Biodiesel Production Technology

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Biodiesel Production Processes

- Definition and standards
- Transesterification
- Fatty acid chains
- Standard recipes
- Production techniques
- Process issues

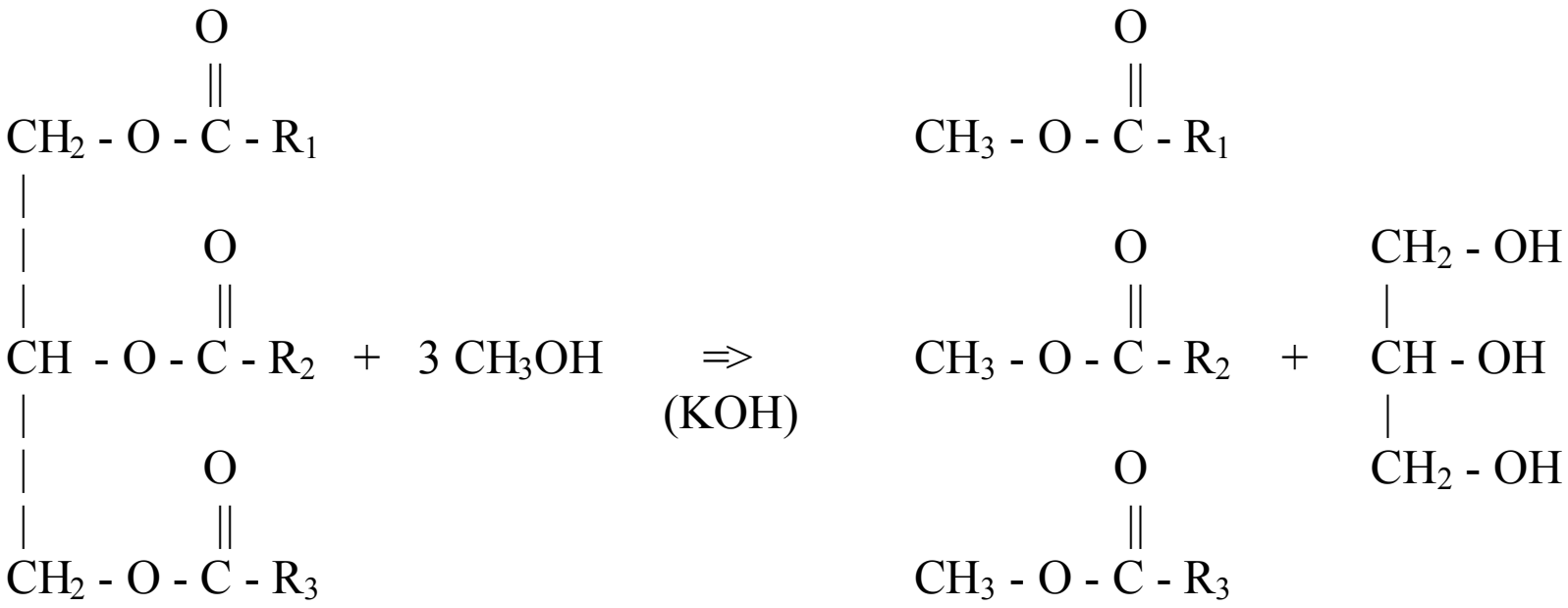
Definition of “Biodiesel”

- Biodiesel – a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B 100.
- Biodiesel must meet the specifications of ASTM D 6751

ASTM D 6751-02

Property	Method	Limits	Units
Flash point, closed cup	D 93	130 min	° C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 ° C	D 445	1.9 – 6.0	mm^2/s
Sulfated ash	D 874	0.020 max	wt. %
Total Sulfur	D 5453	0.05 max	wt. %
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to customer	° C
Carbon residue	D 4530	0.050 max	wt. %
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	wt. %
Total glycerin	D 6584	0.240	wt. %
Phosphorus	D 4951	0.0010	wt. %
Vacuum distillation end point	D 1160	360 °C max, at T-90	% distilled

Transesterification



Triglyceride methanol mixture of fatty esters glycerin

Standard Recipe

100 lb oil + 21.71 lb methanol

_ 100.45 lb biodiesel + 10.40 lb glycerol + 10.86 lb XS methanol

Plus 1 lb of NaOH catalyst

Biodiesel Production Techniques:

- Batch Base Catalyzed
- Continuous Base Catalyzed
- Acid Catalyzed Processes
- Non-Catalytic Processes

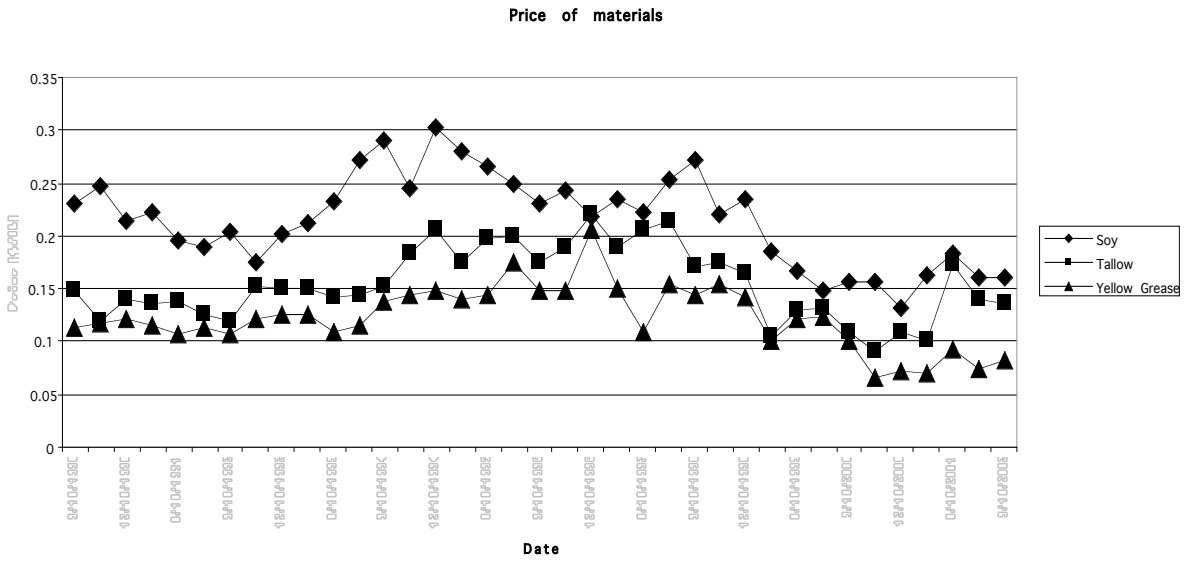
Feedstocks Used in Biodiesel Production

- Triglygeride (triacylglycerol) or fats and oils (e.g. 100 kg soybean oil)
- Primary alcohol (e.g. 10 kg methanol)
- Catalyst (e.g. 0.3 kg sodium hydroxide)
- Neutralizer (e.g. 0.25 kg sulfuric acid)

Triglyceride Sources

- Rendered animal fats: beef tallow, lard, Vegetable oils: soybean, canola, palm, etc.
- chicken fat
- Rendered greases: yellow grease (multiple sources)
- Recovered materials: brown grease, soapstock, etc.

Price Patterns for Biodiesel Sources



Primary Alcohol Sources

- Methanol: Molecular Weight - 32.04
  Density - 0.792 g/cc
  Boiling Point - 64.7 °C

- Ethanol: Molecular Weight - 46.07
  Density - 0.789 g/cc
  Boiling Point - 78.4 °C

Catalyst Options

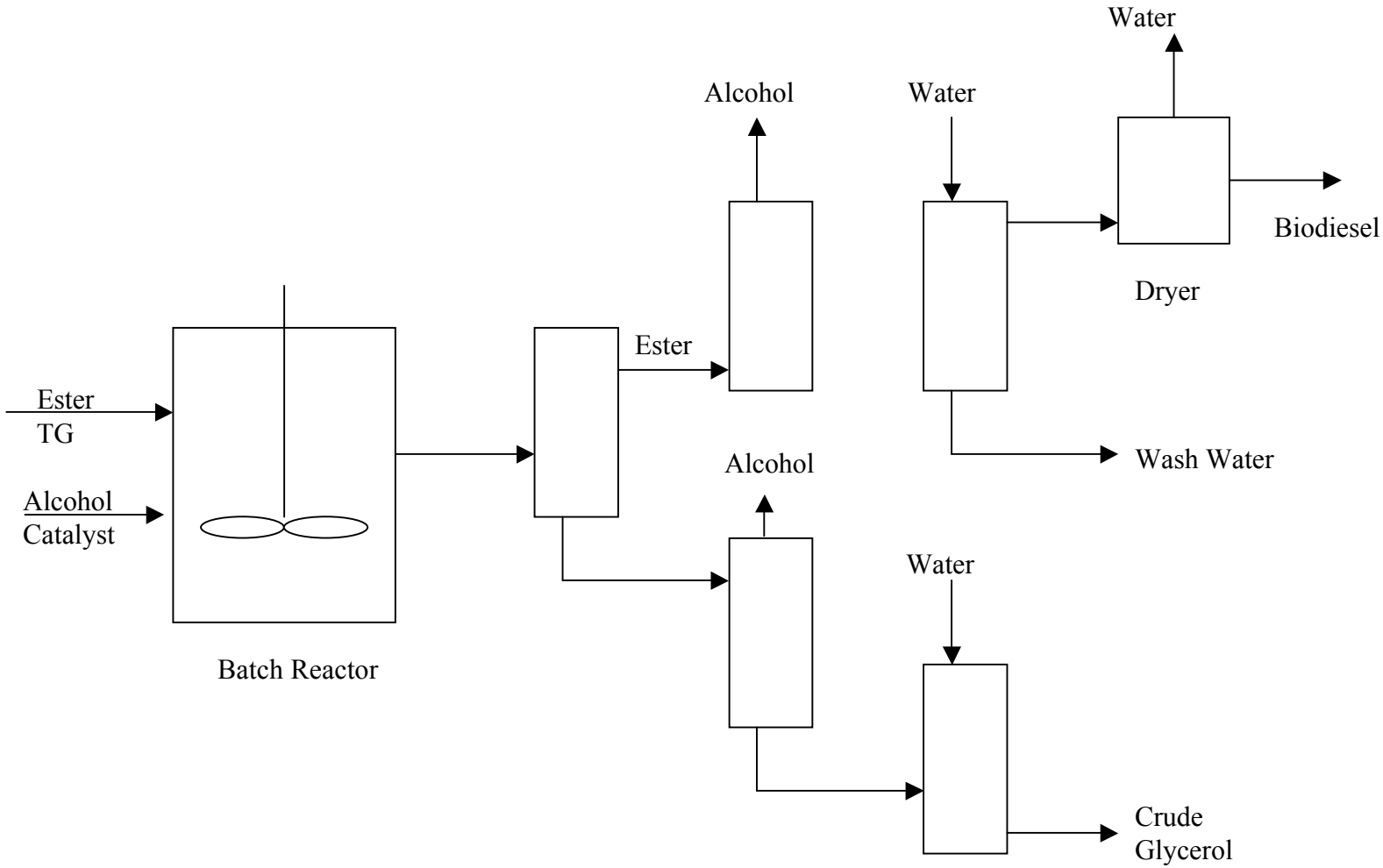
- Base Catalysts: NaOH, KOH, NaMeO
- Acid Catalysts: H_2SO_4, H_3PO_4, $CaCO_3$
- Lipase Enzymes: activity depends on source
- Non-catalyst options: supercritical, co-solvent system

Base Catalyzed Processes

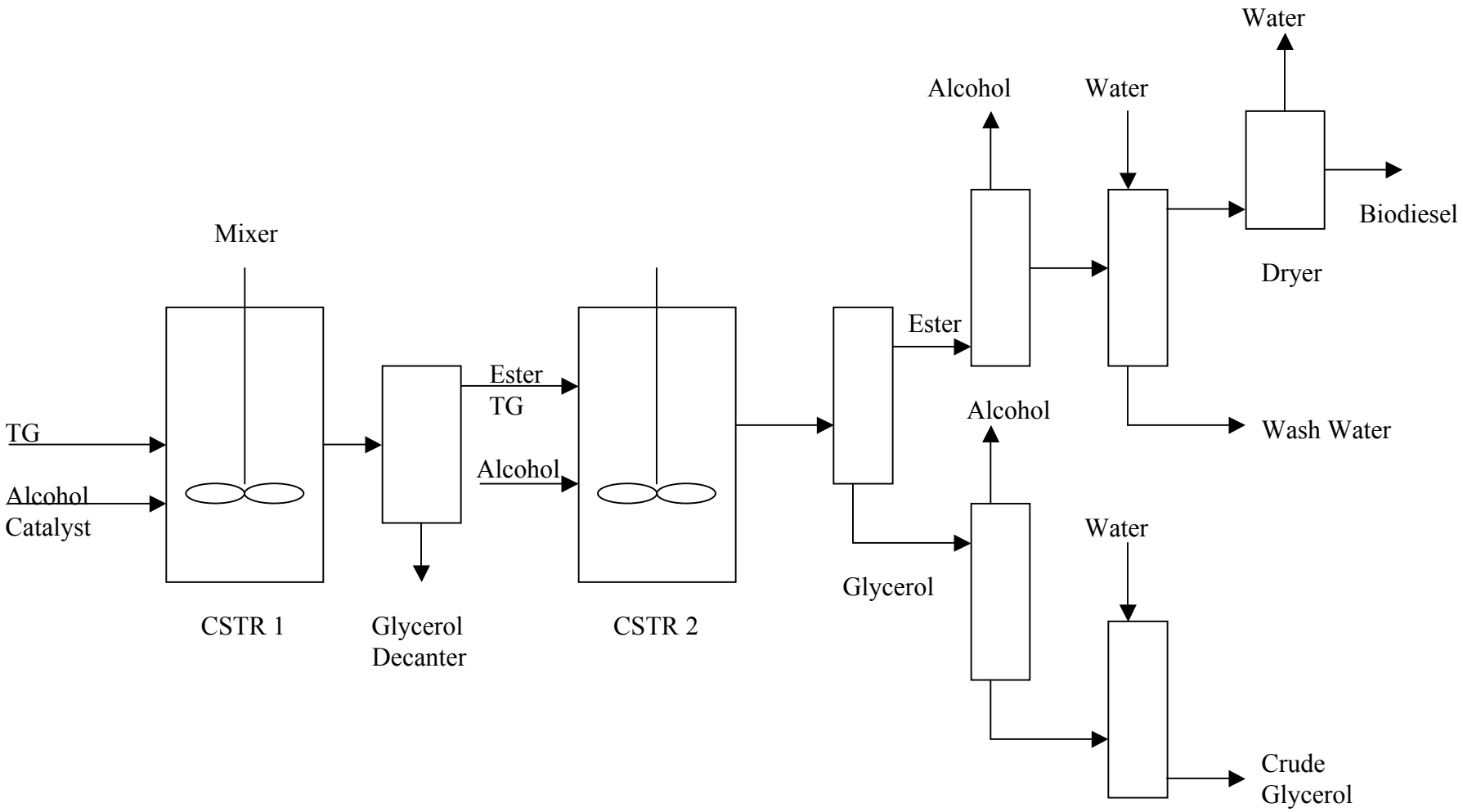
- Base catalyzed processes dominate current commercial production.
- Base catalysts are sensitive to : water, FFA
- Typical alcohol:TG ratio is 6:1 for base catalyzed reactions.
- Typical base concentrations are (5 w/w oil):
  NaOH/KOH – 0.3 to 1.5 %

  NaMeO – 0.5 % or less

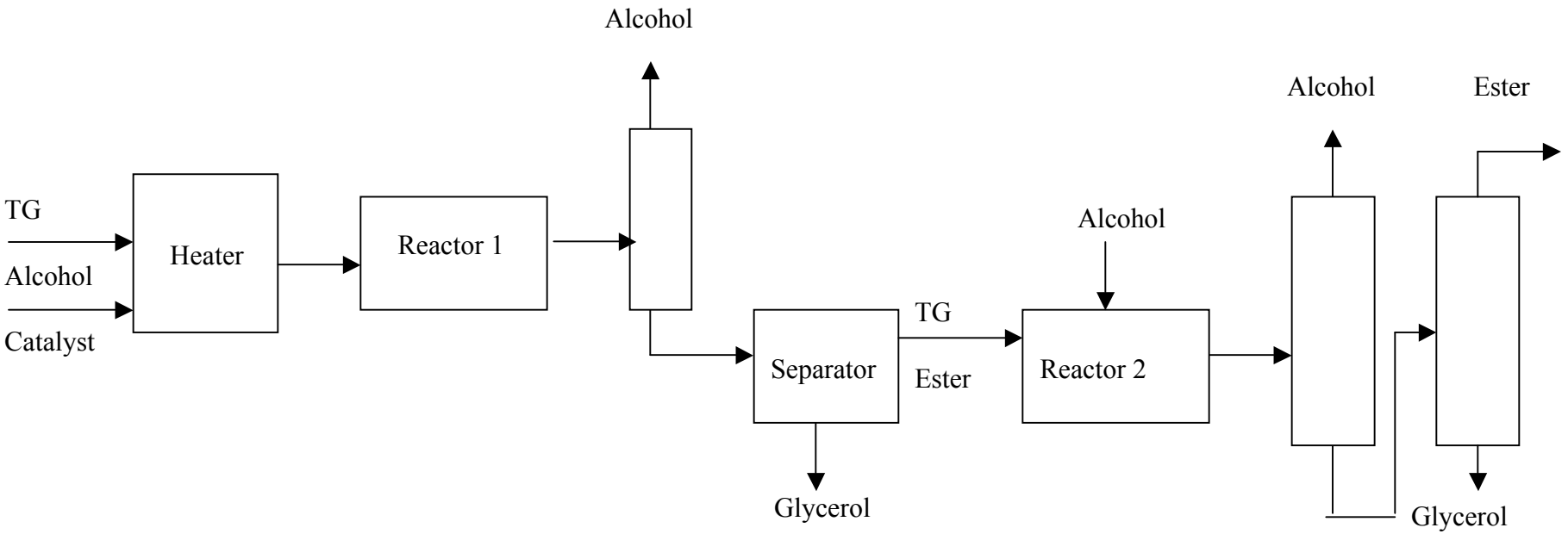
Batch, Base Catalyzed Process



Continuous, Base Catalyzed Process



PFR, Base Catalyzed Process



Acid Catalyzed Processes

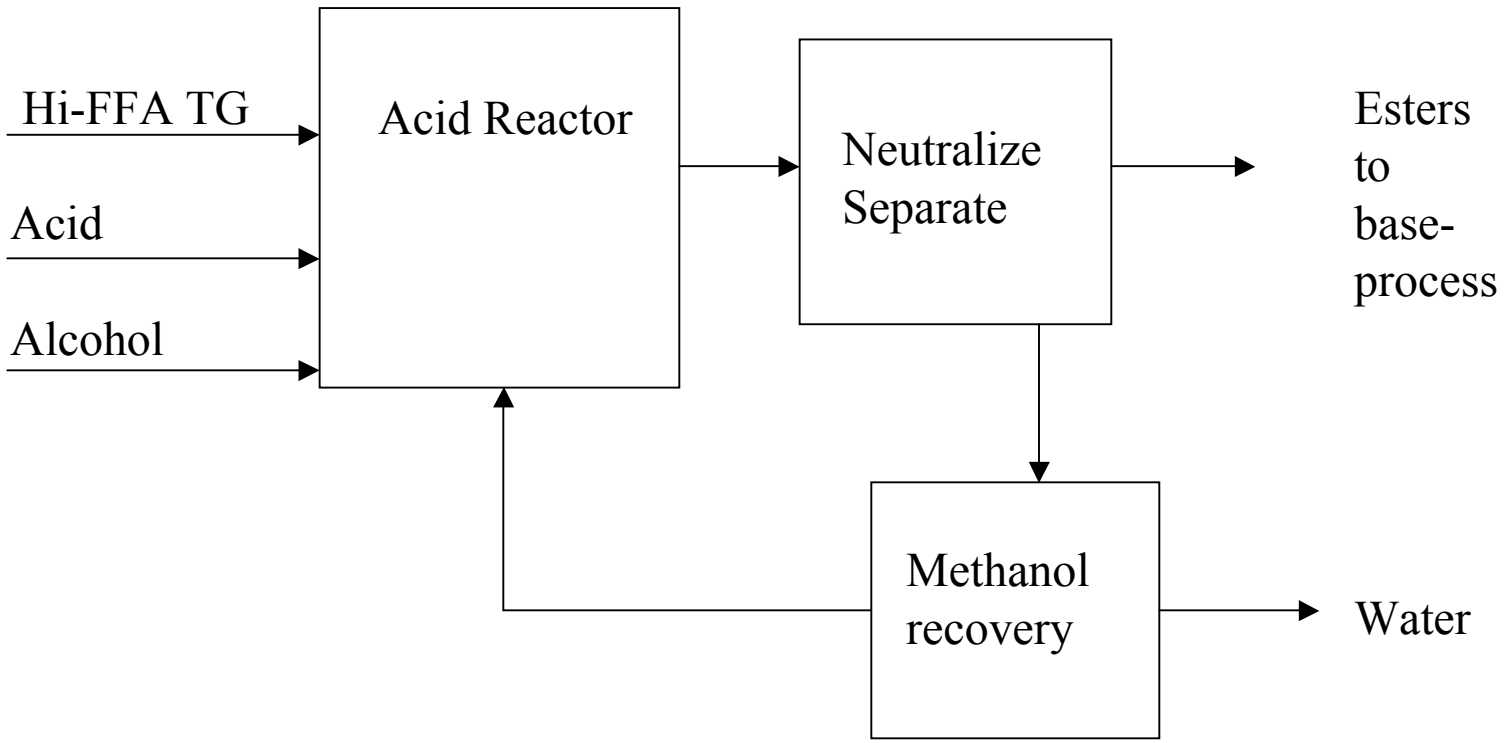
- Acid catalyzed processes are used for direct esterification of free fatty acids in a high FFA feedstock, or to make esters from soapstock.
- Sensitivities:

  High FFA content requires water removal during reaction.

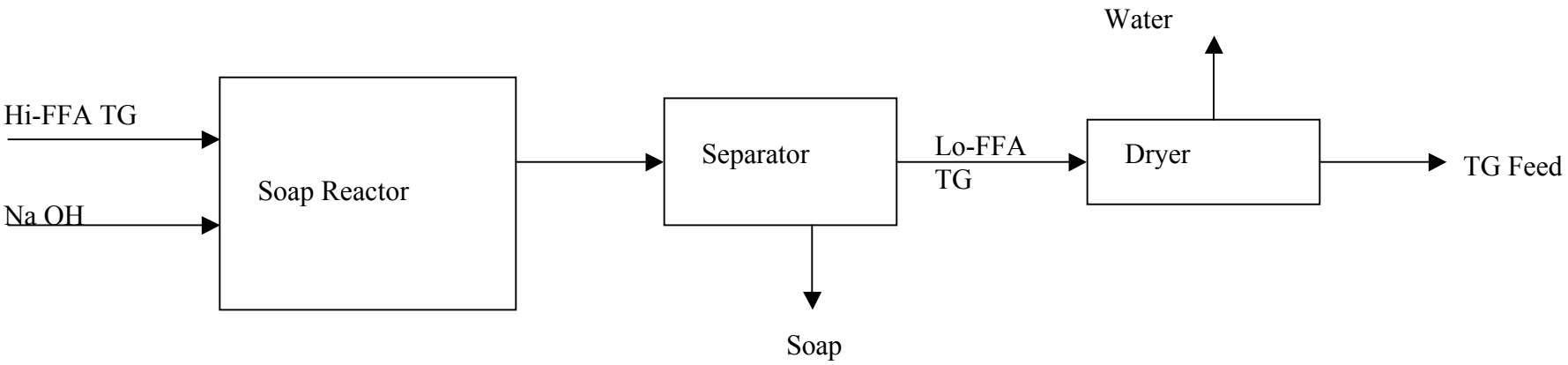
  High alcohol:FFA ratio required – about 40:1

  Large amounts (5 to 25 %) catalyst may be required.

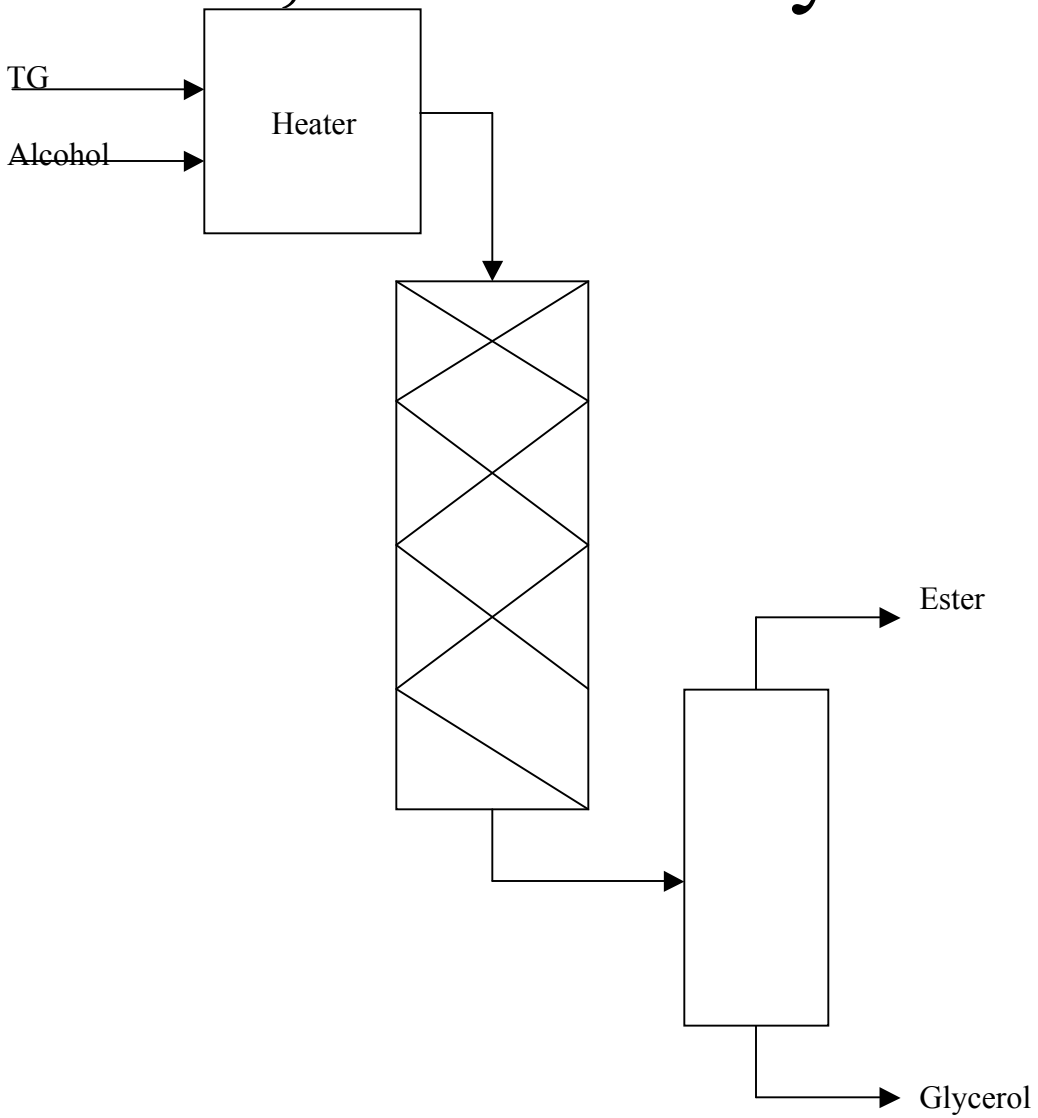
Acid Catalyzed FFA Pretreat System



Base-High FFA Soapstock Removal



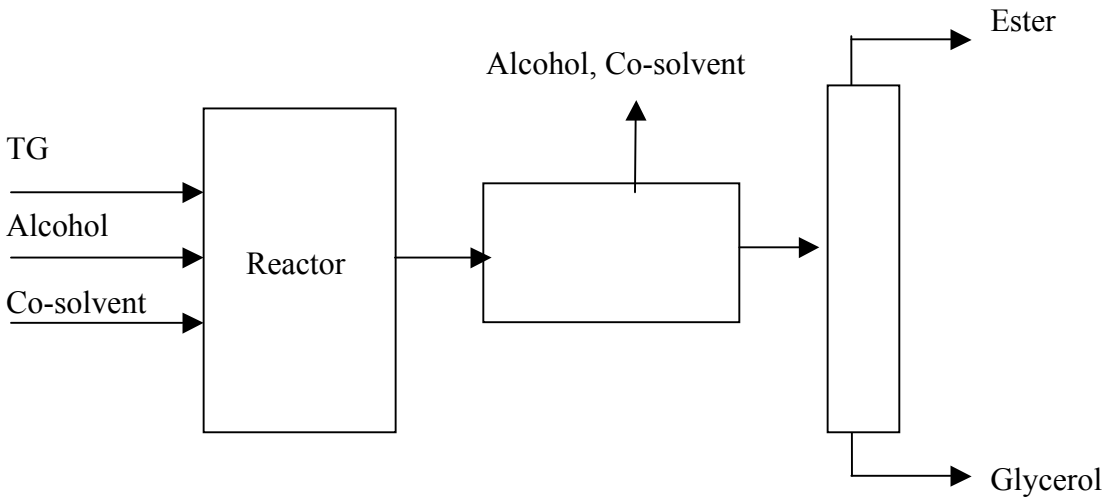
Fixed-Bed, Base Catalyzed Reactor



Non-Catalytic Systems

- Esterification is a three-step reaction sequence:
  - Induction phase
  - Rate limiting phase
  - Glycerol inhibition phase
- Base and acid catalysts serve as solubilizers to speed the induction reaction.
- Non-Catalytic Strategies:
  - Co-solvent
  - Supercritical system

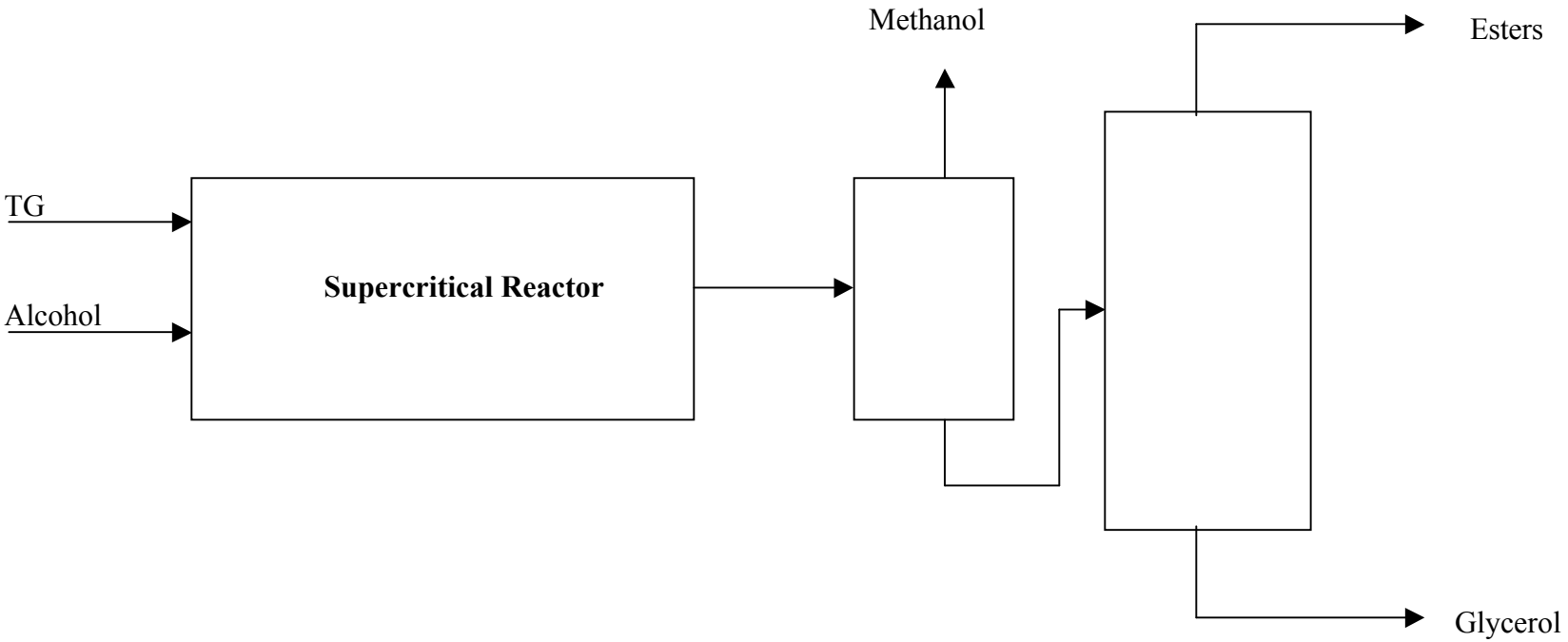
Biox Co-solvent Process



Reaction time

- Transesterification reaction will proceed at ambient (70°F) temperatures but needs 4-8 hours to reach completion.
- Reaction time can be shortened to 2-4 hours at 105°F and 1-2 hours at 140°F.
- Higher temperatures will decrease reaction times but require pressure vessels because methanol boils at 148°F (65°C).
- High shear mixing and use of cosolvents have been proposed to accelerate reaction.

Supercritical Methanol System



Process Issues

- Feedstock requirements
- Reaction time
- Continuous vs. batch processing
- Processing low quality feedstocks
- Product quality
- Developing process options

Product Quality

- Product quality is important – modern diesel engines are very sensitive to fuel.
- It is not biodiesel until it meets ASTM D6751.
- Critical properties are total glycerol (completeness of reaction) and acid value (fuel deterioration). Reaction must be >98% complete.

Developing Process Options

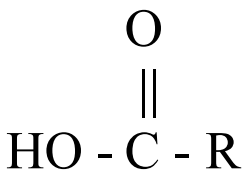
- Schemes for accelerating the reaction
  - Supercritical methanol
  - High shear mixing
  - Cosolvents (Biox)
- Solid (heterogeneous) catalysts
  - Catalyst reuse
  - Easier glycerol clean-up

Summary

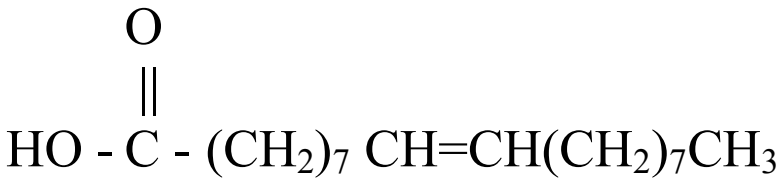
- Biodiesel is an alternative fuel for diesel engines that can be made from virtually any oil or fat feedstock.
- The technology choice is a function of desired capacity, feedstock type and quality, alcohol recovery, and catalyst recovery.
- The dominant factor in biodiesel production is the feedstock cost, with capital cost contributing only about 7 % of the product cost.
- Maintaining product quality is essential for the growth of the biodiesel industry.

Competing Reactions

- Free fatty acids are a potential contaminant of oils and fats.

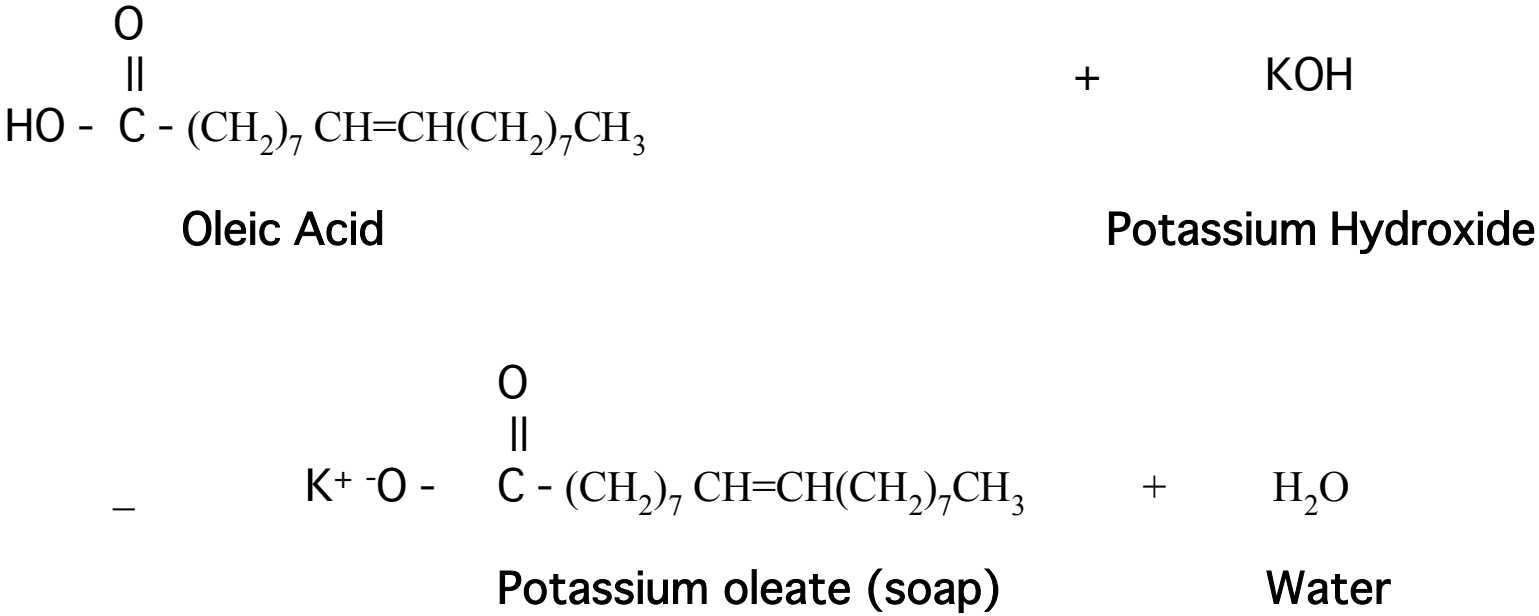


Carboxylic Acid (R is a carbon chain)



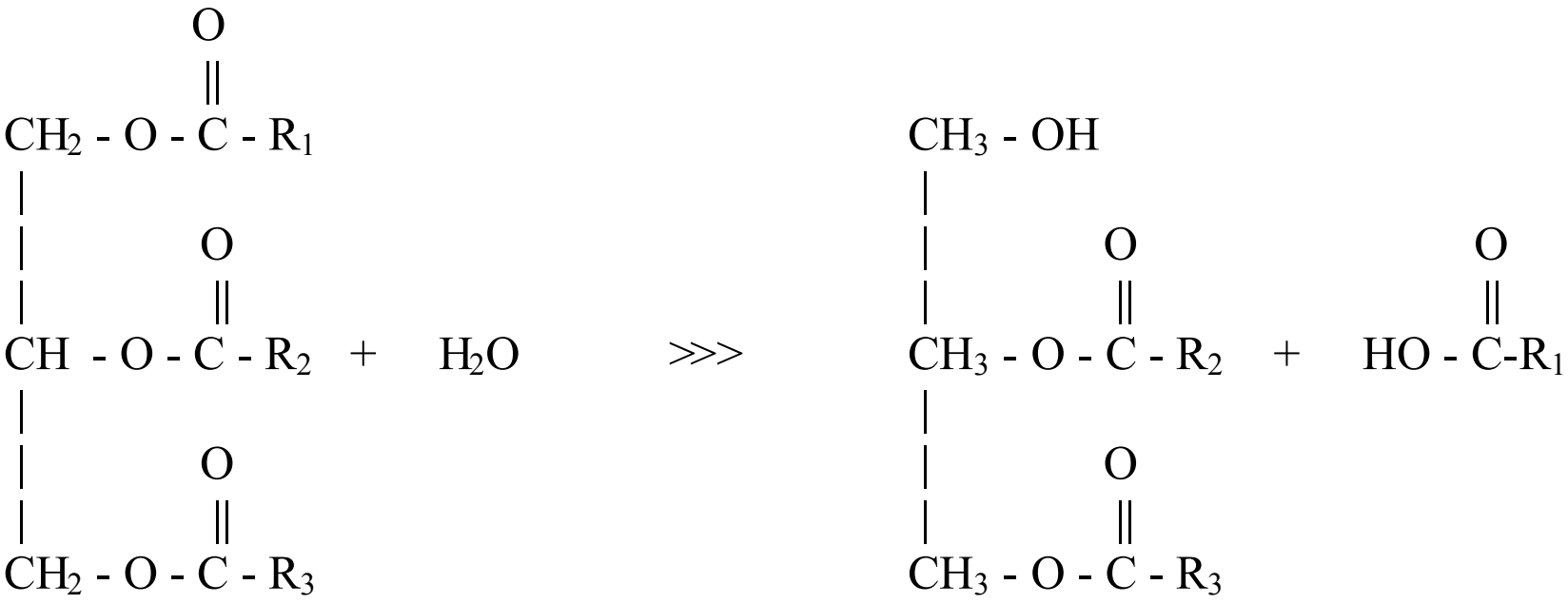
Oleic Acid

Fatty acids react with alkali catalyst to form soap.



Water is also a problem

Water hydrolyzes fats to form free fatty acids, which then form soap.



Triglyceride **Water** **Diglyceride** **Fatty acid**

Soap

- Soaps can gel at ambient temperature causing the the entire product mixture to form a semi-solid mass.
- Soaps can cause problems with glycerol separation and washing.

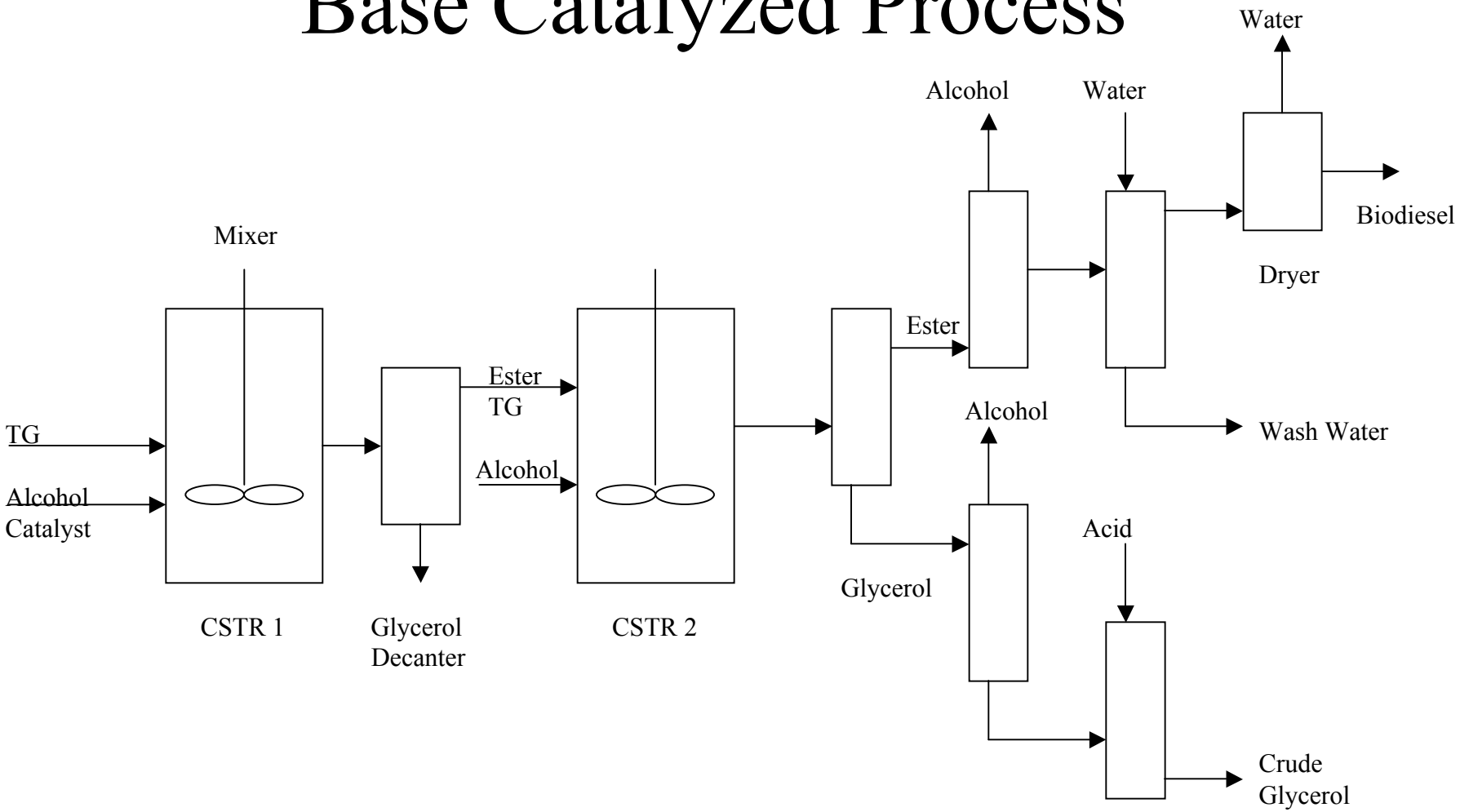
Feedstocks Used in Biodiesel Production

- Triglygeride or fats and oils (e.g. 100 kg soybean oil) – vegetable oils, animal fats, greases, soapstock, etc.
- Primary alcohol (e.g. 10 kg methanol) – methanol or ethanol (44% more ethanol is required for reaction)
- Catalyst (e.g. 0.3–1.0 kg sodium hydroxide)
- Neutralizer (e.g. 0.25 kg sulfuric or hydrochloric acid)

Batch vs Continuous Flow

- Batch is better suited to smaller plants (<1 million gallons/yr).
- Batch does not require 24/7 operation.
- Batch provides greater flexibility to tune process to feedstock variations.
- Continuous allows use of high-volume separation systems (centrifuges) which greatly increase throughput.
- Hybrid systems are possible.

Hybrid Batch/Continuous Base Catalyzed Process



Processing Lower Quality 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%

Price decreases as FFAs increase but processing demands increase, also.

Not suitable for high FFA feeds because of soap formation.

Preferred method for High FFA feeds: Acid catalysis followed by base catalysis

1. Use acid catalysis for conversion of FFAs to methyl esters, until FFA < 0.5%.
   - Acid esterification of FFA is fast (1 hour) but acid-catalyzed transesterification is slow (2 days at 60°C).
   - Water formation by

     FFA + methanol ==> methyl ester + water

     can be a problem.
2. Then, add additional methanol and base catalyst to transesterify the triglycerides.