors were immersed in a preheated, isothermal fluidized sand bath for a desired time and then promptly removed and cooled in water. Hydrolysis reactions at each condition were carried out simultaneously in two reactors. The larger reactor (10 mL) was loaded with dry algae (1 g) and water (4 g) to represent 80% moisture content of algae paste and reacted for 15, 30, 45, and 60 minutes at 250 $^\circ$C. Drying and then rehydrating the biomass allowed for improved sample preservation during storage and precise control of solids loading in downstream reactions. No difference in the solids yield, elemental composition, or moisture content of hydrolysis solids was found when reactions were completed with freshly harvested biomass.

Upon cooling, the aqueous phase and solids were separated by filtering under light vacuum (pre-dried, pre-weighed 934-AH filter paper, Whatman). No additional water was used to rinse the reactor housing. For some reactions, the aqueous phase was hexane-extracted to detect lipid components. The wet hydrolysis solids were stored at 4 $^\circ$C prior to use; a portion of these solids was dried to determine its moisture content. The yield of hydrolysis solids was determined from a parallel reaction in which dry algae (0.5 g) and water (2.0 g) were loaded into smaller reactors (4 mL). Upon cooling, 15 mL H_2O was used to ensure complete solids recovery from the reactor. Filter-separated hydrolysis solids were then dried (65 $^\circ$C, 24 hours) and massed.

SC-IST/E was carried out in 1.6 mL SS reactors with wet hydrolysis solids (60 mg) derived from the hydrolysis reaction at 250 $^\circ$C for 45 min. An exploratory 2^3 factorial experiment was carried out to determine the effects of reaction temperature (275 and 325 $^\circ$C), and reaction time (60 and 120 minutes), and ethanol loading (ca. 2 and 8 w/w dry solid) on the yield and composition of crude biodiesel. Following the reaction, reactor contents were filtered as described above; ethanol (95%; 15 mL) was used to wash the reactor. Hexane (1 mL) was added to the empty reactor to ensure complete ester recovery without exposing solids to this solvent. The ethanol-biodiesel mixture was collected in a round bottom flask and ethanol was evaporated under vacuum at 70 $^\circ$C. The crude biodiesel was re-suspended in hexane (5 mL), combined with the 1 mL hexane reactor wash, centrifuged to remove any remaining fine particles, and transferred to a sample vial. The hexane-biodiesel mixture was analyzed for FAEEs directly by gas

chromatography with flame ionization detection (GC-FID) and the mass of crude biodiesel was determined gravimetrically, as described below. The crude biodiesel (5-10 mg) was then analyzed for fatty acids (FAs), monoglycerides (MGs), diglycerides (DGs), triglycerides (TGs), and glycerol following derivatization with N-trimethylsilyl-N-methyl trifluoroacetamide (MSTFA, Sigma), as described below. Each reaction condition was analyzed in duplicate.

Lipid analysis via solvent extraction.

Lipids within algal biomass and hydrolysis solids were extracted and analyzed to determine their composition (relative amounts of FA, TG, DG, MG). Dry solids (ca. 30 mg) were loaded into glass tubes (16 mm x 100 mm) with teflon-lined screw caps and extracted at 60 °C for 4 hours with 6 mL of *n*-hexane or a mixture of *n*-hexane:isopropanol (HIP, 3:2 v/v). *n*-Hexane was chosen based on its commercial relevance in oilseed extraction and previous use to extract heterotrophic algal lipids, [3-7] whereas HIP was employed as a less toxic alternative to chloroform:methanol mixtures [8]. Upon cooling, the tubes were centrifuged (2000 RCF, 15 minutes) and 2 mL of the upper solvent layer (i.e. crude lipid extract, CLE) was transferred to a 2 mL GC-vial and stored at 4 °C prior to analysis.

The CLE (50 to 500 µL) was transferred to two pre-weighed GC vials using the Agilent 7693A Automated Liquid Sampler. The solvent was evaporated under N_2 (Visiprep Solid Phase Extraction Vacuum Manifold**,** Supelco) and the mass of the CLE was determined gravimetrically (XS205DU, Mettler Toledo, readability = 0.01 mg). Prior to analysis by high-temperature (HT) GC/FID, the CLE was derivatized with MSTFA to improve the volatility of lipid components containing free hydroxyl groups (e.g., FA, MG, DG). A modified micro-scale EN14105 procedure was adopted to automate standard and sample preparation, include FA quantification, increase analysis throughput, and reduce experimenter exposure to hazardous solvents [9, 10]. Three internal standards (1,2,4-butanetriol, dodecanoic acid, and tricaprin) in pyridine (10 µL each; 6,000-8,000 ppm) and MSTFA (20 µL) were added to a vial, the vial was stirred for 1 min, and then allowed to react for 30 min at room temperature. The sample was diluted in *n*-heptane (700 µL), stirred again, and injected in an Agilent 7890 GC-FID with an

ASTM6584 column (15 m x 320 mm x 0.25 µm, Agilent J&W). Injection (1.0 µL) was made to a cool-on-column inlet in oven-track mode with an initial oven temperature of 50 °C. After a 1 min hold, the temperature was ramped to 180 °C at 15 °C/min, 230 °C at 7 °C/min, and 380 °C at 30 °C/min. Helium was the carrier gas at a constant flow rate of 3.0 mL/min. FID detector temperature was 380 °C and N_2 served as make-up gas (30 mL/min). Peaks corresponding to FA, MG, DG, and TG were identified by their retention time and quantified based on internal standard calibrations of oleic acid, monoolein, diolein, and triolein, respectively.

Lipid analysis via acid-catalyzed in-situ transesterification.

Lipids from all classes in algal biomass, hydrolysis solids, and residual solids from SC-IST/E reactions were simultaneously extracted and catalytically transesterified to determine the total lipid content. Since acid-catalyzed in-situ transesterification has repeatedly been shown to recover more FAs than traditional two-step extraction and transesterification procedures [11-14], this procedure provided the theoretical maximum ester yield possible from process solids. This method has been applied successfully to dry algae on both an analytical [13-16] and larger scale [17, 18].

Dried algae (30 mg) or hydrolysis solids (15 mg) were weighed into glass tubes (16 mm x 100 mm) with teflon-lined screw caps and reacted with 2 mL freshly prepared ethanol (99%) containing 5% acetyl chloride at 100 °C for 90 minutes with vigorous stirring. Water (1 mL) was added to stop the reaction and FAEEs were extracted into 6 mL total *n*-hexane. The tubes were vortexed for 1 minute and centrifuged (2000 RCF, 10 min). Approximately 2 mL of the upper hexane-FAEE mixture were transferred to a GC vial. FAEEs were identified and quantified by GC-FID with a modified version of EN14103 [19] and the mass of biodiesel was determined gravimetrically in a manner similar to the CLE. A new vial containing the sample (195 µL) and internal standard (5 µL, tricosanoic methyl ester, C23:0 FAME, Supelco) was prepared by the 7963A Automated Liquid Sampler and injected (1µL; 15:1 split ratio; 260 °C inlet temperature) onto an HP-InnoWax column (30 m x 0.32 mm x 0.25 µm, J&W 1909BD-113) with an initial oven temperature of 170 °C. After a 3 minutes hold, the temperature was ramped at 3 °C/min to 250 °C. Helium was the carrier gas at a constant flow rate of 1.0 mL/min.

FID detector temperature was 260 °C and N_2 served as make-up gas (30 mL/min). FAEE were identified based on retention time using a C4-C24 FAEE mix (Supelco); total FAEE calculations reflect all integrated area between FAEE C14:0 and C24:0, as designated by EN14103. Vials containing pure *n*-hexane served as negative controls (gravimetric yield on blanks was never greater than 0.1 mg).

3.2 Modeling

3.2.1 Pressure Calculation

In addition to the laboratory experiments, we also performed phase equilibrium calculations using ASPEN Plus version 2006.5 process simulation software. We used the FLASH2 block to perform vapor-liquid equilibrium calculations. These calculations provided estimates for the reactor pressure and compositions and amounts of co-existing phases when multiple phases were present. As recommended by Carlson [20] for high-pressure, non-electrolyte systems, we used the PRMHV2 thermodynamic property option. This option employs the Peng-Robinson equation of state with modified Huron-Vidal mixing rules. Temperature, the initial amounts of ethanol and oleic acid, and an assumed pressure were the inputs to the process simulation software. We adjusted the pressure manually until the calculated results provided the total molar density of the mixture that existed at the experimental conditions.

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CHAPTER 4

Feasibility Study of Noncatalytic Subcritical Esterification

This following three chapters will present the experimental/model results and discuss the significant findings in depth. As mentioned earlier in the motivation of the work, two-step noncatalytic biodiesel production is an interesting process that might allow biodiesel to become more competitive with petroleum based diesel, in terms of cost. The two-step noncatalytic process involves the hydrolysis of triglyceride, which is then followed by the esterification of fatty acid. The first step is a well-known reaction and has been studied for many years. The second reaction, esterification, was done under supercritical conditions in the two-step noncatalytic biodiesel production scheme [1].

In this Chapter, we first show the possibility of esterification under sub-critical conditions, which shows the potential for lower energy use in the process. We then examine the influence of the ethanol to oleic acid feed ratio, the water content, and the metal surfaces on esterification at mild conditions.

In Chapter 5, we demonstrate the method with a real biomass reactant, carbonized solid from algae, to produce biodiesel without drying and extraction of the lipid. Drying and extraction processes consume a considerable amount of energy, which is undesirable. Therefore, we showed the possibility of applying the two-step noncatalytic concept to lower the cost of biodiesel production from algae.

After that we explore the kinetics of esterification to determine how fast the system works under specific conditions in Chapter 6. The kinetics was studied at both the phenomenological and mechanistic level. The phenomenological kinetics studies start with a set of single-phase esterification experiments (simple model) and then the kinetics model is extended by combining the esterification and hydrolysis experimental

data (Fatty acid catalytic model). We show the ability of the kinetics model to predict the conversion in single phase reaction both within and outside the parameter space studied. We also applied the phenomenological kinetics model to predict the conversion at conditions that have 2 phases present. The model includes both kinetics and the thermodynamics of the system. A more complex mechanistic kinetics model is included next to provide an even better understanding of the reaction path of the system.

Finally chapter 7 presents conclusions and chapter 8 provides future direction for the work.

4.1 Feasibility at milder conditions

Since most of the previous work on noncatalyzed esterification used methanol as the alcohol and supercritical conditions [2, 3], we sought to determine whether appreciable rates could be obtained with ethanol at temperatures and/ or pressures below its critical values (T_c = 243 °C, P_c = 6.3 MPa). We conducted experiments at 250 °C and 320 °C with f = 0.04. These conditions led to calculated initial pressures of around 2.0 MPa for both reaction temperatures. These values are well below the critical pressure of ethanol, suggesting the feasibility of esterification at milder subcritical pressures. The ASPEN calculations also revealed that most of the material loaded into the reactor resides in the vapor phase at these reaction conditions. The vapor fractions on a total molar basis were 0.87 at 250 °C and 0.93 at 320 °C. We also conducted an experiment at 250 °C with f = 0.26, conditions which led to a calculated pressure of 5.3 MPa. At these conditions, two phases existed. 52% of the total moles were in the liquid phase according to the ASPEN phase equilibrium calculations. Others feasibility experiments were at 150 °C with f=0.80, 200°C with f=0.80, and 230 °C with f=0.56. A single liquid phase existed at these subcritical temperatures, and the calculated pressure was about 38.5 MPa, 74.5 MPa, 5.5 MPa respectively.
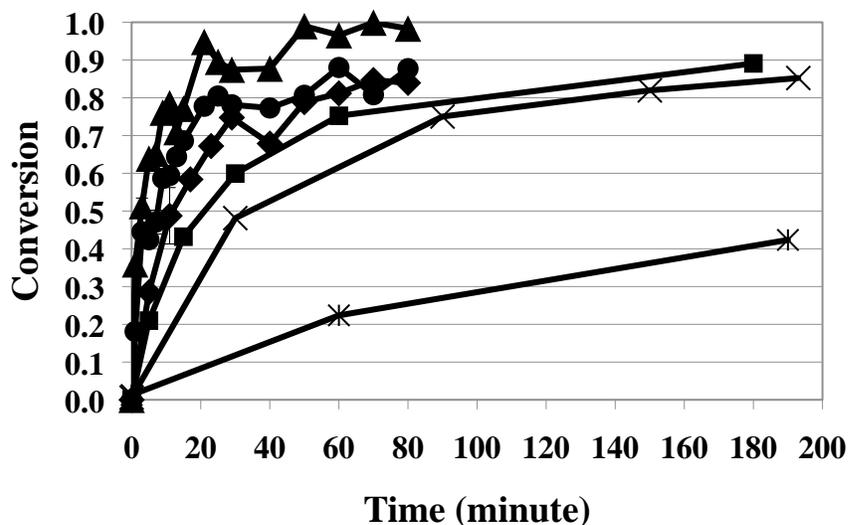
Figure 4.1: Temporal variation of esterification conversion at different reaction conditions 320 °C f= 0.04, R_{EtOH} = 10 (▲); 250 °C f= 0.04, R_{EtOH} = 10 (•); 250 °C f= 0.26, R_{EtOH} = 10 (♦); 230 °C f= 0.56, R_{EtOH} = 10 (■); 200 °C f= 0.80, R_{EtOH} = 7 (x); 150 °C f= 0.80, R_{EtOH} = 7 (∗)

Table 4.1 shows the phases and conditions used here, where R_{EtOH} is the molar ratio of ethanol to oleic acid, and C^0_{OA} is initial concentration of oleic acid.

Table 4.1: Conditions used in Figure 4.1

T (°C)	P (MPa)	f	R_{EtOH}	C^0_{A0} (mol/L)	mol % Liquid	vol % Oleic Acid in Liquid
150	38.5	0.80	7	1.1	100	100
200	74.5	0.80	7	1.1	100	100
230	5.5	0.56	10	0.6	100	100
250	5.3	0.26	10	0.29	52	96.1
250	2.0	0.04	10	0.05	13	96.1
320	2.0	0.04	10	0.04	7	68.9

Figure 4.1 shows the experimental results as discrete points. The line segments in Figure 4.1 are intended solely to guide the reader's eye. Complete conversion occurred within about 60 minutes at 320 ^{o}C, f = 0.04, 2 MPa. To compare with previous work in noncatalytic esterification, note that Minami and Saka [4] obtained around 90% yield of FAME in 10 minutes at 320°C, 20 MPa and a molar ratio of methanol: oleic acid of 10:1. Another researcher, Alenezi [3] also observed a high yield of around 95% in 5 minutes with esterification of FFA (88% Oleic acid) with molar ratio of methanol to FFA of 7 at 320 ^{o}C, 10 MPa. Our result adds to the literature by revealing that pressures above P_c for ethanol are not required for noncatalytic esterification. Our results at 320 ^{o}C used lower pressure of 2 MPa but longer time to reach complete conversion. However, this might be due to the different type of alcohol used in this work. Ethanol might have lower reactivity than methanol resulting a longer reaction time.

The conversion for 250 °C, f = 0.04 was always lower than that at 320 °C, which is consistent with the kinetics being faster at the higher temperature [5, 6]. The two experiments at 250 °C but different filling fractions (f = 0.04, f = 0.26) show that the conversion at a given time less than 20 minutes is higher at the lower pressure (f = 0.04). Again, high pressures are not required for this reaction to proceed at an appreciable rate. These experimental conditions at 250 ^{o}C involved two phases. The higher conversion obtained from the experiment with lower pressure might be due to the different compositions in each phase. For example, at 250 ^{o}C, f=0.04, most of the oleic acid is in the liquid phase and as the reaction proceeds, the water produced might exist in the vapor phase. This partitioning might help shift the reaction more to the right side with less product in the liquid phase compared to the higher pressure case (250 ^{o}C f=0.26). If this hypothesis is true, the long time conversion at 250°C, f=0.04 should be higher than the one at 250 ^{o}C, f=0.26. However, we did not observe such a trend here at our longest study time. Perhaps longer reaction time is required to see the effect.

At 150 °C, the lowest temperature tested here, the noncatalytic esterification proceeded with slow rate. Around 45% conversion was reached at 200 minutes. Increasing temperature to 200 °C, the noncatalytic esterification proceeded with an appreciable rate (~80% conversion) in 2 hours. However, at these conditions

supercritical pressures exist at 38.5 MPa and 74.5 MPa for 150 °C and 200 °C, respectively.   Increasing temperature further to 230°C but with a lower loading, the pressure at this condition is 5.5 MPa.   These conditions represent a subcritical temperature and pressure. Acceptable conversion of around 75% was obtained for one hour of reaction time. Note that the error of the experiment in all conditions was less than 5%. The repitition was done at longer time so it was not included in figure 4.1 for 150°C, and 200°C.

Taken collectively, these results demonstrate that high conversions can be obtained for noncatalytic fatty acid esterification with ethanol at temperatures and/or pressures below the critical values for ethanol. Having demonstrated this feasibility, we next explored the influence that different process variables have on the rate of this reaction.

4.2 Effect of ethanol to oleic acid molar ratio

The molar ratio of alcohol to fatty acid is an important variable in the esterification reaction. Since the reaction is reversible, more alcohol is expected to drive the reaction to higher conversions at equilibrium. For a commercial process, however, it would be desirable to use as low a ratio as possible to reduce costs. The exploration of Kusdiana and Saka [1] showed that oleic acid could be completely converted to methyl ester at an alcohol to acid molar ratio of only 3:1 using 270 °C, 20 MPa and 20 minutes as the reaction conditions. This result is encouraging, but we desired to learn the effect of this ratio on the conversion from noncatalytic esterification at lower temperatures and pressure (subcritical temperature and/or pressure) with ethanol as an alcohol. Therefore, we performed new experiments and selected 30 minutes as the reaction time. We considered three different reaction conditions. At 230 °C, f=0.56, the reactions are mostly in the liquid phase and under subcritical temperature and pressure. At 250 °C with f=0.26 the system is about 50/50 liquid and vapor. At 250 °C and f=0.04 the reactor contains mostly vapor. These two conditions at 250 °C are under subcritical pressure.

Figure 4.2, which displays the results of the three reactions, shows that at the stoichiometric ratio (1:1), conversions of at least 50% were observed. At 230°C, the

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conversion was highest at the 3:1 ratio, and the conversion decreased slightly as the molar ratio increased. This behavior might have occurred because the oleic acid concentration decreased as the molar ratio increased (since the total fluid volume added to the reactor was fixed). At 250°C f=0.04, the conversion increased to 70% when the molar ratio increased to 3:1. Further increases in the molar ratio do not appear to have a significant effect. At 250°C f=0.26, the molar ratio does not seem to have an effect on conversion. Taken together, these results show that low, rather than high, alcohol to fatty acid ratios are sufficient for noncatalytic ethyl esterification even at a subcritical temperature and/or pressure.

Our observation at 230°C f=0.56 is similar to those from Minami and Saka [4]. They obtained a decrease in yield with increases in the molar ratio of methanol in the esterification of oleic acid. Their methanol to oleic acid molar ratio range of study is 5-29. Alenezi et al. [3] observed an increase in yield with an increase of molar ratio of methanol to FFA from 0.7, 1, 1.6, 3 and then a decrease in yield from molar ratio of 3 to 7.

Both kinetic and thermodynamic effects are likely at work in causing the changes in conversion with the alcohol to fatty acid ratio in our work (Figure 4.2) as Figure 4.1 shows that at this batch holding time the reactions have not yet reached equilibrium. It is difficult to decouple these effects in the present data due to the existence of two separate fluid phases in the reactor under these reaction conditions (see Table 4.2). The vapor and liquid phases had different concentrations of oleic acid and ethanol (and products as they formed), so the esterification reaction would proceed at different rates and to different equilibrium conversion values in the two phases. This discussion shows that understanding the phase behavior and how it changes throughout the course of the reaction is required to fully understand the reaction behavior.
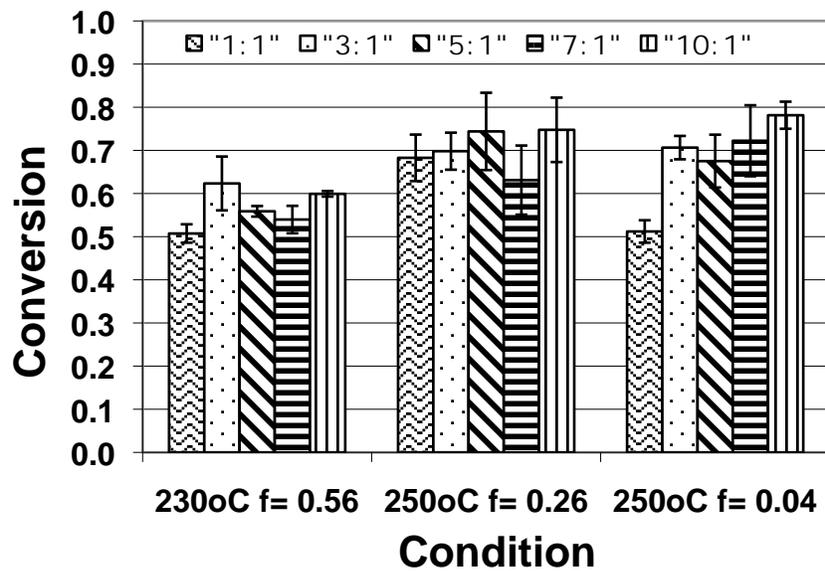
Figure 4.2: Effect of ethanol to oleic acid feed molar ratio on esterification conversion at 30 minutes

Table 4.2: Conditions used in Figure 4.2

T (^{o}C)	P (MPa)	f	R_{EtOH}	C^0_{A0} (mol/L)	mol% Liquid	vol% Oleic Acid in Liquid
230	2.4	0.56	1	1.49	95	99.9
230	3.7	0.56	3	1.13	96	99.9
230	4.0	0.56	5	0.92	98	99.9
230	4.2	0.56	7	0.77	100	100
230	5.2	0.56	10	0.63	100	100
250	2.0	0.26	1	0.68	73	99.8
250	4.0	0.26	3	0.52	57	99.1
250	4.7	0.26	5	0.42	52	98.2
250	5.1	0.26	7	0.35	52	97.3

Table 4.2: Conditions used in Figure 4.2 (continued)

T (°C)	P (MPa)	f	R_{EtOH}	C^0_{A0} (mol/L)	mol% Liquid	vol% Oleic Acid in Liquid
250	5.3	0.26	10	0.29	52	96.1
250	0.8	0.08	1	0.22	59	99.5
250	0.8	0.04	3	0.07	30	98.2
250	1.1	0.04	5	0.05	18	97.1
250	1.2	0.04	7	0.04	16	96.7
250	2.0	0.04	10	0.05	13	96.1

4.3 Effect of water

Water is a common impurity in low cost feedstocks such as waste cooking oils, and its presence is undesired in the feed to a conventional base-catalyzed biodiesel process. However, water has less effect on the two-step noncatalytic system because water is used in the first step (triglyceride hydrolysis). However, because water is a product of the reversible esterification reaction, its presence in the feed is expected to reduce the conversion at equilibrium. For all of these reasons, knowledge of the influence of water on the esterification reaction is vital.

Water was shown to inhibit acid catalyzed esterification reaction because water consumes the catalyst. Therefore, we will study the effect of water content in catalyst-free esterification under subcritical temperature and/or pressure.

We performed experiments with different amounts of added water, up to 15% by volume. This highest water loading is equivalent to 0.6 wt % water and also to the molar ratio of water to oleic acid in the reactor feed being 9:1. Figure 4.3 provides the results from the experiments. At all three conditions investigated, the conversions with no water, 1% water, and 3% water are approximately the same, given the experimental

uncertainties. The reduction in conversion at higher water loadings could be due to kinetic effects, chemical equilibrium effects, or phase equilibrium effects, either individually or collectively. Adding water to the feed dilutes the reactant concentration so there could be kinetic effects. Adding water will reduce the equilibrium conversion, which could lead to chemical equilibrium effects. Adding water influences the phase behavior, which could result in phase equilibrium effects. At 250 °C and f = 0.04, the system exists as two phases at reaction conditions when no water is present. According to the ASPEN calculations, the liquid portion decreases as more water is added, and the water content in the liquid phase decreases. At 250 °C and f = 0.26, the reaction also proceeds in two phases, but as more water is added to the system, the liquid fraction increases (see Table 4.3). This difference in the phase behavior might occur because the pressure is higher at this higher loading, causing more of the water to be driven into the liquid phase resulting in lower conversion. This might be the reason for the sharper decrease in this condition (250 ^{o}C f = 0.26) compared to 250 ^{o}C f = 0.04.
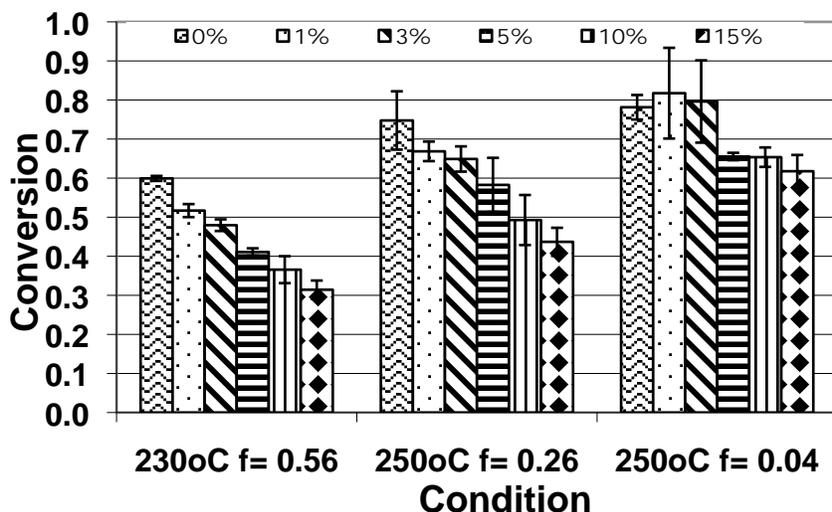
Figure 4.3: Effect of water (vol %) on conversion at 30 minutes and molar ratio of ethanol to oleic acid of 10:1

Table 4.3: Conditions used in Figure 4.3

T (°C)	P (MPa)	f	vol% water	C^0_{A0} (mol/L)	mol% Liquid	vol% Oleic Acid in Liquid
230	6.5	0.56	1	0.62	100	100
230	7.2	0.56	3	0.61	100	100
230	7.8	0.56	5	0.60	100	100
230	8.6	0.56	10	0.57	100	100
230	8.7	0.56	15	0.53	100	100
250	5.4	0.26	1	0.29	54	96.1
250	5.6	0.26	3	0.28	57	95.9
250	5.8	0.26	5	0.27	62	95.9
250	6.0	0.26	10	0.26	69	96.1
250	6.1	0.26	15	0.24	74	96.5
250	1.4	0.04	1	0.03	11	95.3
250	1.5	0.04	3	0.03	10	95.1
250	1.7	0.04	5	0.03	9	94.6
250	2.0	0.04	10	0.03	8	94.0
250	2.3	0.04	15	0.03	6	91.4

4.4 Effect of Reactor Surface Material

Dasari et al. [7] showed that a metal reactor wall can catalyze even a nominally noncatalytic transesterification reaction. Product yields in a metal reactor were about 10% higher than in a glass tube. The authors also showed that adding stainless steel and

nickel to the glass reactor increased the reaction rate by 30- and 400-fold, respectively [7]. We sought to determine whether metal reactor walls had a catalytic effect on esterification at our reaction conditions. The effect of a metal reactor wall was tested here by performing esterification in both stainless steel and quartz reactors at the same conditions (230 °C, f = 0.56, ethanol:oleic acid molar ratio of 1:1, 10 minutes). The conversion in the stainless steel reactor was $49 \pm 4\%$ and in the quartz reactor it was $48 \pm 4\%$. These results indicate that the 316 stainless steel walls did not catalyze the esterification reaction at these conditions. Therefore, both stainless steel and quartz reactors can be used to investigate the noncatalytic esterification of oleic acid.

The results presented thus far demonstrate the feasibility of noncatalytic esterification. High conversions are available at conditions milder than supercritical processing. The results also show that low alcohol to acid ratios of around 3:1 are adequate for the reaction and that the reaction is inhibited as the amount of water increases.

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CHAPTER 5

Biodiesel Production from Wet Algal Biomass Through In-situ Lipid Hydrolysis and Supercritical (trans)esterification

This chapter will demonstrate an alternative method to produce biodiesel from microalgae without drying and extraction using two steps: hydrolysis and (trans) esterification. This work was conducted jointly with Robert Levine and the contribution of this thesis was on the esterification step.

Interest in oleaginous microalgae as a non-edible biodiesel feedstock has grown considerably, largely on the promise of high oil yields (5,000 to 100,000 L/ha-y), the opportunity to capture waste CO_2, and the ability to cultivate algae on abandoned or unproductive land using brackish, salt or wastewaters instead of freshwater.

Unlike terrestrial oilseeds (e.g., soy), which can be easily harvested, dehulled, flaked, and dried to ~10% moisture prior to extraction with n-hexane, microalgae grow in dilute aqueous suspensions that complicate lipid recovery. A recent life-cycle assessment (LCA) of algal biodiesel production from *Chlorella vulgaris* indicated that drying and hexane extraction accounted for up to 90% of the total process energy [1]. These data indicate that drying algal biomass and treating it as a substitute for terrestrial oilseeds in traditional solvent extraction and subsequent transesterification processes is not likely to be a net energy positive route towards sustainable biodiesel production.

A biodiesel production process that obviates biomass drying and organic solvent use for oil extraction could lead to significant energy and cost savings. Previous attempts to eliminate even one of these steps have met with only limited success. For example, efforts to combine extraction with acid-catalyzed transesterification in one step have been successful with dry algal biomass, but the reaction is severely inhibited by water [2, 3]. Herein we propose a two-step, catalyst-free biodiesel production process involving

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intracellular lipid hydrolysis coupled with supercritical in-situ (trans)esterification (SC-IST/E). Figure 5.1 provides a process schematic. The wet algal biomass we reacted contained about 20% solids and 50% lipids on a dry weight basis. In the first step, wet algal biomass (ca. 80% moisture) reacts at subcritical water conditions to hydrolyze intracellular lipids, conglomerate cells into an easily filterable solid that retains the lipids, and produce a sterile, nutrient-rich aqueous phase. In the second step, the wet fatty acid (FA)-rich solids are subjected to SC-IST/E with ethanol to produce biodiesel in the form of fatty acid ethyl esters (FAEEs). This process eliminates both biomass drying and TG extraction (e.g., with an organic solvent such as *n*-hexane).
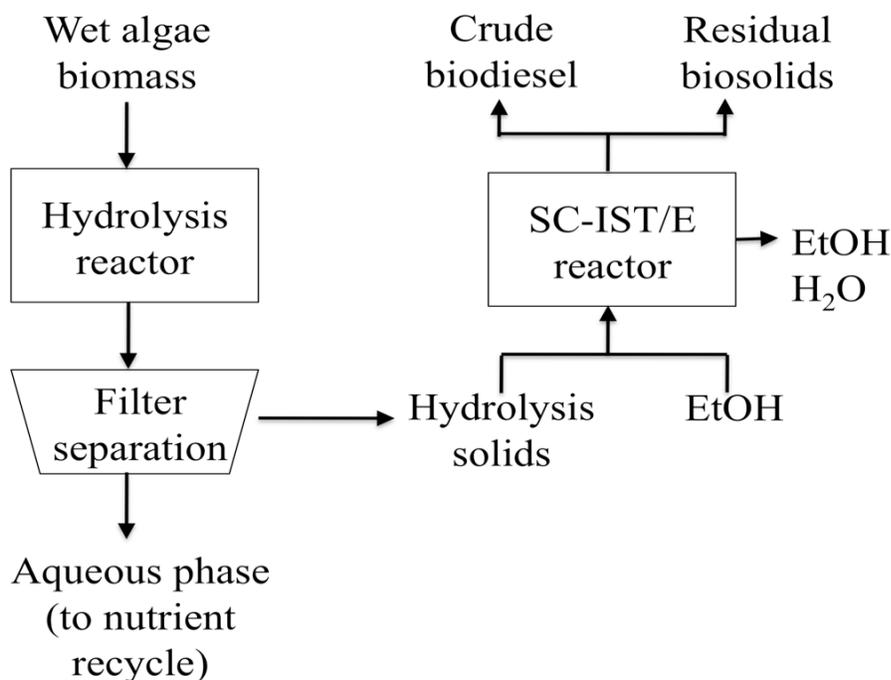
Figure 5.1. Process flow diagram for biodiesel production through intracellular lipid hydrolysis and supercritical in-situ (trans)esterification (SC-IST/E) using ethanol (EtOH).

The temperature of 250 °C at 45 minutes was chosen for hydrolysis. Hydrolysis solids contained approximately 80% and 70% total lipids measured as the HIP CLE, hexane:isopropanol crude lipid extract) from the solvent extraction and FAEE (from acid-catalyzed in-situ transesterification), respectively as shown in Table 5.1. (Both lipid measurements refer back to page 51-52 in chapter 3). Unexpectedly, FAEE yields were lower than the yield of the HIP CLE. Although unlikely, it is possible that the acid-

catalyzed in situ transesterification did not go to completion or that non-lipid constituents liberated during hydrolysis were extracted into the CLE and perhaps co eluted with detected lipid components.

Table 5.1 displays the FA profiles for the lipids in the hydrolysis solids recovered at 45 minutes compared to the algae feedstock. There was little variation in the distribution of the major FAEE in comparison to the original algal feedstock. This result indicates that there is no selective retention or rejection of certain FAs during the hydrothermal treatment. However, we did see evidence for isomerization and minor decomposition of linolenic acid (C18:3). About 13% of the total FAEE detected was C18:3. Note that standard deviation is given for the mean of duplicate reactions/extractions; ester percentages all had a standard deviation less than 0.6%. Other fatty acids detected, present at less than 5% of total fatty acids, included: C12:0, C16:1, C17:0, C20:0, C22:0, and C24:0. The percentages of C18:1, C18:2, C18:3 include all isomers.

Table 5.1. Characterization of feedstock and hydrolysis solids

	Feedstock	Hydrolyzed Solid
FAEE yield (wt%)		
Gravimetric	52.9 ± 1.9	73.5 ± 2.8
GC-FID	53.3 ± 1.3	73.1 ± 1.0
Fatty acid (% of esters)		
C14:0	0.4	bdl
C16:0	17.8	17.8
C18:0	2.1	2.0
C18:1	45.5	45.5
C18:2	9.0	8.7
C18:3	12.7	12.8

Table 5.1. Characterization of feedstock and hydrolysis solids (continued)

	Feedstock	Hydrolyzed Solid
HIP CLE (wt%)		
Gravimetric	45.6 ± 3.4	82.8 ± 0.4
GC-FID	47.1 ± 2.3	77.4

Table 5.2. Lipid composition and lipid retention in solids recovered from hydrolysis at 250 °C 45 minutes.

	Algae Paste	Hydrolyzed Solid
Lipid retention (%)	-	86.5
FA (%)	2.3	37.0
MG (%)	0.3	8.8
DG (%)	2.2	24.1
TG (%)	95.2	30.1

Lipid composition is the proportion of fatty acids (FAs), monoglycerides (MGs), diglycerides (DGs), and triglycerides (TGs) in the crude lipid extract (CLE) obtained by hexane:isopropanol extraction. Lipid retention was calculated from the dry weight yield of hydrolysis solids and the lipid content of both algal biomass and hydrolysis solids as determined by their fatty acid ethyl ester composition from GC-FID analysis of acid catalyzed in-situ transesterification as in equation (5.1).

$$Lipid\ retention = \frac{Lipid\ in\ hydrolyzed\ solid}{Lipid\ in\ algae\ paste} \times 100 \qquad (5.1)$$

The solids from this reaction time provide high lipid retention (87%) and significant TG hydrolysis (~ 70% conversion) in Table 5.2.

Solids generated from the hydrolysis of wet algal biomass were used for supercritical in-situ (trans)esterification (SC-IST/E) experiments. The hydrolysis solids were not dried prior to SC-IST/E and contained approximately 46 wt% water. The ability to convert FA and remaining glycerides in this wet solid into biodiesel through a

noncatalytic reaction with ethanol was assessed in exploratory experiments with two levels each of time, temperature and ethanol loading (Table 5.3).

Note that the ethanol loading is the mass ratio of ethanol to dry hydrolysis solids. H_2O % is the mass percentage of water in the reactor. Crude biodiesel yield is a gravimetric determination (average standard deviation for the mean of at least two gravimetric determinations was less than 6%) and is reported as a percentage of total lipids (hexane-isopropanol extraction) in the hydrolysis solids loaded on a dry basis. The crude biodiesel was analyzed directly for fatty acid ethyl esters (FAEEs) and for fatty acids (FAs), monoglycerides (MGs), diglycerides (DGs), and triglycerides (TGs) following derivatization with MSTFA.

In general, longer reaction time and higher temperature led to higher crude biodiesel yields and significantly fewer non-FAEE components therein, particularly FA and MG. In contrast, the higher ethanol loading led to significantly greater gravimetric yields of crude biodiesel but with concomitant increases in its non-FAEE content. In the discussion that follows, the influence of key process parameters on lipid extraction and conversion is elucidated through an analysis of the yield and composition of biodiesel.

Table 5.3. Supercritical in-situ (trans)esterification conditions and crude biodiesel yield and composition

	Reaction conditions and loading					Crude biodiesel composition (wt%)					
Run	T (°C)	Time (min)	EtOH (w/w)	H_2O (%)	Crude biodiesel yield (%)	FAEE	FA	MG	DG	TG	Other
1	275	60	2.2	21.0	56.4	53.5	11.7	10.1	2.1	2.1	20.5
2	275	60	8.3	8.4	80.5	39.8	14.0	16.7	6.7	2.7	20.1
3	275	120	2.3	20.4	68.3	79.2	9.3	5.3	1.7	1.3	3.1
4	275	120	7.5	9.1	94.0	56.6	9.7	13.2	2.2	0.8	17.5
5	325	60	2.1	21.6	65.8	33.4	9.9	3.2	0.8	0.6	52.2
6	325	60	7.2	9.4	87.7	52.0	13.9	10.7	0.8	0.4	22.3
7	325	120	2.3	20.4	58.7	58.6	8.6	2.0	0.6	0.1	30.1
8	325	120	6.6	10.1	100	58.7	9.0	4.3	0.3	0.1	27.6

Table 5.3 provides information about the composition of the crude biodiesel. In general, its ester content decreased with ethanol loading at 275 °C, while at 325 °C it increased or remained the same. Ester content increased with time, though with a less pronounced effect at the higher temperature. The highest ester content (79.2%) was achieved at 275 °C, 120 minutes, and a low (2.3) EtOH:solids mass ratio. The ester contents reported here compare well with data reported for SC-EtOH transesterification of soybean oil in systems containing 10% water: at 275 °C, the ester content of the recovered product was approximately 50% at 52.5 min residence times, respectively, and 70.8% esters at 325 °C [4]. In addition, they compare favorably to a previous report regarding in-situ transesterification of dry rice bran containing 17.4% total oil (comprising 73.7% TG and 12.3% FA): the FAME yield was 51% and FAMEs composed 52.5% of the product mixture following reaction with SC-MeOH and a CO_2 co-solvent (300 °C, 30 MPa, 5 min, 271 MeOH:oil molar ratio) [5]. As detailed in Table 5.3, the crude biodiesel contained unreacted glycerides and FA in addition to esters. TGs and DGs were typically present in low amounts, especially at 325 °C. At both temperatures, increasing the amount of ethanol resulted in crude biodiesel containing a higher proportion of FA and MG. For example, in runs 4 and 8, FAEE accounted for only 57-59% of the crude biodiesel product; a significant amount of FA (9.0-9.7%) and MG (4.3-13.2%) were present. The prevalence of MGs can be explained by their increased stability relative to other glycerides and previous work demonstrating their conversion is the rate-limiting step in TG transesterification [6]. Likewise, FA in the crude biodiesel most likely resulted from incomplete esterification or from FAEE hydrolysis. Since EN14214 mandates that esters comprise more than 96.5% of biodiesel and limits the amount of FA, MG, DG, and TG in biodiesel to 0.4, 0.8, 0.2, and 0.2 (w/w), respectively, the crude biodiesel produced by SC-IST/E under the conditions examined herein does not meet the specifications for finished biodiesel. In general, non-FAEE components could be removed with a warm alkaline water wash followed by centrifugation [7] or with new techniques that require less water [8, 9]. FA and glycerides recovered from the crude biodiesel could be recycled back to the supercritical reactor, generating additional FAEE. Clearly, further work is required to explore the parameter space more fully and identify

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optimal conditions for producing fuel-grade biodiesel from wet, FA-rich solids via uncatalyzed, SC-EtOH reactions.

Both the ethanol and water content of SC-IST/E reactions may have impacted the yield and quality of biodiesel produced. Water may play both beneficial and detrimental roles during supercritical (trans)esterification. The benefit arises from low water contents increasing the conversion of glycerides to FAEE at 250-325 °C, most likely through increased glyceride hydrolysis prior to esterification and decreased decomposition of unsaturated FAEE [4]. The detriment arises from higher water contents diluting the system (thereby reducing reaction rates) and facilitating FAEE hydrolysis (loss of desired product). These phenomena are likely responsible for the reduced ester yields reported from SC-EtOH (trans)esterification reactions done in the presence of water [10-12]. Likewise, the ethanol loading can have positive and negative impacts on the FAEE yield. The equilibrium conversion to esters increases with ethanol loading, but high EtOH:FA molar ratios (>15-30) can result in lower ester yields, [13, 14] perhaps because of dilution effects that reduce reaction rates. In the SC-IST/E reactions we ran with low ethanol loading, the molar ratios of ethanol to FA, MG, DG, and TG (estimated based on C18:1 FA groups) were in the ranges of 45-50, 240-260, 150-170, and 170-190, respectively. In all of the esterification reactions in Table 5.3, the initial water-to-oil ratio was constant (ca. 1.1 w/w water to HIP CLE of hydrolysis solids). Therefore, reactions with a higher ethanol loading necessarily had a lower water content on a total mass basis (cf. 8-10% to 20-21%). This conflation of the effects of ethanol loading and water content makes it difficult to isolate the effect of either component in our experiments, but given the large excess of water and ethanol, relatively long residence times, and the prevalence of FA in the product mixtures, it is likely that dilution of the reactant mixture and FAEE hydrolysis limited ester yields. Therefore, future work should consider lower ethanol loadings and perhaps removing some or all of the water from the hydrolysis solids. In addition to improving the ester yield from SC-IST/E, these process changes may also reduce process costs and energy inputs.

In this complex, multiphase reaction system, lipids were both extracted from the hydrolysis solids and (trans)esterified. The crude biodiesel yield, which indicates overall

extraction efficiency, ranged from about 56 to 100% (relative to the total lipids in the hydrolysis solids as determined by HIP extraction). As shown in Table 5.3, yields from reactions lasting 120 minutes with an EtOH:solids mass ratio of 6.6-7.5 were between 94 and 100%, suggesting that lipid removal from the solids was nearly complete under these conditions. This result was confirmed by examining residual solids from SC-IST/E and finding the FAEE content to range from 1 to 4% on a dry weight basis. Although nearly all lipids may have been removed from the hydrolysis solids during these reactions, total FAEE yields (60-66%) indicate that (trans)esterification was somewhat inhibited (Table 5.4).

Table 5.4. Fatty acid ethyl ester yields from supercritical in-situ (trans)esterification

	Ester yield (%)		Yield reduction (%)		
Run	Total	Saturated	C18:1	C18:2	C18:3
1	34.2	37.2	1.4	1	9.3
2	36.3	39.7	1.4	2.3	8.5
3	49.5	55.4	0.6	8	21.9
4	60.2	65.1	-0.5	3.6	17.5
5	43.0	58.4	4.4	28.5	48.2
6	51.6	59.7	0.7	8.7	32.3
7	38.9	60.6	9.9	42.3	60.6
8	66.4	81.3	2.1	18.2	56.5

Note that all yields in Table 5.4 are based on GC-FID determinations of FAEE from the acid catalyzed in-situ transesterifaction of hydrolysis solids and of FAEE recovered from supercritical in-situ (trans)esterification. Saturated FAEE yield is the average yield of C16:0 and C18:0 FAEEs. The difference between the average yield of saturated FAEE and the yield of all isomers of either C18:1, C18:2, or C18:3 is the yield reduction of those corresponding FA.

Supercritical alcohol treatment has been noted to cause trans-isomerization and decomposition or polymerization of unsaturated FA [15-17]. Though some have suggested that isomerization reduces fuel stability [18] and negatively impacts cold flow properties, [16] there is little conclusive evidence that trans-isomers of unsaturated FAEE are actually detrimental to fuel quality. Nevertheless, we estimated the extent to which isomerization occurred by examining GC retention time shifts in the elution of unsaturated FAEE. Note that both isomerization and decomposition can contribute to changes in the FAEE profile of the synthesized crude biodiesel. Since no isomerization of C18:2 was detected in the hydrolysis solids, the appearance of C18:2 isomers following exposure to SC-EtOH permits a useful analysis of the effects of time, temperature, and ethanol loading on isomerization. Table 5.5 shows that at 275 °C, between 6 and 8% of the C18:2 synthesized was in a non-native form, with the exception of the reaction lasting 60 min with high ethanol, in which no isomerization was detected. Significantly more C18:2 isomerized at 325 °C; between 34-44% and 56-57% of the C18:2 synthesized was in a non-native form after 60 or 120 minutes, respectively. At both temperatures, higher amounts of ethanol led to a reduction in isomerization, with a more prominent effect evident at shorter times. Similar but more pronounced trends were observed for C18:3 FAEE. Although analysis of C18:3 isomerization is complicated by the fact that the hydrolysis solids already contained some isomerized linolenic FA, about 35-60% and 77-83% of C18:3 FAEE detected in the crude biodiesel was isomerized at 275 °C and 325 °C, respectively. In summary, higher temperatures and longer reaction times resulted in greater trans-isomerization of C18:2 and C18:3 FAEE, in agreement with previous reports [11, 15].

Table 5.5 Fatty acid ethyl ester composition of biodiesel produced through supercritical in-situ (trans)esterification

| | Fatty acid profile (% of total FAEE) | | | | | | Percent isomerized (% of total species) | |
Run	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C18:2	C18:3
1	0.0	19.3	2.2	47.7	9.3	11.8	8.0	42.2
2	0.0	18.5	2.3	48.1	9.0	12.4	0.0	34.9
3	0.5	20.1	2.3	50.4	8.4	9.8	8.4	59.1
4	0.4	19.1	2.2	49.6	8.9	11.4	6.3	53.9
5	0.6	23.2	2.9	57.1	6.1	3.4	43.8	77.2
6	0.5	20.1	2.4	52.1	8.6	7.7	34.5	83.6
7	0.7	24.9	3.5	59.4	4.1	0.0	57.1	-
8	0.4	21.0	2.6	54.3	8.3	5.4	55.9	80.7

Note that isomerized ethyl esters correspond to both positional and geometric isomers, which demonstrated earlier (typically *trans*) and later (typically *cis*) retention times compared to compounds with the same chain length and number of double bonds in unreacted algal biomass where only single peaks were detected. C18:1, C18:2, and C18:3 data include all isomers detected, with the percent isomerized indicated in the two rightmost columns. No C18:3 FAEE was detected in Run 7.

In addition to isomerization, unsaturated FA can undergo a variety of reactions that may impact their usefulness as fuel components. It has been suggested that polyunsaturated FA can polymerize into higher molecular weight compounds and decompose into gaseous products in the presence of methanol above 300 °C, thereby reducing ester yields [16]. For example, when methyl linolenate was reacted with methanol at 350°C and 43 MPa for 20 and 40 min, total ester recovery was only 20.6% and 14.4%, respectively [16]. We examined the decomposition of unsaturated FAs during SC-EtOH treatment of the hydrolysis solids. Decomposition is indicated when the yield of all isomers of an unsaturated FAEE is less than the yield of saturated FAEEs, which are assumed to be thermally stable under these conditions [16]. We also implicitly

assume that the (trans)esterification rates in SC-EtOH are identical for both saturated and unsaturated FAs. The data in Table 5.4 show that decomposition was most prevalent in the polyunsaturated FAEE at higher temperatures and longer times. For example, the difference between the C18:3 yield and the yield of saturated FAEE increased between 3-5 and 1.2-1.5 fold from 275 to 325 °C and 60 to 120 minutes, respectively. In addition, yields of C18:2 and C18:3 FAEE, inclusive of all isomers, were closer to the average yield of saturated FAEE in reactions containing more ethanol, with the exception of those carried out at 275 °C and 60 minutes. In contrast, the yield of native C18:1 was within 2% of the average yield of saturated FAEE in all treatments, with the exception of reactions at 325 °C containing low amounts of ethanol. Here, C18:1 yields were about 4.4 and 10% less than the average yield of saturated FA at this temperature and 60 or 120 minutes, respectively. These data suggest that thermal reactions consume unsaturated FAEE, generating compounds that were not detected in this study.

Some of these products, such as glycerol decomposition products and short chain FAEE, may still contribute to the biodiesel as fuel components and may even improve the biodiesel viscosity and cloud/pour point [19]. Recall from Table 5.3 that in most reactions about 20-30% of the gravimetric mass of the crude biodiesel remained unidentified by GC-FID. This result is consistent with findings of Kasim et al., [5] who suggested unidentified matter was most likely degradation products of proteins, carbohydrates, and hydrocarbons. While biodiesel may be narrowly defined by international specifications to contain only long-chain mono-alkyl esters, we suggest that the total fuel yield from SC reactions may contain non-FAEE components that are still valuable. In addition, exposing feedstocks rich in polyunsaturated FA to SC-EtOH may be a useful way to generate biodiesel that meets EN14103 specifications (i.e., C18:3 content < 15% of esters).

In general, the FAEE yield from both SC oil transesterification and FA esterification tends to increase with residence time until a critical point, after which it decreases. The competing phenomena of conversion and decomposition define this optimum time, which tends to occur earlier at higher temperatures [15]. Since isomerization and thermal decomposition were less pronounced at 275 °C, the longer

reaction time increased crude biodiesel and FAEE yields. At 325 °C, increasing the reaction time from 60 to 120 minutes decreased both crude biodiesel and FAEE yields at the lower ethanol loading but increased yields at the higher ethanol loading. These data highlight how the decomposition of unsaturated FAEE, evidenced in part by the complete absence of C18:3 FAEE in run 7, can influence fuel yields when considering esters only. Since data in the factorial experiment was collected at only two time points, little can be inferred about whether a maximum in yield occurred at intermediates times. However, in additional SC-IST/E experiments carried out for 60, 90, and 120 minutes at 290 °C, crude biodiesel and FAEE yields were highest at 90 min by 10-20%. Taken together, these data suggest that reaction time must be chosen wisely to optimize conversion and limit decomposition.

Finally, residual solids remaining after SC-IST/E were found to contain approximately 68-72% C, 5.6% H, and 3.1% N. We suspect these defatted solids can be used as a soil amendment, providing both fertilizer value and enhancing soil carbon content and microbial activity as has been demonstrated for other biochars [20].

We have demonstrated the feasibility of a two-step hydrolysis-solvolysis process to produce biodiesel from lipid-rich, wet algal biomass. This process obviates biomass drying, organic solvent extraction, and catalysts, while providing a mechanism for nutrient recycling. A cursory investigation of the influence of some key process variables led to crude biodiesel and FAEE yields as high as 100 and 66%, respectively, on the basis of lipids within the hydrolysis solids. Considering that about 80-90% of lipids in the original algal biomass were retained in the solids recovered after hydrolysis, the total process yield was somewhat lower. The optimal time and temperature for hydrolysis must appropriately balance the desire for increased lipid hydrolysis with the likelihood of reduced lipid retention and solids yields at more severe conditions. In addition, it is imperative to improve the ester yield from SC-IST/E, which may have been limited by incomplete (trans)esterification, decomposition/polymerization of unsaturated FA, hydrolysis of FAEE, or incomplete lipid extraction from the solid. More remains to be understood regarding how whole cells, hydrothermally processed algal biomass, and intracellular constituents influence SC-IST/E and potentially contribute to non-ester

components in the final fuel product. Additional research and process optimization are likely to improve yields and reduce process inputs (e.g., ethanol), thereby minimizing the overall environmental impact of algal biodiesel production. To be economically viable, biodiesel yields must be above 95% and preferably higher than current norms achieved with alkali-catalyzed processes (~97%) [21].

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CHAPTER 6

Kinetics of Noncatalytic Esterification

Having demonstrated that noncatalytic esterification of fatty acids with ethanol was feasible even at subcritical reaction conditions, we next focused on determining the reaction kinetics. This chapter will present the development of a kinetic model for noncatalytic esterification.

This thesis studied esterification kinetics in two levels: phenomenological level and mechanistic level. In the development of the phenomenological kinetics model, we seek to find the model that can be used to make a reasonable prediction of the conversion with a few input parameters. This knowledge will be useful for scaling up the reaction. We proposed two phenomenological kinetics models: simple power-law and fatty acid catalytic model. The former model was developed early in the project because of its simplicity and, at the time, only esterification data were available for parameter estimation. The latter model was developed based on the possibility of fatty acid acting as an acid catalyst during esterification. This fatty acid catalytic model was proposed after hydrolysis data (the reverse path of esterification) become available from the work of Shujauddin Changi in our laboratory. This allows accurate correlation of both forward and reverse rate. The second level of kinetics was developed to go beyond phenomenology into the underlying chemistry. The mechanism of the reaction was studied on how the reaction proceeds. This will point out the path of the reaction.

To study reaction kinetics, conditions were selected at five different temperatures such that all of the material loaded into the batch reactors would reside in a single fluid phase at reaction conditions, according to vapor-liquid equilibrium calculations done in

ASPEN. To ensure single-phase conditions, we used large filling fractions, f, at low temperatures and large ethanol to oleic acid ratios at higher temperatures. Figure 6.1 and Table 6.1 show the results and reaction conditions that were used. At subcritical temperatures, the reaction took place in a liquid phase. At supercritical temperatures (with respect to ethanol: T_c =243°C, P_c =6.3 MPa), a single vapor or supercritical fluid phase was present at reaction conditions. The experiments were used to determine the conversion achieved at several different batch holding times for each temperature. Long batch holding times (Table 6.1) were used here so that we could obtain results near equilibrium, where the reverse reaction would be important. The conversions were close to unity for most of the long-time experiments, owing to the large excess of ethanol (driving the esterification reaction nearly to completion). Esterification data with initial water present is also used to help capture the effect from the reverse path (Table 6.2). The conversion in this study is calculated using conversions of the reactant and yields of product and assuming that the small difference between their sum and 100% (perfect mass balance) can be apportioned equally between the two yields. Experimental uncertainties reported herein are the run-to-run variations, which we determined as the 95% confidence statistic calculated from replicated experiments. The repetition was done at longest time of 1440 minutes experiments and values are shown in Table 6.1.
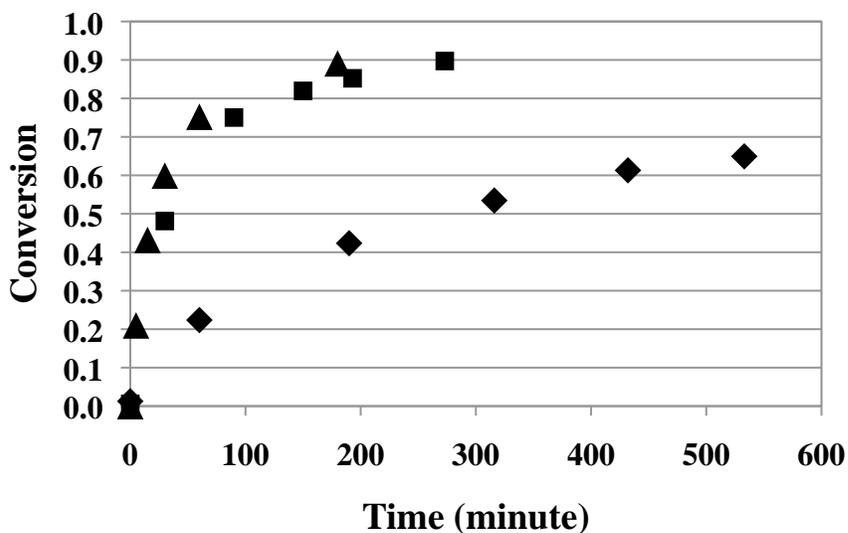
(a)
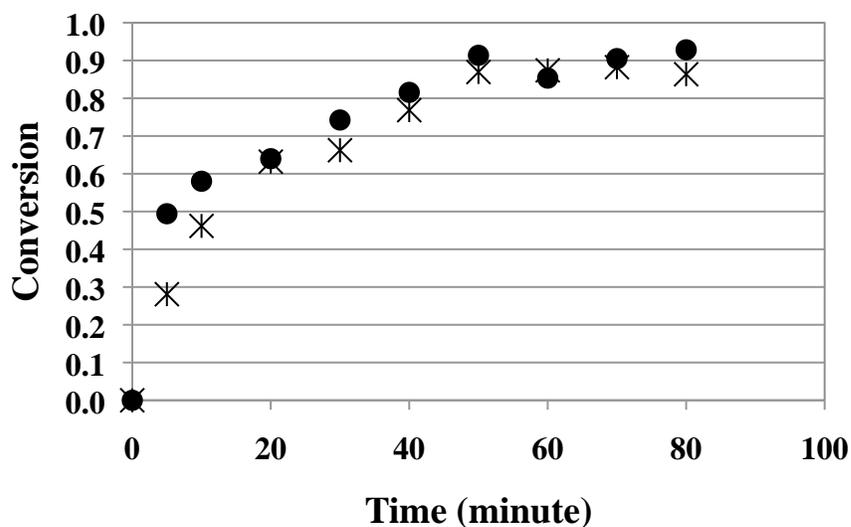
(b)

Figure 6.1: Esterification data at different temperature and time: (a) 150 ^{o}C ($\blacklozenge$), 200 ^{o}C ($\blacksquare$), 230 ^{o}C ($\blacktriangle$); (b) 270 ^{o}C ($*$) and 290 ^{o}C ($\bullet$)

Table 6.1: Conversion from esterification at 1440 minutes

T (°C)	C_{OA}^o(mol/L)	R_{EtOH}	X
150	1.11	7.5	0.83 ± 0.004
200	1.11	7.0	0.97 ± 0.003
230	0.63	9.8	0.99 ± 0.003
270	0.08	35.2	0.96 ± 0.025
290	0.08	35.2	0.98 ± 0.011

Table 6.2: Conversion from esterification with various initial water content at 250 ^{o}C 30 minutes, R_{EtOH} = 10

C_{OA}^o(mol/L)	R_W	X
0.51	10	0.46 ± 0.05
0.38	30	0.24 ± 0.04
0.31	50	0.20 ± 0.03

6.1 Simple Power Law Kinetics Model

We start by developing a power law kinetics model that incorporates the reverse of esterification into the model. First we assumed that the reaction is first order with respect to each reactant. We use the notation $OA + EtOH \leftrightarrow EO + W$, where OA is oleic acid, EtOH is ethanol, EO is ethyl oleate, and W is water. The design equation for a reaction in a constant-volume batch reactor with this rate equation is

$$-\frac{dC_{OA}}{dt} = k_1 C_{OA} C_{EtOH} - k_{-1} C_{EO} C_W \tag{6.1}$$

where C_i is the concentration of species i, and k_1 and k_{-1} are the forward and reverse rate constants respectively. The concentration of each species can be written in terms of the oleic acid conversion (X) for this isothermal system, $C_i = C_{OA}^{\circ} (R_i + \nu_i X)$, where C_{OA}° is initial concentration of oleic acid; R_i is the molar ratio of component i with respect to the limiting reactant, oleic acid; ν_i is stoichiometric coefficient. We get the differential equation as in equation (6.2).

$$\frac{dX}{dt} = k_1 C_{OA}^0 (1 - X)(R_{EtOH} - X) - k_{-1} C_{OA}^0 (R_{EO} + X)(R_W + X) \tag{6.2}$$

The calculated conversion was obtained by integrating the differential equation (6.2) using Euler's method. We use the Arrhenius equation, $k_i = 10^{a_i} \exp(-E_a/RT)$, and fit 4 parameters ($a_1$, a_{-1}, Ea_1, Ea_{-1}) using non-linear regression (Solver function in Microsoft Excel 2007). The objective function for the non-linear regression was the sum of the squared differences between the experimental and calculated conversions at the six temperatures investigated. The Arrhenius parameters obtained from the fit are shown in Table 6.3.

A parity plot (Figure 6.2) shows a good agreement between calculated conversion using the Arrhenius parameters in Table 6.3 and experimental conversion. If the model provided a perfect fit for all the data, all points would fall on the diagonal line. Clearly,

the model fit is not perfect, but it is very good. Moreover, the data are scattered on both sides of the diagonal indicating the absence of systematic errors.
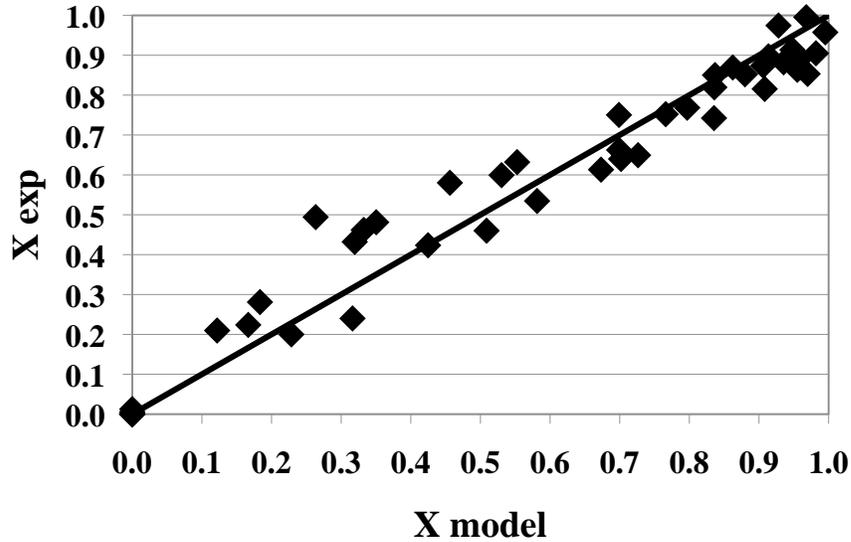
Figure 6.2: A parity plot for oleic acid conversion from esterification reaction (simple power-law kinetics model)

Table 6.3: Arrhenius parameters for esterification reaction

Reaction path	log A (L.mol^{-1}.min^{-1})	$E_{a,i}$ (kJ/mol)
k_1	3.06	52.3
k_{-1}	-0.94	18.7

To test the kinetics obtained from the model, we used it to predict the results from independent single-phase esterification experiments at 200 ^{o}C with R_{EtOH} = 10 and at 230 ^{o}C with R_{EtOH} = 7. These data were not used to determine any of the model parameters. The model gave a good prediction at these conditions (Figure 6.3).
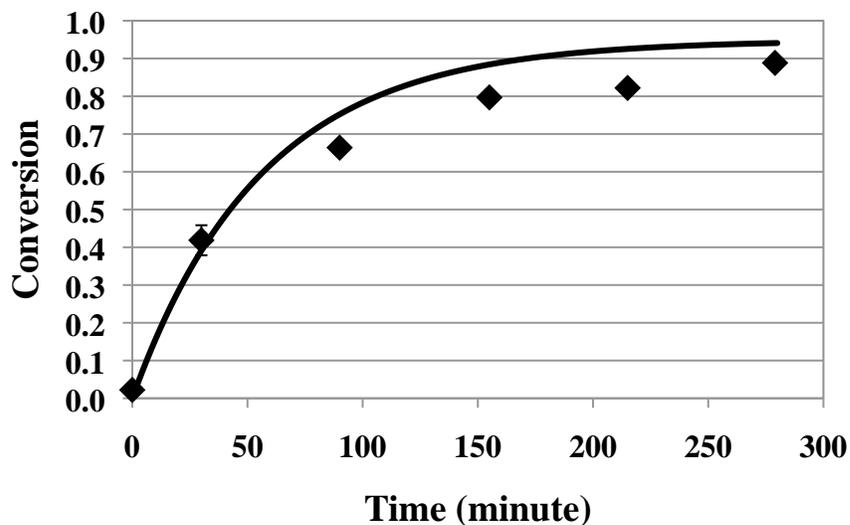
(a)
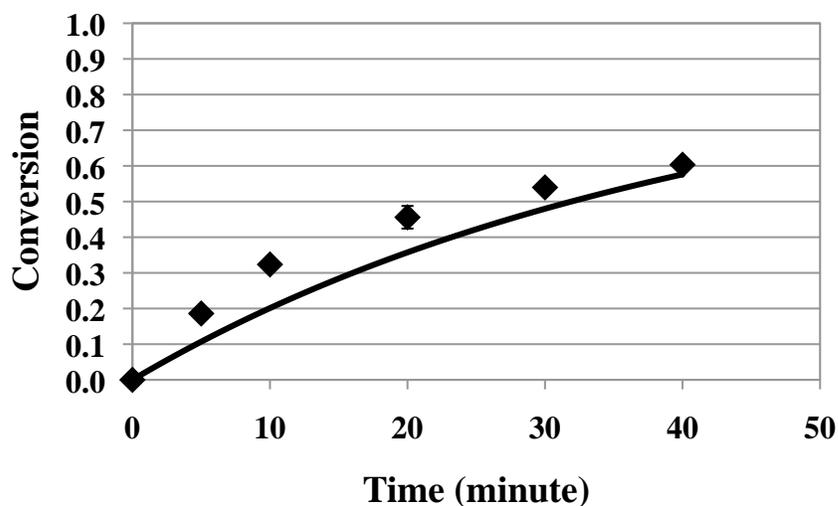
(b)

Figure 6.3: Calculated conversion from simple power-law kinetics model (smooth curve) compared to the experimental results (discrete points) at (a) 200 ^{o}C, C^{0}_{OA} = 0.90 mol/L, R_{EtOH} = 10 and (b) 230 ^{o}C, C^{0}_{OA} = 0.77 mol/L, R_{EtOH} = 7

We also used the simple power-law kinetics model to predict conversion reported in the literature [1] at conditions outside the parameter space used experimentally (oleic acid esterification at 300 ^{o}C, 15 MPa, R_{EtOH} = 42, and C^{0}_{OA} = 0.139 mol/L). The

comparison is shown in Figure 6.4 and the model gave acceptable prediction of the conversion except at long times. Note here that Warabi et al. [1] did not give the oleic acid initial concentration, but we calculated it from the given conditions in their study.
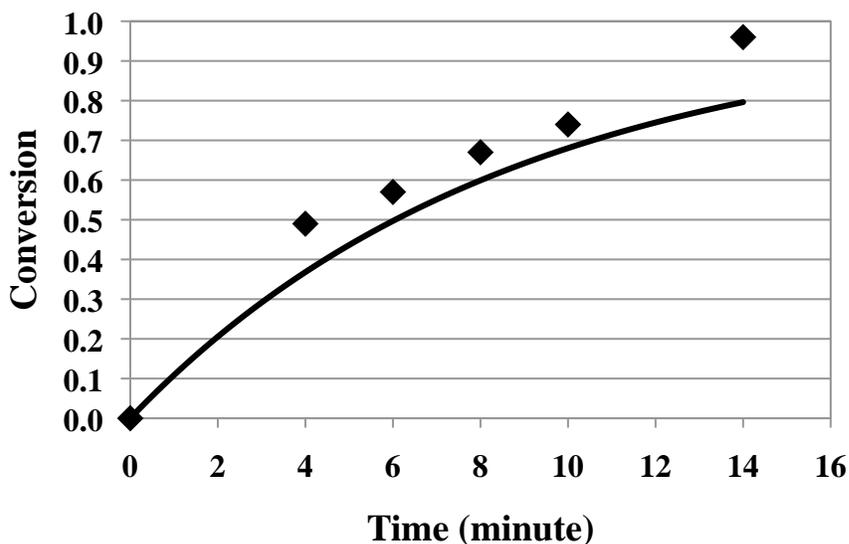
Figure 6.4: Calculated conversion from simple power-law kinetics model (smooth curve) compared to the experimental results (discrete points) from Warabi et al. [1] at 300 $^{\circ}$C, 15 MPa, $R_{EtOH} = 42$, $C^0_{OA} = 0.14$ mol/L

We also investigate the case with added product (water and FAEE) using this kinetics model. The model gave a reasonable predicted conversion for the case of small initial water content of $R_W = 1$ (Figure 6.5 a) but tended to over predict the conversion at higher initial water condition, $R_W = 9$ in Figure 6.5 b. Figure 6.6 shows under predicted conversion from the model compared to experimental data for conditions with added FAEE. The deviation of the predicted conversion from the experimental values might be caused by the lack of accuracy for the kinetics of the reverse path. In this simple power-law model, the experimental data used to calculate the kinetics parameter are based only on the forward direction (esterification). This might result in poor prediction at long time and for the case that product is initially present. In these conditions, the reverse reaction impacts the system. This shows that information from esterification experiments alone might not properly capture the effect of the reverse path resulting in the conversion deviation. If the reverse reaction experimental data is included, the model might give a

closer prediction. Another possibility is that the deviation might be from the assumption of power law kinetics with first order behavior for each component. A different kinetics model might help improve conversion prediction. We will introduce a different model (fatty acid catalytic model) in the next section.
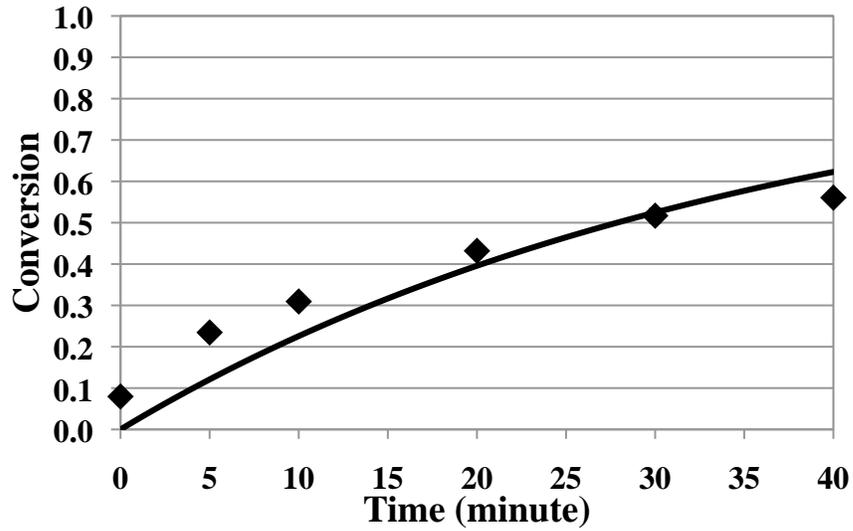
(a)
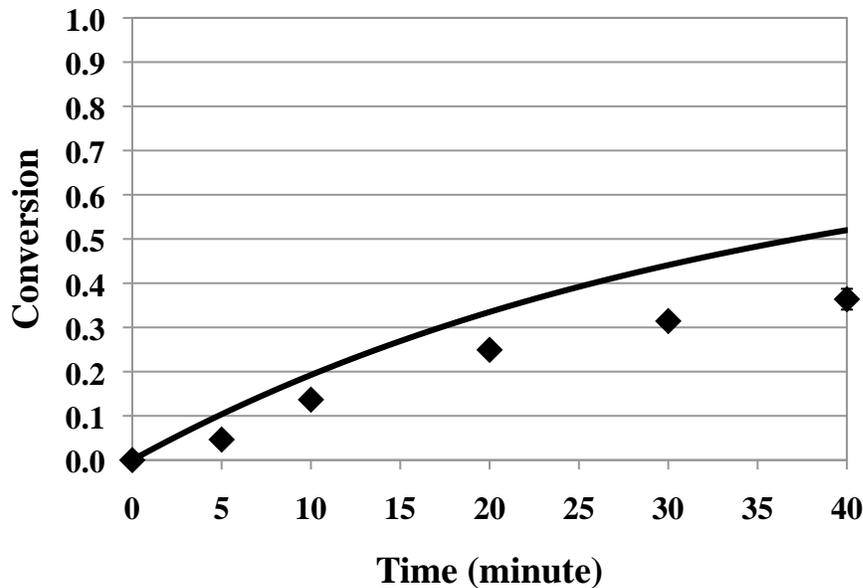
(b)

Figure 6.5: Calculated conversion from simple power-law kinetics model compared to experimental data in case of water initially present in the system at 230 ^{o}C (a) $R_{EtOH} =10$, $R_W =1$, $C^0_{OA} = 0.62$ mol/L ; and (b) $R_{EtOH} =10$, $R_W = 9$, $C^0_{OA} = 0.53$ mol/L
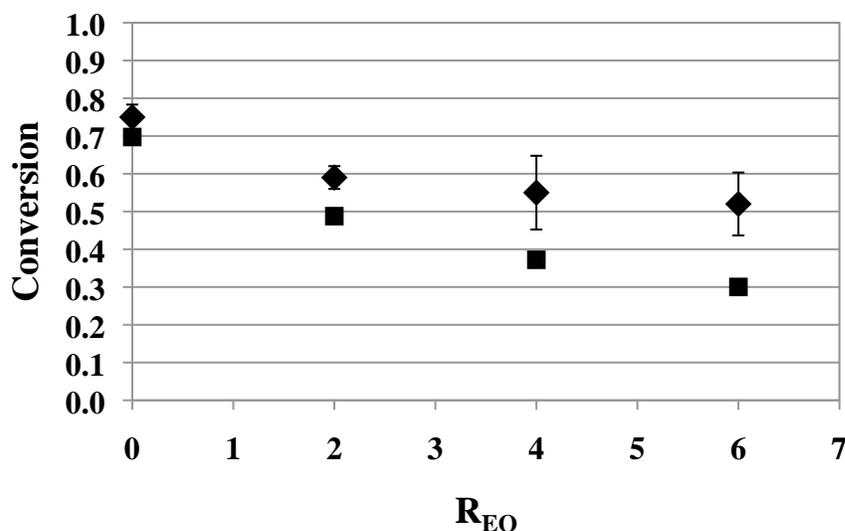
Figure 6.6: Calculated conversion from simple kinetics model compared to experimental data in case of ethyl oleate initially present in the system at 250 $^{\circ}$C, f = 0.55, R_{EtOH} = 10 with various R_{EO} (C_{OA} = 0.34 mol/L, 0.24 mol/L, 0.18 mol/L at R_{EO} = 2, 4, 6 respectively) at 30 minutes with experiment ($\blacklozenge$) and model ($\blacksquare$)

The value of the forward rate constant at 250 $^{\circ}$C we obtained is 0.0069 L.mol^{-1}.min^{-1} The one obtained from Alenezi et al. is 0.035 (mol/mol of FFA)$^{-1}$.min^{-1} [2]. The conditions used in their study are noncatalytic supercritical methanol in the temperature range of 250 $^{\circ}$C – 320 $^{\circ}$C with methanol to fatty acid molar ratio of 7. Alenezi et al. used the same kinetics model as our. Note here that Alenezi work was not published at the time when our project started.

Based on the values of the activation energies, we estimate the heat of reaction over the temperature range studied (150 $^{\circ}$C to 290 $^{\circ}$C) to be 33.6 kJ/mol. Heats of formation for ethyl oleate, water, oleic acid, and ethanol were taken from Vatanai *et al.* [6] to obtain the theoretical ΔH_r = 42.4 kJ/mol (at 25 $^{\circ}$C). Our experimental estimate for ΔH_r is in good agreement with this thermochemical estimate.

6.2 Fatty Acid Catalytic Model

As shown in the previous section, the simple power-law kinetics model can be used to predict the esterification conversion that occurs in one phase, but it still gave some deviation in the conversion prediction especially at long time and/or with initial

product present, which might be caused by the lack of accuracy in the kinetics for the reverse path (hydrolysis reaction) and/or the assumption of power law kinetics with first order for each component. To address this issue, the new kinetics model that combines information from both forward path (esterification) and reverse path (hydrolysis) was proposed and is discussed in this section. This study was conducted jointly with Shujauddin Changi.

A more advanced model that incorporates catalysis by fatty acid is introduced as there is evidence that esterification and hydrolysis can be catalyzed by fatty acids [3, 4]. The sigmoidal trends in conversion vs. time for hydrolysis [3, 4] suggest the kinetics should not follow first order behavior with each component. These reasons lead us to propose a fatty acid catalytic model for this esterification/ hydrolysis system.

In previous studies, the kinetics of fatty acid esterification and ester hydrolysis have been studied as disparate topics [2, 3, 5-7]. In reality their kinetics are coupled since these reactions are the reverse of one another. Therefore, this section presents a unified kinetics model for both the esterification and hydrolysis reactions. The results from oleic acid esterification in near- and supercritical ethanol (Figure 6.1 and Table 6.1) and ethyl oleate hydrolysis [4] in high temperature liquid water were used in this unified kinetics model. The phenomenological model comprises the two reversible reactions shown below.

$$OA + EtOH \xleftrightarrow{k_1} EO + W \qquad\qquad (6.3)$$

$$2OA + EtOH \xleftrightarrow{k_2} EO + W + OA \qquad\qquad (6.4)$$
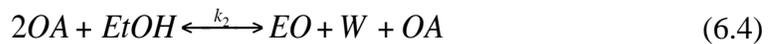
Note here that Liu et al. [8] proposed two similar catalytic routes but they neglected the reverse paths and used only esterification data from their study of acetic acid with methanol at $60^{o}C$, catalyzed by added sulfuric acid.

The first reaction is a reversible esterification of oleic acid to produce ethyl oleate. In the second step, the oleic acid itself can catalyze the reaction to give another mole of the ethyl oleate and water and give back oleic acid. We assumed that the reaction orders are equal to the stoichiometric coefficients, v_i. Thus, rate equations for the consumption of oleic acid (for esterification experiments) and the consumption of ester (for hydrolysis experiments) can be written. For example, the rate equation for oleic acid esterification is

$$-r_{OA} = k_1 C_{EO} C_W - k_{-1} C_{OA} C_{EtOH} + k_2 C_{EO} C_W C_{OA} - k_{-2} C_{OA}^2 C_{EtOH} \tag{6.5}$$

where C_i is the concentration of component i.

Note here that the second step (equation (6.4)) of our proposed model is similar to the one proposed by Minami and Saka [3] for esterification reaction. However, the addition of the first step here is necessary if we want to model both esterification and hydrolysis simultaneously. The reason for this is that hydrolysis cannot occur with only the second step since there is no oleic acid present initially (a reverse path of equation (6.4)).

We next combined the rate equations with the design equation for a constant volume batch reactor. Substituting the expressions for the concentration of each component in terms of the conversion of the limiting reactant, $C_i = C_i^o (R_i + v_i X)$, into equation (6.5) leads to a differential equation describing how the oleic acid conversion changes with batch holding time.

$$\frac{dX}{dt} = k_1 C_{OA}^0 (R_{EO} + X)(R_W + X) - k_{-1} C_{OA}^0 (1-X)(R_{EtOH} - X) + k_2 C_{OA}^{0\,2}(1-X)(R_{EO} + X)(R_W + X) - k_{-2} C_{OA}^{0\,2}(1-X)^2(R_{EtOH} - X)$$

$$\tag{6.6}$$

We then again assume that the rate constants follow Arrhenius form (equation 6.7), where 10^{ai} and E_i are the respective pre-exponential factor and activation energy.

$$k_i = 10^{a_i} \exp(\frac{-E_i}{RT}), \qquad i = 1, 2, -1, -2 \tag{6.7}$$

The ratios of forward and reverse rate constants for the first (uncatalyzed) and second (catalyzed) reactions should be the same, because they share a common equilibrium constant. This thermodynamic constraint leads to equations (6.8) and (6.9). This reduces the total number of parameters in the model to six.

$$a_{-1} = a_1 - a_2 + a_{-2} \qquad (6.8)$$

$$E_{-1} = E_1 - E_2 + E_{-2} \qquad (6.9)$$

We numerically integrated the differential equations using Euler's method and simultaneously performed parameter estimation to get estimates for a_1, a_2, a_{-2}, E_1, E_2, and E_{-2}. These calculations were performed using Microsoft Excel 2007 and its Solver function. The objective function to be minimized was the sum of the squared differences between the experimental and calculated conversions. We combined and used together esterification data (Figure 6.1 and Table 6.1) and hydrolysis data [4] to estimate numerical values for the parameters in the model. To the best of our knowledge, this is the first study to treat fatty acid esterification and ester hydrolysis data together to develop a unified model for this reaction system. Table 6.4 displays the parameter estimates.

Table 6.4: Arrhenius parameters for esterification reaction: FA catalytic kinetics model (min, L, mol)

Reaction i	log A	E_i (kJ / mol)
1	8.6	123.6
2	7.5	87.9
-1	4.3	86.7
-2	3.1	51.1

The parity plot in figure 6.7 demonstrates the ability of the model with the parameters in Table 6.4 to correlate the experimental results for esterification. The plot shows a good fit of calculated conversion and experimental conversion.
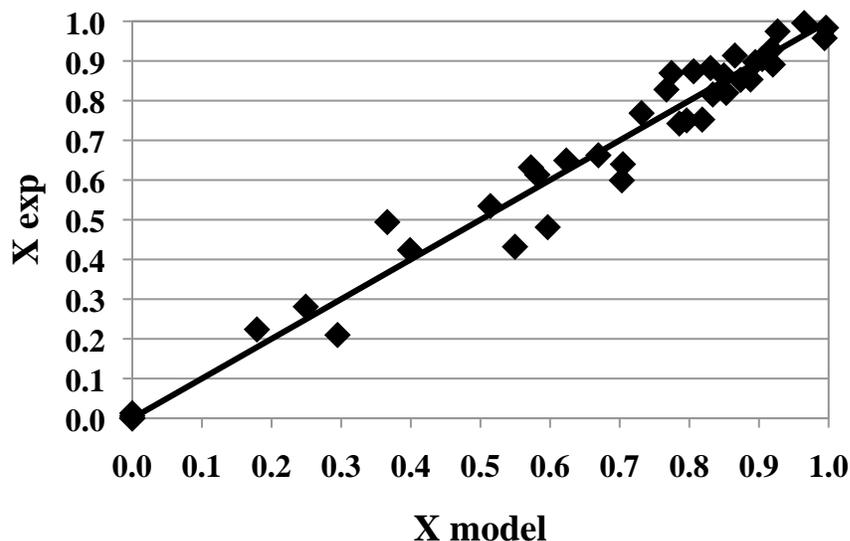
Figure 6.7: Parity plot for oleic acid conversion from esterification (FA catalytic model)

To verify that the parameters in Table 6.4 are reasonable on a thermochemical basis, we calculated the heat of reaction for oleic acid esterification using the estimated activation energies and compared it to the value obtained using heats of formation of the reactants and products. The heat of reaction is simply the difference between the activation energies for the forward and reverse reaction. The activation energies in Table 6.4 lead to $\Delta H_r = 35.7$ kJ/mol. Heats of formation for ethyl oleate, water, oleic acid, and ethanol were taken from Vatanai et al. [9] to obtain the theoretical $\Delta H_r = 42.4$ kJ/mol (at 298 K). Our experimental estimate for ΔH_r is in good agreement with this thermochemical estimate.

To test the predictive ability of the model, experiments done both within and outside the parameter space used to determine the model parameters were used. Thus, they provide an opportunity to assess the predictive ability of the model as it interpolates within the parameter space and also as it extrapolates beyond.

First, we tested the ability of the model to predict the outcome of experiments done within the parameter space used to determine the model parameters. The results for esterification at 200 $^{\circ}$C, with $R_{EtOH} = 10$ and 230 $^{\circ}$C with $R_{EtOH} = 7$ show a reasonable prediction (Figure 6.8).
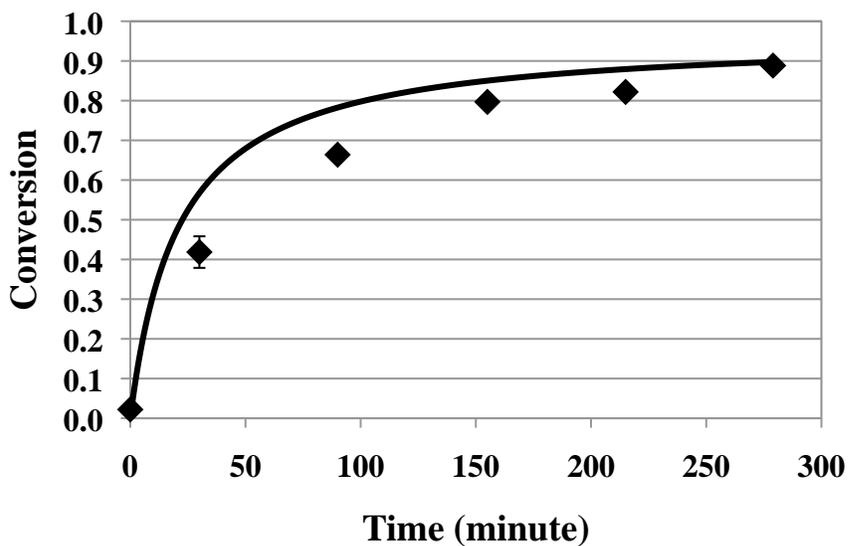
(a)
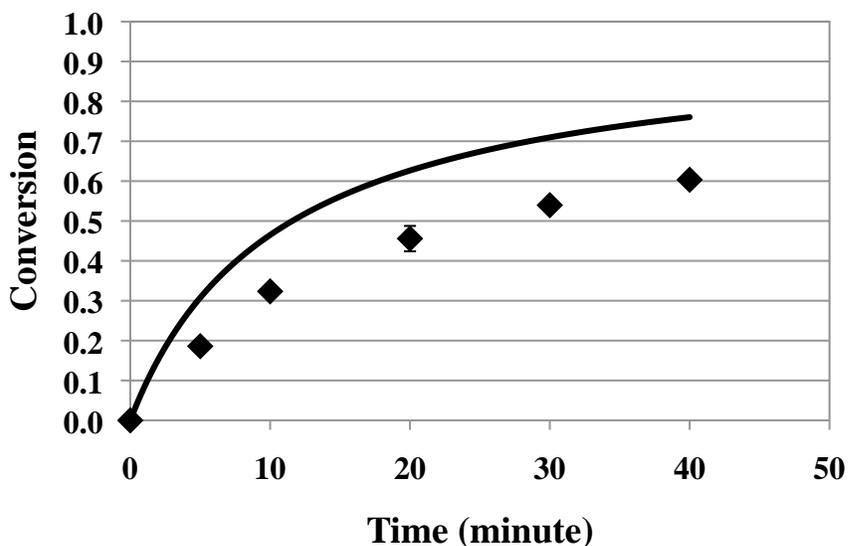
(b)

Figure 6.8: Calculated conversion from FA catalytic kinetics model (smooth curve) compared to the experimental results (discrete points) at (a) 200 $^{\circ}$C, $C^0_{OA} = 0.90$ mol/L, $R_{EtOH} = 10$ and (b) 230 $^{\circ}$C, $C^0_{OA} = 0.77$ mol/L, $R_{EtOH} = 7$

Next, we use the model to predict results in the literature. Warabi et al. [1] report yields of ethyl oleate from oleic acid esterification at 300 °C, 15 MPa, and $R_{EtOH} = 42$. Figure 6.9 compares their experimental results at different batch holding times with the yields predicted by the FA catalytic kinetics model. Even though the experimental conditions used by Warabi et al. [1] are not within our parameter space, the model still gives accurate prediction of the product yields, except at the longest time.
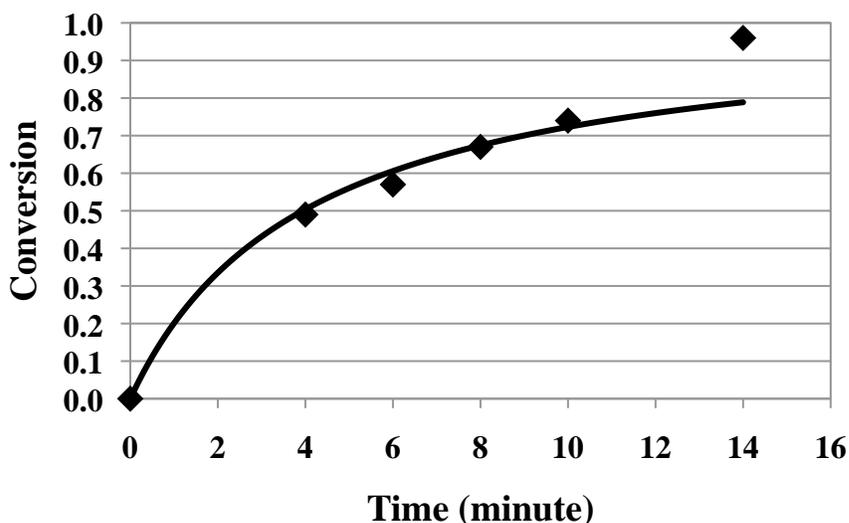
Figure 6.9: Calculated conversion from FA catalytic kinetics model (smooth curve) compared to the experimental results (discrete points) from Warabi et al. [1] at 300 °C, 15 MPa, $R_{EtOH} = 42$, $C^0_{OA} = 0.14$ mol/L

As a final test of the predictive ability of the model, we used the model to predict experimental conversions for cases where one of the reaction products was added to the reactor. No data from experiments with added product water or ester were used to determine the model parameters. Thus, the comparisons test the predictive ability of the model outside its parameter space for that case. For esterification with varying initial water (Figure 6.10) and ester (Figure 6.11) amounts, the model over predicted the experimental data but still gave the proper trends (i.e. adding water and ester reduces the conversion for esterification). The conversion prediction from this FA catalytic model gave a higher deviation from experimental data compared to the prediction from the simple power-law kinetics model. This might be because the FA catalytic model tried to

describe a larger set of data to fit both esterification and hydrolysis data. Another possible reason for the model's lack of quantitative predictive ability in these cases when extrapolated is that the model is phenomenological and is not based on the elementary steps that govern the reaction chemistry. For example, one could build a detailed mechanistic model that includes charged intermediates, dissociation of oleic acid in high temperature water, and catalysis by H^+. Such a model will be presented in section 6.3.
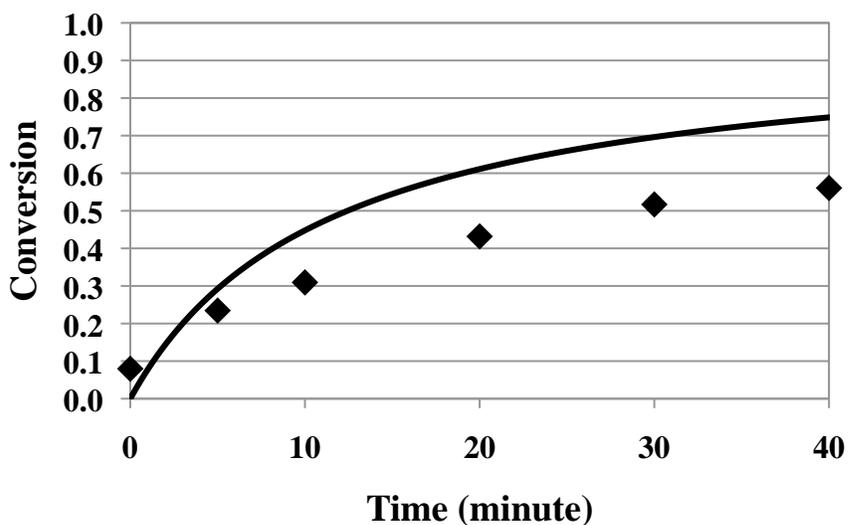
(a)
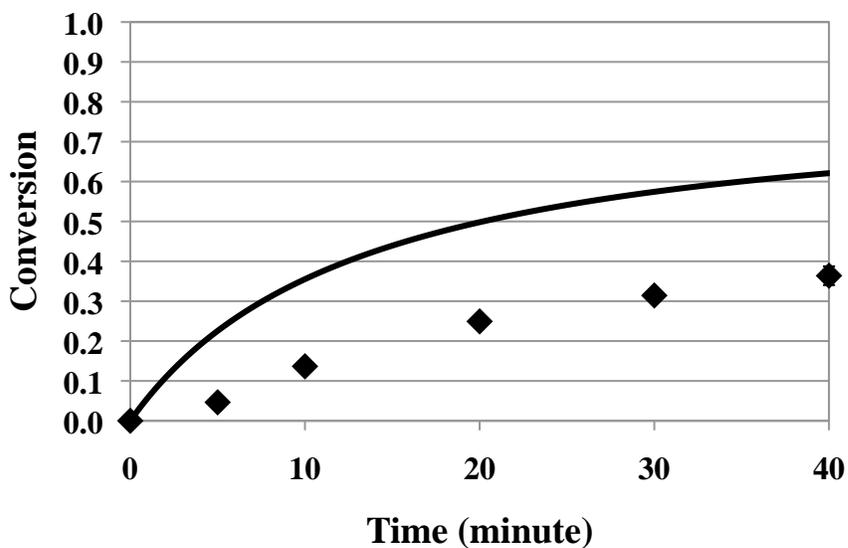
(b)

Figure 6.10: Calculated conversion from FA catalytic kinetics model compared to experimental data in case of water initially present in the system at 230 $^\circ$C (a) $R_{EtOH} = 10$, $R_W = 1$, $C^0_{OA} = 0.62$ mol/L ; and (b) $R_{EtOH} = 10$, $R_W = 9$, $C^0_{OA} = 0.53$ mol/L
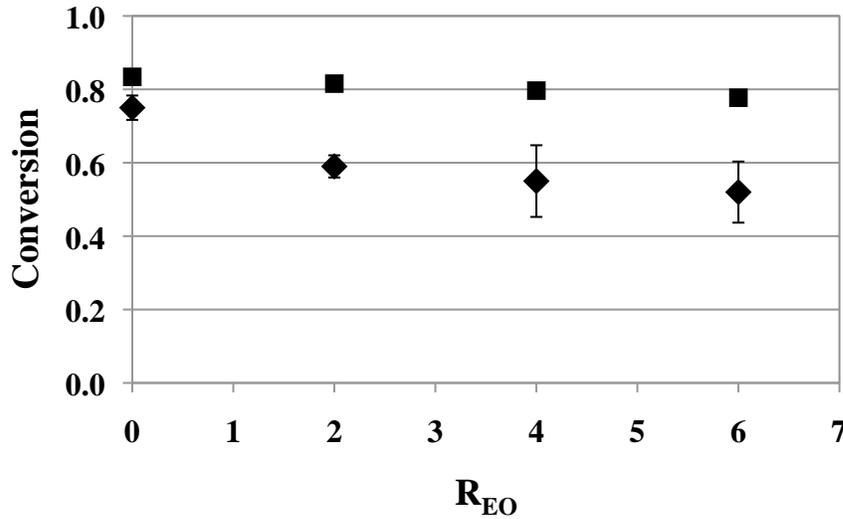
Figure 6.11: Calculated conversion from FA catalytic kinetics model compared to experimental data in case of ethyl oleate initially present in the system at 250 $^\circ$C, f = 0.55, $R_{EtOH} = 10$ with various R_{EO} ($C_{OA} = 0.34$ mol/L, 0.24 mol/L, 0.18 mol/L at $R_{EO} = 2$, 4, 6 respectively) at 30 minutes with experiment ($\blacklozenge$) and model ($\blacksquare$)

To sum up this section on model validation, we have demonstrated that the model makes quantitatively accurate predictions within, and at times outside, the parameter space for conditions starting with only oleic acid and ethanol. It also accurately predicts trends when extrapolated outside the original parameter space for cases that have products (water or ester) initially present.

To determine the sensitivity of the calculated conversion to small changes in the estimated Arrhenius parameters, we calculated normalized sensitivity coefficients, NSC, as shown in equation (6.10), where S is sensitivity, which is the change in conversion caused by a small change in P; P represents one of the parameters.

$$NSC = \frac{S}{(X_{Cal}/P)} \qquad S = \frac{X(P + \Delta P) - X(P)}{\Delta P} \qquad (6.10)$$

These coefficients indicate the relative change in conversion that would result from some small change in a parameter. A normalized sensitivity coefficient of unity, for example, indicates that a small relative change (say 1%) in a parameter leads to an identical relative change in conversion. We used Berkeley Madonna 8.3.18 to compute the sensitivity coefficients, which are functions of the initial concentrations, reaction time, and temperature. We conducted this sensitivity analysis at the experimental conditions used to test the predictive capability of the model, as discussed above. Table 6.5 summarizes the sensitivity analysis results.

Table 6.5: Normalized sensitivity coefficients for oleic acid esterification and ethyl oleate hydrolysis on calculated conversion by FA catalytic model

Run	Rxn	t (min)	T (^{o}C)	X	R_w	R_{EtOH}	R_{EO}	Normalized Sensitivity Coefficient					
								a_2	E_2	a_{-1}	E_{-1}	a_{-2}	E_{-2}
1	Est.	10	270	0.40	0	35	0	5.1	-5.7	0.0	0.0	0.0	0.0
2	Hyd.	60	240	0.18	569	0	0	0.0	0.0	7.7	-16.5	7.0	-11.1
3	Hyd.	60	300	0.96	510	0	0	-0.3	0.3	0.3	-0.6	0.9	-1.3
4	Est.	30	250	0.62	0	10	2	6.7	-7.9	0.0	0.0	-0.2	0.2
5	Est.	30	250	0.70	10	10	0	7.5	-8.9	0.0	0.1	-1.3	2.1
6	Hyd.	30	300	0.45	450	25	0	-2.9	3.1	3.9	-7.6	5.5	-7.8

Run 1 shows that for esterification at moderate conversion, the model is sensitive to only a_2 and E_2, the kinetics for the esterification reaction. For hydrolysis, Run 2 and 3, the model is highly sensitive to a_{-1}, E_{-1}, a_{-2}, and E_{-2}, the reverse rate constants for both reactions 1 and 2, but not sensitive to a_2 and E_2. Collectively, runs 1-3 show that to estimate reliable values for all six of the model parameters one needs to use data from both hydrolysis and esterification reactions, as we have done.

Runs 4 and 5 list the normalized sensitivity coefficients for the cases of added ester and water, respectively, for esterification. The calculated conversion is sensitive not only to a_2 and E_2 but it is also modestly sensitive to a_{-2} and E_{-2}. This result implies that the hydrolysis path is also important when ester or water is present during esterification under those conditions with more pronounce effect for condition with added ester than the one with added water. The similar results for hydrolysis with added ethanol, Run 6

show that conversion in this case not only sensitive to reverse rate constant (a_{-1}, E_{-1}, a_{-2}, and E_{-2}) but also to forward rate constant (a_2 and E_2).

To summarize the sensitivity of the calculated conversions to the model parameters under different conditions, a_2 and E_2 are most important for esterification, with a_{-1}, E_{-1}, a_{-2}, and E_{-2} being least important. The latter become important only in the presence of added water and/or ester. Similarly for hydrolysis, a_{-1}, E_{-1}, a_{-2} and E_{-2} are most important. Thus, one needs a combination of both the esterification and hydrolysis data to get accurate estimates for all of the kinetics parameters.

The FA catalytic model can be used to predict an acceptable conversion for a single phase system with initial reactant being oleic acid and ethanol. We next sought to determine how well this FA catalytic kinetics model could be used to model results from esterification reactions conducted with two phases. To calculate the conversion for conditions that had two phases present, we use two approaches. In the first, we neglect the fact that two phases exist and treat the system as single pseudo-homogeneous phase when performing the kinetics model calculations. Of course, since this approach ignores the fact that two phases actually exist in the reactor and that the rates are likely different in the separate phases, the model was not expected to be accurate in this case.

Figure 6.12 (dash line) shows the results of the model calculations along with the experimental data for two-phase esterification experiments at 250 °C. The model considerably under predicted the experimental conversions for the low-density experiment, f = 0.04 (case a). At this condition, most of the material added to the reactor was in the vapor phase (87% by mole). But most of the limiting reactant, oleic acid is in the liquid phase at the start of the reaction. Also in this Run, a lower than stoichometric ratio of ethanol to oleic acid ratio in liquid phase was observed ($R_{EtOH,\ Liq}$ = 0.4). The conversion in the vapor phase was perhaps very rapid in the experiments because of the large excess of ethanol present in that phase. As the oleic acid in the vapor phase becomes depleted, more oleic acid from the liquid phase could be transferred into the vapor phase to maintain the vapor-liquid equilibrium. Thus, the fast-reacting phase could be continually resupplied by fast mass transfer from the slowly reacting phase. Also ethanol in the vapor phase can transfer to the liquid phase. Ethanol , the limiting reactant

in the liquid phase, could become more abundant and drive more reaction in that phase. This interplay of mass transfer, vapor-liquid equilibrium, and reaction kinetics could account for the high experimental conversions observed in this low-density, two-phase reaction system.

At a higher density ($f = 0.26$), the model did a better job of predicting the experimental conversions when treating the system as one pseudo-homogeneous phase (Figure 6.12 b). At this condition, the vapor and liquid phases enjoyed nearly an equimolar split at $t = 0$ (49% mole in liquid phase), and both phases contained excess amounts of ethanol ($R_{EtOH, Liq} = 20$, $R_{EtOH, vap} = 109$). This better level of agreement is probably due to the liquid and vapor phases being similar in composition and perhaps concentration. Both phases had a large excess of ethanol present. Perhaps the model predictions were more accurate here because the actual compositions and concentrations in the two phases did not differ dramatically from those obtained by assuming a single phase. However, the model predictions still deviated from the experimental data in this Run.

This comparison of model predictions assuming a single phase exists in the reactor with experimental results for two-phase esterification shows that the prediction was poor at low densities where one of the phases has a substoichiometric amount of ethanol. Clearly, a rigorous and more accurate treatment of the physics and chemistry governing these two-phase constant-volume batch reactions would require the use of a reliable thermodynamics model to handle vapor-liquid equilibrium, a mass transfer model to handle interphase transport of reactants and products, and a reaction engineering model to monitor the reaction progress in both phases. Taken collectively, these elements would allow for the computation of the compositions and amounts of the co-existing phases at each time step throughout the reaction.
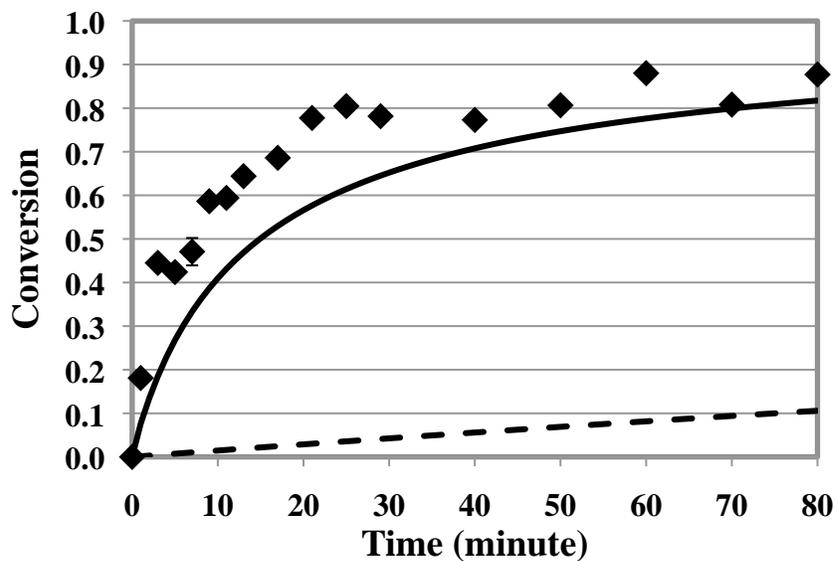
(a)
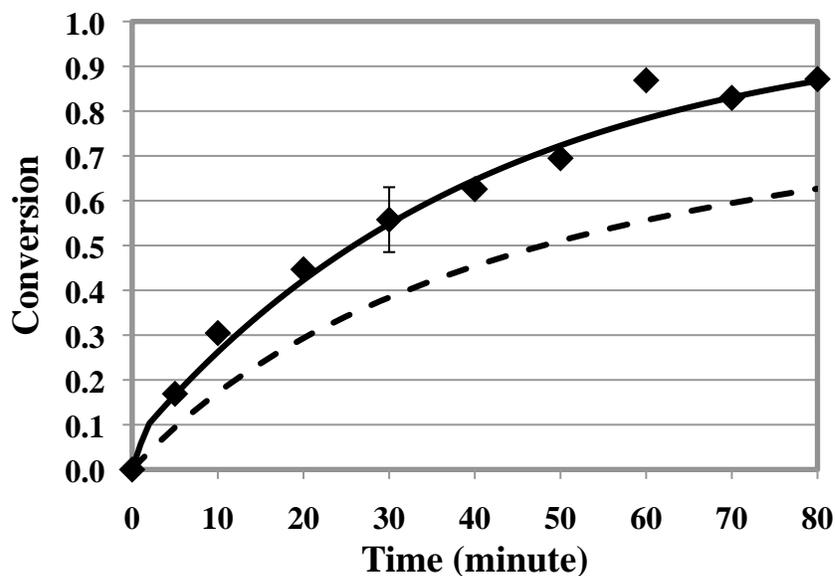
(b)

Figure 6.12: Comparison of conversions predicted by kinetics model (curve) and measured by experiment (discrete points) at 250 ^{o}C for two-phase esterification systems by treated system as single pseudo homogeneous phase (dash line) and multi-phase (solid line) (a) C^0_{OA} = 0.05 mol/L, f = 0.04, R_{EtOH} = 10, P = 2 MPa; and (b) C^0_{OA} = 0.11 mol/L, f = 0.26, R_{EtOH} = 35, P = 6 MPa

Though a rigorous model would account simultaneously for reaction, mass transfer between phases, and vapor-liquid equilibrium (VLE), we opted for a simpler model that accounted explicitly only for reaction and VLE. Rather than treating mass transfer rigorously as a rate-based process, we assumed that transport between the phases would be faster than the reactions taking place within each phase. We accounted for VLE and reaction by using ASPEN (FLASH2 block) to calculate first the compositions and amounts of the co-existing vapor and liquid phases. This information was then used in the fatty acid catalyzed kinetics model to calculate the reaction progress in each phase. We allowed the reaction to proceed for one minute. The results from the kinetics model were then used as input to ASPEN, which updated the compositions and amounts of the vapor and liquid phases that now existed at equilibrium. This new information was then used in the kinetics model to allow the reaction to proceed for another one minute. This procedure (flash, react, mix) was repeated after each minute of reaction time until the desired final reaction time was reached. The results in Figure 6.12 (solid line) show that the predicted conversion got closer to the experimental data compared to when we treated the system as a single pseudo-homogeneous phase.

We further tested if a smaller reaction time step would affect the prediction. The time step was reduced from 1 minute to 0.5 minute. However, the change showed no significant difference in the predicted conversions. Hence, one minute time step appears to be adequate.

We also observed that the molar density of the mixture changed after the reaction step, because the composition changed while pressure was held constant in ASPEN. In reality, the molar density should stay the same since the reaction is equi-molar. Therefore, we adjusted the pressure (as trial and error in ASPEN) to keep the molar density constant. Then we used the new pressure to calculate compositions in each phase by Flash 2. The results did not show any significant difference between the case of pressure change and constant pressure in the calculation.

To summarize this work on predicting results from two-phase reaction system, the use of a small reaction time step in each phase allows the calculation to become closer to

the actual system and enables the model to better predict the conversion with two-phase conditions.

6.3 Mechanistic Kinetics Model

A detailed mechanism of the reactions (esterification-hydrolysis) will help us understand reactions at the molecular level. This knowledge can help clarify how the reaction is catalyzed and produces the desired product. With this in mind, we are motivated to elucidate the mechanism for combined esterification of the fatty acid and hydrolysis of fatty acid ester reaction without added catalyst. One can then use this mechanism to develop a detailed chemical kinetics model that can predict conversions for a multi-component system of fatty acid, alcohol, water, and ester, at a given condition. Such a model is useful because we can adjust the reaction condition in the system to help accelerate the reaction in the desired direction, which can be useful for industrial process development. This study was also conducted jointly with Shujauddin Changi.

According to the mechanistic classification, acid-catalyzed esterification is usually $A_{AC}2$ [10]. $A_{AC}2$ refers to acid catalyzed (A), acyl cleavage (AC) and rate limiting step is bimolecular (2). Esterification is reversible and symmetrical with hydrolysis. Therefore, the mechanisms for both esterification and hydrolysis are the same. There is evidence that $A_{AC}2$ describes esterification data in the low temperature range [11]. Therefore, we will use $A_{AC}2$ for our system. In the reverse $A_{AC}2$ mechanism, which we suspect to dominate in conditions with no added catalyst, the first step is the protonation of the fatty acid by H^+ to generate a carbocation. The carbocation is subsequently attacked by an alcohol molecule and, after a series of steps, forms the corresponding ester and water.

Liu et al. [8] have proposed a modified mechanism for sulfuric acid catalyzed esterification of acetic acid with methanol at 60 °C, wherein the alcohol gets protonated by the sulfuric acid. The protonated alcohol then protonates the acetic acid. The protonated acetic acid attacks another alcohol molecule, in a rate–limiting step to generate ester and water. However, such a mechanism would be favorable if there is a strong acid catalyst present initially, to protonate the alcohol. In our case we do not have

any strong acid to catalyze esterification. Hence, such a mechanism would not be very likely for our system.

We proposed a mechanism with esterification catalyzed by [H+] from dissociation of oleic acid. For the hydrolysis reaction, apart from the [H+] catalyzed route (Krammer et al. [12]), we also include the possibility of general acid catalysis by water molecules, as proposed by Comisar et al. [13]. The ability of water molecules to catalyze the hydrolysis in HTW would most likely be due to the higher thermal energy available in HTW. Additionally, we proposed that the fatty acid (hydrolysis product) could be a general acid catalyst for the reaction by reacting with the ester. Oleic acid would be able to catalyze the reaction with ester due to its acidity at elevated temperatures. Fitting the proposed mechanistic model with our experimental data will test the hypothesis.

Figure 6.13 shows all the steps of our proposed mechanism. The forward reactions in this scheme pertain to esterification, while the reverse reactions refer to hydrolysis.

$$C_{17}H_{33}\overset{O}{\overset{\|}{C}}\text{-OH} \quad \underset{}{\overset{K_a}{\rightleftharpoons}} \quad C_{17}H_{33}COO^- + H^+ \qquad \text{Step 0}$$

(OA)   (O⁻)

$$C_{17}H_{33}\overset{O}{\overset{\|}{C}}\text{-OH} + H^+ \quad \underset{k_{10}}{\overset{k_{01}}{\rightleftharpoons}} \quad C_{17}H_{33}\overset{OH}{\underset{+}{-C-OH}} \qquad \text{Step 1}$$

(X₁)

$$C_{17}H_{33}\overset{OH}{\underset{+}{-C-OH}} + CH_3CH_2OH \quad \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \quad C_{17}H_{33}\overset{OH}{\underset{OH}{-C}}\overset{+}{-O}-CH_2CH_3 \qquad \text{Step 2}$$

(EtOH)   (X₂)

$$C_{17}H_{33}\overset{OH}{\underset{OH}{-C}}\overset{+}{-O}-CH_2CH_3 \quad \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \quad C_{17}H_{33}\overset{OH}{\underset{+OH_2}{-C}}-O-CH_2CH_3 \qquad \text{Step 3}$$

(X₃)

104
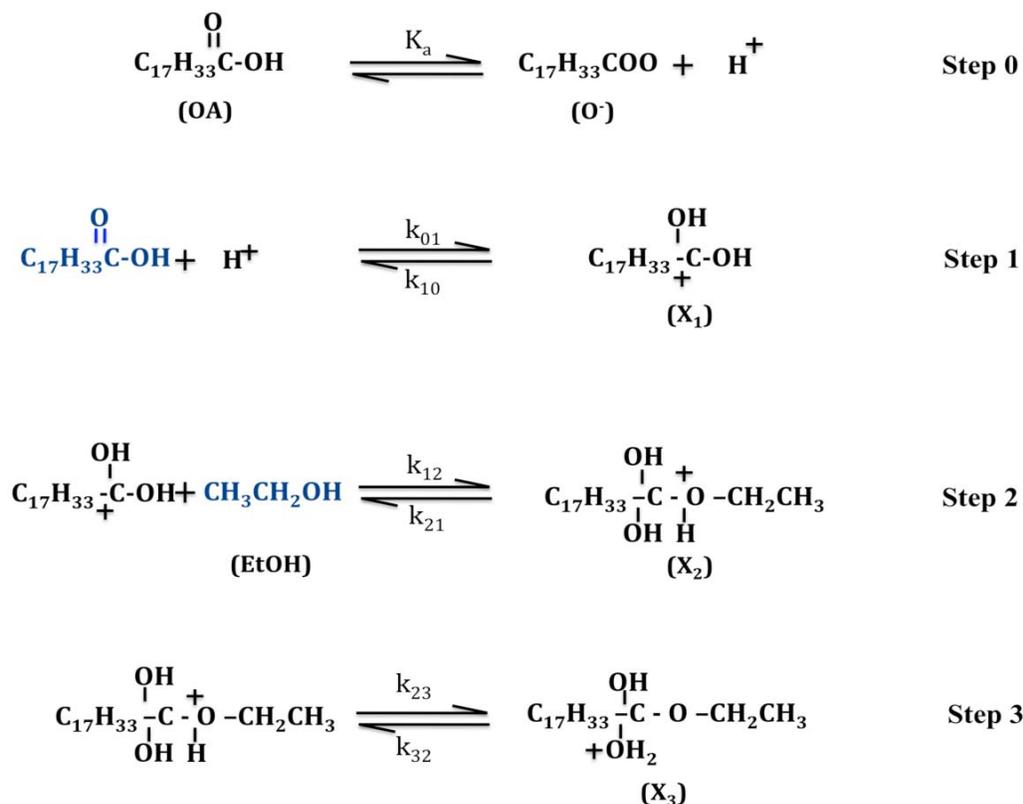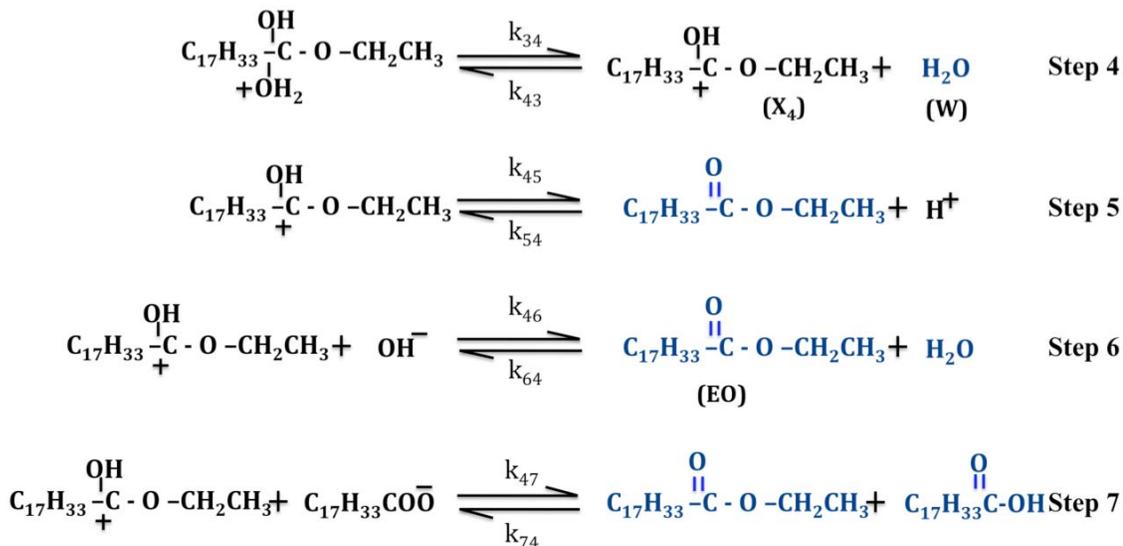
Figure 6.13: The mechanism of esterification of oleic acid (C18:1) to ethyl oleate

In step 0, oleic acid dissociates to give $[H^+]$ and $[C_{17}H_{33}COO^-]$. The dissociation constant (Ka) of the acid at the reaction conditions governs the formation of H^+ ions. The first step for esterification is the protonation of oleic acid (OA) to give a carbocation intermediate (X_1), which then is attacked by ethanol (EtOH) to form another intermediate (X_2) in step 2. In step 3, this intermediate X_2 undergoes rearrangement to give another intermediate X_4, which in step 4 loses a molecule of water to form a carbocation (X_4). Intermediate X_4 can subsequently form the product ester (EO) and water through parallel steps 5, 6, and 7: in step 5, X_4 forms ester and regenerates $[H^+]$; in step 6, X_4 reacts with $[OH^-]$ to produce ethyl oleate and water; and in step 7, it reacts with $[C_{17}H_{33}COO^-]$ to produce ethyl oleate and oleic acid.

The ester hydrolysis reaction takes place in the reverse direction, and parallel steps 5-7 catalyze it. We consider the possibility that the hydrolysis can be catalyzed by H+ obtained from dissociation of fatty acid and water (step 5), water (step 6), and oleic acid (step 7). The reaction mechanism can be written in a simpler manner as:

$$
\begin{array}{ccccccccccccc}
& 0 & & \overset{\textbf{H}^+}{} & 1 & & \textbf{EtOH} & 2 & & 3 & & \overset{7}{\textbf{EO}} & 4 & & \overset{\textbf{OH}^-}{} & 6 \\
& \textbf{OA} & \rightleftarrows & & \textbf{X} & \rightleftarrows & & \textbf{X} & \rightleftarrows & \textbf{X} & \rightleftarrows & \textbf{X} & \rightleftarrows & \textbf{EO} \\
\end{array}
$$

(reaction scheme: OA $\overset{H^+}{\rightleftarrows}$ X$_1$ $\overset{EtOH}{\rightleftarrows}$ X$_2$ $\rightleftarrows$ X$_3$ $\rightleftarrows$ X$_4$ $\overset{OH^-}{\rightleftarrows}$ EO$_6$; X$_4$ with O$^-$/OA to EO$_7$ above, W below; X$_4$ with H$^+$ to EO$_5$ below, W)

This reaction scheme involves a network of both sequential and parallel steps as part of a multistep pathway. The rate of formation of ester (R_{EO}) or rate of consumption of fatty acid (R_{OA}) can be written analytically using the streamlined method outlined by Helffrich [14], as written below. The only assumptions made are that each step is an elementary reaction and each intermediate is present in trace levels and in a quasi-stationary state. No assumptions need to be made regarding the identity or existence of any rate determining steps. Moreover, all steps are taken to be reversible.

$$
-R_{OA} = \frac{(k_{45} + k_{46}C_{OH^-} + k_{47}C_{O^-})k_{01}C_{H^+}C_{EtOH}C_{OA} - k_b C_W(k_{54}C_{H^+}C_{EO} + k_{64}C_W C_{EO} + k_{74}C_{OA}C_{EO})}{k_b C_W + (k_{45} + k_{46}C_{OH^-} + k_{47}C_{O^-})(C_{EtOH} + k_c + k_c k_d + k_c k_e)}
$$

(6.13)

With

$$
k_b = k_{10}\frac{k_{21}}{k_{12}}\frac{k_{32}}{k_{23}}\frac{k_{43}}{k_{34}}, \qquad k_c = \frac{k_{10}}{k_{12}}, \qquad k_d = \frac{k_{21}}{k_{23}}, \qquad k_e = \frac{k_{21}}{k_{23}}\frac{k_{32}}{k_{34}}
$$

(6.14)

where k_{ij} is a rate constant for reaction step i to j.

Next we combined the rate equation with the design equation for a constant volume batch reactor. Substituting the expressions for concentration for each component (C_i) in terms of the conversion of the limiting reactant, $C_i = C_i^0 (R_i + v_i X)$ into equation (6.13), leads to a differential equation (equation (6.15)) describing how the oleic acid conversion changes with the batch holding time. A similar differential equation can be written for ethyl oleate conversion during its hydrolysis.

$$\frac{dX}{dt} = \frac{(k_{45} + k_{46}C_{OH^-} + k_{47}C_{O^-})k_{01}C_{H^+}C_{OA}^0(R_{EtOH} - X)(1-X) - k_b(R_w + X)\left[k_{54}C_{H^+}C_{OA}^0(R_{EO} + X) + k_{64}C_{OA}^{0\,2}(R_w + X)(R_{EO} + X) + k_{74}C_{OA}^{0\,2}(1-X)(R_{EO} + X)\right]}{k_bC_{OA}^0(R_W + X) + (k_{45} + k_{46}C_{OH^-} + k_{47}C_{O^-})(C_{OA}^0(R_{EtOH} - X) + k_c + k_ck_d + k_ck_e)}$$

$$(6.15)$$

with $\quad C_{H^+} = \sqrt{K_w + K_aC_{OA}^0(1-X)}, \qquad\qquad C_{OH^-} = \frac{K_w}{C_{H^+}}$ $\qquad$ (6.16)

for the case of esterification in pure ethanol with no added acid catalyst.

We assume that the rate constants follow Arrhenius form (equation 6.17), where 10^{a_i} and E_i are the respective pre-exponential factor and activation energy.

$$k_i = 10^{a_i}\exp\left(\frac{-E_{a,i}}{RT}\right), \quad i = 01, b, c, d, K_a \qquad (6.17)$$

The value of the dissociation constant of water K_w is temperature dependent and calculated using the correlation from Marshall and Franck [15]. Since we do not have any correlation for the dissociation constant (K_a) for oleic acid, we have used K_a as one of the adjustable parameters. Also the K_a value will be different in water, ethanol and water-ethanol mixture. To overcome this problem, we define a common K_a based on the mole fraction of water and ethanol as is shown in equation (6.18). We obtain this relationship based on the linear dependence of log K vs mole fraction [16]. Furthermore, we allow $K_{a,h}$ and $K_{a,e}$ to have Arrhenius dependency.

$$log\ K_a = x_w\, .log\ K_{a,h} + x_e\, .log\ K_{a,e} \qquad (6.18)$$

where x_w, x_e are a mole fraction of water and ethanol respectively with $x_e = 1 - x_w$
$K_{a,h}$ and $K_{a,e}$ are the dissociation constants of oleic acid in water and in ethanol, respectively.

We numerically integrated the differential equations for esterification and hydrolysis using Euler's method and simultaneously performed parameter estimation to determine values for a_i and E_i. These calculations were performed using Microsoft Excel 2007 and its Solver function. The objective function to be minimized was the sum of the

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squared differences between the experimental and calculated conversions, from both hydrolysis and esterification experiments. For hydrolysis we have used data as reported in Changi et al. [4] and for esterification we have used data reported in Figure 6.1, Table 6.1 and Table 6.2.

Using the methodology outlined above, we obtained values of the Arrhenius parameters for the different collections of rate and equilibrium constants at different conditions. We found that the model was largely insensitive to k_{46}, k_{64}, k_c, k_d and k_e. The values of k_{46} and k_{64} were also small compared to k_{45}, k_{54}, k_{47} and k_{74}. For esterification, k_c, k_d and k_e could be neglected as they were smaller than C_{EtOH}. Neglecting the less significant kinetics parameters (k_c, k_d, k_e, k_{46}, k_{64}), the reaction pathway can be further simplified to the form shown below.
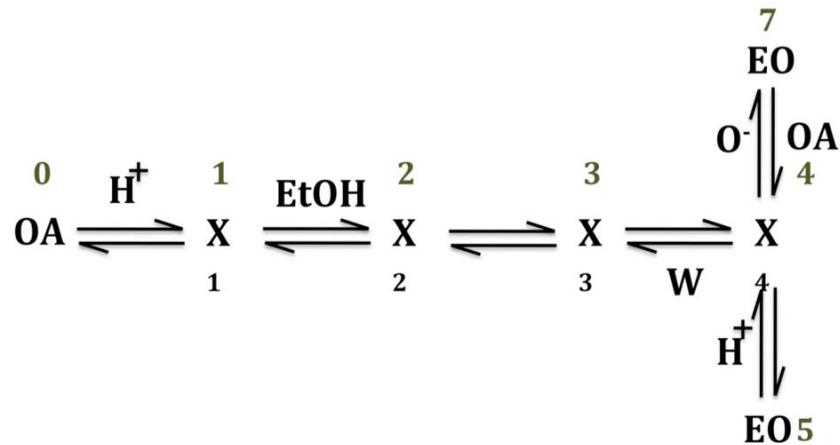
The differential equation for the conversion during esterification reduces from eq.(6.15) to eq. (6.19).

$$\frac{dX}{dt} = \frac{(k_{45} + k_{47}C_{A^-})k_{01}C_{H^+}(R_{EtOH} - X)(1 - X) - k_b(R_W + X)(k_{54}C_{H^+}(R_{EO} + X) + k_{74}C_{OA}^0(1 - X)(R_{EO} - X))/C_{OA}^0}{k_b(R_W + X) + (k_{45} + k_{47}C_{A^-})(R_{EtOH} - X)} \quad (6.19)$$

Next, we use the reduced model to re-estimate the parameters using the same data set and method listed above. Table 6.6 shows the values of the reduced model's Arrhenius parameters determined for the different collections of rate and equilibrium constants that constitute the model parameters.

Table 6.6: Arrhenius parameters for esterification reaction: mechanistic kinetics model (min, L, mol)

| Kinetics constant, k_i	log A	E_i (kJ/mol)	k at 230°C
01	4.4	42.2	0.99
45	2.2	47.4	2×10^{-3}
47	2.1	65.2	2×10^{-5}
54	4.3	40.7	1.33
74	3.7	42.5	0.18
b	1.5	48.8	3×10^{-4}
$\mathbf{K_{a,h}}$	1.5	45.6	5×10^{-4}
$\mathbf{K_{a,e}}$	2.1	43.8	4×10^{-3}

When we extrapolate the parameters $K_{a,h}$ and $K_{a,e}$ and use equation (6.18) at room temperature we get pKa between 6 and 7 for various mole fractions of ethanol and water. This is slightly different from the pKa of 7 to 9.24 reported for palmitic acid and pKa of 7.47 to 9.35 reported for stearic acid at different mole fractions of ethanol (Rahman et al. [16]). The small discrepancy may be attributed to difference in fatty acid type between unsaturated, oleic acid and the saturated ones used by Rahman et al. [16] and probably to the fact that the latter have used KOH solution as their solvent medium. Based on this reasoning, the dissociation constant value obtained through the parameters from the model seems reasonable.

Figure 6.14 demonstrates the ability of the model with the parameters in Table 6.6 to correlate the experimental results for esterification. Clearly, the model fit is not perfect, but it is very good and indicates the absence of systematic errors.
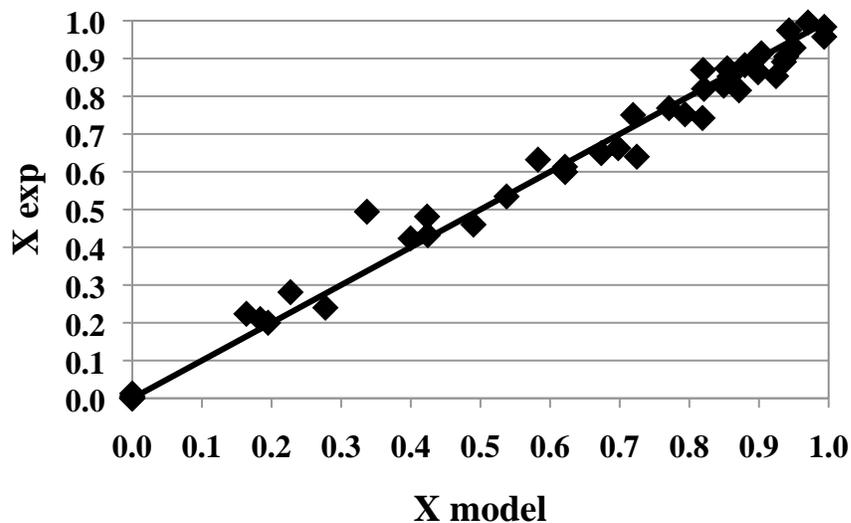
Figure 6.14: Parity plot for oleic acid conversion from esterification reaction (mechanistic kinetics model)

We then used the mechanistic model to predict the conversion for conditions that came from experiments done both within and outside the parameter space used to determine the model parameters. First, we tested the ability of the model to predict the outcome of experiments done within the parameter space. Figure 6.15 shows the experimental and model conversions for esterification carried out at 200 °C and 230 °C. Good agreement can be seen of the model and experimental conversions.
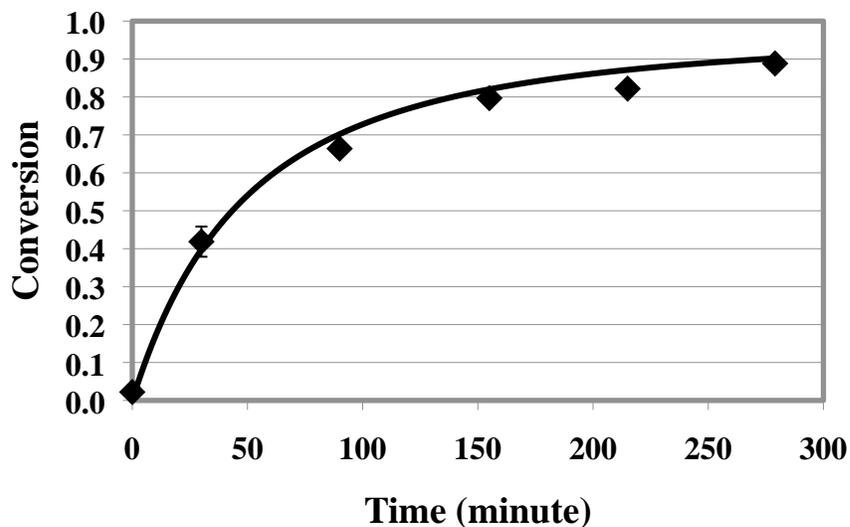

(a)
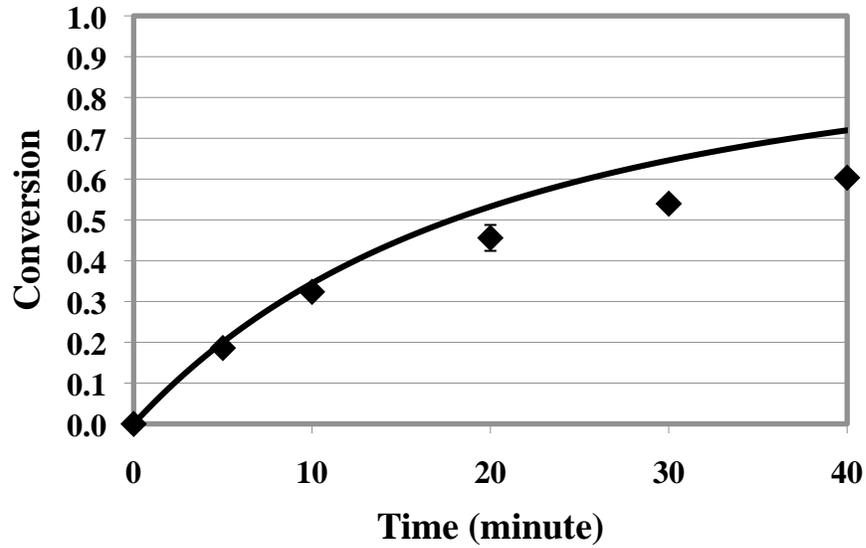
(b)

Figure 6.15: Calculated conversion from mechanistic kinetics model (smooth curve) compared to the experimental results (discrete points) at (a) 200 $^{\circ}$C, $C^0_{OA} = 0.90$ mol/L, $R_{EtOH} = 10$ and (b) 230 $^{\circ}$C, $C^0_{OA} = 0.77$ mol/L, $R_{EtOH} = 7$

We tested the ability of the model to predict results of experiments conducted outside the parameter space for case with only oleic acid and ethanol. The model conversion is compared with experimental conversions from the Warabi et al. [1] data set in Figure 6.16. It does a fairly good job of predicting esterification results published by Warabi et al. [1]. The slight deviation might be attributed to a higher ratio of ethanol to fatty acid ($R_{EtOH} = 42$) used by Warabi et al. [1].
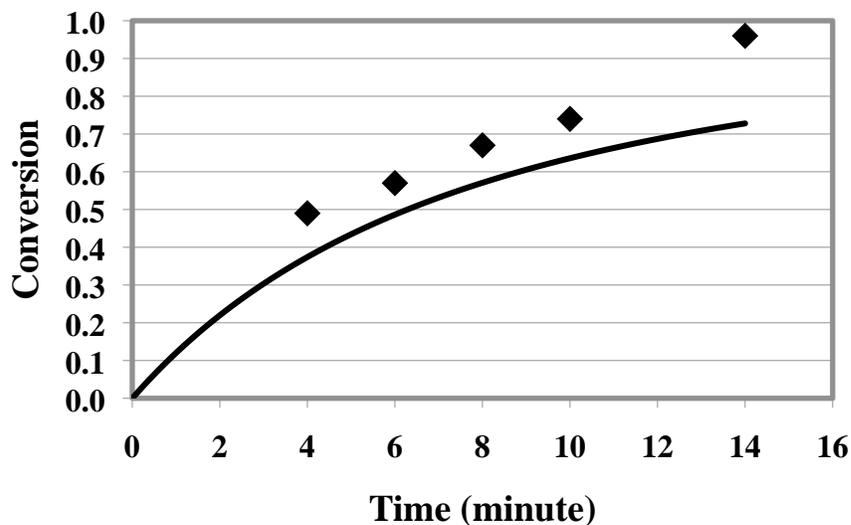
Figure 6.16: Calculated conversion from mechanistic kinetics model (smooth curve) compare to the experimental results (discrete points) from Warabi et al. [1] at 300 °C, 15 MPa, $R_{EtOH} = 42$, $C^0_{OA} = 0.14$ mol/L

The model's predictive capability was also tested for esterification carried out with added water within the parameter space ($R_w = 1$ and $R_w = 9$; cases of multicomponent system). Figure 6.17 shows good agreement between model and the experimental conversions.
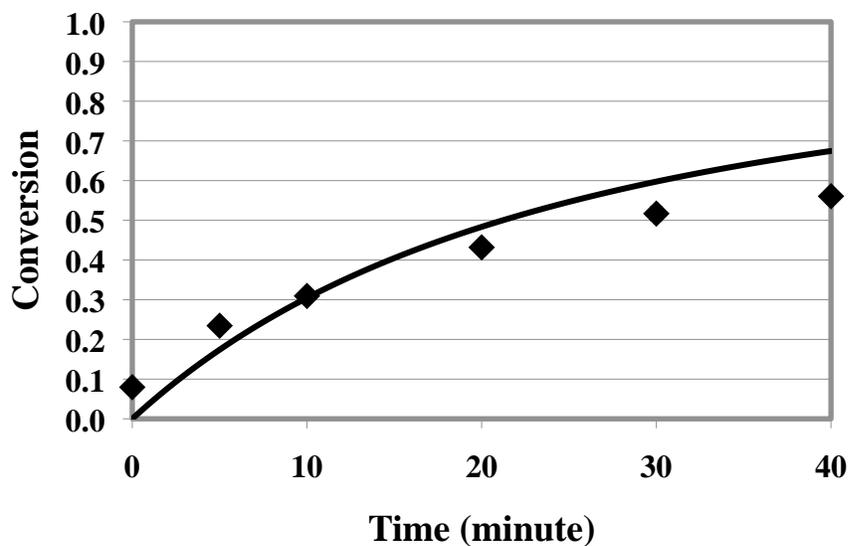

(a)
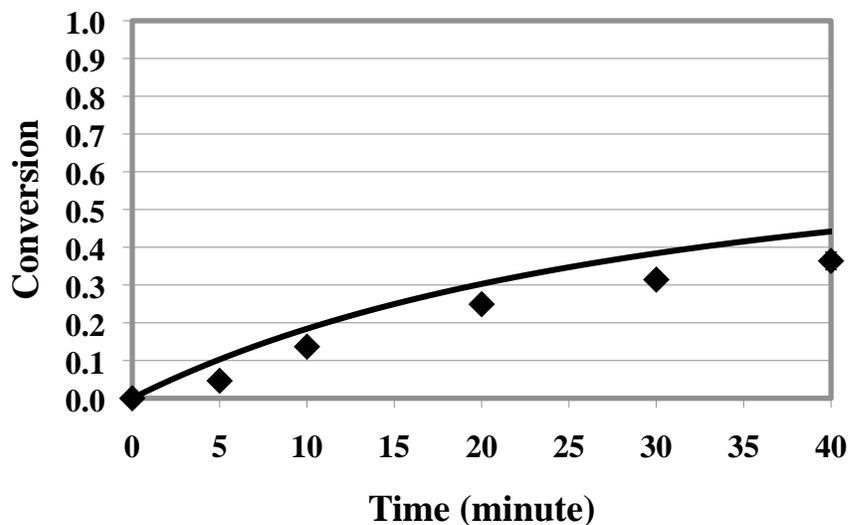
(b)

Figure 6.17: Calculated conversion from mechanistic kinetics model compared to experimental data in case of water initially present in the system at $230^{\circ}C$ (a) $R_{EtOH} = 10$, $R_W = 1$, $C^0_{OA} = 0.62$ mol/L ; and (b) $R_{EtOH} = 10$, $R_W = 9$, $C^0_{OA} = 0.53$ mol/L

For esterification with added ethyl oleate, the model makes good predictions as shown in Figure 6.18.
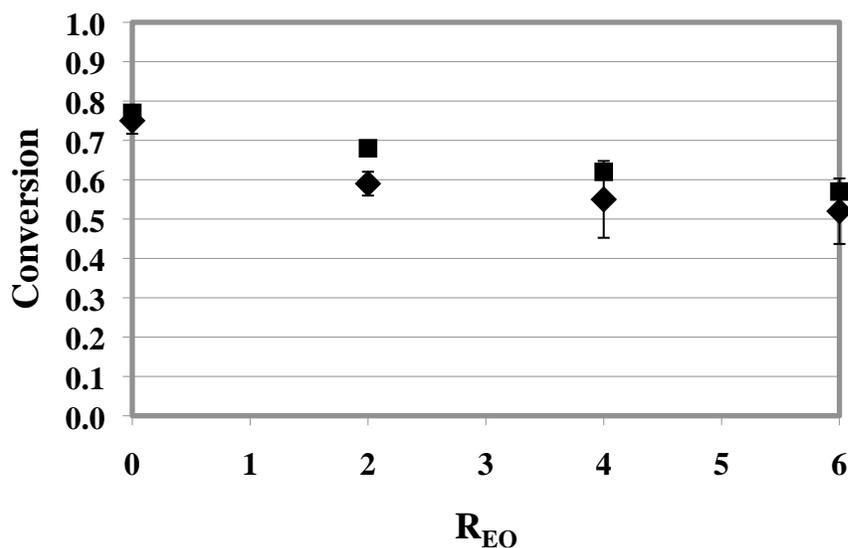
Figure 6.18: Calculated conversion from mechanistic kinetics model compared to experimental data in case of ethyl oleate initially present in the system at $250^{\circ}C$, f = 0.55, $R_{EtOH} = 10$ with various R_{EO} ($C_{OA} = 0.34$ mol/L, 0.24 mol/L, 0.18 mol/L at $R_{EO} = 2, 4, 6$ respectively) at 30 minutes with experiment (♦) and model (■)

Table 6.7: Normalized sensitivity coefficients for oleic acid esterification on calculated conversion by mechanistic model at 250 °C, $R_{EtOH} =10$, and at 30 minutes

R_w	R_{EO}	C^0_{OA}	Normalized Sensitivity Coefficient (NSC)													
			a_{45}	E_{45}	a_{54}	E_{54}	a_{74}	E_{74}	a_{01}	E_{01}	a_b	E_b	a_{ah}	E_{ah}	a_{ae}	E_{ae}
0	0	0.6	0.1	-0.2	-0.1	-0.1	0	0	3.1	-3.0	-0.1	0.2	0	0	0.7	-1.5
50	0	0.3	3	-7	-1.6	1.5	-2.8	3.2	8.6	-8.2	-2.3	7.3	1	-3	0.3	-0.6
0	6	0.4	-1	-1	-0.5	0.5	-0.3	0.3	5.1	-4.9	-0.3	0.9	0	0	1.1	-2.3

From the normalized sensitivity coefficients, it suggested that the protonation of oleic acid is the rate-determining step in the case of system without initial water or ethyl oleate and the dissociation constant of oleic acid in ethanol-water is important parameters (row 1 of Table 6.7). For esterification with added water or ethyl oleate, the calculated conversion becomes sensitive to all parameters, and no rate-determining step exists (row 2 and 3 of Table 6.7). Note that in all cases, the model is insensitive to k_{-1}, a_{47} and E_{47}.

This work is the first of its kind to explore the combined dynamics of fatty acid esterification and ester hydrolysis and propose a common mechanism. Our mechanistic model is a modification of the $A_{AC}2$ mechanism and includes three pathways catalyzing ester hydrolysis, namely, H^+-catalyzed, water catalyzed, and fatty acid catalyzed, whereas esterification is primarily catalyzed by H^+ (step 01). We make further simplification based on the parameters obtained on fitting the model to experimental data, wherein the water catalyzed pathway is not important for ester hydrolysis. Thus, hydrolysis is mostly catalyzed by H^+ and the fatty acid, which has not been included before at the mechanistic level. This work is an improvement to the existing mechanisms in this area.

The model makes reliable quantitative predictions within the experimental conditions used to determine its parameters. It makes reliable predictions when extrapolated outside this parameter space. The model also makes reliable predictions when there is a multicomponent system of fatty acid, ester, water and alcohol.

The knowledge of this mechanistic study helps us in the design of both esterification and hydrolysis reaction. Our model suggests that esterification can be accelerated if we add in acid catalyst to the system or if we subject the system to the low pH environment that could create more $[H^+]$ in the system. In a similar manner, the

hydrolysis path can be catalyzed by the addition of fatty acid to the system, since the $[H^+]$ is obtained mainly from the fatty acid dissociation and also the rate of the fatty acid catalyzed reaction is significant. We can therefore reduce cost and minimize waste using fatty acid instead of mineral acid catalyst in the system.

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CHAPTER 7

Conclusions

This thesis shows the feasibility of noncatalytic oleic acid esterification with ethanol under subcritical conditions. An acceptable conversion around 75% can be achieved at 230 $^{\circ}$C, f=0.56, 5.5 MPa in an hour of reaction (the pressure and temperature of this condition is lower than the critical point of ethanol). The experimental data at 250 $^{\circ}$C with different pressure also show that higher rate was obtained with the system that has lower pressure. These conditions at 250 $^{\circ}$C lead to the existence of two phases. The composition of reactant and product in each phase is different for both conditions, which might play an important role in the change in conversion. For example, if water that is being produced during the reaction were in the vapor phase, while the reactants are in the liquid phase, it might help drive the reaction toward the product side of reaction. After confirming the feasibility of esterification under subcritical temperature and/or pressure, two main parameters that effect the reaction: amount of ethanol and water, were studied. The amount of ethanol to oleic acid affects the reaction since esterification is a reversible reaction. We found an increase of conversion from molar ratio of ethanol to oleic acid of 1 to 3 and no significant change after more ethanol is added. Both kinetic and thermodynamic effects are likely at work in causing the changes in conversion with the ethanol to oleic acid ratio. It is difficult to decouple these effects in the present data due to the existence of two separate fluid phases in the reactor under these reaction conditions. Another important parameter, amount of water, has a negative effect on the reaction even at a small amount of 3 vol%. We also showed that a stainless steel reactor wall does not have a catalytic effect on esterification at the conditions that we study.

We demonstrate here for the first time an alternative way to produce biodiesel from algae without prior drying and extraction of lipid by using two-steps: hydrolysis and

noncatalytic (trans) esterification. The results show the potential of the method. The hydrolysis was done at 250 °C and 45 minutes to produce an easy to filter lipid-rich solid. The hydrolyzed solid was then processed without drying (46% water) in the (trans) esterification reaction to obtain biodiesel. The highest yield of FAEE obtained based on lipid within the hydrolyzed solid is 66% at 325 °C, 6.6 w/w Ethanol, 10% water, with 2 hours of reaction.

Another main portion of this thesis is the esterification kinetics. The kinetics of esterification was studied at 2 levels: phenomenological and mechanistic. The phenomenological models give a reasonable prediction of conversion with a few input parameters. Two models were proposed at the phenomenological level. First, the simple kinetics model based on the power rate law was used to fit the esterification data with four parameters. The model gives a good prediction for one phase conditions that start with only oleic acid and ethanol. Some deviation was observed in the case of added water or ester product. The second model, FA catalytic kinetics, was proposed based on the evidence that fatty acid can catalyze the reaction. This model used data sets from both esterification and hydrolysis. This study is the first to explore the dynamics of fatty acid esterification and ester hydrolysis reactions in tandem. The kinetics model comprised a two-step path using six parameters to fit the experimental conversion data obtained over a range of temperatures of 150°C to 300°C. The parameter values are thermodynamically consistent and reasonable on a thermochemical basis. The model makes reliable quantitative predictions within the experimental conditions used to determine its parameters. It makes reliable qualitative predictions when extrapolated outside the parameter space. Sensitivity analysis also confirms the need of using both esterification and hydrolysis data to obtain reliable estimates of the kinetics parameters for both forward and reverse reactions. This phenomenological FA catalytic model was then used to predict the results from esterification taking place in two phases. The calculation was done in multiple small time steps using the same kinetics in both vapor and liquid phase. ASPEN was used to calculate the composition in each phase as an input for the initial concentrations at each time step. This simple approach provided good predictions for the two-phase system without explicitly including mass transfer in the model.

A more detailed mechanistic model was introduced to study the reaction path. The model suggested that esterification is mainly catalyzed by [H+] from the dissociation of oleic acid. The validation of the model was done within and outside the parameter space of the model, which shows a good conversion prediction.

CHAPTER 8

Future Work

According to the study in this thesis, there are many further important studies that need to be investigated. This chapter will discuss some of the future directions in the field.

In the feasibility study, the vapor and liquid phases had different concentrations of oleic acid and ethanol (and products as they formed), so the esterification reaction would proceed at different rates and to different equilibrium conversion values in the two-phase condition. This phase behavior leads to a different conversion being observed at 250 $^{\circ}$C with different reactor loadings. The lower loading, which led to a lower pressure, gave higher conversion in the first 30 minutes of reaction. The vapor fractions on a total molar basis were 0.87 at the lower loading (f =0.04) and 0.48 at the higher loading (f=0.26).

The discussion above shows that understanding the phase behavior and how it changes throughout the course of the reaction is required to understand fully the reaction behavior at the high temperature for the mixture of oleic acid, ethanol, FAEE, and water. It will be useful to be able to predict the composition in each phase at specific conditions.

We demonstrated an alternative way to produce biodiesel from algae without prior drying and extraction of lipid by using two-steps: hydrolysis and (trans) esterification. The results show the potential of the method. However, more study has to be done to improve the system. According to EN14214, esters have to comprise more than 96.5% of biodiesel and the amount of FA, MG, DG, and TG in biodiesel cannot exceed 0.4, 0.8, 0.2, and 0.2 (w/w), respectively. The crude biodiesel produced by SC-IST/E under the conditions examined in this study does not meet the specifications for finished biodiesel. Therefore, a further investigation on the effect of water and amount of

alcohol to find the optimum condition to use in the esterification is required. The future work should also consider lower ethanol loadings since there is evidence of FA catalyzing the esterification reaction. Less ethanol will lead to a higher concentration of FA to start the reaction. In addition, removing different amounts of the water from the hydrolysis solids would allow one to determine the influence that might exist with the presence of water. In addition to improving the ester yield from SC-IST/E, these process changes may also reduce process costs and energy inputs. A techno-economic study should also be done to compare this two-step catalyst-free method with the traditional method of biodiesel production from algae. The techno-economic study also should be done to identify if the supercritical conditions with short time or subcritical condition at longer time will be more beneficial in the commercial scale.

In the kinetics study section, we demonstrate the conversion prediction of two phase conditions with a simple approach that does not explicitly include mass transfer. We used a small time step for the reaction with the same kinetics in both vapor and liquid phase. ASPEN was used to calculate the composition in each phase as an input for initial concentration at each time step. This simple approach allowed the calculation to get close to the real system without building mass transfer into the model. However, the kinetics model that has mass transfer as one of the features in the model would help improve the ability of the model to predict the conversion of the esterification with multiple phases. Clearly, a rigorous and more accurate treatment of the physics and chemistry governing these two-phase constant-volume batch reactions would require the use of a reliable thermodynamics model to handle vapor-liquid equilibrium, a mass transfer model to handle interphase transport of reactants and products, and a reaction engineering model to monitor the reaction progress in both phases. Taken collectively, these elements would allow for the computation of the compositions and amounts of the co-existing phases at each time step throughout the reaction.

The mechanistic study showed that there is a need for data on the dissociation constant of oleic acid in the water-ethanol mixture at high temperature. This information would lead to more accurate results in the model prediction.