

# Biodiesel Tech

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## PRETREATMENT OF HIGH FREE FATTY ACID FEEDSTOCKS

When working with feedstocks that contain 5% FFA or higher, it is important to convert the FFAs to biodiesel or the process yield will be low. There are at least four techniques for converting the FFAs to biodiesel:

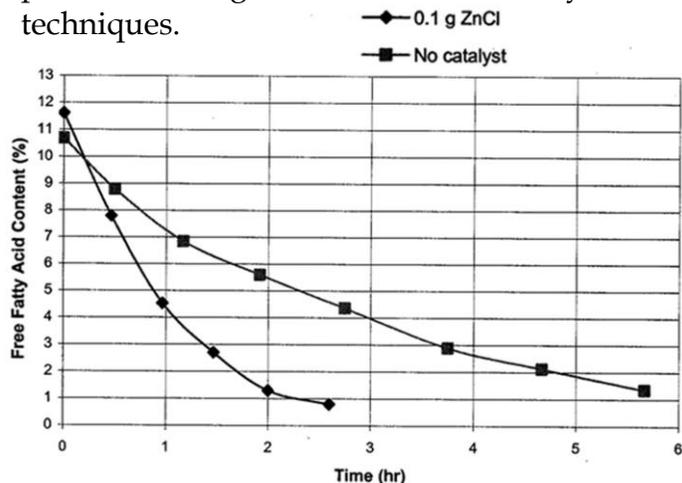
**1. Enzymatic methods:** These methods require expensive enzymes but seem to be less affected by water. At the present time, no one is using these methods on a commercial scale.

**2. Glycerolysis:** This technique involves adding glycerol to the feedstock and heating it to high temperature (200°C), usually with a catalyst such as zinc chloride. The glycerol reacts with the FFAs to form mono- and diglycerides as shown in the following reaction.

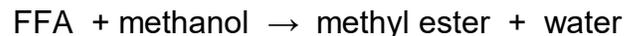


The drawback of glycerolysis are the high temperature and that the reaction is relatively slow. An advantage is that no methanol is added during the pretreatment so that as water is formed by the reaction the water immediately vaporizes and can be vented from the mixture.

The figure below shows the rate of decrease of the fatty acid level in a batch of animal fat. This technique produces a low FFA feed that can be processed using traditional alkali-catalyzed techniques.



**3. Acid Catalysis:** This technique uses a strong acid such as sulfuric acid to catalyze the esterification of the FFAs and the transesterification of the triglycerides. The reaction does not produce soaps because no alkali metals are present. The esterification reaction of the FFAs to alcohol esters is relatively fast, proceeding substantially to completion in one hour at 60°C. However, the transesterification of the triglycerides is very slow, taking several days to complete. Heating to 130°C can greatly accelerate the reaction but reaction times will still be 30-45 minutes. Another problem with acid catalysis is that the water production from the following reaction stays in the reaction mixture and ultimately stops the reaction, usually well before reaching completion.



**4. Acid catalysis followed by alkali catalysis:** This approach solves the reaction rate problem by using each technique to accomplish the process for which it is best suited. Since acid catalysis is relatively fast for converting the FFAs to methyl esters, it is used as a pretreatment for the high FFA feedstocks. Then, when the FFA level has been reduced to 0.5%, or lower, an alkali catalyst is added to convert the triglycerides to methyl esters. This



process can convert high free fatty acid feedstocks quickly and effectively. Water formation is still a problem during the pretreatment phase. One approach is to simply add so much excess methanol during the pretreatment that the water produced is diluted to the level where it does not limit the reaction. Molar ratios of alcohol to FFA as high as 40:1 may be needed. The disadvantage of this approach is that more energy is required to recover the excess methanol. Another approach would be to let the acid-catalyzed esterification proceed as far as it will go until it is stopped by water formation. Then, boil off the alcohol and water. If the FFA level is still too high, then additional methanol and, if necessary, acid catalyst can be added to continue the reaction. This process can be continued for multiple steps and will potentially use less methanol than the previous approach. Again, the disadvantage is the large amount of energy required by the distillation process.

A less energy intensive approach is to let the acid-catalyzed reaction mixture settle. After a few hours, a methanol-water mixture will rise to the top and can be removed. Then, additional methanol and acid can be added to continue the reaction. It is also possible to use

fluids such as glycerol and ethylene glycol to wash the water from the mixture.

### Procedure for High FFA Acid Catalysis

1. Measure FFA level
2. Add 2.25 g methanol and 0.05 g sulfuric acid for each gram of free fatty acid in the oil or fat. Sulfuric acid and methanol should be mixed first and then added slowly to the oil.
3. Agitate for one hour at 60-65°C.
4. Let mixture settle. Methanol-water mixture will rise to the top. Decant the methanol, water, and sulfuric acid layer.
5. Take bottom fraction and measure new FFA level.
6. If FFA is > 0.5%, return to step 2 with new FFA level. If FFA is < 0.5%, proceed to step 7.
7. Add an amount of methanol equal to  $0.217 \times [\text{grams of unreacted triglycerides}]$  and an amount of sodium methoxide equal to  $[0.25 + (\% \text{FFA})0.190]/100 \times [\text{grams of unreacted triglycerides}]$ . Mix the sodium methoxide with the methanol and then add to the oil. This corresponds to a 6:1 molar ratio of methanol to oil for the unreacted triglycerides. It ignores any methanol that may have carried over from the pretreatment.
8. Agitate for 1 hour at 60°C.

#### Example: 100 g of 12% FFA animal fat

Pretreatment:  $2.25 \times 12 \text{ g} = 27.0 \text{ g}$  methanol  
 $0.05 \times 12 \text{ g} = 0.6 \text{ g}$  H<sub>2</sub>SO<sub>4</sub> (sulfuric acid)

Mix acid with methanol. Then add mixture to fat. Agitate for one hour at 60°C. Let settle and separate bottom phase. Acid value should decrease substantially, to at least 5-6 mg KOH/g. Therefore, FFA = 2.5%

Second step of pretreatment:

$2.25 \times 2.5 \text{ g} = 5.6 \text{ g}$  of methanol  
 $0.05 \times 2.5 \text{ g} = 0.13 \text{ g}$  H<sub>2</sub>SO<sub>4</sub>

Mix with oil, agitate at 60°C for 1 hour. FFA should be < 0.5%. Removal of upper phase is usually optional at this point.

Then add  $0.217 \times (88) = 19.1 \text{ g}$  methanol  
 $[0.25 + (0.5)(0.190)]/100 \times 88 = 0.30 \text{ g}$  sodium methoxide

Agitate at 60°C for one hour. If glycerol and ester do not separate, add 50 g of warm distilled water to encourage separation. Wash 3-4 times.

