Biodiesel Analysis

Here we describe the use of Raman spectroscopy to monitor the production of biodiesel in both batch and continuous flow reactors. We also used Raman spectroscopy to quantify the concentration of biodiesel in product blends.

Biodiesel has become the foremost alternative biofuel being developed to reduce the Nation's dependence on fossil fuels. One of the most attractive processes is the conversion of vegetable oils and animal fats to biodiesel via the transesterification reaction (Figure 1A). However, the rate of reaction and yield can change dramatically due to variability in these feedstocks (composition and stage of degradation). Not only must these feedstocks be qualified for use, but the transesterification reaction needs to be monitored and controlled in real-time to optimize yield and minimize energy usage. Currently, samples are extracted and measured off-line by chromatographic or spectroscopic techniques. This does not allow changing process conditions to compensate for variations in the feedstocks, such as adjusting co-reactant concentrations, catalyst loading or process temperature.

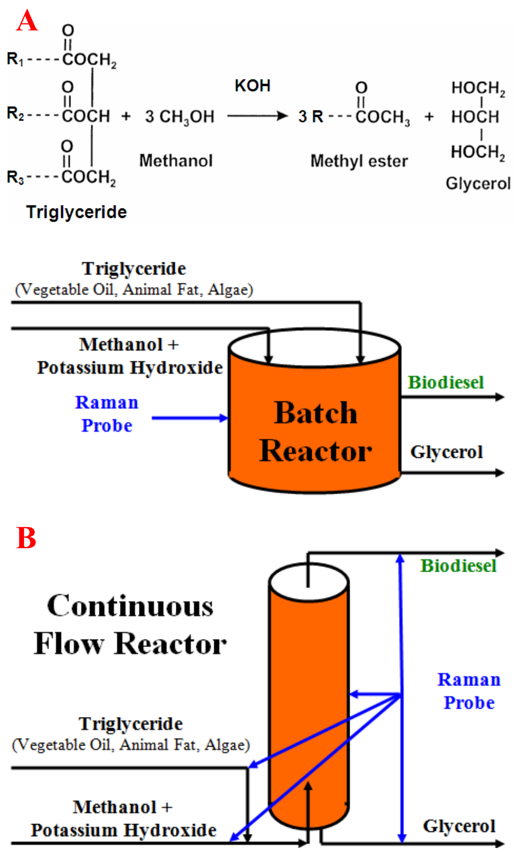

Figure 1. A) Transesterification Reaction, B) Illustrations of Batch and Continuous Feed Biodiesel Reactors.

In an effort to overcome some of these production limitations we used Raman spectroscopy to monitor the transesterification reaction in both batch and continuous feed reactors (Figure 1B). We used the former reactor to establish the ability of Raman to observe the chemical changes, and the latter reactor to demonstrate process control. A 3-neck round-bottom flask was used to perform the reaction as a batch process. Raman spectra were collected through the glass side wall, as well as through one of the necks using a ball probe. Both methods produced quality spectra (Figure 2). The by-product glycerol has an isolated Raman peak at 1040 cm^{-1}, and its production was easily monitored (Figure 2 Inset, the scatter in the data is

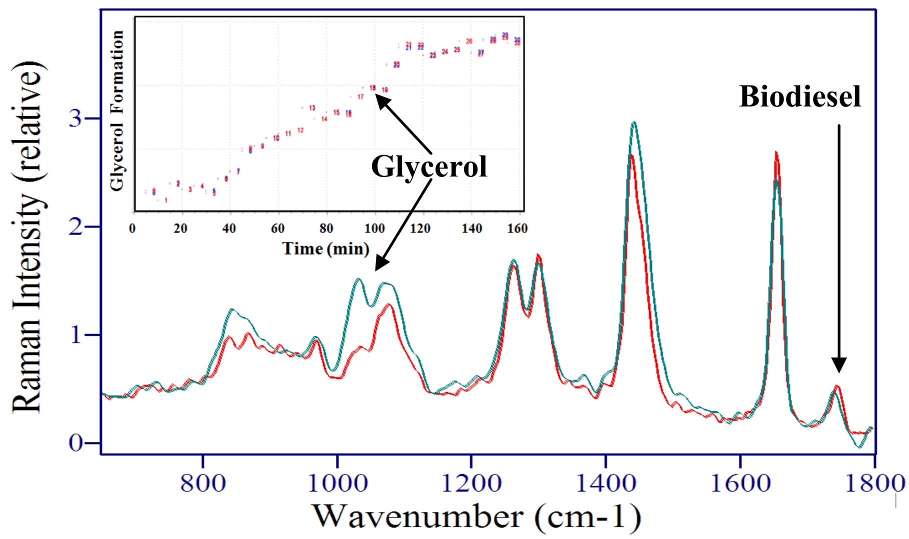

Figure 2. Raman spectra collected at the start and end of the batch reaction. Inset shows peak height of glycerol as a function of the reaction time. Conditions, 0.5 W 1064 nm laser excitation, 1 minute spectra.

real and due to the glycerol forming as higher density phase droplets). This was not the case for the primary product biodiesel (methyl ester), where most of the Raman peaks are the same as the triglyceride reactant, and it simply shows a shift in the Raman ester peak at 1740 cm^{-1}.

Next we performed Raman measurements using RTA's ***RamanPro*** analyzer on a continuous flow reactor designed and built at the University of Connecticut (Department of Chemical Engineering), by inserting a fiber optic probe into the reactor inlet lines and the product exit lines (Figure 1B above, and Figures 3 and 4 below). Measurement of the reactants allows verifying the quality of the triglyceride feedstock and the methanol to KOH concentration ratio. Although not

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done here, the ratio of the two reactants after mixing could also be monitored. Note that the biodiesel product exits the top of the reactor, while the glycerol by-product exits the bottom. This is due to the fact that both products have significantly different densities and polarity (glycerol has a higher density and is highly polar. In fact, glycerol forms droplets that fall to the bottom of the reactor and looks very much like rain.

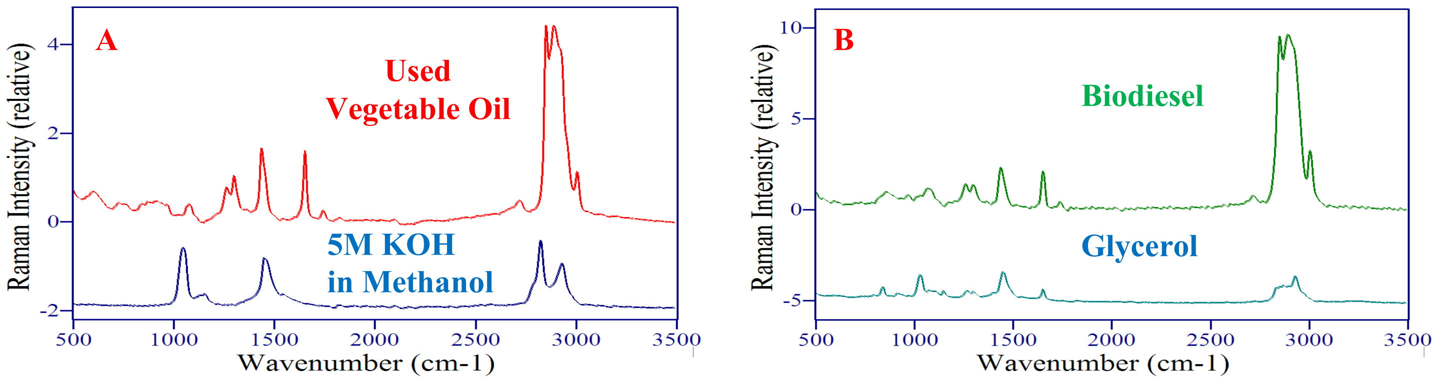

Figure 3. Raman spectra collected at A) the inlet lines and B) the exit lines of the continuous feed reactor. Condition as above.

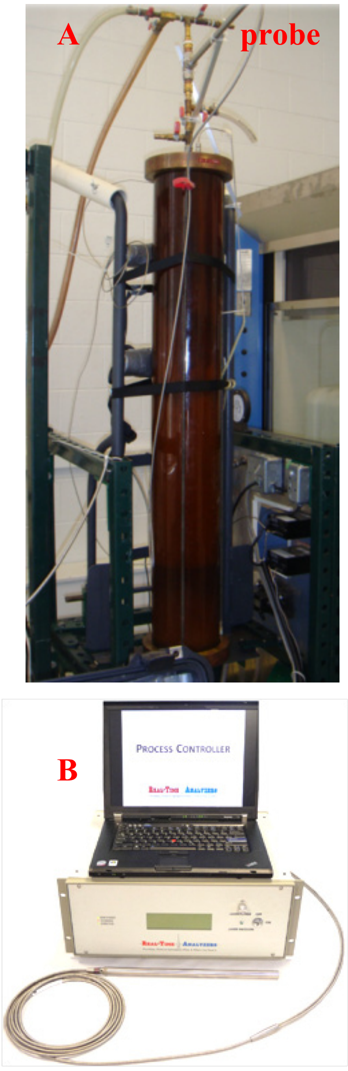

Figure 4. A) Photographs of A) the Continuous Reactor Fiber Probe inserted at top) and B) RTA's ***RamanPro***.

Next, measurements were performed in the middle of the reactor (Figure 4). For these measurements, RTA's ***Process Controller*** software was used to monitor each of the reactants and products (Figure 5). These continuous measurements allowed monitoring the effects of reactant flow rates and the column temperature on the product yield and energy efficiency (heat in). This data will ultimately be used to optimize and control the reactor.

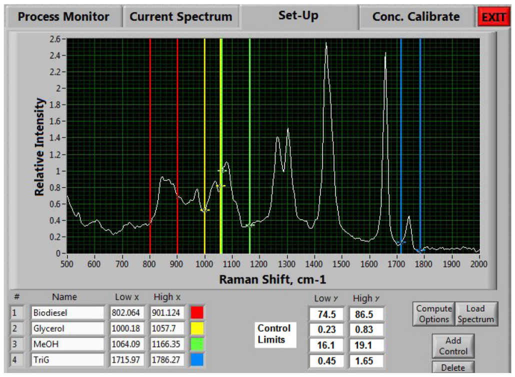

Figure 5. Image of RTA's ***Process Monitor*** Set-Up screen showing peak selection for reactants and products.

Finally, the ***RamanPro*** analyzer was used to quantify the blending process. Commercial Biodiesel is typically sold as B-5, B-20, B-50, or B-100, which represents 5, 20, 50 or 100% biodiesel in regular diesel 2. Figure 6 shows the Raman spectra and calibration plot for this concentration series. As can be seen the Raman spectral measurements can easily quantify the amount of biodiesel within 1%.

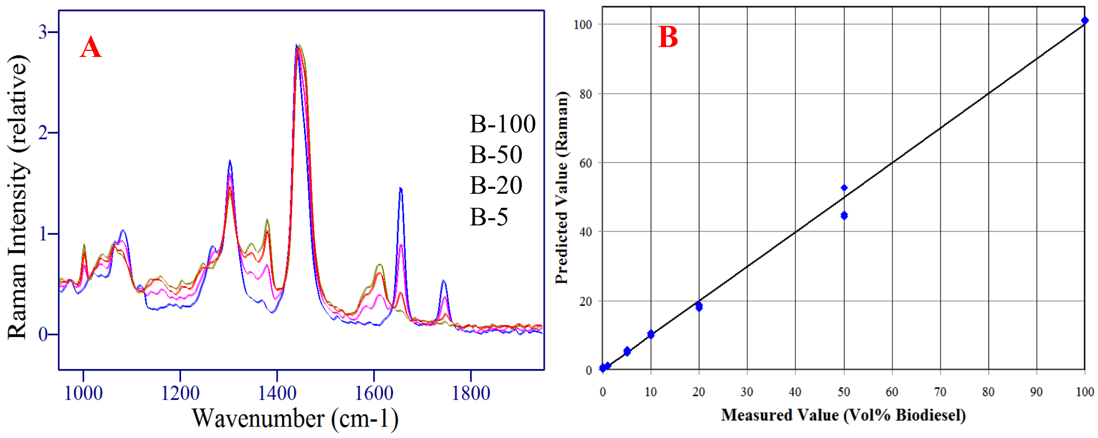

Figure 6. A) Raman spectra of 5, 20, 50 or 100% biodiesel in regular diesel 2. B) Concentration plot of the 0,1,5,10, 20, 50 (repeated) and 100% biodiesel in diesel 2.