

ACID/BASE CATALYZED REACTION

(a.k.a. Two-Stage Process)

Why a two stage process?

- The single stage, base-catalyzed transesterification process we carried out in previous labs is inefficient because soap is made.
- Soap is formed when sodium ions from the lye or potassium ions from the potassium hydroxide combine with free fatty acids (FFAs) present in used vegetable oil, some virgin oils, and animal fats.
- The soaps diminish the yield because they bond the methyl esters to water.
- The bonded esters get washed out at the washing stage but make water separation more difficult (emulsification occurs) and increase water consumption.
- An acid-catalyzed esterification process before the base-catalyzed transesterification process will eliminate most of the free fatty acids from the vegetable oil.
- FFAs = bad.

Process Overview: Stage 2

- The second-stage process is transesterification and uses basic catalyst as usual, but uses less than the single stage process
- The sulfate ion in the sulfuric acid combines with the sodium or potassium ion during the second-stage reaction to form a water-soluble salt (sodium or potassium sulfate) that gets removed during the water wash phase.
- No sulfur remains in the biodiesel fuel product.

Process Overview: Stage 1

- The first-stage process is not *trans*-esterification it is simple esterification
- We turn FFAs into biodiesel thus significantly decreasing the possibility of saponification (soap making)
- We use an acid as the catalyst for the esterification of the FFAs
- Sulfuric acid is battery acid and needs to be 95% pure (battery acid is around 50%)
- Sulfuric acid is one of the most common chemicals on Earth, just like lye. It is also extremely corrosive so wear chemical protective gloves and eye protection when handling strong acids.

Pretreatment of High Free Fatty Acid Feedstocks

- Biodiesel feedstocks vary in the amount of free fatty acids they contain:

Refined vegetable oils	< 0.05%
Crude soybean oil	0.3-0.7%
Restaurant waste grease	2-7%
Animal fat	5-30%
Trap grease	75-100%

Alkali Catalysts

- Not suitable for high FFA feeds because of soap formation.

- Typical catalyst amounts:

Sodium hydroxide: 1% of triglyceride weight

Potassium hydroxide: 1% of triglyceride weight

Sodium methoxide: 0.25% of triglyceride weight

High FFA feeds must be pretreated

Four methods

1. Enzymatic methods – very costly, not currently a popular choice.
2. Glycerolysis
3. Acid catalysis
4. Acid catalysis followed by base catalysis.

Glycerolysis

- Add glycerol to high FFA feedstock with catalyst (ZnCl) at 200°C.
- Converts FFAs to monoglycerides and diglycerides. These can be transesterified to methyl esters with a base catalyst.
- Water formed by

FFA + glycerol \gg monoglyceride + water
is vented as it is formed.

Glycerolysis

- Disadvantages:
- Requires high temperature, 200°C
- Fairly slow process.
- Requirement for clean glycerol is not known.

Approach for low levels of FFA

- Can add additional catalyst and allow soap formation (similar to caustic stripping).
- It takes one mole of catalyst to neutralize one mole of FFA.

Sodium hydroxide: $[\%FFA](0.144) + 1 \%$

Potassium hydroxide: $[\%FFA](0.197)/0.86 + 1 \%$

Sodium methoxide: $[\%FFA](0.190) + 0.25 \%$

- This approach will work up to 5-6% FFA, less if emulsifiers or water are present.

Acid Catalysis

- Use acid such as sulfuric acid to catalyze both esterification and transesterification reactions.
- Esterification of FFA is fast (1 hour) but transesterification is slow (2 days) at 60°C.
- Water formation by

FFA + methanol \gg methyl ester + water

Can be a problem.

Acid catalysis followed by base catalysis

- Use acid catalysis for conversion of FFAs to methyl esters, until FFA $< 0.5\%$.
- Then, add additional methanol and base catalyst to finish the reaction.

Lab Procedure

- Measure the acid value of the WVO sample
- Note: Acid value is twice the %FFA
- Measure out 200g of WVO sample
- Heat sample to 60°C
- Measure out 2.25g methanol for every gram of FFA in the WVO sample
- Calculate amount of sulfuric acid to add
- 0.05 g of sulfuric acid for every gram of FFA in sample

Lab Procedure (part 2)

- Add the acid to the alcohol
- Gently agitate the alcohol-acid mixture until completely mixed
- Add the alcohol-acid mixture to the 200g of WVO sample
- Agitate mixture at 60oC for 1 hour
- Let mixture settle- Methanol-water mixture will rise to the top
- After the mixture cools, drain a sample from the bottom fraction and measure new FFA level via acid value measurement

(Directions taken from Iowa State Lab procedure, “Pretreatment of High Free Fatty Acid Feedstocks”)

Acid catalysis followed by base catalysis

After measuring the acid value or %FFA, your results will

Determine your next step:

If FFA is $> 0.5\%$, return to step 2 with new FFA level. If FFA is $< 0.5\%$, proceed to step 7.

Add an amount of methanol equal to $0.217 \times$ [grams of unreacted triglycerides] and

an amount of sodium methoxide equal to

$[0.25 + (\%FFA)0.190]/100 \times$ [grams of unreacted triglycerides].

Mix the sodium methoxide with the methanol and then add to the oil.

Agitate for 1 hour at 60°C .

References

- Canakci, M. and J. Van Gerpen, 1999, “Biodiesel Production via Acid Catalysis,” ASAE Transactions, 42(5):1203-1210.
- Canakci, M. and J. Van Gerpen, 2001, “Biodiesel Production from Oils and Fats with High Free Fatty Acids,” ASAE Transactions, 44(6):1429-1436.
- www.me.iastate.edu/biodiesel