

Biodiesel



What is Biodiesel?

- Biodiesel consists of alkyl-esters derived from a biological source
- Biodiesel can be used as a fuel in compression ignition engines (i.e. diesels)
- Can be blended with petroleum diesel in any ratio (e.g. B2, B20, B100)

What is Biodiesel?

- Vegetable oils (soy, canola, palm) are the most commonly used oils for biodiesel production.
- All common oils can be converted (i.e. plant oils, animal fats, waste cooking oil)



Why Biodiesel?

IT'S RENEWABLE!

Why Biodiesel?

- **Non-toxic**
 - LD50 of 17.4 g/kg
 - ten times less toxic than table salt
 - Less skin irritation than a 4% soap solution
 - very mild irritation
 - Insignificant aquatic toxicity
 - 1000mg/L is lethal to bluegill

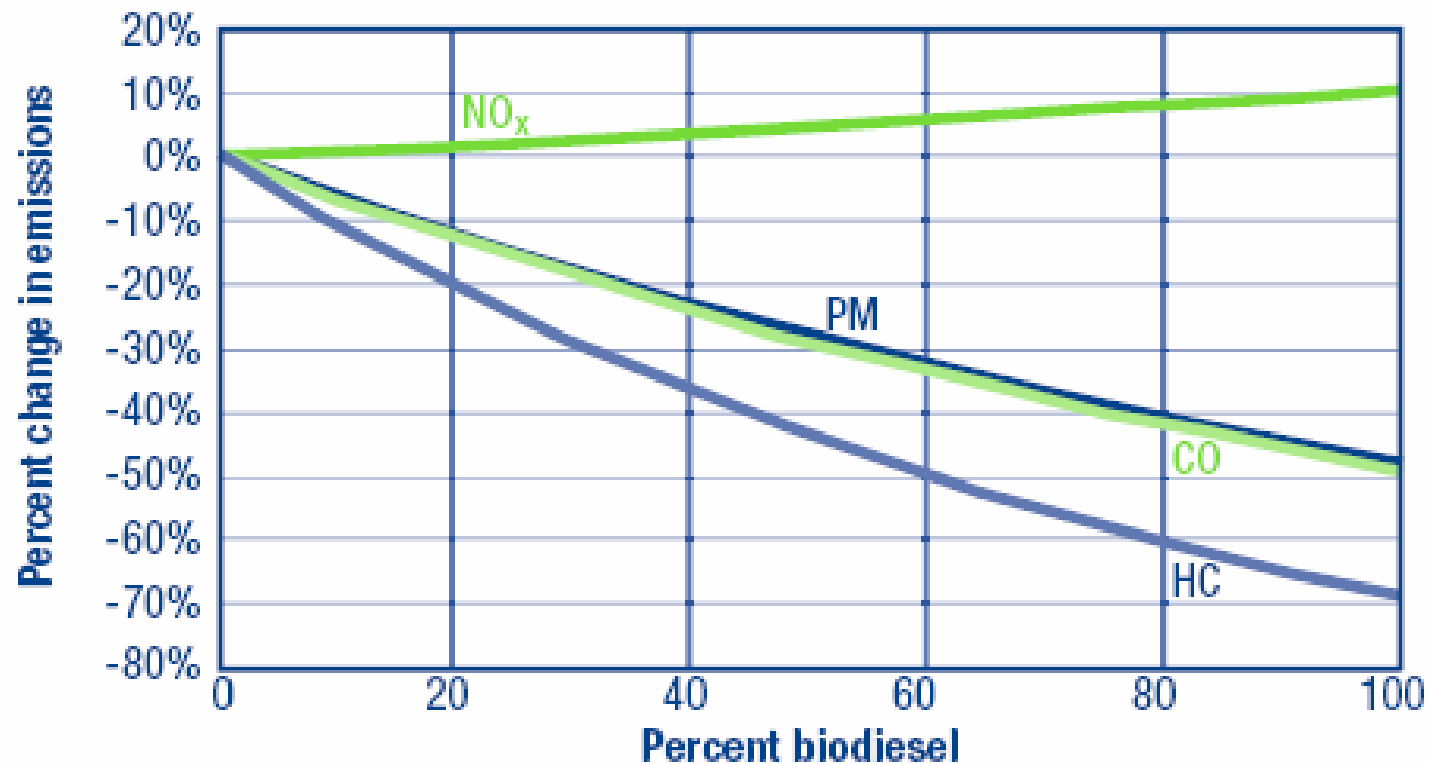
Why Biodiesel?

- **Reduced air pollution**
 - Sulfur emissions are greatly reduced
 - Equivalent to ultra low sulfur diesel now required by EPA
 - EPA Criteria pollutants are reduced
 - unburned hydrocarbons
 - carbon monoxide
 - particulate matter

Effects on Air Quality

- **Reduced air pollution**
 - Reduces health risks associated with petroleum diesel:
 - **75-85%** reduction of polycyclic aromatic hydrocarbons (PAH)
 - **90%** reduction of nitrated polycyclic aromatic hydrocarbons (nPAH).
 - These have been identified as carcinogens

Biodiesel vs. Petrodiesel



Basic Emission Correlation. Average emission impacts of biodiesel for heavy-duty highway engines. Source: U.S. EPA².

AVERAGE BIODIESEL EMISSIONS COMPARED TO CONVENTIONAL DIESEL, ACCORDING TO EPA

Emission Type	B100	B20
<u>Regulated</u>		
Total Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
Nox	+10%	+2% to -2%
<u>Non-Regulated</u>		
Sulfates	-100%	-20%*
PAH (Polycyclic Aromatic Hydrocarbons)**	-80%	-13%
nPAH (nitrated PAH's)**	-90%	-50%***
Ozone potential of speciated HC	-50%	-10%

* Estimated from B100 result

** Average reduction across all compounds measured

*** 2-nitrofluorine results were within test method variability

Source: EPA Emissions Evaluation for the National Biodiesel Board

Environmental Benefits

- **Homegrown**
 - Can be grown from local oil crops
 - Reduce long distance transport of fuels
- **Biodegradable**
 - Biodiesel degrades at ~the same rate as dextrose
 - Environmentally positive (no oil spill disasters)



Some other important considerations

- Fits existing fuel infrastructure
 - Runs in current diesel engines
 - Can be stored at existing petrol stations
 - Can be transported like petroleum diesel
- Higher flashpoint than petroleum diesel
 - Classified as non-flammable by OSHA (150 °C)
 - Safer to handle and transport, safer in accidents
- Provides lubricating properties
 - Reduces engine wear
 - Extends engine life

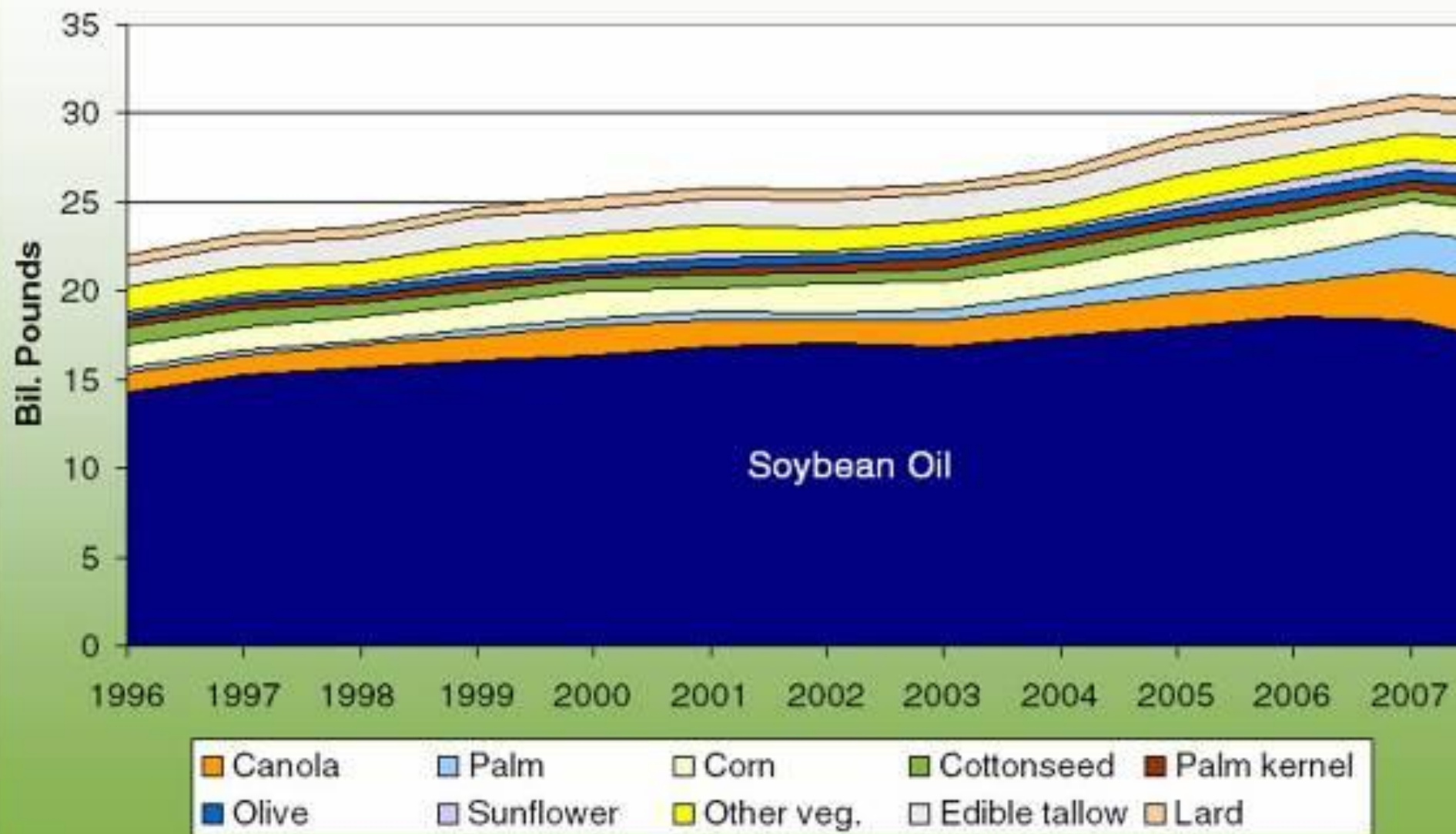
What's the Catch?

What's the Catch?

Feedstock Supply

There simply isn't enough oil to turn into biodiesel!

Figure 1. U.S. Domestic Vegetable Oils and Animal Fat Usage



Data source: USDA, ERS

Feedstock Supply

- Devoting all 2005 U.S. soybean production to biodiesel would have offset 6.0% of U.S. diesel demand.

Source: Hill et al. 2006. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. Proceedings of the National Academy of Sciences, 103:30 11206-11210

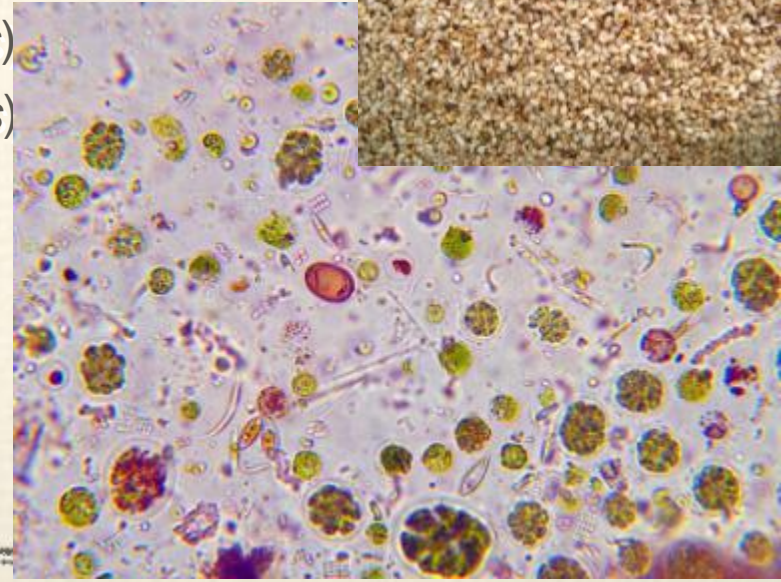
Feedstock Supply

- However, because of the fossil energy required to produce biodiesel, this change would provide a net energy gain equivalent to just 2.9%.

Source: Hill et al. 2006. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. Proceedings of the National Academy of Sciences, 103:30 11206-11210

Feedstock Supply Solutions

1. Use less fuel by increasing efficiency
2. Recycle waste cooking oil
3. Get creative in oil crops!
 - Tremendous botanical potential
 - ✓ Sesame (*Sesamum indicum*)
 - ✓ Camelina (*Camelina sativa*)
 - ✓ Jatropha (*Jatropha curcas*)
 - ✓ Castor (*Ricinus communis*)
 - ✓ Tallow (*Sapium sebifera*)
 - ✓ Algae (~40,000 species)

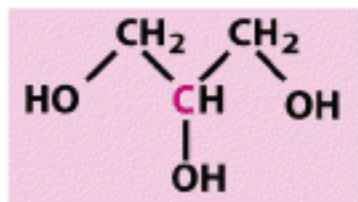




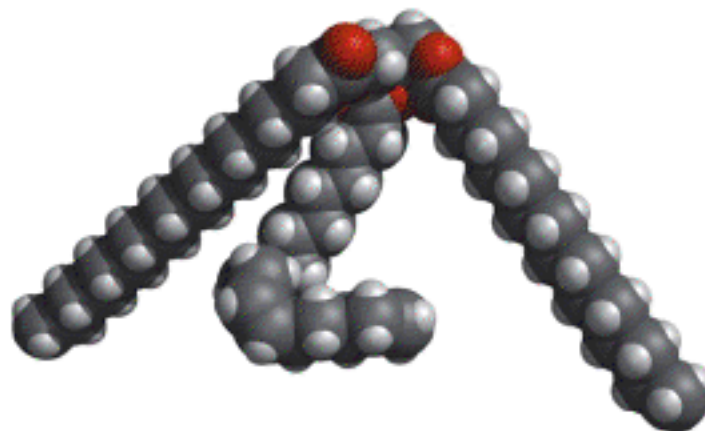
THE CHEMISTRY OF BIODIESEL

Important Families of Organic Compounds in Relation to Biodiesel

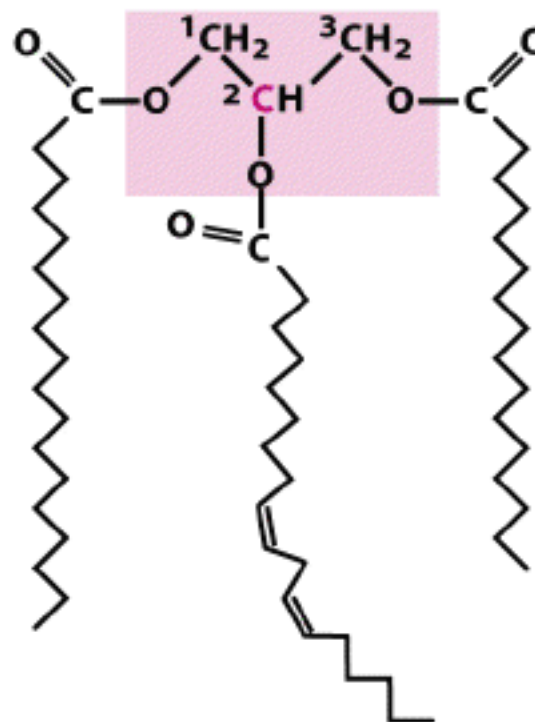
- Alcohols
 - Methanol
 - Ethanol
- Carboxylic acids
 - Free fatty acids
- Lipids
 - Triacylglycerols (oils)
 - Phospholipids
 - Waxes
- Esters
 - Methyl esters
 - Ethyl esters



Glycerol



Triacylglycerol



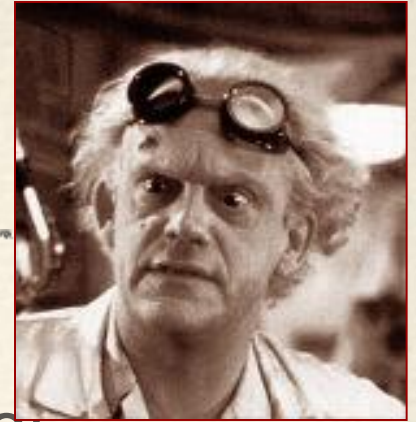
**1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol,
a mixed triacylglycerol**

Figure 10-3

Lehninger Principles of Biochemistry, Fifth Edition

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How is Biodiesel Made?



- A TRANSESTERIFICATION reaction of **vegetable** (or **animal**) lipids with a low molecular weight alcohol (**methanol**) produces biodiesel
- This reaction is catalyzed by a **base**, typically: Sodium Hydroxide (NaOH) or Potassium Hydroxide (KOH)

Transcendental Transesterification

- TRANS= CHANGE
- ESTERIFICATION= CREATING AN ESTER
- OIL + ALCOHOL = GLYCEROL + ALKYL ESTERS (BIODIESEL)

A BASE AND HEAT ARE REACTION CATALYSTS

- In the context of biodiesel transesterification is:
 - the replacment of the glycerol portion of the oil with methanol or ethanol

[TRANSESTERIFICATION]

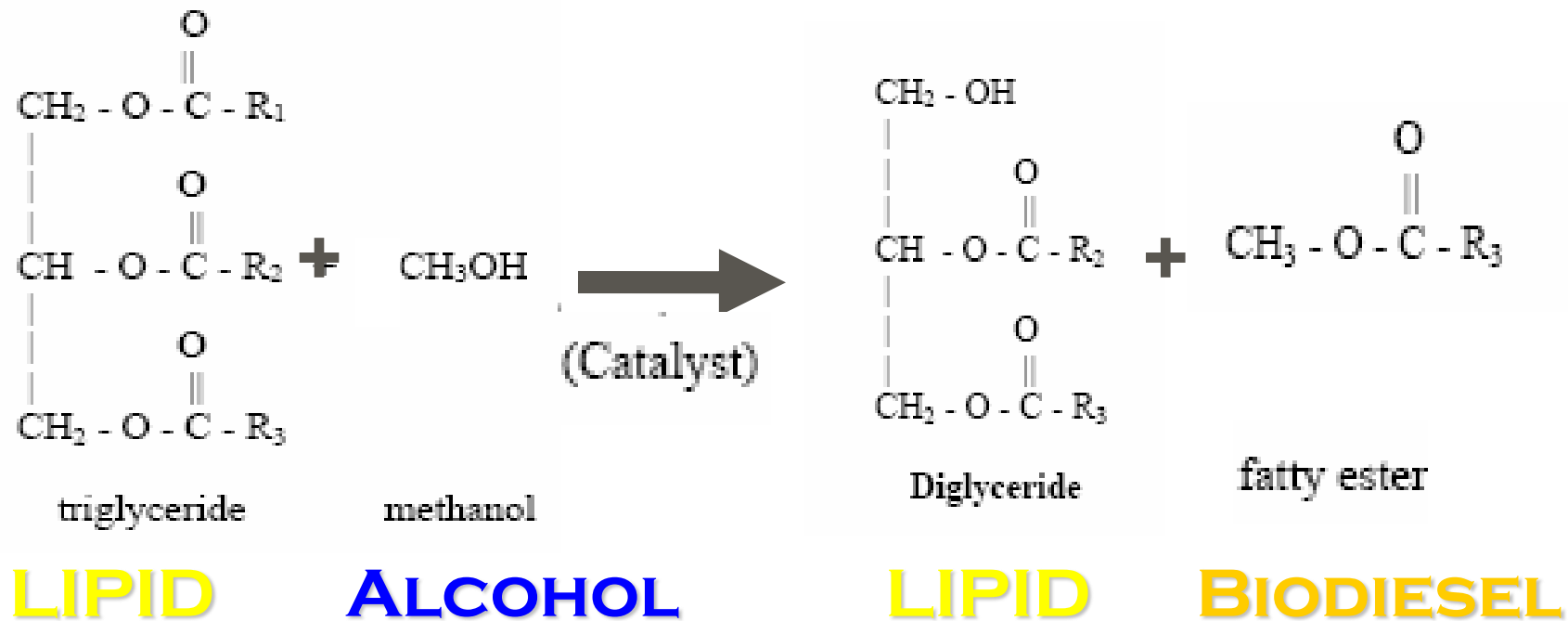
a step-by-step visual guide



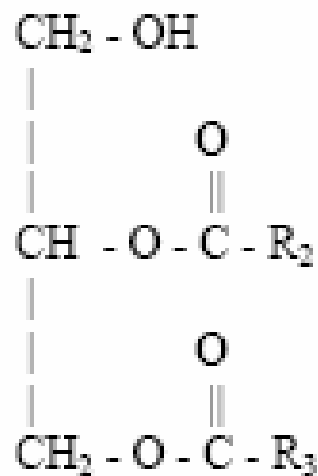
Catalyst



Step 1



Step 2:



Diglyceride

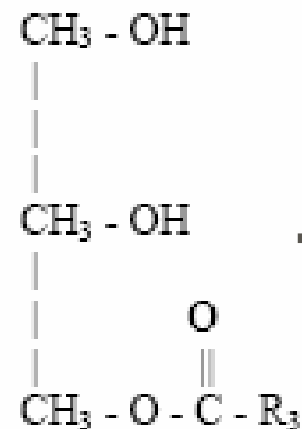
LIPID

+



methanol

ALCOHOL



Monoglyceride

LIPID

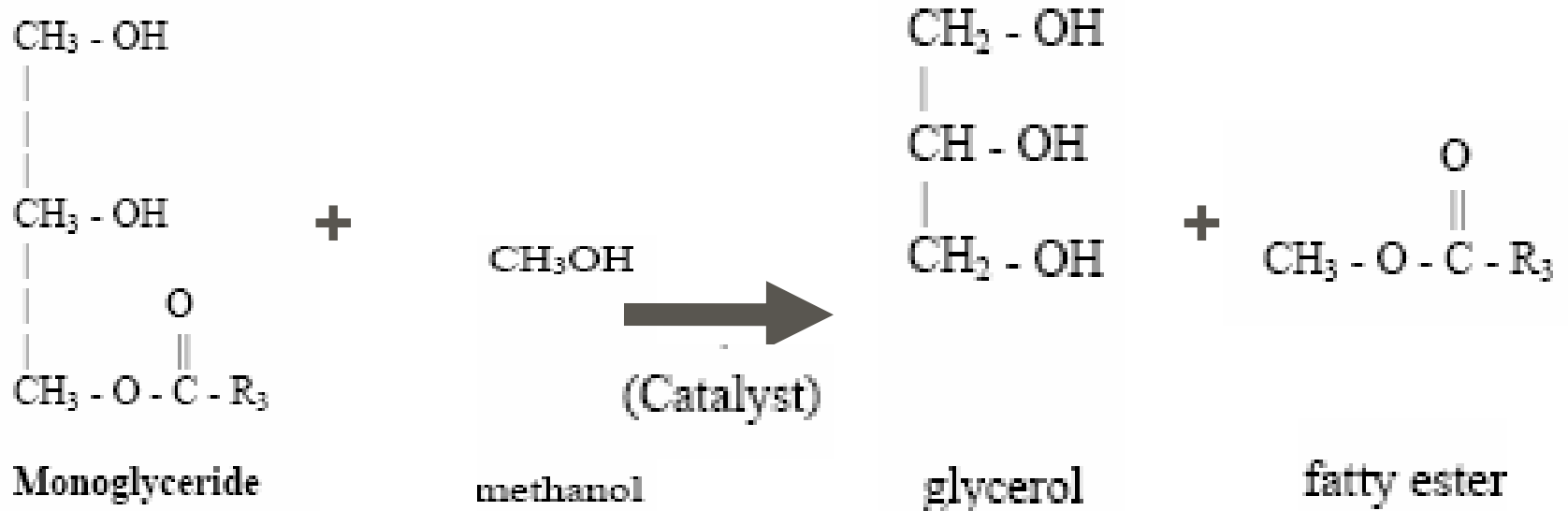
+



fatty ester

BIODIESEL

Step 3



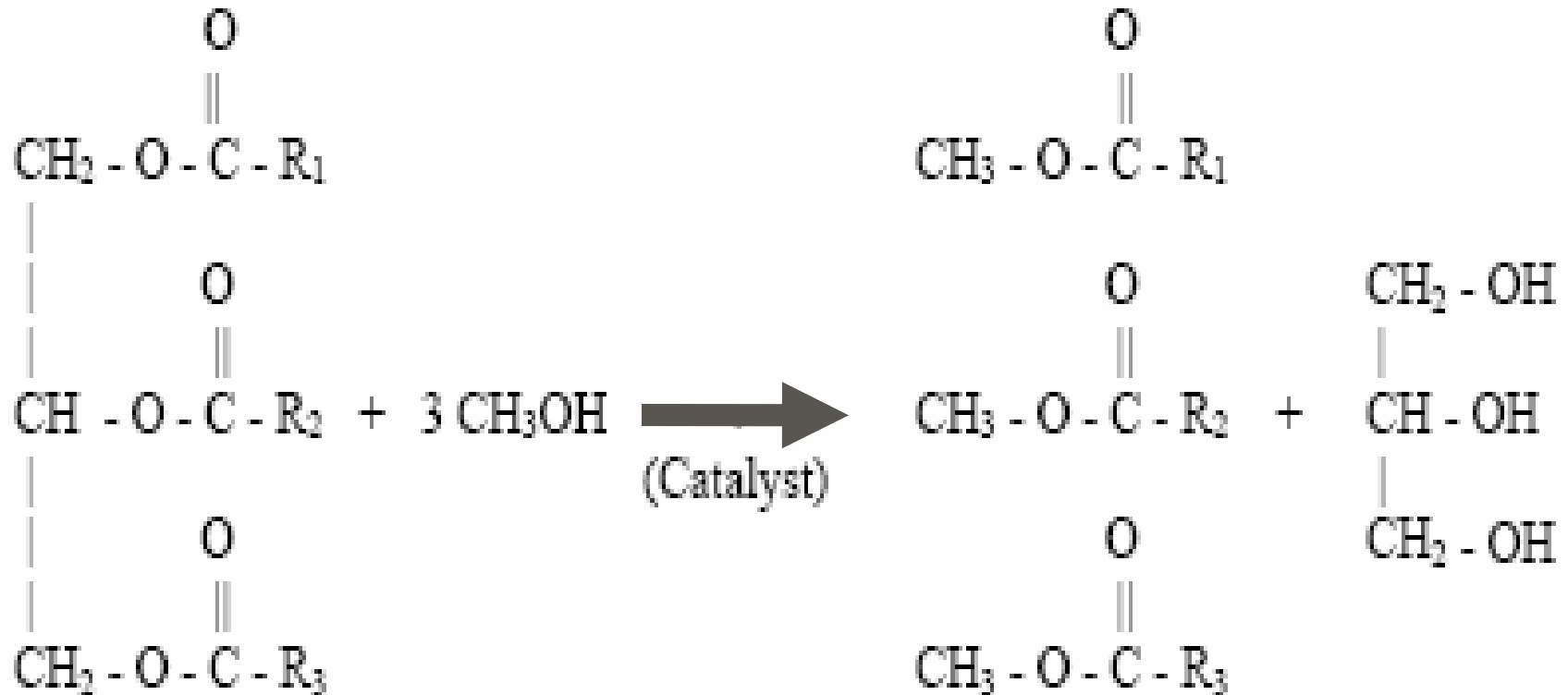
LIPID

ALCOHOL

GLYCEROL

BIODIESEL

Combined Reaction



triglyceride

methanol

mixture of fatty esters

glycerol

LIPID

ALCOHOL

BIODIESEL

GLYCEROL

The Biodiesel Production Process

THE REACTION TANK



- Location of the transesterification
- The reaction tank is a closed vessel
- The tank must be made of solvent resistant materials: polyethylene or stainless steel

The “Appleseed Reactor”

Heating the Oil

- .Heat acts as a catalyst to drive the transesterification reaction
- .The oil can either be heated in the reaction tank or heated prior to adding to the tank
- .Oil in the reaction tank is at a temperature of $\sim 55^{\circ}\text{C}$
- .Temperature is critical as methanol boils at 64.7°C

Transesterification of the Oil

- An **alcohol**, usually methanol, is combined with a strong **base**, potassium hydroxide (KOH) or sodium hydroxide (NaOH)
- This creates **methoxide**, which is then added to the reaction tank with the oil to initiate the transesterification reaction
- Methanol is added at 20% by volume of oil, only 10% needed in reaction.

Glycerol Settling

- During the transesterification reaction two products are created:
 - **Alkyl esters** and **Glycerol**
- **Glycerol** settles to the bottom of the reaction vessel and the **Alkyl esters** float on top
- The **glycerol** is drained from the bottom of the reaction vessel
- Glycerol typically constitutes 10% of total oil volume

Washing the Biodiesel

- The remaining alkyl esters contain small amounts of the **base catalyst**, free **glycerol**, and saponified **fatty acids**
- These are all **water soluble** and can be washed out of the biodiesel
- 1:1 ratio of water used per biodiesel made
- Wash water is drained off the bottom of a washing tank

Drying Biodiesel

- Water, however, is undesirable within a diesel engine
- All residual wash water must be removed from the washed biodiesel
- Either through intensive heating (100°C), passive evaporation, settling, or centrifugation

Ready to use Fuel!

- Raw **vegetable** (or **animal**) **oil** has now been transesterified into **alkyl esters**
- These **alkyl esters** have been **washed** to increase the purity level
- And dried to remove all water
- The fuel is ready to run in any diesel engine

Producing 100 liters of biodiesel also:

- Consumes at least 350g base catalyst
- Consumes 20 liters methanol
- Produces 10 liters glycerol
- Produces 100 liters wash water

A Note on Safety

- An alcohol is required in the production of Biodiesel
 - methanol is used in our biodiesel lab
- Methanol is a **flammable neurotoxin**
 - However, so is gasoline (a quite common fuel)

- **Safety precautions** must be used when handling, transporting, or producing methanol:

- no sparks
- no smoking
- proper ventilation
- proper safety equipment: gloves, goggles, lab coats,

etc.