"And all I've outlined here today are interim strategies short-term and interim strategy. The truth of the matter is, the long-term strategy is to power our automobiles with something other than oil something other than gasoline, which is derived from oil."

President Bush on Energy Policy
Marriott Wardman Park Hotel
Washington, D.C.
April 25, 2006

BIODIESEL

Grant Landrum

Joline Munoz

Outline

- Introduction to Biodiesel
- Biodiesel vs. Petrol Diesel
- Oil Sources
- Our Source
- Location Selection
- Genetic Modification
- Scenarios Evaluated
- Transesterfication
- Byproducts
- Economics
- Conclusions

Introduction

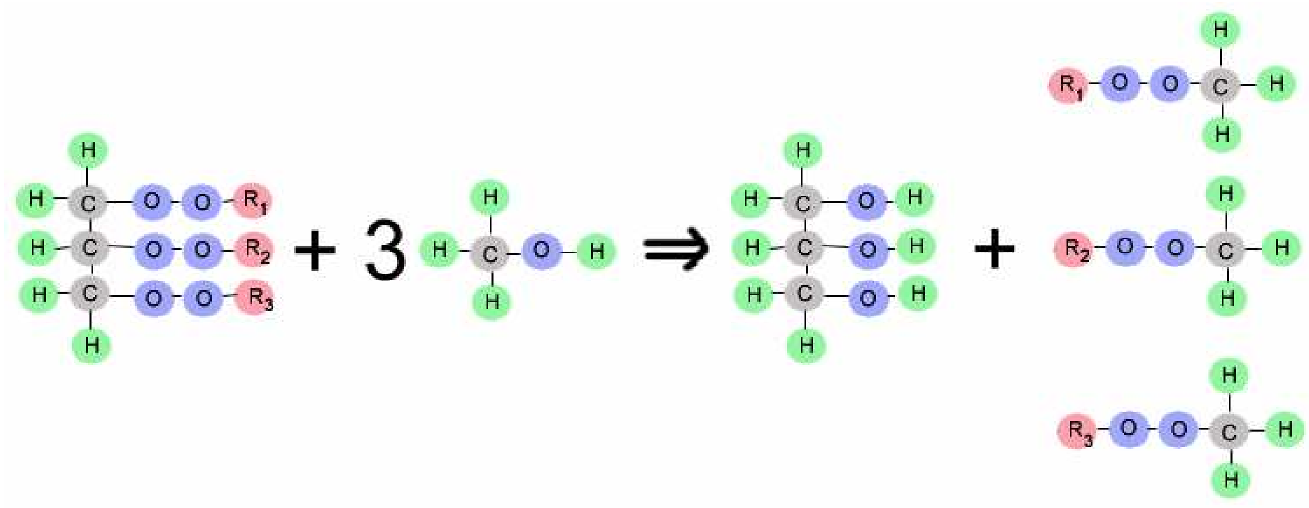
What is Biodiesel?

- **Biodiesel is a completely natural, alternative fuel source that is applicable in almost all situations in which petrol diesel is used.**

Transesterification

	Base Catalyst	
Triglyceride + Alcohol (Oil)	→	**Methyl Esters + Glycerol** (Biodiesel)

– ***Oil can come from animal oil / fats, vegetable oil, and waste oil from restaurants (after degumming)***



Triglycerides Alcohol Glycerol Methyl Esters

Biodiesel vs. Petrol-Diesel

- **Biodiesel**
  - Reduces emissions
  - Cetane #: 48-65
  - Increases lubricity
  - Longer engine life
  - Higher Flash Point
  - Requires no modification
  - Dissolves rubber and some plastic
  - Slightly lower heating value

- **Petroleum Diesel**
  - High emissions
  - Cetane #: 40-55
  - Low sulfur diesel lacks lubricity
  - High sulfur
    - poisons catalyst in exhaust system
    - Reduces effective reduction of emissions in exhaust system

Average Density and Heating Value of Biodiesel and Diesel Fuel		
Fuel	**Net Heating Value Avg., Btu/gal.**	**% Difference vs. No. 2 Diesel Avg.**
No. 2 Diesel	129,500	
Biodiesel (B100)	118,296	8.65 %
B20 Blend (B20)	127,259*	1.73 %*
B2 Blend (B2)	129,276*	0.17 %*

* Calculated Values from those of No. 2 Diesel and Biodiesel (B100)

http://www.biodiesel.org/pdf_files/fuelfactsheets/BTU_Content_Final_Oct2005.pdf

Cetane number = ease of ignition / smoothness of combustion.

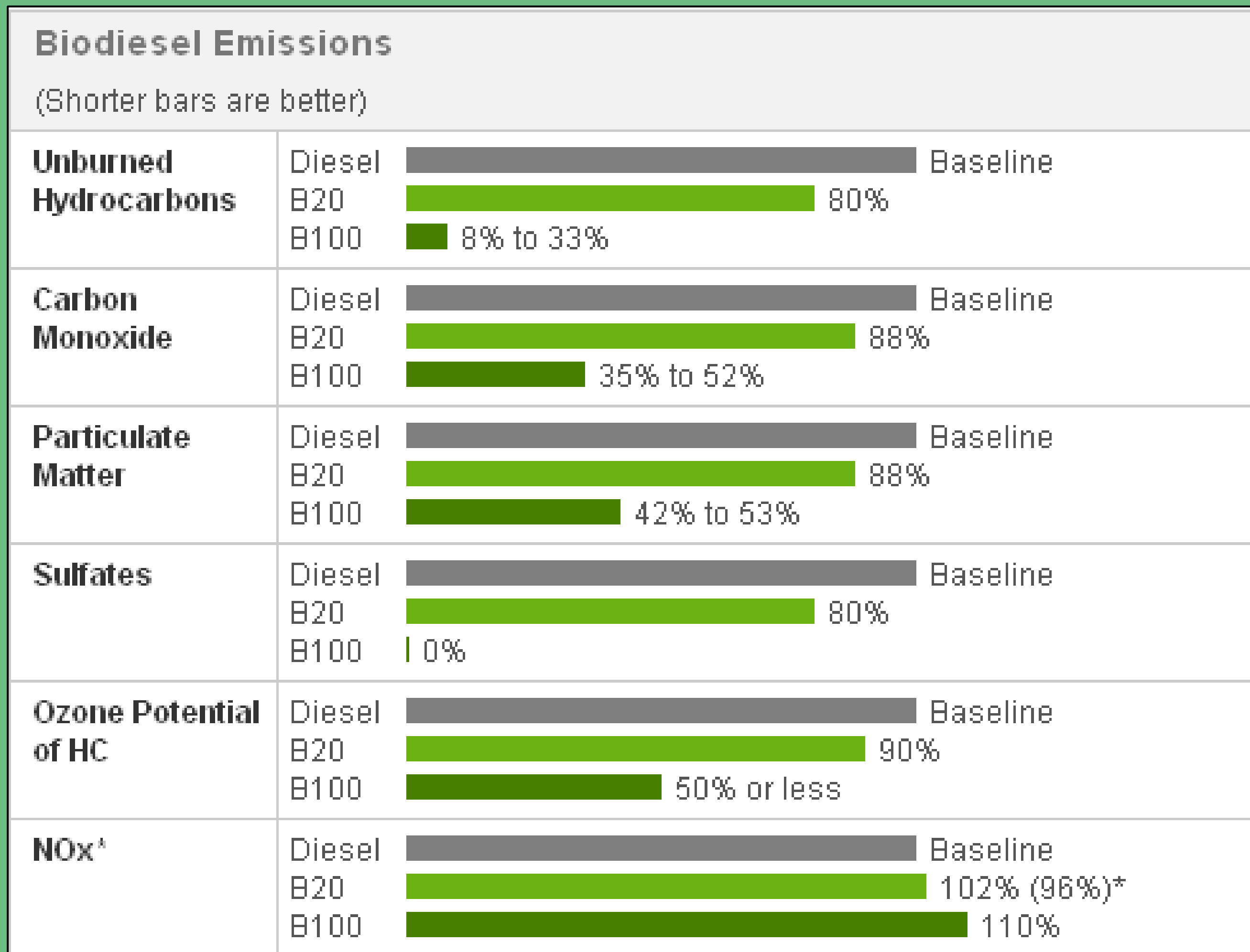
High cetane = easy starting, at low temperature, low pressures, lower knocking characteristics.

Low cetane = poor ignition causes misfiring, rough operation, higher knocking.

http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19940101_gen-297.pdf

Acute Oral Toxicity/Rates	The lethal dose is greater than 17.4 g/Kg body weight. table salt (NaCL) is 10 times more toxic.
Skin Irritation - Humans	Very mild irritation. Less than 4 percent soap and water solution.
Aquatic Toxicity	Deemed "insignificant" according to NIOSH (National Institute for Occupational Safety and Health)
Biodegradability	Within 28 days, pure biodiesel degrades 85 to 88 % in water.
Flash Point	Biodiesel's flash point is 260° Fahrenheit Petroleum based diesel's is 125° Fahrenheit

http://www.biodiesel.org/pdf_files/fuelfactsheets/Environment_Safety1.pdf



http://www.propelbiofuels.com/site/aboutbiodiesel.html

Potential Oil Sources

U.S. Department of Argiculure Statistics						
Canola: Area Planted, Harversted, Yield, and Production by State and United States, 2001-03						
State	Area Planted			Area Harvested per 1,000 Acres		
	2001	2002	2003	2001	2002	2003
MN	80	80	57	75	45	56
ND	1,300	1,300	970	1,285	1,160	960
Other Sts 1/	114	79	55	95	70	52
US	1,494	1,459	1,082	1,455	1,275	1,068

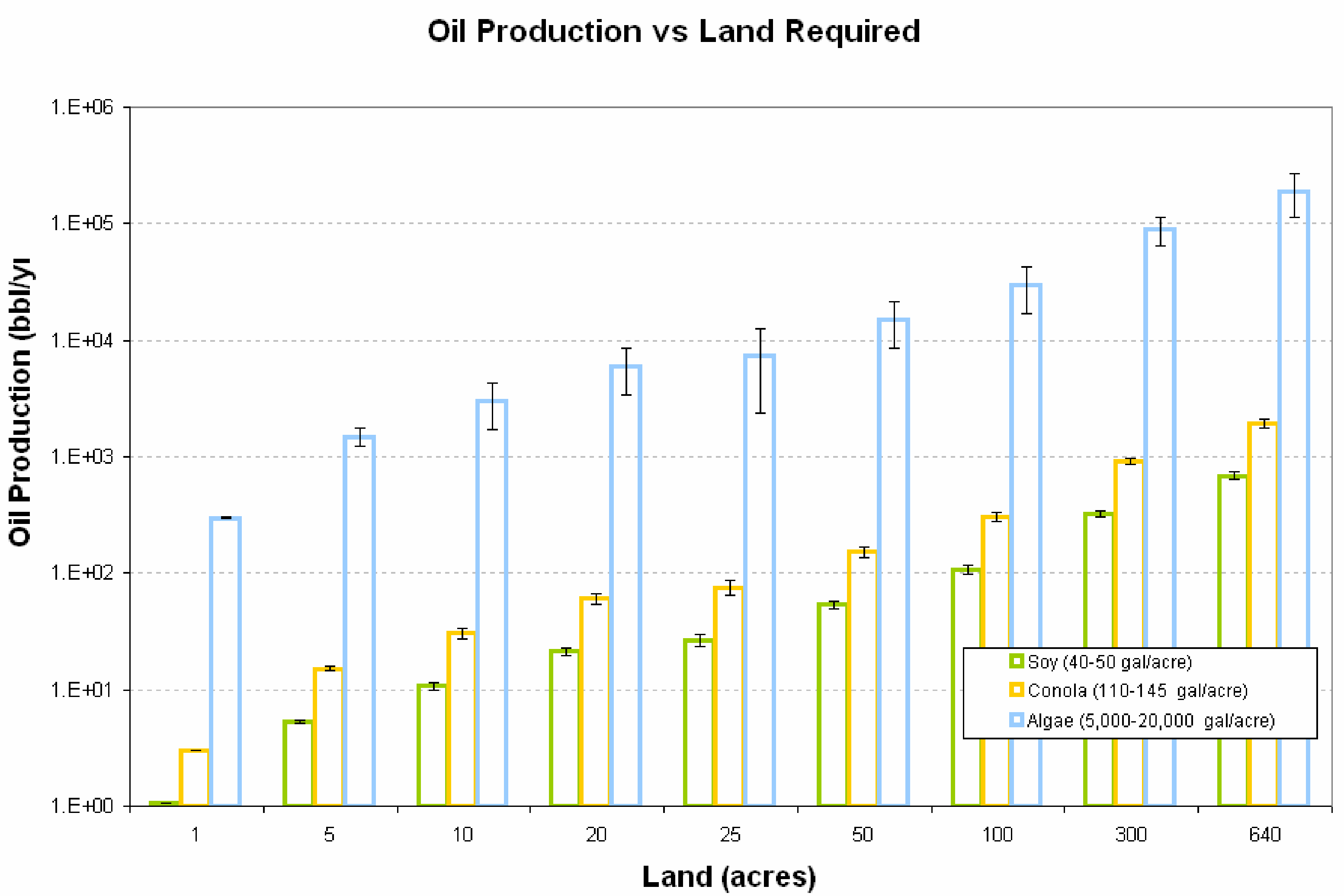
http://www.uscanola.com/index.asp?Type=B_BASIC&SEC={5CDA1D60-89B2-4F79-B96F-0B5AB2FBF781}

Soybean

- Biodiesel plants in U.S. use soy
- Commodity Credit Corporation (CCC)
  - Incentives: $1.45 - 1.47 / gallon till mid-2006
- 30% of the plants are not profitable without government incentives
- 24% are still unprofitable with incentives
  - High cost oil feed stock for biodiesel
  - High production costs
  - Increase lipid content-lower production costs

http://www.farmgate.uiuc.edu/archive/2006/04/what_is_the_fut.html

Land Requirements



Algae

- NREL Aquatic Species Program Study (*National Renewable Energy Laboratory*)
  - Factors to consider
    - High adaptability to variety of environments
    - Large growth rate
    - Higher lipid content

Algae Requirements

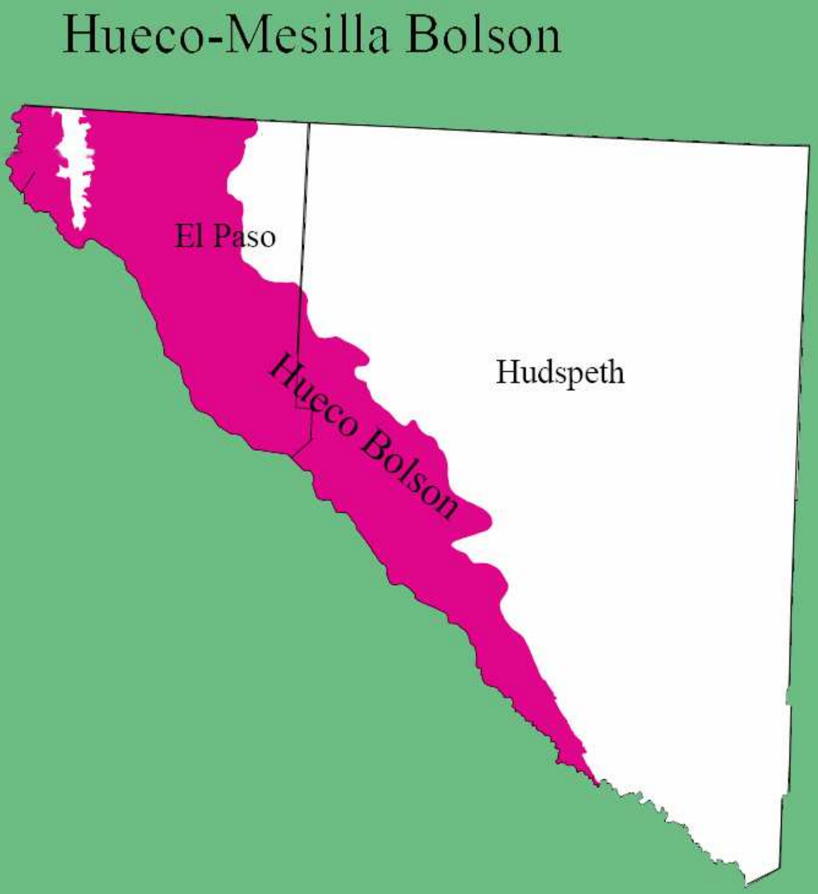
- Growth $6H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2$
  - Sunlight
  - CO_2
  - Nutrients (N and Si)
  - Water (*can be saline*)
  - Warm Climate
  - Circulation or Aeration

Algae

- Environment
  – Different Media
    - Type I: 2,000 to 16,000 mg/l
    - Type 2: 1,500 to 26,000 mg/l
    - Seawater
  – Majority algae survive well in seawater

Brine Water Source

- Hueco Bolson Aquifer
  - Salt concentrations range from 1000 to 3000 mg/L
    - 600 times the amount of fresh water
    - Possible alternative to evaporation ponds- reinjection

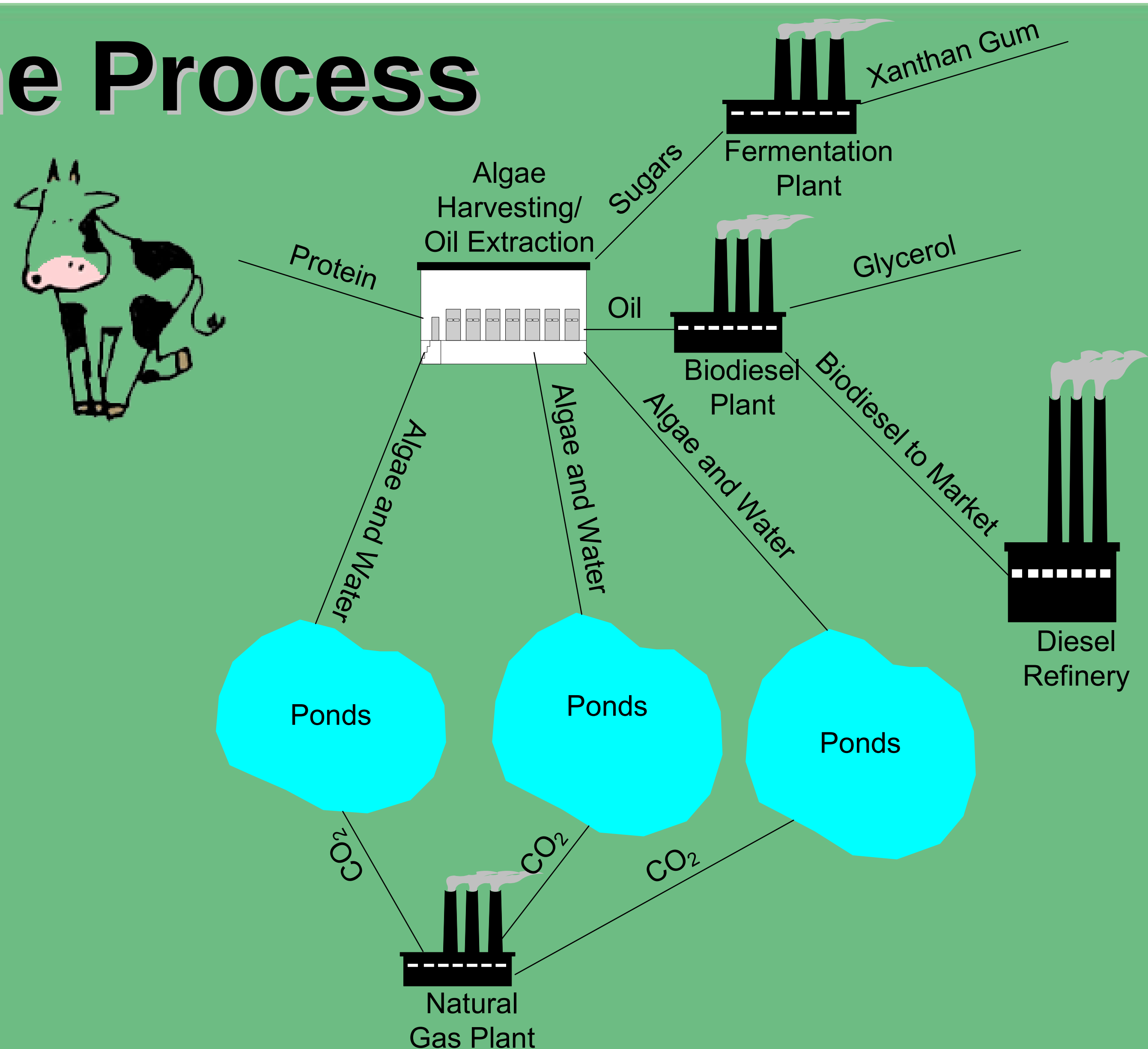


http://www.twdb.state.tx.us/publications/reports/GroundWaterReports/GWReports/R345%20Aquifers%20of%20Texas/Majors/hueco.pdf

Algae Selection

- Arizona State University - New Mexico / Texas Area
  - Amphora Bacillariophyceae
    - Hard to harvest (10 X 4 µm)
    - Salinity: ~9000-18000 mg/L
  - Oscillatoria Cynaophyceae
    - Adaptive
    - Harder to harvest (0.2 X 0.1 µm)
    - Salinity: ~2000-12000 mg/L

The Process



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Sugars
Algae Harvesting/ Oil Extraction
Protein
Glycerol
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Biodiesel Plant
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Diesel Refinery
Algae and Water
Algae and Water
Algae and Water
Ponds
Ponds
Ponds
CO_2
CO_2
CO_2
Natural Gas Plant

Location: West TX

- 24 oil refineries
- 8% diesel transportation

Newman, TX		
Stack	CO_2	SO_2
	tons / year	*tons / year*
1	90,069	0.4
2	88,858	0.5
3	109,273	0.6
4	130,436	0.7
5	135,758	0.6
SUM	**554,395**	**2.8**

Tolk Station, TX		
Stack	CO_2	SO_2
	tons / year	*tons / year*
1	1,537,026	4,543
2	2,112,768	5,993
SUM	**3,649,794**	**10,536**

Jones, TX		
Stack	CO_2	SO_2
	tons / year	*tons / year*
1	355,086	1.8
2	374,686	1.9
SUM	**729,773**	**3.7**

Newman Power Plant, El Paso TX.

Pond Nutrients

	$\%_{carbon}$	C_{algae} (lb/day)	$\%_{absorbed}$
1 mile^2	40%	80,000	3.9%
	50%	100,000	4.9%
	60%	120,000	5.8%
4 mile^2	40%	320,000	15.6%
	50%	390,000	19.0%
	60%	470,000	22.9%
7 mile^2	40%	550,000	26.8%
	50%	690,000	33.6%
	60%	830,000	40.5%

CO_2 Availible (lb/day)
7,515,059

C Availible (lb/day)
2,051,611

The CO_2 utilization efficiencies of 96 ±11% were achieved by bubbling CO_2 into the culture with the use of a counterflow sump system.

	Concentration		
	1 mi^2	4 mi^2	7 mi^2
	M	M	M
SO_2	2.71E-08	6.77E-09	3.87E-09
NO_x	1.00E-05	2.51E-06	1.44E-06

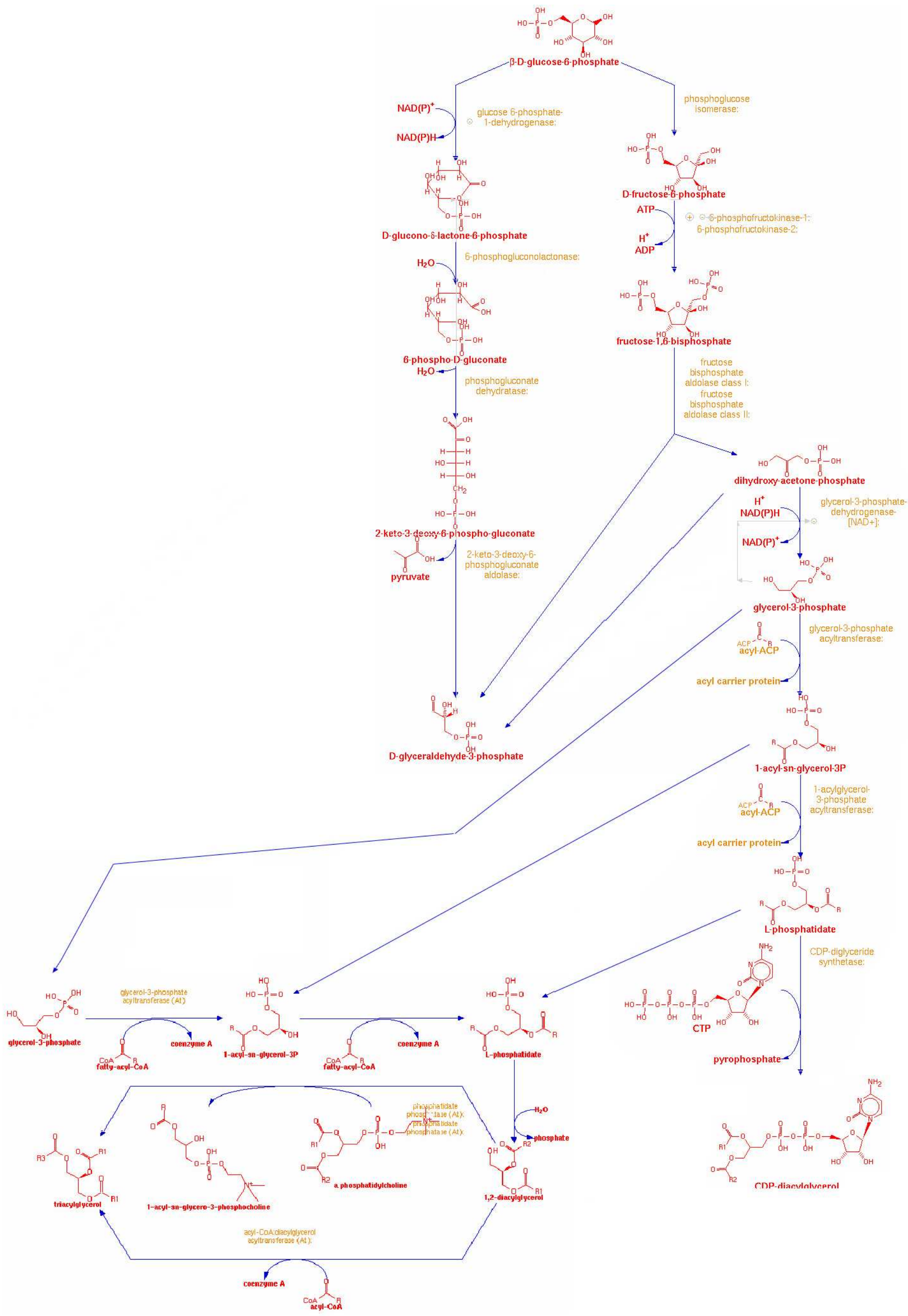
SO_2 Availible (mol/day)
278

NO_x Availible (mol/day)
103,152

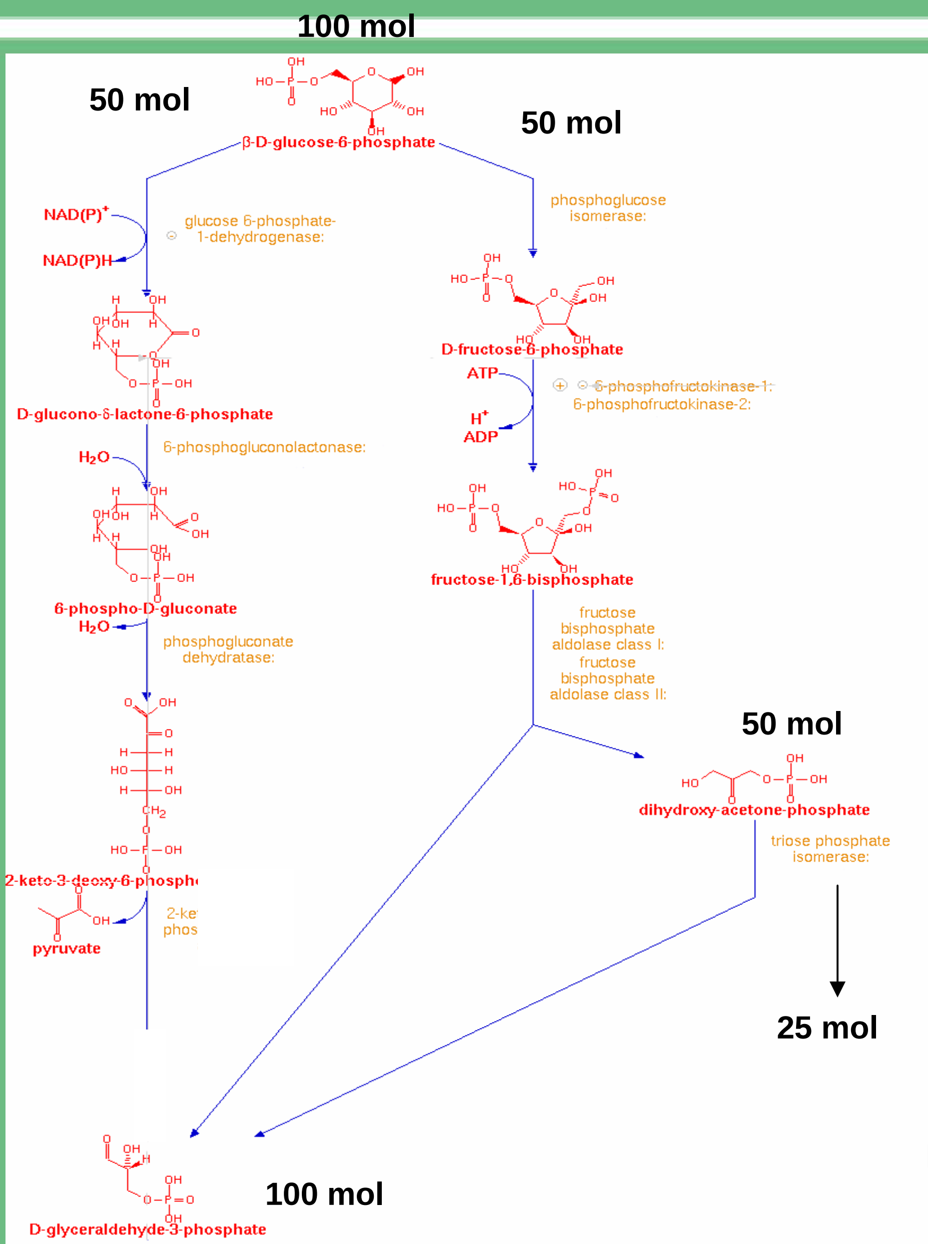
A Study of the Energetics and Economics of Microalgal Mass Culture with the Marine Chlorophyte *Tetrase/mis suecica:* Implications for Use of Power Plant Stack Gases*

Algae

- Lipid Content
  - Starvation
    - A minimum amount of food (nitrogen source or Si source) added to ponds
    - 7-day cycle, algae have run out of food and have begun to starve
      - Pro-Causes many different algae to increase lipid content
      - Con-Stuns cell growth
  - Genetic Engineering
    - Metabolic processes in the specific algae
    - Manipulate these processes to maximize lipids



Overall Metabolic Pathway of Lipid Synthesis



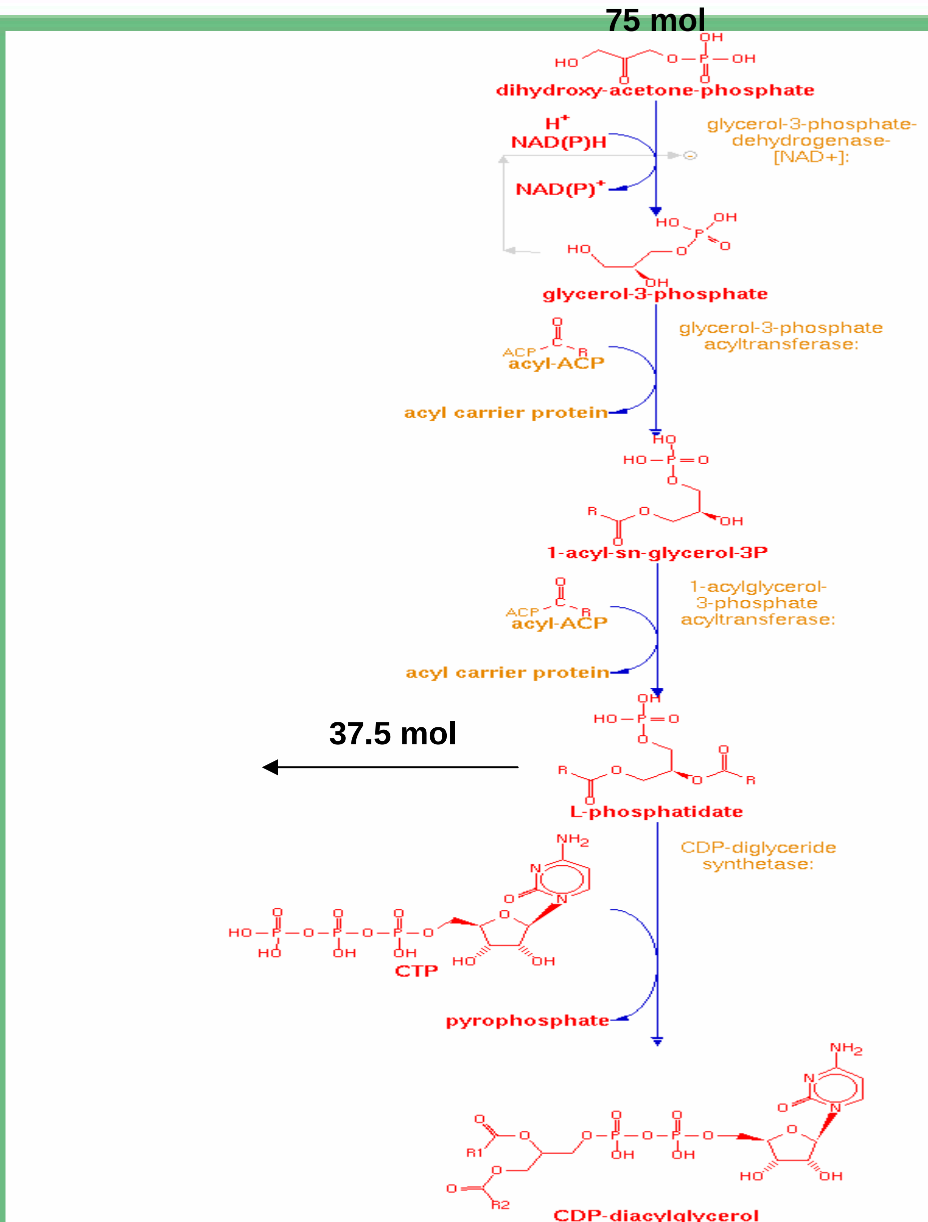
Entner-Doudoroff & Glycolysis I

Genetic engineering algae starting with glucose-6-phosphate

Want to produce dihydroxy-acetone-phosphate

http://biocyc.org/

Phospholipid Biosynthesis



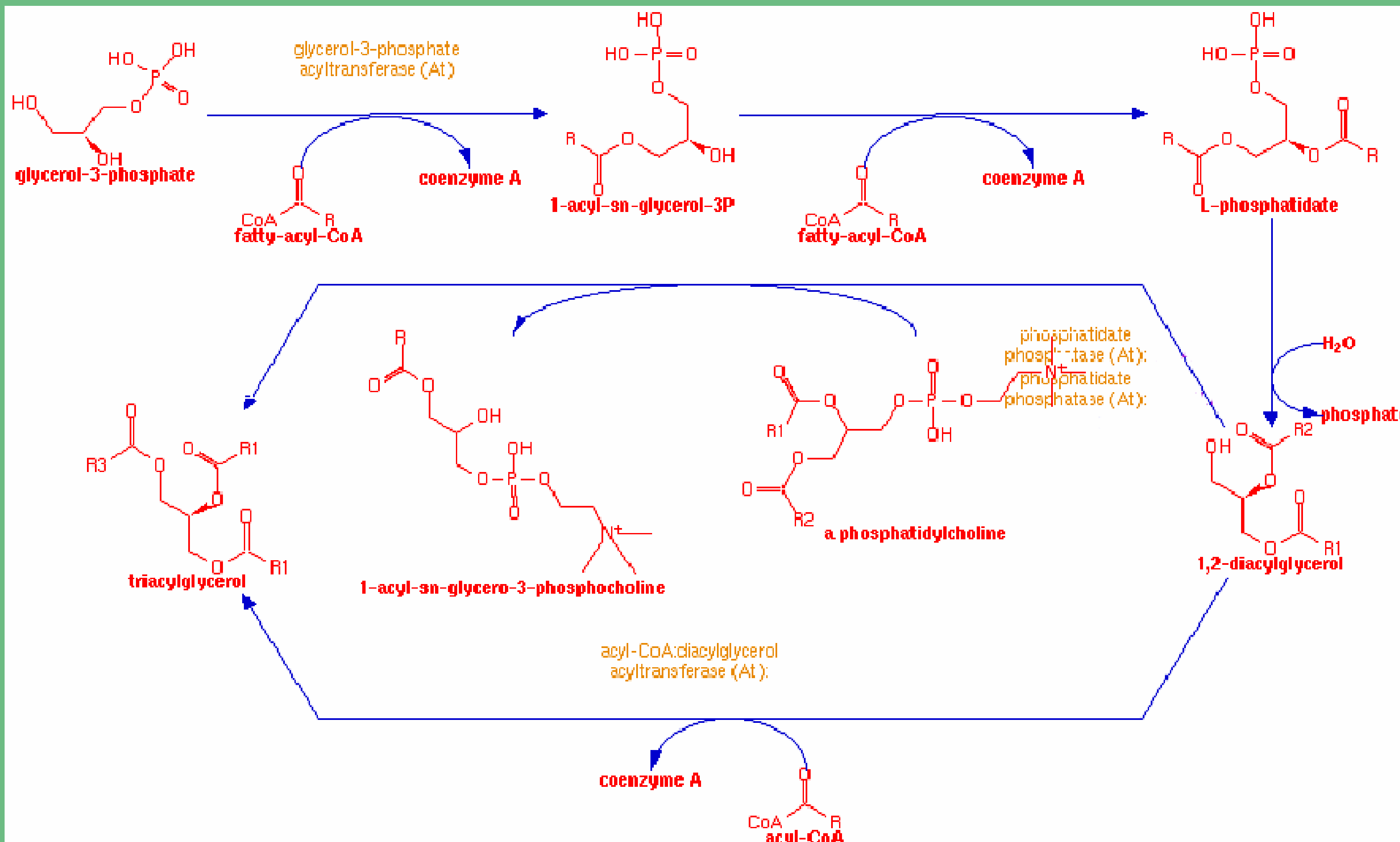
37.5 mol

Want to produce glycerol-3-phosphate or L-phosphatidate

http://biocyc.org/

Triacylglycerol Biosynthesis

Initially 37.5 mol tri / 100 mol G-6-P   Now 56.25 mol tri / 100 mol G-6-P



Genetic Engineering

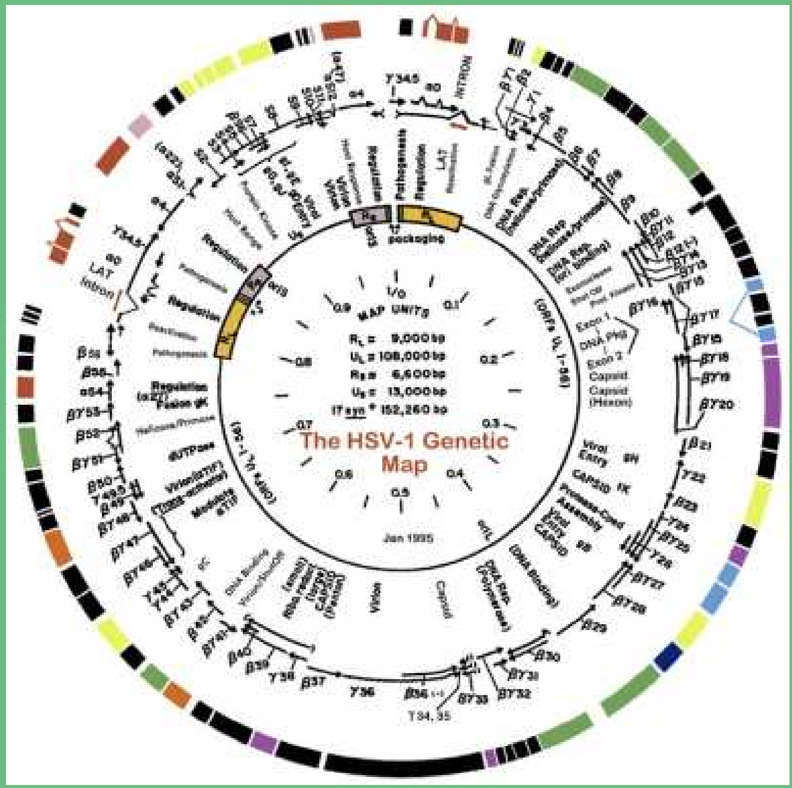
- Why genetically modify the algae?
  - *Maximize algal lipid content*

- How to genetic engineer the algae?
  - *Complete genome study on the species*
  - *Isolation, Manipulation, and Re-introduction*
  - *Polymerase Chain Reaction (PCR)*
  - *Loss of Function / Gain of Function / Tracking*

What is a genome?

- Contains all the biological information needed to build / maintain a living example of that organism

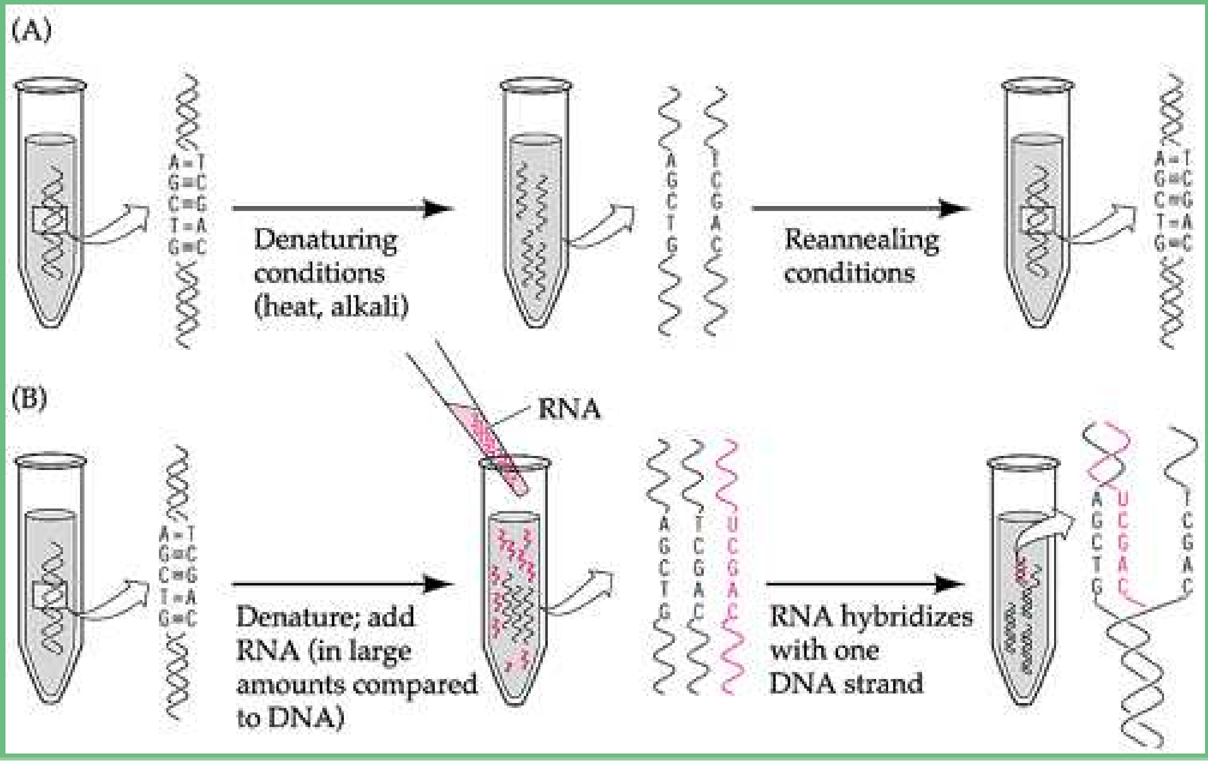
- Biological information in a genome is encoded in its DNA and is divided into discrete units called genes



http://darwin.bio.uci.edu/~faculty/wagner/hsvimg04.jpg

Nucleic Acid Hybridization

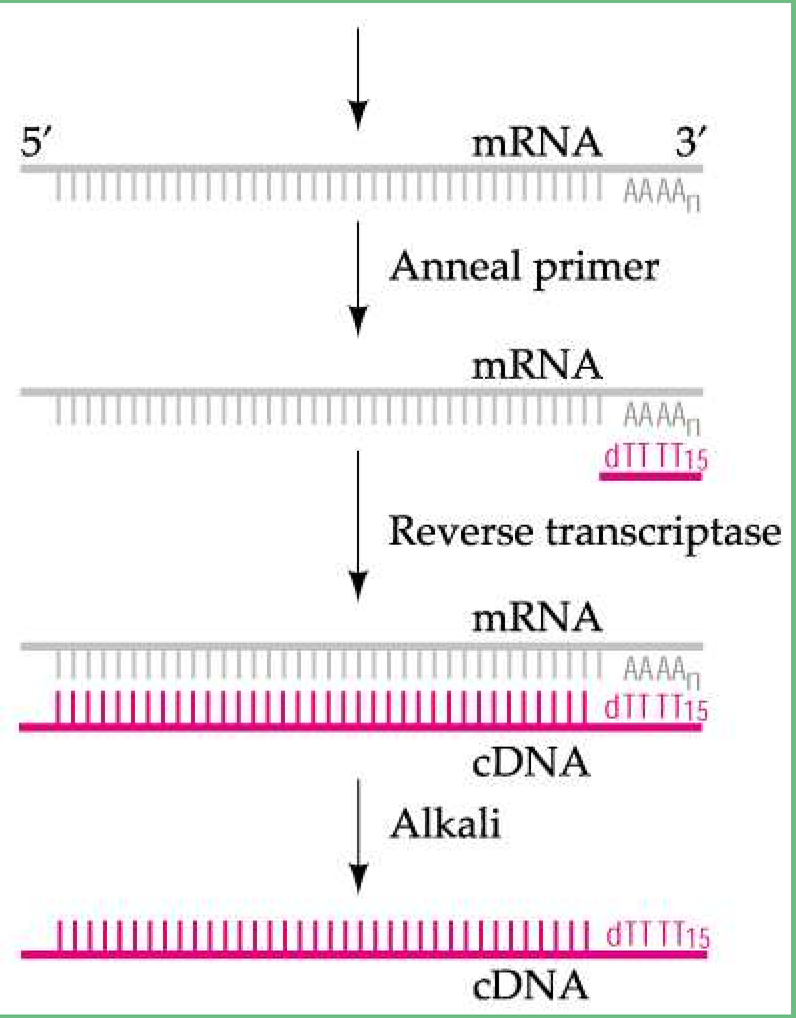
- DNA is separated into its two strands
- $C_{RNA} >> C_{DNA}$ the RNA will replace one of the DNA strands in this region



http://7e.devbio.com/image.php?id=126

Complementary DNA (cDNA)

- RNA isolated and converted to cDNA
- cDNA isolated
  - raising the pH (*denature helix*)
  - cleaving RNA



http://7e.devbio.com/image.php?id=127

Reverse Transcription Polymerase Chain Reaction

- PCR followed by transcription with reverse transcriptase (to convert the RNA to cDNA)
- Expression mapping: determining when and where certain genes are expressed

(1) Denaturing at 94°C
(2) Annealing at 68°C
(3) Extension at 72°C
(4) Rinse and Repeat

Options

	Year			
	1	4	7	10
Option				
A	1 sq. mile	4 sq. miles	4 sq. miles	7 square miles
B	7 sq. miles	7 sq. miles	7 sq. miles	7 sq. miles

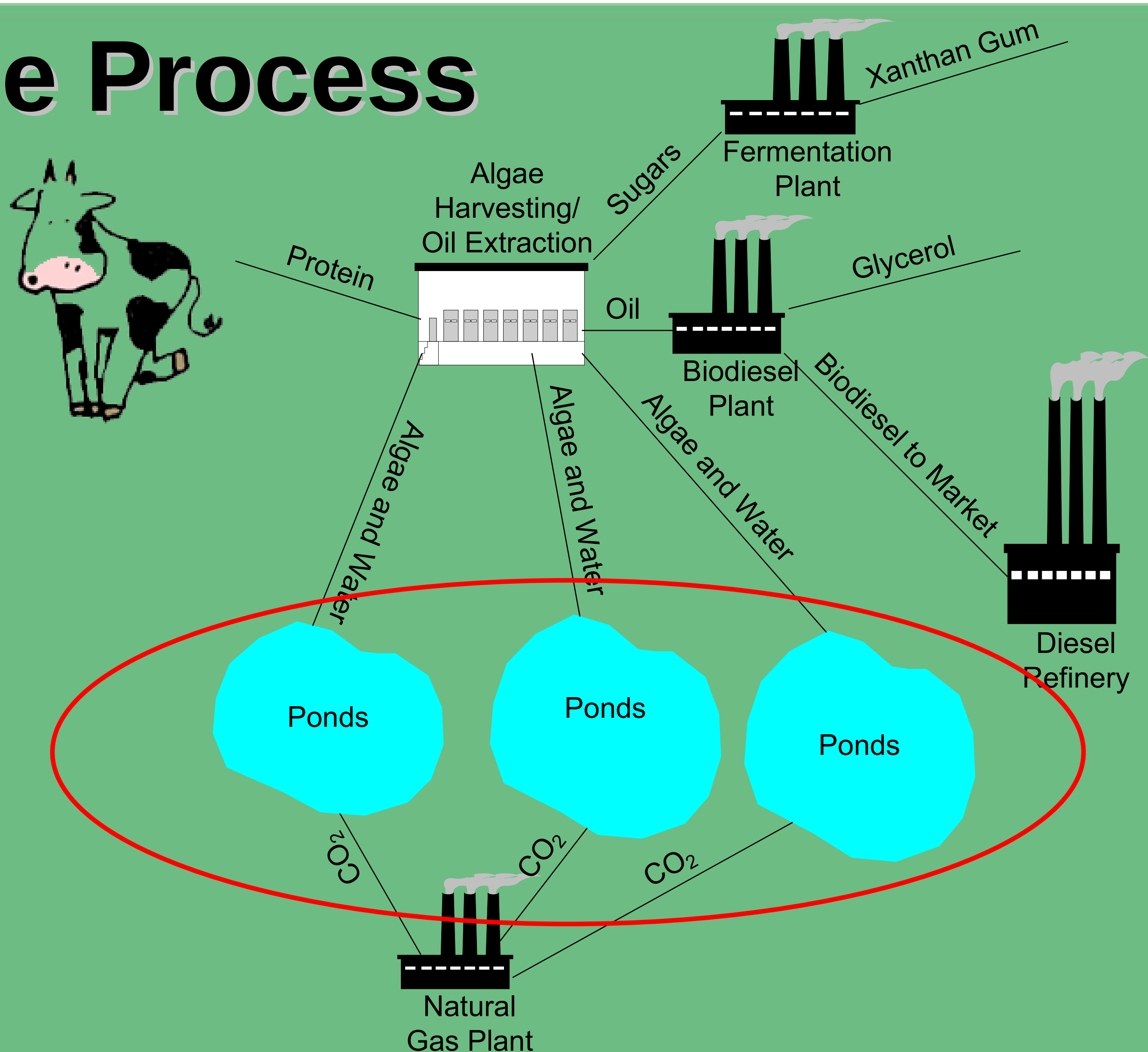
- 15 year production term
- Evaluate profitability based on different starting capital investments
- Expansion vs. One time Build
- Possibility of recycling profits advantage

Options Cont.

Production Rate (million gallons/year)			
Land Usage (sq. miles)	20% Lipid	30% Lipid	40% Lipid
1	1.4	2.1	2.8
4	5.6	8.4	11.2
7	9.8	14.7	19.6

- **Varied Lipid Content to evaluate profitability based on different lipid yields**

The Process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Sugars
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Plant
Xanthan Gum
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Diesel
Refinery
Algae and Water
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Ponds
Ponds
Ponds
CO_2
CO_2
CO_2
Natural
Gas Plant

Pond Production Plan

1. 7 day cycle
2. Drain at night
3. Refill pond w/ ~85% old water
4. Pump rest to evaporation pond
5. Add ~15% reclaimed water

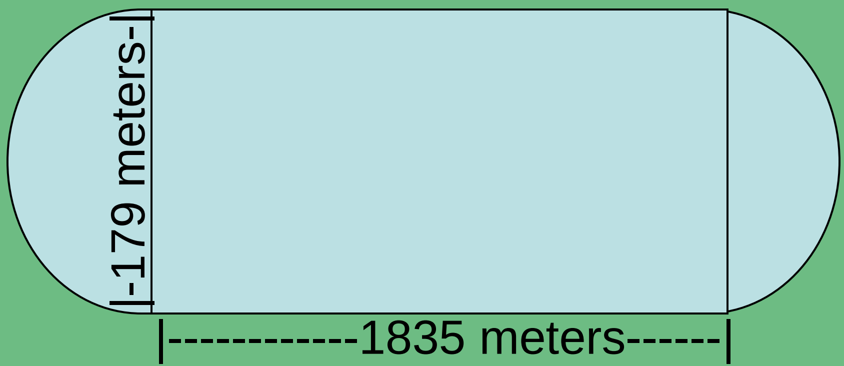
Ponds

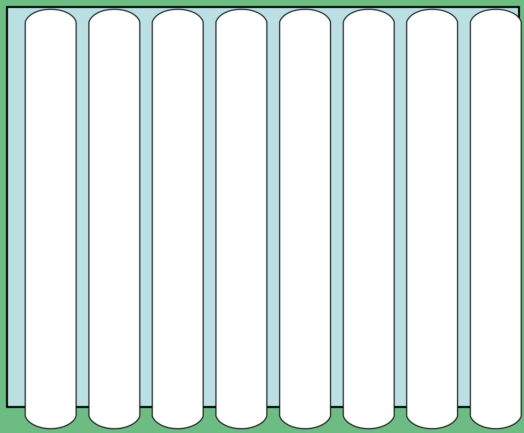
- Length = 1835 m
- Width = 179 m

- Based on 1 mile^2

(*8 ponds to per mile^2*)

  - 7 ponds for growth
  - 1 pond for cyclic process

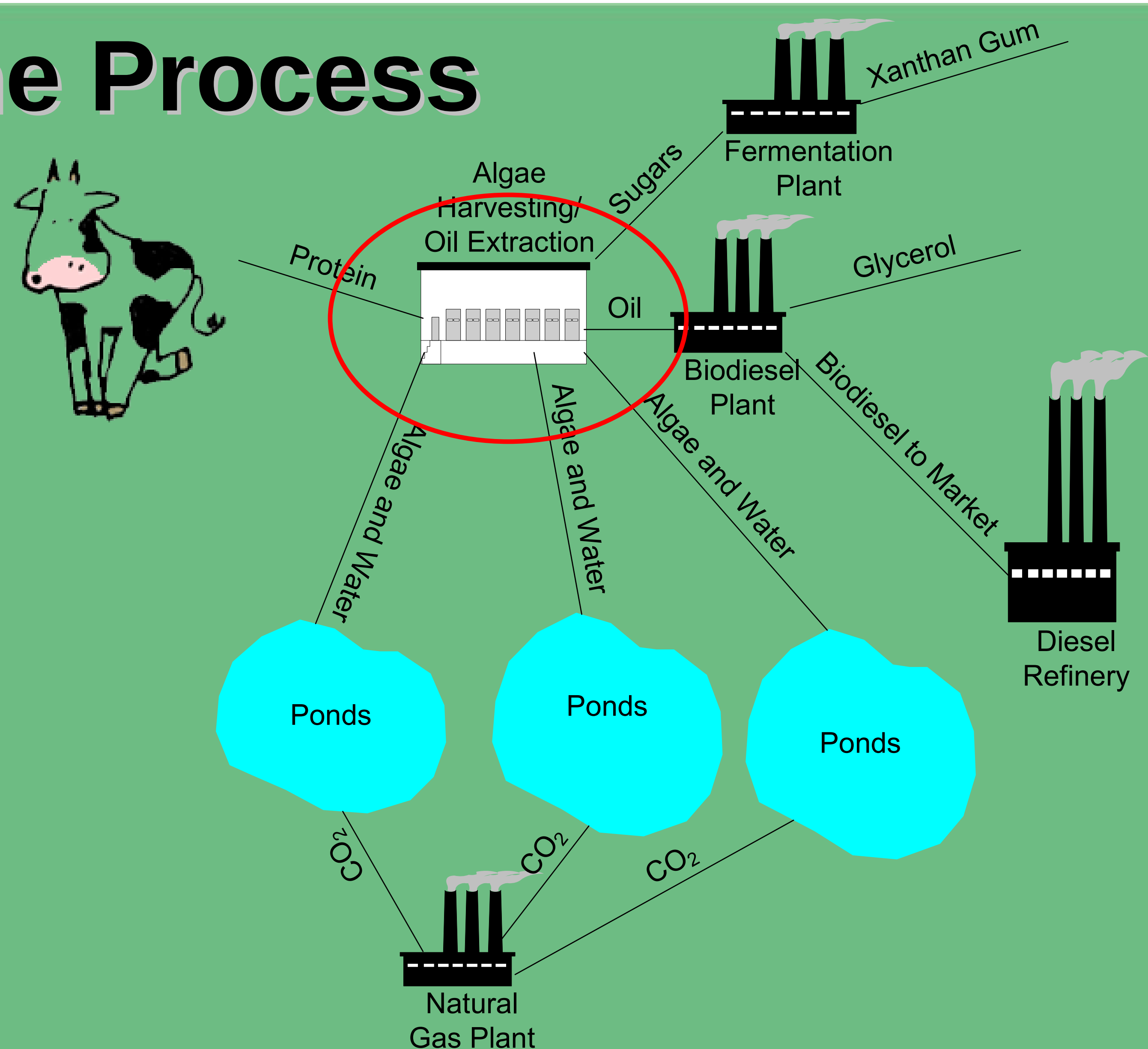




Ponds

- Evaporation Ponds
  - According to NREL
    - West Texas Region 1 cm water/day will evaporate
  - Brine Waste disposed at land fill $8/yd^3
  - Supplement with reclaimed water. $0.94/1000 gallons.

The Process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CO_2
CO_2
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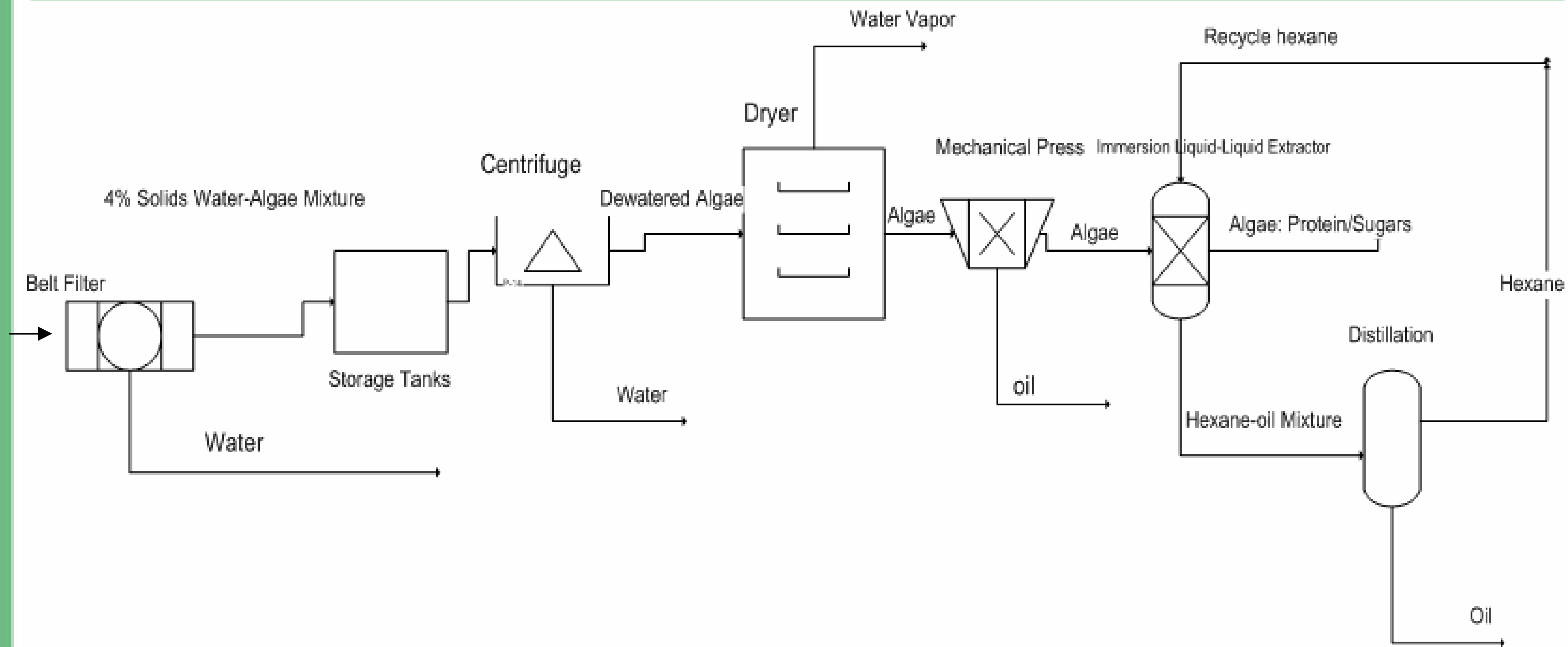
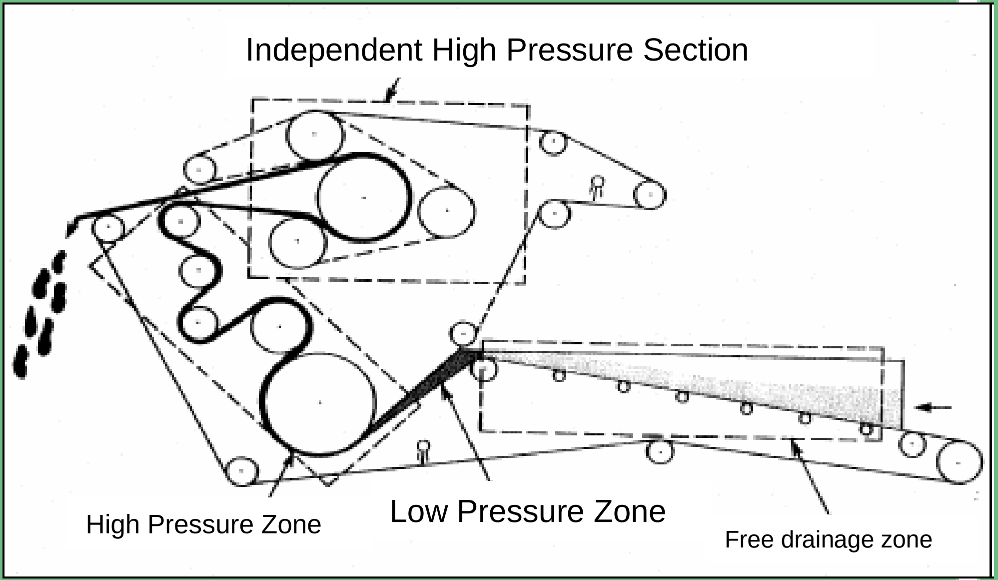
Natural Gas Plant

Harvesting / Oil Extraction



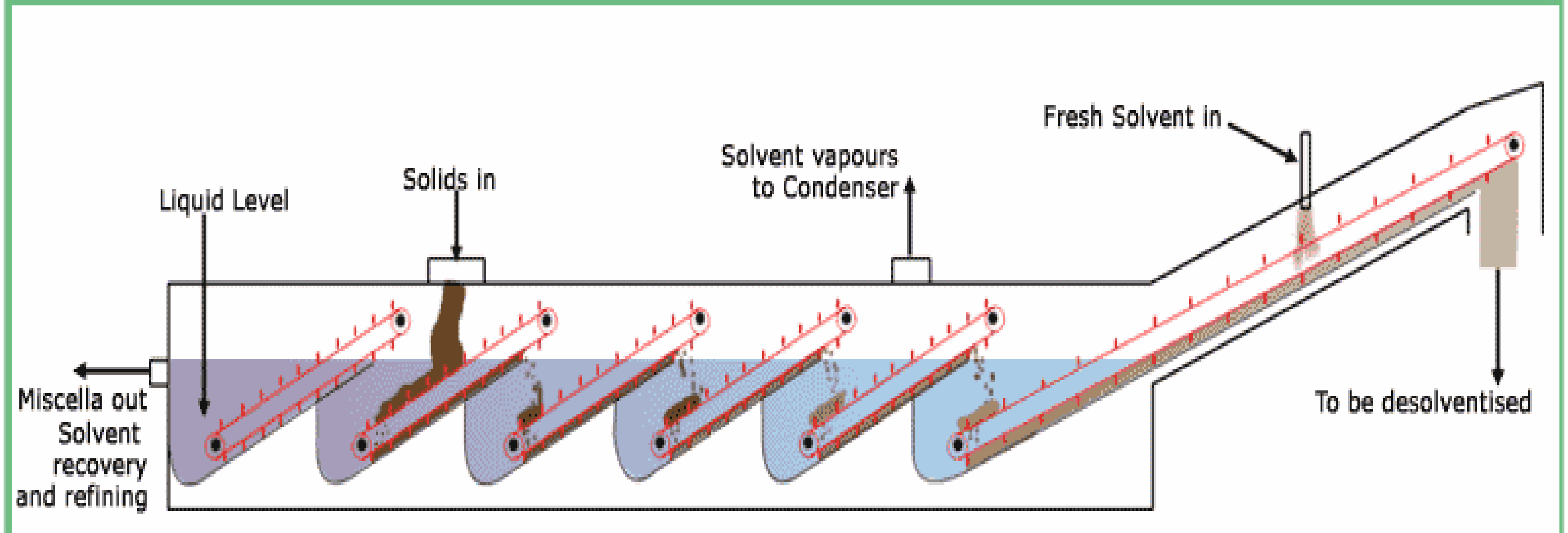
Harvesting

- Empty ponds overnight
- Belt Filtration
  (0.04 - 4% solids)
- Centrifuge
  (4% - 60% solids)
- Dryer
  (60% - 90% solids)



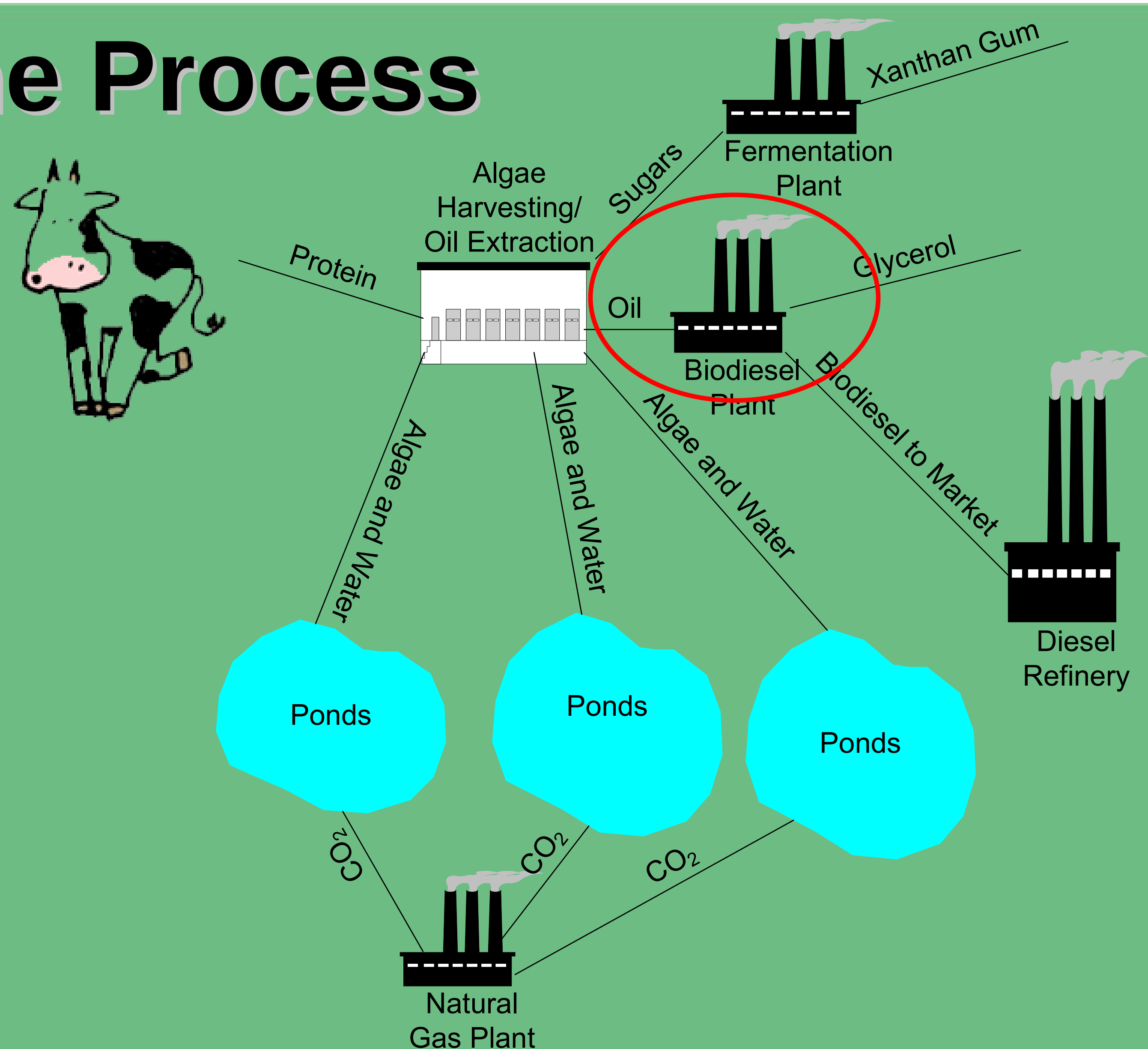
Belt Filtration

Oil Extraction



- Mechanical press yields 70% oil
- Immersion extractor w/ hexane yields 95-99% oil

The Process



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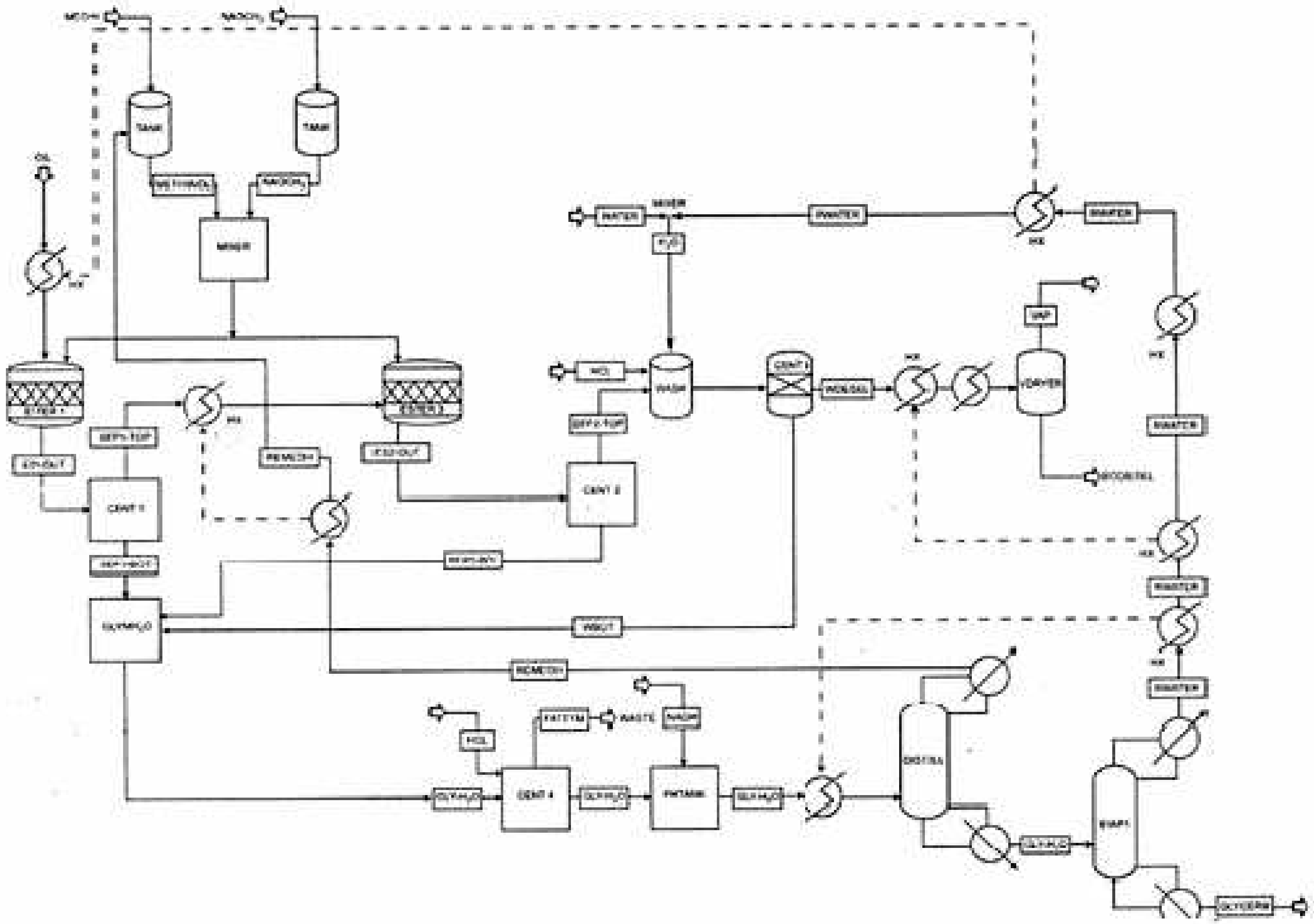
Transesterification



A process model to estimate biodiesel production costs (Michael J. Haas, Andrew J. McAloon, et al)

Transesterification

- Base Catalyzed Reaction Model
- KOH as catalyst; interchangeable w/ NaOH
- MeOH = cheap, eases separation
- 6:1 ratio of MeOH to triglyceride
  - Highest yield
  - Actual stoichiometry is 3:1
- 90% conversion assume in each reactor
- Yields 99% total conversion

Kinetics

Three reactions that compose transesterifcation

*Tri-tryglyceride, Di-diglyceride, Mono-monoglyceride, MeOH-methanol, R_1-methy ester 1, R_2-methyl ester 2, R_3-methyl ester 3

$$Tri + MeOH \Leftrightarrow Di + R_1$$

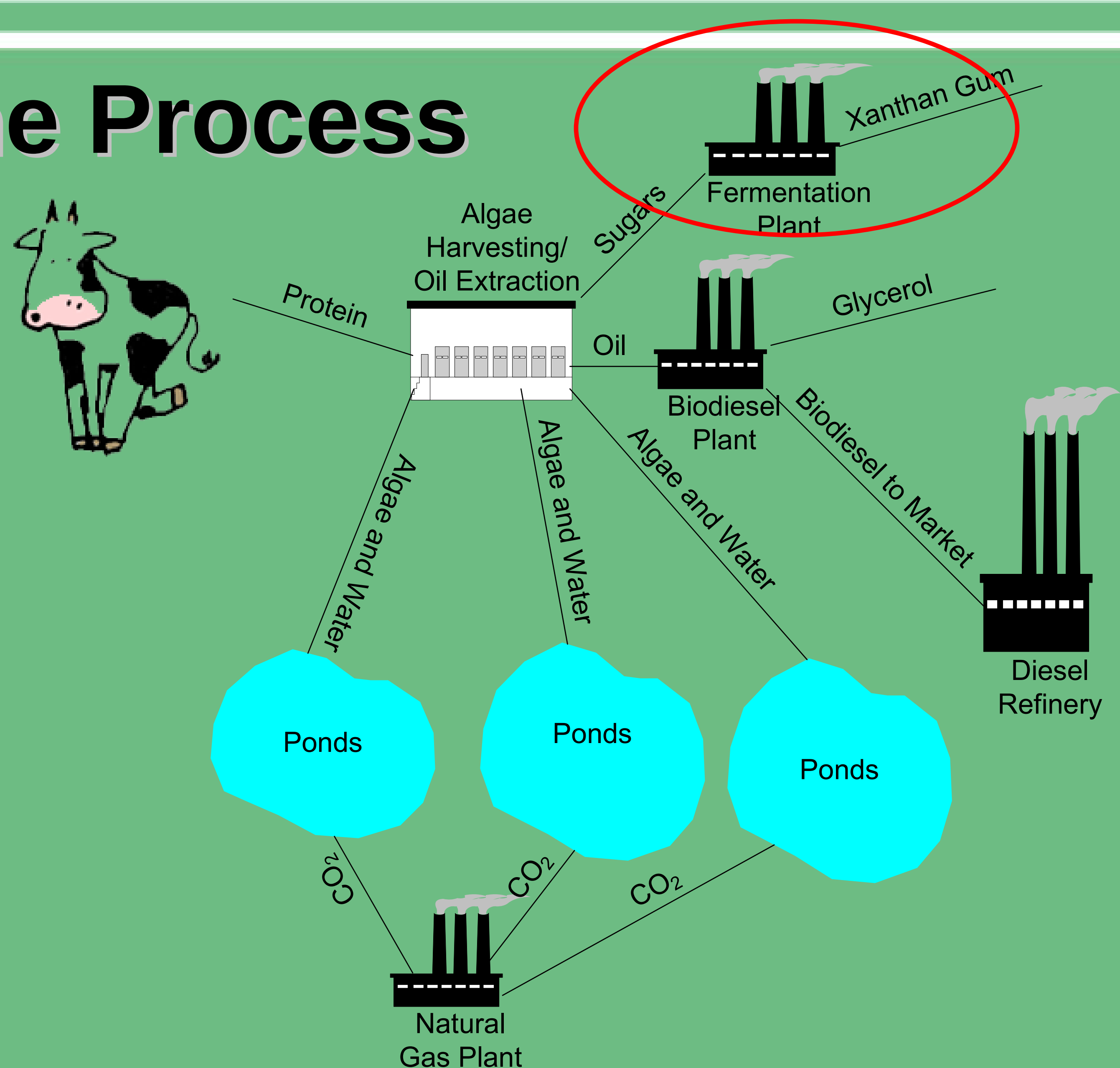
$$Di + MeOH \Leftrightarrow Mono + R_2$$

$$Mono + MeOH \Leftrightarrow Glycerol + R_3$$

Mole Balance on Triglyceride Reaction

$$0 = F_{Tri0} - (F_{Tri0} - \xi_1)$$
$$+V[-k_1(F_{Tri0} - \xi_1)/\upsilon * (F_{MeOH} - \xi_1 - \xi_2 - \xi_3)/\upsilon$$
$$+k_2(F_{Di0} + \xi_1 - \xi_2)/\upsilon * (F_{R1} + \xi_1)/\upsilon]$$

The Process



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Byproducts

- What are we going to do with the biomass?
  - Pyrolysis of biomass
    - Yields bio-oil, charcoal, and flue gas
  - Fermentation of carbohydrates / sell protein
    - Yields a multitude products
- Glycerol produced during transesterfication

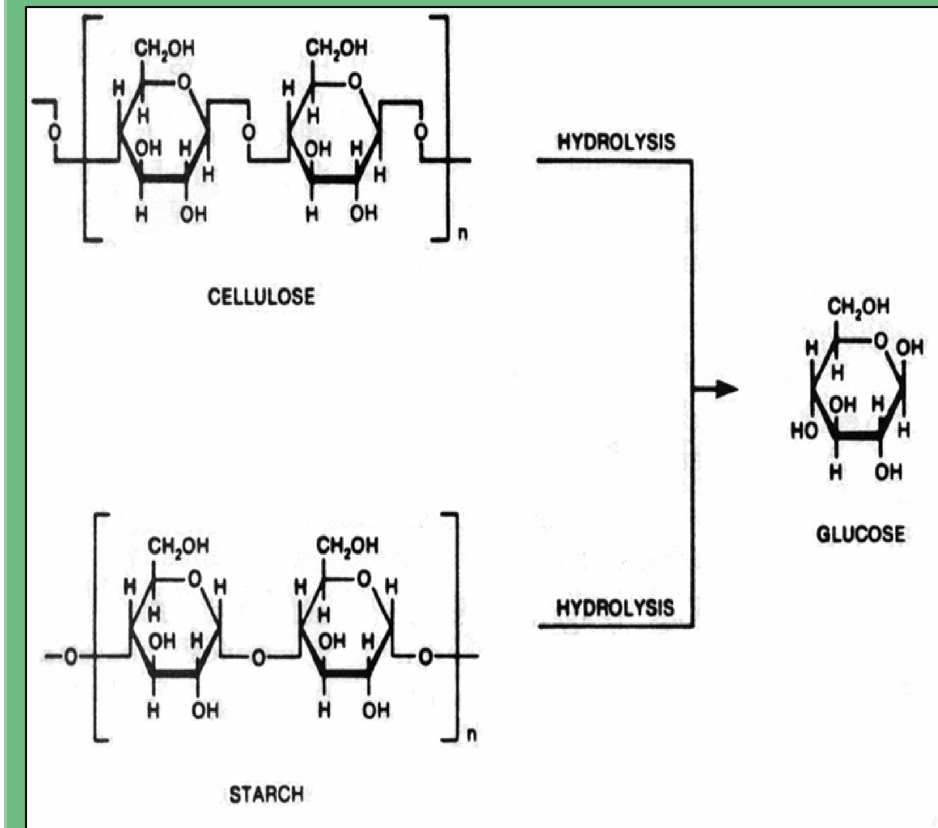
Pyrolysis of Biomass

- Produces Bio-oil (*Don't know its composition)*
  - Burns at half the heating value of diesel
  - Stability questioned
  - Acidic

- Questionable Market
  - $ 2 MM / yr for 100 tpd facility *(Dynamotive)*

- Algae contain very small amounts of lignin, an important constituent in the pyrolysis process

Acid Hydrolysis of Biomass

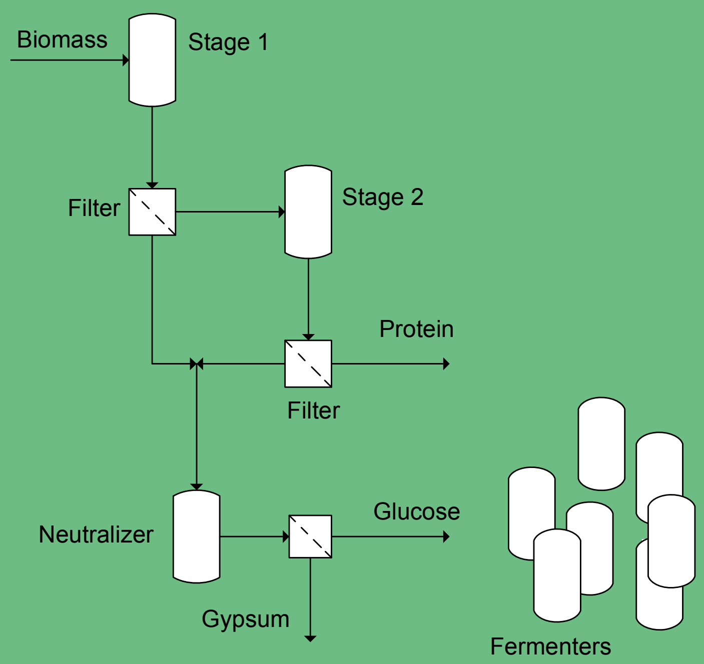


- Increases glucose yield
- Low concentration acids and high temperatures to process the cellulosic biomass

Two Stage Acid Hydrolysis

- **Stage 1:**
  - Targets hemicellulose
  - 0.7% sulfuric acid
  - 190°C

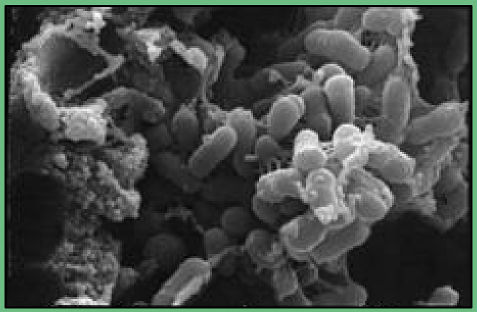
- **Stage 2:**
  - Targets cellulose
  - 0.4% sulfuric acid
  - 215°C



Fermentations

- Succinic acid w/ *Escherichia coli*
  - – 59 hour fermentation
  - – 0.105 kg glucose/L
  - – 54 fermenters at 7 mi^2

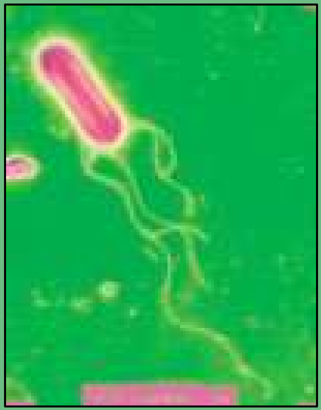
- Propionic acid w/ *Propionibacterium freudenreichii ssp. Shermanii*
  - – 148 hour fermentation
  - – 0.02 kg glucose/L
  - – 115 fermenters at 7 mi^2



$$\frac{(kg\_glucose/day)\left(\frac{hrs\_fermented}{24hrs}\right)}{1000(kg\_glucose/L)(m^3/fermenter)} = \#\_fermenters$$

Fermentations Cont.

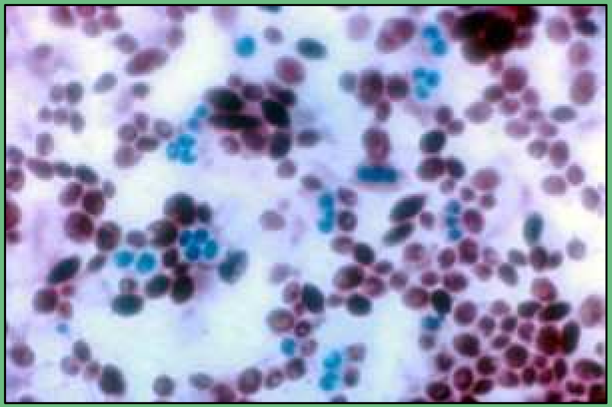
- 2,3-Butanediol w/ *Aerobacter aerogenes*
  - 0.195 kg glucose/L
  - 35 fermenters at 7 mi^2
  - 390 tons at $1.98/kg

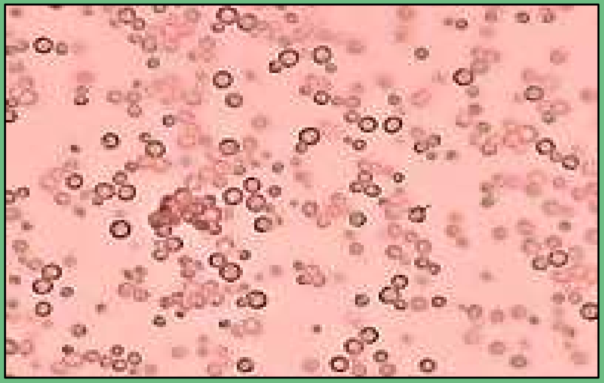


- Butyric acid w/ *Clostridium butyricum*
  - 48 hour fermentation
  - 0.016 kg glucose/L
  - 145 fermenters at 7 mi^2

Fermentation Cont.

- Ethanol w/ *Saccharomyces cerevisiae*
  - 18 - 94 hour fermentation
  - 0.05 - 0.2 kg glucose/L
  - 5.1 - 91.8 g ethanol/L
  - 16 fermenters at 7 mi^2
  - Selling price $1.91/gallon
  - 30,000 gallon/batch
  - $13 M/yr (revenue)





Hyaluronic Acid

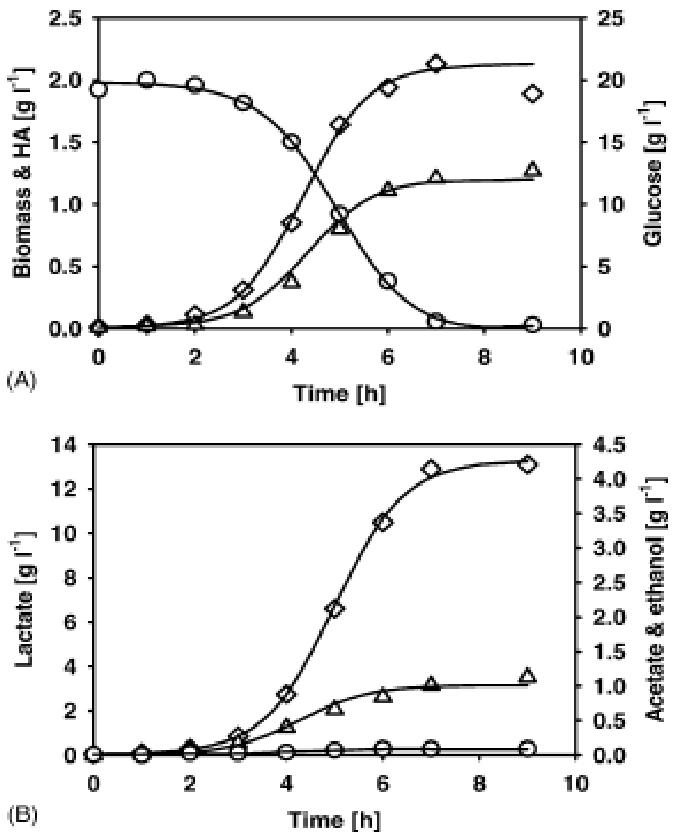


Fig. 3. Growth and product profiles for cells grown in an aerobic batch culture containing $20\,g\,l^{-1}$ glucose. The main metabolic products were lactic acid and acetic acid. HA was produced in a growth-associated manner until the glucose was depleted.

- **Low temperatures (28^{o}C) and high glucose concentration (40 g/L)**
- **Hyaluronic acid $100,000 / kg**
- **Small market requires extreme purity**

*Aerobic cultivation of *Streptococcus zooepidemicus* and the role of NADH oxidase
Barrie Fong Chong, Lars K. Nielsen

Xanthan Gum

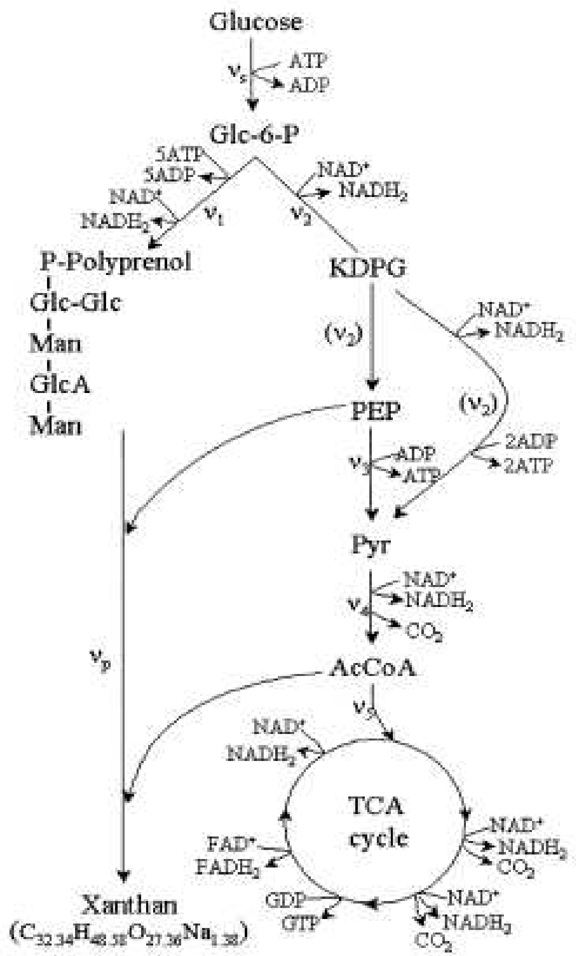


Fig. 2. Simplified metabolic network of xanthan synthesis for *campestris*.

Characterization of xanthan gum biosynthesis in a centrifugal, packed-bed reactor using metabolic flux analysis
Chia-Hua Hsu, Y. Martin Lo

Xanthan Gum: $ 11 / kg
Market volume: 40 – 50 M tons/yr

Multiple industries:
Food: Beverages, Dairy, Sauces, Meats, Frozen Deserts, Bakery

Consumer / Industrial: Cleaners, Oral Care, Paints, Cosmetics, Pharmaceutical, Printing

Oil: Mud's / Drilling Fluids

Paper:

http://www.apsnet.org/education/IntroPlantPath/Topics/plantdisease/images/fig07.jpg

Traditional Xanthan Fermentation

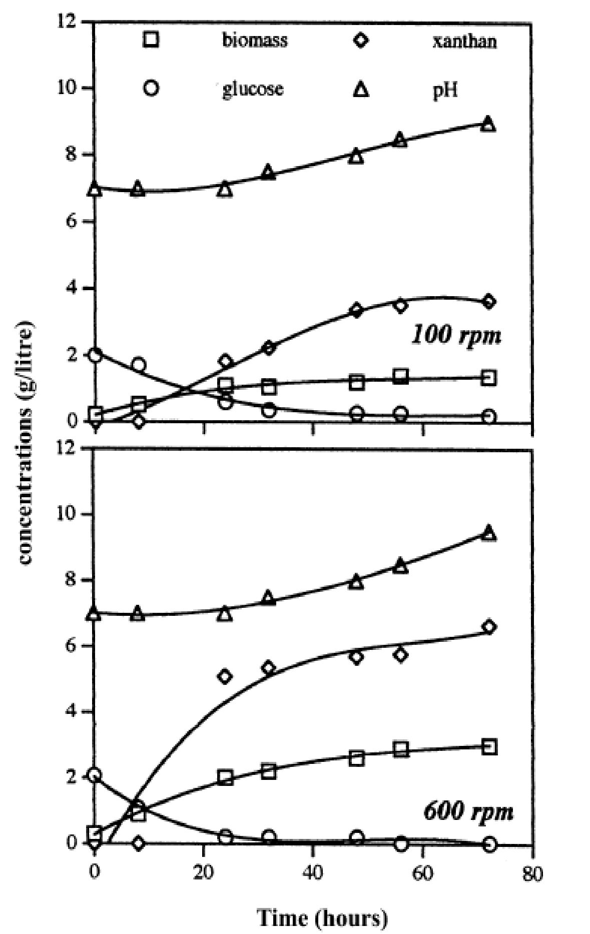


Fig. 1. Xanthan gum fermentation time-courses at 100 and 600 rpm.

- Production dependent upon mixing speed
- Aeration is an issue
- 72 hour fermentation
- 0.05 kg glucose/L
- 77 fermenters at 7 mi^2

Xanthan production by *Xanthomonas campestris* in batch cultures
M. Papagianni a, S.K. Psomas a, L. Batsilas a, S.V. Paras a, D.A. Kyriakidis b, M. Liakopoulou-Kyriakides

CPBR Xanthan Fermentation

- 24 hour fermentation
- 0.05 kg glucose/L
- 26 fermenters at 7 mi^2
- Repeatable fermentations once cells adsorbed
- Cell-free broth

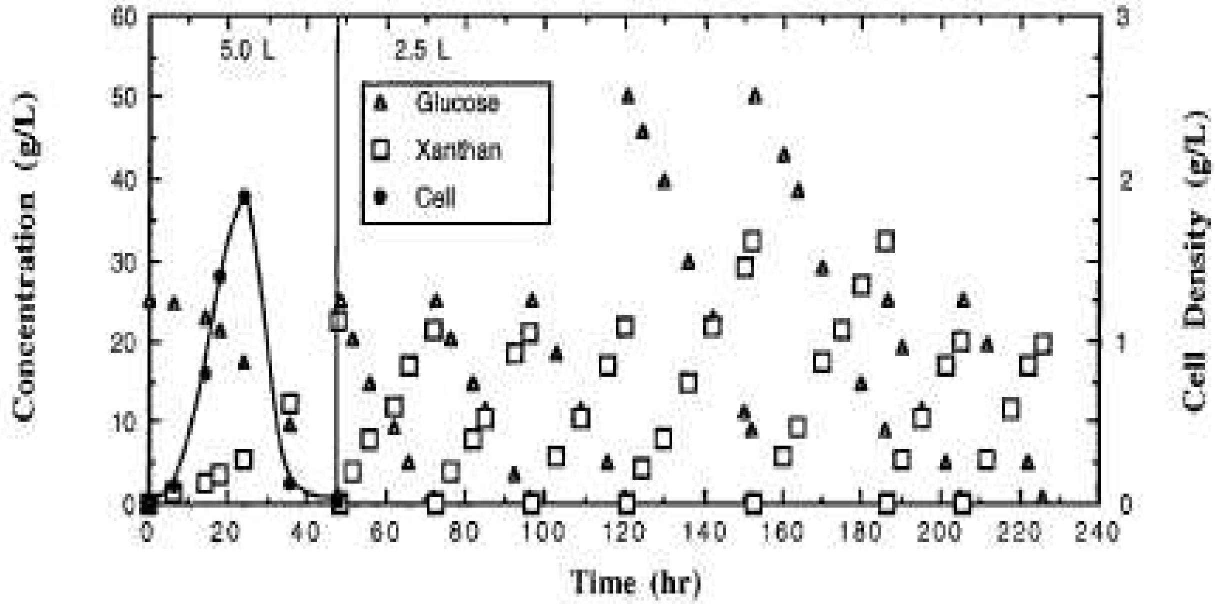


Figure 6. Fermentation time course data for repeated batch xanthan fermentations with CPBR at 350 rpm rotational speed for the fibrous bed under gas continuous condition (CPBR-GC).

Xanthan Gum Fermentation by *Xanthomonas campestris* Immobilized in a Novel Centrifugal Fibrous-Bed Bioreactor
Shang-Tian Yang, Yang-Ming Lo, and David B. Min

Centrifugal Packed Bed Reactor

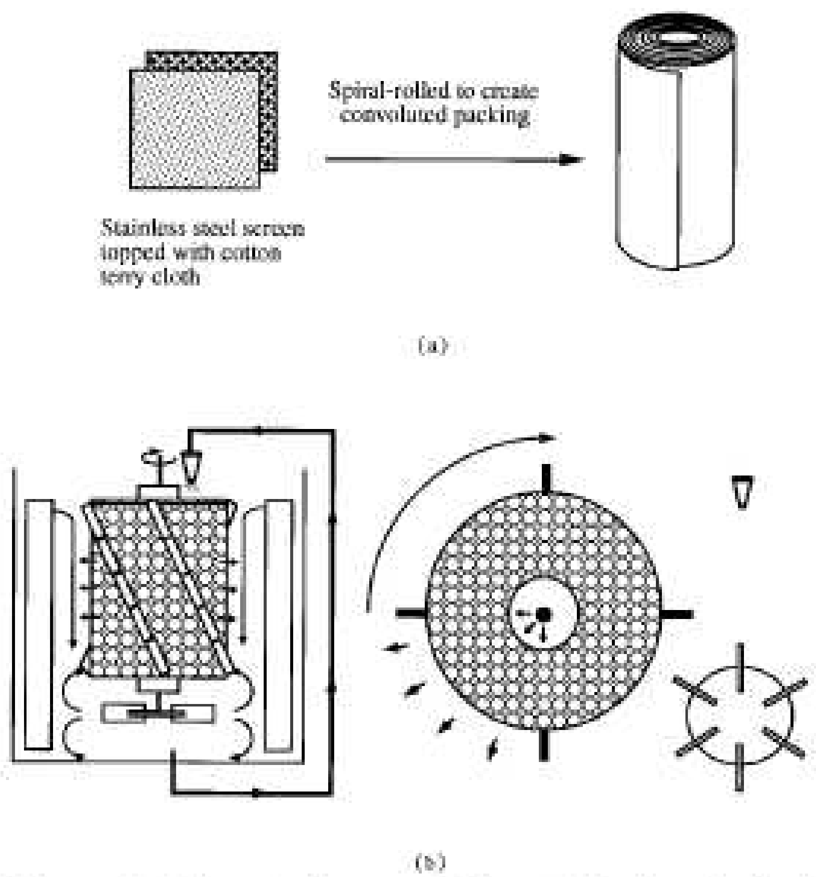


Figure 1. Schematic diagram of the centrifugal, packed-bed reactor (CPBR) for xanthan gum fermentation: (a) construction of fibrous matrix and (b) fluid flow pattern in the reactor.

- Improves the energy-intensive, low-yield process due to limited aeration
- Produces cell-free broth with elevated productivity

Xanthan Gum Fermentation by *Xanthomonas campestris* Immobilized in a Novel Centrifugal Fibrous-Bed Bioreactor
Shang-Tian Yang, Yang-Ming Lo, and David B. Min

http://www.vikingpump.com/products/rotary_lobe_pumps/images/LobePumpLarge.gif

Xanthan Production

- 4.4 tons xanthan gum / batch

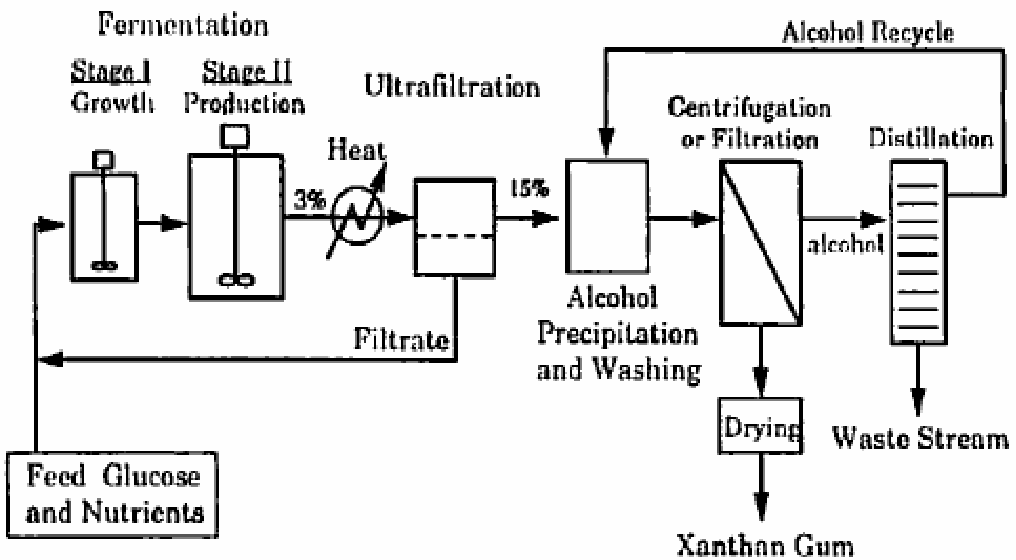


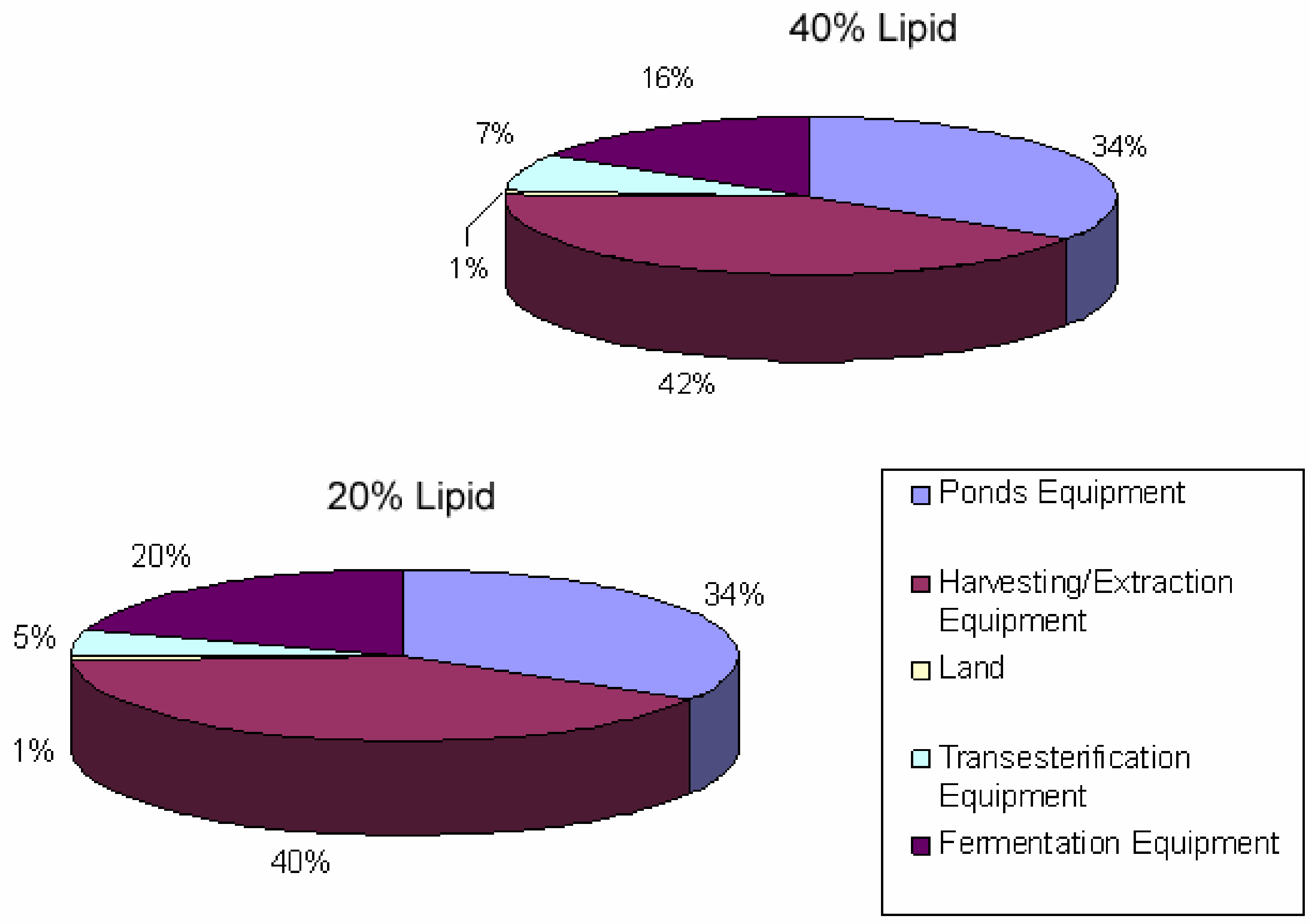
Fig. 1. A process flowsheet for xanthan gum production from fermentation, ultrafiltration and alcohol precipitation.

What to do with the glycerol?

- Foods and Beverages
  - Soft Drinks, Candies, Meat & Cheese Casings
- Drugs
  - Capsules, Suppositories, Lozenges, Gargles
- Cosmetics / Toiletries
  - Emollient (softening agent)
  - Moisturizer
- Tobacco
- Paper / Printing
- Textiles
  - Lubricant

Sell at $0.15/lb

Cost Breakdown



Economics

Option	Lipid Content	TCI	FCI	NPW	ROI
A	20%	574,000,000	488,000,000	-304,000,000	-53%
	30%	569,000,000	484,000,000	-329,000,000	-58%
	40%	563,000,000	479,000,000	-336,000,000	-60%
B	20%	364,000,000	309,000,000	113,000,000	31%
	30%	362,000,000	308,000,000	47,000,000	13%
	40%	359,000,000	306,000,000	24,000,000	7%

- Biodiesel: $2.00/gallon
- Payout Time
  - Option B : 5 - 7

Pricing

Cost B20 =

%Diesel * Production * Cost

+ %BioDiesel * Production * (Cost – α)

ΔProfit =

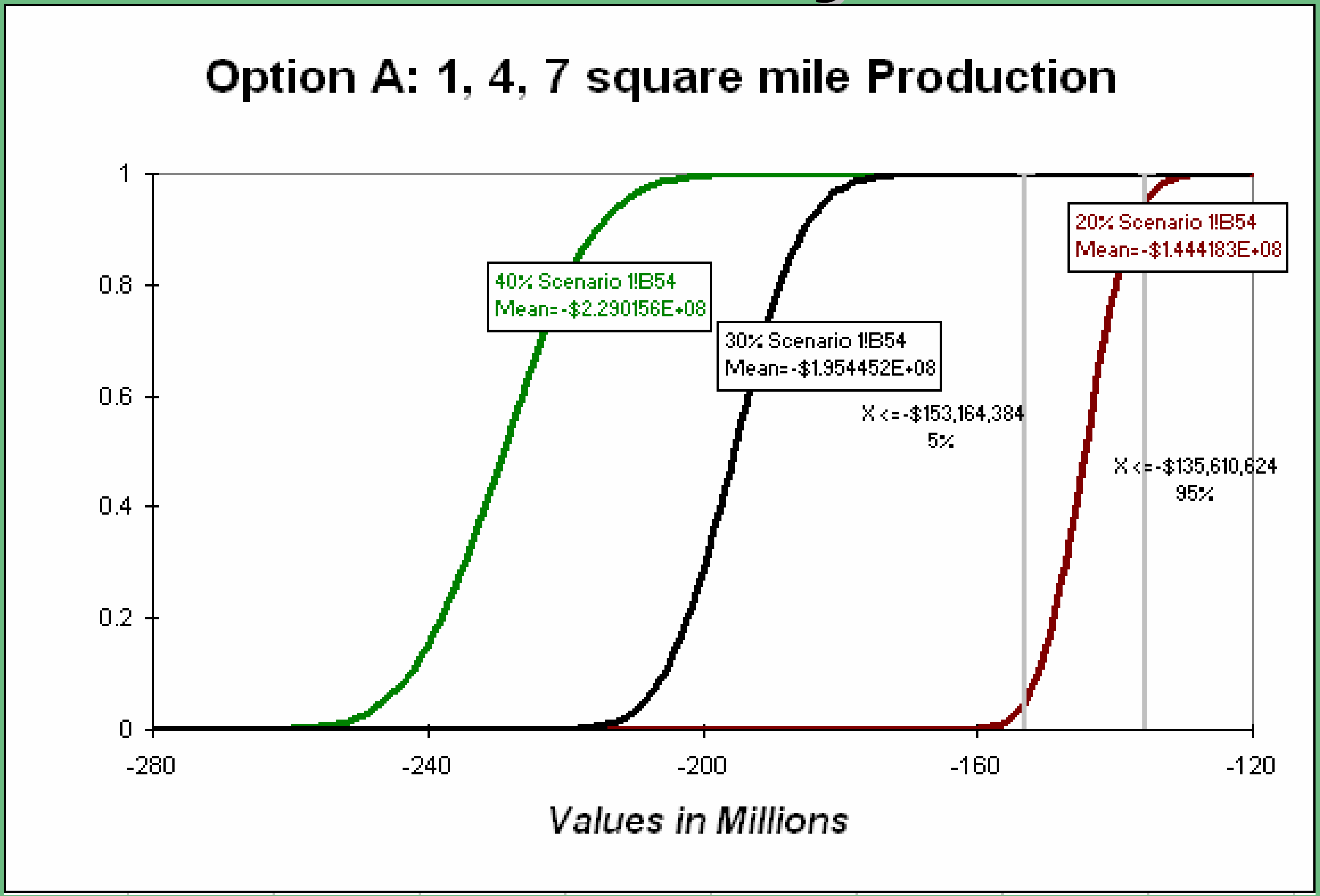
Production * (Selling Price – Cost B20)

– Production * (Selling Price – Cost)

Solved for α such that their equipment costs are paid off in one year (α = .05)

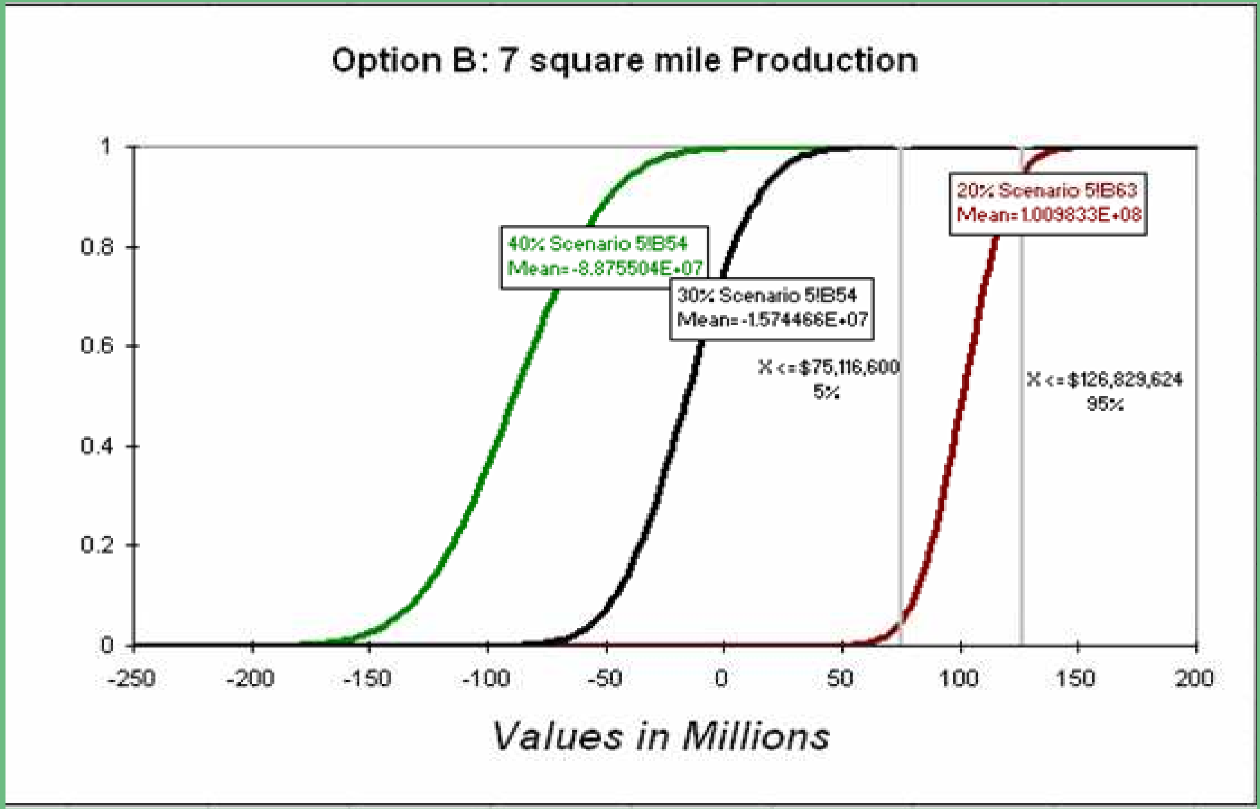
Sell to biodiesel to refinery for B20 (20% Biodiesel) blend $0.72/gallon

Risk Analysis



- Risk Curves, and Minimax
- Explain high TCI and low ROI

Risk



- The risk is extremely large since everything relies on production of algae.
  - Cold weather
  - Alternative algae take over
  - High Cost of Making Ponds and Harvesting Algae
  - Overall high TCI and long payout time
- Varied Selling price of Biodiesel

Price Effects

		Net Present Worth (15 years)			
	Selling Price of Biodiesel	$0.72	$1.50	$2	$3.14
Option A	20% Lipid	-$356,000,000	-$324,000,000	-$304,000,000	-$257,220,000
	30% Lipid	-$407,000,000	-$359,000,000	-$329,000,000	-$258,950,000
	40% Lipid	-$440,000,000	-$377,000,000	-$336,000,000	-$243,200,000
Option B	20% Lipid	$13,000,000	74,000,000	$113,000,000	$202,800,000
	30% Lipid	-$104,000,000	-12,000,000	$47,000,000	$181,100,000
	40% Lipid	-$177,000,000	-55,000,000	$24,000,000	$203,200,000

- As biodiesel price increases NPW goes up
- $3.14/gallon biodiesel becomes more profitable than byproduct fermentation
- $9.50/gallon Option A becomes Profitable

Conclusion

- Algae
  - Good source for oil
  - High Cost Harvesting
  - High TCI
  - Profitable but risky
  - Further research is necessary to make the process more economically feasible

Recommendations

- Evaluate algae types with onsite experimentation
- Explore the cost of bioreactors with the rising diesel prices
- Explore more economical ways of harvesting
- Utilize Tax Incentives

BIODIESEL

Questions?