



A Computer-Controlled Biodiesel Experiment

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Abstract

In this poster we describe a new computer-controlled, base-catalyzed transesterification experiment to produce biodiesel from vegetable oil that we have implemented in our unit operations laboratory. The main educational goal of the experiment is to measure the reaction kinetics at several temperatures and evaluate the activation energy of the reaction. Using a computer control panel to operate the process that is contained in a hood gives it the feel of a larger scale industrial process and minimizes some of the dangers from the hazardous and flammable materials involved. The new experiment provides experience with an industrially relevant, “green” technology and affords us a chance to reinforce safety concepts and provide experience with standard operating procedures and electronic batch records.

Introduction

Renewable fuels such as biodiesel are becoming increasingly popular alternatives to petroleum based fuels. Vegetable oil can be burned directly, but is not a good engine fuel due to its high viscosity. Transesterification converts the high viscosity oil into 3 biodiesel molecules with viscosity and other properties similar to those of petroleum diesel fuel¹. The overall reaction for production of biodiesel from vegetable oil is



Vegetable oil is primarily composed of triglycerides with long chain aliphatic groups of the form $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$, but different types of oils have different amounts of saturated and unsaturated fats of various types². The methyl esters, also called fatty acid methyl esters (FAMEs), are the biodiesel product we seek. The reaction can be either base-catalyzed or acid-catalyzed.

The apparent simplicity of the process along with the readily available supply of waste vegetable oil from deep fry food preparation has given rise to a large number of small scale and “home brew” processors who usually use potassium hydroxide as catalyst. This base-catalyzed biodiesel process is neither particularly simple nor particularly safe, however. Methanol is both poisonous and highly flammable. KOH is caustic and when mixed with methanol forms an extremely dangerous potassium methoxide solution. A web search on accidents involving this reaction readily turns up news reports on fires at homes, barns, and industrial sites. Despite the enthusiasm of the four undergraduate student authors for developing a “green” experiment as their senior thesis, these safety concerns made us hesitant to introduce the process in an

undergraduate lab. Ultimately, the recent ABET emphasis on teaching safety convinced us to make safety a feature of the new lab exercise we developed.

The first objective for a pre-lab exercise for this experiment is, therefore, to obtain and read the MSDS information for KOH, methanol, and potassium methoxide. Students are asked to write a brief discussion of the safety precautions required for handling and processing these materials and the safeguards we have included in the lab. The second objective for the pre-lab is to locate (on the web or elsewhere) a report of an accident involving a fire with this process. Students are asked to write a brief summary of the accident and a discussion of what could have been done to prevent it.

The third objective of the pre-lab is to understand the theory presented below and show how results for glycerol concentration as a function of time can be used to obtain coefficients for an approximate rate expression. The final objective of the pre-lab exercise is for students to explain how they plan to use the equipment described below to study the temperature dependence and evaluate the activation energy for conversion of canola oil to biodiesel with 0.5 weight % KOH and 6:1 methanol to oil ratio.

In the lab, student groups use a computer-controlled mini pilot plant to run the reaction safely at several different temperatures. They collect samples from the reactor at specified times and later analyze them for glycerol content. Fitting the glycerol results to a pseudo 2nd order rate equation at three different temperatures allows them to estimate the activation energy for the reaction as explained below.

Theory

As noted above, biodiesel production is more complex than it may seem. It has been observed that the production process depends on the type of oil used, the water and free fatty acid content of the oil, the type and amount of catalyst, the alcohol to oil ratio, and operating conditions such as temperature, pressure, and mixing rate^{3,4}. The reaction is believed to involve multiple steps



where it can be seen that triglyceride (TG) is first attacked by the methoxide ion CH_3O^- (present in the basic KOH/methanol solution) to produce one biodiesel (BD) and a di-glyceride (DG). The DG is next converted to a second BD and a mono-glyceride (MG). Finally, in a third reaction step, the MG is converted to a third BD and glycerol (G). Each of these reactions can be considered reversible, giving rise to a forward and a reverse rate constant for each of the three reactions. Side reactions that produce soap (via saponification) instead of biodiesel often occur, especially if water is present in the mixture, but we neglect side reactions in our analysis. To

complicate matters further, methanol and oil are essentially insoluble in one another, requiring good stirring to bring them into contact. The reaction mixture begins as two phases, then goes to one phase, and finally back to two phases because the glycerol and biodiesel are also essentially insoluble in one another. This has caused many researchers to believe that the reaction cannot be properly modeled without understanding the phase behavior and droplet size changes that occur during the course of the reaction^{5,6}. Others have shown that in cases with sufficient stirring, experimental data can be modeled using only the reversible reactions of Equations 2 - 4.

For example, Vicente et al.⁷ studied base-catalyzed transesterification of sunflower oil with 6:1 mole ratio of methanol to oil and stirring rates that they believed were sufficient to avoid mass transfer limitations. They varied the KOH catalyst concentration and the process temperature and measured the concentration of TG, DG, MG, BD, M, and G with time during the reaction. Assuming that the forward rate constants for reactions 1, 2, and 3 are given by k_1 , k_3 , and k_5 , while the reverse rate constants for the three reactions are given by k_2 , k_4 , and k_6 , they found the values of the rate constants that fit their data according to the mathematical model shown in Figure 1.

$$\begin{aligned}
 TG(0) &= TG_0 & M(0) &= M_0 & DG(0) &= MG(0) = BD(0) = G(0) = 0 \\
 TG'(t) &= -k_1 \cdot TG(t) \cdot M(t) + k_2 \cdot BD(t) \cdot DG(t) \\
 DG'(t) &= k_1 \cdot TG(t) \cdot M(t) - k_2 \cdot BD(t) \cdot DG(t) - k_3 \cdot DG(t) \cdot M(t) + k_4 \cdot BD(t) \cdot MG(t) \\
 MG'(t) &= k_3 \cdot DG(t) - k_4 \cdot BD(t) \cdot MG(t) - k_5 \cdot MG(t) \cdot M(t) \\
 M'(t) &= -k_1 \cdot TG(t) \cdot M(t) + k_2 \cdot BD(t) \cdot DG(t) - k_3 \cdot DG(t) \cdot M(t) + k_4 \cdot BD(t) \cdot MG(t) - k_5 \cdot MG(t) \cdot M(t) \\
 BD'(t) &= k_1 \cdot TG(t) \cdot M(t) - k_2 \cdot BD(t) \cdot DG(t) + k_3 \cdot DG(t) \cdot M(t) - k_4 \cdot BD(t) \cdot MG(t) + k_5 \cdot MG(t) \cdot M(t) \\
 G'(t) &= k_5 \cdot MG(t) \cdot M(t)
 \end{aligned}$$

Figure 1. Mathematical model equations for multistep biodiesel reaction.

Note that in Figure 1, the symbol $TG'(t)$ represents the time derivative of the triglyceride concentration, $dTG(t)/dt$. At 35 °C and 0.5 weight percent KOH (on a percent weight of oil basis) they found the following rate constants with units of L/(mol min): $k_1 = 0.20$, $k_2 = 0.98$, $k_3 = 1.67$, $k_4 = 2.18$, $k_5 = 0.27$, and $k_6 = 0.01$ (sufficiently small that it has been omitted in the model). Our students are presented with a Mathcad file that solves this model and provides graphical and tabular results for the concentration of all components as a function of time, starting with 1 mol/L of TG and 6 mol/L of M.

To minimize cost, our studies use canola oil from a local grocery rather than sunflower oil, and we only follow overall reaction conversion by following the glycerol concentration with time. It is not possible to fit all six rate constants from our experimental data. Fortunately, some researchers have suggested that it is advantageous to consider the reaction in three stages: a brief initial mixing/mass transfer limited stage (which diminishes with increasing temperature), an

irreversible chemical reaction controlled stage, and a reversible equilibrium reaction controlled stage near the end⁸. These authors have further suggested that the pseudo 2nd order reaction:

$$O'(t) = -k \cdot O(t)^2 \quad (5)$$

provides an approximate model for the overall reaction, at least in the middle stage. The symbol, O for total oil (TG, DG, and MG) is used instead of TG here since we are not able to follow the intermediate species.

As part of their pre-lab work, our students are asked to test this hypothesis using the Mathcad model of the reaction at 35 °C. That is, they are asked to use the multistep model results for concentration with time to test if a pseudo 2nd order model could fit those results and determine the pseudo 2nd order rate constant, k.

Students should know (or consult a reaction engineering text about) how to test for a 2nd order rate law by plotting 1/O versus t as shown in Figure 2. For a 2nd order reaction, the slope should equal the rate constant and the intercept should be the reciprocal of the initial oil concentration as shown. Since the intercept at time zero equals 1/(1 mol/L), there does not appear to be an appreciable mass transfer limited stage in this case.

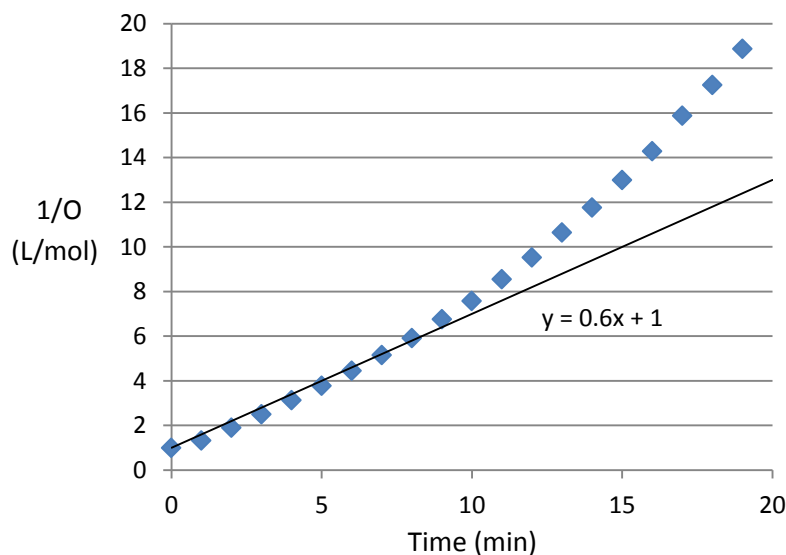


Figure 2. Expected results for students plotting 1/O versus t to obtain 2nd order rate constant.

Using the rate constant of 0.6 L/(mol min) obtained from Figure 2, students should be able to generate a comparison of the multistep model (the data they were given) and the approximate pseudo 2nd order model as shown in Figure 3. Although the 2nd order model appears to be only approximately valid at early times according to Figure 2, it can be seen in Figure 3 that it provides a reasonable approximation to the more complex multistep model over the course of the reaction.

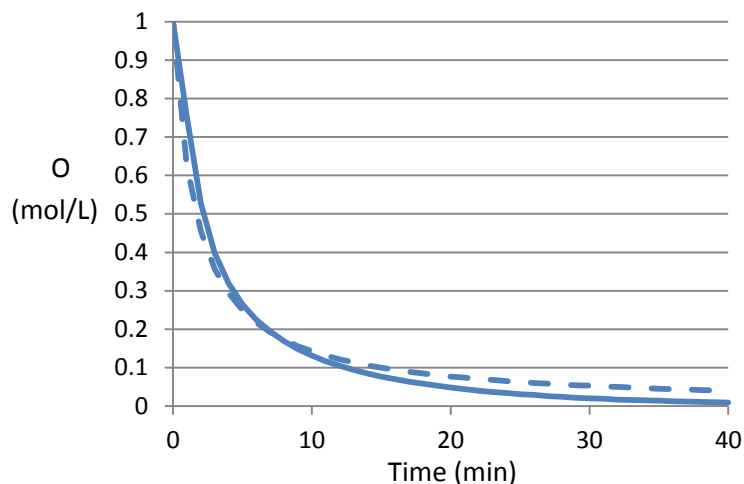


Figure 3. Comparison of oil concentration as a function of time with the multistep reaction model (solid) and psuedo 2nd order model (dashed).

For convenience, students are also provided with Table 1 showing the densities and molecular weights for reactants and products they will study.

Table 1. Densities and molecular weights of canola biodiesel reactants and products⁹.

component	density (g/ml)	molecular weight (g/mol)
canola oil	0.92	887.3
methanol	0.792	32.0
glycerol	1.26	92.1
biodiesel	0.88	297.1

Experiment

We have converted a 5 foot wide fume hood into a mini biodiesel pilot plant as shown in Figure 4. A computer-controlled reactor system was purchased from Syrris, Inc.¹⁰ and consists of a 250 ml jacketed glass catalyst preparation reactor and a 500 ml jacketed glass process reactor connected to feed and product vessels and each other via peristaltic pumps. Sparkless and brushless overhead electronic stirrers are used to control and monitor the stirrer rpms and torque in each reactor. A constant temperature is maintained with a separate temperature bath circulating water through the jacket of each reactor. A third circulating temperature bath is used to circulate chilled water through condensers attached to each reactor vessel to minimize evaporation losses at elevated process temperatures. Using a computer control panel outside of the hood to operate the process gives it the feel of a larger scale industrial process and minimizes some of the dangers from the hazardous and flammable materials involved.

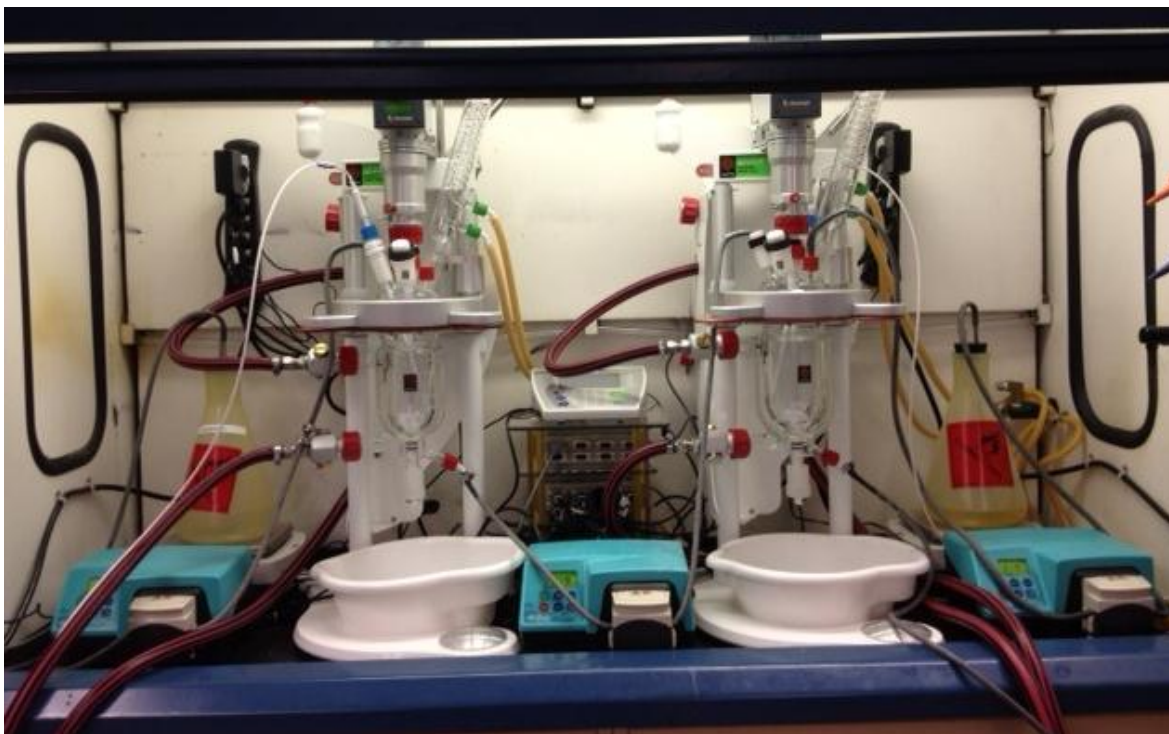


Figure 4. Five foot fume hood converted to two-reactor biodiesel mini pilot plant.

For a typical experiment, 100 ml methanol and 400 ml canola oil were introduced into the catalyst prep reactor and process reactor, respectively, by computer-controlled gravimetric dosing from feed vessels on electronic balances working together with the peristaltic pumps. The catalyst prep reactor was stirred at 400 RPM and the process reactor at 800 RPM, the recommended maximum allowable. Once both reactors reached the target temperature (usually 25, 35, or 45 °C), 1.8 g solid KOH catalyst was manually added and dissolved in the catalyst prep reactor. The process reaction was initiated by pumping the contents of the catalyst prep reactor into the process reactor. Small volume samples were withdrawn from the process reactor at regular intervals and analyzed for glycerol content via an enzymatic assay to follow the reaction progress. At the end of the experiment, all samples were analyzed at once using a 96-well plate reader at a wavelength of 570 nm. The reactor system was washed with acetone and allowed to air dry between experimental runs. The acetone wash, as well as the draining of the reactors to waste containers, was also accomplished with the peristaltic pumps. Thus, the student's exposure to hazardous materials was limited to weighing solid KOH and adding it to the catalyst prep reactor via a funnel and pipetting small volumes of the reaction mixture.

The ReactorMaster software from Syrris that controls the process also collects data on each piece of equipment, allows for pauses to insert comments, and effectively keeps an electronic batch record of everything that happens in each experimental run. Students were required to input comments into the batch record indicating that they either performed or witnessed various aspects of the standard operating procedure as is often required in industry. A screenshot of the

software given in Figure 5 shows the block diagram, programming recipe on the upper right, some student comments added to the batch record on the upper left, and plots of the temperatures in the two reactors for a typical run.

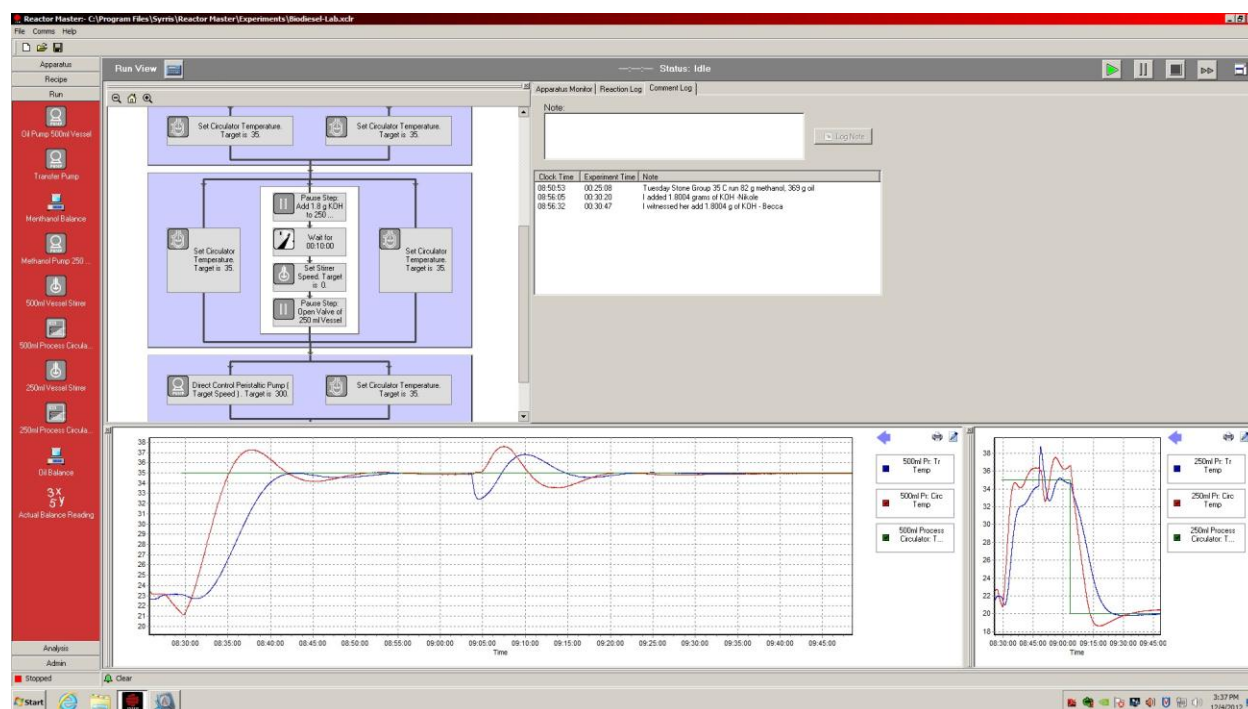


Figure 5. Screenshot from ReactorMaster software during a typical run.

The enzymatic glycerol assay (cat # EGLY-200) purchased from BioAssay Systems¹¹ is very sensitive to low levels of glycerol like those found in blood. For our purpose, it was necessary to dilute the reactor samples 1000 fold to get them in the appropriate range. We found it convenient to take 40 μ l samples and quench them in 40 ml of cold water pre-loaded into 50 ml plastic centrifuge tubes to prepare them for analysis. This 1000 fold dilution was convenient because the colorimetric assay method yields results in the range 0 – 1 mM which translates into samples from the reactor in the range 0 – 1 mol/L. For our process, the maximum glycerol concentration at complete conversion should be about 0.83 mol/L.

To conduct the assay, 10 μ l of each diluted sample was incubated with 100 μ l of a freshly prepared enzyme/dye working reagent for 20 minutes at room temperature in a separate well of a 96-well plate. Glycerol standards were also included on the same plate to generate a calibration curve. The absorbance of all the samples for a given run were measured simultaneously at 570 nm using a Molecular Devices 340PC 386 plate reader.

As visual evidence that the transesterification reaction has the desired effect, we filled one burette with the original canola oil and a second burette with purified biodiesel product (prepared in advance by a teaching assistant). Students can time the fall of a steel ball through each fluid and estimate the viscosity using Stokes law.

Results and Discussion

Glycerol assay results as a function of time for three operating temperatures are shown in Figure 6. As expected, the glycerol concentration increases with time and shows a more rapid increase at higher temperature. Figure 7, showing before and after photos of the reaction mixture, helps explain two other features of the results shown in Figure 6.

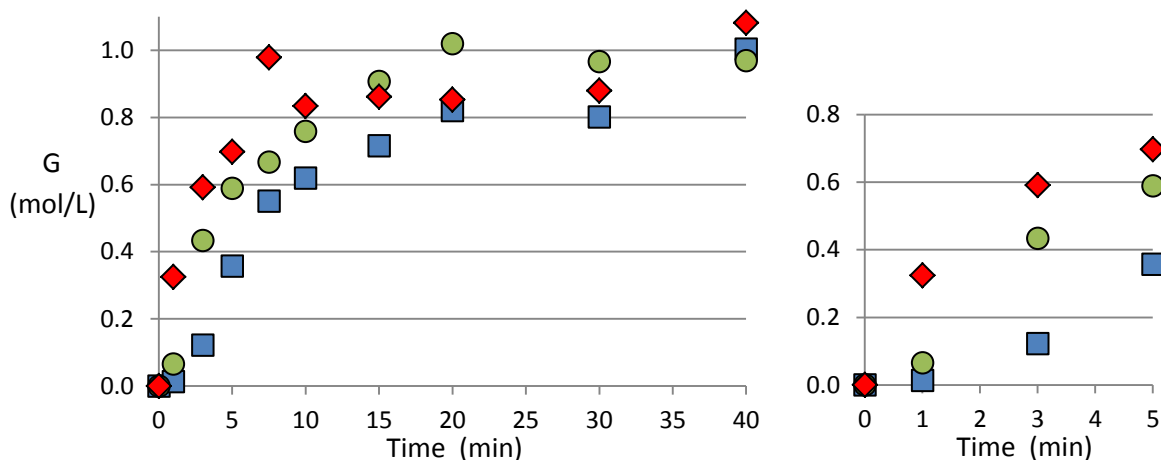


Figure 6. Glycerol assay results as a function of time for three temperatures: squares = 25 °C, circles = 35 °C, diamonds = 45 °C. The right hand figure is an expanded view of early time results.

As shown in the “before” picture (prepared for this illustration by adding methanol with no KOH to the oil and letting it settle, when in practice the methanol/KOH solution was added to the oil under vigorous stirring) the methanol and oil do not mix. This explains why there is a lag in the reaction progress of about 2 minutes at 25 °C and about 1 minute at 35 °C. The decrease in viscosity and increase in diffusivity as temperature increases explains why this mass transfer limited stage decreases with increasing temperature. The “after” picture of Figure 7, taken after the reaction mixture was allowed to settle for several hours, indicates that the upper biodiesel rich-phase and the more dense glycerol-rich phase do not mix. This explains why some of the glycerol results at later times were erroneously found to be above the maximum expected value of 0.83 mol/L. Even though the reaction mixture was vigorously stirred at 800 RPMs, samples taken at later times, when there was sufficient glycerol to form a separate phase, could contain more or less of one phase or the other.

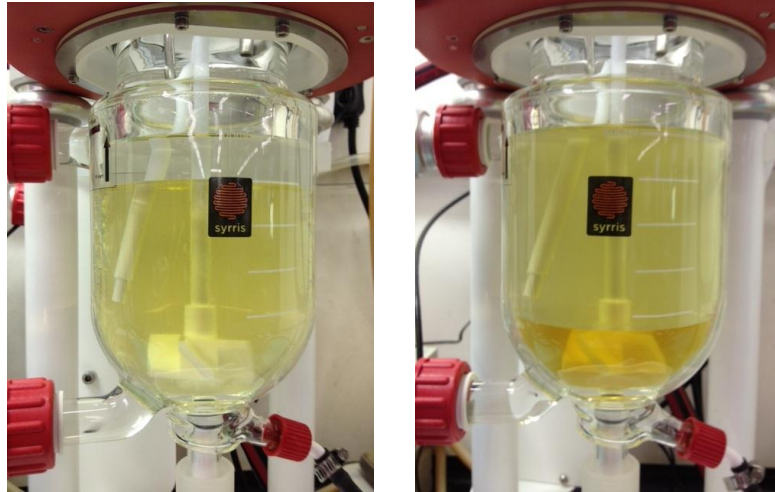


Figure 7. Before and after photos of reaction mixtures in the process reactor.

We believe that samples taken at intermediate times - between the initial, mass transfer limited, lag stage and the later times - provided sufficiently accurate results to estimate the pseudo 2nd order rate constants as shown in Figure 8.

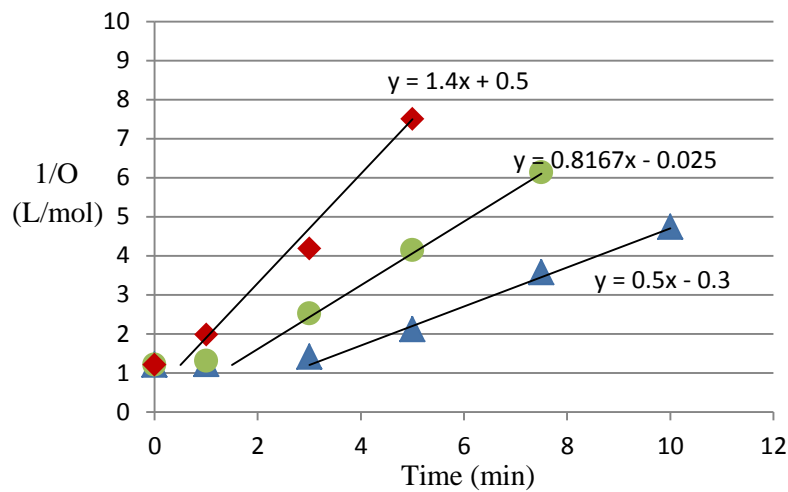


Figure 8. Pseudo 2nd order rate law fit to results in middle stage (after initial mixing stage) at three temperatures; 25 °C (lower line), 35 °C (middle line), 45 °C (upper line). Rate constants in L/(mol min) are given by the slopes of the lines as indicated.

Due to the one-to-one stoichiometry of oil to glycerol shown in Equation 1, the oil concentration, O, for preparing Figure 8 was easily determined as (0.83 mol/L – G). The lines shown in Figure 8 were drawn to accommodate the mass transfer limited stage that was observed in Figure 6. That is, they intersect the reciprocal of the initial oil concentration ($1/0.83 = 1.2$) at approximately the end of the lag stage instead of time zero. The slopes of the lines yield rate constants of 0.50, 0.82, and 1.4 (L/mol min) at $T = 25, 35,$ and 45 °C, respectively.

The Arrhenius plot shown in Figure 9 yields an activation energy of 41 kJ/mol which compares favorably with the value of 54 kJ/mol for sunflower oil found by Stamenkovic et al.⁸.

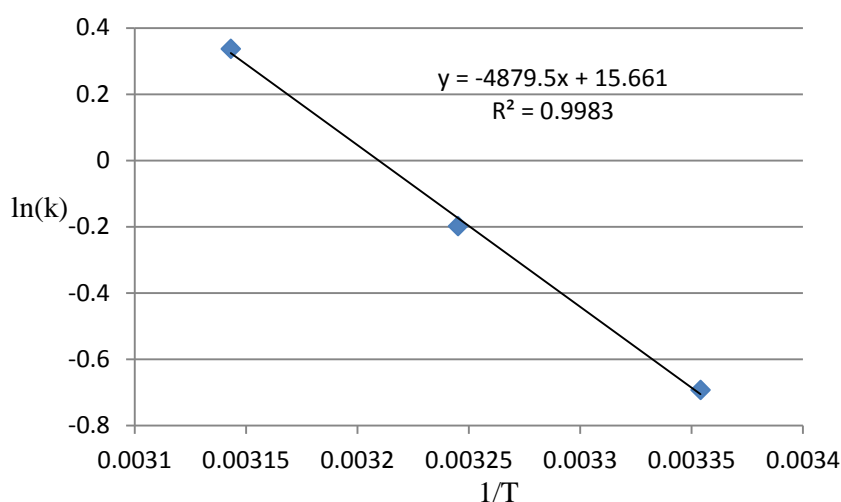


Figure 9. Arrhenius plot for pseudo 2nd order rate constants at 3 temperatures; activation energy = 41 kJ/mol.

We implemented the new experiment for the first time in Fall 2012 and used it on a trial basis with three lab groups. The students seemed enthusiastic about working with a pilot plant reactor system to produce a product of current interest and seemed to appreciate the concept that the computer-controlled process would be the same if the reactors were of a larger, industrial scale. All of the groups did well researching safety aspects and learned to wear gloves and eye protection when adding the KOH and taking samples. Most of the students had completed one course in kinetics and reactor design, but some still had trouble generating pre-lab results like Figures 2 and 3 to verify that a pseudo 2nd order rate law can approximate the multistep reaction. More guidance on this aspect will be offered in the future.

The glycerol assay required preparing standards, reagents, and samples using small volumes with microliter pipettes. This type of precision lab work was new to most of these students and resulted in more scatter than that shown in Figure 6 for some groups. Nevertheless, with some imagination (and in some cases using previously obtained results provided to them to supplement those that they obtained) all groups were able to approximate the results with a 2nd order model and obtain an Arrhenius plot similar to Figure 9. In our implementation, each group came to the lab on two separate occasions and was only able to study one temperature each time. Each group, therefore, shared one of their sets of results with another group to provide results at three temperatures for each group. In the future it should be possible to have each group conduct two different experiments in each lab session. Possible variations on the experiment include studying different types of oil, different catalysts, and different amounts of stirring as well as higher temperatures.

It would be good to use a chromatographic method^{12,13} to follow the composition of all species in the reaction more precisely, but no such method was readily available to us. These methods would be quite time consuming even if they were available. An even better approach would be to follow the reaction in real time with an in-situ spectroscopic method¹⁴, but this was not available to us either. Despite the limitations, we believe the glycerol assay used yielded acceptable reaction rate results.

Conclusion

We are pleased with our new computer-controlled, two-reactor, pilot plant system that we purchased from Syrris, Inc. and believe we have developed a safe, interesting, and meaningful unit operations laboratory experiment using it to measure biodiesel reaction kinetics. This new biodiesel experiment provides students the opportunity to learn about green technology and the use of precision pipetting for an enzymatic glycerol assay that they would not learn from any of our other lab exercises. In addition, it gives us the opportunity to address important safety issues as required by ABET and expose our students to standard operating procedures and electronic batch records.

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