Biodiesel as an Alternative Fuel and its Impact on Air Pollution

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Diesel Use in U.S.

- In 2006, 49.6 billion gallons of diesel fuel consumed in U.S.
  - 79% of this for highway transportation (mostly big trucks)
  - Rest for farm machinery, construction, military, rail, and marine craft
- Biodiesel is a potential replacement for petroleum diesel
  - Derived from plant or animal lipids
  - Oils and fats can't be used directly in engines because their higher viscosity, higher cloud points, and lower vapor pressures put extra pressure on filters and pumps and cause deposits in cylinders and injectors.

Comparison of Biodiesel and Petroleum Diesel

	Average Biodiesel	Average Diesel
Natural cetane number	55	44
Sulfur, ppm	54	333
Nitrogen, ppm	18	114
Aromatics, vol%	0	34
T10, ^{o}F	628	422
T90, ^{o}F	666	603
Specific gravity	0.88	0.85
Viscosity, cSt at 40 ^{o}F	6.0	2.6
Cloud point, ^{o}C (soybean)	2	-19
Flash point, ^{o}C (soybean)	141	85
Combustion pt, ^{o}C (soy)	171	92

Biodiesel Production

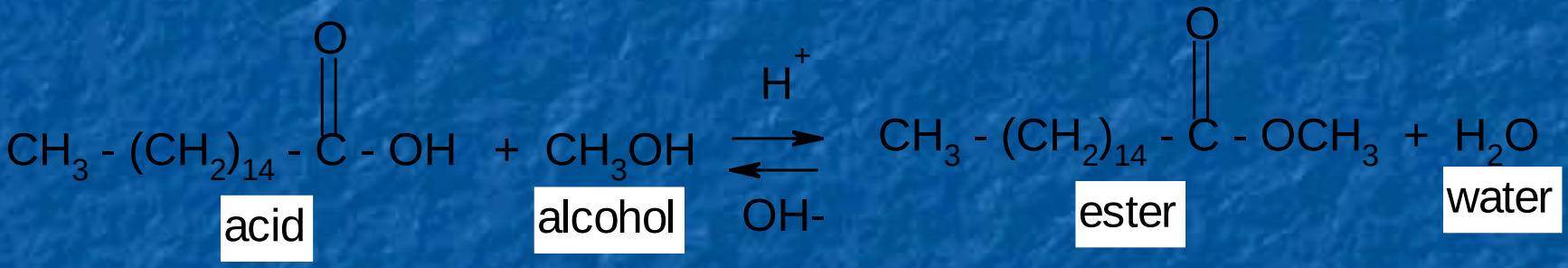
- Biodiesel production in U.S.
  - 75 million gallons in 2005
  - 450 million gallons in 2007 (0.9% of total diesel use)
- Almost all biodiesel in U.S. made from soybeans. In Europe, mainly from rapeseed (canola) oil.
- Land Use
  - Assuming a yield of 118 gallons/ha for soybeans, then 420 million ha of cropland are needed to replace all diesel used in U.S.
  - Currently 182 million ha of cropland, so you would need 230% of the available cropland.
  - Yield of oil from rapeseed more than twice that of soybeans.

Options

- Virgin oils not a feasible solution to replace diesel
  - Impact on land use
  - Cost of oil feedstock almost same as price of biodiesel. Feedstock can account for 75% of cost of biodiesel.
  - Impact on food costs
- Two other possibilities for feedstocks
  - Waste oil
  - Algae
- Amount of waste oils
  - 2.5 billion pounds of waste fats collected annually from U.S. restaurants
  - 11.6 billion pounds of animal fats produced annually
  - Potentially could replace 4% of petroleum diesel

Oils (Lipids)

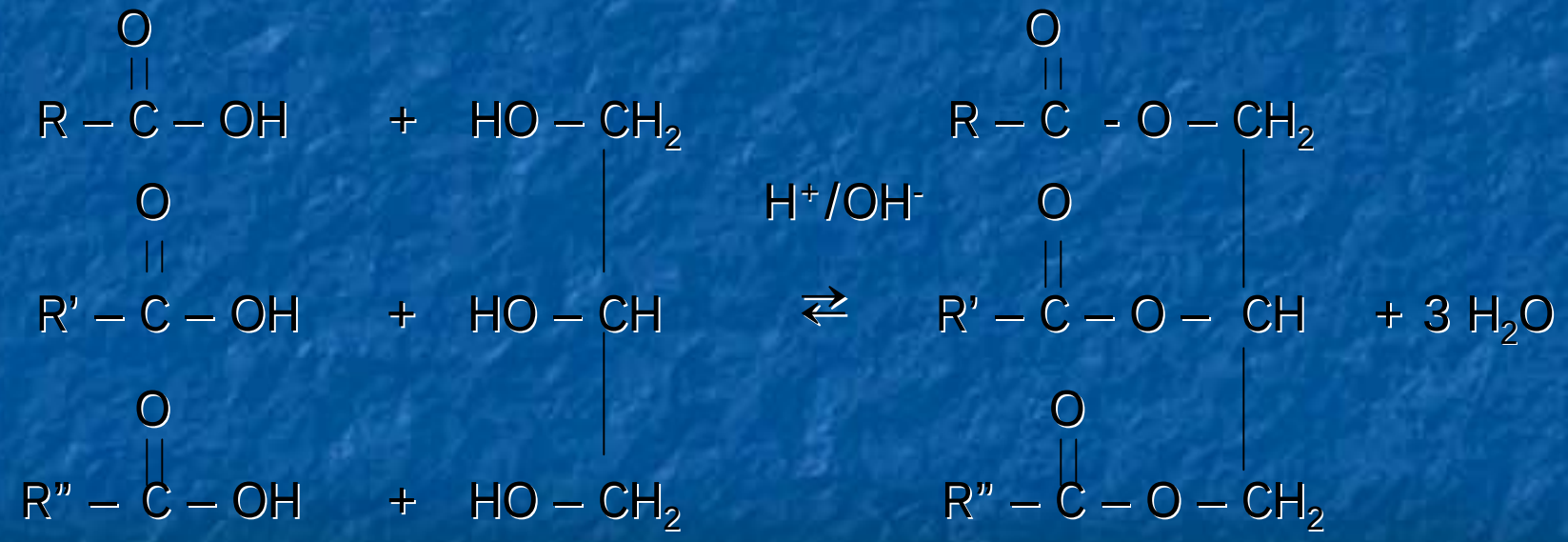
- Lipids consist of long chain fatty acids (such as C16, palmitic acid or C18, oleic acid) which are esterified to a glycerol molecule to give a *triglyceride*.
- An ester is formed from reaction of a carboxylic acid and an alcohol. Catalyzed by acid or base.



- Reaction is reversible, so esters can be hydrolyzed to give fatty acid and alcohol. Presence of water reduces ester formation

Triglycerides

- Glycerol molecule can be esterified to as many as 3 fatty acids .The resulting triglyceride (or fat) is non-polar and not water soluble.
- Free fatty acids (FFA) in blood are very toxic. Very important to take them out of blood plasma and store them as triglycerides.



fatty acid glycerol triglyceride water

Saturated vs Unsaturated Fatty Acids

Figures from Lubert Stryer, *Biochemistry*, W.H. Freeman, 1975.

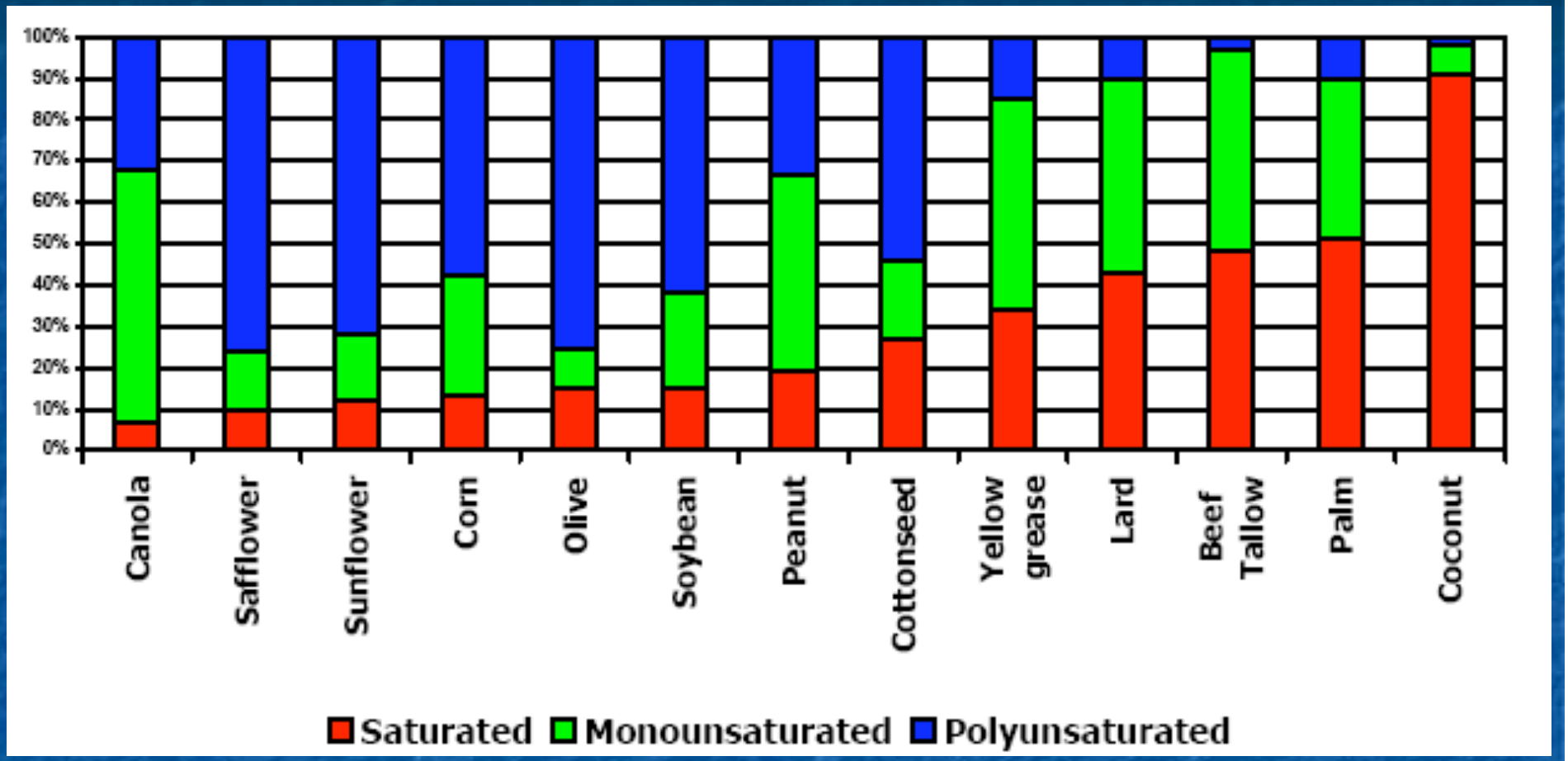
Top is palmitic acid (C 16, saturated) and bottom is oleic acid (C 18, Mono-unsaturated). *cis* double bond produces "kink". Fatty acid chains don't "pack" as well. One or more cis bonds decreases boiling point and viscosity.

Triglycerides

- Animal fat (lard) is mostly made of saturated fatty acids. Because the saturated fatty acid chains can pack closely together, van der Waals forces are strong and the melting point of lard is above room temperature.
- Vegetable oils have mostly unsaturated C=C double bonds. Packing is harder. Makes it a liquid at room temperature. The more double bonds (polyunsaturated), the lower the melting point.
- Iodine Value measures extent of double bonds (g I_2/100 g oil). Higher Iodine Value means more unsaturation. Also corresponds to lower cloud point because melting point decreases.

Fatty Acid Distribution in Oils and Fats (% by Weight)

	C16:0	C18:0	C18:1	C18:2	C18:3	% Sat	Iodine Value
Rapeseed Oil	3.49	0.85	64.40	22.30	8.23	4.34	98
Sunflower Oil	6.08	3.26	16.93	73.73	-	9.34	125
Soybean Oil	10.58	4.76	22.52	52.34	8.19	15.34	130
Lard	28-30	12-18	40-50	7-13	-	41-50	60-70



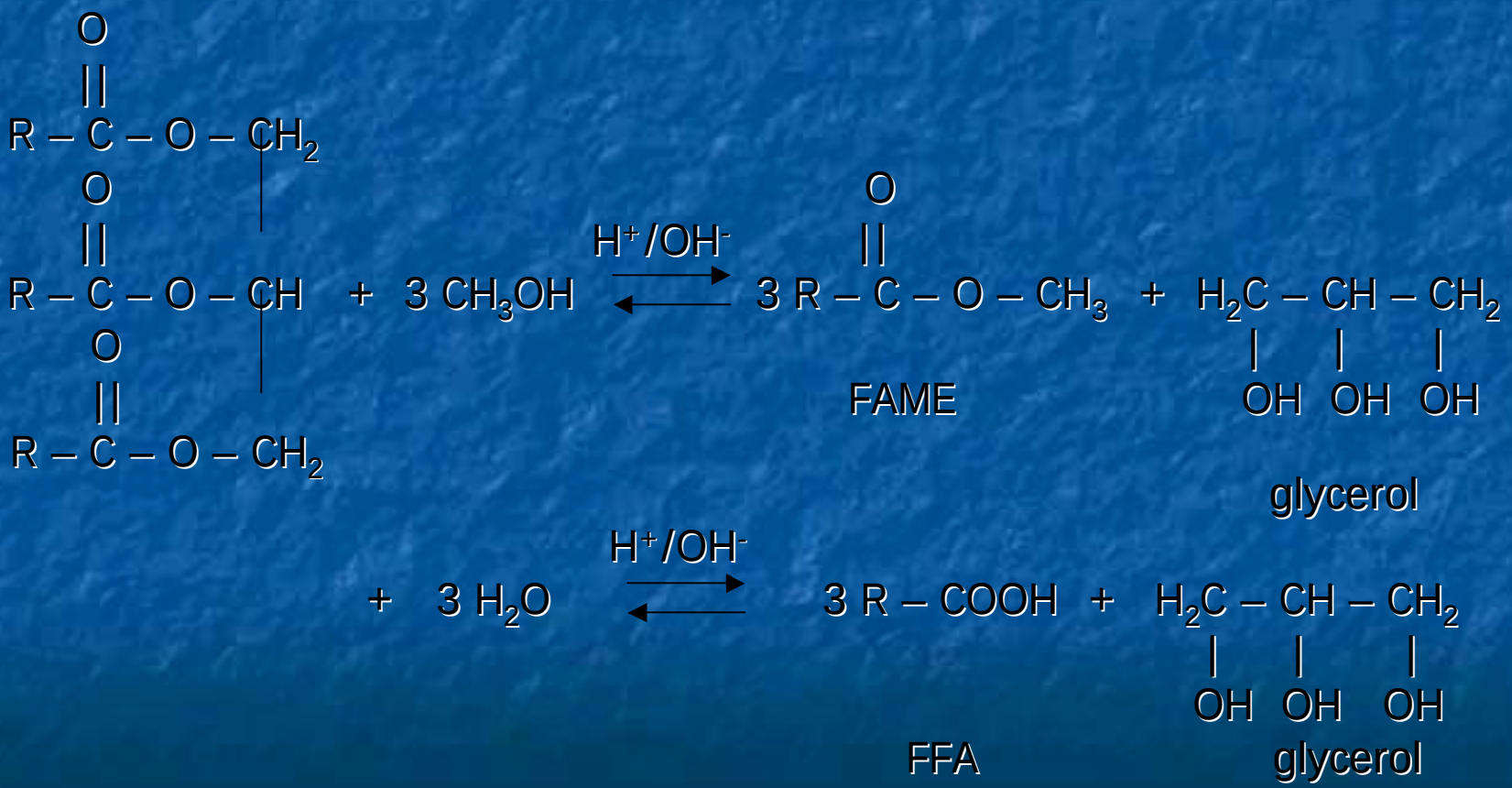
U.S. Dept of Energy (March 2006), Biodiesel Handling and Use Guidelines

Trans-esterification

- The reaction between a triglyceride and an alcohol to produce another ester and is called *trans*-esterification.
- Biodiesel is mostly made from reacting methanol with triglycerides to give a fatty acid methyl ester (FAME). The MW of the FAME is much smaller than the triglyceride which greatly affects properties such as viscosity, boiling point, cloud point, flash point, etc., all of which are closer to petroleum diesel than the vegetable oils themselves.

Trans-esterification

- But presence of water provides a competing reaction to generate a free fatty acid (FFA). **So transesterification is inhibited by water.**



Technical Issues with Biodiesel Production from Waste Oils

- Deep frying subjects oils to 160 – 200 ^{o}C for relatively long periods of time in presence of air and light. Three types of reactions result:
  - Hydrolytic – Steam produced from cooking foods causes hydrolysis of triglycerides to produce FFA, mono and diglycerides, and glycerol.
  - Thermolytic – High temperatures in absence of O_2 can decarboxylate triglycerides to produce CO_2, acids, hydrocarbons, and other compounds.
  - Oxidative – Unsaturated fatty acids react with O_2 to produce hydroperoxide free radicals which can then produce many different chemicals including polymers. Higher iodine number leads to higher viscosity and acid number.

Challenges of Waste Cooking Oil

- Thus, polar content of cooking oils increases with repeated heating.
- Results in
  - Increased FFA, solids, and water content
  - Different viscosity, iodine number, and density than virgin oil
  - Possible contamination with proteins, carbohydrates, and other unsaponifiables

Greases

- Yellow (recycled) grease is limited to 15% FFA. Animal tallows can vary, depending upon the grade, from less than 1% to 15% FFA. Can be mixture of vegetable oils and animal fats. Fats with higher FFA are sold as brown grease.
- Trap greases can contain between 50 – 100% FFA. There is currently no market for these and most are landfilled. Use of trap greases to make biodiesel is a significant challenge, not only because of organic impurities, but silts and emulsifications make processing very difficult.

Yellow and Brown Grease

- Excluding capital costs for plant construction, but including all production costs including feedstock, electricity, natural gas and consumables, estimated costs are:
  - Methyl ester from soybean oil $1.58/gallon
  - Methyl ester from yellow grease $1.20/gallon
  - Methyl ester from brown grease $0.91/gallon

Algae as Oil Source

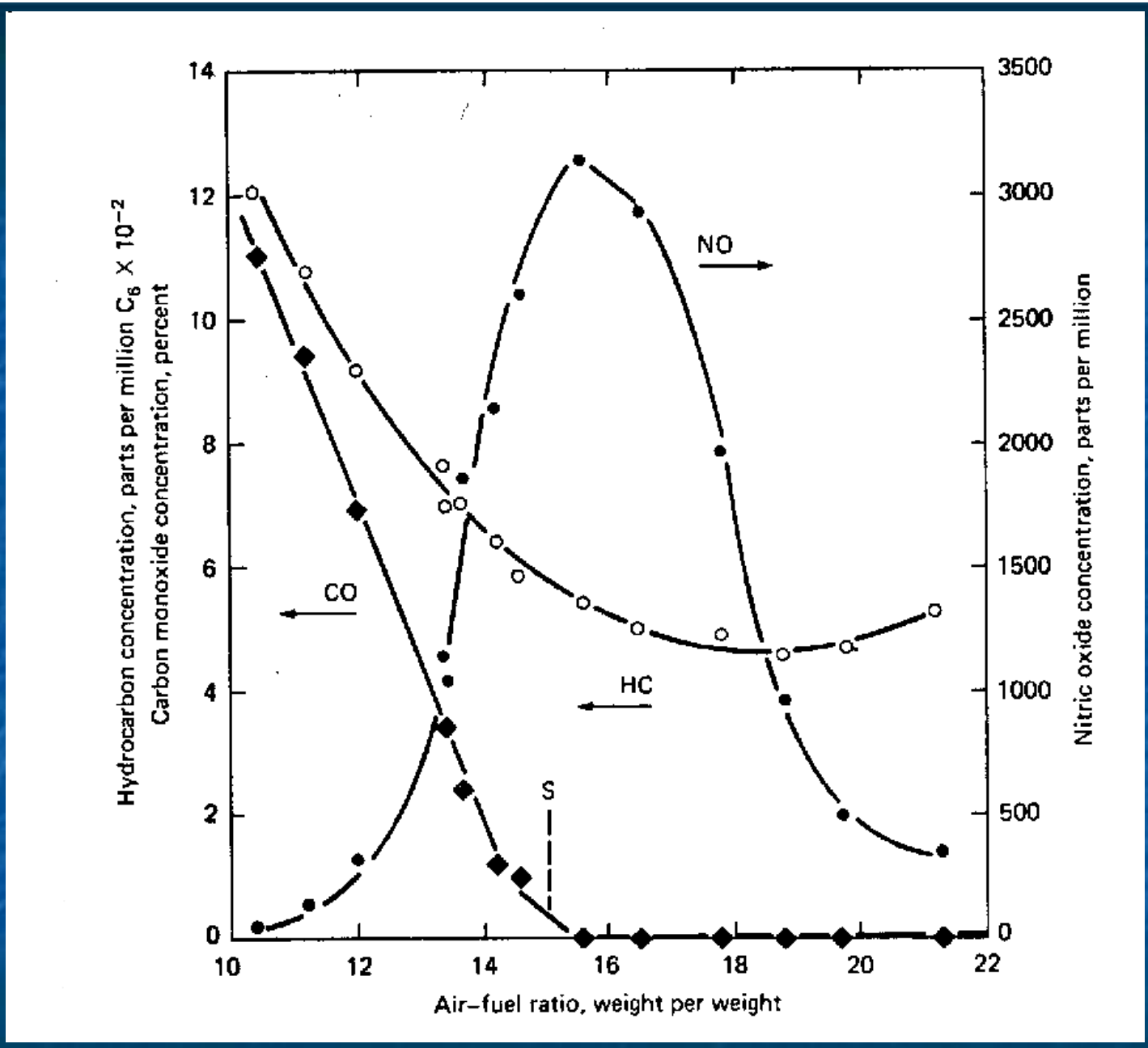
- Microalgae can exceed 80% oil content by dry weight, with 20-50% being common.
- As photosynthetic organisms, basic requirements are
  - Sunlight
  - CO_2
  - Water
  - Essential nutrients like N and P
- Much effort currently underway on design of large scale photobioreactors. Also need improvement of recovery of oil from biomass.
- Oil content somewhat different from vegetable oils (more polyunsaturated fatty acids).

Algae as Oil Source

- Great advantage of microalgae is that it doesn't require arable land or potable water.
- Potentially could replace U.S. petroleum diesel with 2-4% of existing cropland.
- Only real option for replacing significant percentage of existing diesel fuel.

Effect of Biodiesel on Air Pollution

- Primary pollutants emitted from engines
  - HC (VOCs)
  - CO
  - NO
  - PM
  - SO_2
- Air/Fuel ratio in combustion chamber plays critical role.



K. Wark, et al, 1998, Air Pollution: Its Origin and Control, 3rd Ed.

NOx

- Don't need N in the fuel to form NO.
- "Combustion NOx" is formed from reaction of N_2 and O_2 in air.

$$N_2 + O_2 + ht \rightleftharpoons 2\,NO \qquad \Delta H^o = +180\ kJ$$

$$\Delta G^o = +173\ kJ$$

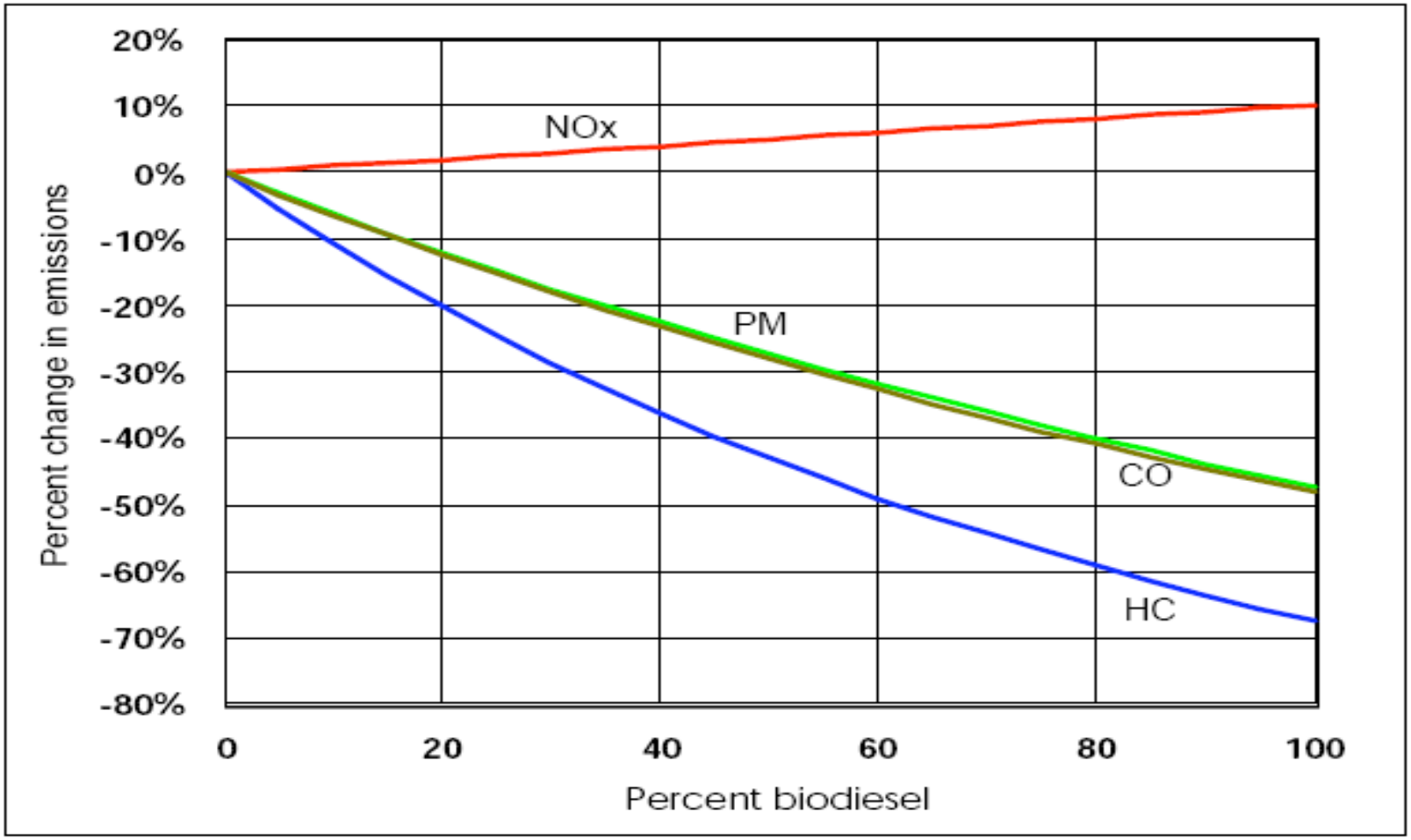
Higher temperatures favor formation of NO

- Once temperature drops, NO could dissociate back to N_2 and O_2, but this reaction is slow.
- Instead what happens is that NO reacts with O_2 to produce NO_2. The sum of NO and NO_2 is called NOx.

$$2\,NO + O_2 \rightarrow 2\,NO_2 \qquad \Delta H = -113\ kJ$$

Biodiesel and Emissions

Figure ES-A
Average emission impacts of biodiesel for heavy-duty highway engines



http://www.epa.gov/otaq/models/analysis/biodsl/p02001.pdf

Emissions

- Extent of changes in emissions depends upon percentage of biodiesel in fuel.
- For 20% blend

Table ES-A
Emission impacts of 20 vol% biodiesel
for soybean-based biodiesel added to an average base fuel

	Percent change in emissions
NOx	+ 2.0 %
PM	- 10.1 %
HC	- 21.1 %
CO	-11.0 %

http://www.epa.gov/otaq/models/analysis/biodsl/p02001.pdf

Biodiesel Energy Content

- Biodiesel reduces fuel economy of 1-2% for a 20% blend. Slightly more reduction for animal based biodiesel.

Table IV.A.2.a-3.
Difference in energy content between biodiesel and conventional diesel fuel

Conventional diesel	129,500 Btu/gal
Animal-based biodiesel	115,720 Btu/gal
Percent difference	-10.6 %

Conventional diesel	129,500 Btu/gal
Plant-based biodiesel	119,216 Btu/gal
Percent difference	-7.9 %

Table IV.A.2.b-1
Fuel economy impacts of biodiesel use

	% reduction in miles/gallon
20% biodiesel	0.9 - 2.1
100% biodiesel	4.6 - 10.6

http://www.epa.gov/otaq/models/analysis/biodsl/p02001.pdf

Conclusions

- Biodiesel is a proven substitute for petroleum diesel in existing engines.
- Almost all current biodiesel is produced from virgin oils. Cost of raw material and potential impact on food costs and land use are major factors.
- Waste oils have potential to substantially reduce costs of biodiesel, but there is limited capacity. There are ancillary environmental benefits from redirecting waste.
- Substantial technical problems exist in converting waste oil into FAME.

Conclusions

- Microalgae could be a renewable source of biodiesel without compromising arable land and potable water.
- Biodiesel slightly reduces fuel economy compared to petroleum diesel.
- Emissions of CO, SO_2, HC, and PM are substantially reduced with biodiesel. Emissions of NO increase slightly.