ABSTRACT

TURNER, TIMOTHY LAWRENCE. Modeling and Simulation of Reaction Kinetics for Biodiesel Production. (Under the direction of Richard R. Johnson and William L. Roberts)

Biodiesel has emerged as a viable substitute for petroleum diesel. The fuel can be made easily from either virgin or waste vegetable oil. A common means of production is base-catalyzed transesterification. After twenty-five years of study, the description of the kinetics of transesterification for biodiesel remains controversial. There are conflicting findings as to the order of reaction, and estimates of reaction rate constants vary widely.

After analyzing the prior work on kinetics, this thesis gives support to a kinetic model based on careful examination of chemical mechanisms and of competing reactions. It then describes the extensions to the model that are needed in order to build a predictive model for biodiesel reactions. A computer simulation of the rate equations, with extensions for the effect of temperature, is used to analyze the implications of the model.

Modeling and Simulation of Reaction Kinetics for Biodiesel Production

by

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DEDICATION

This thesis is gratefully dedicated to my parents,

Peter C. Turner and the late Betty Donovan Turner.

PERSONAL BIOGRAPHY

Timothy Lawrence Turner attended public schools in New York, New Jersey, and North Carolina. He has prior BS and MS degrees in Electrical Engineering from NC State. He worked on manual control of robotic manipulators at Jet Propulsion Laboratory from 1980 to 1982. He then worked at Research Triangle Institute from 1982 to 1993, designing and writing software for research in aircraft cockpit displays and decision support systems for rocket launch safety. He started a consulting company, Turner Engineering, in 1993, building software for scientific and research engineering applications. After taking undergraduate courses for a year in preparation, he entered the MS program in Mechanical Engineering at NC State in fall 2003, where he has focused on sustainable energy technologies. He received an NSF Graduate Research Fellowship in the spring of 2004.

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I would like to thank the members of my committee, Drs. Richard Johnson, William Roberts, and Gregory Buckner for their collaboration, guidance, and support.

Other faculty members at NC State were also helpful. Dr. Philip Brown, a fellow biodiesel enthusiast, gave me the use of his organics lab, bought supplies, and talked me through the fine points of chemical analysis. I had many enlightening conversations with Drs. Laura Sremaniak, Charles Orji, and Ratna Sharma. Pedro Ordoñez of Universidad de San Carlos, Guatemala, worked with me for several months to analyze samples from ethanolysis of waste vegetable oils.

At the outset of my graduate program, I worked at the NC Solar Center, where I first learned about biodiesel, and gained knowledge and experience in a variety of sustainable technologies. I am grateful to the director, Dr. Alex Hobbs, former Manager of the Alternative Fuel Vehicle Program, Kurt Creamer, and my co-workers John Garner and Morgan Crawford.

I learned the nuts and bolts of fuel making from my North Carolina colleagues Rachel Burton and Leif Forer of Piedmont Biofuels in Pittsboro, and Eric Henry of T.S. Designs in Burlington

Finally, I must thank my wife, Elizabeth Martinez, and our daughters Jessica, Adrienne, Amelia, and Sophia. Elizabeth had the selflessness and vision to

recommend that I attend graduate school full time. And our daughters are an endless source of joy and discovery.

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LIST OF SYMBOLS, ABBREVIATIONS, AND NOMENCLATURE

FFA Free Fatty Acid

LMA Law of Mass Action

RLS Rate-Limiting Step assumption

SVO Straight Vegetable Oil. Vegetable oil burned directly in diesel engines.

WVO Waste Vegetable Oil. Vegetable oil that that has been used for cooking.

1 INTRODUCTION

1.1 General context

Humanity's dependence on petroleum for transportation fuel comes at a high cost. Global production of petroleum has arguably already peaked, while demand will soar in the future as the huge populations of India and China will require more fuel as those economies continue to grow (Campbell 1997). The environmental impact of fossil fuels is well known. It contributes to global warming by transferring previously sequestered carbon molecules into the atmosphere as carbon dioxide, a greenhouse gas. It also is a major source or air pollution through other combustion products found in exhaust. Finally, the nations that cannot supply their own petroleum needs are forced into an unfavorable balance of payments with petroleum exporters. Among the net petroleum importers are the United States, most of Europe, and Japan.

Biofuels offer a partial solution to many of these problems. It has been claimed that biofuels do not contribute to global warming. Like petroleum, exhaust from biofuels contains carbon dioxide. Since plants remove carbon dioxide from the atmosphere during photosynthesis, the net production of CO_2 is arguably zero. The levels of other pollutants are also generally lower with biofuels than with petroleum. The fuelstocks for biofuels are produced by domestic agriculture, which means that biofuel production occurs domestically as well.

Biodiesel is an attractive alternative to petroleum diesel. Production of biodiesel is easily done and requires low energy inputs. While it can be made from animal fat, the main fuelstock is vegetable oil, which can be obtained from an amazing variety of

plants. In northern climates, the main source is rapeseed, whose oil is often called canola oil. In warmer regions such as North Carolina, the oil source is often soybeans.

The main drawback of biodiesel is the availability of vegetable oil. There is not enough arable land in the US to meet current domestic diesel consumption. It may be possible to produce enough oil by farming microbes, such as algae, whose oil yields per unit land area could be two orders of magnitude higher than with conventional oil crops (Pahl 2005).

Currently, there is no shortage of vegetable oil for biodiesel in the US. In fact, hundreds of small producers are making quality fuel from the waste vegetable oil (WVO) discarded by restaurants and food processors. While the methods for making biodiesel from WVO require slight modification from those for virgin oil, the quality of the fuel produced is comparable.

For the private citizen who wants to take control of his or her own energy needs, biodiesel is the transportation fuel of choice. It does not require a breakthrough technology to make it feasible. It also will run in existing diesel engines without modification, although rubber components such as fuel hoses must be replaced with synthetic materials if biodiesel is to be used long-term.

An alternative to biodiesel is straight vegetable oil, or SVO. This second approach is to burn vegetable oil directly in diesel engines. While SVO has its own following of dedicated enthusiasts, modification is required to run it in existing engines. The main

change is to provide a means to preheat the oil before it enters the injection pump. This is necessary because the viscosity of SVO is much higher than diesel fuel at room temperature.

The trade-off between SVO and biodiesel is cost. Assuming both are obtained from waste vegetable oil, SVO is essentially free, while biodiesel has material costs associated with the other reactants, alcohol and catalyst. Also, making biodiesel in small batches is labor-intensive.

1.2 History of biodiesel

The diesel engine was invented by Otto Diesel in 1892. His engine was designed to run on a wide variety of fuels. Although he demonstrated a diesel engine running on peanut oil at the Paris Exhibition of 1900, the first commercial diesel engines ran on kerosene. Due to their large size, diesels were first used in manufacturing plants. The new engine first appeared in transportation vehicles in ships in the 1900's. They showed up in trains in 1914, but "did not seriously displace the steam engine until after World War II". Diesels were first used in automobiles in 1924 (Pahl 2005).

Chemically, biodiesel is a mixture of fatty alkyl esters, or esters formed by fatty acids and an alcohol. Alkyl esters are commonly made from vegetable oil through a chemical reaction called transesterification. Although this process has had long use in making detergents, the resulting compound was first used as a diesel fuel by Austrian researchers around 1980 (Mittelbach 1983). Mittelbach's group is also responsible for using waste vegetable oil as an inexpensive alternative to virgin oil as the fuelstock for biodiesel.

In the U.S., research in biodiesel has taken place at various laboratories and universities. Some of the defining work on biodiesel kinetics took place at US Department of Agriculture. Iowa State University has led in establishing production standards and methods especially for methyl esters, while the production and testing of ethyl esters has been the province of Idaho State University.

1.3 Biodiesel work at NC State

The goal of biofuels work in the Department of Mechanical and Aerospace Engineering (MAE) at NC State is to maximize the efficiency and sustainability of biofuel production. This work has had a practical component and a theoretical component.

On the practical side, students have participated in ongoing batch production of biodiesel, and occasional batch production of ethanol since the summer of 2004. The author began working with then graduate student John Garner to complete a batch reactor that Mr. Garner had built, while both were working for the NC Solar Center. The reactor consists of an 80-gallon HDPE conical reactor tank, and a 30-gallon HDPE conical methoxide tank. The reactor tank has a 1 ½ in ID recirculation line with a 1 hp pump to stir the reaction mixture. The reactor was fitted with spray nozzles in the top for washing the reacted fuel with water. In the original configuration, methanol and catalyst were mixed in the methoxide tank, then introduced by gravity feed into the reactor tank containing waste vegetable oil. We quickly discovered that the feed line was prone to clogging, and that it was very difficult to solve the problem with the toxic methoxide mixture high overhead.

The author worked with Morgan Crawford of NC Solar Center to change the method of introducing the methoxide to the reaction. In the new system, a venturi on the outlet side of the recirculation pump pulls the methoxide into the recirculation line. The idea for the venturi came from Dr. Alex Hobbs, Director of NC Solar Center, who had used one in an earlier reactor. On that system, the venture was placed on the inlet side of the pump. Although that arrangement provides better suction, the pump would often foul due to air introduced through the methoxide line. The current arrangement eliminates that problem. The final design has a bypass line so that the venture does not restrict the recirculation flow once all the methoxide has been introduced.

The reactor, housed at MAE's Applied Energy Research Lab (AERL), has been used to make biodiesel for on-road use since October 2004. The author has run his 1983 Mercedes on 100% biodiesel, or B100, since March 2004.

On the theoretical side, the work has focused on the chemistry of biodiesel making. The author began making biodiesel in the laboratory, using ethanol instead of the usual reactant, methanol. Although ethanol has been used successfully to make biodiesel for more than twenty years (Peterson 2002), the production methods are more challenging. We found that making biodiesel using virgin soy oil and ethanol was quite easy. However, when we used the same methods with ethanol and waste vegetable oil, we only succeeded in creating a tea-colored mixture.

With the help of Pedro Ordoñez, a visiting lecturer from the University of San Carlos, Guatemala, we analyzed product samples using GC-MS. We discovered that the

samples contained high concentration of the desired product as well small concentrations of intermediate products known as di- and mono-glycerides. This meant that we were successfully making biodiesel, but that the reaction products were not separating as they customarily do.

We then turned our attention to speeding the separation process. That work is still underway.

In the process of experimentation, the author began trying to understand the chemical explanation for the difference encountered between various alcohols, catalysts and fuelstocks. The original motivation was to understand why the reaction with waste oil and ethanol was so much more difficult than with virgin oil. He became fascinated by Bikou's investigation of the effect of water on the transesterification of vegetable oil with ethanol (Bikou 1999). After reading through a number of papers, he decided that Komers' analysis of the reaction kinetics of transesterification for biodiesel was the most grounded in the fundamentals of chemical mechanisms. Komer's conclusions are the basis for the work described here.

1.4 Chemical foundations of biodiesel-making

Biodiesel is fuel made from fat. It can be produced from vegetable oil or animal fat. Either virgin vegetable oil or waste vegetable oil (WVO) can be used to make quality fuel. Fats are converted to biodiesel through a chemical reaction involving alcohol and a catalyst.

1.4.1 Chemical building blocks

It is instructive to think of the chemistry of biodiesel in terms of the building blocks that comprise the larger molecules involved in the biodiesel-making reactions.

Fatty acids are a component of both vegetable oil and biodiesel. In chemical terms, they are carboxylic acids of the form

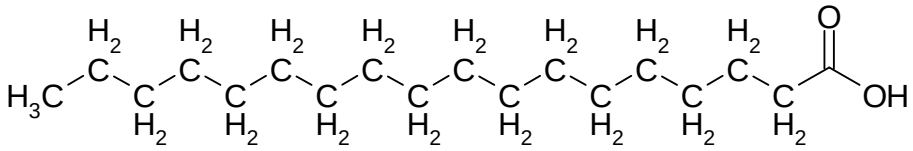


Figure 1-1. Molecular structure of an idealized fatty acid

Fatty acids which are not bound to some other molecule are known as free fatty acids.

When reacted with a base, a fatty acid loses a hydrogen atom to form soap.

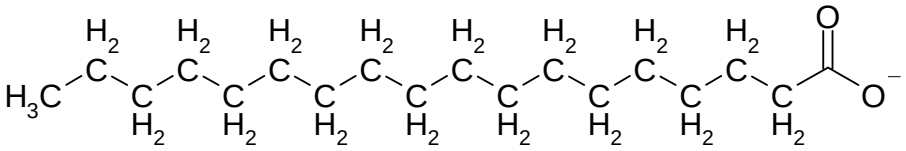


Figure 1-2. Molecular structure of soap

Chemically, soap is the salt of a fatty acid.

The structures of fatty acids shown in this section are highly idealized. Real fatty acids vary in the number of carbon atoms, and in the number of double bonds. Glycerol, a component of vegetable oil and a by-product of biodiesel production, has the following form:

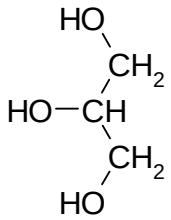


Figure 1-3. Molecular structure of glycerol

Alcohols are organic compounds of the form *R-OH*, where *R* is a hydrocarbon. Typical alcohols used in biodiesel-making are methanol, ethanol, 1-propanol, and 1-butanol:.

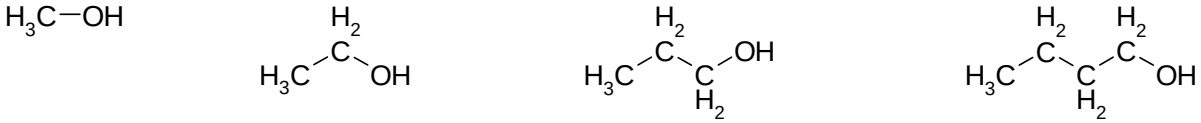


Figure 1-4. Molecular structure of methanol, ethanol, 1-propanol, and 1-butanol.

Of these, methanol is the most commonly used to make biodiesel. Since ethanol is easily obtained from plant sugars, while methanol is commonly produced from natural gas, using ethanol makes for a more sustainable fuel. Ethanol is harder to use because it forms emulsions easily, making the separation of end products more difficult. This is especially true if the oil source is WVO.

Transesterification is sometimes called alcoholysis, or if by a specific alcohol, by corresponding names such as methanolysis or ethanolysis.

Chemically, biodiesel is a fatty acid alkyl ester:

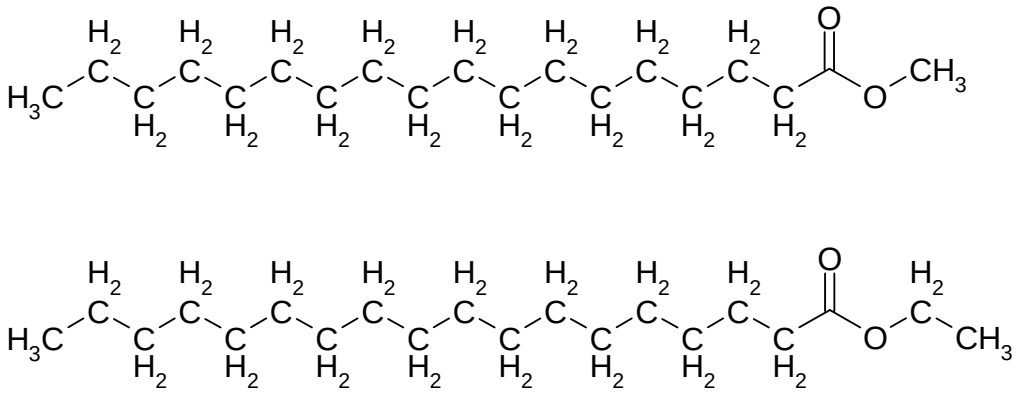


Figure 1-5. Biodiesel molecules. Above is a methyl ester; below, an ethyl ester.

An ester is a compound of the form:

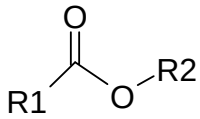


Figure 1-6. Form of the ester compound.

The biodiesel ester contains a fatty acid chain on one side, and a hydrocarbon called an alkane on the other. Thus, biodiesel is a fatty acid alkyl ester. Usually, the form of the alkane is specified, as in “methyl ester” or “ethyl ester”.

Vegetable oil is a mixture of many compounds, primarily triglycerides and free fatty acids. A triglyceride is a tri-ester of glycerol and three fatty acids:

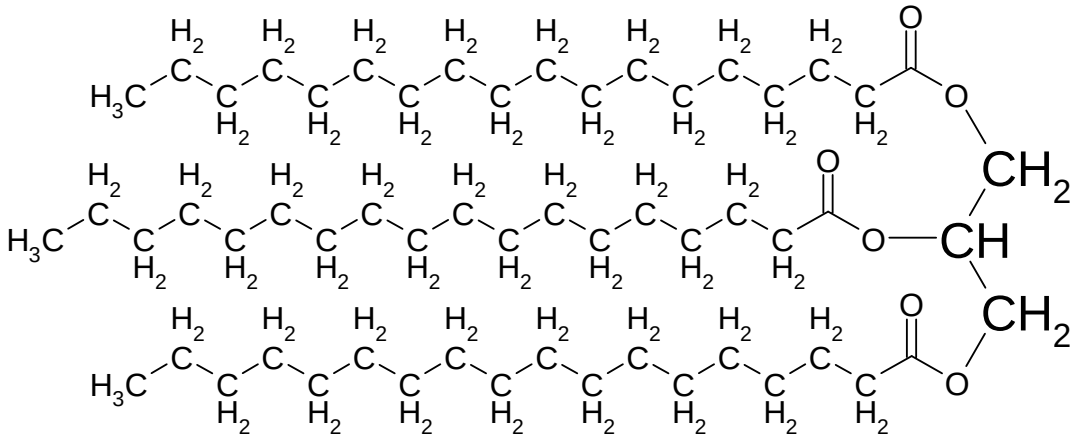


Figure 1-7. Molecular structure of triglyceride.

Virgin oil contains a low percentage of free fatty acids. Waste vegetable oil contains a higher amount of FFA's because the frying process breaks down triglyceride molecules.

Petroleum diesel and biodiesel are both mixtures of organic compounds. The idealized petroleum molecule is cetane, a pure paraffin. Compared to cetane, alkyl esters are somewhat longer, and more importantly, contain two oxygen atoms.

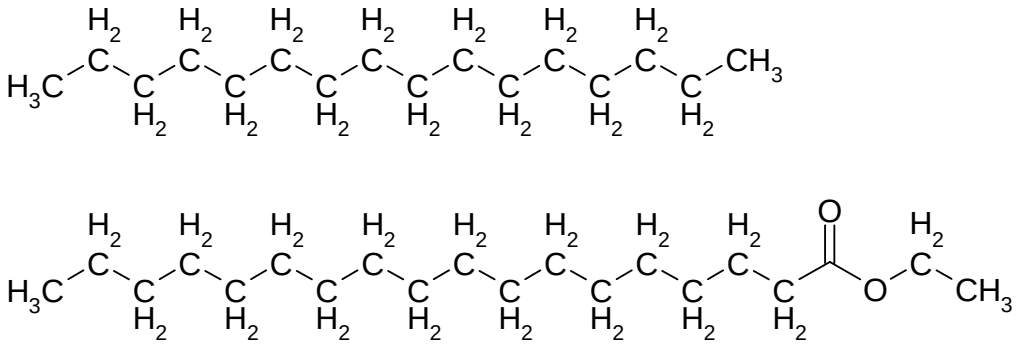


Figure 1-8. Cetane molecule, above, versus ethyl ester, below

Since combustion is an oxidation reaction, the heating value of cetane, which contains no oxygen atoms, is higher than that of biodiesel. For this reason, diesel engines running biodiesel experience a loss of power on the order of 5%.

The principal ways of making biodiesel are by transesterification of triglycerides and esterification of free fatty acids.

The transesterification reaction of triglycerides is as follows:

$$Triglyceride + 3Alcohol \xrightarrow{catalyst} 3Biodiesel + Glycerol$$

The esterification reaction of free fatty acids:

$$FFA + Alcohol \xrightarrow{acid\ catalyst} Biodiesel + Water$$

In the first reaction, a tri-ester is converted to three individual esters, thus the term transesterification. In the second reaction, a new ester is created, thus it is called esterification.

Transesterification reactions can be base-catalyzed, acid catalyzed, or enzymatic. The base-catalyzed reaction takes about one hour at room temperature. It suffers from competing saponification reactions, which convert the same ingredients as well as any free fatty acids to soap. Acid-catalyzed and enzymatic transesterification require three to four days to complete. The acid-catalyzed reaction also requires heat.

There is no competing saponification reaction with the acid-catalyzed and enzymatic reactions. In fact, even free fatty acids are converted to biodiesel by esterification.

The associated acid-catalyzed esterification reaction requires only about two hours to completion. A combined strategy called the two-stage process can be used to maximize the amount of biodiesel produced, while minimizing the amount of soap produced. The first stage is acid-catalyzed esterification of the free fatty acids. This is followed by base-catalyzed transesterification. This approach is especially effective for waste vegetable oil and animal fats, which have high free fatty acid content.

This thesis only deals with base-catalyzed transesterification. The basic steps involved are given in Table 1-1.

Table 1-1. Steps in base-catalyzed transesterification process

1. Add vegetable oil to reactor tank, begin stirring
2. Add alcohol to secondary tank. Add catalyst, stir until dissolved
3. Slowly mix alcohol+catalyst into reactor tank
4. Stir one hour
5. Allow to sit overnight
6. Drain off glycerol, alcohol, catalyst, soap, and water from lower, aqueous layer
7. Wash with water several times and filter

1.4.2 Principles of kinetics

Derivation of the kinetics of a reaction is based upon a few generally accepted principles. The main ones are presented here, for use in the succeeding chapters.

Chemical reactions are classified as either irreversible or reversible. An irreversible reaction proceeds in only one direction, which by convention is assigned to be from left to right:

$$FFA + OH^- \xrightarrow{k_{12}} A + W \qquad \text{(Equation 1-1)}$$

This reaction shows the saponification of free fatty acid by a hydroxide base, to form soap (*A*) and water (*W*). The reaction can only proceed in the direction that creates soap and water; it cannot make free fatty acids and hydroxide from soap and water. The rate of reaction is governed by the rate constant k_{12}.

A reversible reaction can proceed in either direction:

$$ROH + OH^- \underset{k_{1r}}{\overset{k_1}{\Leftrightarrow}} RO^- + H_2O \qquad \text{(Equation 1-2)}$$

This shows the conversion between an alcohol and the hydroxide base on the left, and alkoxide and water on the right. Alkoxide is formed when the hydroxide hydrogen of an alcohol is removed by a base. This reaction can proceed in either direction. The forward rate is governed by the rate constant k_1, while the rate of the reverse reaction is governed by k_{1r}. With reversible reactions, it is important to control the conditions of the reaction to favor the desired direction of conversion.

Kinetics describes the rate of chemical reactions. Rate equations are typically written in terms of the concentrations of the reactants, for example,

$$\frac{-d[TG]}{dt} = k[TG]^2 \qquad \text{(Equation 1-3)}$$

In words, this equation says that the rate of disappearance of triglycerides is proportional to the square of the molar concentration of triglycerides. This rate expression appeared in a recent paper (Darnoko 2000), it is not the expression used in the model described here.

Rate equations can be obtained by application of the law of mass action (LMA), which relates the rate of reaction to the concentrations of reactants. For example, LMA applied to Equation (1-1) produces the rate expression

$$\frac{dW}{dt} = k_{12}[FFA]^1[OH^-]^1 \qquad \text{(Equation 1-4)}$$

Under LMA, the rate of reaction in a given direction is proportional to the products of the reactant concentrations, each raised to the power of its coefficient in the reaction. The law of mass action only applies to elementary reactions, those which reflect the mechanism at the molecular level, and which occur as a single event. Chemists use simplicity tests to determine whether a reaction is elementary. These include number of collisions, number of bonds broken, number of bonds formed, integer reaction coefficients, and simplicity of reverse reaction. Even with simplicity tests, the order of reactions predicted by LMA should be verified by experiment.

When a reversible reaction proceeds at the same rate in the forward and reverse directions, it is said to be in equilibrium. The relative proportions of the reactants is

given by the equilibrium constant. The equilibrium condition for Equation (1-2) is given by

$$K_1 = \frac{k_1}{k_{1r}} = \frac{[RO^-][H_2O]}{[ROH][OH^-]} \qquad \text{(Equation 1-5)}$$

The overall reaction for transesterification can be written symbolically as

$$TG + 3ROH \xrightarrow{KOH} G + 3E \qquad \text{(Equation 1-6)}$$

This reaction occurs in three steps:

$$\begin{aligned} &TG + ROH \Leftrightarrow DG + E \\ &DG + ROH \Leftrightarrow MG + E \\ &MG + ROH \Leftrightarrow G + E, \end{aligned} \qquad \text{(Equation 1-7)}$$

where *TG* means triglycerides*, DG* means diglycerides*, MG* means monoglycerides*, G* means glycerol*, ROH* means alcohol*, E* means alkyl ester*, and A* means soap*.*

The catalyst is usually either potassium hydroxide (KOH), or sodium hydroxide (NaOH), also known as lye. When the catalyst dissolves in the alcohol, it forms an ionic solution, in which the K^+ or Na^+ ions and the OH^- ions are not directly bound to each other. The active ingredient is the hydroxide ion, OH^-. When describing chemical reactions and rate equations, the K^+ or Na^+ ions are never written out explicitly.

Hydroxide ion is the catalyst for base-catalyzed transesterification. It is also a reactant in the competing saponification reactions, in which it is consumed. Thus,

saponification robs the transesterification reaction not only of reactants that could be made into biodiesel, but also of the catalyst needed for the reaction to proceed.

2 KINETIC MODEL AND SIMULATION

2.1 Background

Although the importance of biodiesel as an alternative fuel has grown in the last twenty years, the chemical kinetics of transesterification, the most common means of producing biodiesel, remain controversial. Most efforts in the literature have focused on finding the best fit of empirical data to simple models of reaction order. Some of these results are contradictory. The one paper that develops a kinetic model based on chemical mechanisms has never been referenced. (Komers 2002)

Work on chemical kinetics specific to biodiesel production began with Freedman and colleagues at USDA in the early 1980's (Freedman 1984, 1986). In Freedman's model, the overall reaction,

$$TG + 3ROH \xrightarrow{KOH} G + 3E \,, \qquad \text{(Equation 2-1)}$$

occurs as a sequence of three steps:

$$\begin{aligned} TG + ROH &\Leftrightarrow DG + E \\ DG + ROH &\Leftrightarrow MG + E \\ MG + ROH &\Leftrightarrow G + E, \end{aligned} \qquad \text{(Equation 2-2)}$$

where

TG means triglycerides,
DG means diglycerides,
MG means monoglycerides,
G means glycerol, and
E means alkyl esters, or biodiesel.

While this is not stated explicitly, Freedman's kinetic model appears to derive from the application of the law of mass action to the three steps of the reaction. For example, the first forward reaction would proceed according to

$$-\frac{d[TG]}{dt} = k_1[TG][ROH], \qquad \text{(Equation 2-3)}$$
$$\text{where } [S] \equiv \text{the concentration of species } S$$

The forward reactions are said to be second order, referring to the overall order of the proposed forward reaction step. When the molar ratio of alcohol to triglyceride is very high, then the concentration of alcohol can be assumed constant. The rate of reaction is then dependent solely on the concentration of triglyceride, a condition which Freedman calls "pseudo-first-order".

Finally, where the data does not fit the sequential model, Freedman proposes a "shunt reaction", in which three alcohols simultaneously attack a triglyceride. The shunt reaction is said to be fourth order, presumably proportional to

$$[TG][ROH]^3. \qquad \text{(Equation 2-4)}$$

Freedman investigated transesterification of soy oil using butanol and methanol, with molar ratios of alcohol to oil of 30:1 and 6:1, at temperatures ranging from 20°C to 60°C. With butanol, he found the forward reactions to be second order at 6:1 and pseudo-first order at 30:1. With methanol, he found the forward reactions to be fourth order at 6:1, implying the shunt reaction, and pseudo-first order at 30:1. All reverse reactions were found to be second order.

He found the rate constants as a function of temperature, and derived the activation energies by taking the slope of the plot of ln(k) vs. 1/T. This method is derived from the Arrhenius equation, which relates reaction coefficients to temperature:

$$k = A\exp(-E_a / RT) \qquad \text{(Equation 2-5)}$$

where

A is the Arrhenius pre-factor, and

E_a is the activation energy of the reaction.

Taking the log of both sides of the equation,

$$\ln(k) = -\frac{E_a}{RT} + \ln(a) \qquad \text{(Equation 2-6)}$$

This equation is linear with respect to 1/T. If k is determined for varying temperatures, the plot of ln(k) vs. 1/T should produce a straight line of slope $-E_a / R$.

In 1990, Mittelbach and Trathnigg of Karl Franzen University, Austria, discussed the kinetics of methanolysis of sunflower oil. Although they did not propose any rate equations or derive any rate constants, they did discuss the parameters affecting the transesterification reaction. Although Freedman had considered the reaction to be single phase, Mittelbach found that "a two-phase system could be observed for the first 2 minutes, followed by a period of about 5 to 10 minutes, where almost complete solution occurred. As soon as a considerable amount of glycerin had formed a two phase system was established again. These facts complicating kinetic conditions have to be taken into consideration."

Mittelbach found that the conversion of triglycerides did not follow second-order kinetics as indicated by Freedman. He found that the rate of reaction is temperature dependent, but the per cent conversion is not a strong function of temperature provided that the reaction proceeds at least ten minutes (Mittelbach 1990).

In 1997, Noureddini and Zhu of the University of Nebraska again studied the kinetics of transesterification of soybean oil. They used the same reaction model proposed by Freedman. However, they took measurements at differing mixing intensities, as measured by the Reynolds number of the stirrer. They also computed Arrhenius parameters for both the standard Arrhenius equation, above, and the modified equation

$$k = AT^n \exp(-E_a / RT) \qquad \text{(Equation 2-7)}$$

where *n* is an experimentally derived parameter.

The authors used the value n = 1. They found no correlation of the data to the shunt reaction, that is, the reaction constants for the shunt reaction were negligibly small. They also found that the activation energies varied with Reynolds number. Even more surprising, their rate constants for the reverse direction of the first two reactions are larger than the rate contants in the forward direction (Noureddini 1997).

In 1998, Boocock and colleagues at the University of Toronto commented on anomalies in Freedman's results. Their study suggests that the reaction rate drops off over time, due both to inadequate mixing and to reduced effectiveness of the catalyst because of reduced polarity (Boocock 1998)

In 1999, Bikou and others at the National Technical University of Athens investigated the effect of water on the kinetics of ethanolysis of cotton seed oil. Remarkably, their data fitting suggested that each of the three reaction steps should be third order with respect to ethanol. However, the remainder of the paper does not depend on the kinetic model. Instead, they investigated the effect of water on the equilibrium constants of the three steps in the overall reaction. They found that presence of water shifted the direction of the reaction to the left for all three steps (Bikou 1999)

In 2002, Darnoko and Cheryan at the University of Illinois studied the kinetics of palm oil transesterification. They found that the best fit to their data was a "pseudo-second-order model for the initial stages of the reaction, followed by first-order or zero-order kinetics." However, by second order kinetics, they mean, for example, (Darnoko 2002)

$$\frac{-d[TG]}{dt} = k[TG]^2 \qquad \text{(Equation 2-8)}$$

In 2002, Komers and colleagues at the University of Pardubice, Czech Republic, derived a kinetic model from proposed mechanisms for all the competing reactions that take place during transesterification. These include formation of methoxide, methanolysis, and saponification. After simplifying assumptions, they derived a system of six rate equations involving eight reaction species and ten rate constants. The resulting model explicitly treats the amount of water and catalyst present. Theirs is the only model we have found that does this. The model supports Bikou's research

on the negative effect of water on the equilibrium reactions. The model is described in detail in the following section (Komers 2002).

2.2 Komers' kinetic model

Komers' model considers the methanolysis of vegetable oil using potassium hydroxide (KOH) as the catalyst. Here, we generalize for any alkyl alcohol, designated ROH, and any base catalyst. We also change Komer's notation slightly, reducing the number of special symbols.

The development of the kinetic model begins with simplifying assumptions:

1. The concentration of free fatty acids is negligible.
2. Of all the theoretically possible reactions only two proceed to form products: the alcoholysis of glycerides (TG, DG, MG) and the saponification of TG, DG, MG, or alkyl esters (E).
3. All of the isomers of TG, DG, MG, and E proceed at the same rate, with the same mechanism.
4. Alcoholysis is catalyzed by OH^- or RO^- (alkoxide) ions. Concentrations of OH^- and RO^- ions are much smaller than those of TG and ROH.

The possible reactions are then

Formation of alkoxide:

$$ROH + OH^- \underset{k_{1r}}{\overset{k_1}{\Leftrightarrow}} RO^- + H_2O \qquad \text{(Equation 2-9)}$$

Alcoholysis:

$$TG + RO^- \underset{k_{2r}}{\overset{k_2}{\Leftrightarrow}} DG^- + E$$

$$DG^- + ROH \underset{k_{3r}}{\overset{k_3}{\Leftrightarrow}} DG + RO^-$$

$$DG + RO^- \underset{k_{4r}}{\overset{k_4}{\Leftrightarrow}} MG^- + E$$

$$MG^- + ROH \underset{k_{5r}}{\overset{k_5}{\Leftrightarrow}} MG + RO^-$$

$$MG + RO^- \underset{k_{6r}}{\overset{k_6}{\Leftrightarrow}} G^- + E$$

$$G^- + ROH \underset{k_{7r}}{\overset{k_7}{\Leftrightarrow}} G + RO^-$$

(Equation 2-10)

Saponification:

$$E + OH^- \xrightarrow{k_8} ROH + A$$

$$TG + OH^- \xrightarrow{k_9} DG + A$$

$$DG + OH^- \xrightarrow{k_{10}} MG + A$$

$$MG + OH^- \xrightarrow{k_{11}} G + A$$

(Equation 2-11)

where *A* is the soap of the corresponding fatty acid chain.

The above reactions are assumed to be elementary, thus obeying the law of mass action (LMA). Straightforward application of LMA produces thirteen differential equations describing the thirteen species present in the reactions. The number of differential equations and their complexity can be reduced through simplifying assumptions. There are two common approaches. The rate-limiting step assumption holds that the slowest reaction controls the rate of conversion, and that faster reactions can be assumed to have reached equilibrium. The steady state assumption holds that certain species react so much faster than others that their rate of change is essentially zero. The steady-state assumption is the weaker of the two. Its application results in an algebraic equation which contains the rate constants for every reaction in which the species in question participates. The rate-limiting step assumption, on the other hand, leads to a set of equilibrium conditions which typically contain fewer terms for a given species.

The approach taken by Komers, and the one that will be followed in this work as well, is the steady-state assumption.

Reactions (1), (3), (5), and (7) in Equation (2-10), which are simple exchanges of hydrogen atoms, proceed much faster than the others, that is

$$\begin{aligned} &k_2, k_{2r} << k_3, k_{3r} \\ &k_4, k_{4r} << k_5, k_{5r} \\ &k_6, k_{6r} << k_7, k_{7r} \\ &k_3, k_{3r}, k_5, k_{5r}, k_7, k_{7r} > k_8, k_9, k_{10}, k_{11} \end{aligned} \qquad \text{(Equation 2-12)}$$

It therefore follows that

$$\frac{d[H_2O]}{dt} = \frac{d[RO^-]}{dt} = \frac{d[DG^-]}{dt} = \frac{d[MG^-]}{dt} = \frac{d[G^-]}{dt} = 0 \qquad \text{(Equation 2-13)}$$

Eliminating small terms and substituting the equilibrium relations into the rate equations for the corresponding species, we obtain

Komers normalizes the remaining species by the initial concentrations of triglyceride and alcohol, as follows:

$$
\begin{aligned}
TG &= [TG]/a, \\
a &= [TG]_0 \\
DG &= [DG]/a \\
MG &= [MG]/a \\
G &= [G]/a \\
A &= [A]/a \\
OH &= [OH^-]/a \\
W &= [H_2O]/a \\
ROH &= [ROH]/b, \\
b &= [ROH]_0 \\
E &= [E]/b
\end{aligned}
\qquad \text{(Equation 2-14)}
$$

The resulting differential equations are

$$
\begin{aligned}
-\frac{dTG}{dt} &= b \cdot OH \cdot (k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E) + a \cdot OH \cdot k_9 \cdot TG \\
-\frac{dDG}{dt} &= b \cdot OH \cdot (-k_2' \cdot TG \cdot ROH + k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E) \\
&\quad + a \cdot OH \cdot (-k_9 \cdot TG + k_{10} \cdot DG) \\
-\frac{dMG}{dt} &= b \cdot OH \cdot (-k_4' \cdot DG \cdot ROH + k_{4r}' \cdot MG \cdot E + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E) \\
&\quad + a \cdot OH \cdot (-k_{10} \cdot DG + k_{11} \cdot MG) \\
\frac{dG}{dt} &= b \cdot OH \cdot (k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E) + a \cdot OH \cdot k_{11} \cdot MG \\
-\frac{dROH}{dt} = \frac{dE}{dt} &= b \cdot OH \cdot (k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E \\
&\quad + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E - k_8 \cdot E) \\
-\frac{dOH}{dt} = \frac{dA}{dt} &= b \cdot OH \cdot k_8 \cdot E + a \cdot OH \cdot (k_9 \cdot TG + k_{10} \cdot DG + k_{11} \cdot MG)
\end{aligned}
$$

(Equation 2-15)

where

$$k_2' = \frac{k_2 K_1}{W}$$
$$k_{2r}' = \frac{k_{2r} K_1}{K_3 W}$$
$$k_4' = \frac{k_4 K_1}{W}$$
$$k_{4r}' = \frac{k_{4r} K_1}{K_5 W}$$
$$k_6' = \frac{k_6 K_1}{W}$$
$$k_{6r}' = \frac{k_{6r} K_1}{K_7 W}$$

(Equation 2-16)

and

$$K_1 = \frac{k_1}{k_{1r}} = \frac{[RO^-][H_2O]}{[ROH][OH^-]}$$
$$K_3 = \frac{k_3}{k_{3r}} = \frac{[DG][RO^-]}{[DG^-][ROH]}$$
$$K_5 = \frac{k_5}{k_{5r}} = \frac{[MG][RO^-]}{[MG^-][ROH]}$$
$$K_7 = \frac{k_7}{k_{7r}} = \frac{[G][RO^-]}{[G^-][ROH]}$$

(Equation 2-17)

The following balance equations also apply:

$$
\begin{aligned}
&TG + DG + MG + G = 1 \\
&ROH + E = 1 \\
&OH + A = p, \\
&p = \frac{[OH^-]_0}{[TG]_0} \\
&nE + 3TG + 2DG + MG + A = 3, \\
&n = \frac{[ROH]_0}{[TG]_0}
\end{aligned}
\qquad \text{(Equation 2-15)}
$$

There are four balance equations in Equation (2-18). The first keeps track of the glycerol backbone common to all the glycerides: TG, DG, MG, and G. Since this backbone is never destroyed, the sum of these chains must equal the initial amount, which in Komers' model is found solely in the triglyceride molecules. In the overall reaction, the alcohol molecules are only consumed to make alkyl esters. Thus, the second balance equation states that the sum of the alcohol molecules and the ester molecules must equal the original quantity of alcohol molecules. Similarly, the hydroxide ions are only consumed in the production of soap. Therefore, the number of hydroxide ions plus the number of soap molecules must equal the original amount of hydroxide ions, as indicated in the third balance equation. Finally, since fatty acid chains are not destroyed either, their total number is also constant, equal to three times the initial amount of triglyceride. The fourth balance equation enforces this condition. The ester variable, E, is multiplied by the initial molar ratio of alcohol to triglycerides in order place each nondimensional variable on the same scale.

The initial conditions are

$$
\begin{aligned}
&TG_0 = 1 \\
&ROH_0 = 1 \\
&OH_0 = p \\
&DG_0 = MG_0 = G_0 = E_0 = A_0 = 0
\end{aligned}
\qquad \text{(Equation 2-16)}
$$

Using equilibrium relations, Komers was able to develop an algebraic solution for the end product concentrations. Assuming that all reactions have reached equilibrium, we have the additional equilibrium equations

$$
\begin{aligned}
K_2 &= \frac{k_2}{k_{2r}} = \frac{[DG^-][E]}{[TG][RO^-]} \\
K_4 &= \frac{k_4}{k_{4r}} = \frac{[MG^-][E]}{[DG][RO^-]} \\
K_6 &= \frac{k_6}{k_{6r}} = \frac{[G^-][E]}{[MG][RO^-]}
\end{aligned}
\qquad \text{(Equation 2-17)}
$$

Combining with Equation (2-17), he defines the new equilibrium constants:

$$
\begin{aligned}
K_2' &= K_2 K_3 = \frac{[DG][E]}{[TG][ROH]} = \frac{DG \cdot E}{TG \cdot ROH} = \frac{k_2'}{k_{2r}'} \\
K_4' &= K_4 K_5 = \frac{[MG][E]}{[DG][ROH]} = \frac{MG \cdot E}{DG \cdot ROH} = \frac{k_4'}{k_{4r}'} \\
K_6' &= K_6 K_7 = \frac{[G][E]}{[MG][ROH]} = \frac{G \cdot E}{MG \cdot ROH} = \frac{k_6'}{k_{6r}'}
\end{aligned}
\qquad \text{(Equation 2-18)}
$$

This leads directly to

$$DG = K_2' \frac{1-E}{E} TG$$

$$MG = K_4' \frac{1-E}{E} DG = K_2' K_4' \left(\frac{1-E}{E} \right)^2 TG \qquad \text{(Equation 2-19)}$$

$$G = K_6' \frac{1-E}{E} MG = K_2' K_4' K_6' \left(\frac{1-E}{E} \right)^3 TG$$

Substituting (2-22) into the molecule balance for glycerol backbone (2-18) provides

$$TG = \frac{1}{1 + K_2' \left(\frac{1-E}{E} \right) + K_2' K_4' \left(\frac{1-E}{E} \right)^2 + K_2' K_4' K_6' \left(1 + K_6' \frac{1-E}{E} \right)^3} \qquad \text{(Equation 2-20)}$$

Finally, substituting (2-22) and (2-23) into the fatty acid molecule balance (2-18) gives the desired result:

$$n = \frac{1}{E} \left\{ 3 - \frac{3 + 2K_2' \left(\frac{1-E}{E} \right) + K_2' K_4' \left(\frac{1-E}{E} \right)^2}{1 + K_2' \left(\frac{1-E}{E} \right) + K_2' K_4' \left(\frac{1-E}{E} \right)^2 + K_2' K_4' K_6' \left(1 + K_6' \frac{1-E}{E} \right)^3} - p \right\}$$

(Equation 2-21)

Here we use -p instead of +p in the paper, which appears to have been a typographical error. The use of p, the molar ratio of hydroxide (catalyst) to triglyceride, reflects the assumption that all hydroxide will be converted to soaps.

For any choice of E and p, the evaluation of (2-24) establishes the amount of alcohol that is needed.

2.3 Analysis of prior work

There are two, complementary approaches to establishing a kinetic model for a given set of reactions. The first is empirical: take a lot of data and attempt to establish the order of the reaction. The second is theoretical: propose a set of mechanisms, and then derive the rate equations using the law of mass action.

In fact, both approaches are required to establish a predictive model. The best theory requires data to validate it, and a model based purely on fitting of empirical data cannot be used to predict outcomes outside of the range of experiment.

The early work by Freedman (Freedman 1984, 1986) has set the tone for much of the kinetics work to follow. There has been a great deal of fine laboratory work, with accompanying attempts to fit the data to simplistic models. As a result, the efforts to fit the experimental data have met with mixed success. Most papers suggest non-kinetic reasons, from heterogeneity to loss of polarity of catalyst, for these disparities.

Of the papers reviewed in the previous section, the work by Komers and colleagues contains the only serious attempt to establish the reaction mechanisms. The resulting rate equations are the only ones that treat the concentrations of hydroxide and water explicitly. They also are the only ones that explicitly consider the side saponification reactions. Komer claims to be able to predict the reactions with 78% probability, considering only kinetic factors.

It does seem worthwhile to get the kinetic model right before attempting to assess the contribution of non-kinetic effects. Also, since only Komer's model is parameterized

by reaction conditions, it appears to offer the best hope for a predictive model that will allow the evaluation of alternative reactor designs.

As part of this effort, a Fortran simulation has been written to assess Komer's model. The program solves the differential equations using fourth-order Runge-Kutta integration. After each integration step, the program checks for molecule balance of glycerol backbone and fatty acid chains, adjusting the state variables if these vary beyond a given threshold.

The first task was to simulate the experiment described in their paper. The test used an alcohol-to-triglyceride molar ration of 2.0233, and a catalyst-to-triglyceride molar ratio of 0.1225. The alcohol ratio is below the stoichiometric value of 3.

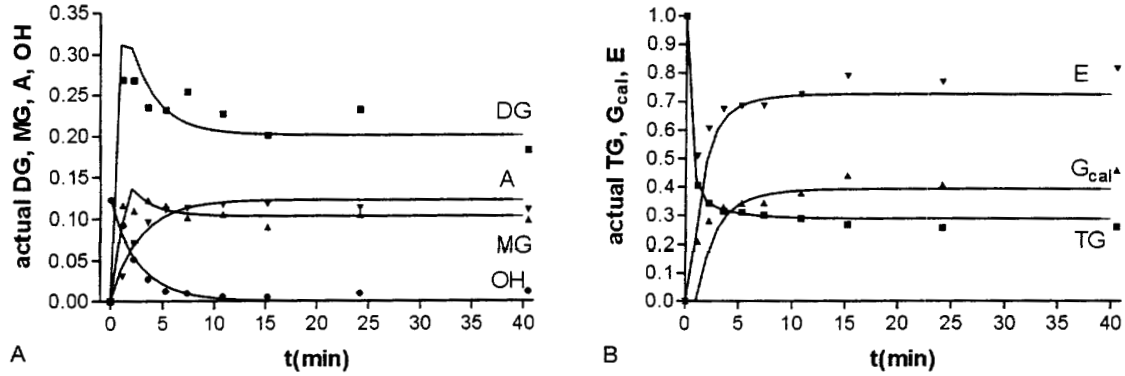


Fig. 1. Experiment No. 2 (n = 2.0233, p = 0.1225). Comparison of the theoretical dependences of actual relative concentrations TG, DG, MG, G_{cal}, E, A and OH *vs.* t , computed with the optimal combination of the rate constants (see Tab. 2, column 1), for this experiment by means of the program *Runge-Kutta* with optimization (full curves), with the experimental data (points), see [3], Tab. 2. S% = 16.3 %.

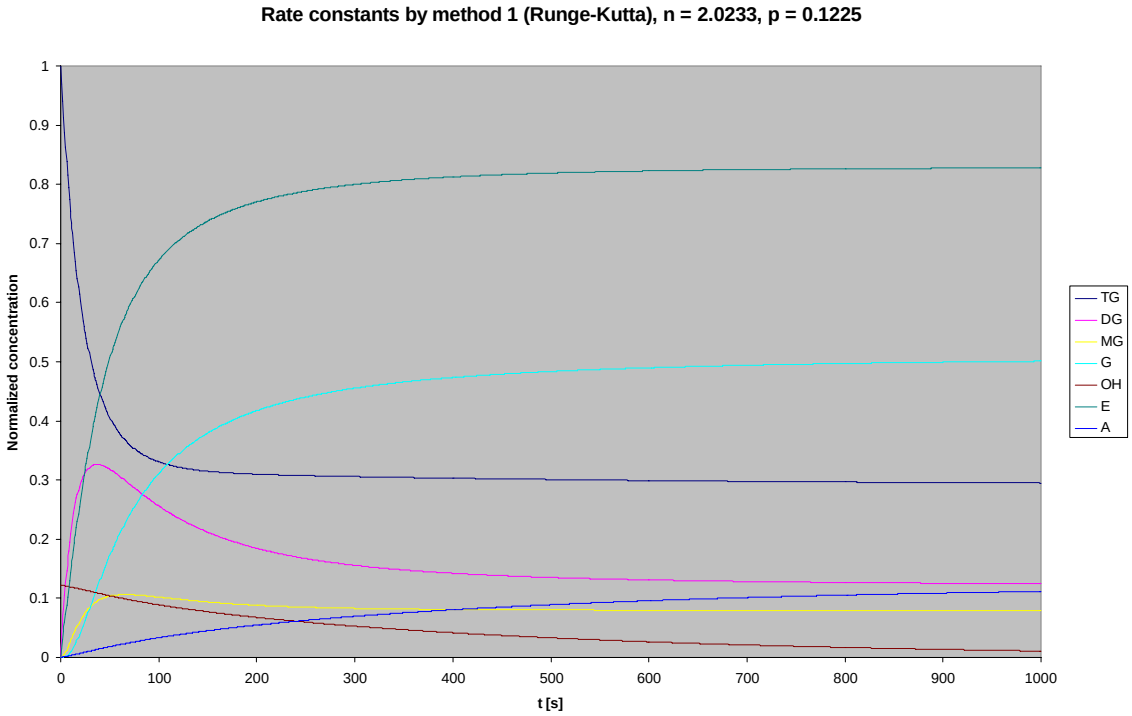
Figure 2-1. Experimental results from (Komers 2002)

Komers employed three different methods to determine the reaction rate constants. The values for the three methods are as follows:

Table 2-1. Reaction rate constants [$dm^3mol^{-1}min^{-1}$] by three different methods, from (Komers 2002).

Rate Constant	Method 1	Method 2	Method 3
k_2'	7.779	5.949	5.005
k_{2r}'	3.843	2.980	3.545
k_4'	8.594	9.399	4.929
k_{4r}'	2.528	7.311	2.987
k_6'	23.65	15.18	29.67
k_{6r}'	0.7029	0.6982	0.7932
k_8	0.0234	0.0133	0.127
k_9	0.1365	0.3436	0.194
k_{10}	0.3504	0.7474	0.3591
k_{11}	0.1925	0.4654	0.727

The simulations were run using the three sets of rate constants. The results of the kinetic simulation are shown in Figure 2-2. Based on the figure from Komers' paper, the best way to compare the three methods is by end concentrations. These can be seen in the table following the figures.



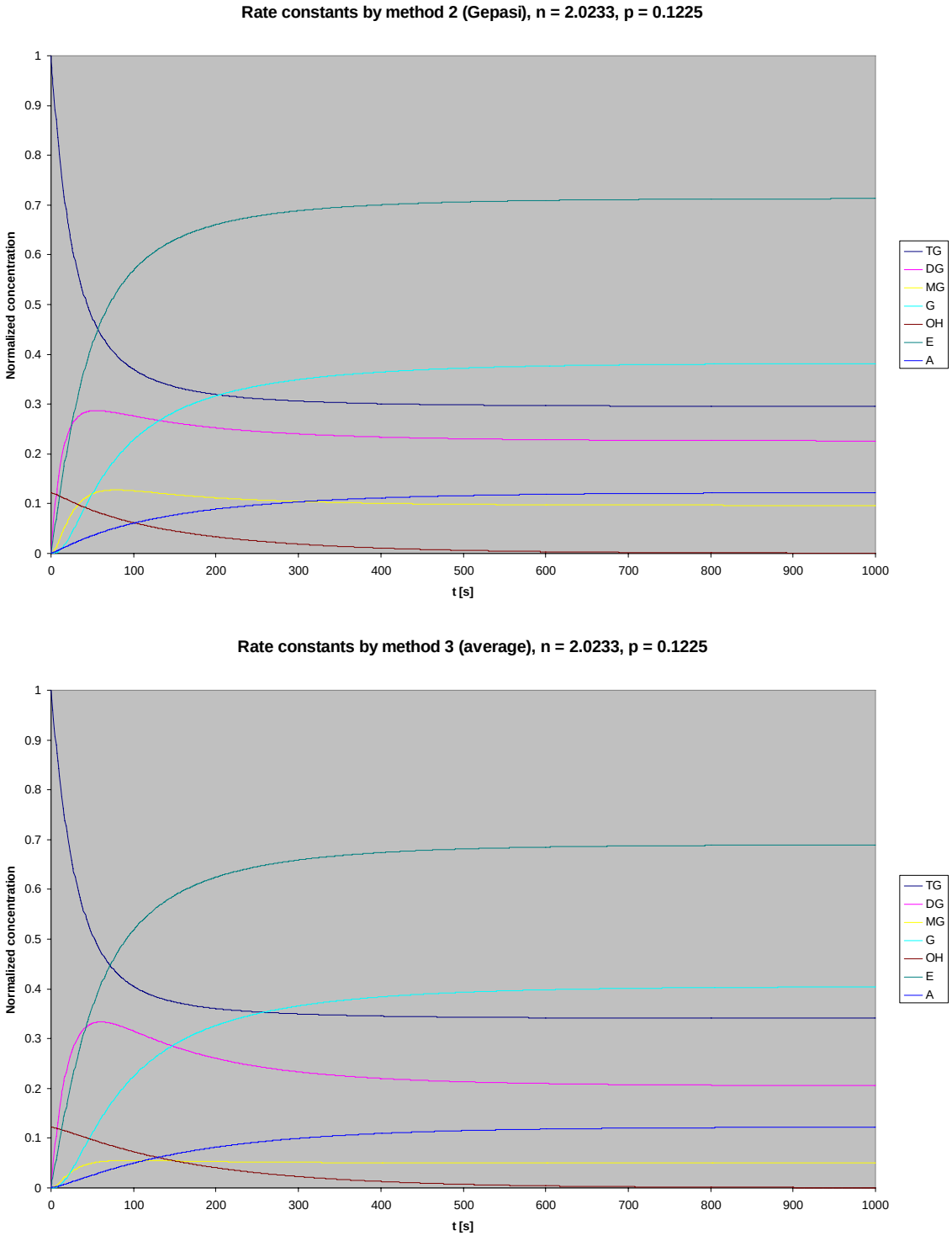


Figure 2-2. Simulation of Komers' experiment using rate constants determined by three different methods.

Table 2-2. Comparison of final concentrations by Komers and by simulation using Bodkin

Source	TG	DG	MG	G	E
Komers theoretical	0.30	0.21	0.10	0.39	0.72
Komers measured	0.28	0.20	0.10	0.40	0.8
Sim 1	0.295	0.125	0.080	0.501	0.828
Sim 2	0.296	0.226	0.097	0.382	0.713
Sim 3	0.341	0.206	0.050	0.404	0.689
Komers predicted by rate constants	0.328	0.186	0.0678	0.418	0.779
Komers predicted by average end values	0.358	0.132	0.060	0.456	0.740

The rate constants by method 2 give the best fit to both the experimental and the theoretical numbers from the paper. The last two rows show the predicted end values based on (2-24). In the upper row, the equilibrium constants were computed from the rate constants. In the lower row, the equilibrium constants were calculated by taking an average from the end values of the experiments. Interestingly, neither of these predictions matches any of these data particularly well.

This discrepancy was quite troubling at first, since one would expect a numerical simulation to reach the theoretical steady state values with only small errors. The problem is that the competing saponification reactions consume the catalyst required by the transesterification reactions, preventing these from achieving the predicted equilibrium state. To illustrate this point, two additional simulations were run using

fictitious saponification rates. In the first, the saponification rate constants were set to zero. In the second, the saponification rate constants were set to ten times their actual values. The results after 2000 seconds are tabulated below. The theoretical values are based on equilibrium constants based on the associated rate constants.

Table 2-3. Comparison of end concentrations by Komers' algebraic formula with simulated values using varying saponification rates.

Source	TG	DG	MG	G	E
Komers theoretical, p=0	0.3281	0.1856	0.0678	0.4182	0.7790
Komers theoretical, p=0.1225	0.2982	0.1791	0.0693	0.4533	0.7687
Simulation, zero saponification rate	0.3281	0.1859	0.0678	0.4182	0.7790
Simulation, actual saponification rate	0.2954	0.2260	0.0964	0.3823	0.7133
Simulation, 10x actual saponification rate	0.6518	0.2401	0.0776	0.0305	0.1800

With saponification turned off, the final concentration of soap is zero. Setting the value of p, the initial molar ratio of catalyst to triglycerides, to zero in (2-24) provides the correct prediction for this fictitious test case.

If saponification is the culprit, we would expect that the simulation run with saponification turned off should match the theoretical prediction with the amount of

catalyst set to zero, since both of these correspond to a zero-soap condition. In addition, if the rate of saponification is fictitiously increased in the model, we can expect the end concentrations to differ from the theoretical prediction even more so than with the actual saponification rates. This is indeed the case. The high amount of triglycerides, and low amounts of esters and glycerol vs. the prediction show that the extent of the reaction was greatly reduced in the case of high saponification rates. The saponification proceeded so quickly that there was no catalyst available for transesterification.

There are two possible explanations for the failure of the predictive equation (2-24). Either the transesterification reactions reach equilibrium in such a way that the forward and reverse reaction rate constants do not predict the final equilibrium constant, or else the reactions never reach equilibrium.

The second explanation is more plausible. First, it is hard to see why the end equilibrium constants should not be given by the ratio of the forward and backward reaction rate constants. Second, in order to achieve equilibrium, there must be a balance between the non-zero forward and reverse reaction rates.

While the transesterification reactions are proceeding, they are not in equilibrium. That would require that the transesterification reaction rates to be much faster than the rate-limiting saponification reactions, or

$$k_2, k_{2r}, k_4, k_{4r}, k_6, k_{6r} >> k_8, k_9, k_{10}, k_{11} \qquad \text{(Equation 2-22)}$$

Considering the rate constants from method 2, the smallest value on the left side of the inequality (2-25) is only four times larger than the largest value on the right side. As long as there is catalyst present, saponification is still taking place, and the transesterification reactions are not at equilibrium. Once virtually all the catalyst has been converted to soap, all the reaction rates approach zero. The transesterification reactions do not reach equilibrium because there is not enough activity forward and backward for the equilibrium balance to be achieved.

If condition (2-25) is only weakly met, then the predicted values will match the actual end concentrations only very approximately. This appears to be what is occurring with Komers' analysis.

3 PROPOSED EXTENSIONS TO KINETIC MODEL

Komer's model holds the promise of predicting the behavior of transesterification under varying conditions, such as temperature, choice of catalyst, choice of alcohol, molar ratio of catalyst to triglycerides, molar ratio of alcohol to triglycerides, overall water content, and non-zero initial concentrations of free fatty acids. This last item is important if waste vegetable oil is to be considered. As it stands, the existing model already addresses the choice of catalyst, molar ratio of catalyst to triglycerides, molar ratio of alcohol to triglycerides, and overall water content. The review in the previous section has already generalized Komer's model for various alcohols.

To this end, the following enhancements to Komer's model are proposed:

1. Re-cast the state variables so that all are non-dimensionalized by the same scale factor.
2. Generalize the model by relaxing certain of the model assumptions.
3. Determine all rate constants as a function of temperature
4. Determine rate constants for various alcohols
5. Consider possible limiting factors, such as transport, partitioning of catalyst, and reduced polarization of catalyst
6. Attempt to find an analytical solution for the end concentrations.

These enhancements are considered below.

3.1 Re-cast state variables

In Komer's model, most of the concentrations are scaled by the initial concentration of triglycerides in the reaction mixture. The variables for alcohol, alcoxide, and alkyl esters are scaled by the initial concentration of methanol in the reaction mixture. The

main advantage to the second scale factor is that the steady-state concentrations have a closed-form solution. The choice of scale factors is carefully considered so that the equilibrium balance equations apply to both the actual concentration values as well as the scaled values. However, the resulting formulation is not entirely intuitive. In particular, the concentration of alkyl esters scaled by the initial concentration of triglycerides in the reaction mixture does not provide any sense of the extent of conversion of the reaction.

Since the analytical prediction of end products is of limited use given real-world saponification rates, we propose to scale all concentration states by the same factor, the total concentration of bound and unbound glycerol in the reaction mixture.

Thus,

$$\begin{aligned} TG &= [TG]/a \\ DG &= [DG]/a \\ MG &= [MG]/a \\ G &= [G]/a \\ A &= [A]/a \\ OH &= [OH^-]/a \\ W &= [H_2O]/a \\ ROH &= [ROH]/a \\ E &= [E]/a, \\ a &= [TG]_0 + [DG]_0 + [MG]_0 + [G]_0 \end{aligned} \qquad \text{(Equation 3-1)}$$

The differential equations then take on the somewhat simpler form

$$
\begin{aligned}
-\frac{dTG}{dt} &= a \cdot OH \cdot (k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E + k_9 \cdot TG) \\
-\frac{dDG}{dt} &= a \cdot OH \cdot (-k_2' \cdot TG \cdot ROH + k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E \\
&\quad - k_9 \cdot TG + k_{10} \cdot DG) \\
-\frac{dMG}{dt} &= a \cdot OH \cdot (-k_4' \cdot DG \cdot ROH + k_{4r}' \cdot MG \cdot E + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E \\
&\quad - k_{10} \cdot DG + k_{11} \cdot MG) \\
\frac{dG}{dt} &= a \cdot OH \cdot (k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E + k_{11} \cdot MG) \\
-\frac{dROH}{dt} = \frac{dE}{dt} &= a \cdot OH \cdot (k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E \\
&\quad + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E - k_8 \cdot E) \\
-\frac{dOH}{dt} = \frac{dA}{dt} &= a \cdot OH \cdot (k_8 \cdot E + k_9 \cdot TG + k_{10} \cdot DG + k_{11} \cdot MG)
\end{aligned}
$$

(Equation 3-2)

The initial conditions are now

$$
\begin{aligned}
&TG_0 = \frac{[TG]_0}{a}, \\
&a = [TG]_0 + [DG]_0 + [MG]_0 + [G]_0 \\
&ROH_0 = \frac{[ROH]_0}{a} = n, \\
&OH_0 = \frac{[OH^-]_0}{a} = p, \\
&DG_0 = \frac{[DG]_0}{a}, MG_0 = \frac{[MG]_0}{a}, G_0 = \frac{[G]_0}{a}, E_0 = \frac{[E]_0}{a}, A_0 = \frac{[A]_0}{a}
\end{aligned}
$$

(Equation 3-3)

The initial value of ROH is simply the molar ratio of alcohol to triglycerides. The balance equations become

$$
\begin{aligned}
&TG + DG + MG + G = 1 \\
&ROH + E = n \\
&OH + A = p \\
&E + 3TG + 2DG + MG + A = d, \\
&d = E_0 + 3TG_0 + 2DG_0 + MG_0 + A_0
\end{aligned}
\qquad \text{(Equation 3-4)}
$$

It is hoped that this representation, while equivalent to the original, is a bit more intuitive. For example, under the new scheme, the variable E is the molar ratio of alkyl esters to the initial concentration of triglycerides in the reaction mixture. Since there are three fatty acid chains per triglyceride molecule, the percent yield is simply E/3.

3.2 Generalization of the model

If waste oil is used, then the participation of free fatty acids must be considered. The FFAs are saponified by the hydroxide ion. This is an undesired side reaction, which requires more catalyst to achieve the same reaction rate, resulting in production of more soap and water. The additional reaction is

$$FFA + OH^- \xrightarrow{k_{12}} A + W$$

The additional reaction has two consequences for the kinetic model. First, the rate equation for the destruction of hydroxide ion will require an additional, positive term,

$$a \cdot OH \cdot k_{12} \cdot FFA \text{, where } FFA = \frac{[FFA]}{a}$$

Second, since water is produced by the saponification of free fatty acids, the concentration of water can no longer be considered constant. An additional rate

equation is required for water, and the water concentration can no longer be lumped into the rate constants. The rate equation for water becomes

$$\frac{dW}{dt} = a \cdot OH \cdot k_{12} \cdot FFA$$

The new system of differential equations is

$$-\frac{dTG}{dt} = a \cdot OH \cdot \left(\frac{k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E}{W} + k_9 \cdot TG \right)$$

$$-\frac{dDG}{dt} = a \cdot OH \cdot \left(\begin{array}{l} \dfrac{-k_2' \cdot TG \cdot ROH + k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E}{W} \\ -k_9 \cdot TG + k_{10} \cdot DG \end{array} \right)$$

$$-\frac{dMG}{dt} = a \cdot OH \cdot \left(\begin{array}{l} \dfrac{-k_4' \cdot DG \cdot ROH + k_{4r}' \cdot MG \cdot E + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E}{W} \\ -k_{10} \cdot DG + k_{11} \cdot MG \end{array} \right)$$

$$\frac{dG}{dt} = a \cdot OH \cdot \left(\frac{k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E}{W} + k_{11} \cdot MG \right)$$

$$-\frac{dROH}{dt} = \frac{dE}{dt} = a \cdot OH \cdot \left(\begin{array}{l} \dfrac{k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E}{W} \\ \quad + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E \\ -k_8 \cdot E \end{array} \right)$$

$$-\frac{dOH}{dt} = \frac{dA}{dt} = a \cdot OH \cdot (k_8 \cdot E + k_9 \cdot TG + k_{10} \cdot DG + k_{11} \cdot MG + k_{12} \cdot FFA)$$

$$\frac{dW}{dt} = -\frac{dFFA}{dt} = a \cdot OH \cdot k_{12} \cdot FFA$$

where

$$k_2' = k_2 K_1$$
$$k_{2r}' = \frac{k_{2r} K_1}{K_3}$$
$$k_4' = k_4 K_1$$
$$k_{4r}' = \frac{k_{4r} K_1}{K_5}$$
$$k_6' = k_6 K$$
$$k_{6r}' = \frac{k_{6r} K_1}{K_7}$$

Written in this form, the differential equations clearly show that the rates of both alcoholysis and transesterification are proportional to the concentration of hydroxide ion, and that the rate of alcoholysis is also inversely proportional to the concentration of water. These dependencies also hold for Komer's original model, but there the concentration of water is lumped into aggregate rate constants.

The balance equations and initial conditions are as before:

$$TG + DG + MG + G = 1$$
$$ROH + E = n$$
$$OH + A = p$$
$$E + 3TG + 2DG + MG + A = d,$$
$$d = E_0 + 3TG_0 + 2DG_0 + MG_0 + A_0$$

$$TG_0 = \frac{[TG]_0}{a},$$
$$a = [TG]_0 + [DG]_0 + [MG]_0 + [G]_0$$
$$ROH_0 = \frac{[ROH]_0}{a} = n,$$
$$OH_0 = \frac{[OH^-]_0}{a} = p,$$
$$DG_0 = \frac{[DG]_0}{a}, MG_0 = \frac{[MG]_0}{a}, G_0 = \frac{[G]_0}{a}, E_0 = \frac{[E]_0}{a}, A_0 = \frac{[A]_0}{a}$$

3.3 Effect of temperature

To develop a predictive model, we must know the rate constants as a function of temperature for each alcohol and catalyst of interest. Komer's paper only provides the lumped constants for one particular test case. Since all his experiments were run at the same temperature, there is nothing to be learned about temperature dependencies from his data.

To establish the dependencies of rate constants on temperature will require further testing in a carefully designed experiment. Additionally, test data from prior research should be obtained, and reconciled with the new model.

While such endeavors are only speculative, it should be possible to estimate the temperature dependencies of the rate constants of the new model, based on prior research.

In general, the process of determining the temperature dependencies is straight-forward. One simply runs the same experiment several times at different temperatures, determining a set of rate constants k_i for each temperature. The Arrhenius equation relates reaction coefficients to temperature:

$$k = A\exp(-E_a / RT)$$

where

A is the Arrhenius pre-factor, and

E_a is the activation energy of the reaction.

Taking the log of both sides of the equation,

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

This equation is linear with respect to *1/T*. If *k* is determined for varying temperatures, the plot of *ln(k)* vs. *-1/RT* should produce a straight line of slope E_a.

For example, Ishchuk examined the affect of temperature on the saponification of trigycerides (Ishchuk 1992). Their data produced the following table:

Table 3-1. Saponification rate constants from (Ishchuk 1992) and derived values vs. temperature

T [K]	k	-1/RT	ln(k)
373	2.17	-0.001349106	7.7473E-01
383	9.82	-0.001313882	2.2844E+00
393	16.68	-0.00128045	2.8142E+00
403	63.98	-0.001248677	4.1586E+00
413	187	-0.001218442	5.2311E+00

Plotting of *ln(k)* vs. *-1/RT*, we obtain

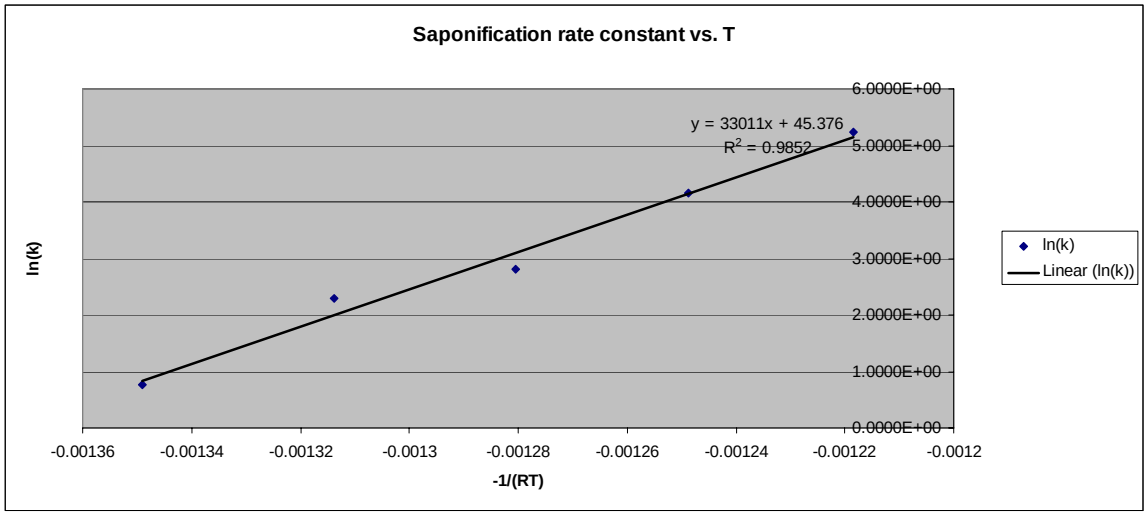


Figure 3-1. Determination of activation energy of saponification

The activation energy is 33011 cal/mol, the slope of the straight line fit to the data points. Once the activation energy is known, the Arrhenius pre-factor is given by

$$A = k \exp(E_a / RT)$$

It turns out that the activation energies for transesterification reported in the literature are fairly consistent, even where different orders of reaction are assumed. We can thus make use of these values as a first approximation to compute temperature dependencies for the transesterification rate constants.

With saponification, the answer is not so simple. Ishchuk's result is an overall rate dependency for all three steps. If we assign the same activation energy to the saponification rate constants in our model, we obtain the results shown in Table 3-2.

Table 3-2. First attempt at estimating temperature dependencies

R [cal/mol/K]	T [^{o}C], experiment	T [K]		
1.987215583	22.75	295.9		
Rate constant	**Value [L/mol s]**	**Activation energy [cal/mol]**	**Arrhenius pre-factor**	**source of Ea**
k2'	5.94900	13145	3.0409E+10	Noureddini
k2r'	2.98000	9932	6.4527E+07	Noureddini
k4'	9.39900	19860	4.3770E+15	Noureddini
k4r'	7.31100	14369	2.9961E+11	Noureddini
k6'	15.18000	6421	8.3880E+05	Noureddini
k6r'	0.69820	9588	8.4223E+06	Noureddini
k8	0.01330	0	1.3300E-02	neglect temp
k9	0.34360	33032	8.5569E+23	Ishchuk
k10	0.74740	33032	1.8613E+24	Ishchuk
k11	0.46540	33032	1.1590E+24	Ishchuk

Since the value of k8 is small relative to the other rate constants, we can neglect its dependency on temperature by setting the activation energy to zero.

If the temperature is raised to 50°C, the rate constants are variously affected as shown in Table 3-3.

Table 3-3. Predicted temperatures at 50°C based on first attempt.

Rate constant	k(22.75) [L/mol s]	k(50), predicted
k2'	5.9490	39.1859
k2r'	2.9800	12.3821
k4'	9.3990	162.1756
k4r'	7.3110	57.3977
k6'	15.1800	38.1223
k6r'	0.6982	2.7614
k8	0.0133	0.0133
k9	0.3436	39.2009
k10	0.7474	85.2700
k11	0.4654	53.0970

The first six constants are for transesterification; the last four are for saponification. Of the transesterification reaction constants, k4p sees the greatest change, by a factor of sixteen. In contrast, the saponification rates all change by a factor of more than 100. If this were the case, it would make no sense to heat the reaction, as most of the benefit would go to the saponification side.

It should be noted that Ishchuk's data was for saponification of triglycerides in a petroleum solvent. It seems likely that the kinetics are different in the presence of methanol. It would be dangerous to assume that Ishchuk's data can be used directly. As further evidence, he reports that saponification in petroleum takes four or five hours, while we know that saponification in methanol is complete in one hour.

Instead, we turn to a plot by Mittelbach showing the effect of temperature on final yield:

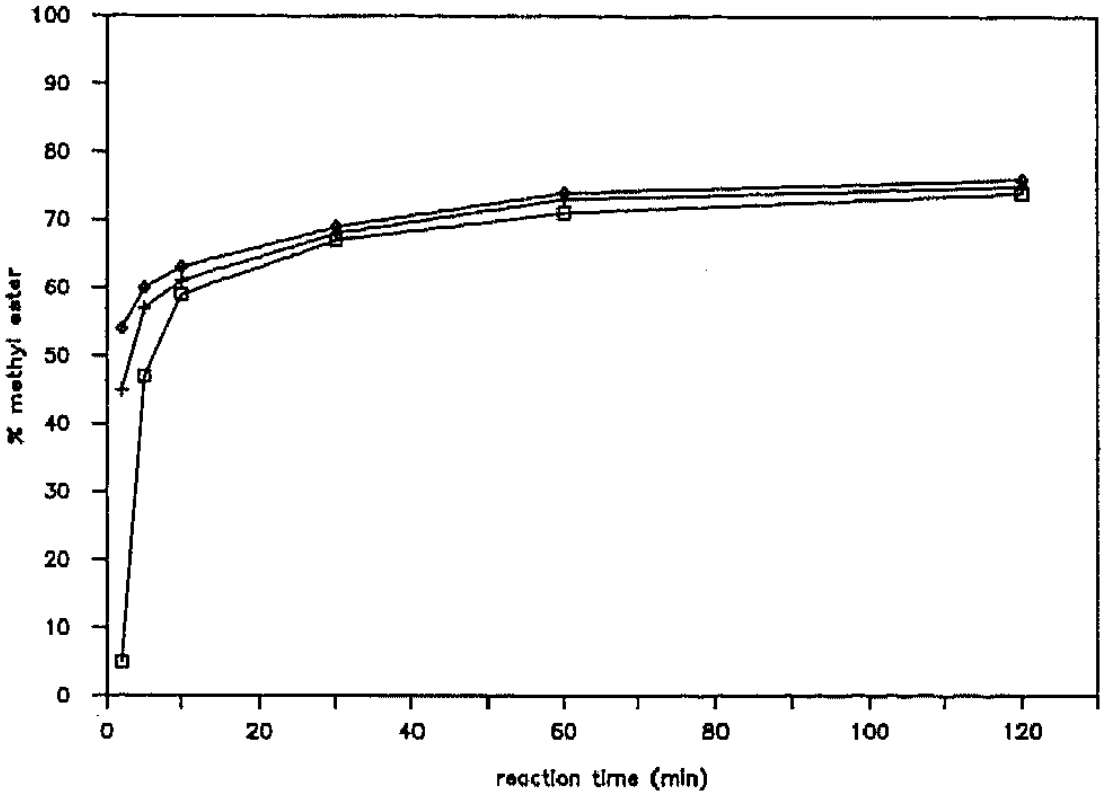


Fig. 4. Effect of temperature on methanolysis for a molar ratio of methanol : sunflower oil = 3 : 1, 0.5 % KOH
□ 25° C, + 40° C, ◇60° C

Figure 3-2. Temperature dependency from (Mittelbach 1990)

The methyl ester yields increase very slightly with temperature. This result can be expected if the changes in activation energies for saponification are slightly less than the corresponding activation energies for transesterification. To try to match Mittelbach's result, we assign values to the activation energies for saponification as follows:

$$E_{a,9} = E'_{a,2} - \Delta E$$
$$E_{a,10} = E'_{a,4} - \Delta E \qquad \text{(Equation 3-5)}$$
$$E_{a,11} = E'_{a,6} - \Delta E$$

Arriving at the value $\Delta E = 2000\ cal/mol$ by trial and error, we obtain the results shown in Table 3-4.

Table 3-4. Second attempt at estimating temperature dependencies

Rate constant	k(22.75) [L/mol s]	Activation energy [cal/mol]	Arrhenius pre-factor	source of Ea
k2'	5.9490	13145	3.0409E+10	Noureddini
k2r'	2.9800	9932	6.4527E+07	Noureddini
k4'	9.3990	19860	4.3770E+15	Noureddini
k4r'	7.3110	14369	2.9961E+11	Noureddini
k6'	15.1800	6421	8.3880E+05	Noureddini
k6r'	0.6982	9588	8.4223E+06	Noureddini
k8	0.0133	0	1.3300E-02	neglect temp
k9	0.3436	13045	1.4817E+09	Ea,k2p - 2000
k10	0.7474	19760	2.9362E+14	Ea,k4p - 2000
k11	0.4654	6321	2.1695E+04	Ea,k6p - 2000

At 50°C, the predicted rate constants in comparison to the base temperature of 22.75 are given Table 3-5.

Table 3-5. Predicted rate constants at 50°C based on second attempt

Rate constant	k(22.75) [L/mol s]	k(50), predicted
k2'	5.9490	39.1859
k2r'	2.9800	12.3821
k4'	9.3990	162.1756
k4r'	7.3110	57.3977
k6'	15.1800	38.1223
k6r'	0.6982	2.7614
k8	0.0133	0.0133
k9	0.3436	1.6989
k10	0.7474	9.6804
k11	0.4654	0.8773

Simulating Mittelbach's experiment at 25°C, 40°C, and 60°C, we obtain the following profiles for methyl esters:

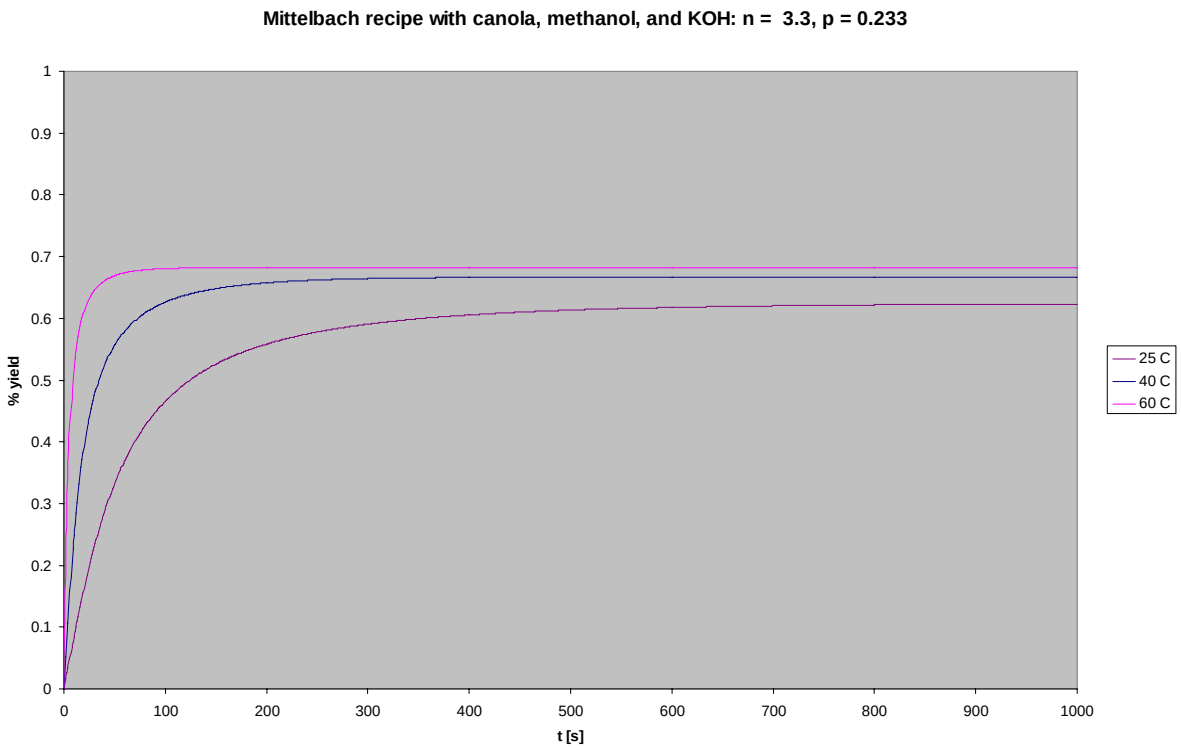


Figure 3-3. Simulation of experiment from (MIttelbach 1990)

After estimating the temperature dependencies using multiple sources, certain discrepancies remain. Noureddini's results show that the activation energies and the overall rate constants are higher for two of the reverse transesterification reactions than for the corresponding forward reactions. Using Noureddini's activation energies and Komer's rate constants, the derived temperature-dependent rate constants are higher in the forward direction than in the reverse direction at all temperatures of interest. We use Noureddini's activation energies on the assumption that the computation of activation energies is less prone to error.

If the activation energies for transesterification are incorrect, then our guess of the activation energies for saponification will also be wrong. The entire exercise is speculative in nature, but does provide our best estimates based upon current information.

In addition, it should be noted that the rates of reaction in the simulations are consistently higher than the plots found in the literature.

All of this bears further investigation. The only way to resolve these discrepancies appears to be to conduct a consistent set of experiments and measurements.

3.4 Limiting factors

All the previous authors have mentioned limiting factors to the kinetic model related to the heterogeneity of the reaction. The reaction begins as a two-phase system of methanol and triglycerides. After a few minutes of mixing, the system behaves as if it were a single phase. After products begin to form, it becomes a two-phase system again, this time with a biodiesel and a glycerol phase.

The factors to be considered are transport, partitioning, and polarization. In the initial two-phase system, the reaction is hampered by the inability of the reactant molecules to contact each other. This is a transport limitation. After products begin to form, the catalyst is drawn disproportionately to the glycerol phase, but it is needed in the biodiesel phase, where the remaining reactants are found. At this stage, transport and partitioning effects are involved. In addition, Booncock has hypothesized a reduced effectiveness of the catalyst due to reduced polarization.

Of the studies reviewed here, only the one by Noureddini and Zhu attempts to quantify the limiting factors. They ran experiments at different mixing intensities, as indicated by Reynolds number, then computed Arrhenius parameters for the rate constants for each mixing level.

The proper way to handle such effects in a predictive model is to apply effectiveness factors to each rate constant as appropriate. The effective rate constant is the product of the kinetic rate constant and its effectiveness factors. For example

$$k_{1,eff} = \eta_t \eta_p \eta_e k_1$$

The computation of the effectiveness factors can be as sophisticated as one desires.

It is an open question to what extent the effectiveness factors affect the reaction rate. Komers claims that his purely kinetic model predicts real-world behavior with a probability of 78%. He concedes that the remaining infidelities of the model may be due to the heterogeneity of the system.

4 POTENTIAL USES OF THE EXTENDED MODEL

The practical application of the model will be to aid the design of a fuel production process that optimizes the use of fuelstocks, reactants, and energy inputs. It will also allow the evaluation of alternative choices of alcohols and catalysts. The goal should be to produce a sustainable fuel as economically as possible. Some of the expected uses of the model are examined below. Where possible, the existing model based on (Komers 2002) is used to demonstrate the intended use.

4.1 Predicting the product yield

The problem is to find the final concentration of all reaction species under given reaction conditions, with specified relative amounts of catalyst and alcohol. A closed-form solution for the end product concentrations along the lines of Equation (2-24) has not been found. Currently, the method of choice is to run the simulation for a long enough time that the model states stop changing in value. As limiting factors are added to the model, it is likely that simulation will remain the most reliable method for computing yields, even if an analytical solution is found. This method has already been presented in Section 2.3.

4.2 Optimizing the amount of alcohol and catalyst

The model should help in the optimization of the reaction to achieve some criteria. For example, we may wish to maximize the per cent yield while minimizing the amount of methanol used.

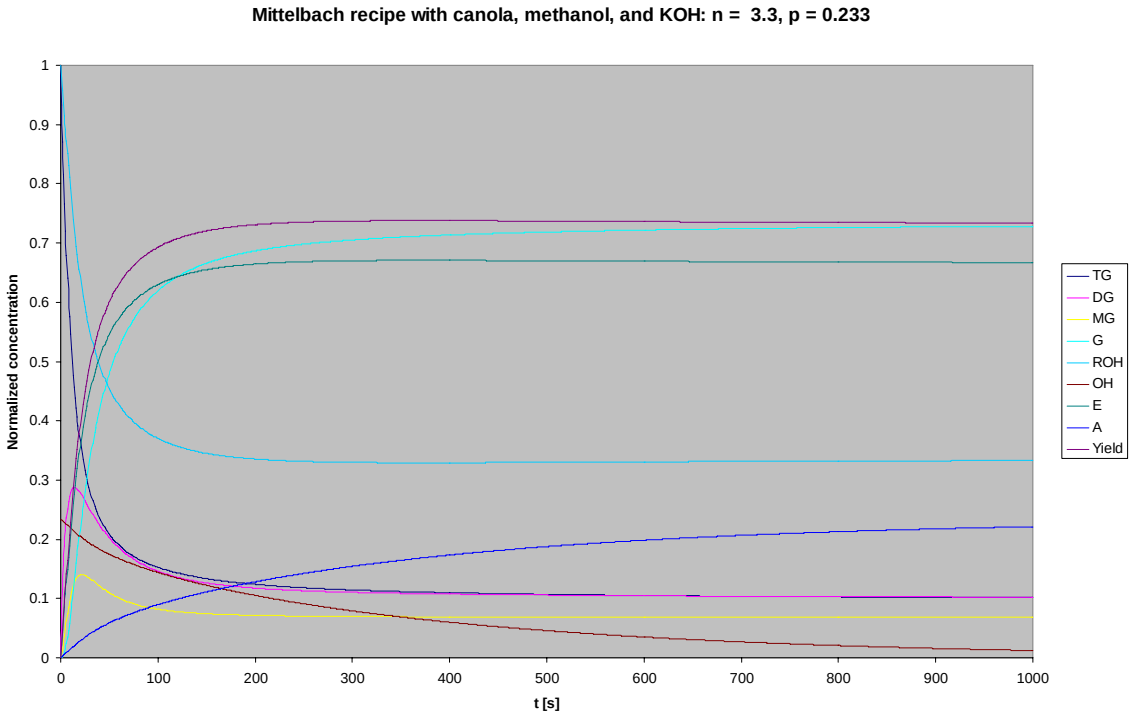
Here we show a comparison between two published recipes at room temperature. The first is from (Mittelbach 1990). His recommendation is to use 10% excess methanol, and 1.5 wt % catalyst. The second method is the standard recipe found on web sites, such as journeytoforever.org. It calls for 20 vol % methanol, with 4.9 g/L KOH for virgin oil.

Clearly, the first task is to express all the proportions as molar ratios. Conversions between wt %, vol %, and molar ratios are obtained through simple ratios involving the densities and average molecular weights of each substance. After establishing the molar ratios, both experiments were simulated for one hour.

The results are seen in Table 4-1 and Figure 4.1.

Table 4-1. Comparison between two biodiesel-making recipes.

Recipe	Standard	Mittelbach
n	4.699	3.300
p	0.084	0.233
TG	0.042	0.100
DG	0.058	0.101
MG	0.054	0.068
G	0.846	0.731
ROH	0.443	0.334
OH	0.000	0.000
E	0.558	0.666
A	0.084	0.233
Yield	0.873	0.732



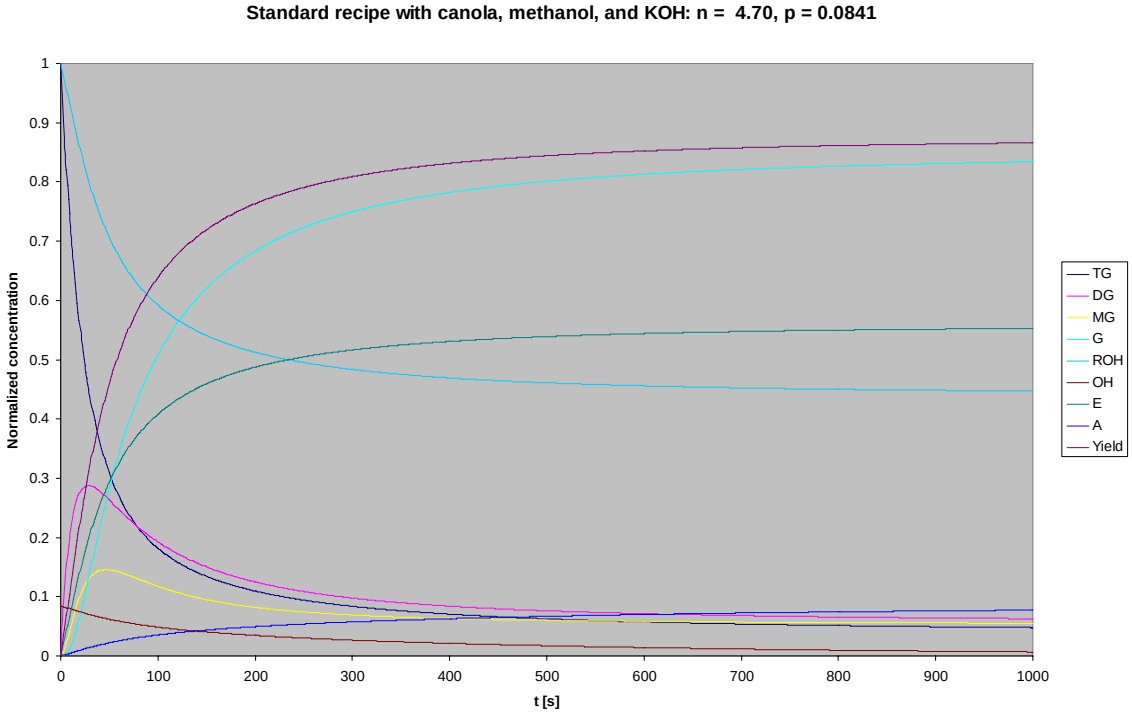


Figure 4-1. Comparison of two biodiesel-making recipes

The choice of recipe depends on what is to be optimized. Mittelbach's recipe minimizes the amount of alcohol required. Not only is the initial amount of alcohol lower than the standard recipe, but the amount of alcohol left over is only 33.4% versus 44.3% for the standard recipe. Although it is possible to recover the remaining methanol, the amount of time and energy required will be much lower with Mittelbach's recipe. Mittelbach also mentions that the separation of products is faster with lower alcohol.

The standard recipe has a higher % yield: 87.3% versus 73.2%. Since the amount of catalyst is lower, there is also less soap produced.

4.3 Designing the production process

The previous discussion assumes that the reaction takes place in a batch reactor. In the ideal case, all reactants are added to the vessel at the beginning, upon which the reaction takes place for some length of time, upon which the reaction products are removed from the vessel.

Of course, there are other reactor configurations, and other methods of mixing the reactants besides adding all ingredients at the outset. The kinetic model can help to determine the best reactor configuration, and the best control strategy.

The three basic types of chemical reactor are the batch reactor, the continuous stirred-tank reactor (CSTR), and the plug flow reactor (PFR).

In the CSTR, reactants are continuously added to the vessel while products are continuously removed. The contents of the vessel are at steady state, and the species concentrations are equal to the outlet concentrations.

In the PFR, the reaction occurs as it moves down a pipe. Assuming that there is no mixing between neighboring volumes, a differential volume within the pipe behaves like a tiny batch reactor. Thus, the reaction dynamics of the batch reactor and the PFR are similar.

For reversible reactions such as transesterification, the higher the concentration of products, the slower the reaction rate. Since the contents of the CSTR are always equal to the final product concentrations, the transesterification reaction will run slowly. From this standpoint, the batch reactor and the PFR are favored.

For irreversible reactions such as saponification, the reaction rate depends only on the concentrations of the reactants. Saponification will also run slower in the CSTR, due to the lower concentration of reactants.

The net result is that the CSTR requires a longer reaction time without providing any advantage for transesterification over saponification. In practice, only batch reactors and PFR's are used for biodiesel production (Peterson 2002).

Since the dynamics of the batch reactor and the PFR are similar, the entire discussion applies equally well to either type.

If one could continuously remove the products from the reactor, then a favorable balance of products and reactants would be maintained for esterification, while the saponification rate would decrease with the available supply of reactants. This scenario is not likely, since the two-phase reaction requires mixing, and separation of products is usually done by settling. It might be possible to place a centrifuge on a recirculation line, which would allow both mixing and separation to take place concurrently.

A simpler approach would be to conduct the reaction in a series of stages, with separation of products after each stage. To test this approach, a two-stage process can be simulated. If the same total amounts of catalyst and alcohol are used, then this approach can be compared directly with the one-stage process.

4.4 Predicting the effect of temperature

As mentioned earlier, temperature can be accounted for using the Arrhenius equation or the modified Arrhenius equation. In the previous section, we provided our best current estimate of the Arrhenius parameters. With the benefit of new experimental data, it should be possible to predict the effect of temperature for all temperatures of interest.

4.5 Predicting the effect of water

Bikou and colleagues examined the effect of water content on the equilibrium and rate constants for the three step reactions of transesterification. She used ethanol as the alcohol, and ran the reactions at the boiling point of ethanol (Bikou 1999). Judging from the data plots, the first two forward reaction rate constants and the first two

equilibrium constants all seem to vary with 1/W. The third forward rate constant seems to be independent of W, and the third equilibrium constant appears to vary exponentially with W.

It is difficult to extrapolate to Bikou's data, since a different alcohol and a much higher temperature were used. However, if the form of Komer's model is correct, and if there are few free fatty acids, then W, the amount of water in the reaction should remain constant. In that case, we would expect all of the rate constants to scale with 1/W, and all the equilibrium constants to be independent of W.

Komers and Bikou both show that the concentration of water has an adverse effect on the rates of reaction. However, the form of the dependency on water is quite different in the two papers. The goal should be to develop the model to the point that simulation can faithfully reproduce experimental results. That would provide some confidence that the model is sufficiently developed to represent the complexities of real reactions.

4.6 Simulation of prior results

A successful model should be able to simulate the experiments of other researchers, and reproduce their results within some margin. Vegetable oil is a mixture of many compounds, and there are many sources of oil. Thus, any two experiments will likely show considerable variation, and any simulation can only approximate the experimental conditions.

Therefore, the goal should be to reproduce the trends found in a particular experiment. Even this limited goal may not be achievable, since many of the experimental results are contradictory. Where this is the case, perhaps the model can lend support to one side or the other.

In the above paragraphs, we have shown that the model has general agreement with some of Mittelbach's results. It will be extremely interesting to investigate kinetic relationships found by other researcher's, such as Bikou's study on the effects of water on transesterification (Bikou 1999).

5 SUMMARY AND CONCLUSIONS

Chemical kinetics alone cannot completely describe the dynamics of reactions for biodiesel production. Clearly transport also plays a role, since the reactions themselves are heterogeneous. The tendency of the products to form emulsions has a considerable impact on the separation of products, if not the reaction rates themselves. Attention has been paid in the literature to these non-kinetic effects.

Most of the research on kinetics of biodiesel has focused on fitting empirical data to order-of-reaction types of models. Authors often cite non-kinetic effects to explain why the experiments do not fit the models.

In general, the amount of catalyst as a function of time and the effects of competing saponification reactions have not been considered. The notable exception is the work of Komers, in particular (Komers 2002), which builds a kinetic model from the ground up by considering all the possible reactions that can go forward, identifying chemical mechanisms, and simplifying the equations based on the rate-limiting step assumption. This model shows that all reaction rates are proportional to the amount of catalyst, which changes over time. The catalyst for transesterification is actually consumed in the competing saponification reactions. The simpler models, that do not treat the amount of catalyst explicitly, lump this term into the rate constants implicitly. Since the amount of catalyst diminishes over time, the lumped rate constants are in fact not constant at all.

The work by Komers (Komers 2002) also puts forward an analytical expression that can be used to predict the end concentrations of products. In this work, we argue that

the accuracy of the prediction is limited by the extent to which saponification competes with transesterification.

Komers' model also shows that the rates of esterification are inversely proportional to the concentration of water in the reaction. This result agrees with Bikou's experimental finding that water adversely affects ethanolysis reactions (Bikou 1999), but the form of the dependency is different in the two studies. It would be fascinating to resolve the differences between Komers' theoretical model, and Bikou's experimental result.

In this work, Komers' model has been extended in a number of ways, and other extensions have been proposed, with the aim of developing a predictive model to aid in the design of biodiesel production processes.

The mathematical model has been extended. After re-casting the state variables, the main change has been to relax Komers' assumptions about the initial concentrations of species. It is no longer assumed that there are no free fatty acids present, and neither is it assumed that all the glycerol resides initially in triglyceride molecules. These are not arbitrary changes. If waste vegetable oil is used in the reaction, then the concentration of free fatty acids can be significant. Also, if the production process contains multiple reactor stages, then all stages after the first will contain a mix of reactants and products.

Another extension is to include the effect of temperature. The method of deriving the Arrhenius constants to describe the dependence of rate constant is demonstrated in

the thesis by example. An attempt has been made to estimate the Arrhenius parameters based on experimental results in the literature. While hopefully better than simply ignoring the effect of temperature, a more precise definition of temperature dependencies must await the results of a carefully designed experiment for this purpose.

Experiments will also allow us to extend the model to include other alcohols besides methanol, and other catalysts.

Once the kinetic model has been extended, it will then make sense to try to quantify the non-kinetic effects. There is an established theory describing the effects of transport on the effective rates of reaction. Our hope is to quantify the effects of transport in terms of existing theory.

Also in this work, the model has been used to show the effect of different biodiesel recipes. The recipe favored by Mittelbach (Mittelbach 1990) minimizes the amount of methanol required. In comparison, the so-called standard recipe maximizes the product yield.

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7 APPENDICES

7.1 PROGRAM "BODKIN"

This program simulates the base-catalyzed transesterification reaction for biodiesel, using rate equations from (Komers 2002). The rate constants have been extended to account for the effect of temperature, using the Arrhenius equation. The program uses fourth-order Runge-Kutta integration. After each integration step, the program checks the balance of glycerol molecules and fatty acid molecules. If the balance equations are not met, a warning is issued. This problem can usually be solved by reducing the integration time step.

The program is written in Fortran. Apart from modern control structures, there is no attempt to take advantage of any advances in software design, such as object-oriented programming. The aim is to make the code understandable to readers with limited knowledge of programming.

```
program bodkin !BiODiesel KINetics

! This program simulates the base-catalyzed transesterification reaction
for biodiesel,
! using rate equations from (Komers 2002).  The rate constants have been
extended
! to account for the effect of temperature, using the Arrhenius equation.
!
! The program uses fourth-order Runge-Kutta integration.
! After each integration step, the program checks the balance of glycerol
molecules
! and fatty acid molecules.  If the balance equations are not met, a
warning is
! issued.  You can usually solve this problem by reducing the integration
time step.

implicit none

logical getDeriv   ! computes the derivatives.  defined below.
external getDeriv
```

```
logical rk4        ! runge-kutta integrator.  defined below.
logical modEuler   ! improved Euler integrator.  defined below.
logical checkBalance ! check atom balance for fatty acids, glycerol
backbone
logical controls   ! control the process

logical status

integer i, j, nStates, iPrint
integer luData
integer source
integer controlMode
real lastPrintTime, lastShoutTime

real densityTG, mwTG, densityROH, mwROH
real C_TG_pure, C_ROH_pure, C_TG_0, C_ROH_0, C_KOH_0

real a ! [TG]0
real b ! [ROH]0
real c ! [KOH]0

real p ! c/a
real n ! b/a

common /params/ a, b, c, n, p

real R, Temperature

real k(11), Arrh(11), Ea(11)

data Arrh / 3.0409e10, 6.4527e7, 4.3770e15, 2.9961e11, 8.3880e5, 8.4223e6,
0.0133, 5.8542e7, 1.1601e13, 8.57170e2 /
data Ea /   13145.,    9932.,    19860.,    14369.,    6421.,    9588.,
0.,     11145.,   17860.,    4421     /

real k2p, k2rp, k4p, k4rp, k6p, k6rp, k8 , k9, k10, k11
common /rc/ k2p, k2rp, k4p, k4rp, k6p, k6rp, k8 , k9, k10, k11

real Keq1, Keq2, Keq3, Keq4, Keq5, Keq6, Keq7
real X, W

real state(6)
real deriv(6)

real sum

real TG, TGdot, DG, DGdot, MG, MGdot, ROH, ROHdot, OH, OHdot, E, G, Gdot
real E

real time, delta, endTime
integer nSteps, nStages
real reserve

luData = 11

open (unit=luData, file='data/biodiesel.dat', status='replace')
```

```
write(*,*) 'Choose Temperature mode.'
write(*,*) '1  Select rate constants from various methods, all at 22.75 C'
write(*,*) '2  Select temperature.  Use Gepasi rate constants'

write(*,*) 'Choose temperature mode: '
read(*,*) source
write(*,*) 'Source = ', source

if (source .eq. 1) then
      write(*,*) 'Choose source of rate coefficients.'
      write(*,*) '1  Runge-Kutta data fit'
      write(*,*) '2  Gepasi data fit'
      write(*,*) '3  average values from 14 experiments'
      write(*,*) '4  Gepasi data fit with fictitious, fast soap-making'
      write(*,*) '5  Gepasi data fit with fictitious, zero soap-making'

      write(*,*) 'Choose source: '
      read(*,*) source
      write(*,*) 'Source = ', source

      if (source .eq. 1) then
            k2p  =  7.779 / 60.
            k2rp =  3.843 / 60.
            k4p  =  8.594 / 60.
            k4rp =  2.528 / 60.
            k6p  = 23.65 / 60.
            k6rp =  0.7029 / 60.
            k8   =  0.0234 / 60.
            k9   =  0.1365 / 60.
            k10  =  0.3504 / 60.
            k11  =  0.1925 / 60.
      else if (source .eq. 2) then
            k2p  =  5.949 / 60.
            k2rp =  2.980 / 60.
            k4p  =  9.399 / 60.
            k4rp =  7.311 / 60.
            k6p  = 15.18 / 60.
            k6rp =  0.6982 / 60.
            k8   =  0.0133 / 60.
            k9   =  0.3436 / 60.
            k10  =  0.7474 / 60.
            k11  =  0.4654 / 60.
      else if (source .eq. 3) then
            k2p  =  5.005 / 60.
            k2rp =  3.545 / 60.
            k4p  =  4.929 / 60.
            k4rp =  2.987 / 60.
            k6p  = 29.67 / 60.
            k6rp =  0.7932 / 60.
            k8   =  0.127 / 60.
            k9   =  0.194 / 60.
            k10  =  0.3591 / 60.
            k11  =  0.727 / 60.
      else if (source .eq. 4) then
            k2p  =  5.949 / 60.
            k2rp =  2.980 / 60.
            k4p  =  9.399 / 60.
```

```
            k4rp =  7.311 / 60.
            k6p  = 15.18 / 60.
            k6rp =  0.6982 / 60.
            k8   =  0.133 / 60.
            k9   =  3.436 / 60.
            k10  =  7.474 / 60.
            k11  =  4.654 / 60.
      else if (source .eq. 5) then
            k2p  =  5.949 / 60.
            k2rp =  2.980 / 60.
            k4p  =  9.399 / 60.
            k4rp =  7.311 / 60.
            k6p  = 15.18 / 60.
            k6rp =  0.6982 / 60.
            k8   =  0.
            k9   =  0.
            k10  =  0.
            k11  =  0.
      else
            write(*,*) 'Source value of ', source, 'is not valid.
exiting.'
            stop
      endif

else if (source .eq. 2) then

      write (*,*) 'Specify reaction temperature in degrees Celsius:'
      read (*,*) temperature

      temperature = temperature + 273.15

      R = 1.9872

      do i = 1, 10

            k(i) = Arrh(i)*exp(-Ea(i)/R/temperature)/60

      end do

      k2p = k(1)
      k2rp = k(2)
      k4p = k(3)
      k4rp = k(4)
      k6p = k(5)
      k6rp = k(6)
      k8 = k(7)
      k9 = k(8)
      k10 = k(9)
      k11 = k(10)

end if

write(*,*) 'rate constants are: ', k2p*60, k2rp*60, k4p*60, k4rp*60,
k6p*60, k6rp*60, k8*60, k9*60, k10*60, k11*60

write (*,*) 'Specify molar ratio of alcohol to TG: '
read (*,*) n
```

```
write (*,*) 'Specify molar ratio of catalyst to TG: '
read (*,*) p

densityTG = 0.925 ! soy
mwTG = 882.82 ! soy

densityTG = 0.914 ! canola
mwTG = 880.3 ! canola (Mittelbach)

densityROH = 0.791 ! methanol
mwROH = 32.04 ! methanol

C_TG_pure = densityTG/mwTG*1000
C_ROH_pure = densityROH/mwROH*1000

C_TG_0 = C_ROH_pure*C_TG_pure/(C_ROH_pure + n*C_TG_pure)
C_ROH_0 = n*C_TG_0
C_KOH_0 = p*C_TG_0

! write(*,*) 'C_TG_pure, C_ROH_pure, C_TG_0, C_ROH_0, C_KOH_0:',
C_TG_pure, C_ROH_pure, C_TG_0, C_ROH_0, C_KOH_0

a = C_TG_0
b = C_ROH_0
c = C_KOH_0

nStates = 6

state(1) = 1.0
state(2) = 0.
state(3) = 0.
state(4) = 0.
state(5) = 1.0
state(6) = p

time = 0.0
delta = 1.0

write(*,*) 'Specify end time in seconds: '
read(*,*) endTime

write(*,*) 'Specify integration time step in seconds: '
read(*,*) delta

nSteps = endTime/delta

write(*,*) 'Specify number of stages: '
read(*,*) nStages

write(*,'(7f10.5)') time, (state(j), j = 1, nStates)
write(luData,'(7f10.5)') time, (state(j), j = 1, nStates)

lastPrintTime = 0.0
lastShoutTime = 0.0

do i = 1, nSteps
```

```
    ! status = controls (state, n, p, time, controlMode)

    time = time + delta

    status = rk4 (state, getDeriv, nStates, delta)

      status = checkBalance (state, n, p)

    if ((time - lastPrintTime) .ge. 0.999) then

            lastPrintTime = time
            write(luData,'(7f10.5)') time, (state(j), j = 1, nStates)

    end if

    if ((time - lastShoutTime) .ge. 59.999) then

            lastShoutTime = time
            write(*,'(7f10.5)') time, (state(j), j = 1, nStates)

    end if

end do

close (luData)

stop
end

logical function getDeriv(state, deriv)
implicit none

    real a, b, c, n, p
    common /params/ a, b, c, n, p

    logical first

    real state(6)
    real deriv(6)

    real TG, TGdot, DG, DGdot, MG, MGdot, ROH, ROHdot, OH, OHdot, E, G,
Gdot
    real E

    real k2p, k2rp, k4p, k4rp, k6p, k6rp, k8 , k9, k10, k11
    common /rc/ k2p, k2rp, k4p, k4rp, k6p, k6rp, k8 , k9, k10, k11

    ! switch names
    TG = state(1)
    DG = state(2)
    MG = state(3)
    G  = state(4)
    ROH  = state(5)
    OH = state(6)

    E = 1. - ROH
```

```
    ! evaluate state rates
    TGdot = -(b*OH*(k2p*TG*ROH - k2rp*DG*E) + a*OH*k9*TG)

    DGdot = -(b*OH*(-k2p*TG*ROH + k2rp*DG*E + k4p*DG*ROH -k4rp*MG*E) + &
              a*OH*(k10*DG - k9*TG))

    MGdot = -(b*OH*(-k4p*DG*ROH + k4rp*MG*E + k6p*MG*ROH - k6rp*G*E) + &
              a*OH*(k11*MG - k10*DG))

    Gdot = b*OH*(k6p*MG*ROH - k6rp*G*E) + a*OH*k11*MG

    ROHdot = -a*OH*(k2p*TG*ROH - k2rp*DG*E +k4p*DG*ROH - k4rp*MG*E + &
                    k6p*MG*ROH - k6rp*G*E -k8*E)

    OHdot = -(b*OH*k8*E +a*OH*(k9*TG + k10*DG + k11*MG))


    deriv(1) = TGdot
    deriv(2) = DGdot
    deriv(3) = MGdot
    deriv(4) = Gdot
    deriv(5) = ROHdot
    deriv(6) = OHdot

    getDeriv = .true.

    return
    end

logical function rk4 (state, getDeriv, n, delta)
integer n
real state(n), newState(n)
logical getDeriv
external getDeriv
real delta

real f1(n), f2(n), f3(n), f4(n), f
logical status

status = getDeriv(state, f1)

do i = 1, n

    newState(i) = state(i) + f1(i)*delta/2.0

end do

status = getDeriv(newState, f2)

do i = 1, n

    newState(i) = state(i) + f2(i)*delta/2.0

end do

status = getDeriv (newState, f3)
```

```
do i = 1, n

    newState(i) = state(i) +f3(i)*delta

end do

status = getDeriv (newState, f4)

do i = 1, n

    f = (f1(i) + 2.0*f2(i) + 2.0*f3(i) + f4(i)) / 6.0
    state(i) = state(i) + f*delta

end do

rk4 = .true.

return
end

logical function modEuler (state, getDeriv, n, delta)
integer n
real state(n), newState(3)
logical getDeriv
external getDeriv
real delta

real f1(n), f2(n), f3(n), f4(n), f
logical status

status = getDeriv(state, f1)

do i = 1, n

    newState(i) = state(i) + f1(i)*delta/2.0

end do

status = getDeriv(newState, f2)

do i = 1, n

    f = (f1(i) + f2(i)) / 2.0
    state(i) = state(i) + f*delta

end do

modEuler = .true.

return
end

logical function checkBalance (state, n, p)
implicit none
real state(6)
real n, p
```

```
      real sum
      integer j

      ! enforce the balance of glycerol backbone
      sum = state(1) + state(2) + state(3) + state(4) ! should equal one

      if (abs(sum - 1.0) .gt. 1.e-3) then

            write (*,*) 'warning: glycerol sum = ', sum

            do j = 1, 4

                  state(j) = state(j) / sum

            end do

      end if

      ! check the fatty acid balance
      sum = n*(1.0 - state(5)) + 3.0*state(1) + 2.0*state(2) + state(3) +
(p - state(6))

      if (abs(sum - 3.0)/3 .gt. 1.e-3) then

            write (*,*) 'warning: FA sum = ', sum
            write (*,*) 'n, p: ', n, p

      endif

      checkBalance = .true.

      return

end
```