Value-Added Products from Biofuels Synthesis

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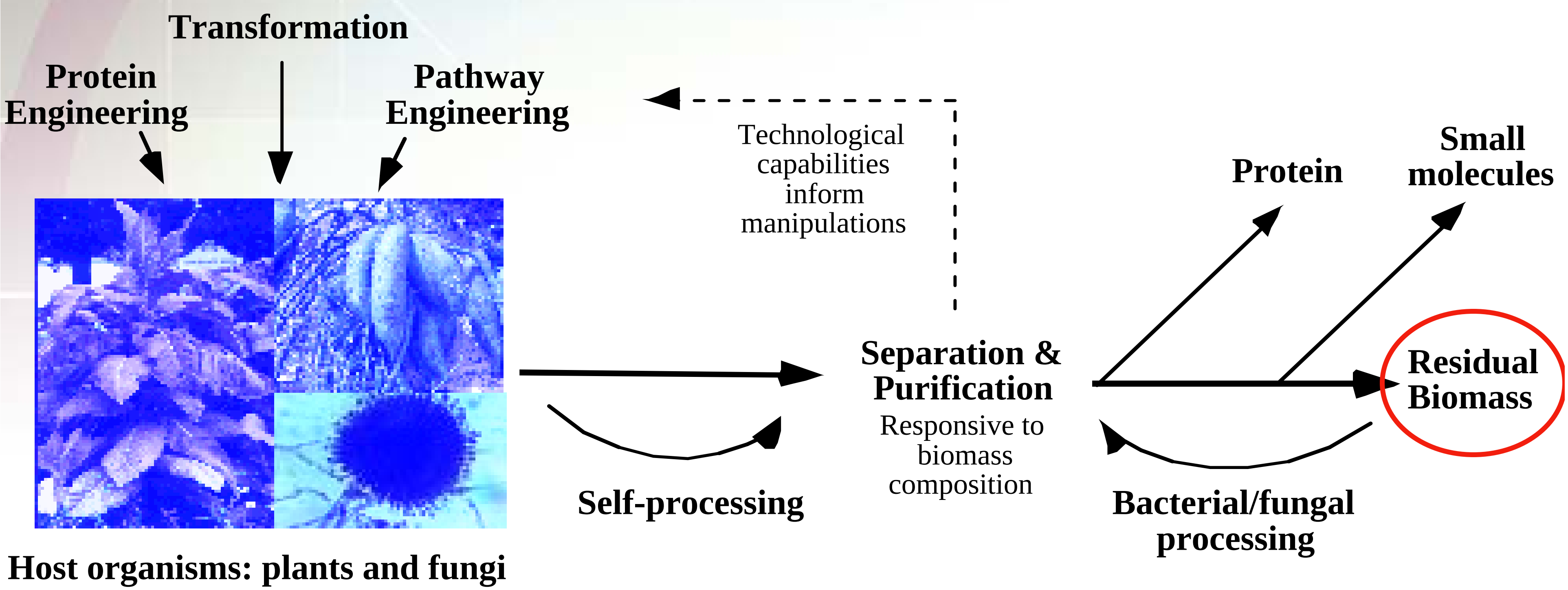
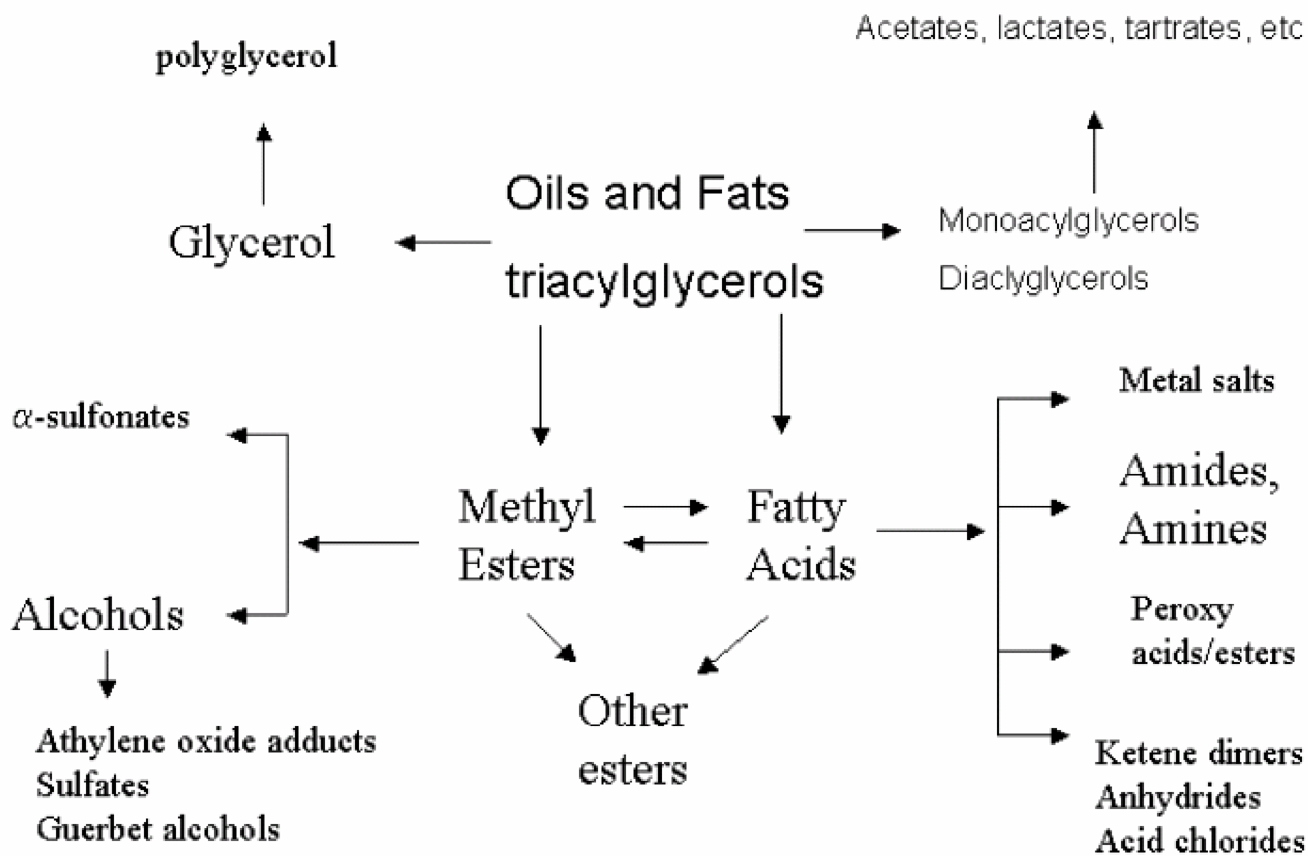
Basic philosophy



- Biofuels are not the driver, they are the passenger!

Oleochemical Plant Product Mix



Industrial sweetpotatoes

- Sweetpotato as a bio-factory
- Plant made industrial products
  - Bio-ethanol
  - High-fructose syrup
  - Bio-plastics

- Nutraceuticals
  - Vitamins
- Plant made proteins
  - Pharmaceuticals
- Other renewable bio-products
  - Purple dye

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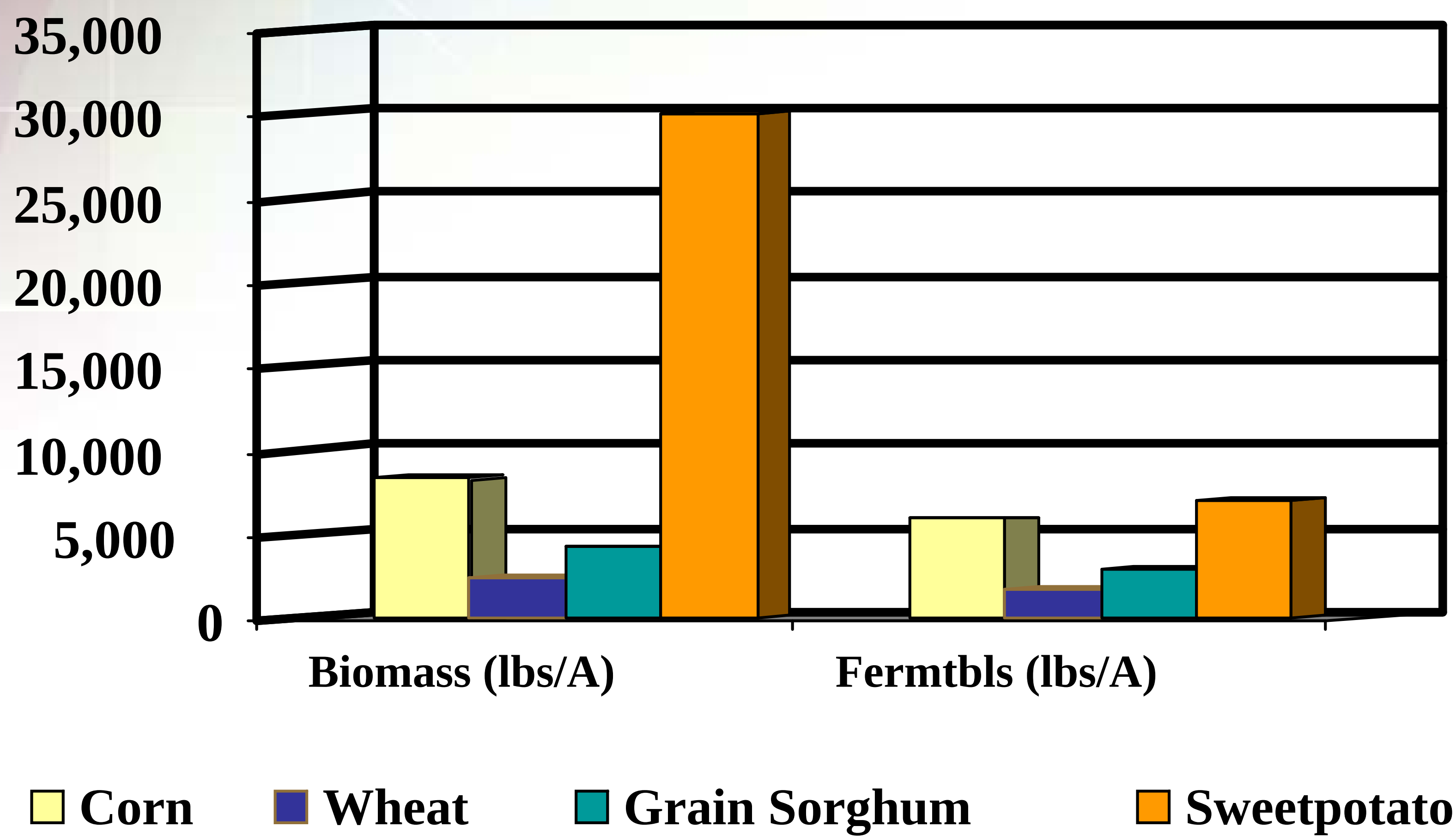
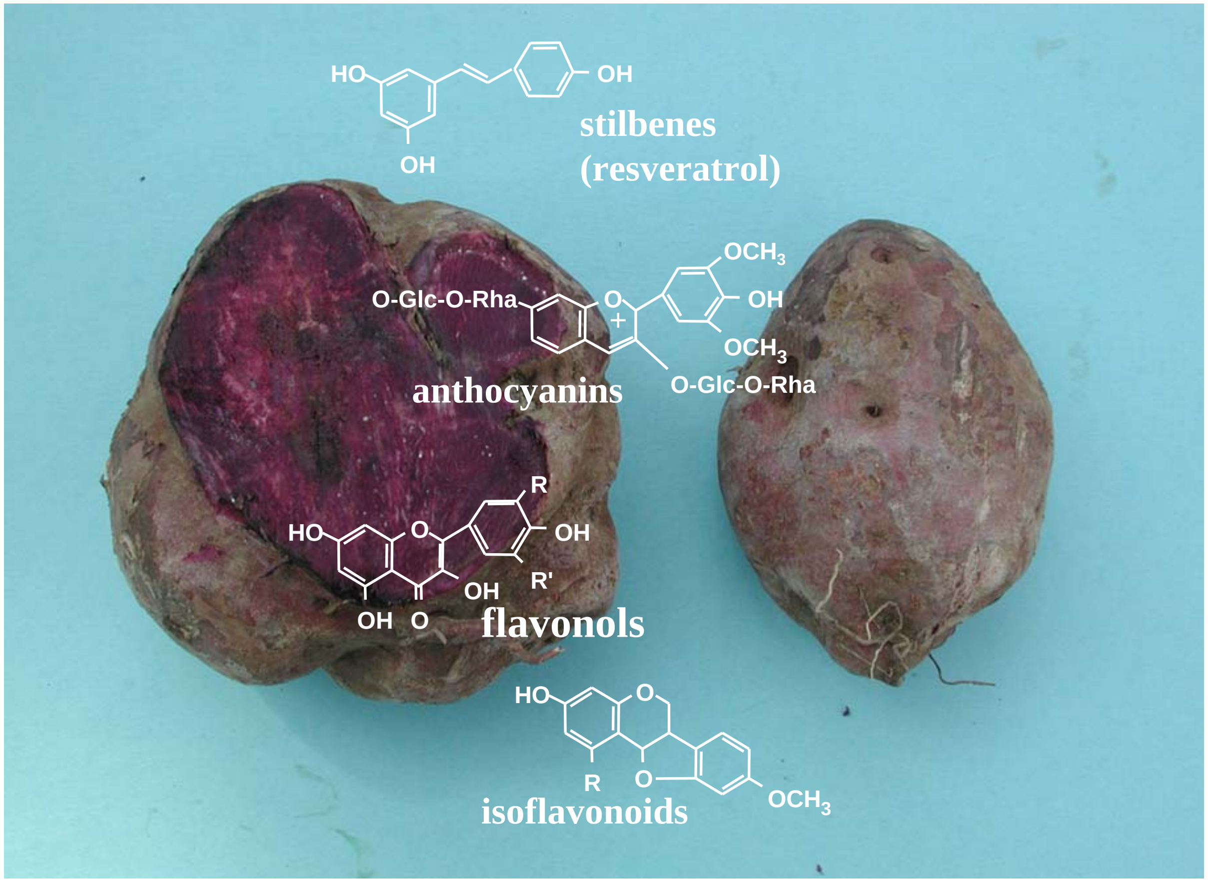
Sweetpotato Biomass Potential



Hall and Smittle. 1993. Industrial-type sweet potatoes: A renewable energy resource for Georgia. UGA Res. Rpt. 429.

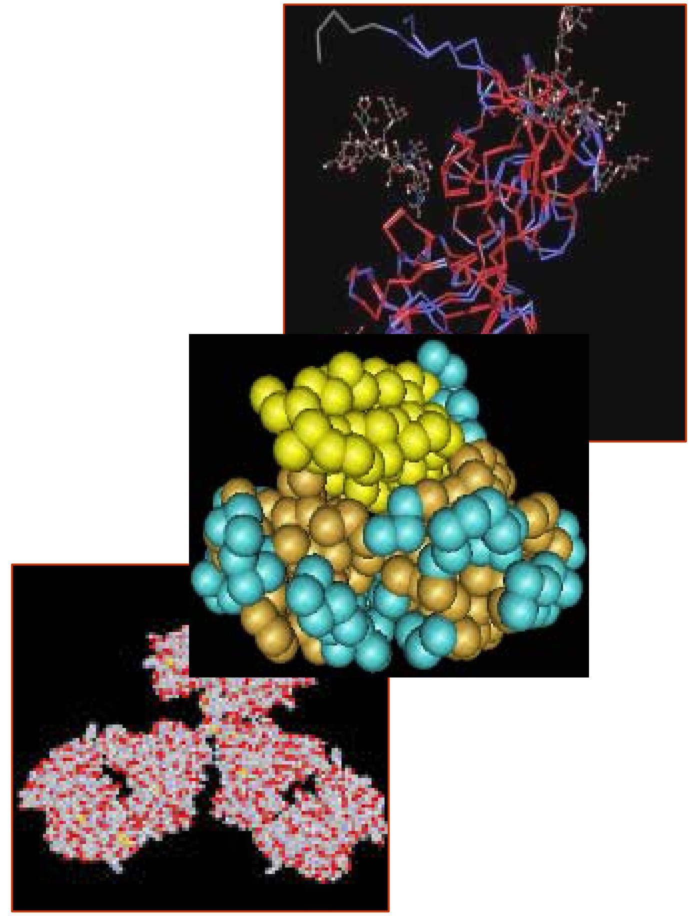
Sweetpotato anthocyanins

- Textiles
  - Bright color
  - Improved potency
- Food
  - nutraceutical
- Co-extraction
  - Proteins
  - Starch by-products
  - Ascorbic acid etc.



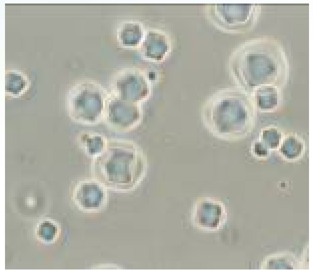
Protein Targets -- **Producing high value proteins representing "prototype" molecules and important commercial targets where plants provide a unique opportunity.**

- **Interleukins (IL-10, 12, 24)**
    - Inflammation, immunity
- **Vaccine adjuvants and antigens**
    - Infectious disease, cancer
- **Hormones (TGF-βs, insulin-like**)
    - Cancers, dermatitis
- **Tumor suppressors (TFF1)**
    - Cancers
- **Therapeutic enzymes**
    - Lysosomal storage disorders



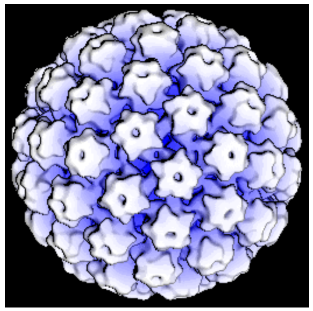
High-Value Products From Tobacco

Native proteins



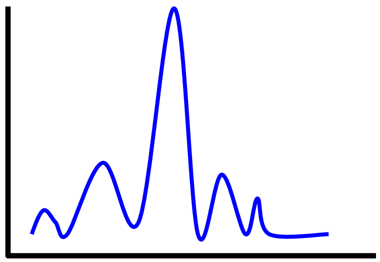
RuBisCO

Transgenic proteins



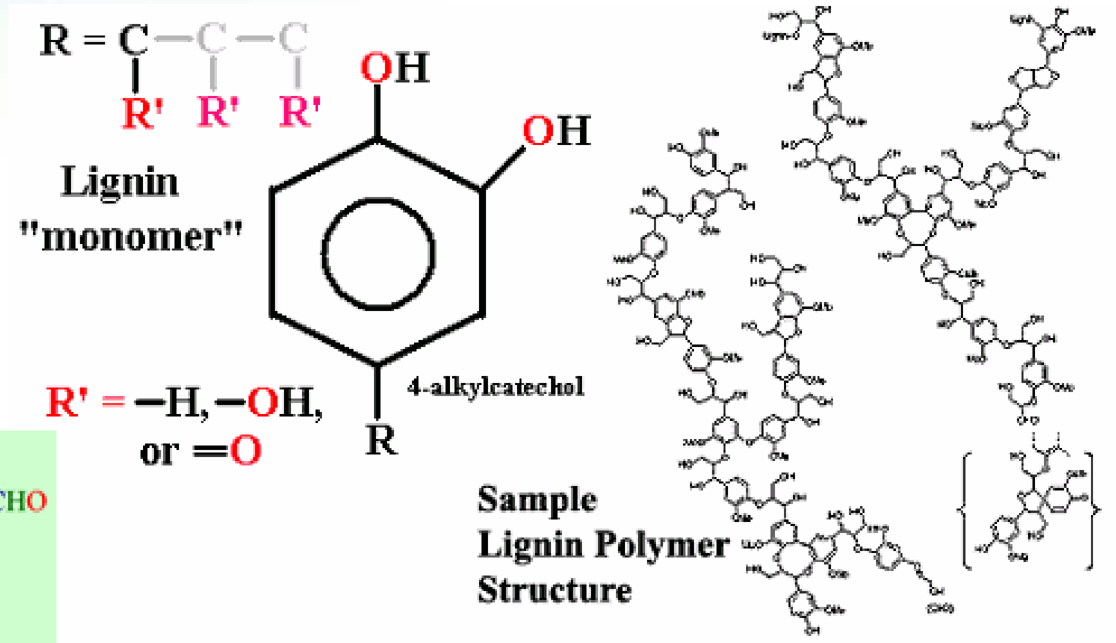
Papillomavirus Vaccines

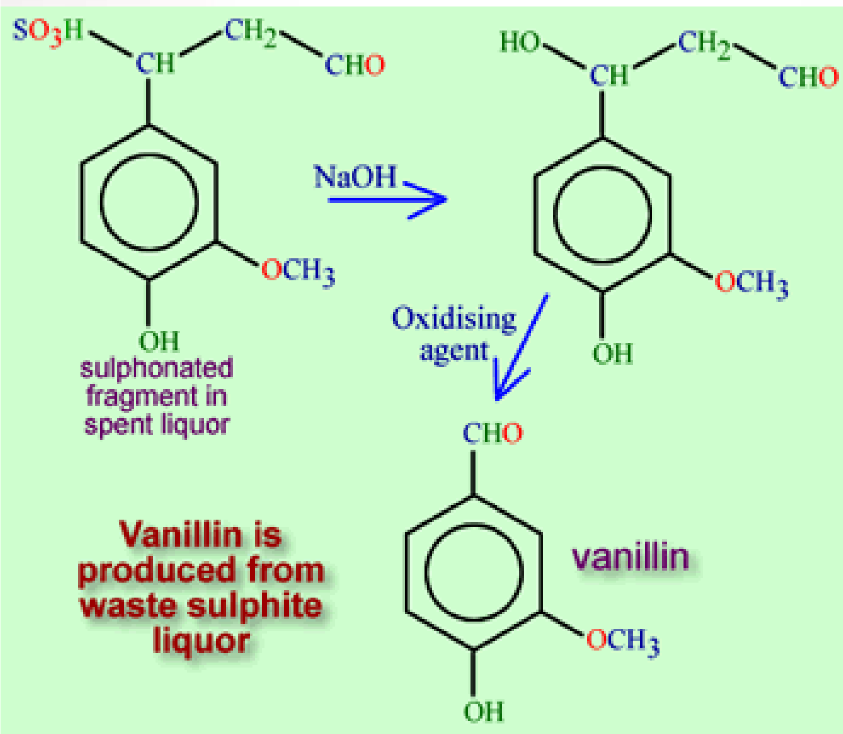
Secondary Compounds



Terpenoids
Sugar Esters
Pigments

What about lignin?





Major producers of bioproducts in the US		
Bioproduct category	Producer	Product
Starch and sugar products	ADM; Arkenol; Cargill; Cargill Dow; Cargill Corn Milling; Minnesota Corn Processors; Midwest Grain Products; DuPont; Grain Processing Company; Tate & Lyle; A.E. Staley; Williams Bio-Energy	Citric acid; Ethanol; Sorbitol; Ethyl lactate; PLA; Sugar; 1,3-propanediol; Starch
Cellulose	Dow Chemical; Celanese	Cellulose derivatives
Wood chemicals	Westvaco; Hercules; Norit America; Arizona Chemical; Georgia Pacific; Akzo Nobel Resins	Activated Carbon; Wood chemicals; Gum rosin
Oils and lipids	Cambrex; Vertec Biosolvents, Inc.; AG Environmental Products LLC; West Central Soy; Lonza	Caster oil derivatives; Soy products; Lubricants; Cleaners; Glycerin; Fatty acids

Biofuel Chemical Markets/Prices

Chemical	Uses	2003 market (M lb/yr)	Market price ($/lb)	2020 market (M lb/yr)
Lactic Acid Derivatives				
Lactic acid	Acidulant (food, drink), electroplating bath additive, mordant, textile/leather	<5 (industrial uses)	$0.70-0.85	Expect GDP-like growth
Polylactide	Film and thermoformed pkg, fiber and fiberfill	Pkg: 21,289 Fiber: 2,769	$0.30-1.50	8,000
Ethyl lactate	Solvent, chemical intermediate	8,000 – 10,000	$0.30 - 1.80	>1,000
Acrylic Acid	Acrylates (e.g., coatings, adhesives), superabsorbent polymers, detergent polymers	2,000	$0.48	Will require technology breakthrough
Propylene Glycol	Unsaturated polyester resins, antifreeze, solvent, humectant, plasticizers, hydraulic brake fluids, non-ionic detergents	1,100	$0.39-0.48	Will compete against conventional petro-based PG as well as biobased PG

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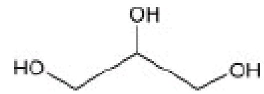
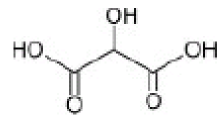
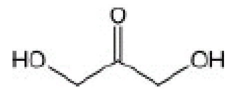
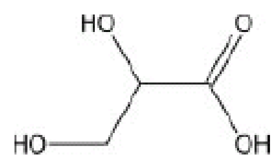
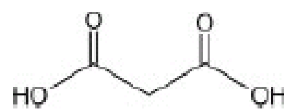
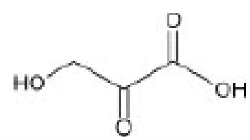
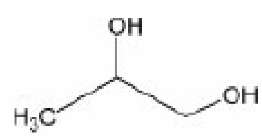
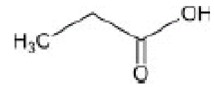
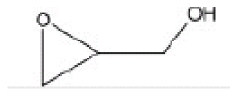
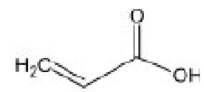
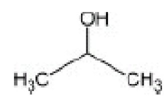
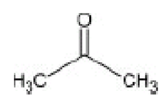
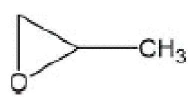
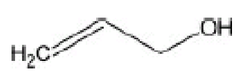
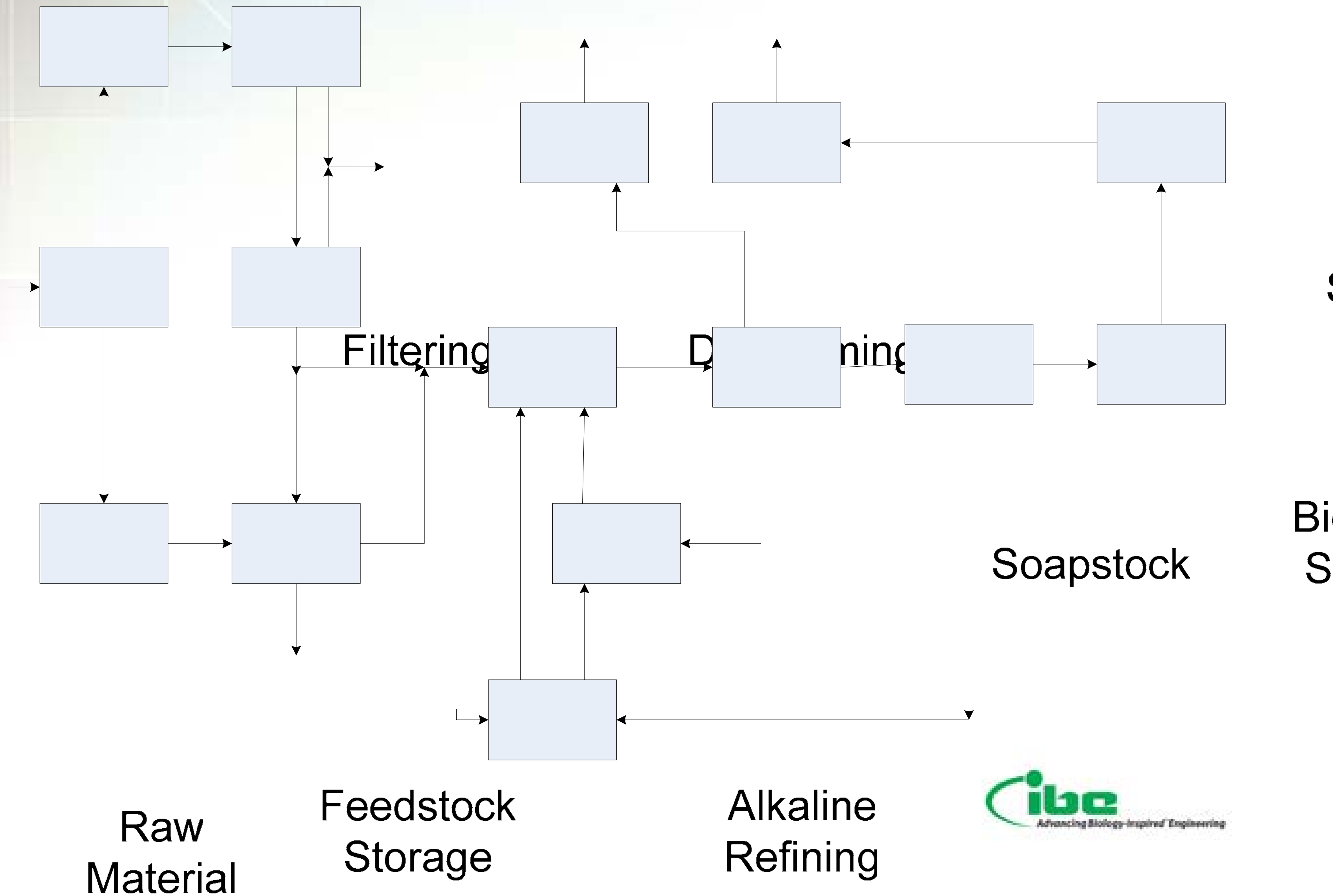
Biofuel Chemical Markets/Prices

Chemical	Uses	2003 market (M lb/yr)	Market price ($/lb)	2020 market (M lb/yr)
Succinic Acid Derivatives				
Tetrahydro furan	Solvent, printing inks, adhesives and mag tapes	255	$1.55	>50
1,4-butanediol	solvent, polybutylene terephthalate, coating resins and chemical/pharmaceutical intermediates	680	$0.65-0.90	>30
n-methyl pyrrolidone	Chemical selective synthesis solvents (paint removers, polyimide coatings,)	80	$1.35	
Bionolle 4,4 polyester	Thermoplastic polymer applications	25,000-60,000	$0.30-1.50	>4,000
Acrylonitrile	ABS polymer, SAN rubber	3,130	$0.31-0.37	Technology developing

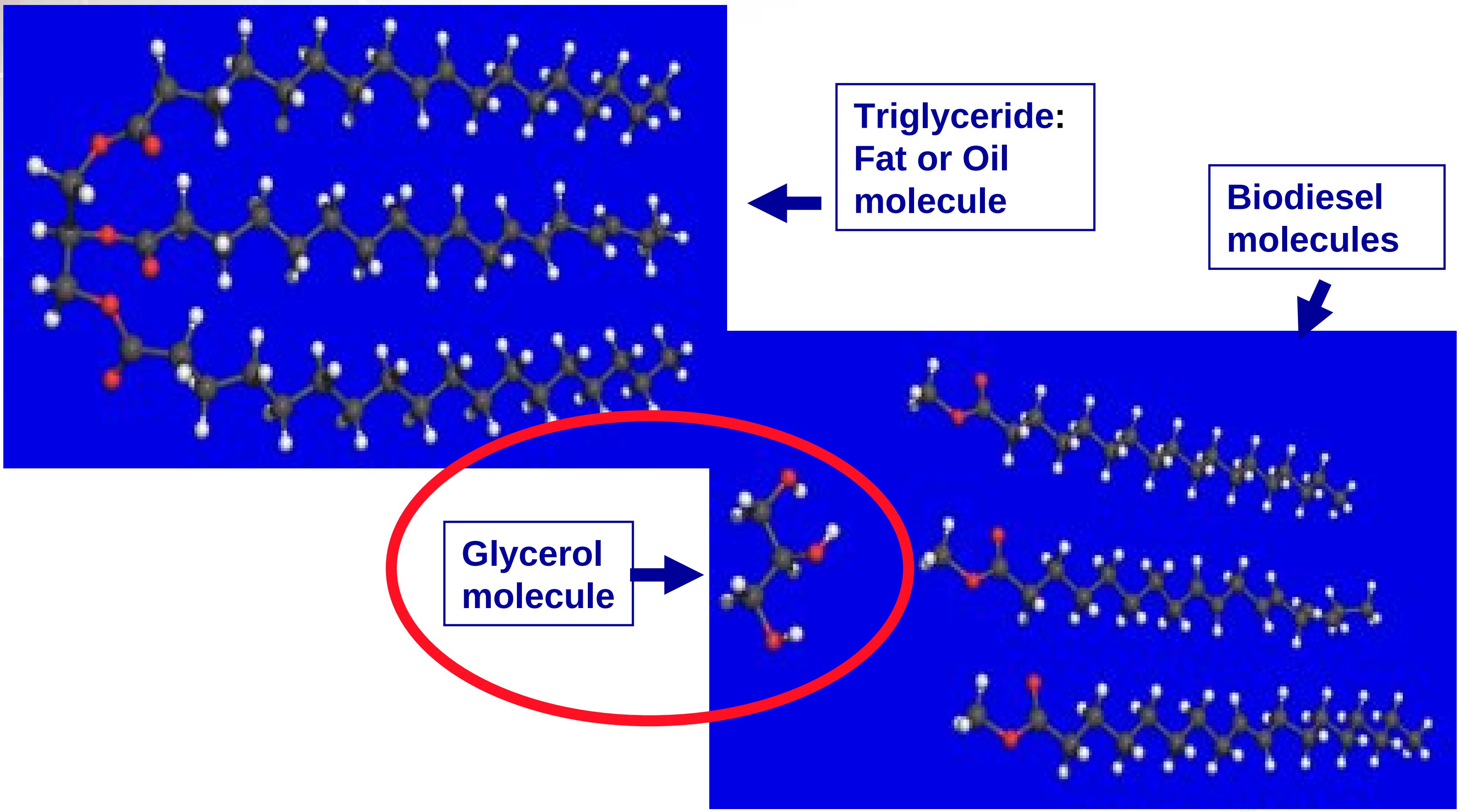
Name	Chemical formula	Chemical structure	Price ($/lbs)	US capacity (MMlbs)
Glycerol	$C_3H_8O_3$		0.05–0.45 [7]	250 [8]
Tartronic acid	$C_3H_3O_5$		N/A	N/A
Dihydroxyacetone	$C_3H_6O_3$		2.00 [9]	N/A
Glyceric acid	$C_3H_6O_4$		Likely high (applications in fine chemicals/ pharma)	N/A
Malonic acid	$C_3H_4O_4$		14 [10]	<1[11]
Hydroxypyruvic acid	$C_3H_4O_4$		High (used for production of amino acids)	N/A
Propylene glycol	$C_3H_8O_2$		0.44–1.00 [12]	1410 [12]

Name	Chemical formula	Chemical structure	Price ($/lbs)	US capacity (MMlbs)
Propionic acid	$C_3H_6O_2$		0.46–0.62 [13]	440 [13]
Glycidol	$C_3H_6O_2$		>$11,000 [14]	N/A
Acrylic acid	$C_3H_5O_2$		0.45–1.01 [15]	2880 [15]
Propanol	C_3H_8O		0.52 [9]	260 [16]
Isopropanol	C_3H_8O		0.28–0.49 [17]	1965 [17]
Acetone	C_3H_6O		0.1325–0.4225 [18]	3441 [18]
Propylene oxide	C_3H_6O		0.64–0.795 [19]	5190 [19]
Propionaldehyde	C_3H_6O		0.40 [9]	400 [16]
Allyl alcohol	C_3H_5O		1.00 [9]	60 [20]
Acrolein	C_3H_4O		0.64 [21]	>250 [22]

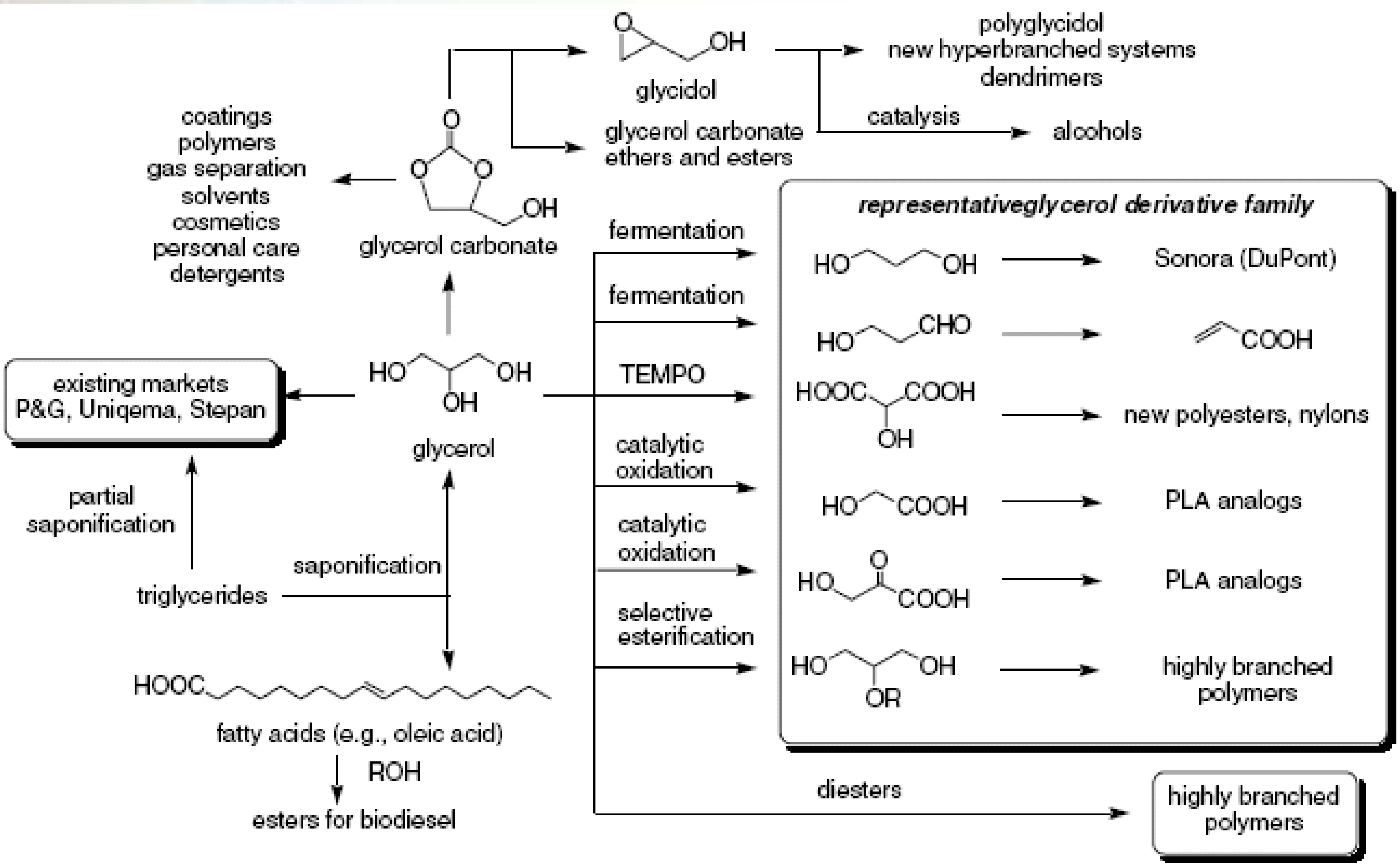
“Typical” Biodiesel Process



Biodiesel Manufacturing



What to do with Glycerol?



Glycerol fermentation

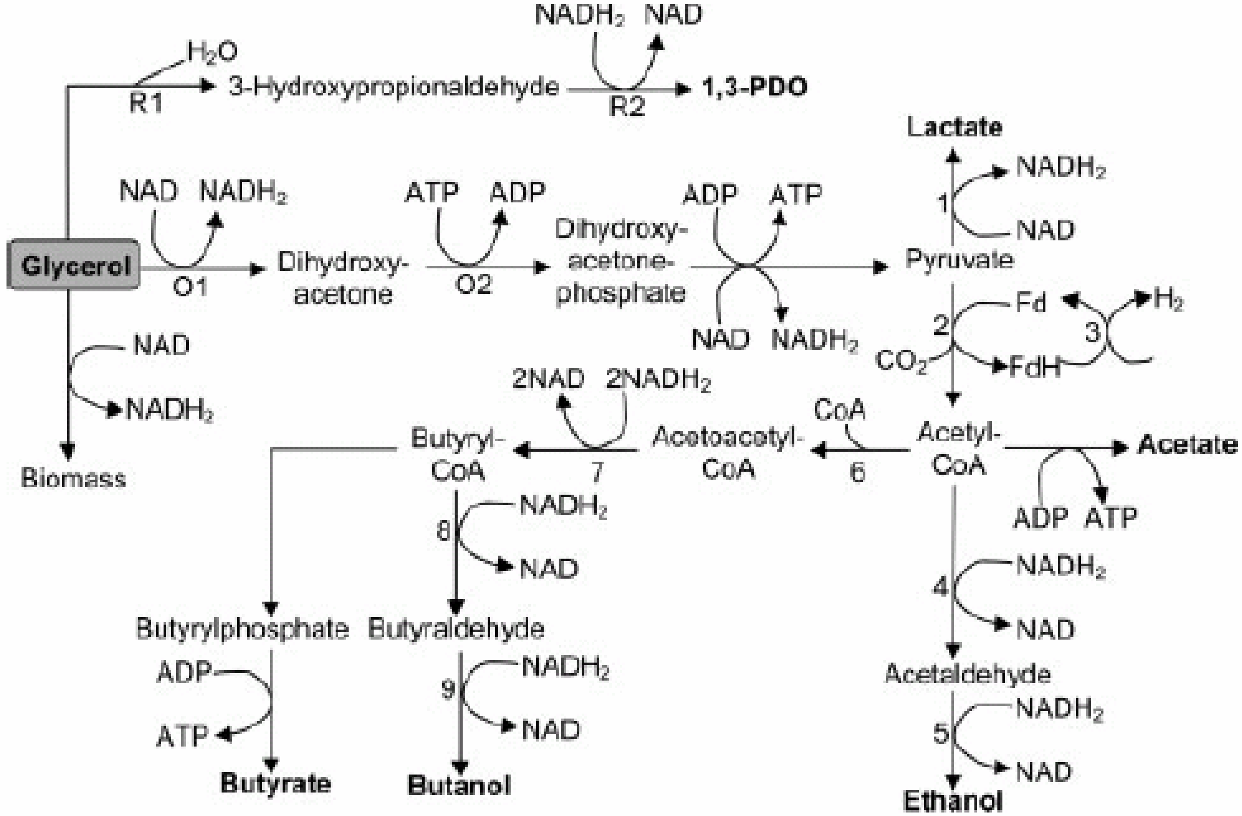
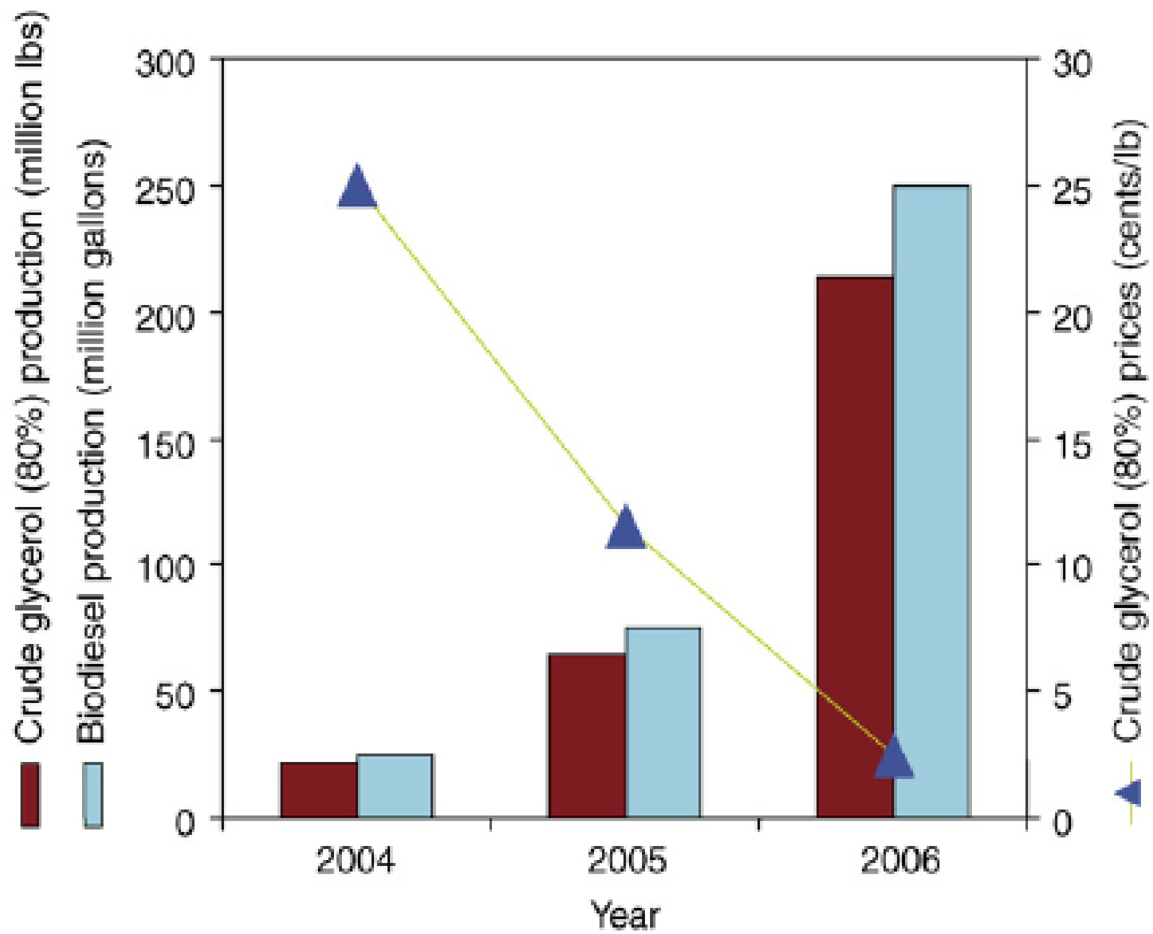


Figure 1. Metabolic pathways for glycerol metabolism in clostridia (R1, glycerol dehydratase; R2, PDO dehydrogenase; O1, glycerol dehydrogenase; O2, dihydroxyacetone kinase; 1, lactate dehydrogenase; 2, pyruvate-ferredoxin oxidoreductase; 3, hydrogenase; 4, acetaldehyde dehydrogenase; 5, ethanol dehydrogenase; 6, thiolase; 7, butyryl-CoA dehydrogenase; 8, butyraldehyde dehydrogenase; 9, butanol dehydrogenase).

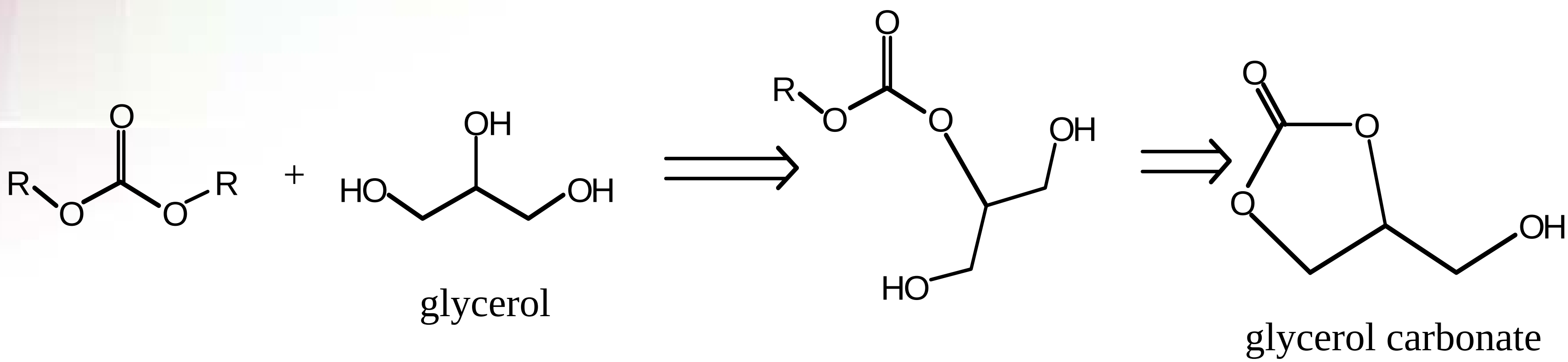
Glycerol Prices



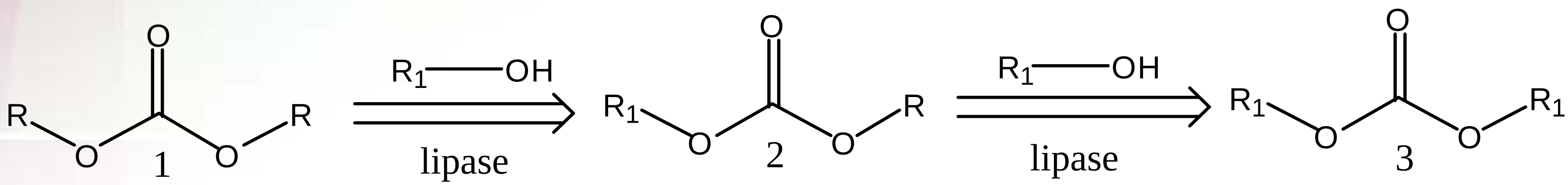
US biodiesel production and its impact on crude glycerol prices.

(Yazdani and Gonzalez 2007)

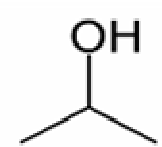
Enzymatic synthesis of glycerol carbonate



Why do we think this reaction is possible?

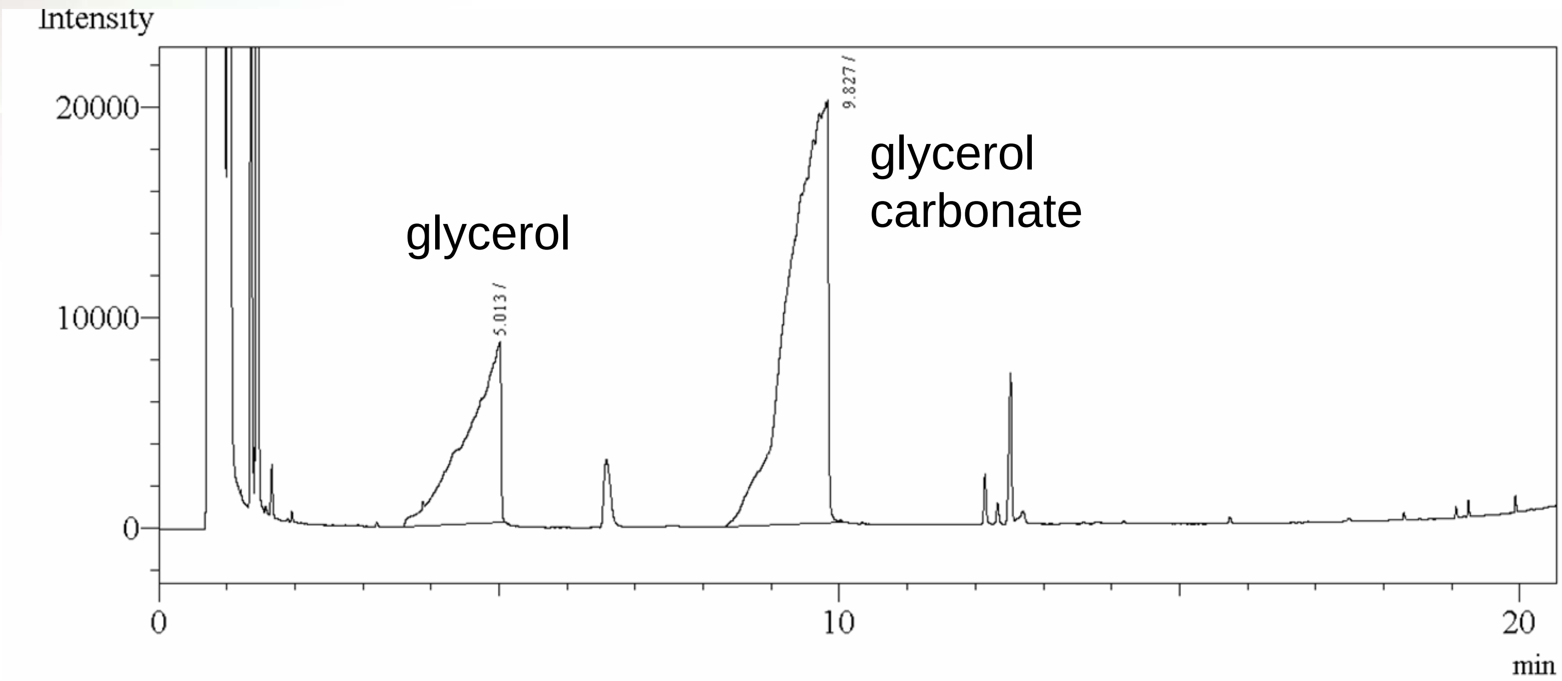


(Chandrasekaran, 2003)

Alcohol	1-propanol 	2-propanol 
Carbonate Products	Mono-substituted Di-substituted	Mono-substituted

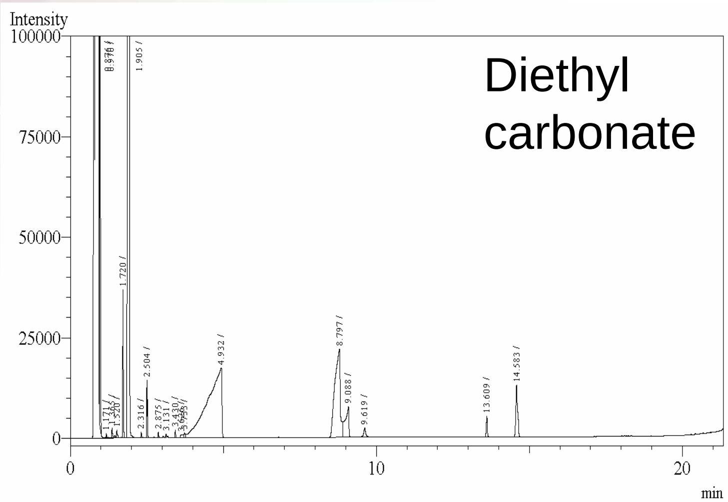
Experimental Results

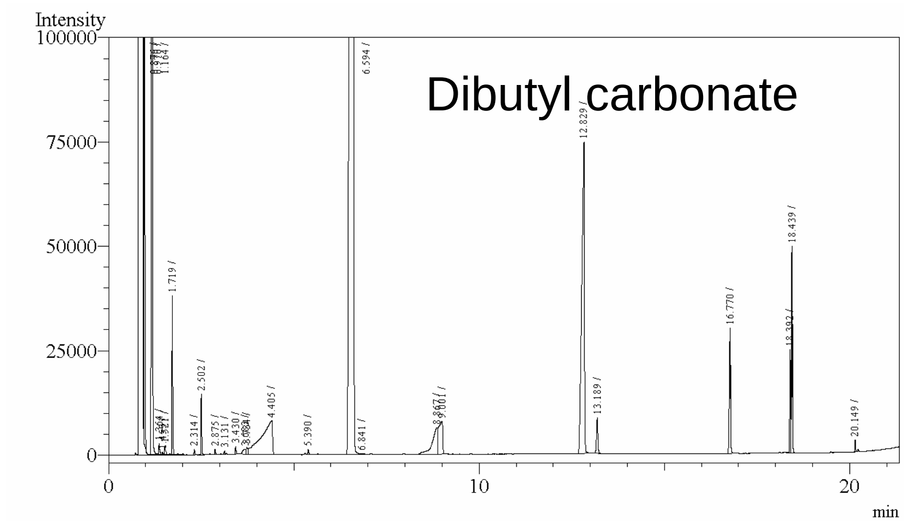
- Glycerol was reacted with dimethyl carbonate in *tert*-butanol
- Catalyzed by *Candida antarctica* lipase B

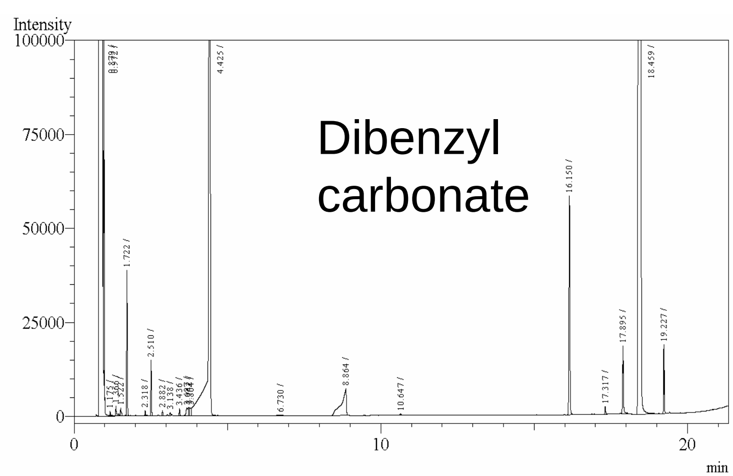


Dialkyl Carbonate Choice

- **Dialkyl carbonate choice effects conversion and specificity.**







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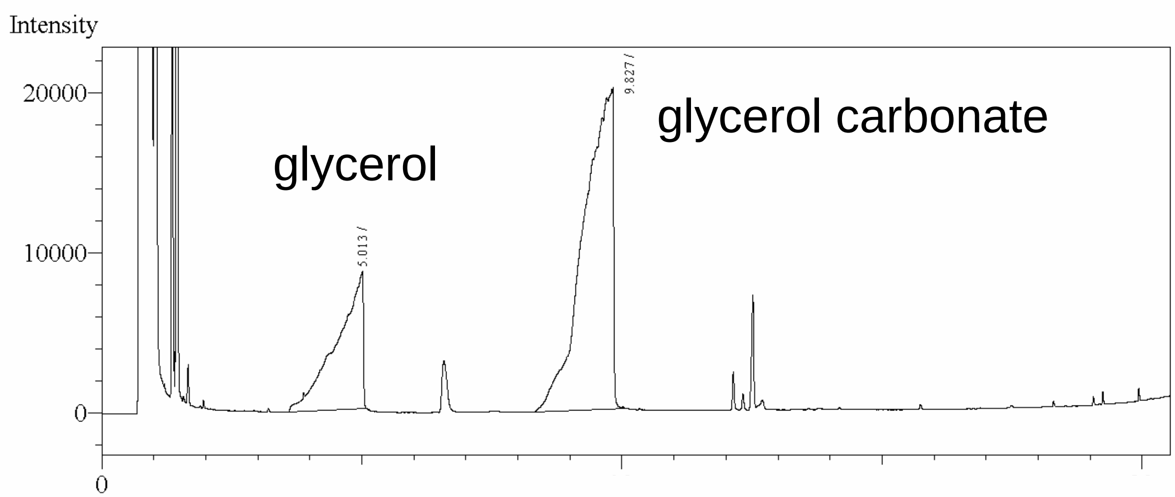
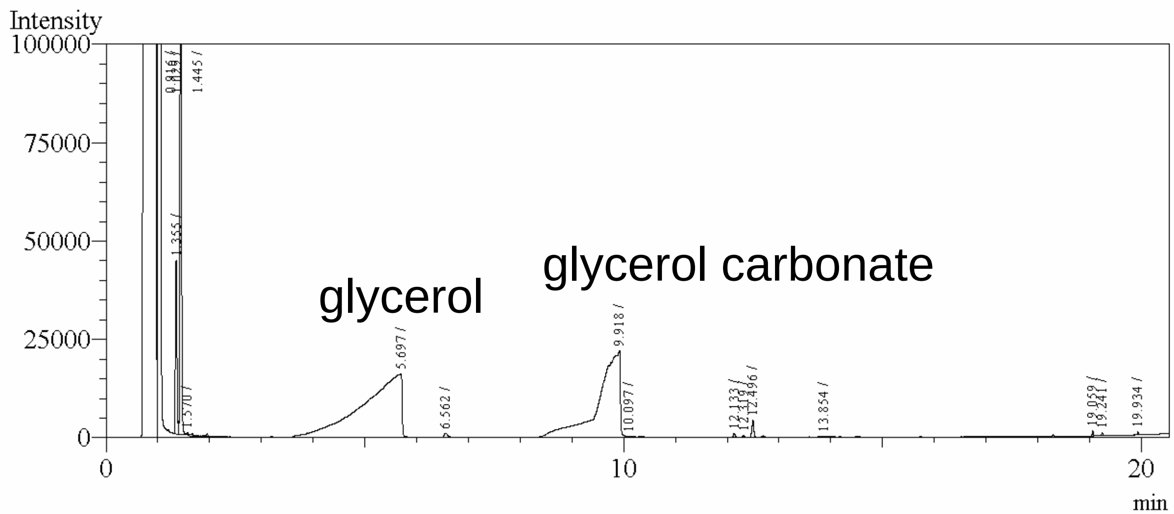
Does solvent matter?



Glycerol, dimethyl carbonate, CalB and

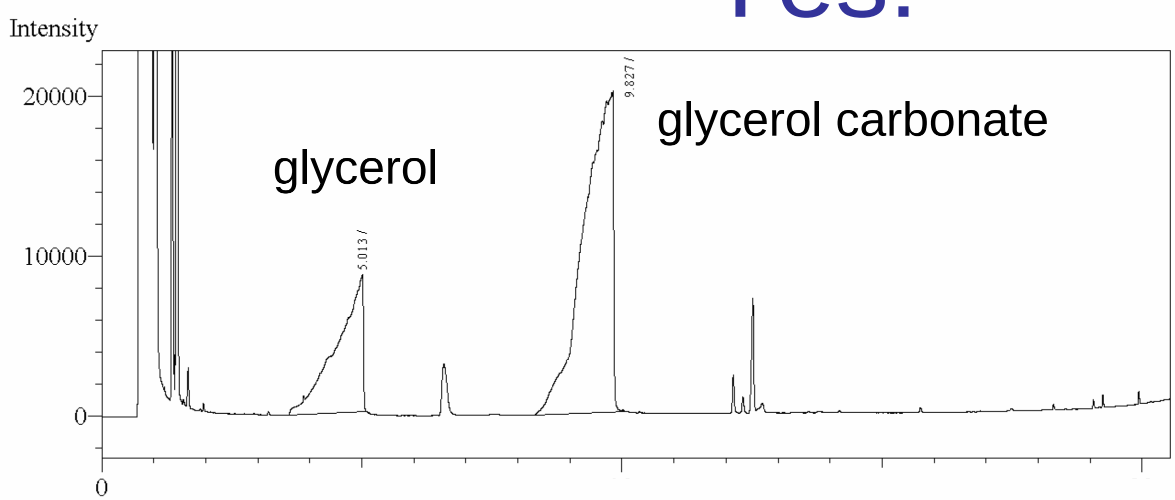
tert- butanol as a solvent

Glycerol, dimethyl carbonate and CalB



Does solvent matter?

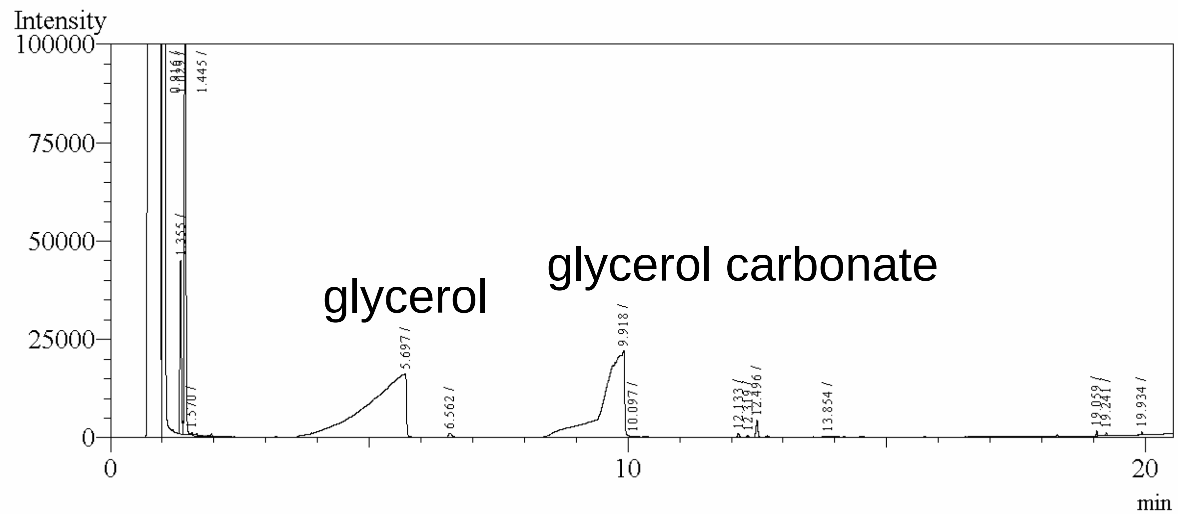
Yes!



Glycerol, dimethyl carbonate, CalB and

tert- butanol as a solvent

→72 % conversion



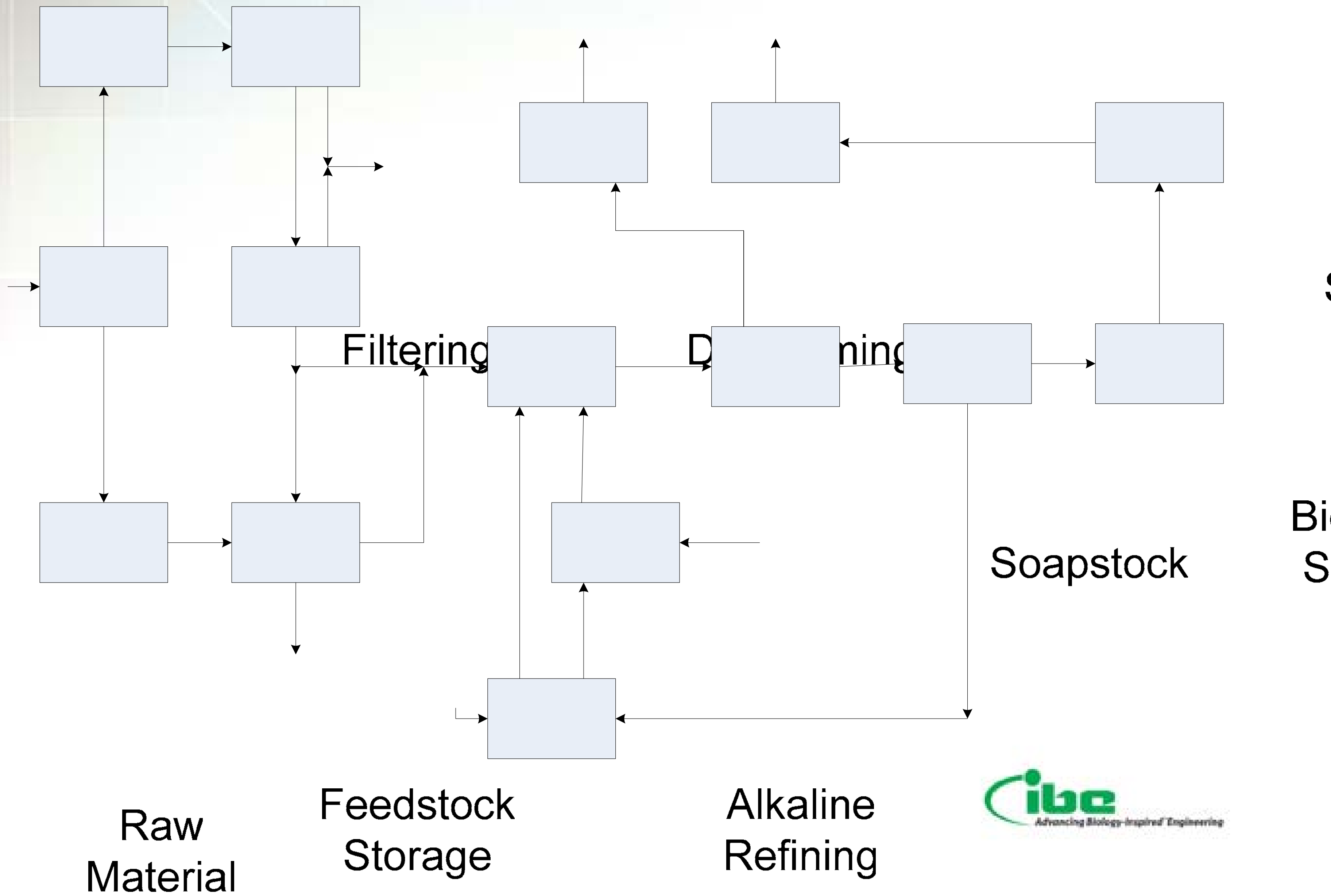
Glycerol, dimethyl carbonate and CalB

→42% conversion

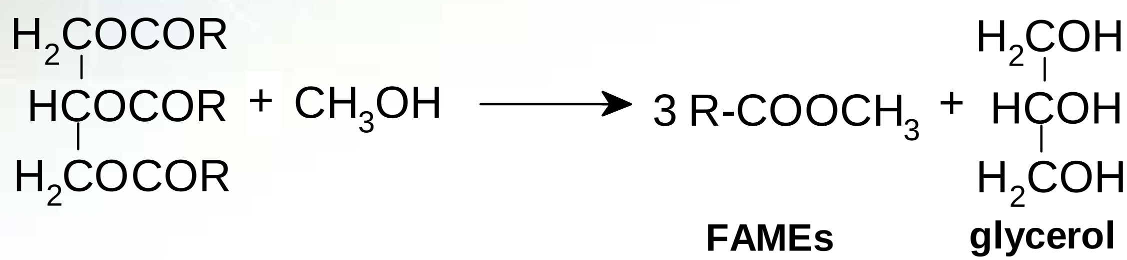
Preliminary results - Glycerol carbonate from glycerol

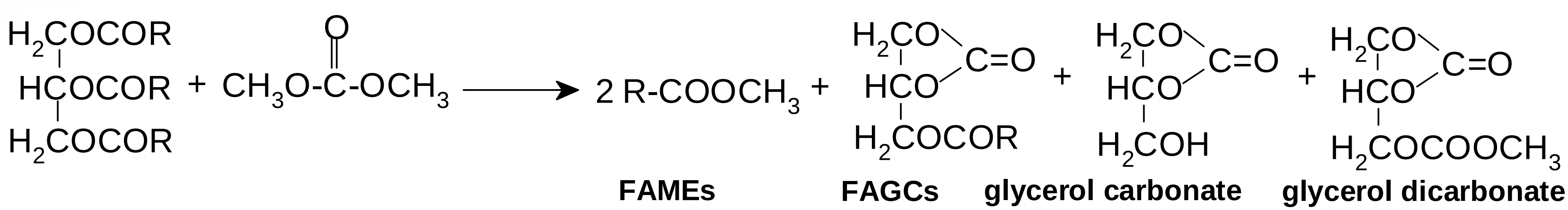
Lipase	Carbonate	Conversion	Time	Selectivity
C. ant B	dibutyl	70%	2 h	30%
C. ant B	dimethyl	70%	20 h	99%+

“Typical” Biodiesel Process



Lipase can also catalyze biodiesel production





Summary of Lipase-catalyzed biodiesel production

- Batch system with 1.5 DMC/oil mole ratio and 2.5% immobilized *Candida antarctica* (based on oil weight) at 50°C
  - 70% fatty acid methyl esters (FAMEs)
  - 12% glycerol carbonate fatty acid monoesters (FAGCs),
  - 0.23% glycerol carbonate
  - 0.08% glycerol dicarbonate
  - less than 2% of mono- and di- glycerides
  - 65% residual activity over fifth recycle was observed at 50°C with 24h run cycle

Implementation

- Immobilized whole cells with surface display of lipase
- Packed column or expanded bed reactor
- Avoided costs of enzyme purification and immobilization
- Protein stability remains an issue

Summary

- Biomass used for biofuel production has multiple uses
  - Fermentation does not have to result in ethanol
  - Lignin is not necessarily a nuisance to be avoided
  - Apply concept of total carbon utilization in approaching starting material
- Many alternate products have specific value > fuel
- Balance high value/low volume with low value/high volume products