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Biodiesel Process Overview

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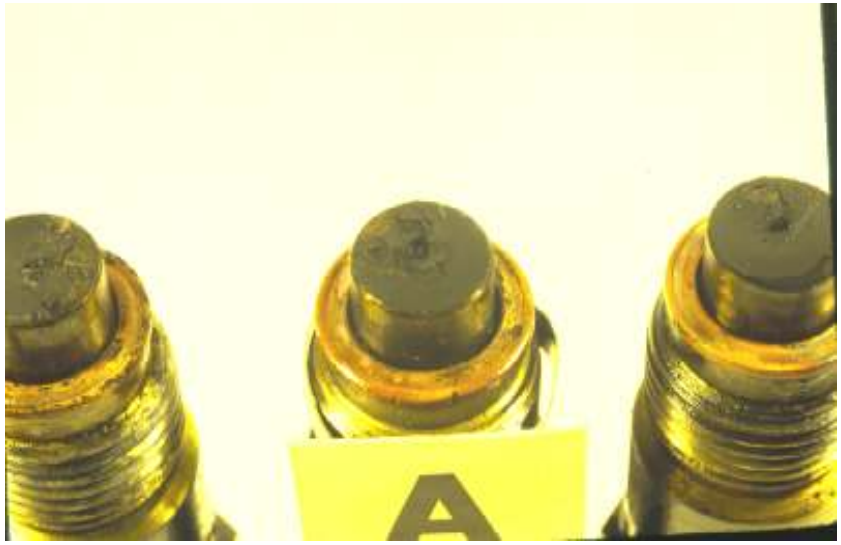
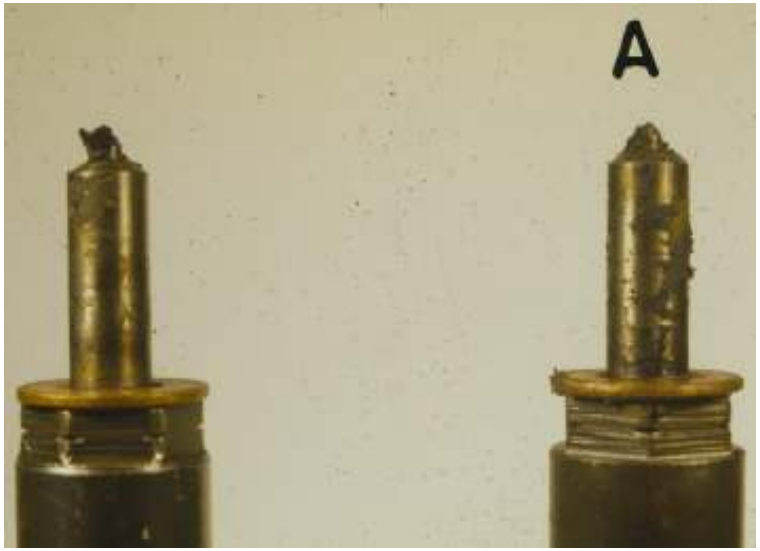
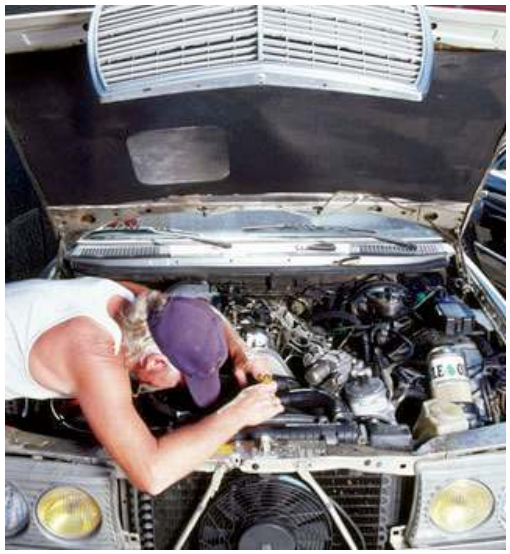
Biodiesel – an established technology





- Straight Vegetable Oils (SVO) will run in a diesel engine to a point.
- Injector coking caused by long term SVO use.
- Biodiesel Studied since 1980s – solved issue of oil viscosity reduction in oils.

Grease Cars – Not a fleet option



- Grease cars use heated SVO to reduce viscosity
- Requires dual tanks/engine modification
- High maintenance
- Void warranties

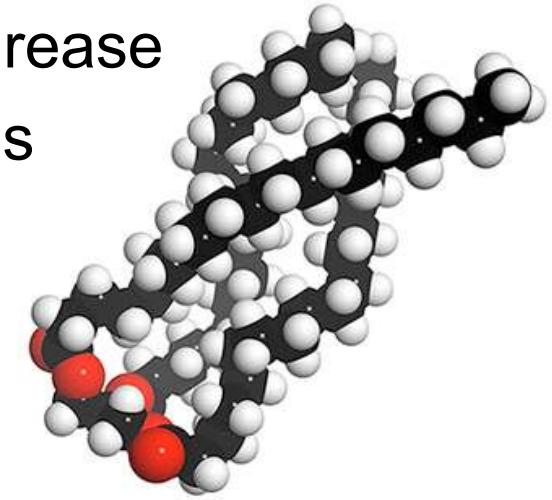
Biodiesel Basics

FATS and OILS
+
ALCOHOL

BIODIESEL
+
GLYCEROL

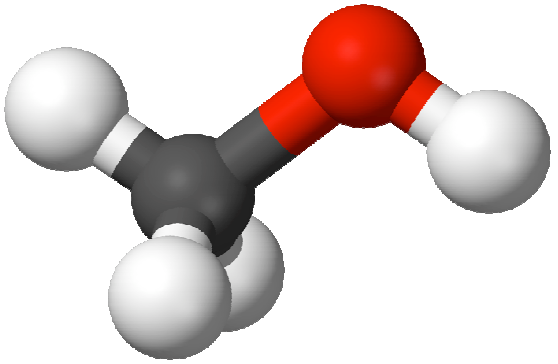
Feedstock

- Feedstock = Starting material used to make fuel
  - US: Soybean Oil
  - EU: Rapeseed – non-food, industrial oil
  - GA: Poultry Fat
  - Municipality/School: Yellow Grease
  - On Farm/Co-op: Energy Crops
    - Oilseed Radish
    - Canola
    - Sunflower



Alcohol

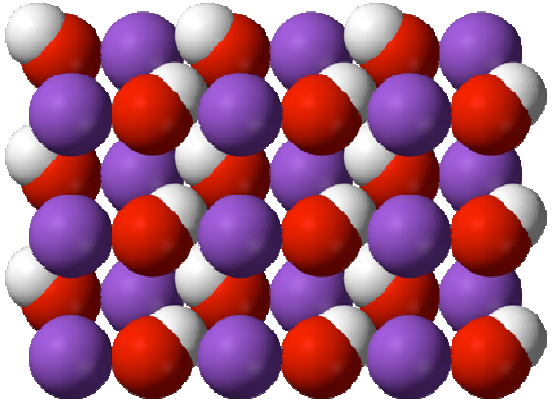
- Methanol:
  - Preferred alcohol for the production of biodiesel
  - Relatively Inexpensive
  - Lower Viscosity Fuel
  - Flammable/Toxic
    - if you can smell it, it is doing damage



- Ethanol
  - Can be used but may complicate reaction
  - EXPENSIVE! Priced against gasoline

Catalyst

- Caustic Catalysts:
  - NaOH – Sodium Hydroxide - Lye
  - KOH – Postassium Hydroxide
    - Flakes are better – dissolve easier
    - Caustic = burns
- Sodium Methylate/Methoxide:
  - Premixed catalyst/alcohol
  - Must be diluted with alcohol to proper concentration
  - Eliminates handling of solid catalyst



Standard Chemical Ratios

Run test batches on feedstock every time it changes to make sure you have the right recipe.

For fresh oil:

1L oil

200 mL Methanol

3.5g NaOH or 4.9g KOH (99%)

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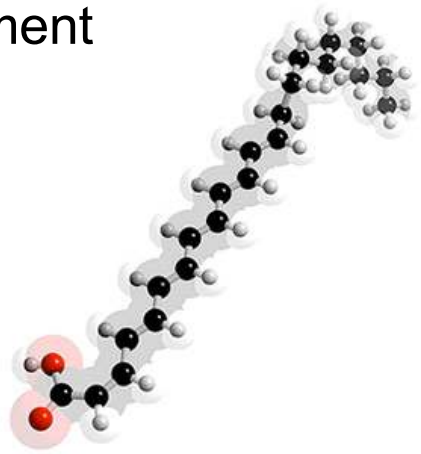
Feedstock Quality - Free Fatty Acids

- Byproduct of oxidative breakdown of fats and oils
- High levels:
  - Poor food quality = rancid
  - Poor fuel feedstock = soap formation
- Must be neutralized/removed before transesterification with caustic catalyst
- Neutralization is accomplished by adding excess catalyst to reaction.
- Catalyst concentration must be calculated.

Free Fatty Acids

Titration: Method for determining the amount of excess catalyst required to neutralize the free fatty acids.

- Can be done with simple equipment
  - Scale
  - Graduated Cylinder
  - Beaker
  - Buret
  - pH meter/indicator



- Excess catalyst is added to the amount required for fresh (0%FFA) oil
- High levels will result in poor quality fuel:
  - poor feedstock in = poor fuel out

Free Fatty Acids

Free Fatty Acid Reduction = Feedstock Improvement

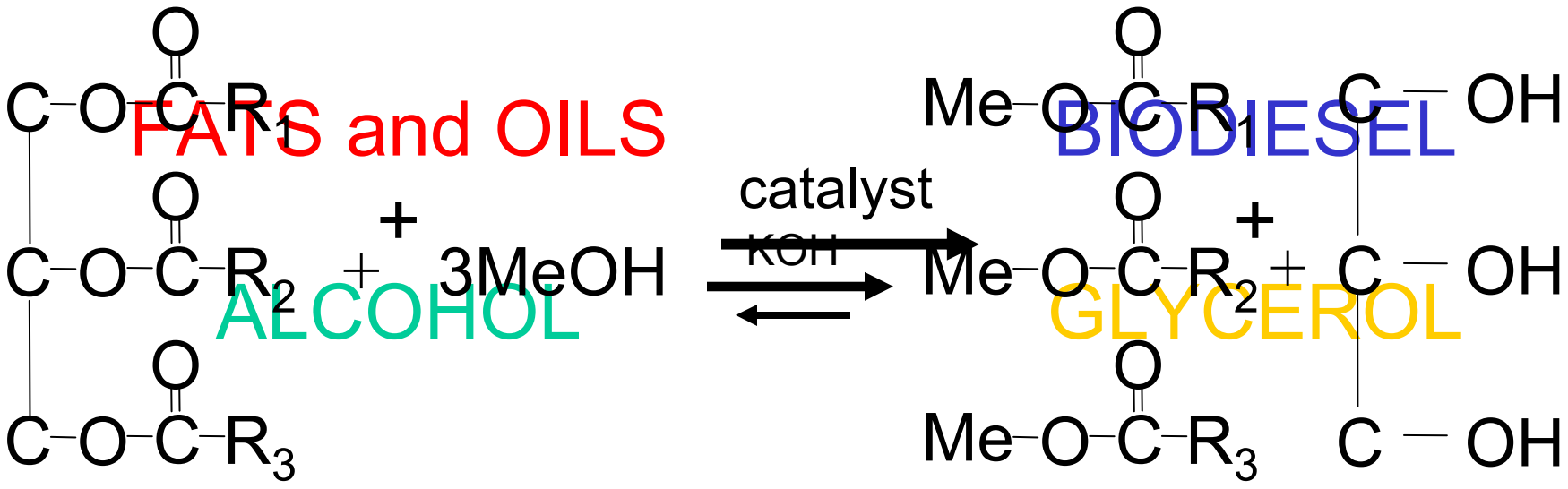
- Acid Esterification
  - Uses two step process
    - 1st step: Acid catalyst allows conversion of FFA to Biodiesel
    - 2nd step: Standard base catalyzed reaction
  - Complicated
  - Slow
- Fresh Feedstock Blending
  - Use clean oils to cut contaminated oils
  - Easy
  - Expensive

Chemical Quality - Water

- Water contamination in chemical components
  - Feedstock
    - Settling time is the best solution to this problem
    - Emulsified feedstock cannot be used
  - Alcohol
    - Methanol is hydroscopic, absorbs water
    - Always seal containers
  - Catalyst
    - Potassium/Sodium Hydroxide absorb water
    - Keep Sealed

Biodiesel Production

Difficult to make right - Biodiesel is made by the transesterification of vegetable oils



Triglyceride (fats and oils)

Methanol (alcohol)

Methyl Ester (Biodiesel)

Glycerol

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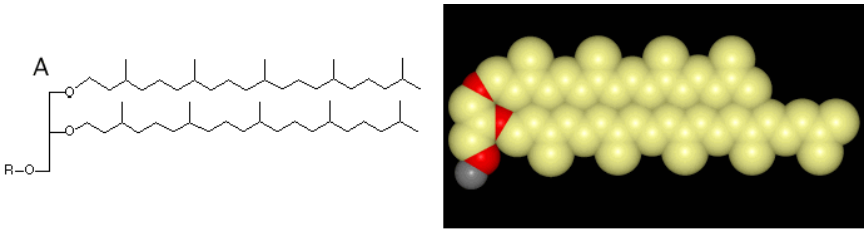
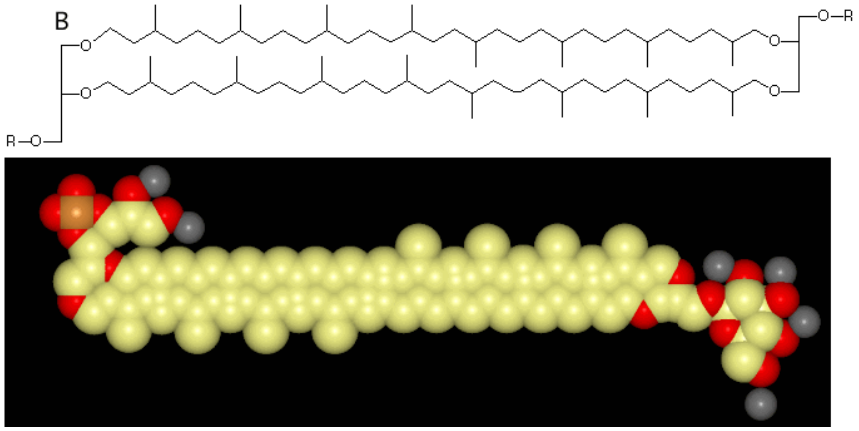
Biodiesel Production is **CHEMICAL PRODUCTION** ask yourself:

"Are you and your team qualified to make chemicals for the _____ industry?"





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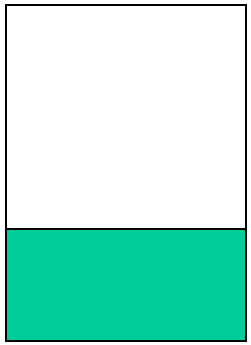
Biodiesel Production

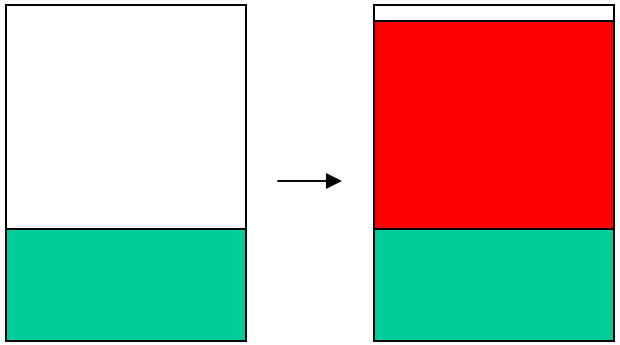
Simple to make



Tank 1 mix alcohol and catalyst

Biodiesel Production

Simple to make



Tank 1 mix alcohol and catalyst

Tank 2 add tank 1 mixture to oil. Mix and heat.

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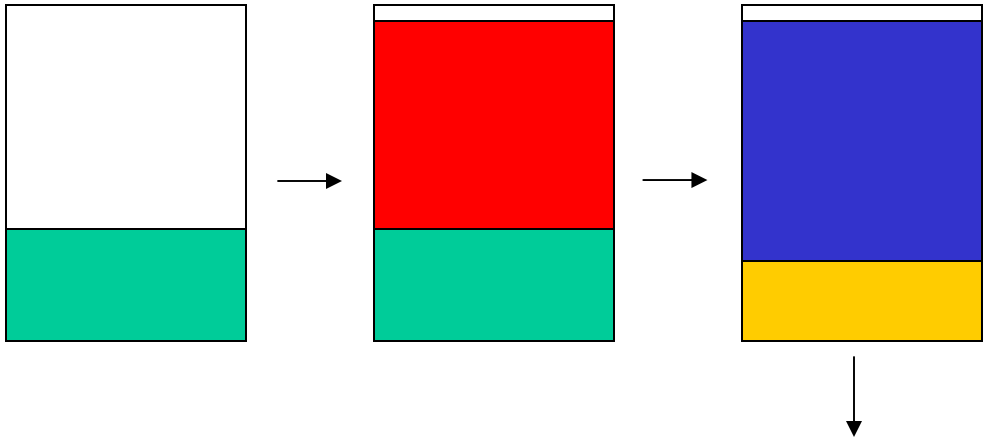
Biodiesel Production

Simple to make



Tank 1 mix alcohol and catalyst

Tank 2 add tank 1 mixture to oil. Mix and heat.

Allow tank to settle, decant bottom glycerol layer

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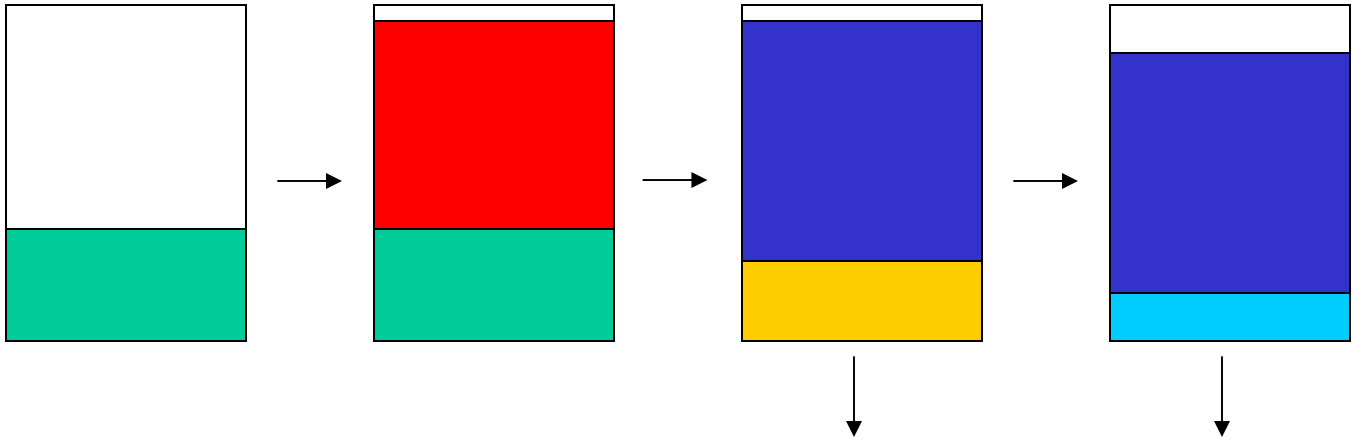
Biodiesel Production

Simple to make



Tank 1 mix alcohol and catalyst

Tank 2 add tank 1 mixture to oil. Mix and heat

Allow tank to settle, decant bottom glycerol layer

Tank 3 wash with water settle, decant bottom water layer - repeat

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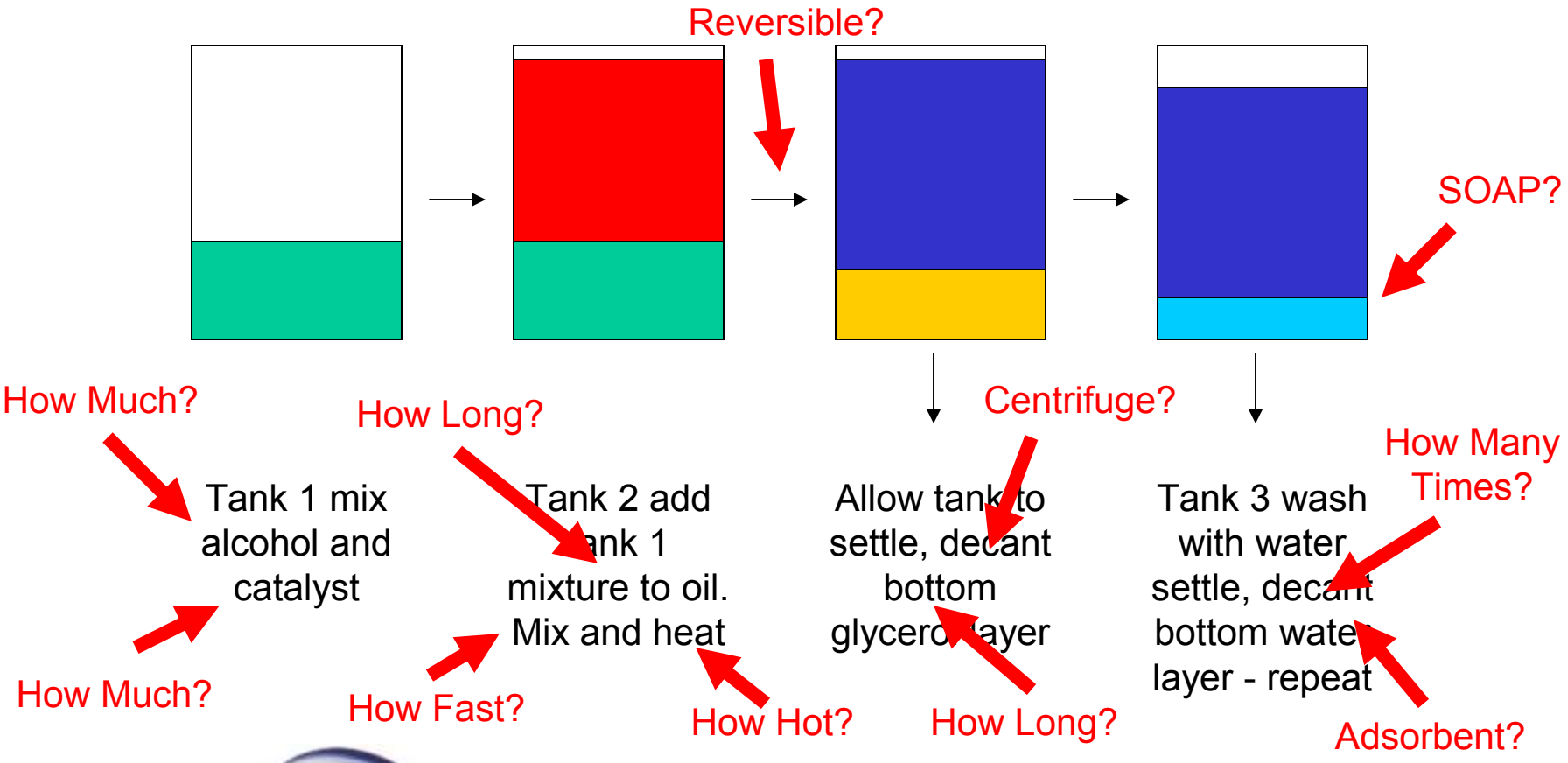
Biodiesel Production

Simple to make, difficult to make right



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The ASTM Specification – D6751

- Designed with OEMs to insure compatibility with modern diesel engines
  - Required for in-warranty vehicles
  - Required to collect federal/state tax credits/incentives
  - Mainly designed to insure fuel quality
  - Also influences feedstock selection

The ASTM Specification – D6751

SPECIFICATION FOR
BIODIESEL (B100) – ASTM D6751-09

Nov. 2008

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines. This specification is for pure (100%) biodiesel prior to use or blending with diesel fuel. #

Property	ASTM Method	Limits	Units
Calcium & Magnesium, combined	EN 14538	5 maximum	ppm (ug/g)
Flash Point (closed cup)	**D 93**	**93 minimum**	**degrees C**
Alcohol Control (One of the following must be met)			
1. Methanol Content	EN14110	0.2 maximum	% volume
2. Flash Point	D93	130 minimum	Degrees C
Water & Sediment	**D 2709**	**0.05 maximum**	**% vol.**
Kinematic Viscosity, 40 C	D 445	1.9 - 6.0	$mm^2/sec.$
Sulfated Ash	D 874	0.02 maximum	% mass
Sulfur			
S 15 Grade	**D 5453**	**0.0015 max. (15)**	**% mass (ppm)**
S 500 Grade	**D 5453**	**0.05 max. (500)**	**% mass (ppm)**
Copper Strip Corrosion	D 130	No. 3 maximum	
Cetane	D 613	47 minimum	
Cloud Point	**D 2500**	**report**	**degrees C**
Carbon Residue 100% sample	D 4530*	0.05 maximum	% mass
Acid Number	**D 664**	**0.50 maximum**	**mg KOH/g**
Free Glycerin	**D 6584**	**0.020 maximum**	**% mass**
Total Glycerin	**D 6584**	**0.240 maximum**	**% mass**
Phosphorus Content	D 4951	0.001 maximum	% mass
Distillation, T90 AET	D 1160	360 maximum	degrees C
Sodium/Potassium, combined	EN 14538	5 maximum	ppm
Oxidation Stability	**EN 14112**	**3 minimum**	**hours**
Cold Soak Filtration	**Annex to D6751**	**360 maximum**	**seconds**
For use in temperatures below -12 C	**Annex to D6751**	**200 maximum**	**seconds**

BOLD = BQ-9000 Critical Specification Testing Once Production Process Under Control

* The carbon residue shall be run on the 100% sample.

\# A considerable amount of experience exists in the US with a 20% blend of biodiesel with 80% diesel fuel (B20). Although biodiesel (B100) can be used, blends of over 20% biodiesel with diesel fuel should be evaluated on a case-by-case basis until further experience is available.

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Fuel Quality and Uses

- ASTM D6751 Spec Grade Biodiesel
  - Industrial production
  - Retail Sale
  - Tax Incentives
  - Consumers
  - Legal, safe fuel
- High Quality Limited Use Fuel
  - Near compliance with key parameters of D6751
  - Must be diluted with petroleum diesel fuel
  - Limited Uses
    - Off Road
    - Municipal/Government
    - Personal

ASTM D6751 - Key Parameters

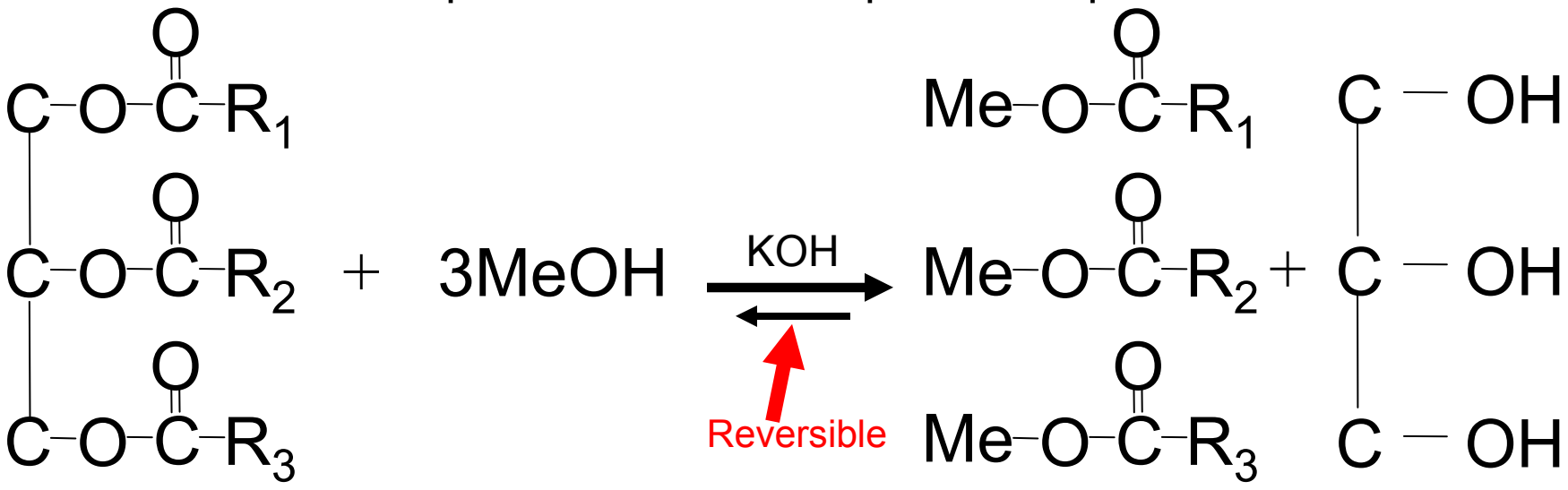
- Complete Reaction
  - Total Glycerine
  - Acid Number
- Adequate Washing
  - Free Glycerine
  - Flash Point
  - Alcohol Content
  - Water and Sediment

pHlip Test

Reversibility

Transesterification reaction is REVERSIBLE

- Too much energy/time = loss of product
- Complete conversion required for spec fuel



Triglyceride
(fats and oils)

Methanol
(alcohol)

Methyl Ester
(Biodiesel)

Glycerol

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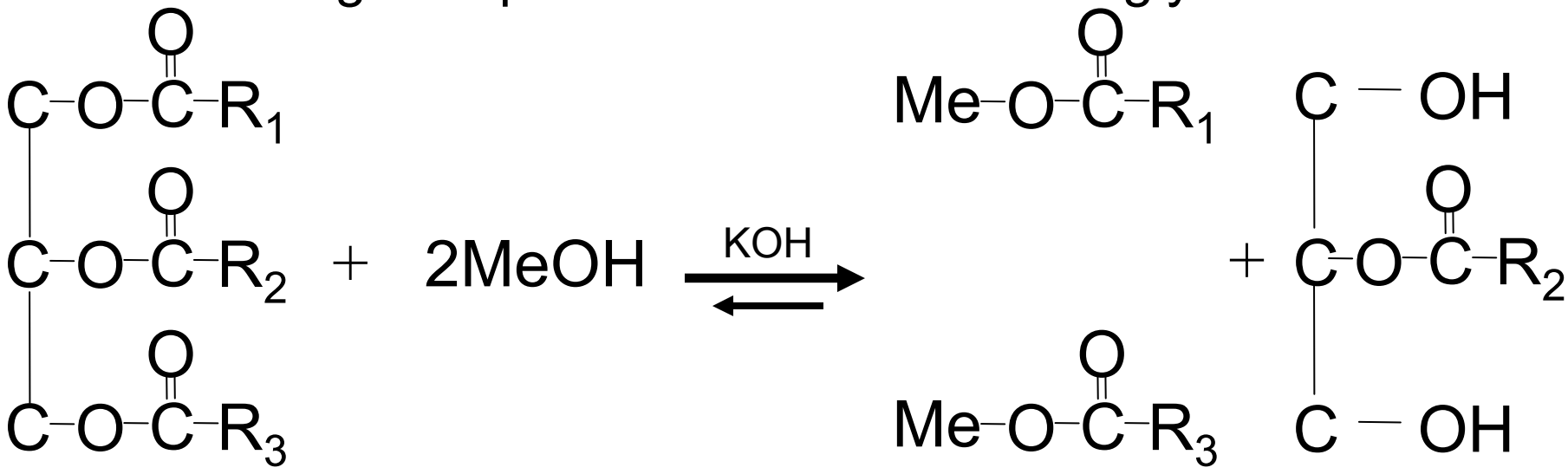
Incomplete Reaction

There are 3 fatty acids on each glycerine backbone.

Incomplete reactions result in 1 or 2 of these remaining

Remaining Components are mono- or di- glycerides



Triglyceride
(fats and oils)

Methanol
(alcohol)

Methyl Ester
(Biodiesel)

Mono-Glyceride

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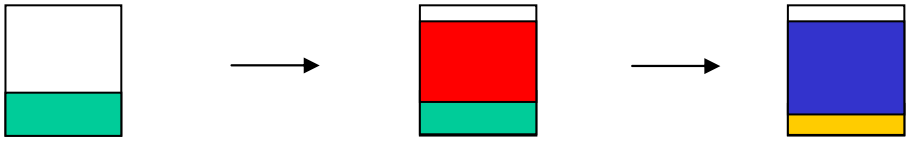
Two Phase Reaction

Basic chemical “trick” to push reaction to completion

PHASE 1

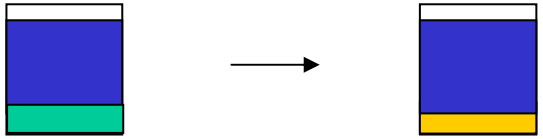


Tank 1 mix alcohol and catalyst

Tank 2 add 80% tank 1 mixture to oil. Mix and heat

Allow tank to settle, decant bottom glycerol layer

PHASE 2



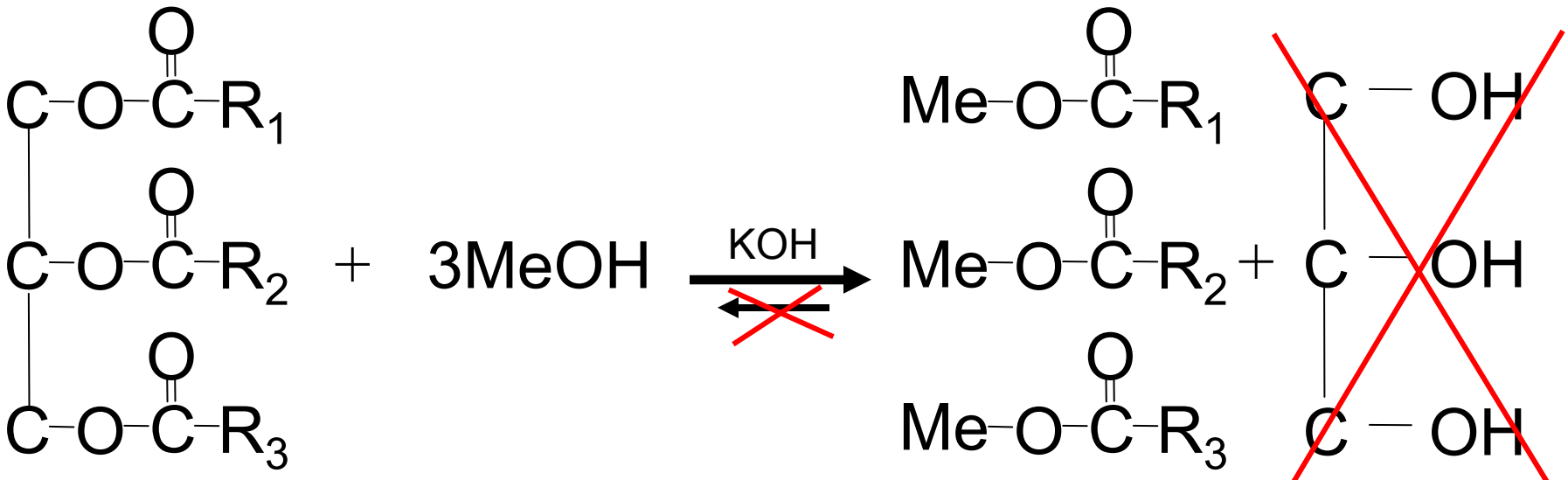
Add remaining alcohol/catalyst

Allow tank to settle. Decant bottom glycerol layer

WASH

Reversibility

Explanation: Removal of one of the products pushes reaction to completion - Equilibrium



Triglyceride
(fats and oils)

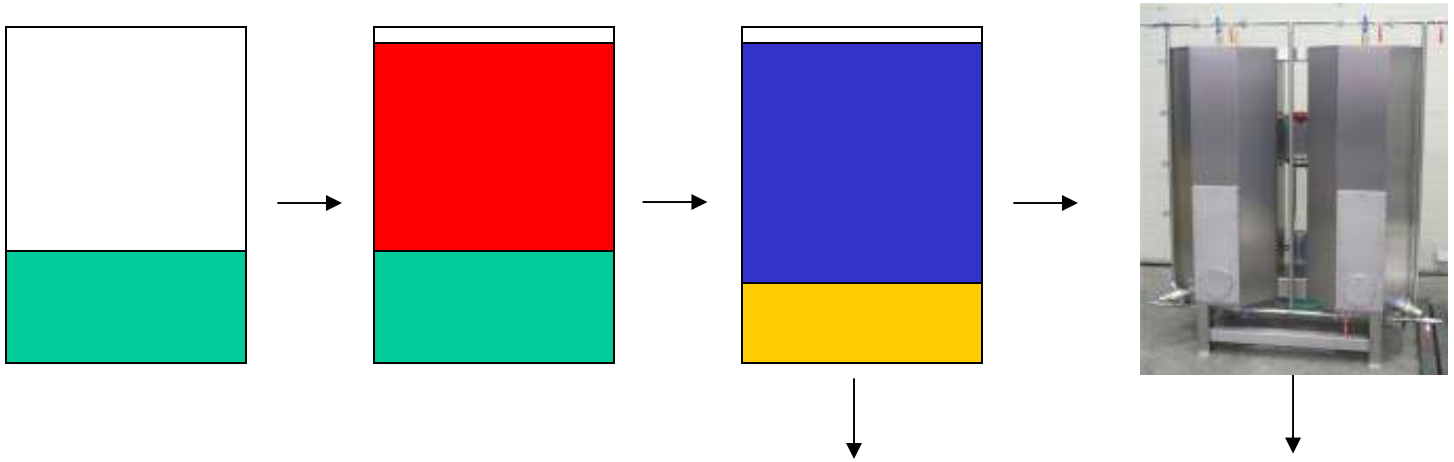
Methanol
(alcohol)

Methyl Ester
(Biodiesel)

Glycerol

Alternative option: Dry Wash

Hydrophilic resins absorb contaminants without use of water



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Tank 2 add tank 1 mixture to oil. Mix and heat

Allow tank to settle, decant bottom glycerol layer

Biodiesel is allowed to pass over column of hydrophilic resin

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Waste Disposal

- Glycerine/Methanol/catalyst solution is caustic, toxic and flammable.
- Stories of “ready markets” abound on internet. – False
- Many biodiesel facilities have had to curtail production due to waste product accumulation

Waste Disposal

- Disposal options:
  - Landfill
  - Use as is
    - » Compost accelerant
    - » Boiler Fuel
  - Methanol removal/neutralization
    - » Animal feed
  - Methanol removal/neutralization/desalting
    - » Value added chemicals

Biodiesel Compatibility

- Uses existing diesel refueling infrastructure
- Biodiesel can be used with most existing vehicles without modification in blends or at 100%
- Biodiesel is *interchangeable* with diesel fuel – can use biodiesel one day and petroleum the next

Biodiesel Considerations

- Non-compatible with natural rubber hoses/seals
- Biodiesel solvent properties cleans fuel system = replacement of fuel filters
- Cold Filter Plug Point is higher in B100 – mixing with D2 compensates for elevated gel temperature

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