Incorporating Lessons on Biodiesel into the Science Classroom

Michael S. Briggs, MS, UNH Physics Department
msbriggs@unh.edu, 862-2828
Joseph Pearson, UNH Chemical Engineering
Dr. Ihab H. Farag, Chemical Eng Dept, 862-2313

University of New Hampshire (UNH) Biodiesel Group
Durham, NH 03824

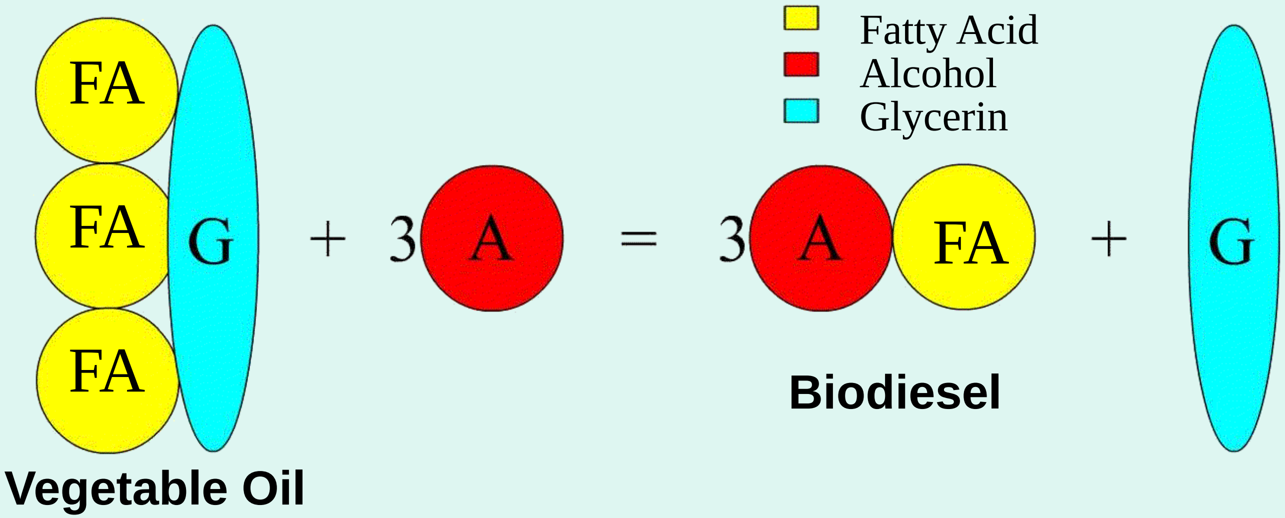
Presentation at the NH Science Teacher Association (NHSTA) Annual Conference, Session 15, March 22, 2005, Philips Exeter Academy. Exeter, NH

Overview

- Biodiesel Background & Advantages
- Making Biodiesel, Glycerin Separation, washing issues
- Chemistry of the process
- Demo: Canola Oil
- Biodiesel properties (double bond location, viscosity, Cetane number, cloud point)
- Biodiesel Challenges (Gelling, additives,..)
- Possible Lesson Plans: Energy efficiency, Vehicle comparison

What is Biodiesel?

- **Alternative fuel for diesel engines**
- **Made from vegetable oil or animal fat**
- **Meets health effect testing (CAA)**
- **Lower emissions, High flash point (>300F), Safer**
- **Biodegradable, Essentially non-toxic.**
- **Chemically, biodiesel molecules are mono-alkyl esters produced usually from triglyceride esters**

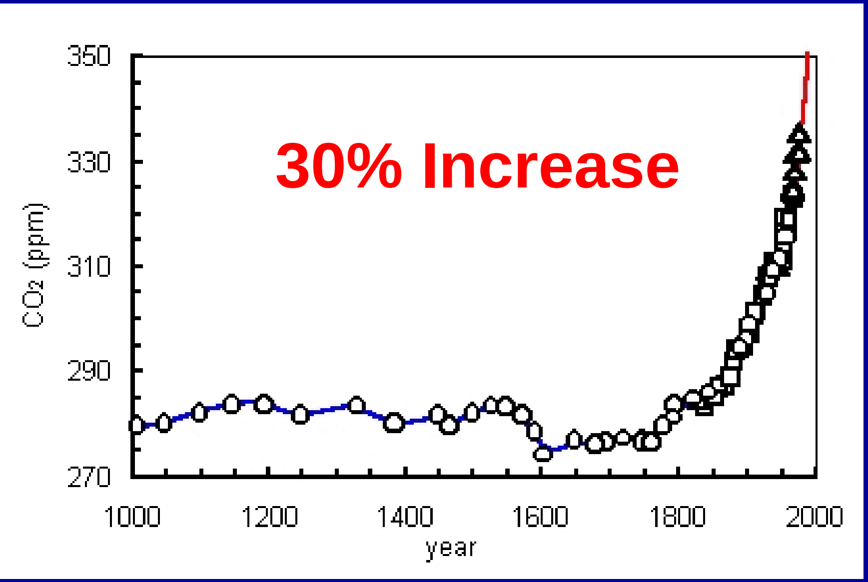


Biodiesel can be used in existing Diesel Engines

- Pure Biodiesel (B100) or blended with petroleum diesel (B20, BXX).
- Rudolf Diesel: peanut oil.
- Little or no engine modifications
- Use existing fuel distribution network.
- Available now

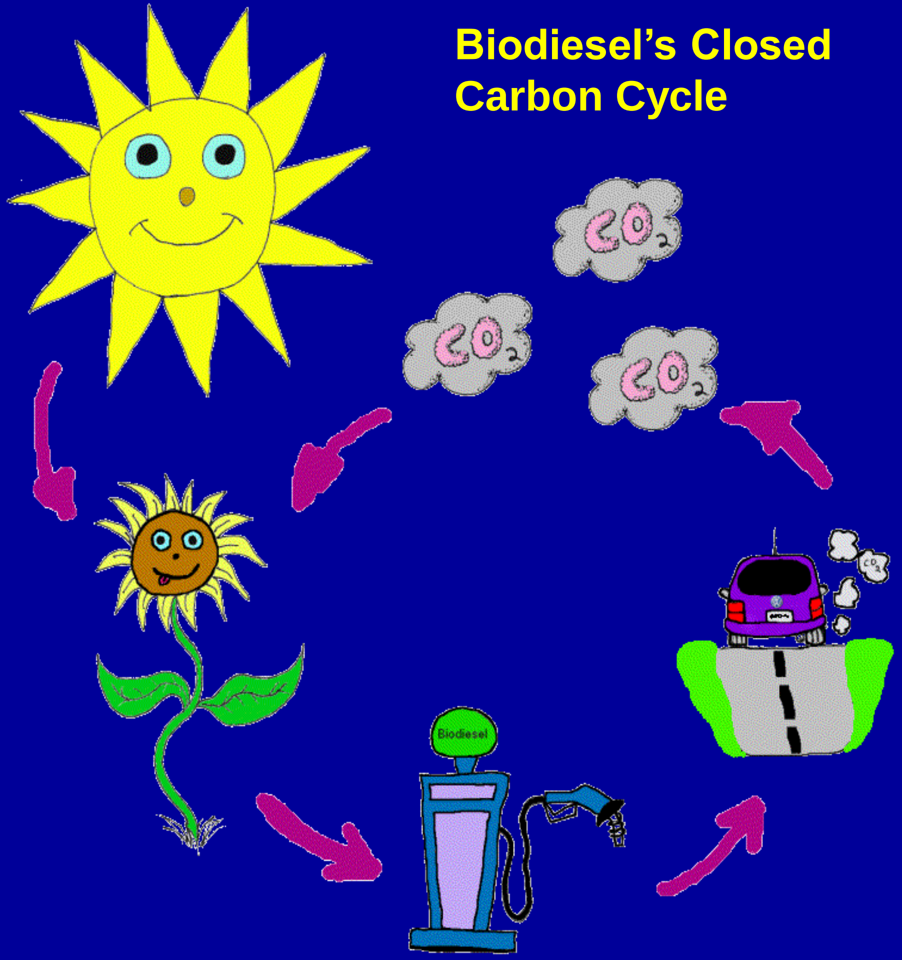
Environmental Issues

- Burning fossil fuels increases atmospheric levels of carbon dioxide
- Fossil fuels are a finite resource



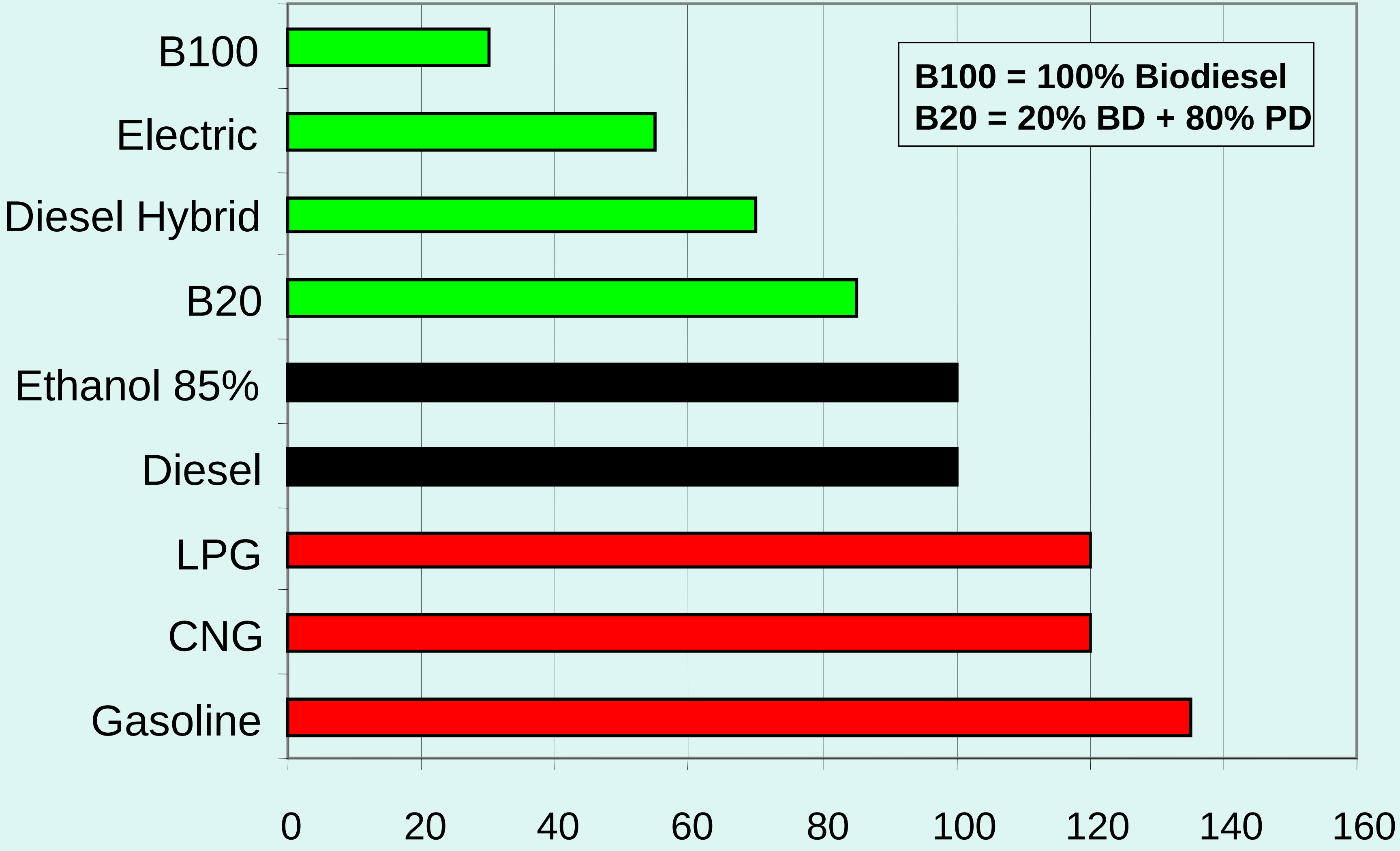
30% Increase

Graph taken from USF Oceanography webpage



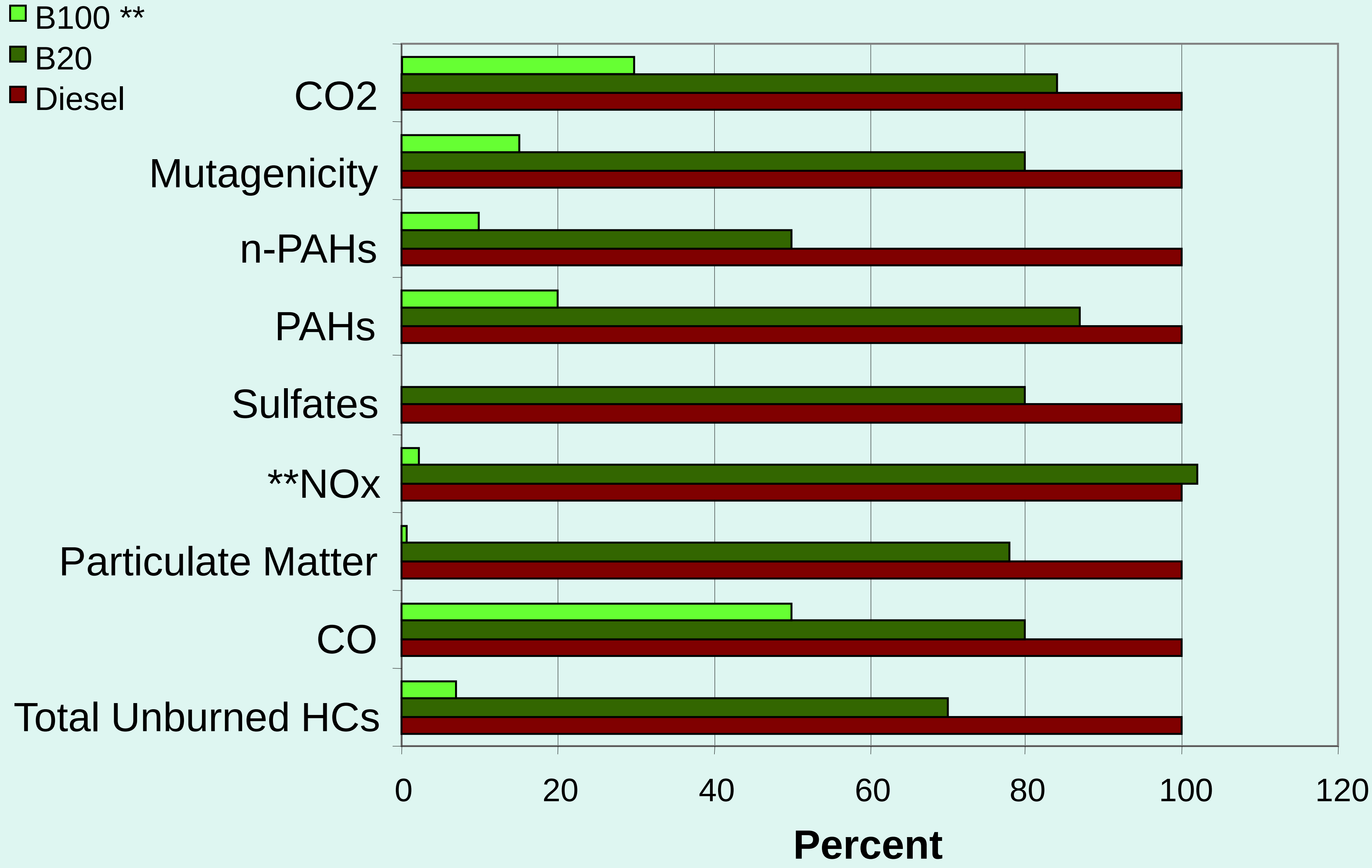
Biodiesel's Closed Carbon Cycle

Relative Greenhouse Gas Emissions



Data from “A Fresh Look at CNG: A Comparison of Alternative Fuels”, Alternative Fuel Vehicle Program, 8/13/2001

Relative emissions: Diesel and Biodiesel

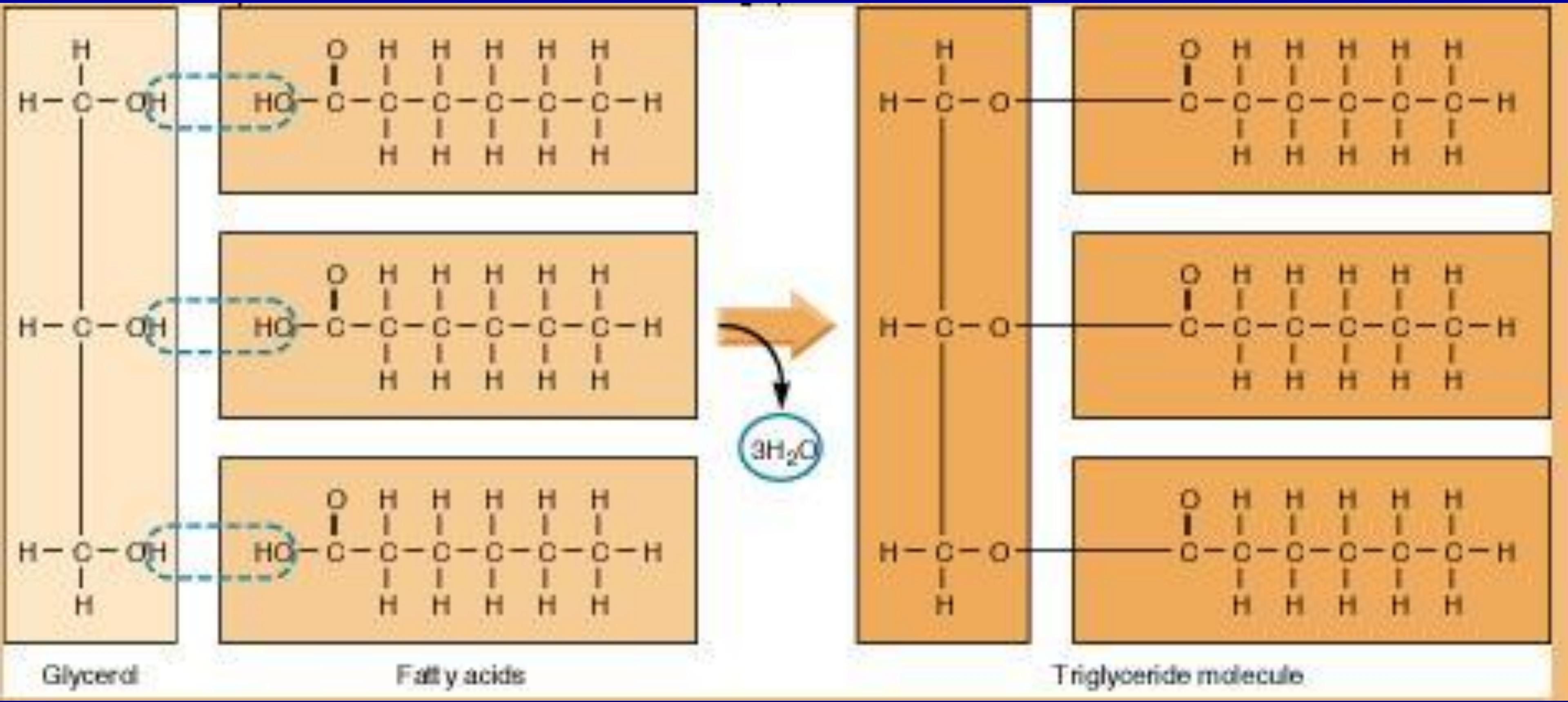


** B100 (100% biodiesel) with NOx adsorbing catalyst on vehicle

Biodiesel Samples

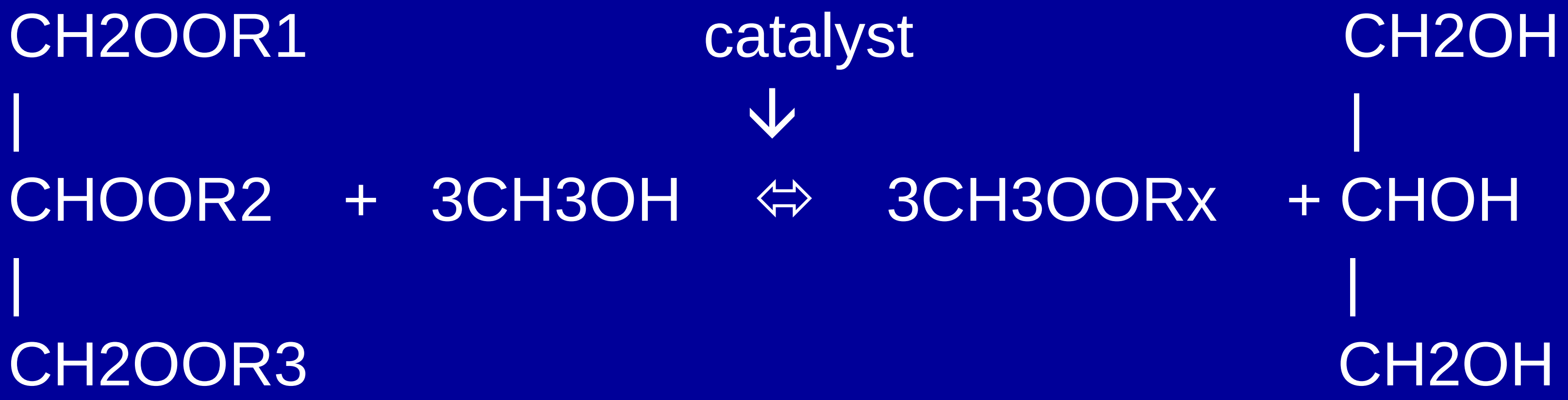
Chemistry of Triglycerides

- Biodiesel is made from the combination of a triglyceride with a monohydroxy alcohol (i.e. methanol, ethanol…).
- What is a triglyceride? Made from a combination of glycerol and three fatty acids:



Transesterification

While actually a multi-step process, the overall reaction looks like this:



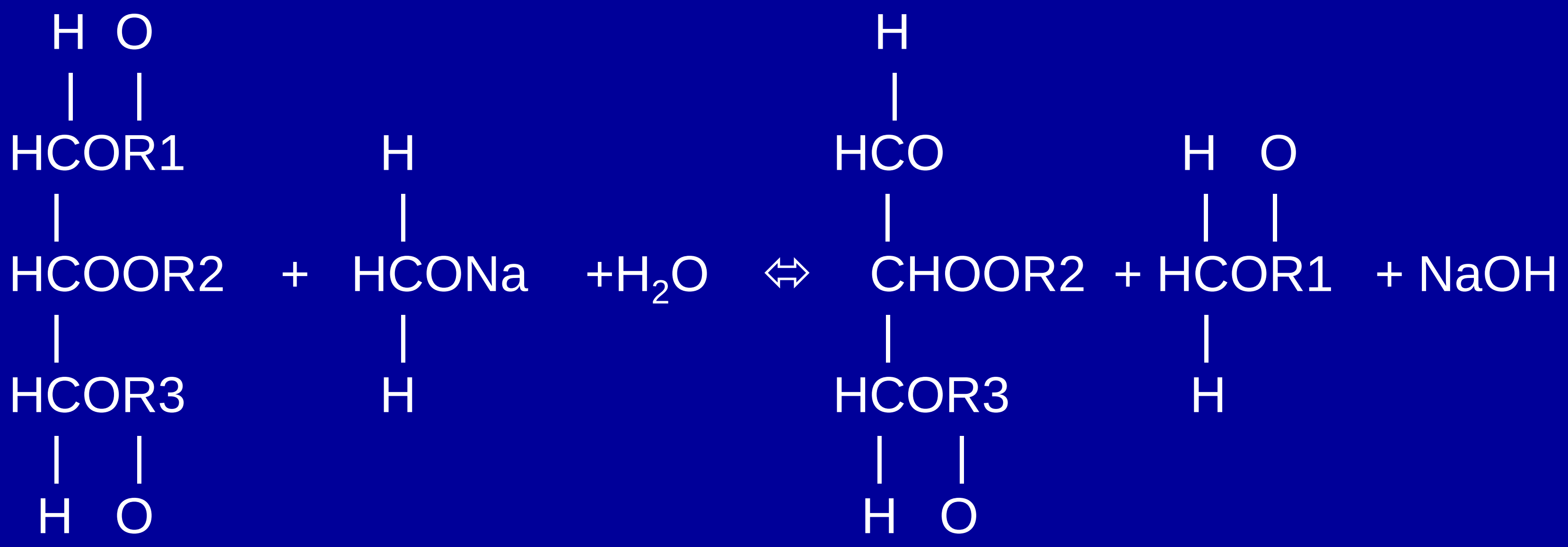
$$\begin{array}{lcccccc} \mathrm{CH2OOR1} & & & \text{catalyst} & & & \mathrm{CH2OH} \\ | & & & \downarrow & & & | \\ \mathrm{CHOOR2} & + & \mathrm{3CH3OH} & \Leftrightarrow & \mathrm{3CH3OORx} & + & \mathrm{CHOH} \\ | & & & & & & | \\ \mathrm{CH2OOR3} & & & & & & \mathrm{CH2OH} \end{array}$$

Triglyceride *3 Methanols* *Biodiesel* *Glycerin*

R1, R2, and R3 are fatty acid alkyl groups (could be different, or the same), and depend on the type of oil. The fatty acids involved determine the final properties of the biodiesel (cetane number, cold flow properties, etc.)

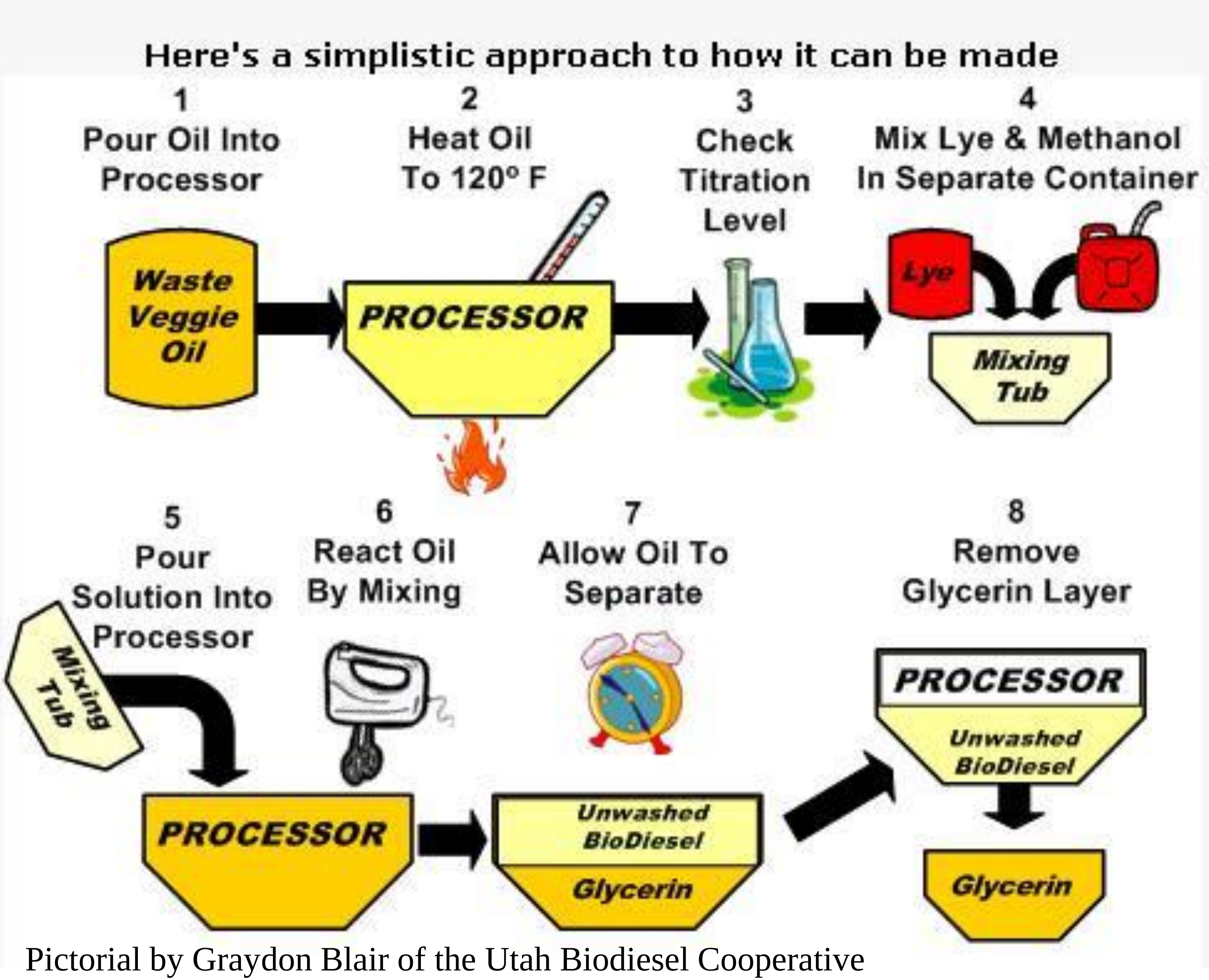
Individual step of Transesterification

First step, triglyceride turned into diglyceride, methoxide (minus Na) joins freed FA to make biodiesel, Na joins OH from water (from methoxide formation) to make NaOH. Other H joins the diglyceride.



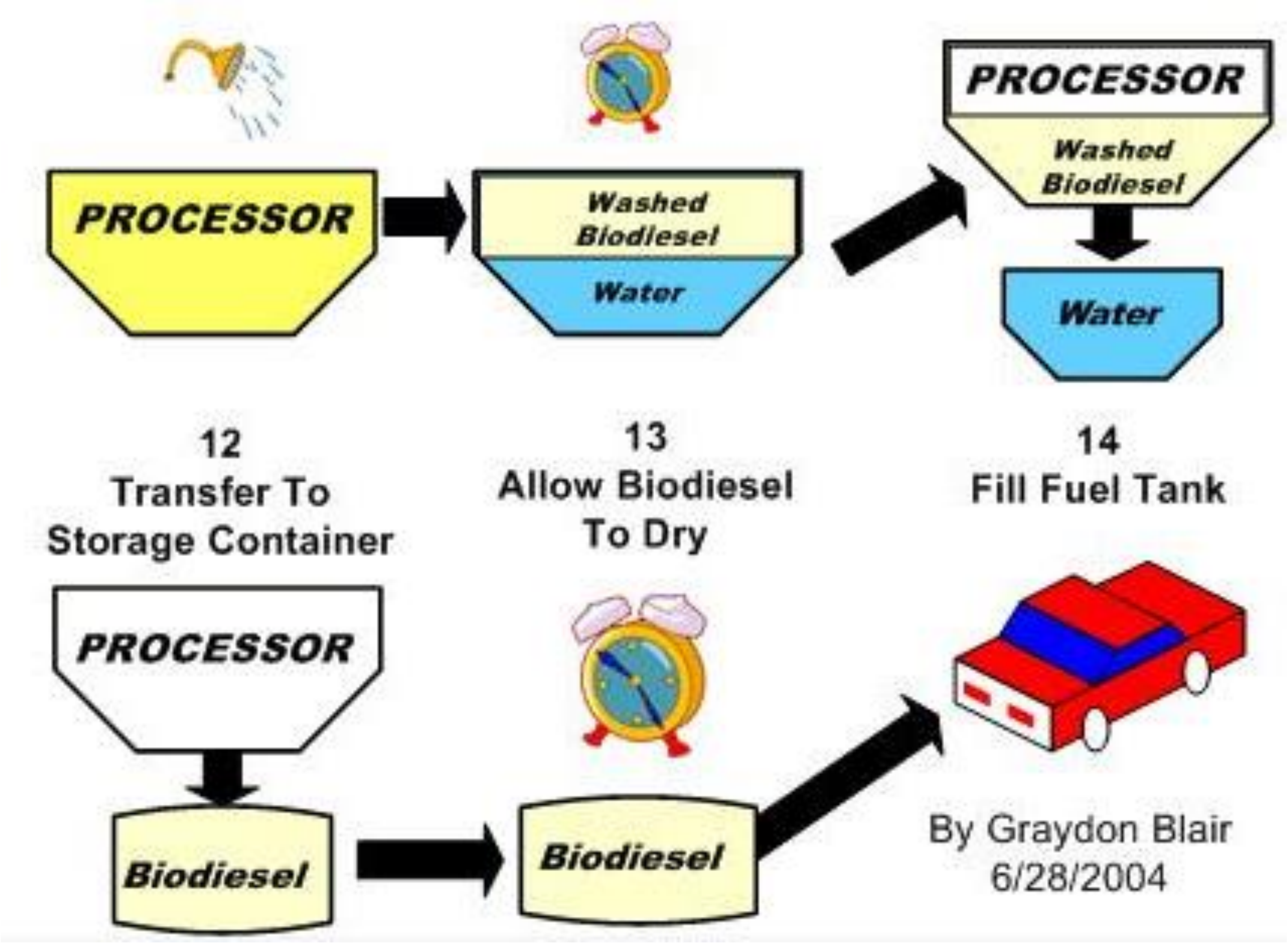
$$\begin{array}{ccccccccc}
\mathrm{H\ \ O} & & & & & \mathrm{H} & & & \\
|\ \ | & & & & & | & & & \\
\mathrm{HCOR1} & & \mathrm{H} & & & \mathrm{HCO} & & \mathrm{H\ \ O} & \\
| & & | & & & | & & |\ \ | & \\
\mathrm{HCOOR2} & + & \mathrm{HCONa} & +\mathrm{H_2O} & \Leftrightarrow & \mathrm{CHOOR2} & + & \mathrm{HCOR1} & +\ \mathrm{NaOH} \\
| & & | & & & | & & | & \\
\mathrm{HCOR3} & & \mathrm{H} & & & \mathrm{HCOR3} & & \mathrm{H} & \\
|\ \ | & & & & & |\ \ | & & & \\
\mathrm{H\ \ O} & & & & & \mathrm{H\ \ O} & & &
\end{array}$$

Triglyceride + Methoxide + H_2O ⇔ Diglyceride + Biodiesel + NaOH



Pictorial by Graydon Blair of the Utah Biodiesel Cooperative
http://www.utahbiodiesel.org/biodiesel_making.html

After Glycerin removal, biodiesel now just needs to be cleaned/purified before use:



“Appleseed” style biodiesel processor (design by Maria (Mark) Alovert). Uses old electric water heater as main unit

Fatty Acids and their Methyl Esters (biodiesel molecules)

Name(s)	**Acronym**	**Molecular Weight**	**Melt°C/°F**	**Boil°C/°F**	**Cetane Number**	**Combustion Heat (kg-cal/mole)**
Caprylic_acid	8:0	144.22	16.5/61.7	239.3/462.7	-	-
Capric_acid	10:0	172.27	31.5/88.7	270.0/518.0	47.6	1453.07
Lauric_acid	12:0	200.32	44.0/111.2	131.0/267.8	-	1763.25
Myristic_acid	14:0	228.38	58.0/136.4	250.5/482.9	-	2073.91
Palmitic_acid	16:0	256.43	63.0/145.4	350.0/662.0	-	2384.76
Stearic_acid	18:0	284.48	71.0/159.8	360.0/680.0	-	2696.12
Oleic_acid	18:1	282.47	16.0/60.8	286.0/546.8	-	2657.40
Linoleic_acid	18:2	280.45	-5.0/23.0	230.0/446.0	-	-
Linolenic_acid	18:3	278.44	-11.0/12.2	232.0/449.6	-	-
Erucic_acid	22:1	338.58	33.0/91.4	265.0/509.0	-	-
Methyl_caprylate	8:0	158.24	-	193.0/379.4	33.6	1313.00
Methyl_caprate	10:0	186.30	-	224.0/435.2	47.7	1625.00
Methyl_laurate	12:0	214.35	5.0/41.0	266.0/510.8	61.4	1940.00
Methyl_myristate	14:0	242.41	18.5/65.3	295.0/563.0	66.2	2254.00
Methyl_palmitate	16:0	270.46	30.5/86.9	418.0/784.4	74.5	2550.00
Methyl_stearate	18:0	298.51	39.1/102.4	443.0/829.4	86.9	2859.00
Methyl_oleate	18:1	296.49	-20.0/-4.0	218.5/425.3	47.2	2828.00
Methyl_linoleate	18:2	294.48	-35.0/-31.0	215.0/419.0	28.5	2794.00
Methyl_linolenate	18:3	292.46	-57.0/-70.6	109.0/228.2	20.6	2750.00
Methyl_erucate	22:1	352.60	-	222.0/431.6	76.0	3454.00

Biodiesel Challenges

- Cold Weather Operation (Chemistry)
- Producing enough feedstock oil to replace a large portion of petroleum (biology, chemistry, physics, economics)
- Engine and emissions optimization (chemistry, physics)

Lesson Ideas

I. Biology

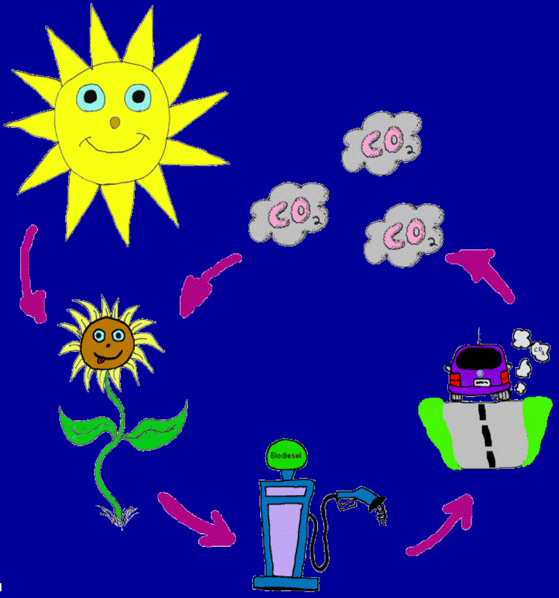
II. Chemistry

III. Physics

IV. Economics

V. Public Policy, Current Events

I. Biology



I.a. Carbon Cycle

I.b. Greenhouse Effect (Chem, Physics)

I.c. Health Issues, Animal Testing (Chemistry)

I.d. Plant suitability - breeding preferable feedstock crops (Chemistry, Economics)

I.e. Photosynthesis – as an energy/fuel production system for humans

II. Chemistry

II.a. Titrations (and general acids/bases)

II.b. Organic Chemistry Terminology

II.c. Freezing and Gelling

II.d. Transesterification reactions

II.e. Catalytic reactions

II.f. Reversible reactions

II.g. Fermentation

II.h. Materials Compatibility

III. Physics

III.a. Thermodynamics, Energy Conservation

III.b. Engines, Combustion (Chemistry)

III.c. Photosynthesis as energy conversion, quantum limits

III.d. Thorough analysis of alternative fuels, particularly efficiency and safety of (combustion science, etc.)

IV. Economics

IV.a. Economics of worldwide petroleum industry, impacts on US (trade deficits, military obligations, etc.)

IV.b. Co-product economics (co-products of feedstocks (i.e. soy meal) and processing (glycerin)

IV.c. Economic incentives for greater fuel efficiency and alternative fuel use

IV.d. Economic analysis of biodiesel production plant

Lesson Possibility - Vehicle comparison (energy efficiency, economics, etc.)

	Jetta TDI on biodiesel	**Jetta TDI on petroleum diesel**	**Jetta 2.0L gasoline engine**	**Toyota Prius on gasoline**	**Toyota Fuel Cell vehicle (hydrogen)**	**Dodge ESX3 (diesel-hybrid) on biodiesel**
Vehicle cost	$19,970	$19,970	$18,790	$21,520	$100,000[3]	$28,500
Fuel efficiency (FE)	41/48.5	42/50	24/31	52/45	5.7[4]	72
Vehicle range (miles)	609/711	609/711	348/450	619/536	155	???
Power (hp)	90	90	115	70	110	???
Torque (ft-lbs)	155	155	122	82	188	???
Cost/mile[2]	$0.047	$0.040	$0.062	$0.035	$0.19[5]	$0.03
Energy density (ED) of fuel (Thousands of BTUs/gal)	127	141	123	123	9	127
Fossil Fuel Energy Balance FEB)[6]	3.2	0.83	0.74	0.74	0.66[7]	3.2
Total fossil energy input/mile[8] (Thousand BTU/mile)	0.89	3.7	6.0	3.4	2.4	0.55

1 Assuming modern catalyst used with the TDI running biodiesel or ULSD.

2 Assuming $1.70/gallon for gasoline, $1.80 for petroleum diesel, and $2.16/gallon for biodiesel, based on 50/50 average of city/highway

3 Honda's estimate for the cost of their fuel cell vehicles in mass production in 2012

4 Miles per gallon of hydrogen compressed to 5,000 psi (35 atmospheres), based on maximum range of Honda's FCV of 170 miles on a 30 gallon tank

5 30 gallons at 5,000 psi equals 3.2 kg of hydrogen (hydrogen density at 14.7 psi is 0.0003142 kg/gal, at 5000 psi it's 0.1069 kg/gal). Typical cost for very large consumers of compressed hydrogen expected to be $10/kg. So, $32 for 170 miles.

6 See http://www.mda.state.mn.us/ethanol/balance.html

7 Assumes hydrogen produced from steam reformation of natural gas, fossil energy balance (net energy ratio) taken from http://www.nrel.gov/docs/fy01osti/27637.pdf

Comparison of Biodiesel and Hydrogen as Fuels of the Future

	Biodiesel	**Hydrogen**
Technological Readiness	Can be used in existing diesel engines, which have already been in use for 100 years	Electrolyzing water (most likely using fossil fuel energy) or reforming fossil fuels. Most likely non-renewable methods with large net CO2 emissions
Fuel Distribution System	Can be distributed with existing filling stations with no changes.	No system currently exists, would take decades to develop. Would cost $176 billion to put one hydrogen pump at each of the filling stations in the US.
Fossil Energy Balance [higher is better]	3.2 units (soy) 4.3 units (rapeseed)	0.66 units (steam reforming of natural gas)
Large scale fuel development cost analysis	For an estimated $169[1] billion, enough algae farms could be built to completely replace petroleum transportation fuels with biodiesel	To produce enough *clean* hydrogen for our transportation needs would cost $2.5 *trillion* (wind power) or $25 trillion (solar)
Safety	Flash point over 300° F (considered “not flammable”)	Highly flammable, high pressure storage tanks pose a large risk due to store mechanical energy, as well as flammability/explosiveness
Time scale for wide scale use	5-15 years	30-70 years optimistic assumption
Cost of engines	Comparable to existing vehicles	Currently 50-100 times as expensive as existing engines.
Tank capacity required for 1,000 mile range in conventional sedan	20 gallons	268 gallons

V. Public Policy, Current Events

- Scientific and engineering advancements are not independent of economics and legislation - they are closely intertwined
- Legislative efforts can make technological advancement more economical while the industry develops (i.e. temporary biodiesel road tax exemption)
- Petroleum is a critical player in world politics, wars, etc. Replacing petroleum vitally important for strategic, economic, and environmental reasons.

Summary

Alternative fuels and energy sources are an issue of increasing importance - not only among the scientific and engineering community, but also in economics and public policy. Alternatives need to be compared on scientific and economic terms - which is not done well in the media.

Alternative fuels and energy sources provide an excellent opportunity to introducing a variety of science topics, and increasing student interest in those topics. Science and engineering fields are increasingly disciplinary - lessons on biodiesel can demonstrate that clearly, by showing the overlapping of biology, chemistry, and physics in studying this and other alternative fuels. It can also demonstrate to students that science is not independent of economics, and advancements in science can yield considerable benefit to the general public (i.e. shifting from petroleum fuels to domestically produced biofuels would create millions of jobs, improve our economy, reduce pollution enormously, and eliminate a key strategic concern for all countries - the dependence on foreign fuels).