The University of Georgia

Biodiesel Process Overview

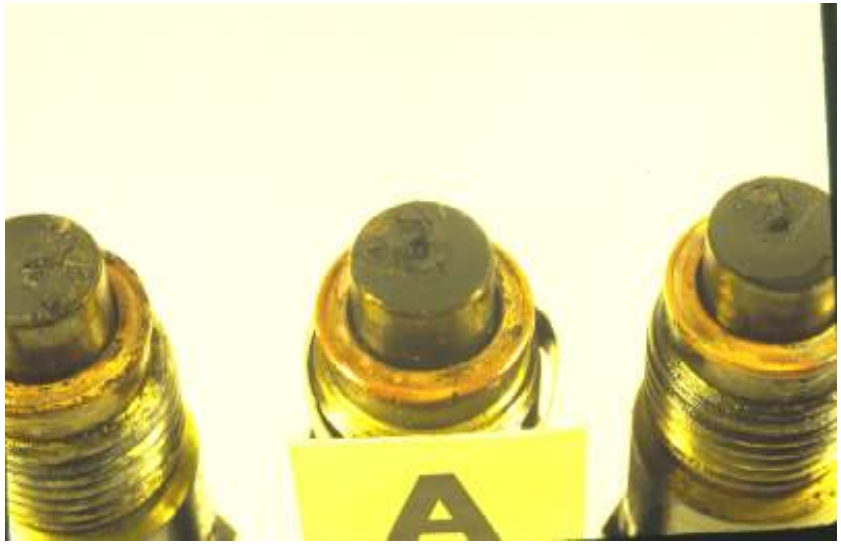
Daniel Geller – UGA Engineering Outreach

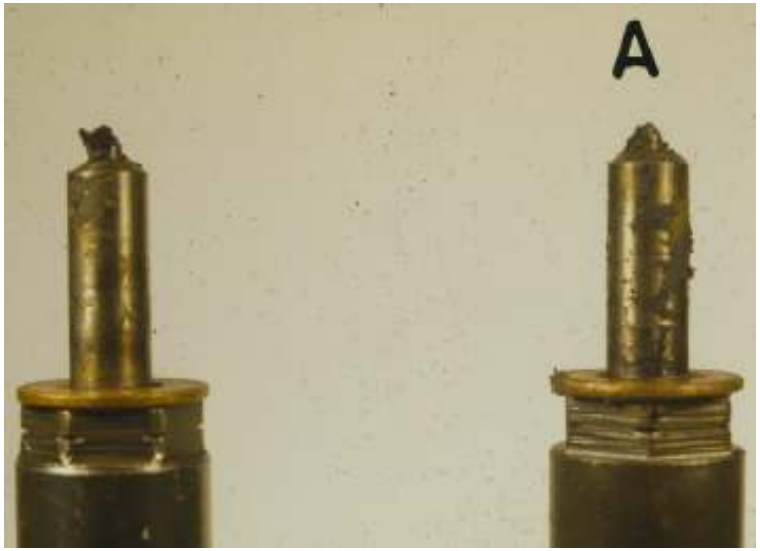
http://outreach.engineering.uga.edu/

FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

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

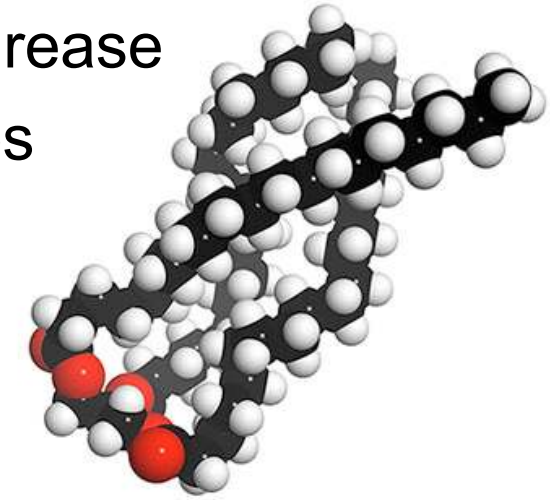
FATS and OILS
+
ALCOHOL

$\xrightarrow{\text{catalyst}}$

BIODIESEL
+
GLYCEROL

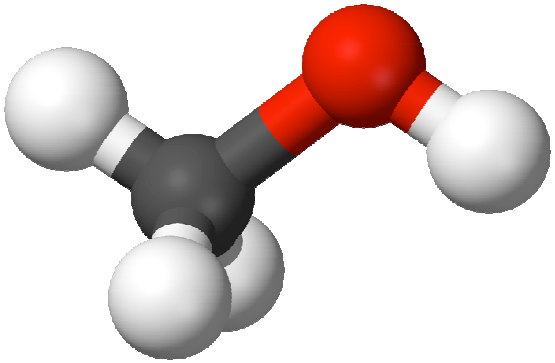
Feedstock

- 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



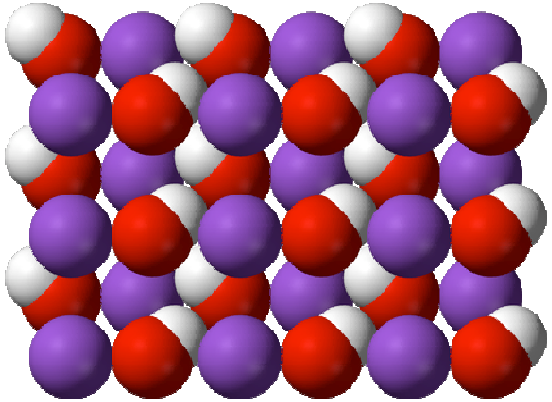
Alcohol

- 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%)

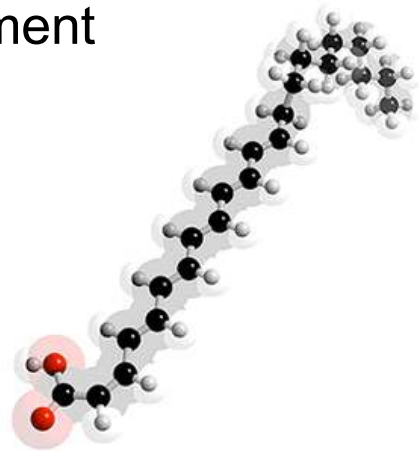
Feedstock Quality - Free Fatty Acids

- 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

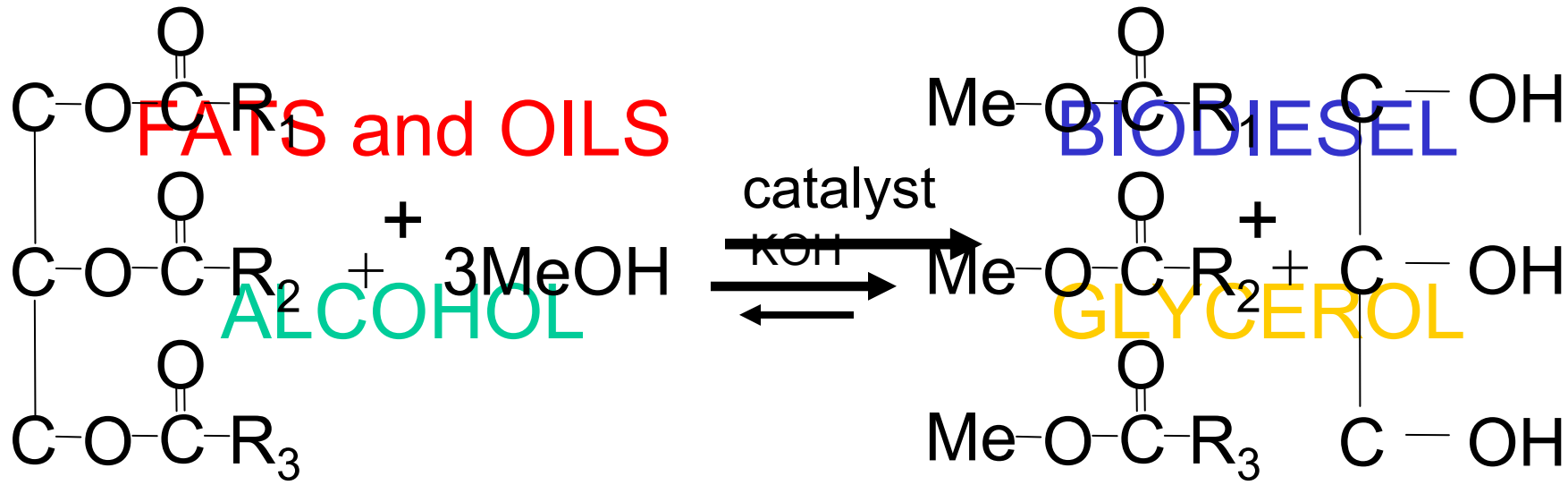
- Acid Esterification
  - Uses two step process
    - 1st step: Acid catalyst allows conversion of FFA to Biodiesel
    - 2nd step: Standard base catalyzed reaction
  - Complicated
  - Slow
- Fresh Feedstock Blending
  - Use clean oils to cut contaminated oils
  - Easy
  - Expensive

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



Triglyceride
(fats and oils)

Methanol
(alcohol)

Methyl Ester
(Biodiesel)

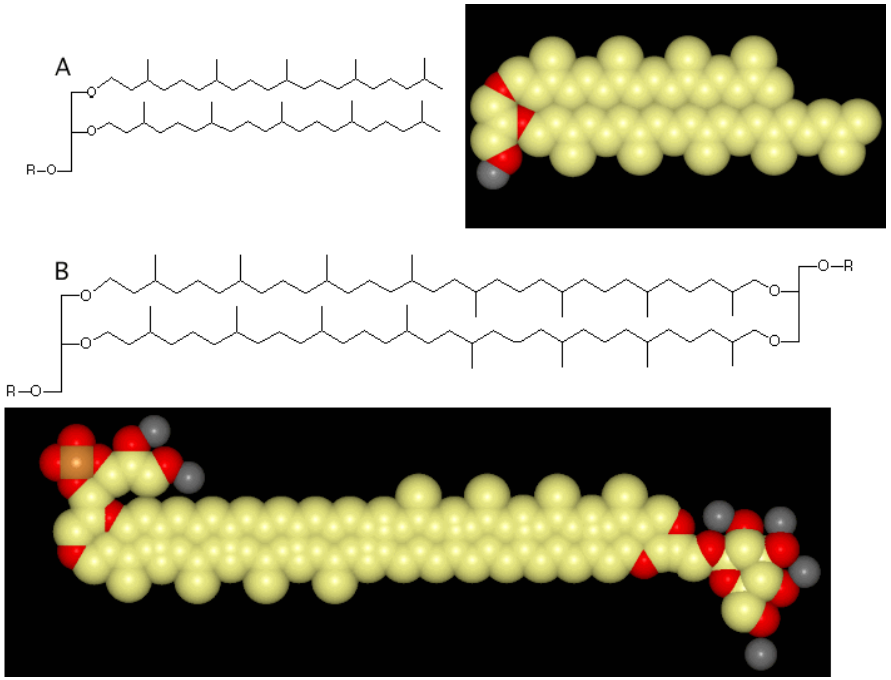
Glycerol

FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

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

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

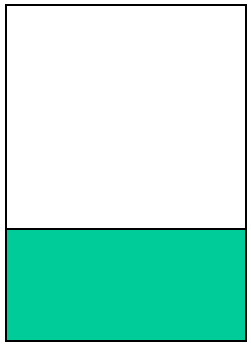


FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

Biodiesel Production

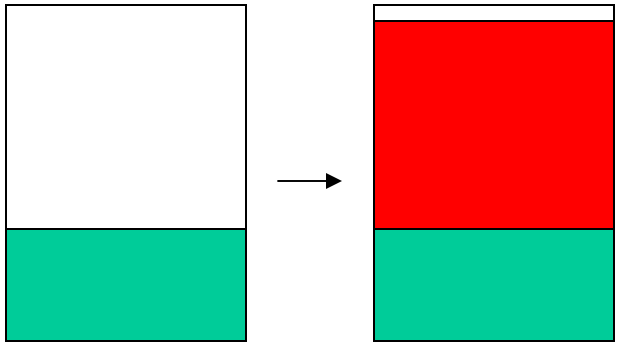
Simple to make



Tank 1 mix alcohol and catalyst

Biodiesel Production

Simple to make

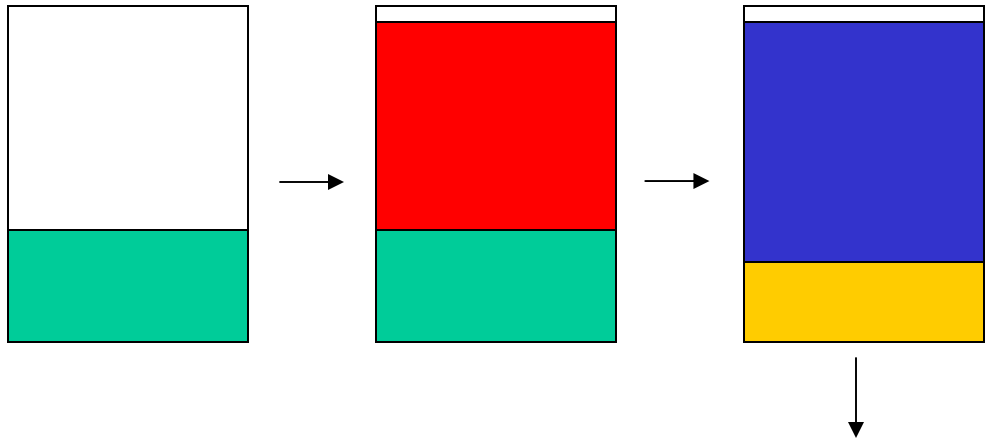


Tank 1 mix alcohol and catalyst

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

Biodiesel Production

Simple to make



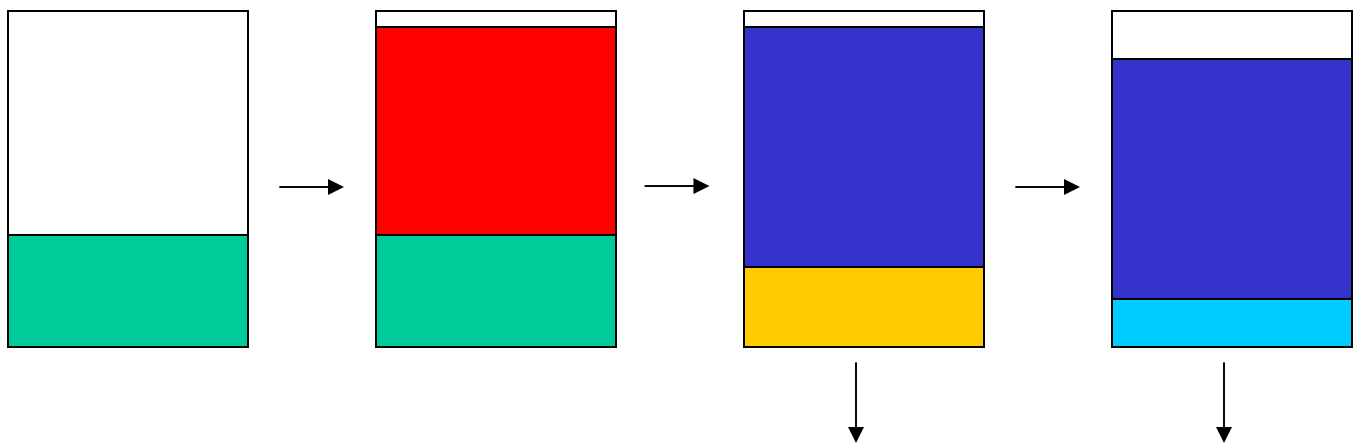
Tank 1 mix alcohol and catalyst

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

Allow tank to settle, decant bottom glycerol layer

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

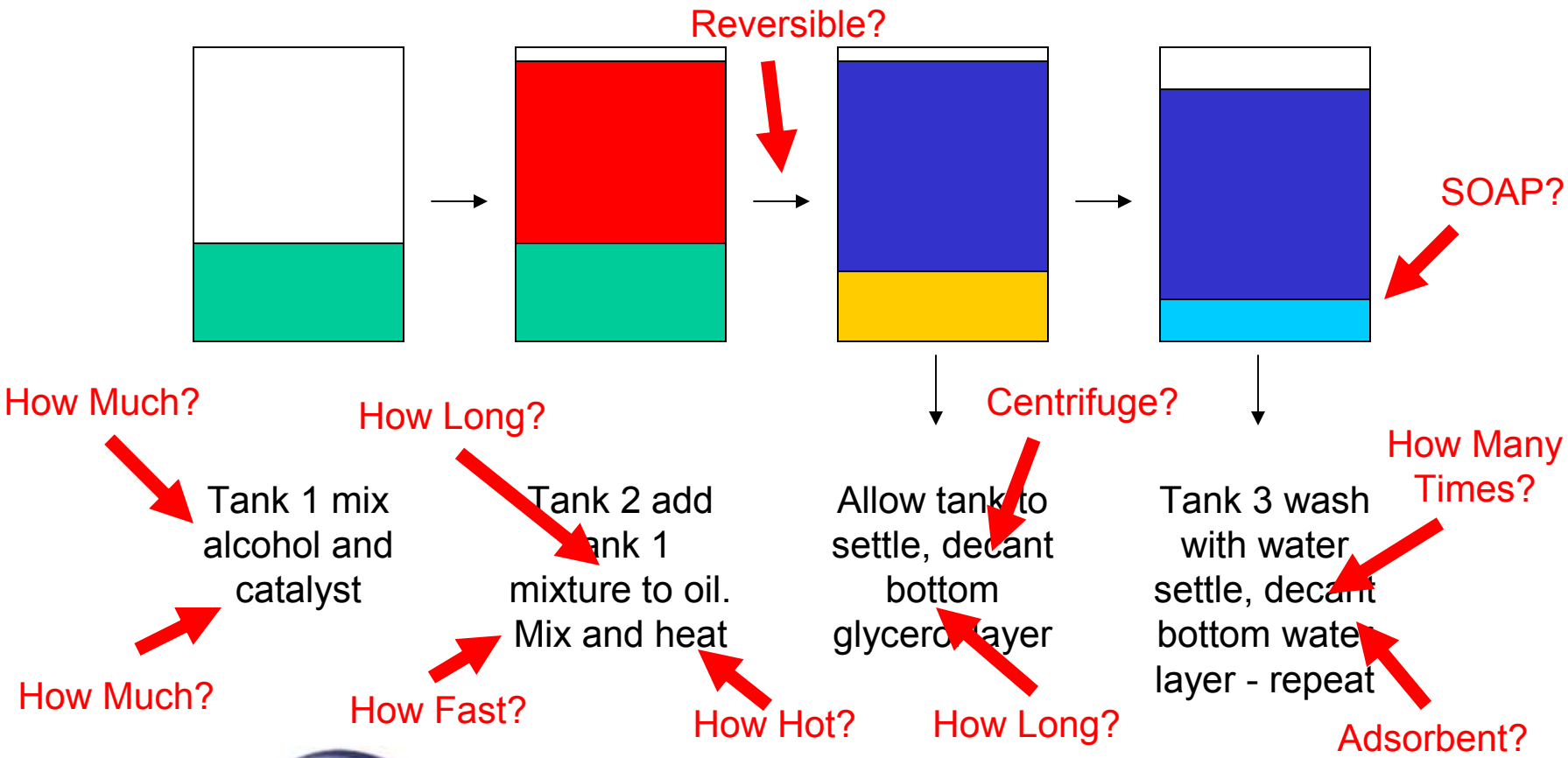
Tank 3 wash with water settle, decant bottom water layer - repeat

FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

Biodiesel Production

Simple to make, difficult to make right



FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

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.

FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

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

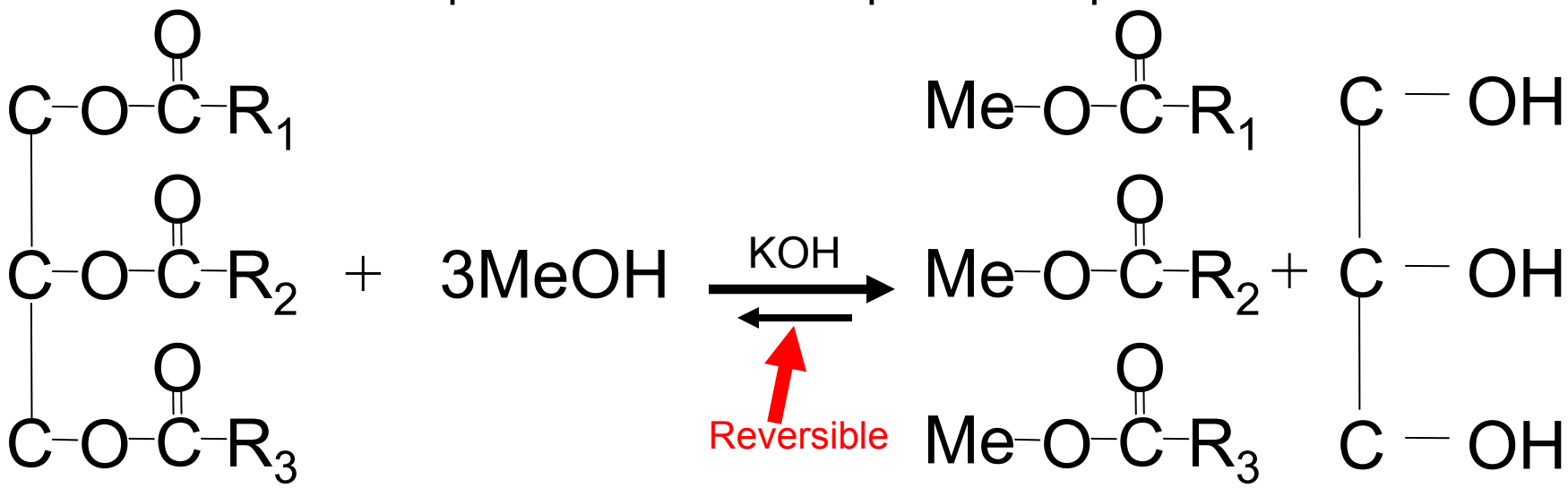
- Complete Reaction
  - Total Glycerine
  - Acid Number
- Adequate Washing
  - Free Glycerine
  - Flash Point
  - Alcohol Content
  - Water and Sediment

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

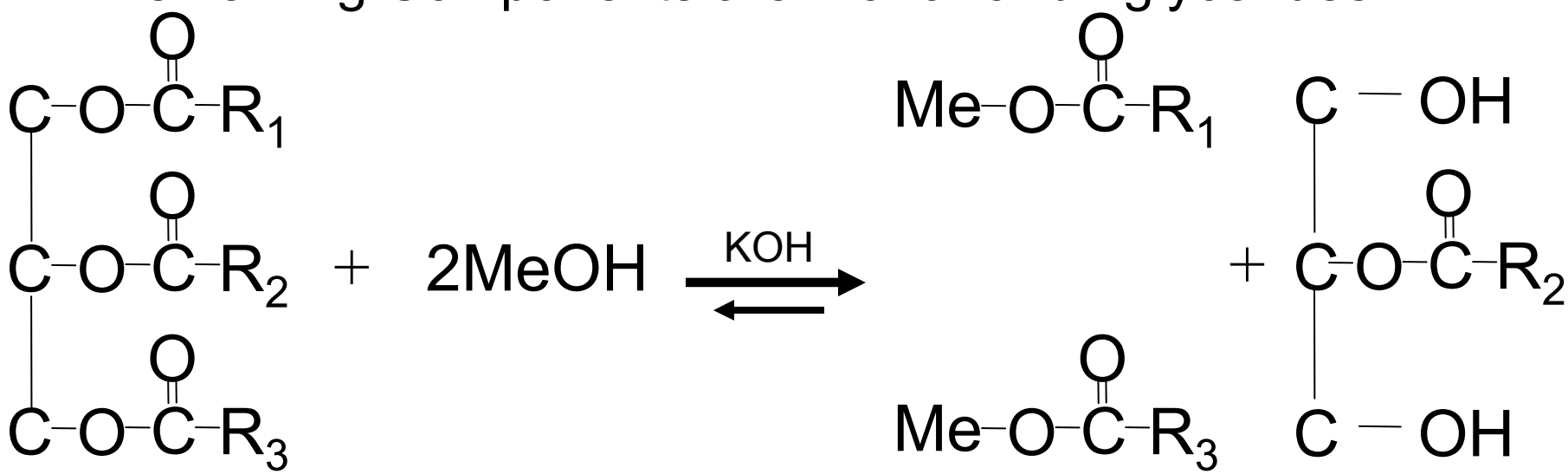
FACULTY of ENGINEERING
An Interdisciplinary Approach to Engineering at The University of Georgia

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)

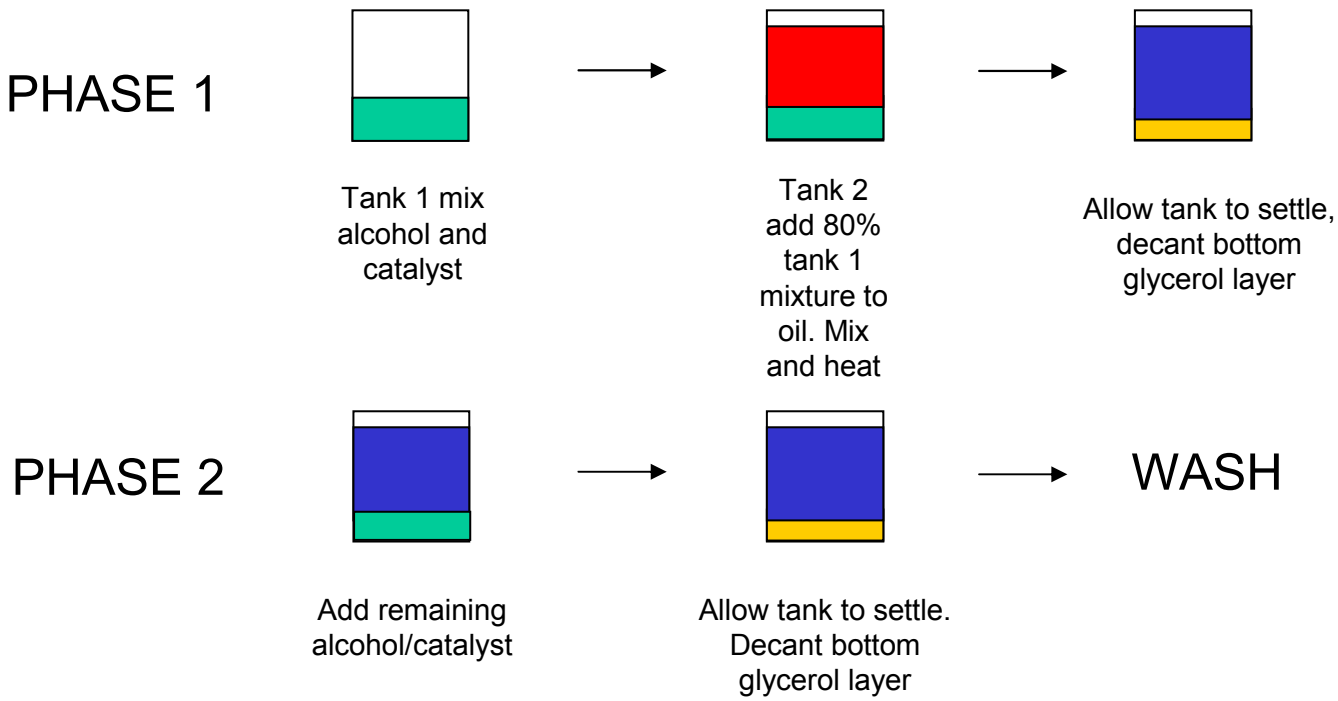
Methanol
(alcohol)

Methyl Ester
(Biodiesel)

Mono-Glyceride

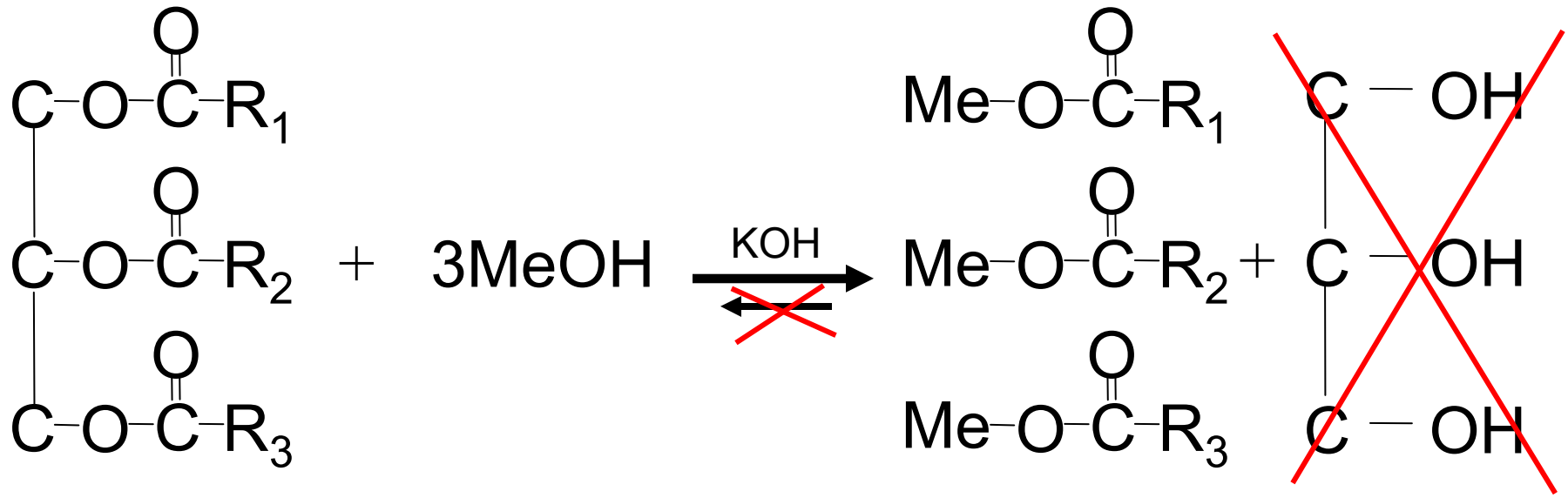
Two Phase Reaction

Basic chemical “trick” to push reaction to completion



Reversibility

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



Triglyceride
(fats and oils)

Methanol
(alcohol)

Methyl Ester
(Biodiesel)

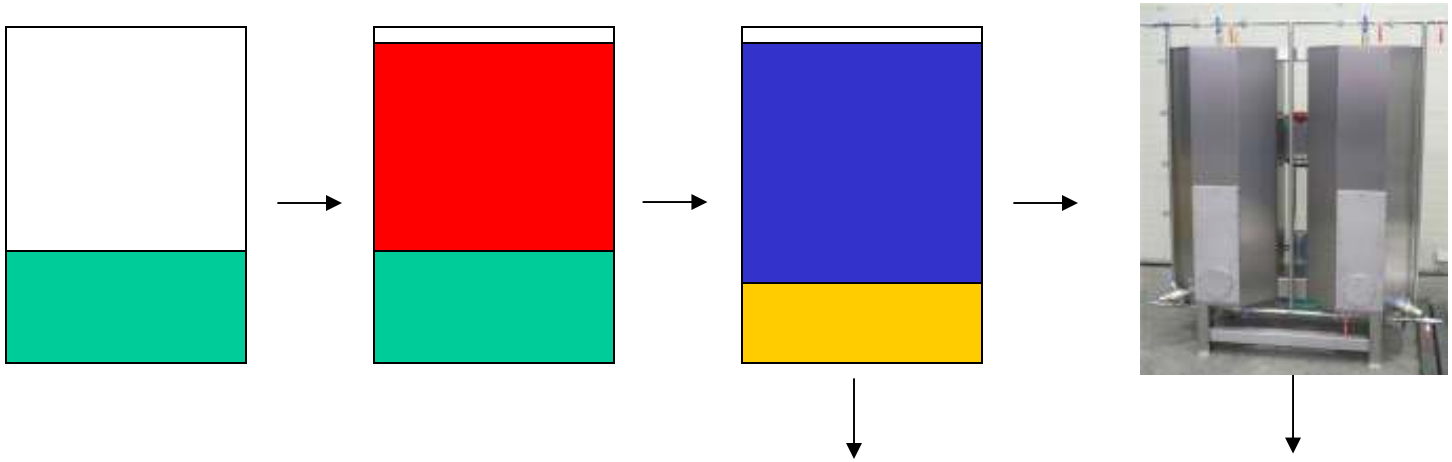
Glycerol

FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

Alternative option: Dry Wash

Hydrophilic resins absorb contaminants without use of water



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

Biodiesel is allowed to pass over column of hydrophilic resin

FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia

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

The University of Georgia

Daniel Geller
dgeller@engr.uga.edu
http://outreach.engineering.uga.edu/

FACULTY of ENGINEERING

An Interdisciplinary Approach to Engineering at The University of Georgia