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Short Communication

## Biodiesel transesterification kinetics monitored by pH measurement

William M. Clark<sup>\*</sup>, Nicholas J. Medeiros, Donal J. Boyd, Jared R. Snell

Chemical Engineering Department, Worcester Polytechnic Institute, Worcester, MA 01609, United States

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### ABSTRACT

Quantification of a pH change that was observed over the course of the transesterification reaction that converts vegetable oil to biodiesel may provide a simple method to monitor the reaction. Transesterification of canola oil at 6:1 methanol to oil ratio with 0.5 wt.% KOH as catalyst was studied at 25, 35, and 45 °C. Reaction conversion was correlated to pH measurements and the results were shown to be in agreement with an independent measure of conversion using an enzymatic assay for glycerol. Rate constants obtained from these measurements are consistent with those in the literature. The measured pH change appears to be related to dilution of OH<sup>-</sup> ions as the oil is converted to products rather than to depletion of OH<sup>-</sup> due to reaction.

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### 1. Introduction

Renewable fuels like biodiesel are becoming increasingly popular alternatives to petroleum based fuels. While vegetable oil can be burned directly, it is not recommended as an engine fuel due to its high viscosity. In the transesterification reaction, vegetable oil, that is predominately made up of triglyceride molecules, is reacted with an alcohol (usually methanol) to produce a by-product, glycerol, and three biodiesel molecules with viscosity and other properties similar to those of petroleum diesel fuel. The recent increase in biodiesel production has also led to increasing interest in developing new uses for the low-cost glycerol by-product (Acosta et al., 2011).

Reaction rate and product quality are influenced by type and amount of catalyst, type of oil feedstock, alcohol to oil ratio, water and free fatty acid content of the oil, and operating conditions such as temperature, pressure, and mixing rate (Freedman et al., 1986; Sing et al., 2006). The complex dependence of rates and yields on a variety of factors makes it of interest to monitor the transesterification reaction for research and development as well as commercial biodiesel production processes.

The base-catalyzed transesterification reaction involves multiple reaction steps: (1) triglyceride is attacked by a methoxide ion CH<sub>3</sub>O<sup>-</sup> (present in the basic methanol solution) to produce one biodiesel (BD) and a di-glyceride, (2) di-glyceride is converted to a second BD and a mono-glyceride, and (3) mono-glyceride is converted to a third BD and glycerol. Methanol and oil are essentially insoluble in one another, as are the glycerol and biodiesel products.

Understanding the phase behavior and droplet size changes that occur during the course of the reaction is important for a complete analysis (Gunvachai et al., 2007; Slinn and Kendall, 2009). In cases with sufficient stirring, however, experimental data can be modeled using only three reversible reactions (Vicente et al., 2005). Stamenkovic et al. (2008) suggested that it is advantageous to consider the reaction in three stages: a brief initial mixing/mass transfer limited stage, an irreversible chemical reaction controlled stage, and a reversible equilibrium reaction controlled stage near the end. They further suggested that the overall reaction can be successfully modeled with a pseudo second order irreversible rate law for the disappearance of oil, O, at least in the middle stage.

Existing methods to monitor the reaction progress include gas and liquid chromatographic methods (Plank and Lorbeer, 1995; Holcapek et al., 1999; Dube et al., 2004; Richard, et al., 2011), FTIR, NIR, NMR, and laser spectroscopic methods (Dube et al., 2004; Richard et al., 2011; Knothe, 2000; De Boni and Da Silva, 2011; Socha et al., 2010), and methods to measure refractive index (Xie and Li, 2006), hydroxyl groups in glycerol (Xie and Li, 2006), and viscosity (Ellis et al., 2008). Most of these require taking samples for off-line analysis which also include significant sample pretreatment steps. The spectroscopic and viscosity methods have been used in situ to monitor the reaction in real time with some success, but they require expensive instruments and complex data analysis, and may be susceptible to interference from impurities or variations in the feedstock.

pH is often used to monitor reactions, normally in aqueous solutions where one of the reactants or products is an acid or base, but it is widely believed that pH measurements are either impossible or unreliable in non-aqueous solutions like vegetable oil. Komers et al. (2001, 2002) determined the total basicity of the biodiesel

<sup>\*</sup> Corresponding author. Tel.: +1 508 831 5259; fax: +1 508 831 5853.

E-mail address: [wmclark@wpi.edu](mailto:wmclark@wpi.edu) (W.M. Clark).

reaction mixture by titrating samples with an analytical solution of strong acid and concluded that the completion of the biodiesel reaction is indicated by the exhaustion of the “strong” basicity (i.e.,  $\text{OH}^- = \text{CH}_3\text{O}^- = 0$ ) due to the consumption of  $\text{OH}^-$  via the saponification reaction that they contend is always present. In this paper it is shown that once methanol and KOH are dispersed in oil, reproducible pH measurements can be taken continuously, in situ, to monitor the reaction progress. The pH measurements were correlated with reaction conversion and fit to a kinetic model. The associated reaction rate constants were compared with those obtained by other means.

## 2. Methods

### 2.1. Materials

Methanol (Pharmco-Aaper, 339000000), KOH (Alfa-Aesar, flake 85%, A16199), sodium methoxide (Sigma–Aldrich, 25 wt.% in methanol, 156256), distilled water, and food grade vegetable oil (canola, soy, and sunflower) were used without further refinement. An enzymatic assay kit for glycerol (EnzyChrom™ EGLY-200) was purchased from BioAssay Systems. Densities and molecular weights for canola oil reactants and products used in calculations were those reported in He et al. (2005).

### 2.2. Equipment

A Syrris, Inc. 500 ml, Globe model, jacketed, glass reactor was used with a Heidolph RZR electronic overhead stirrer to control and monitor mixing. Constant temperature was maintained with a Huber Ministat 230 temperature bath circulating water through the reactor jacket. A Mettler–Toledo Seven Multi pH meter with a Mettler InLab Reach Pt1000 pH probe was used to monitor and record the process temperature and pH. A Molecular Devices 340PC 386 plate reader was used to read absorbance in standard 96-well plates for an enzymatic glycerol assay.

### 2.3. Reaction conditions

Transesterification of canola oil was conducted under the following conditions: 6:1 M ratio of methanol to canola oil, 800 rpm stirring, 0.49 g KOH per 100 g of oil, atmospheric pressure, and 25, 35, or 45 °C reaction temperature. For comparison, water was substituted for methanol to observe the saponification reaction at 40 °C.

### 2.4. Experimental procedure

To obtain the 6:1 M ratio of methanol to oil, 75 ml of methanol was reacted with 300 ml canola oil. Initially, however, only 37 ml of the methanol was mixed with the oil to establish small droplets of methanol dispersed in the oil. 1.35 g of KOH was dissolved in the remaining 38 ml of methanol to make fresh catalyst for each run. Before initiating the reaction, 10  $\mu\text{l}$  of the catalyst mixture was added to the stirring reactor to obtain a stable initial pH reading of about three. Without this step, the pH of the initial stirred mixture of oil and methanol in the reactor usually went below the lower limit of the pH meter and introduced an error. The reaction was initiated by adding the fresh catalyst to the reactor and the pH was recorded at 3 s intervals for a minimum of 40 min. The reactor was cleaned with acetone and allowed to air dry between runs.

### 2.5. Glycerol assay

For an independent measure of reaction progress, 40  $\mu\text{l}$  samples were withdrawn from the well-stirred reactor at regular intervals

and analyzed for glycerol content. Samples were quenched by dilution in 40 ml of cold water. Glycerol concentration was determined from absorbance readings at 570 nm using a calibration curve made according to instructions and a glycerol standard supplied with the assay kit.

### 2.6. pH of KOH in methanol

To aid in interpreting pH measurements during reactions at different temperatures, the composition and temperature dependence of the pH was measured for KOH/methanol solutions. 1.35 g of KOH was dissolved in 375 ml of methanol in the stirred reactor at 800 rpm. The temperature was controlled sequentially at 25, 35, and 45 °C and the pH was measured at each temperature. The temperature was returned to 25 °C and an additional 5.40 g of KOH was added to the reactor with stirring. The pH of this more concentrated solution, equivalent to 1.35 g KOH in 75 ml methanol, was then measured at 25, 35, and 45 °C.

## 3. Results and discussion

Fig. 1 shows the raw pH data as a function of reaction time for four experiments; a soap production run and biodiesel production runs at three different temperatures. In the soap making process, the pH gradually increased until it became constant. In the biodiesel process, there was a rapid increase followed by a gradual decrease in pH until a constant value was reached.

Knowing that the reaction rate and conversion are expected to increase with increasing temperature, it is tempting to conclude from Fig. 1 that a low final pH indicates a high conversion for the biodiesel runs. It was noted, however, that (1) KOH is not expected to be consumed in the biodiesel reaction, (2) little or no soap production (that would consume  $\text{OH}^-$ ) was detected in the biodiesel runs, and (3) the soap production run showed an increase rather than a decrease in pH. It was also noted that both the maximum pH reached and the final pH of the biodiesel runs decreased with increasing temperature as shown in Table 1. This prompted an investigation of the temperature and concentration dependence of pH in KOH/methanol solutions. As shown in the last column of Table 1, the pH values obtained for 1.35 g KOH dissolved in 375 ml of methanol were similar to the constant, final values reached in the biodiesel runs at the various temperatures. To understand the observed maximum pH values in the biodiesel runs, it was hypothesized that these might be similar to the pH for 1.35 g of KOH dissolved in 75 ml of methanol, the initial

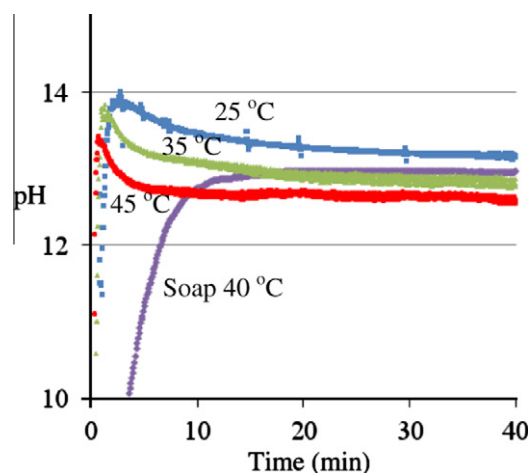


Fig. 1. pH as a function of reaction time for biodiesel and soap production runs.

**Table 1**

Temperature dependence of pH peak time, peak value and final value from Fig. 1, and pH of KOH in methanol solutions at the initial concentration in the methanol only and at the final concentration in the reactor.

Temperature	Peak time (min)	Peak pH	Final pH	pH	
				1.35 g KOH in 75 ml (0.321 mol/L)	1.35 g KOH in 375 ml (0.064 mol/L)
25	3.8	13.90	13.10	13.79	13.00
35	1.5	13.74	12.79	13.55	12.79
45	1.0	13.42	12.58	13.34	12.61

concentration of KOH considering only the methanol in the reactor. It can be seen in the 5th column of Table 1, that this was indeed the case, at least approximately.

Based on the pH results in Table 1, the following correlation to describe the relationship between pH and reaction conversion,  $X$ , was proposed:

$$X(t) = \frac{(10^{-(14-\text{peak pH})} - 10^{-(14-\text{pH at } t)})}{(10^{-(14-\text{peak pH})} - 10^{-(14-\text{final expected pH})})} \quad (1)$$

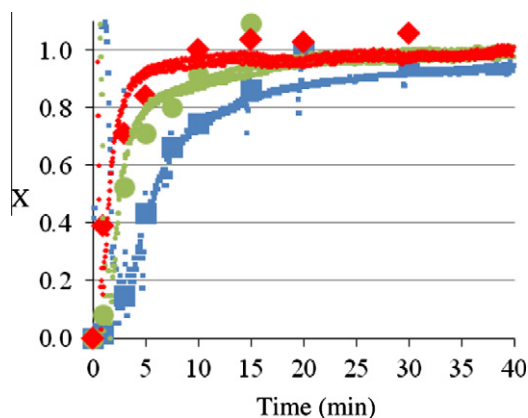
This correlation is a first order approximation based on the idea that pH is a measure of the  $\text{OH}^-$  concentration and that the  $\text{OH}^-$  concentration observable by the pH meter changes during the reaction due to conversion of oil to biodiesel. It appears that the  $\text{OH}^-$  ions do not dissolve in the oil but do dissolve in the biodiesel, glycerol, and methanol. The values obtained for 0.064 mol/L KOH dissolved in methanol were used for the final expected pH. Although the value of 14 in Eq. (1), based on dissociation of water at room temperature, is not technically correct, it serves the purpose of converting from pH to pOH, facilitating estimation of the change in  $\text{OH}^-$  concentration during the reaction. In fact, the  $10^{-14}$  terms cancel out and can be eliminated from Eq. (1).

Fig. 2 shows the conversion results obtained by applying Eq. (1) to the biodiesel production pH data shown in Fig. 1. In agreement with the low temperature methanolysis studies of Stamenkovic et al. (2008), the results show an S-shaped behavior that indicates an initial mixing/mass transfer limited stage that is diminished as temperature increases. The approximate duration of this mass transfer limited stage is indicated by the peak times shown in Fig. 1 and Table 1. Also shown in Fig. 2 are the conversion results obtained from the enzymatic assay for glycerol. Although it can be seen that the two methods yield similar results, it can also be seen that there is scatter in the results of both methods at later times. This scatter can be attributed to the fact that a glycerol rich phase and a biodiesel rich phase are present in the later stage of the reaction. The 40  $\mu\text{l}$  samples withdrawn from the well-stirred

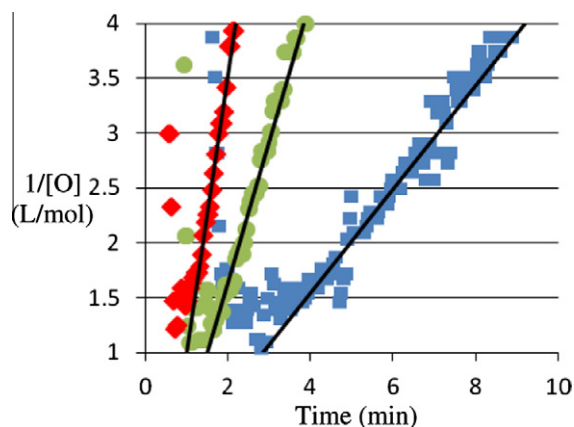
reactor may not all contain representative samples at this later stage; some samples may contain more of one phase or the other. This explains why some later glycerol assay results erroneously showed higher than 100% conversion. The pH results also show some scattered behavior in the later stage of the reaction. Attributing this to phase separation is supported by the fact that when the two phases were separated after the reaction was finished, a higher pH was measured in the glycerol rich phase than in the biodiesel rich phase.

In the middle stage of the reaction, only one phase is present and the glycerol assay results agree well with the pH correlation. Following Stamenkovic et al. (2008), a pseudo second order irreversible rate law has been assumed for this middle stage. A rate constant was estimated at each temperature by calculating  $[O] = [O]_0 (1 - X)$  and plotting  $1/[O]$  versus  $t$  as shown in Fig. 3. In this formulation, the second order rate constant,  $k$ , is given by the slope of a line and the y-intercept at  $t = 0$  is normally equal to  $1/[O]_0$  (Levenspiel, 1972). There is a time shift in the results due to the initial mixing/mass transfer stage, and the time where  $1/[O] = 1/(0.83 \text{ mol/L}) = 1.2 \text{ L/mol}$  on Fig. 3 is approximately equal to the peak time from Fig. 1 for each temperature. The rate constants of 0.47, 1.28, and 2.50  $\text{L}/(\text{mol min})$  obtained at 25, 35, and 45  $^\circ\text{C}$ , respectively, are consistent with those obtained for methanolysis of sunflower oil using 1% KOH as catalyst (Stamenkovic et al., 2008). An Arrhenius plot of  $\ln(k)$  versus  $1/T$  yielded an activation energy of 66  $\text{kJ/mol}$  that is consistent with the value of 54  $\text{kJ/mol}$  obtained by Stamenkovic et al. (2008).

Although it appears that an initial mixing/mass transfer limited stage and a pseudo second order irreversible stage are well characterized by the proposed correlation between pH and conversion, no conclusion can be made at present regarding the accuracy of the final conversion results. The uncertainty in the glycerol assay at later times leads to uncertainty in comparing the final conversion predicted by the pH correlation with the glycerol assay results. Future studies will focus on determining the accuracy of the predicted



**Fig. 2.** Conversion as a function of time for three temperatures; 25  $^\circ\text{C}$  (lower curve), 35  $^\circ\text{C}$  (middle curve), 45  $^\circ\text{C}$  (upper curve). Large symbols are from an enzymatic assay for glycerol, curves are from a correlation with pH measurements.



**Fig. 3.** Pseudo second order rate law tested on pH correlation results in middle stage (after initial mixing stage) at three temperatures; 25  $^\circ\text{C}$  (lower line), 35  $^\circ\text{C}$  (middle line), 45  $^\circ\text{C}$  (upper line).

final conversion, the dissociation and phase distribution of the ions present, and any adjustments to the correlation that are needed to quantify reactions with other operating conditions. A similar rapid increase, then gradual decrease in pH was observed for preliminary studies of biodiesel production under different conditions including using sunflower or soybean oil, increasing the amount of KOH catalyst, using  $\text{NaOCH}_3$  as catalyst, and adding water to the methanol. Although Eq. (1) may not apply in every case, some correlation between pH and conversion seems possible in all cases.

#### 4. Conclusions

Monitoring pH provided at least an approximate measure of the progress of the biodiesel reaction as it appears that the concentration of  $\text{OH}^-$  ions decreases due to dilution as oil, that excludes  $\text{OH}^-$  ions, is converted to more  $\text{OH}^-$  friendly biodiesel. A pseudo second order rate constant of 2.5 L/(mol min) at 45 °C and an activation energy of 66 kJ/mol obtained for transesterification of canola oil are consistent with previously reported values. If this method proves to be robust and precise enough, it could aid in monitoring biodiesel production processes and in research on screening catalysts and optimizing operating conditions.

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