



Oleochemicals in the Biorefinery: Glycerol and Co-Products from Biodiesel Production

***2008 Transition to a Bioeconomy
Integration of Agricultural and Energy Systems***

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Overview

- *The oleochemical operating unit* - a component of the biorefinery
- *Biodiesel* - what are the challenges and the possible impact?
- *Glycerol* - what do we do with it?

The Oleochemical Operating Unit

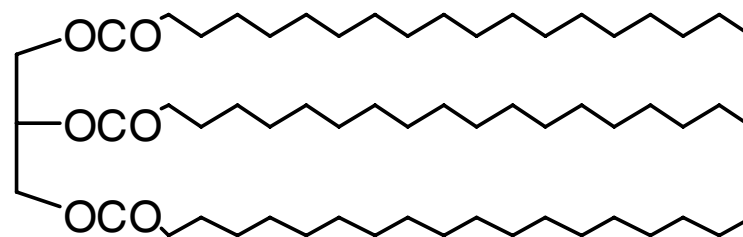
Oil
crops



Triglycerides

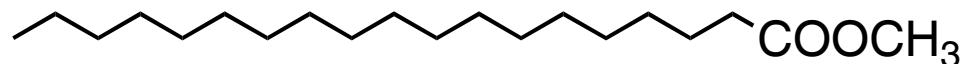
"oils and fats"
"plant oils"

Soy, sunflower
castor, tallow,
canola, algae...

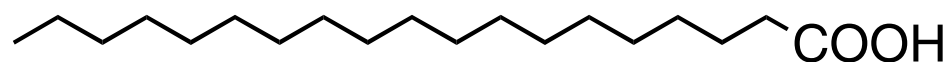


+ plant residue: meal and protein

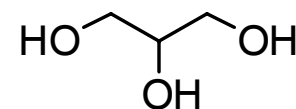
Biodiesel



Fatty acids



Glycerol



2007: 450-500 x10⁶ gal biodiesel produced (NBB)
1998: 101x10⁶ tonnes of fats and oils produced worldwide
14x10⁶ tonnes used by chemical industry; remainder for
food uses (*Pure Appl. Chem.*; 2000, 72, 1255)

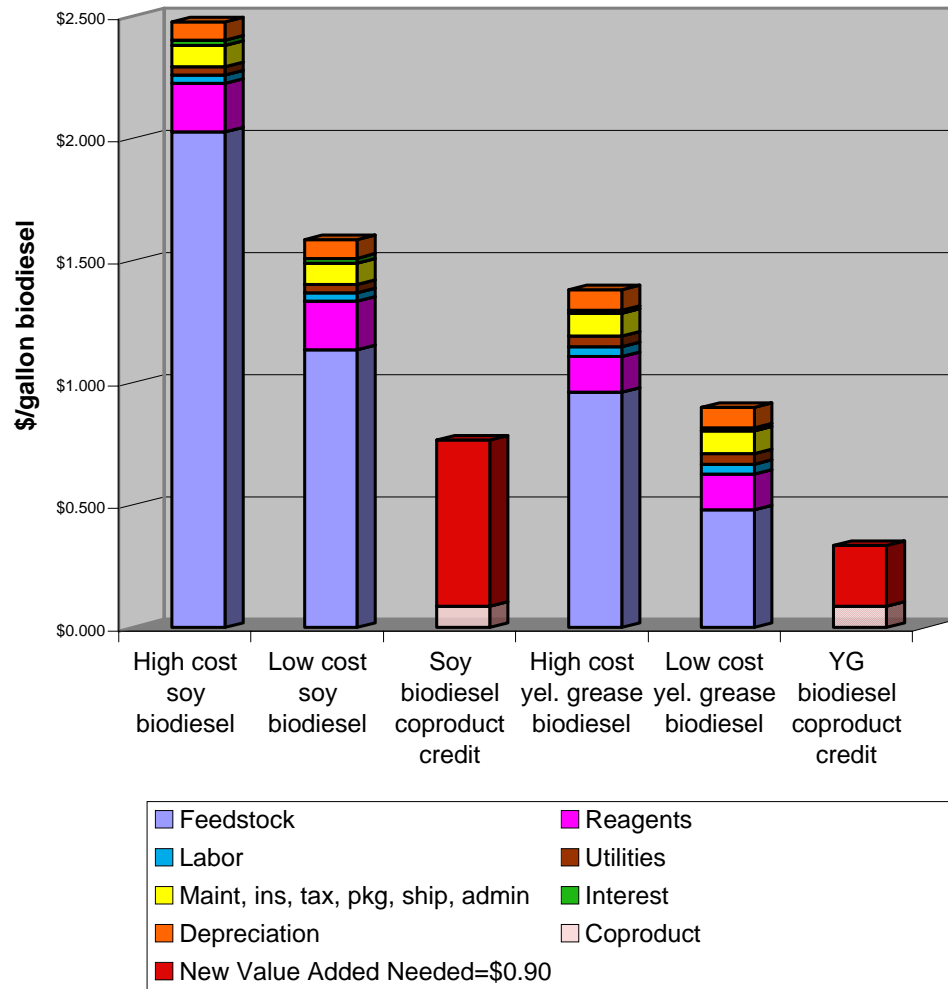
Feedstock Supply Potential for Biodiesel

- *Total* available ~ 10% of U. S. diesel demand. (recent report: soy oil ~ 6% of diesel demand; *Proc. Nat. Acad. Sci.* **2006**, 103, 11206)
- Competition with food impacts supply
- An impact can be made. Is it a significant impact?

Feedstock	Total US Production MM gal/yr 2001	Supply for Biodiesel MM gal/y 2001
Soy	2,432	283
Corn	331	115
Canola	87	0
Sunflower	113	65
Safflower	11	0
Peanut	29	0
Cottonseed	131	18
Tall Oils	171	0
Lard	137	21
Edible Tallow	240	170
Inedible Tallow	487	258
Yellow Grease	412	167
Other Greases	52	52
Trap Greases	495	495
Total	5,128	1,644

Source: Tyson, Shaine K., August 2002. Draft Report "Feedstocks for Biodiesel Production", Submitted to OBP; Original data source: USDA, October 2001, *Oil Crops Situation and Outlook Yearbook*; USDA, *Agricultural Statistics*, 2001; U.S. Census Aug 8, 2001; Render, April 2002.

Biodiesel Production Costs

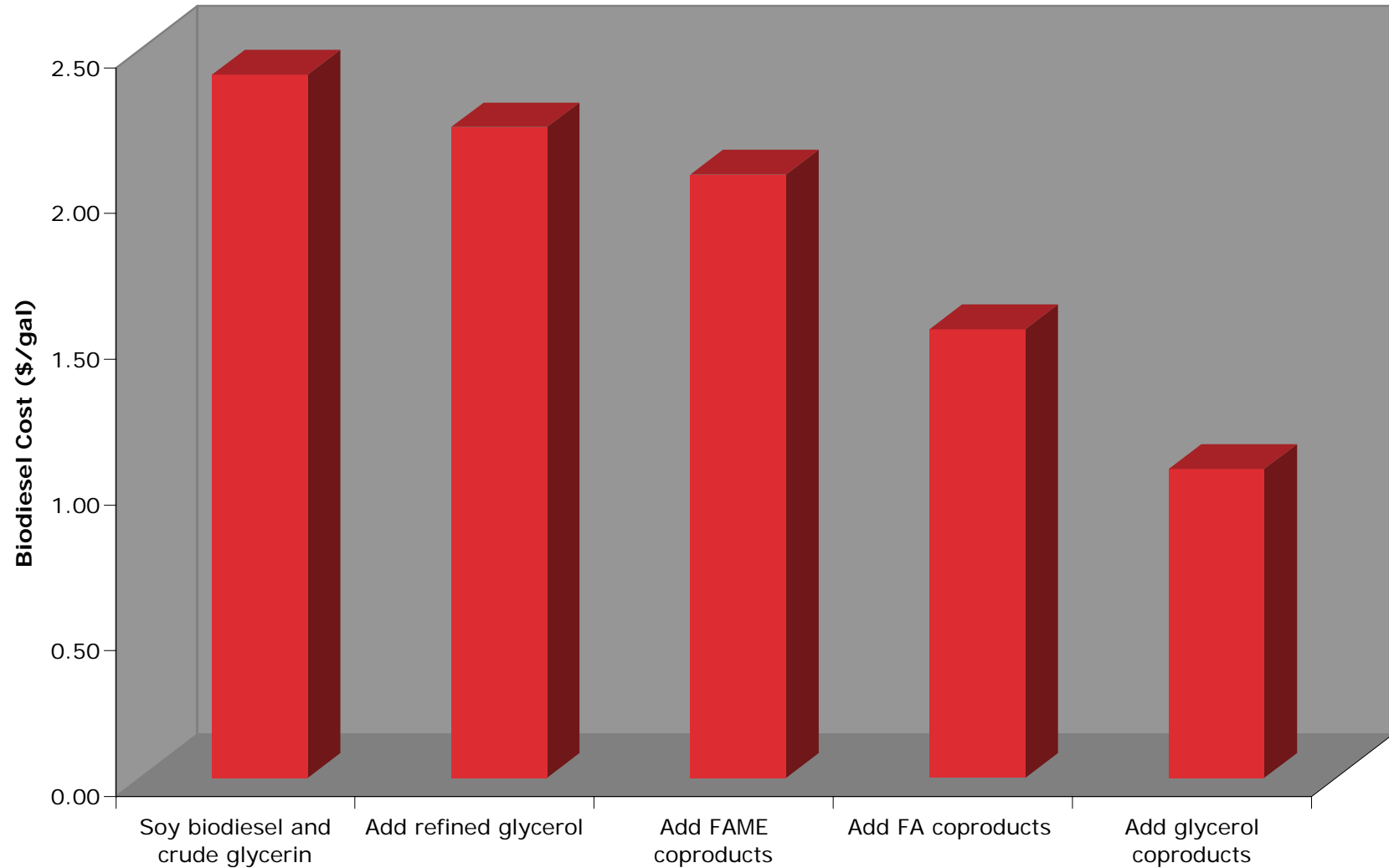


- Largest cost component is feedstock (*7.7 lb oil/gal biodiesel*)
- Coproduct credits have room to contribute
- Needed coproduct value for competitive fuel is challenging

Source: K. S. Tyson, NREL

Coproducts Drive Cost Reduction

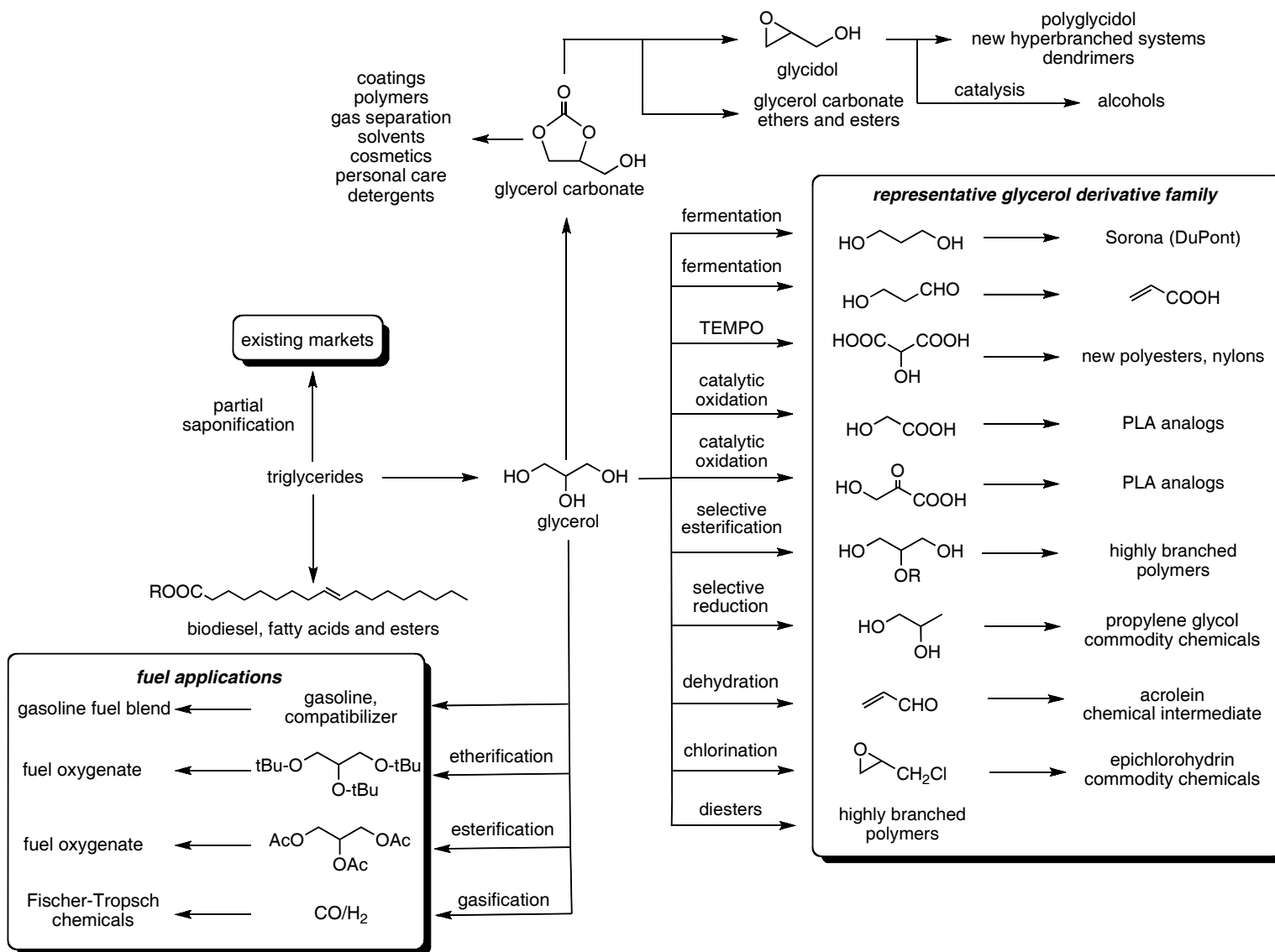
Impact of Coproducts on Biodiesel Cost



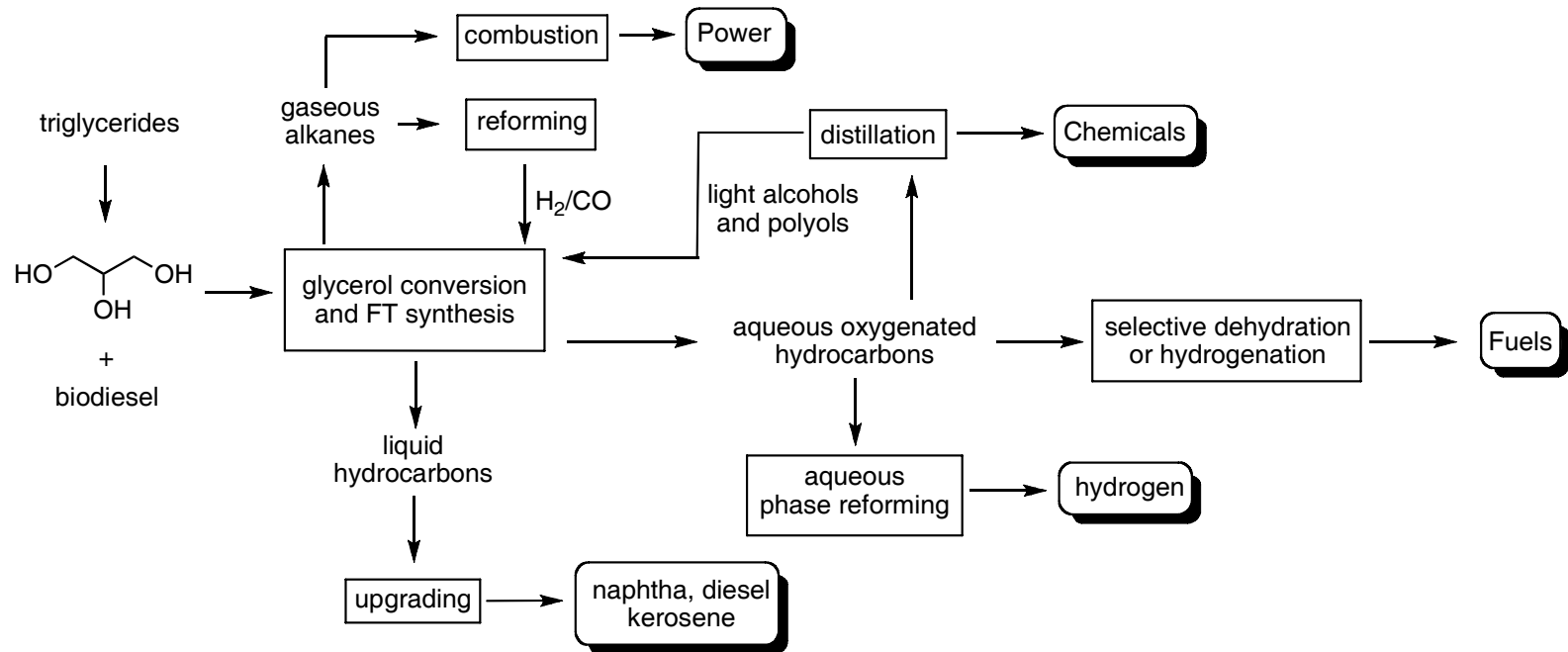
The Glycerol Potential

- Current market: $650 - 700 \times 10^3$ tonnes/yr
- Glycerol is moving from the position of “additive” to that of starting material (platform)
- Capture of 5% of diesel market will lead to availability of 1×10^6 tonnes additional glycerol
- Glycerol can serve as a model for sugar technology development
- *But:* Glycerol may be the limiting factor for the oleochemical operating unit

Glycerol Product Family Possibilities

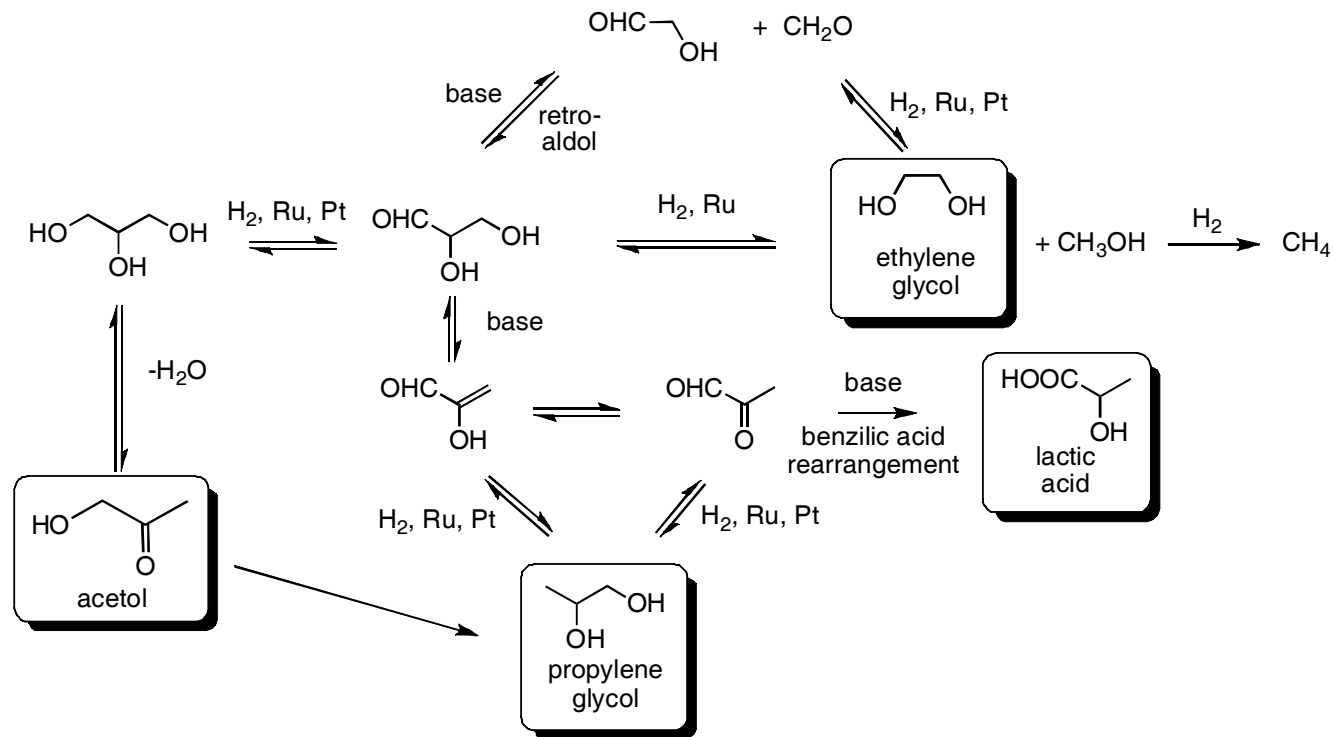


Glycerol Fuel Applications



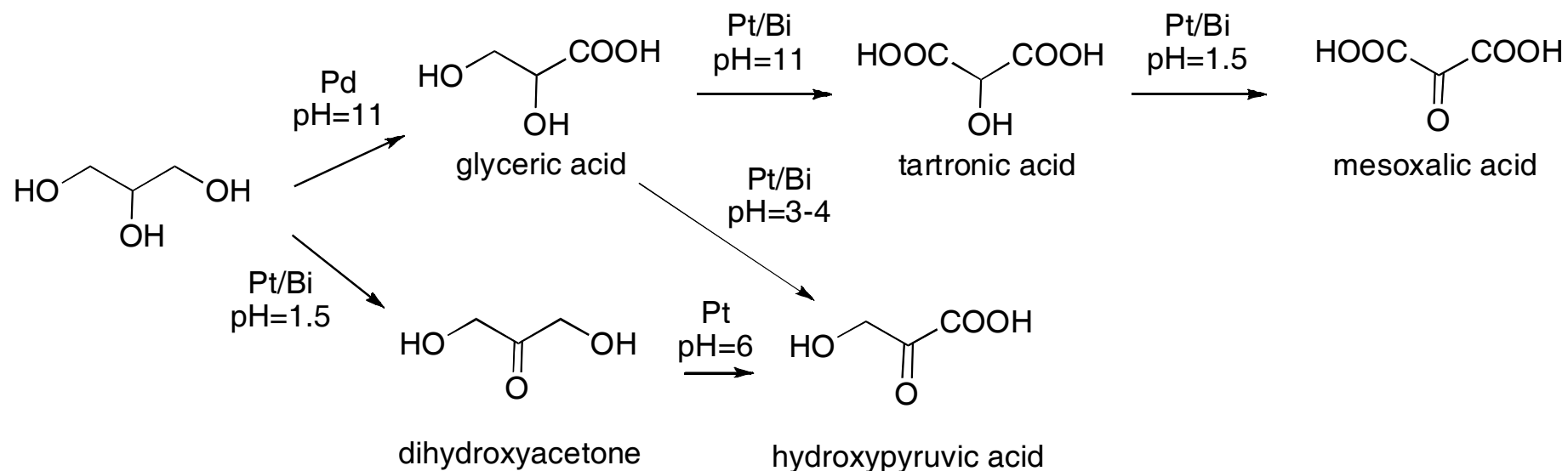
- Fischer-Tropsch synfuels
- Gas turbines
- Hydrogen for fuel cells
- Transportation fuels

Glycerol Reduction Processes



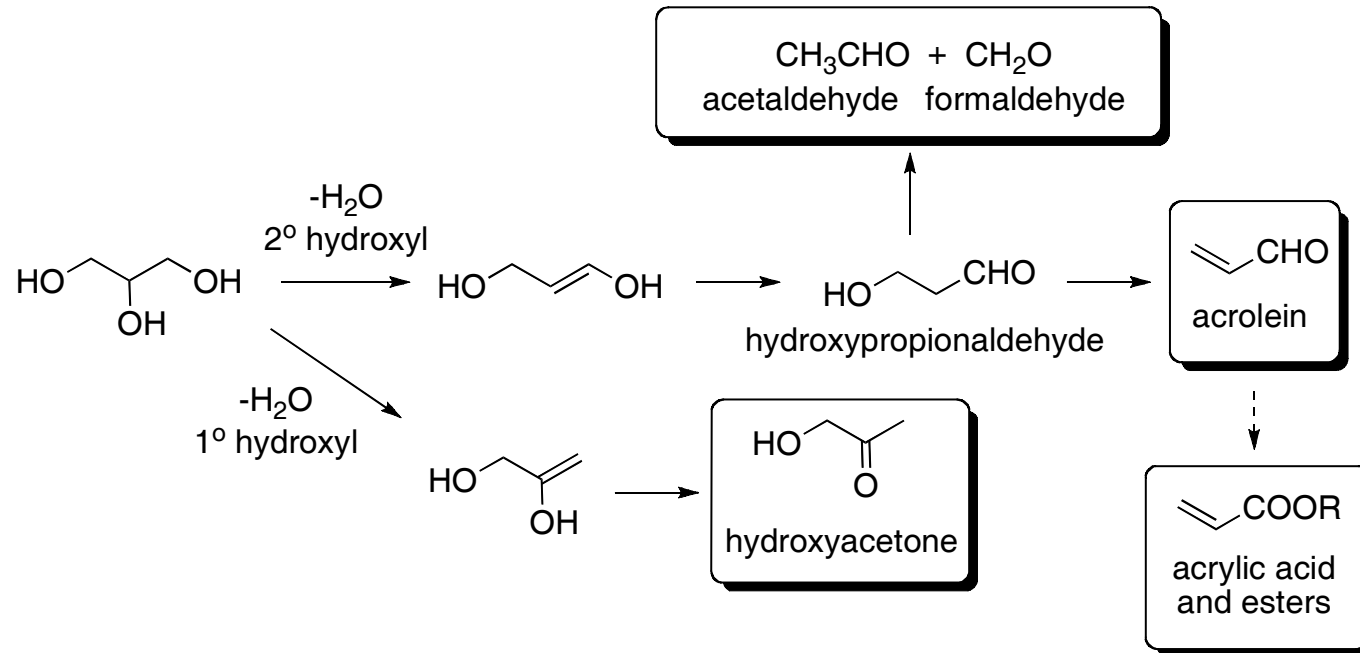
- Antifreeze
- Biobased and conventional plastics
- De-icers
- Paints and coatings

Glycerol Oxidation Processes



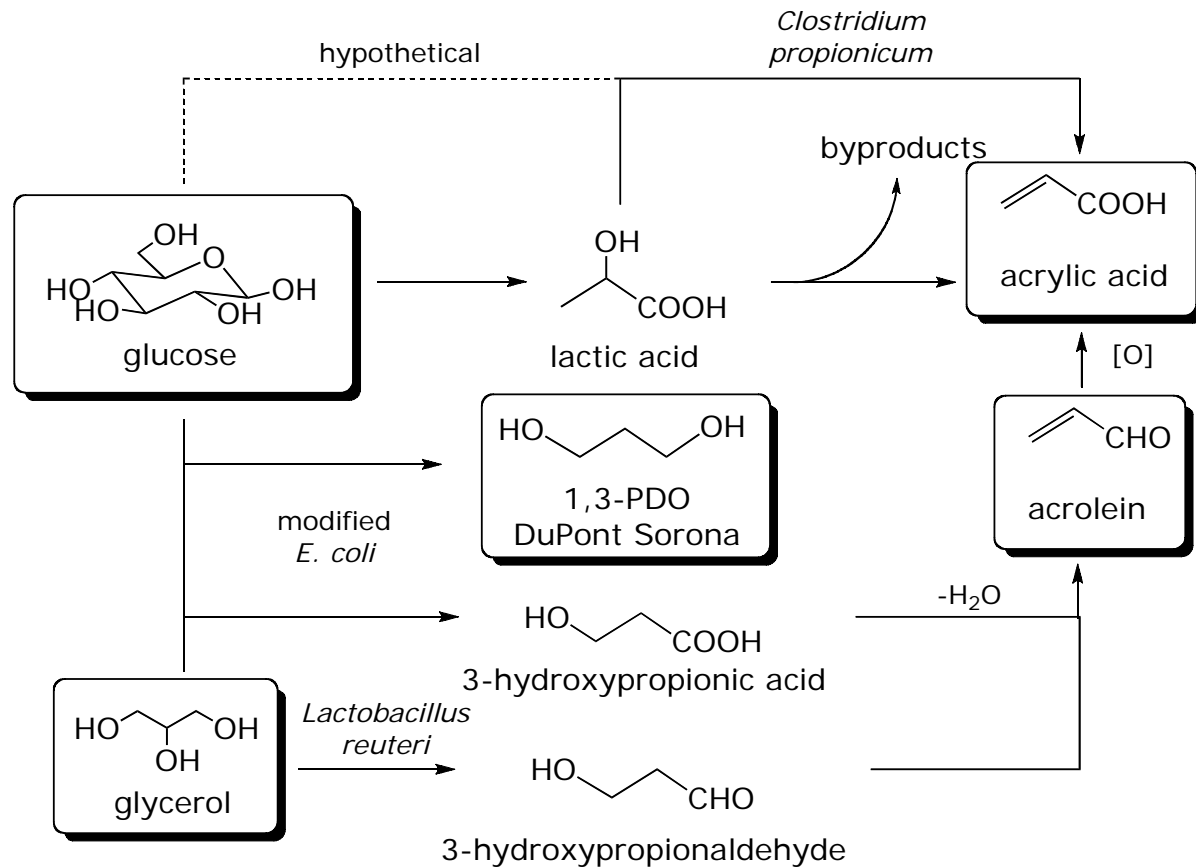
- New chemical intermediates and structures
- Specialty chemicals

Glycerol Dehydration Processes



- High volume chemical intermediates
- Plastics, polymers
- Coatings
- Adsorbents

Biochemical Conversions of Glycerol



- High volume commodities
- New polymers, textiles

Economic Considerations

	Cost/lb (2003)	Cost /lb (current)	% change, 2003 - 2007	Δ propylene	Δ purified glycerol (% difference from propylene)	Δ crude glycerol (% difference from propylene)
Propylene ^a	0.22	0.44	+ 100			
Crude glycerine ^b	0.24	0.05	- 80			
Purified glycerol ^c	0.72	0.25	- 65			
Acrolein/acrylic acid ^a		1.17		0.73	0.92 (+26%)	1.12 (+53%)
Epichlorohydrin ^a		0.97		0.54	0.72 (+33%)	0.92 (+70%)
Propylene glycol ^a		1.05 ^d		0.61	0.80 (+29%)	1.00 (+ 61%)

a) Chemical Economics Handbook;

b) DOE Top 10 Report on Chemicals from Biomass;

c) *Curr. Opin. Biotech.* **2007**, 18, 213, oleochemical industry representatives;

d) list price for industrial grade propylene glycol; USP grade is 0.71/lb

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Derivative Production Potential

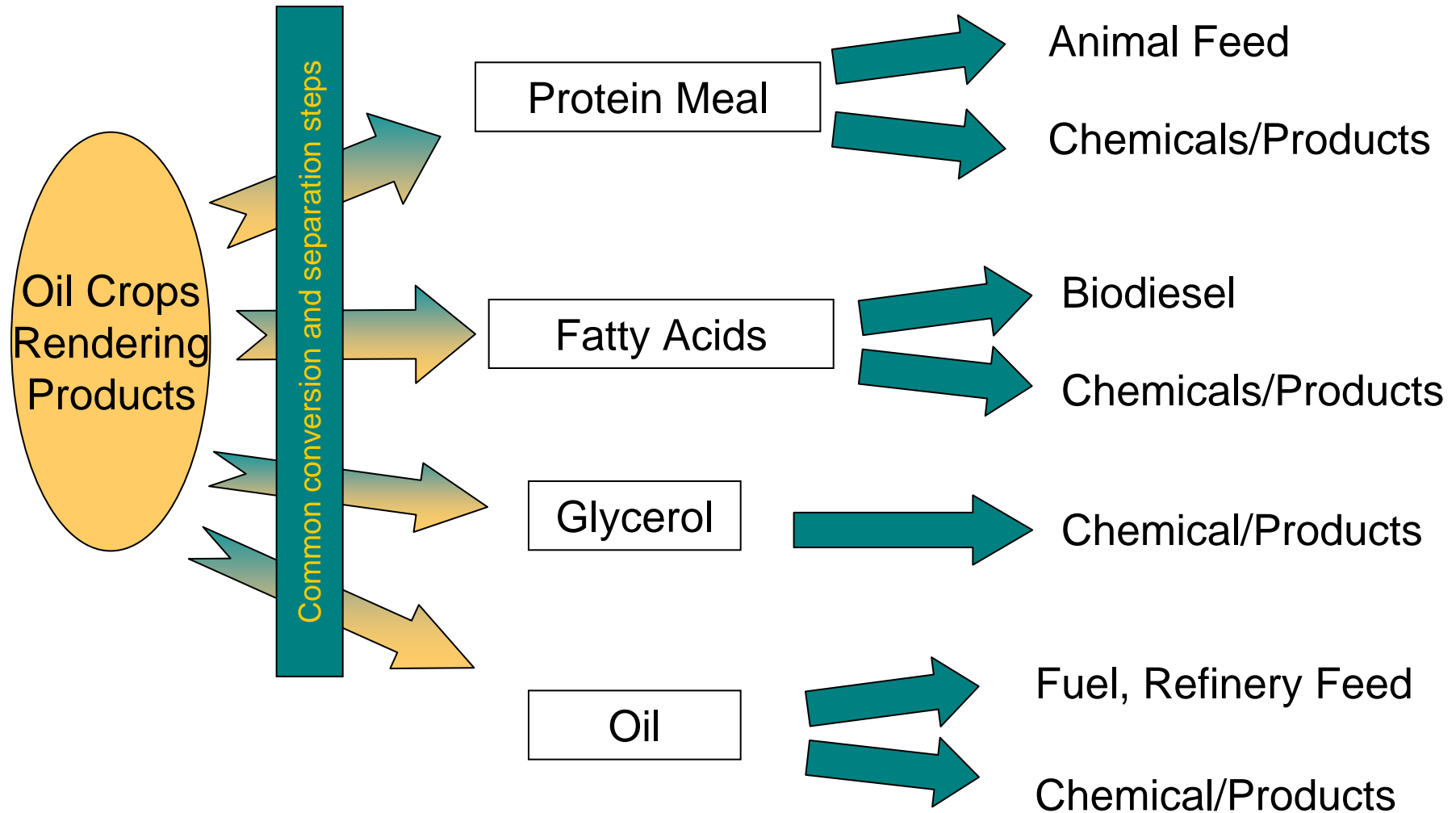
Chemical	Potential available (lb)	Current market (lb)
Glycerol ^a	4.1×10^9	288×10^6 (2004)
Propylene glycol	3.4×10^9	1.17×10^9
Acrolein/acrylic acid	2.5×10^9 (acrolein) 3.2×10^9 (acrylic acid)	2.6×10^9 (acrylic acid)
Epichlorohydrin	4.1×10^9	0.78×10^9

a) Available glycerol calculated assuming a biodiesel industry producing 5×10^9 gal/yr

Summary

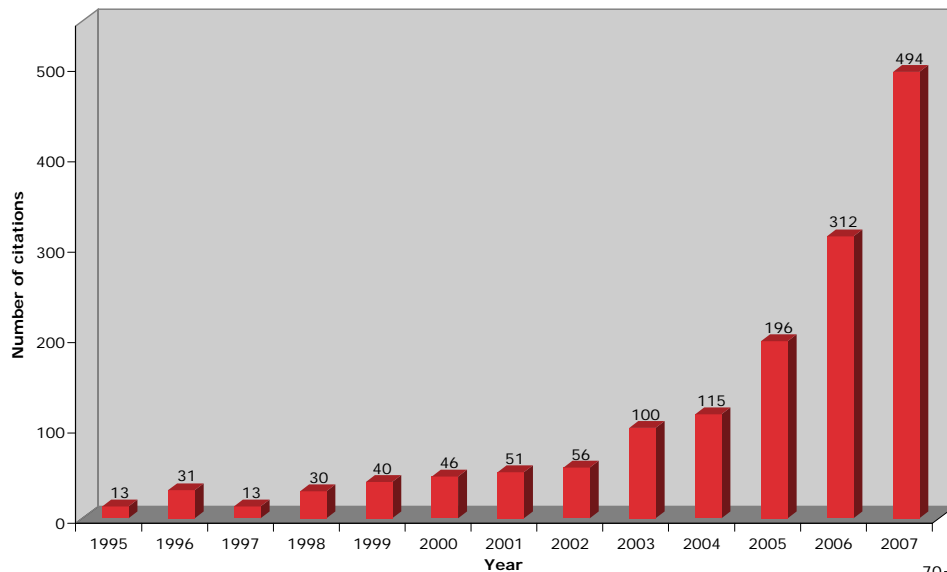
- Oleochemicals are a key component of the integrated biorefinery concept
- Oleochemicals could be the best initial bridge between the biorefinery and the petrochemical refinery
- Integrating biodiesel production with production of chemicals provides an economically attractive process approach
- New uses for glycerol will help drive greater biodiesel production

An Integrated Oleochemical Operating Unit



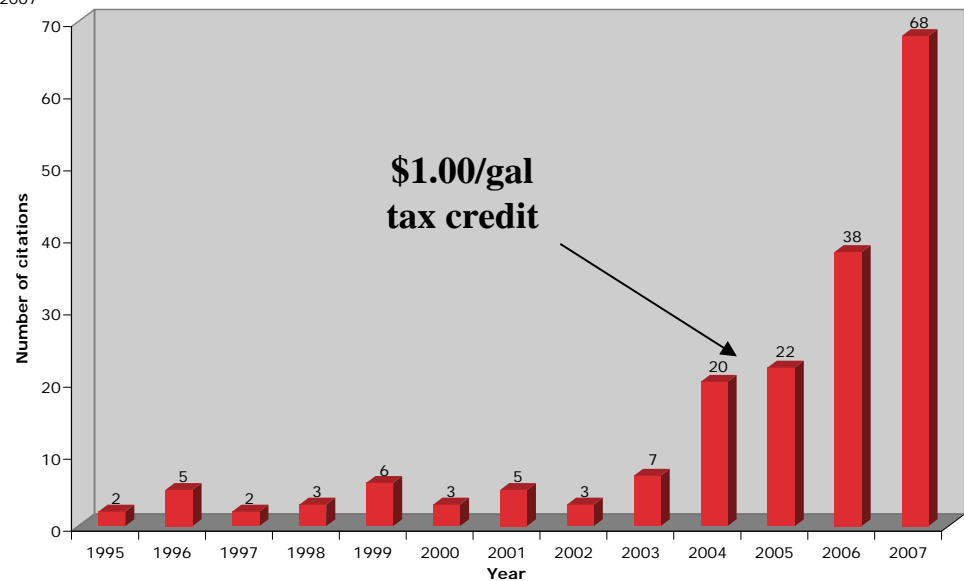
Research Interest in Biodiesel and Glycerol is Booming

Number of WOS citations: biodies*



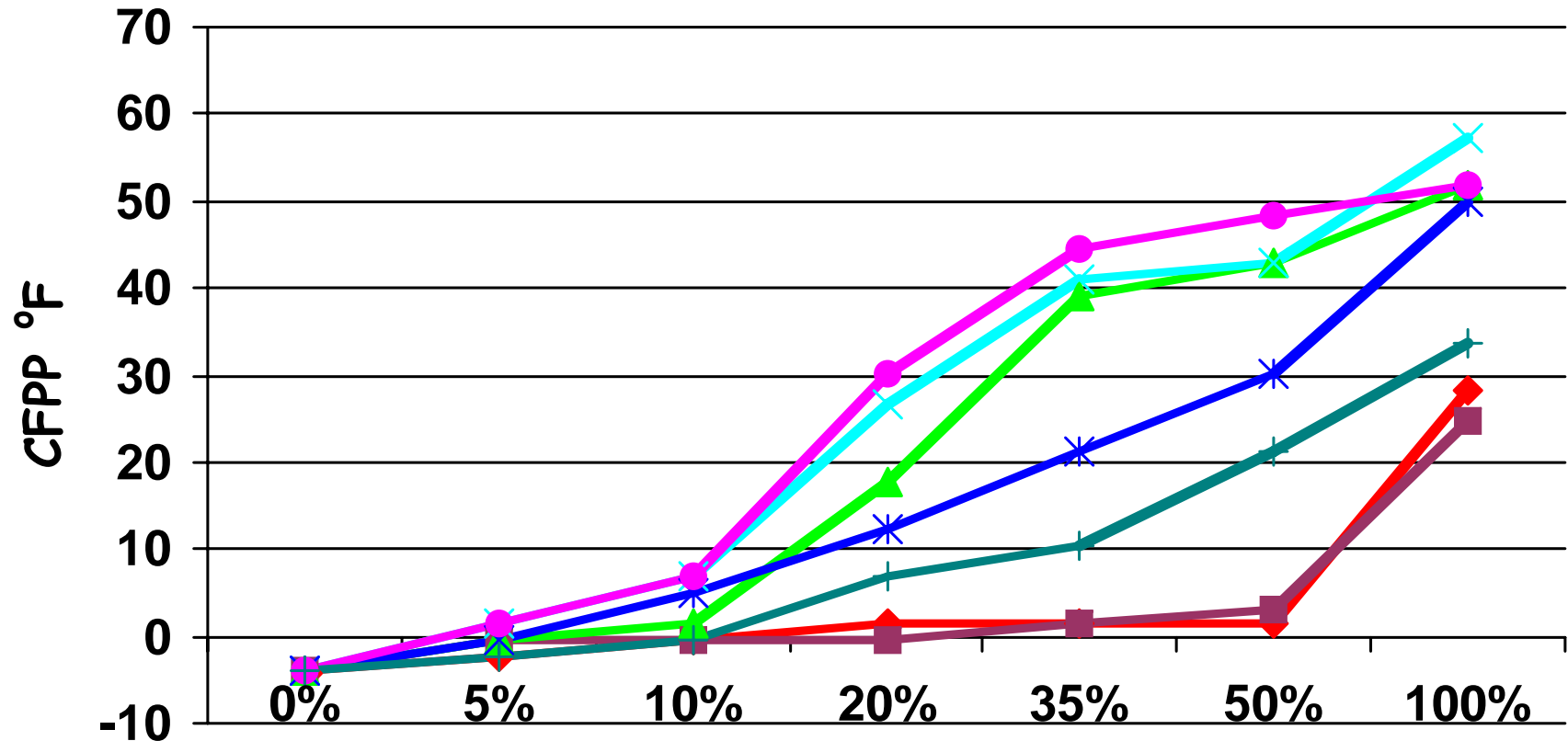
Biodiesel citations

Number of WOS citations - (glycerin* OR glycerol*) AND biodies*



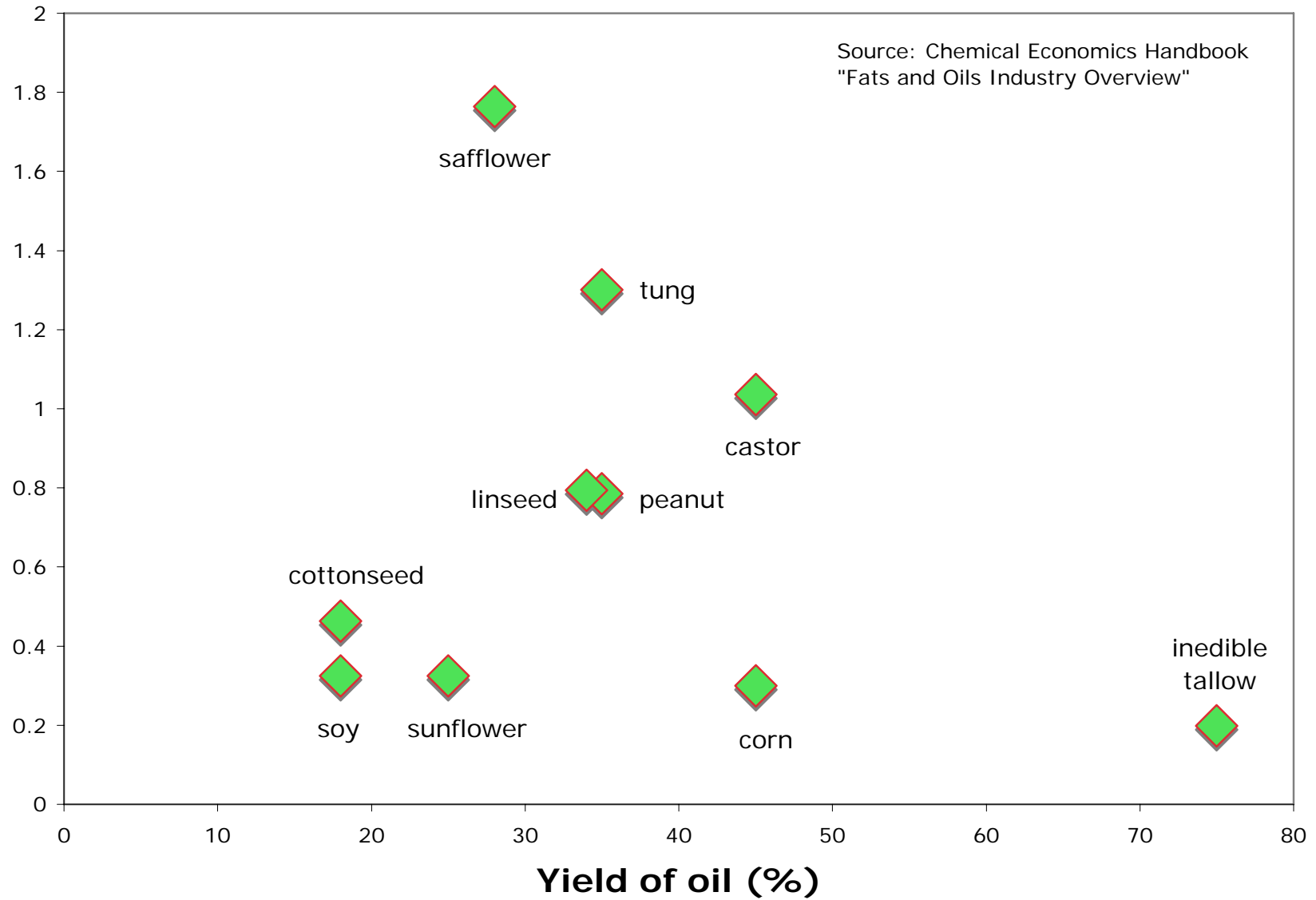
Glycerol citations

Cold Flow Limits Use of Fats and Greases

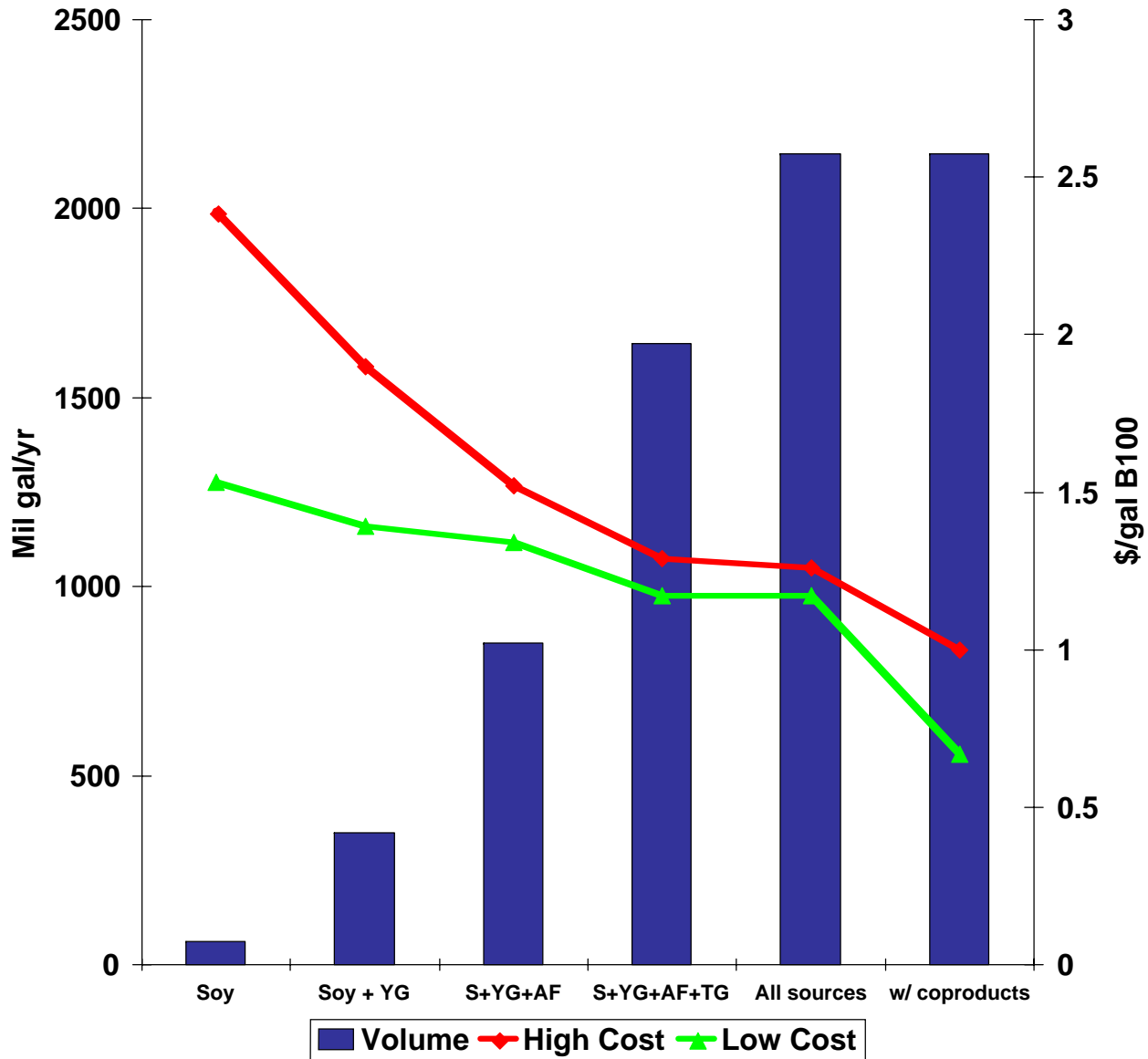


◆ Soy ■ Canola ▲ Lard ✕ Ed. Tallow * ined. Tallow ● YG #1 + YG #2

Oil Prices and Yield



Market Scenarios



Source: K. S. Tyson, NREL

Consumption of New Glycerol Supplies

- Existing markets?
 - New glycerol from “small” biodiesel effort in Europe consumed by existing market
 - No blockbuster markets for glycerol; typical for exhibited price point
 - Growing competition from SE Asia: est. 200×10^3 tonnes of capacity

Consumption of New Glycerol Supplies

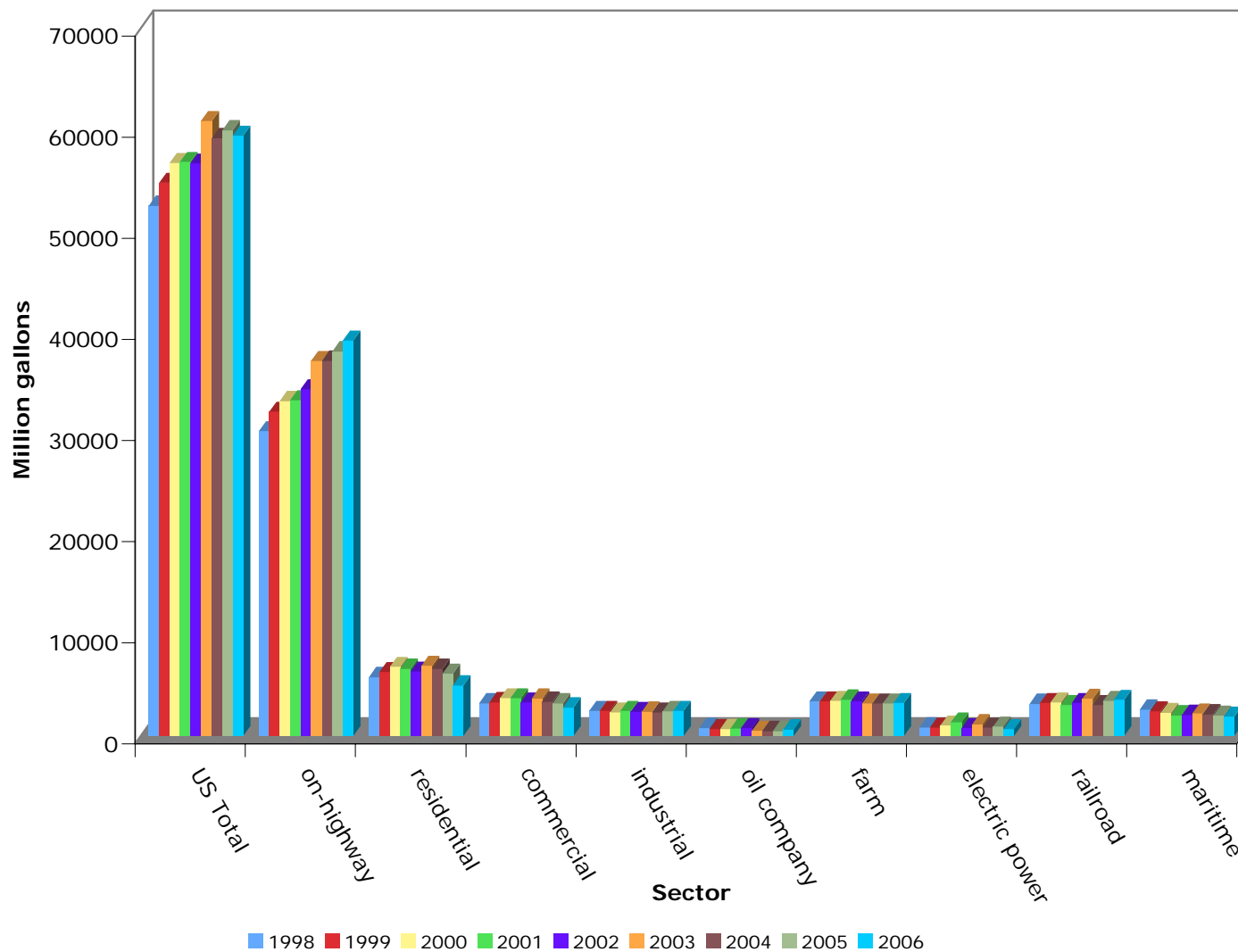
- Recovery of previous markets, capture of new market segments
 - Example: alkyd resins, market size 1691 x10⁶ lb in 2000

<i>Polyol</i>	<i>USD / ton</i>
<i>Glycerol</i>	1200 - 1600
<i>Trimethylol propane</i>	1,278
<i>Pentaerythritol</i>	1,278
<i>Propylene glycol</i>	1,000
<i>Ethylene glycol</i>	667
<i>Sorbitol (70 %)</i>	400

Source: Claude, S. *Fett/Lipid* **1999**, 101, 101

US Consumption of Diesel, 1998-2006

US distillate consumption 1998-2006



Source: http://www.eia.doe.gov/oil_gas/petroleum/info_glance/distillate.html