

Glycerolysis for Lowering Free Fatty Acid Levels

During the last decade, the rendering industry has successfully adapted to changing market conditions. From increased product safety and testing guidelines, to entering new arenas like biodiesel, rendering has remained a vital process. However, these new developments are changing the way renderers look at their products. Technologies to upgrade low-quality oils like brown grease are being researched in order to improve product specifications as well as expand into new industries such as renewable fuels.

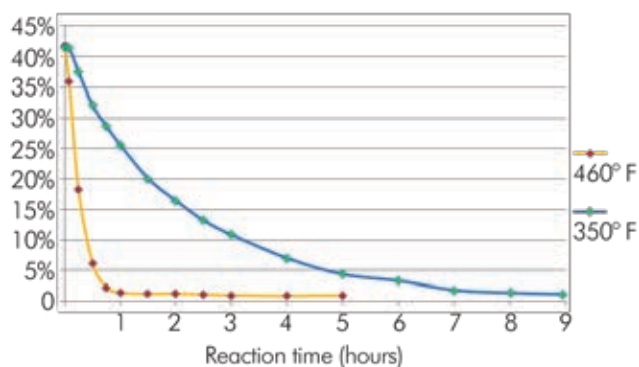
In the case of rendered oils being used for biodiesel, most commercial-scale plants cannot handle high levels of free fatty acid (FFA). Yellow grease and brown grease can be high in FFAs and require processing before being used in traditional biodiesel processes. Methods for FFA reduction, like vacuum stripping and caustic washing, can be very energy intensive and costly, especially when considering yield loss. One technique that has gained popularity recently is glycerolysis, a process that uses glycerin—crude or technical grade—and reacts it with FFAs to create monoglycerides, diglycerides, and water. Since glycerolysis is done at high temperatures, any water formed during the reaction is driven off, resulting in dry product. Glycerolysis has the potential to be used in the rendering industry. For example, an 8,000-gallon batch reactor has the

capacity to upgrade as much as 2.5 million gallons of brown grease per year.

Regarding biodiesel production, glycerolysis reduces the amount of FFA in low-grade oils without the use of acid or methanol, as with acid esterification. It enables the fatty acids to be converted into glycerides rather than removing FFA and reducing product yield. The resulting glycerides can be converted directly to methyl esters via base-catalyzed transesterification without issue.

Research at Superior Process Technologies was conducted to compare glycerolysis at various operational temperatures. Multiple laboratory batch-wise glycerolysis reactions were performed on brown grease at 350 degrees Fahrenheit (F) and 460 degrees F, representing steam-heated and thermal oil-heated systems. Samples were taken over the course of the reaction and analyzed via gas chromatograph-flame ionization detector (GC-FID) to determine compositional makeup versus reaction time. The initial brown grease was determined to have an acid number of 100 (percent FFA equals 50 percent) prior to glycerolysis. Each batch was brought up to its respective temperature under inert conditions using a nitrogen purge before charging glycerin. By graphing the average acid numbers versus time of each reaction, the rates of FFA reduction can be seen in chart 1.

Chart 1. Comparing glycerolysis rates of reaction: % FFA versus time at 350° F and 460° F



At 460 degrees F, the FFA concentration is lowered rapidly in the first hour, and well below one percent FFA within several hours. In comparison, the reaction at 350 degrees F did lower the FFA below two percent, but required nine hours of reaction time. Clearly, the main cause for the slower reaction rate is lower reaction temperature.

Another contributing factor that may affect reaction kinetics is the system's ability to purge water out at 350 degrees F compared to 460 degrees F. Any remaining water shifts the steady-state equilibrium slightly toward the reactants' side of the equation, slowing the reaction. One solution to the problem of remaining traces of water is to place the system under vacuum. At negative pressures, the water will be more effectively removed and an increase in the system kinetics

Chart 2. Glycerolysis system components versus time, at 350° F

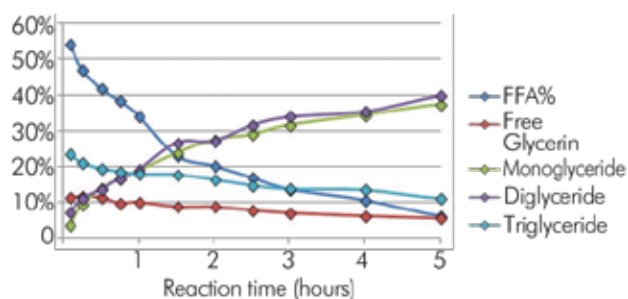
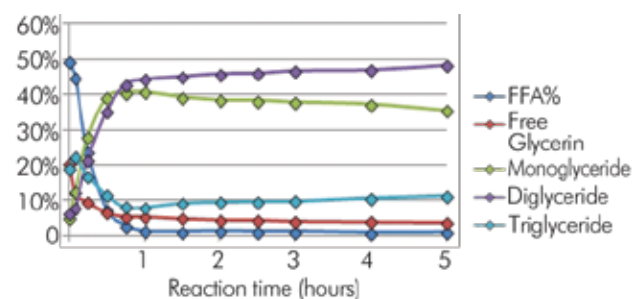


Chart 3. Glycerolysis system components versus time, at 460° F



can be achieved. The drawback to this approach is that there is a fine line between removing water and removing free glycerin, even at 350 degrees F. Also, if vacuum leaks were to occur at glycerolysis temperatures, any air in the system can cause oxidation of the oil. An alternative is to run the reactions at atmospheric pressure, but use nitrogen to purge out water vapor and minimize exposure to air. In large-scale continuous glycerolysis operations, a combination of heat and nitrogen purging can be used with great success.

Combining glycerin with oils containing FFAs, while heating, appears to result in three primary reactions as shown in table 1. The reaction of FFA and glycerin to form monoglycerides and water is initially the primary reaction (R1) during glycerolysis and is responsible for the majority of FFA reduction. A secondary reaction (R2) between glycerin and triglycerides forms monoglycerides and diglycerides; one mole of triglyceride will react with one mole of free glycerin to form one mole each of monoglyceride and diglyceride. A third reaction (R3) is the combination of FFA with monoglycerides to form diglycerides and water; this reaction may become dominant later in the system as monoglyceride concentrations increase and free glycerin concentration diminishes with time.

The oil composition for FFAs, free glycerin, monoglycerides, diglycerides, and triglycerides was determined using GC-FID. This data was analyzed to determine the rate constant, K, for each of the three competing reactions, as shown in table 2. The rate constant is a number that quantifies the speed of the reaction and is dependent only on temperature. The larger the K value, the faster that reaction. The actual laboratory data was modeled mathematically to determine the K values shown in table 2. Although the K value in each case is only a function of temperature, the total rate of reaction for each is also dependent on the concentrations of the starting material.

The K values for each reaction were determined using the compositional data at 350 degrees F (chart 2) and 460 degrees F (chart 3). Glycerolysis at 460 degrees F reaches an equilibrium state within one to two hours, while the reaction at 350 degrees F (steam

Table 1. The three primary reactions modeled for glycerolysis

R1:	Free Fatty Acid	+	Glycerin	=	Monoglyceride	+	Water
R2:	Triglyceride	+	Glycerin	=	Monoglyceride	+	Diglyceride
R3:	Free Fatty Acid	+	Monoglyceride	=	Diglyceride	+	Water

temperatures) continues well beyond five hours. At 350 degrees F, the composition of the oil follows the same trends as glycerolysis at 460 degrees F, just at a slower rate.

Whether glycerolysis is performed at either temperature, end products are essentially the same. Both contain high mole fractions of monoglycerides and diglycerides along with a significantly lowered FFA fraction, and some remaining triglycerides and free glycerin. Glycerolysis at the high temperature has the added benefit of lowering FFA concentrations significantly faster. When scaled up to a continuous system, running glycerolysis at 460 degrees F instead of 350 degrees F will result in at least three times the amount of throughput, while producing a dry product. The end result

Table 2. K values for competing glycerolysis reactions at 350° and 460° F

350° F	460° F
K1 = 0.291	K1 = 1.566
K2 = 0.163	K2 = 0.220
K3 = 0.333	K3 = 1.475

is a glyceride-rich oil with significantly reduced FFA levels.

This study was conducted using very low-grade brown grease in order to be conservative on promoting the advantages of glycerolysis. However, any oil with elevated levels of FFA can be successfully glycerized. The chemical kinetics results of this laboratory batch study have been successfully used to scale up the glycerolysis process to a continuous, industrial design. **R**