Biodiesel

Lecture 8
Biofuels and Bioproducts

Bronx Community College - 2017
Chemistry and BioEnergy Technology for Sustainability NSF ATE 1601636

Types of biomass used for liquid fuel production

Lignocellulosic Biomass (Grasses, Woods)

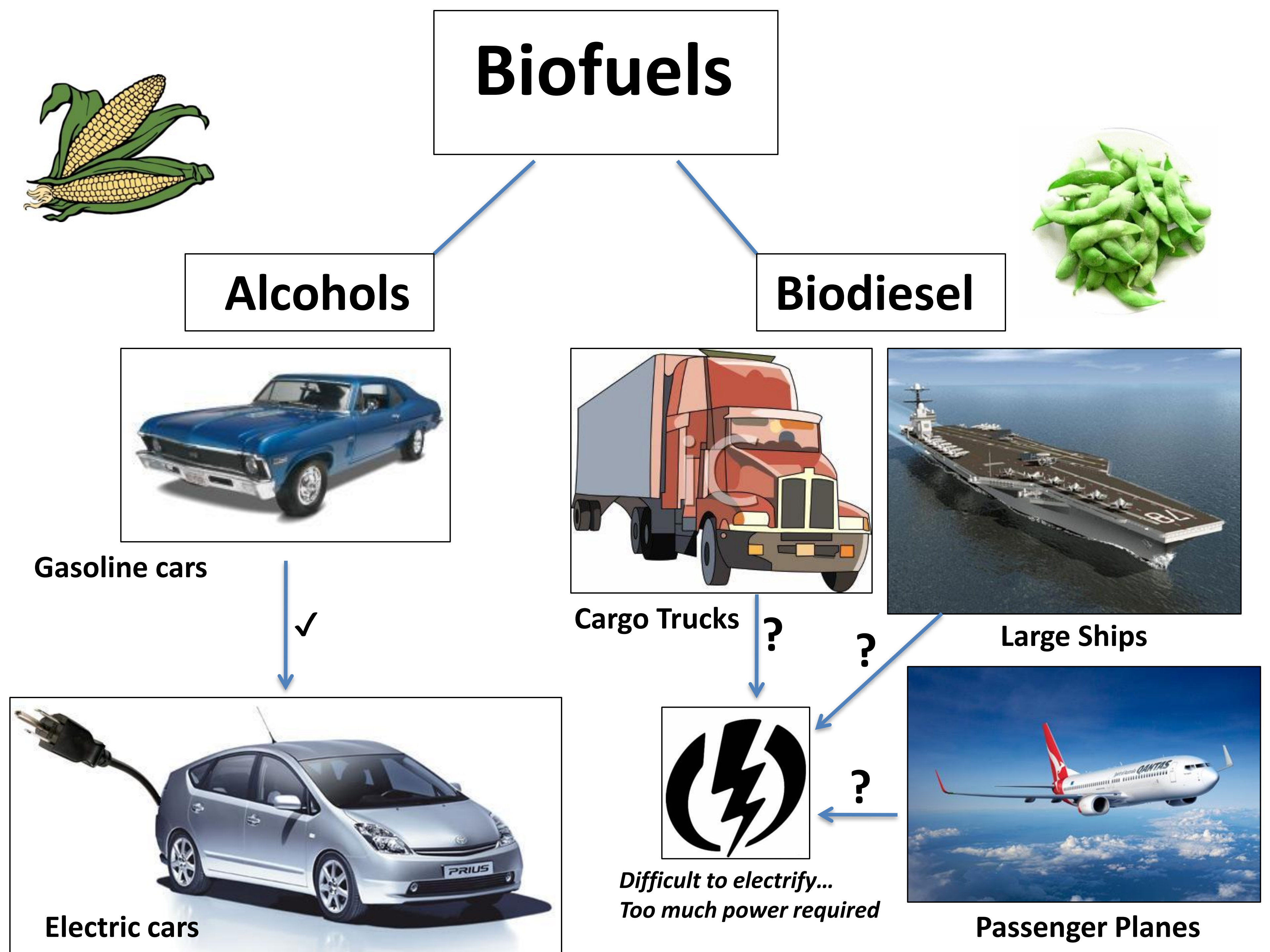
Provide fermentable sugars

For ETHANOL, etc...

Oil Crops (Soy, Palm, Canole, Algae, etc.)

Provide Triglycerides + Fatty Acids

For BIODIESEL


Biofuels
Alcohols
Biodiesel
Gasoline cars
✓
Electric cars
Cargo Trucks
?
Large Ships
?
?
Difficult to electrify…
Too much power required
Passenger Planes

ETHANOL

BIODIESEL

1826 First US internal combustion engine (Samuel Morey) runs on ethanol and turpentine…

1840-1860s Europeans realize importance of ethanol for used in household appliances

1859 Petroleum derived kerosene first used in western PA
Standard Oil Corp. Formed
First fuel/war tax

1872 Rudolf Diesel patents 1st compression ignition "artisanal" engine

1880 Henry Ford develops Model T that can run on ethanol

1910 Prototype Diesel car wins Grand Prize at World's Fair in Brussels

1913 Mysterious death of Dr. Diesel in English Channel

1914 First Diesel locomotive (Prussia to Saxon)

1919 Halliburton founded

1930's First commercial passenger Diesel vehicles (Mack, USA) (Benz, Germany)

1937 Vegetable oil ethyl esters (biodiesel) patent process to G. Chavanne U. of Brussels

1940's Brazil, Argentina, China, India, Japan using vegetable oil alternatives to diesel fuel

1943 Germans produce 36M barrels synthetic hydrocarbons using Fischer-Tropsch Process

1950's Ohio State researchers use cotton seed/corn oil blend to supplement Diesel fuel, spurring US academic research

1972 Crude oil in US = $3/barrel

1973 In retaliation for US/Israeli attack, OPEC initiates oil embargo against Western nations

1974 Crude oil in US = $12/barrel

1977 Trans-Alaskan Pipeline finished (2M barrels/day)

1978 US-DOE initiates biomass fuel research focused on algae

1987 Austrian Chemist Martin Mittelbach describes biodiesel production from waste cooking oil

1999 "Flex Fuel" cars commercially-available worldwide

2001 Tri State Biodiesel founded in Bronx

2003 First commercial algal biofuel company, Solazyme, created

2007 US-DOE funds three high-risk, high-reward bioenergy research centers

2009-2010 Crude oil in US up from $50 to $70 barrel

2011 US Navy contracts private industry to produce 450,000 gallons of biofuel from waste cooking oil and algae for $26/gallon!

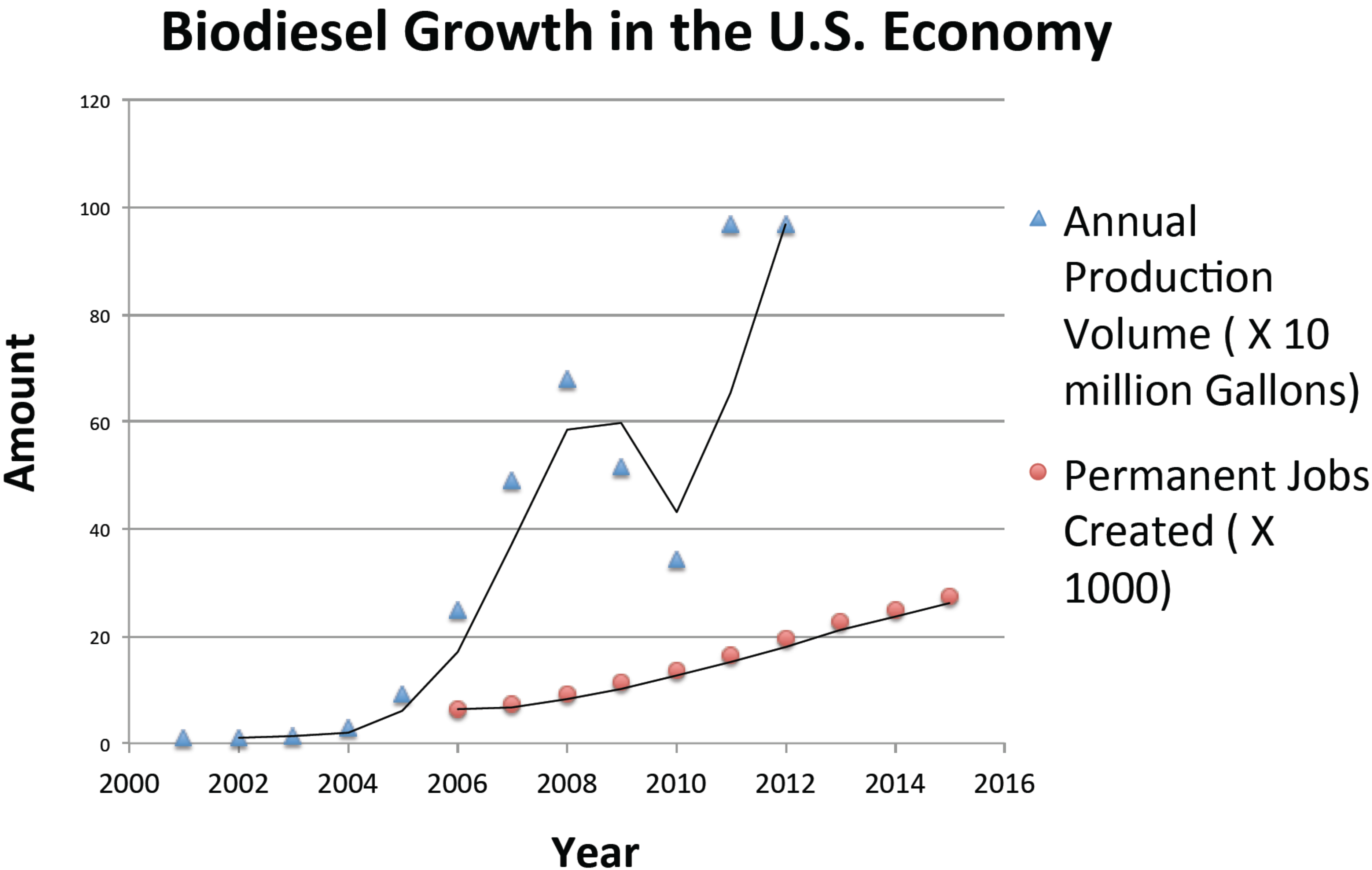
2011 First batch of biodiesel produced at The City University of New York

2012 …Diesel and jet fuels of the future chemically reminiscent of turpentine

Liquid Transportation Fuel Energies

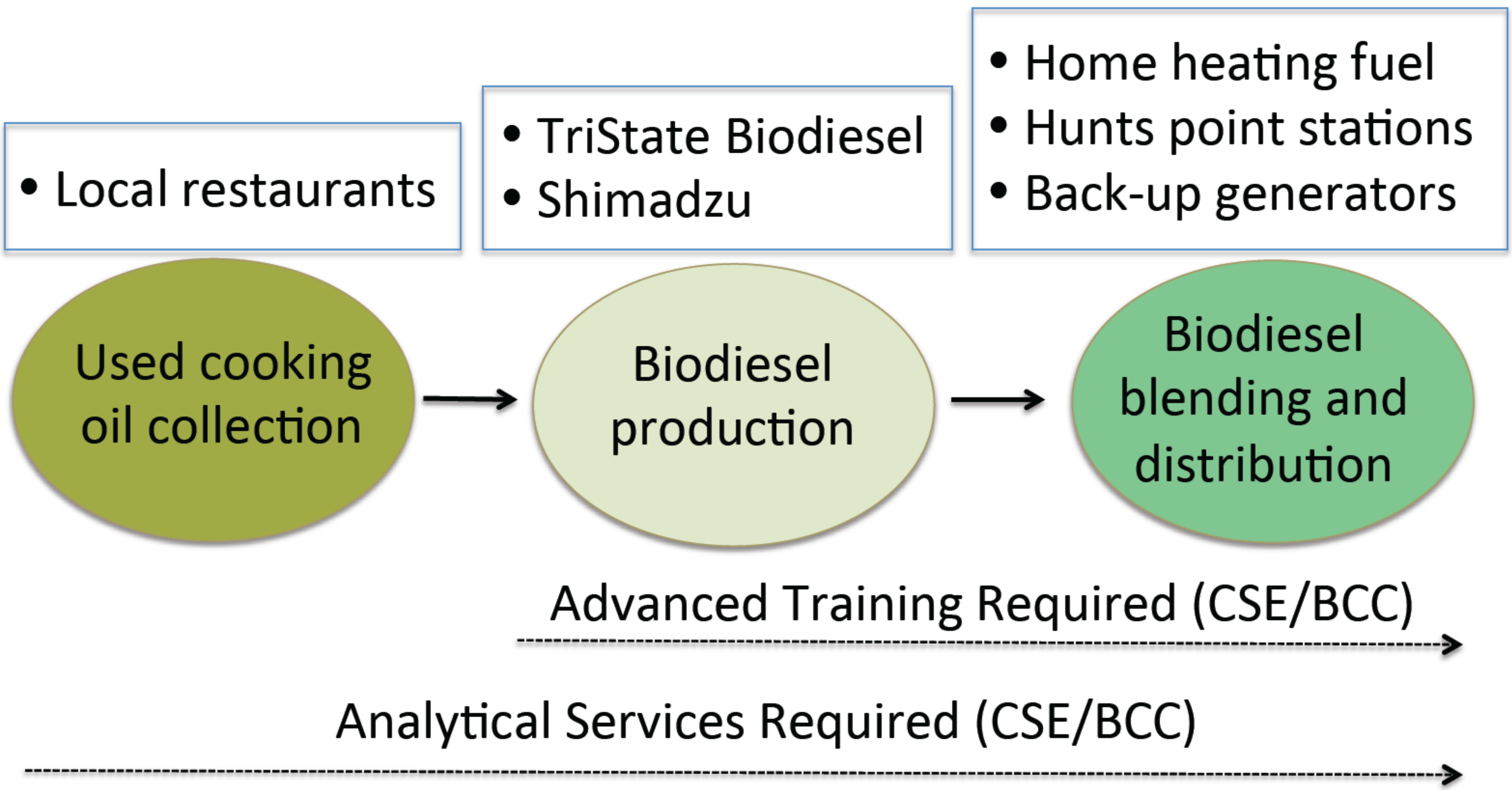
Fuel Type	Engine Type	BTU/Gallon
Methanol	Gasoline	56,800
Liquid Natural Gas	Gasoline	75,000
Ethanol	***Gasoline***	***76,000***
Propane	Gasoline	84,300
Gasoline	***Gasoline***	***114,000***
B100 Biodiesel	***Diesel***	***118,300***
Diesel #2	***Diesel***	***129,500***
Naphtha	Jet	118,000
Kerosene	Jet	128,000

http://en.wikipedia.org/wiki/Gasoline_gallon_equivalent



Biodiesel Growth in the U.S. Economy
Amount
120
100
80
60
40
20
0
2000
2002
2004
2006
2008
2010
2012
2014
2016
Year
Annual Production Volume (X 10 million Gallons)
Permanent Jobs Created (X 1000)

Biodiesel Value Chain in NYC

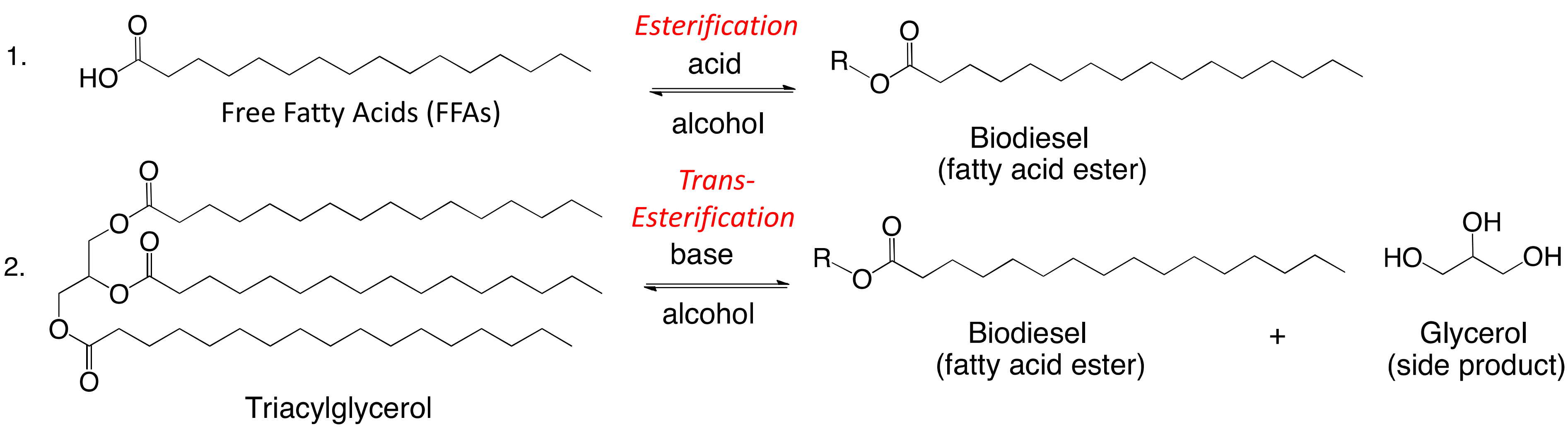


How to Make Biodiesel from Mixed Feedstocks (Fatty Acids and Triglycerides)

Free Fatty Acids (FFAs)

&

Triglycerides



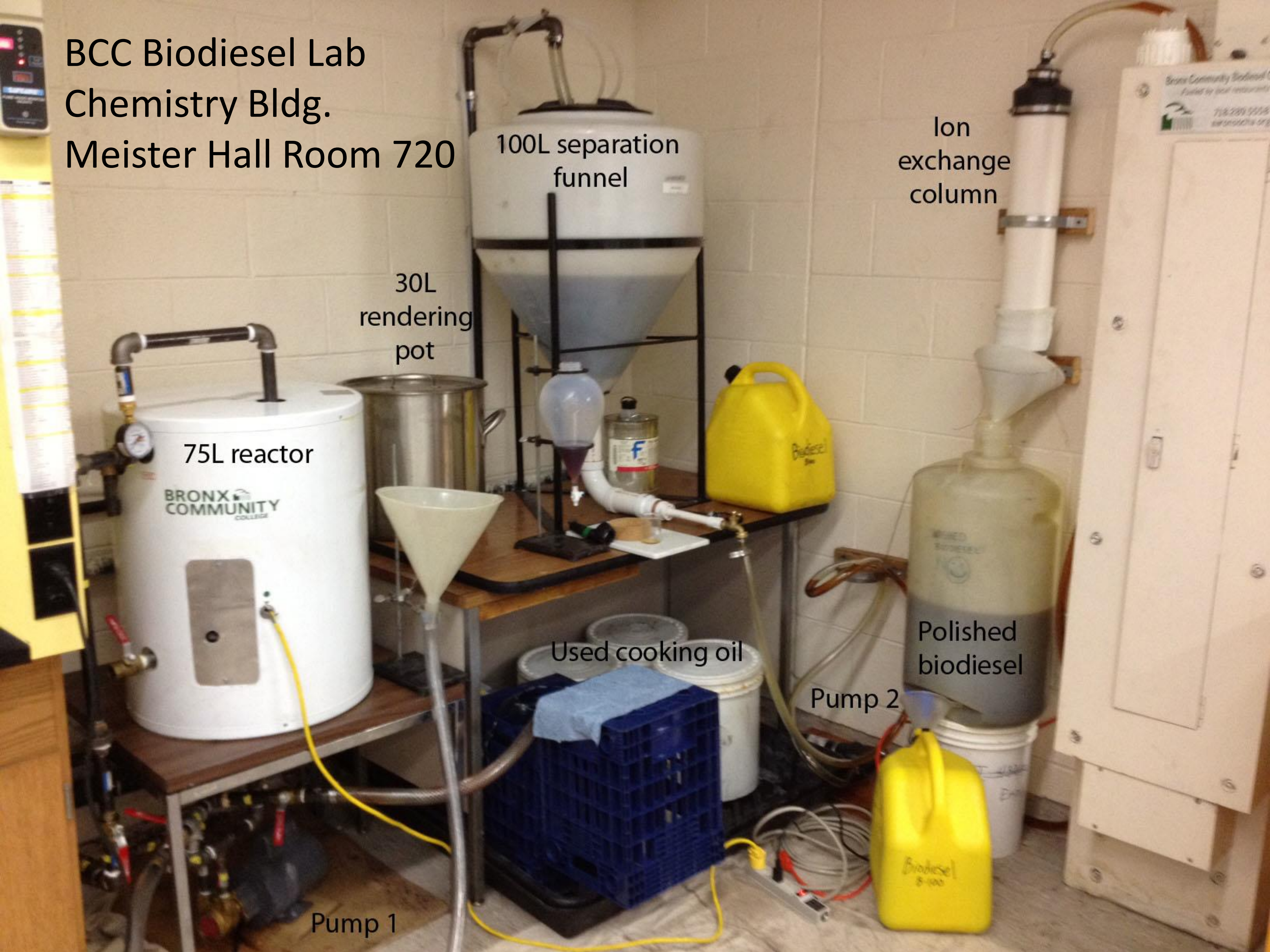
Biodiesel ASTM Testing

Property	ASTM Method	Limits	Units
Flash Points	D93	130.0 min.	°C
Water & Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity, 40°C	D445	1.9-6.0	mm^2/s
Sulfated Ash	D874	0.020 max.	% mass
Sulfur*	D5453	0.0015 max. (S15) 0.05 max. (S500)	% mass
Copper Strip Corrosion	D130	No. 3 max.	
Cetane Number	D613	47 min.	
Cloud Point	D2500	Report to Customer	°C
Carbon Residue**	D4530	0.050 max.	% mass
Acid Number	D664	0.80 max.	Mg KOH/g
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
Phosphorus Content	D4951	0.0001 max.	% max.
Distillation Temperature,	D1160	360 max.	°C

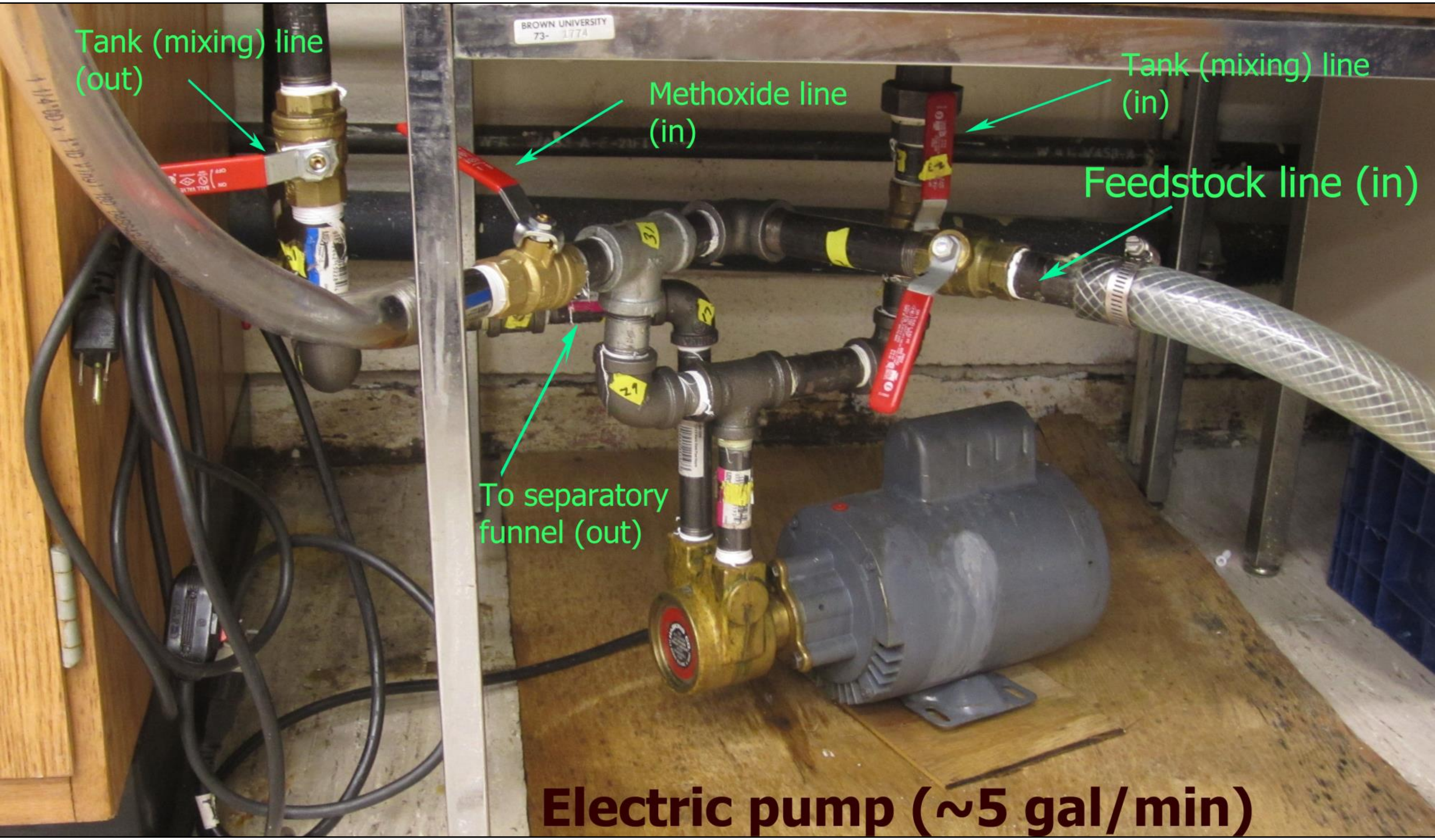
Biodiesel in the Bronx

BCC Biodiesel Car

“Locally-Sourced” Feedstocks


BCC Biodiesel Lab
Chemistry Bldg.
Meister Hall Room 720
100L separation funnel
Ion exchange column
30L rendering pot
75L reactor
BRONX COMMUNITY
Used cooking oil
Polished biodiesel
Pump 2
Pump 1

Reactor Pump/Mixer




BIODIESEL
BIODIESEL
GLYCEROL

Biodiesel Transesterification in a Microwave

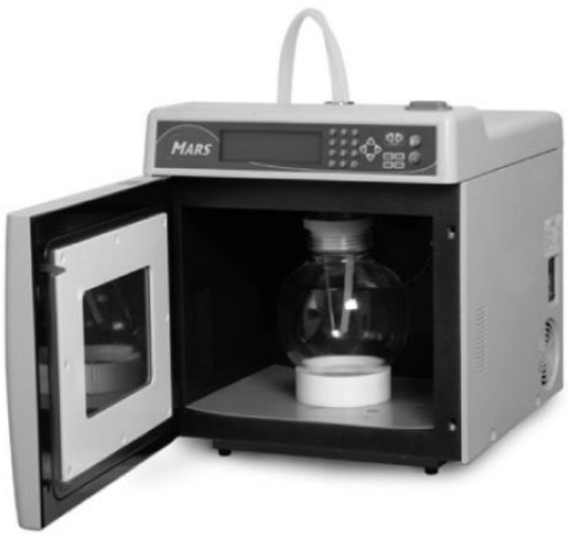
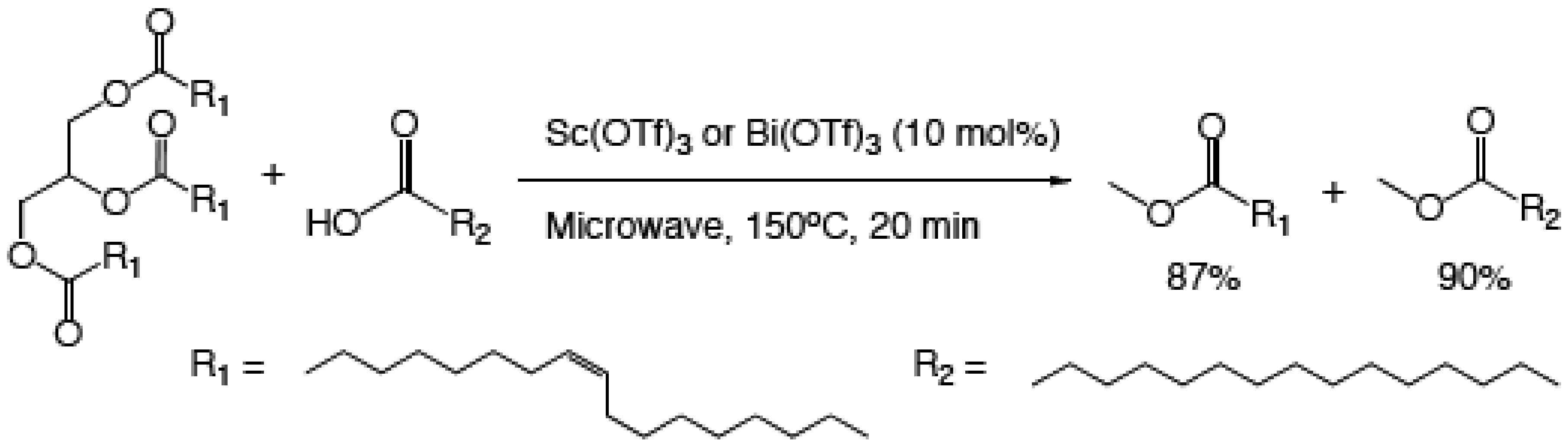


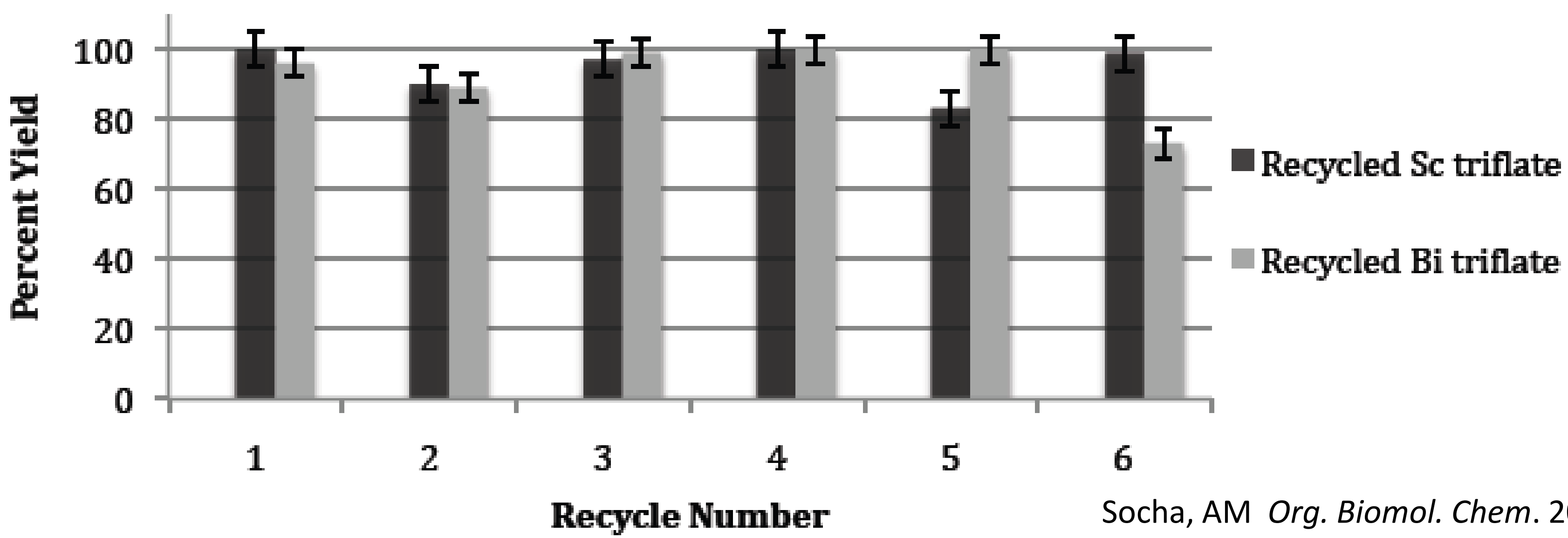
Table 2. Energy Consumption Estimations for the Preparation of Biodiesel Using Conventional and Microwave Heating

entry	reaction conditions	energy consumption (kJ/L)[a]
1	conventional heating[b]	94.3
2	microwave, continuous flow at a 7.2 L/min feedstock flow	26.0
3	microwave, continuous flow at a 2 L/min feedstock flow[c]	60.3 (92.3)[d]
4[e]	microwave heating, 4.6 L batch reaction	90.1

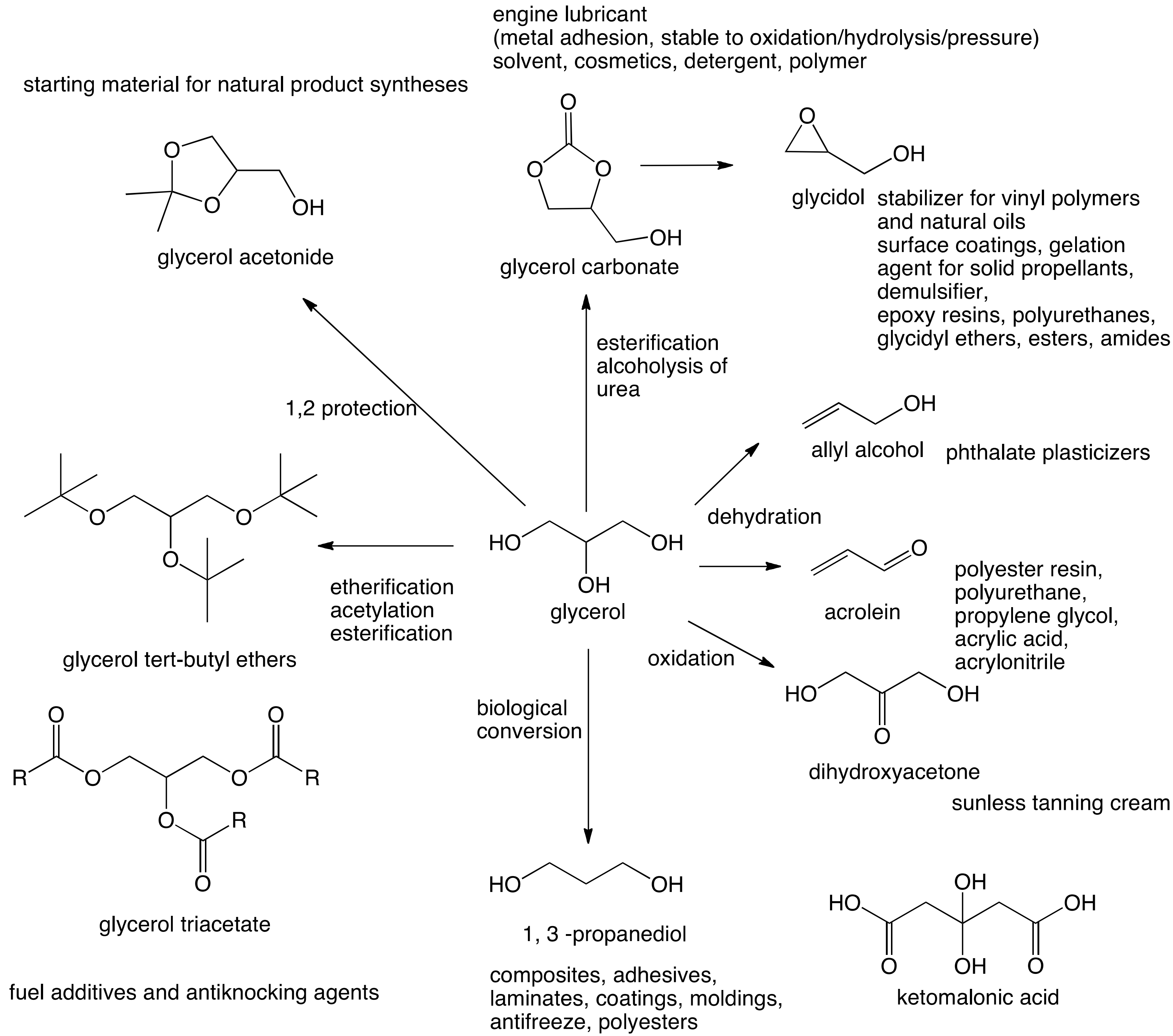
Leadbeater et al *Energy & Fuels* **2007** 21, 1777-1781

One Pot Biodiesel Synthesis in a Microwave

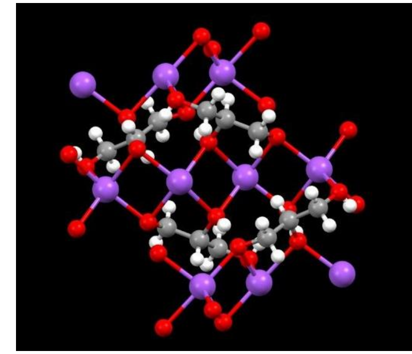


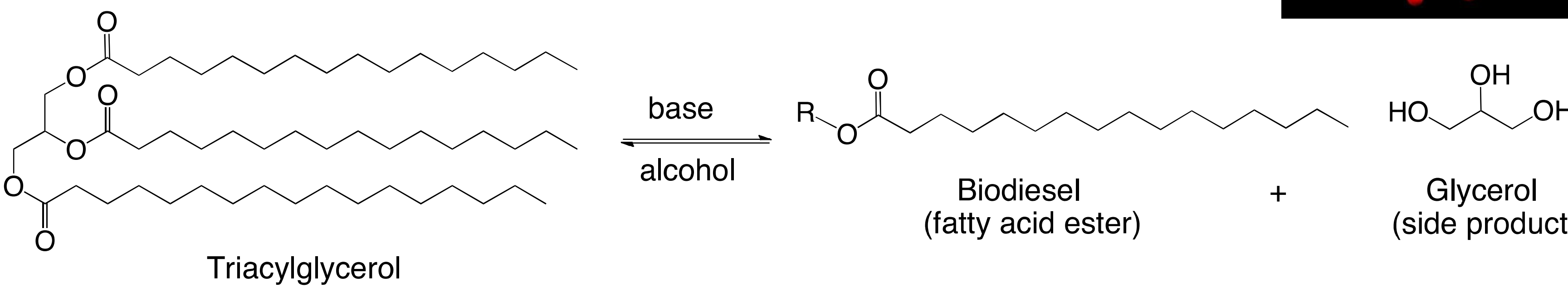


Socha, AM *Org. Biomol. Chem*. 2010


engine lubricant
(metal adhesion, stable to oxidation/hydrolysis/pressure)
solvent, cosmetics, detergent, polymer
starting material for natural product syntheses
glycerol acetonide
glycerol carbonate
glycidol
stabilizer for vinyl polymers and natural oils
surface coatings, gelation agent for solid propellants,
demulsifier,
epoxy resins, polyurethanes,
glycidyl ethers, esters, amides
esterification
alcoholysis of urea
1,2 protection
allyl alcohol
phthalate plasticizers
dehydration
glycerol
acrolein
polyester resin,
polyurethane,
propylene glycol,
acrylic acid,
acrylonitrile
etherification
acetylation
esterification
glycerol tert-butyl ethers
oxidation
dihydroxyacetone
sunless tanning cream
biological conversion
glycerol triacetate
1, 3 -propanediol
composites, adhesives,
laminates, coatings, moldings,
antifreeze, polyesters
ketomalonic acid
fuel additives and antiknocking agents

Sodium Glyceroxide Catalyzed Transesterification Reaction

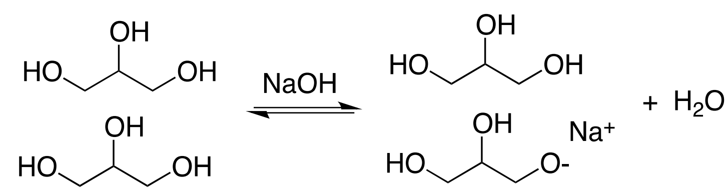




- Sodium methylate production can be cost/safety prohibitive for small scale biodiesel producers
- Sodium glyceroxide offers an *anhydrous alternative* to sodium methoxide (*no soap formation*)
- Effective use of "waste" glycerol from biodiesel industry
- Excellent transesterification catalyst for methyl and ethyl ester synthesis from triglycerides

$$R{-}OH \longrightarrow R{-}O^{-} + H_2O$$

BP MeOH = 64.7°C



BP Glycerol = 290°C

S. Pradhan, et al. Fatty acid methyl ester production with glycerol metal alkoxide catalyst, *Eur. J. Lipid Technology*, 116 (**2014**) 1590-1597

Catalyst Formulation Development: Viscosity and Transesterification Kinetics

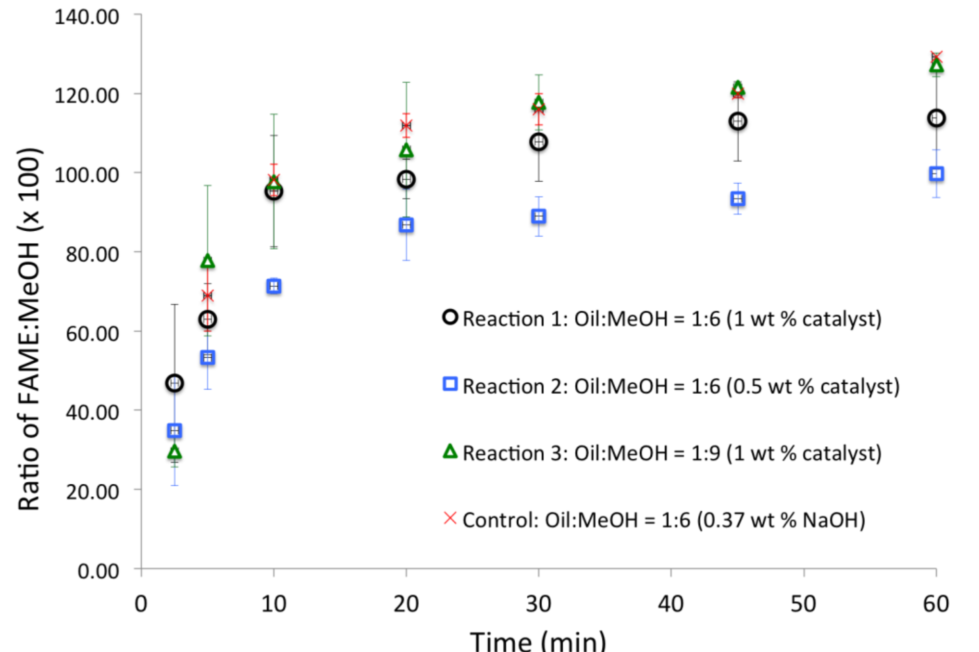
- Transesterification kinetics studied by ^{1}H NMR

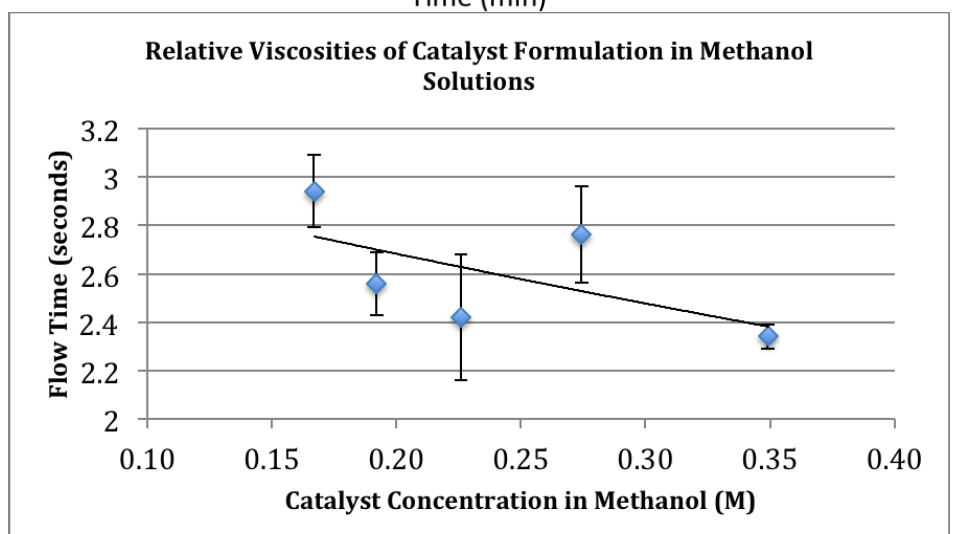
$$\frac{\text{peak area of FAME ester } CH_3\ (\delta = 3.66)}{\text{peak area of methanol } CH_3\ (\delta = 3.46)}$$

- Increased [MeOH] gives increased reaction rate

- 1 wt% catalyst is effective in 10 min reaction time

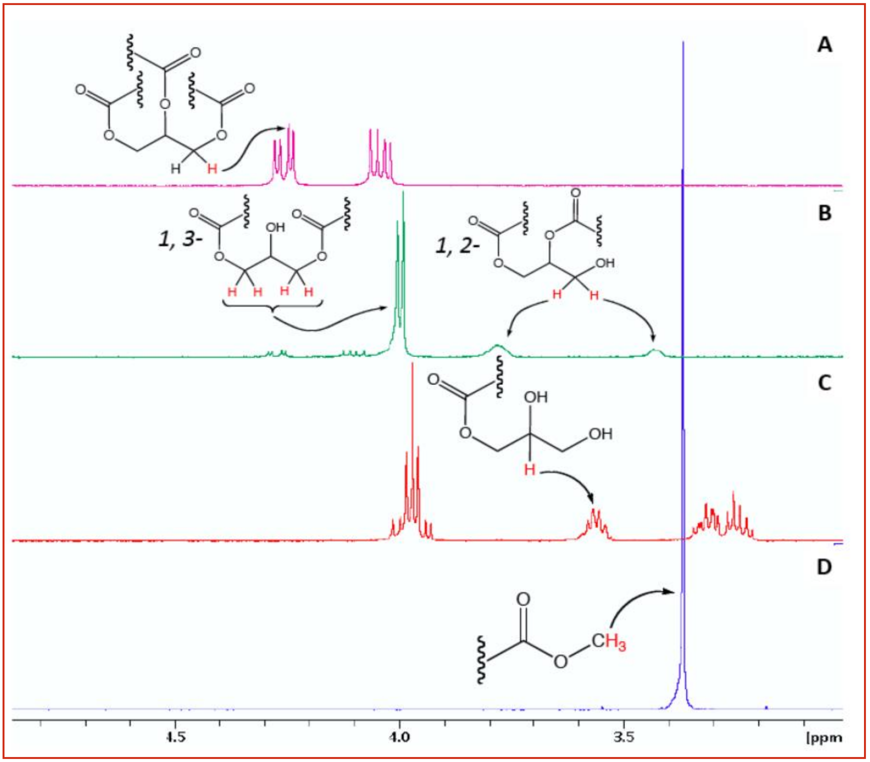
- Increased [Na Glyceroxide] in methanol leads to *decreased* viscosity

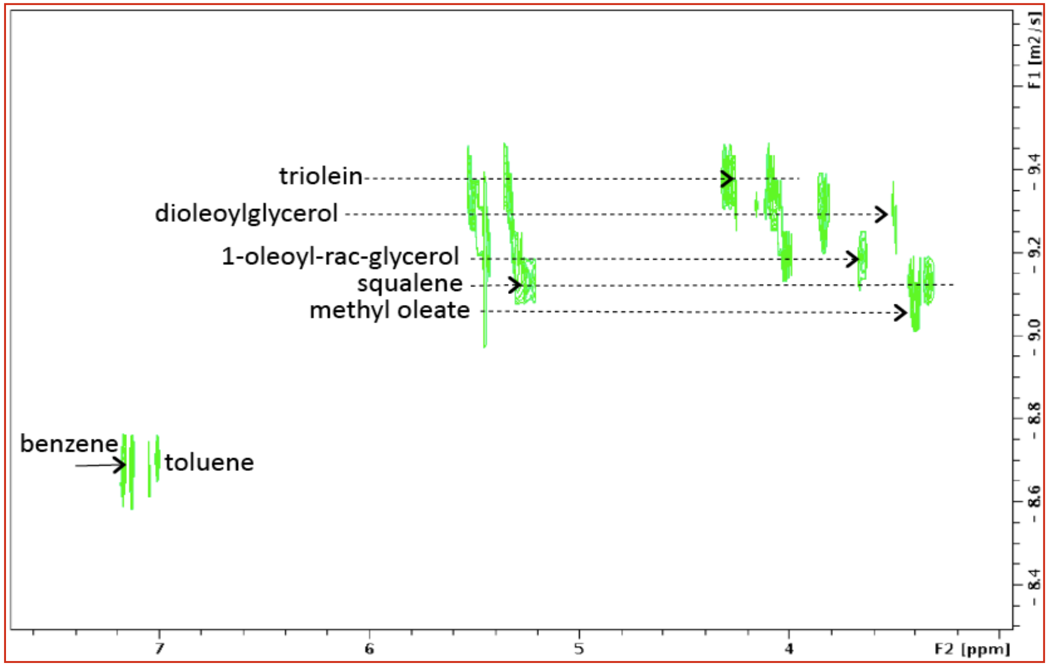




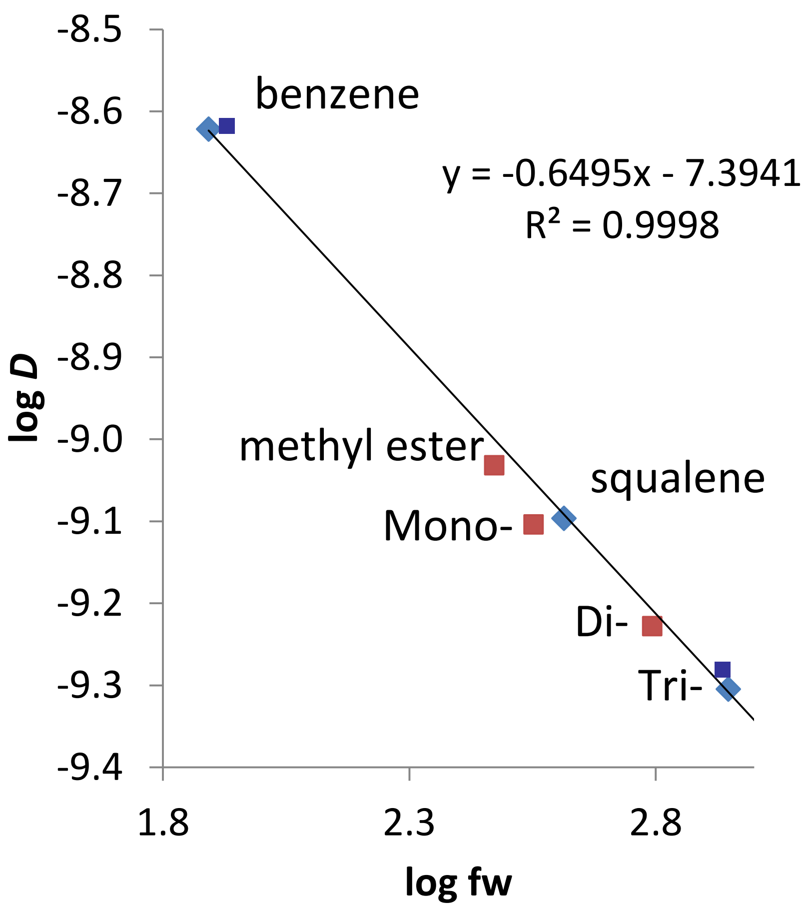
D. Bradley, A.M. Socha et al. Fuel Processing Technology 2016

DOSY NMR spectra of biodiesel oils





Formula weight analysis of reaction products by Diffusion NMR (DOSY)



compnd.	fw	fw*	% error
benzene	78.11	78	0.6
squalene	410.72	418	-1.8
trioleate	885.43	875	1.2
dioleate	620.99	666	-7.3
monooleate	356.54	429	-20.4
Me ester	296.49	332	-12.0

Socha et al., *Energy and Fuels*. **2010**, 24, 4518.