Developing and Integrating Sustainable Chemical Processes into Existing Petro-Chemical Plant Complexes

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Outline

- Introduction to Sustainable Development
- Research Vision
- Biomass conversion processes, Aspen HYSYS 2006® designs, Aspen ICARUS Process Evaluator 2006® cost estimations
- Integration of biotechnology in existing plant complex
- Conclusions

Sustainability

Sustainability refers to integrating development in three aspects

- Economic
- Environmental
- Societal

There are numerous approaches to attempt an integration of these aspects by world organizations, countries and industries.

Corporate Sustainability

- A company's success depends on maximizing the profit as expressed below.

Profit = Σ Product Sales – Σ Raw Material Costs – Σ Energy Costs

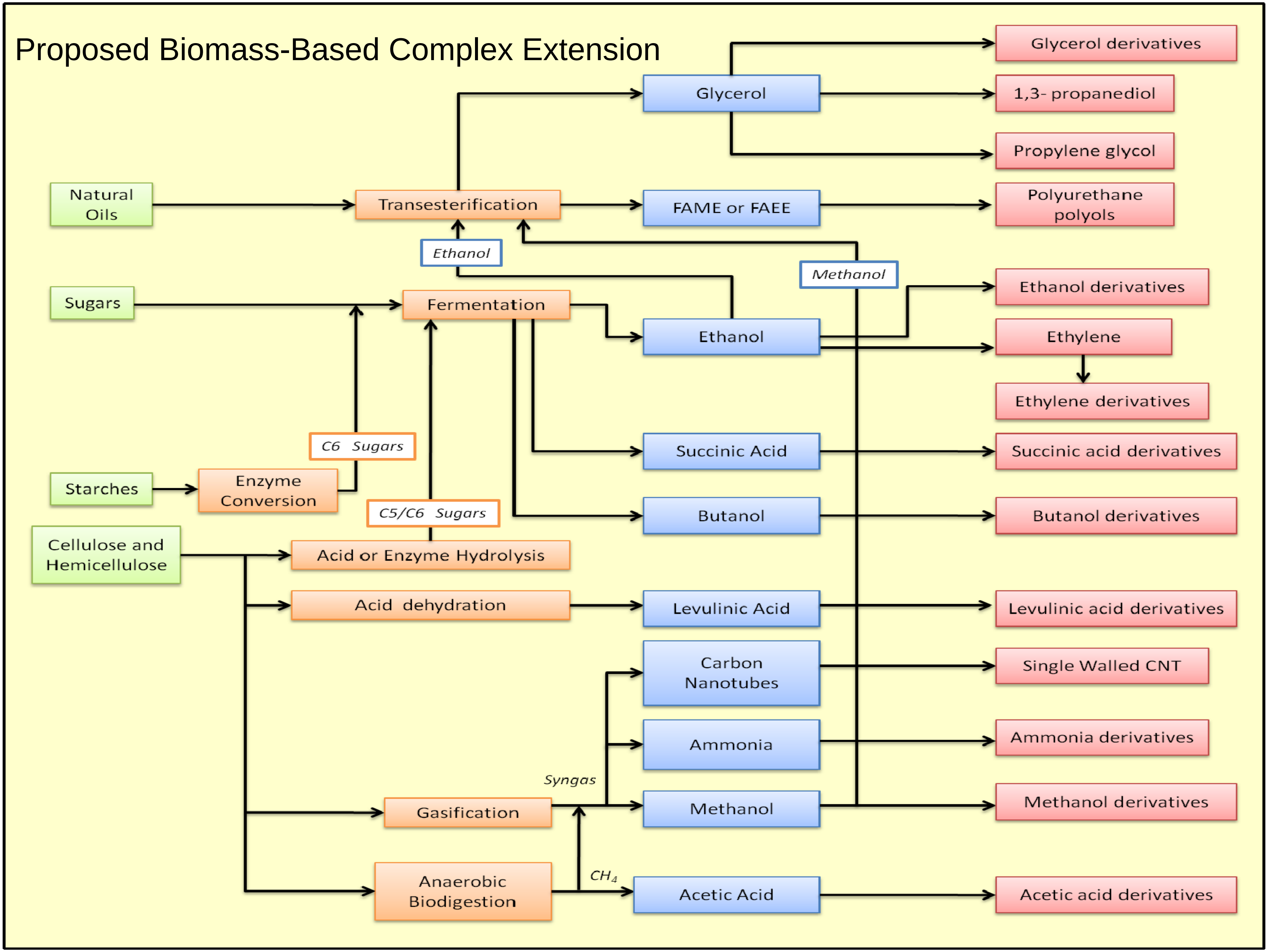
- The profit equation above can be expanded to meet the **"Triple Bottomline"** criteria of sustainability.
- This will incorporate the economic costs expanded to environmental costs and societal costs (also referred to as the sustainable or sustainability costs)

Triple Bottom Line = Σ Product Sales + Σ Sustainable Credits
– Σ Raw Material Costs – Σ Energy Costs
– Σ Environmental Costs – Σ Sustainable Costs

Triple Bottom Line = Profit – Σ Environmental Costs + Σ Sustainable (Credits – Costs)

Research Vision

- Propose a **biomass based chemical industry** in the chemical production complex in the Gulf Coast Region and the Lower Mississippi River Corridor.
- Utilize **carbon dioxide** from all processes in the complex to make chemicals and produce algae for biomass feedstock.
- Assign costs to the **Triple Bottomline Equation** components.
- Propose a **Mixed Integer Non-Linear Programming** problem to maximize the Triple Bottomline based on constraints: multiplant material and energy balances, product demand, raw material availability, and plant capacities
- Use **Chemical Complex Analysis System** to obtain Pareto optimal solutions to the MINLP problem
- Use Monte Carlo simulations to determine **sensitivity** of optimal solution


Proposed Biomass-Based Complex Extension
Natural Oils
Sugars
Starches
Cellulose and Hemicellulose
Transesterification
Fermentation
Enzyme Conversion
C6 Sugars
C5/C6 Sugars
Acid or Enzyme Hydrolysis
Acid dehydration
Gasification
Anaerobic Biodigestion
Syngas
CH4
Ethanol
Methanol
Glycerol
FAME or FAEE
Ethanol
Succinic Acid
Butanol
Levulinic Acid
Carbon Nanotubes
Ammonia
Methanol
Acetic Acid
Glycerol derivatives
1,3- propanediol
Propylene glycol
Polyurethane polyols
Ethanol derivatives
Ethylene
Ethylene derivatives
Succinic acid derivatives
Butanol derivatives
Levulinic acid derivatives
Single Walled CNT
Ammonia derivatives
Methanol derivatives
Acetic acid derivatives

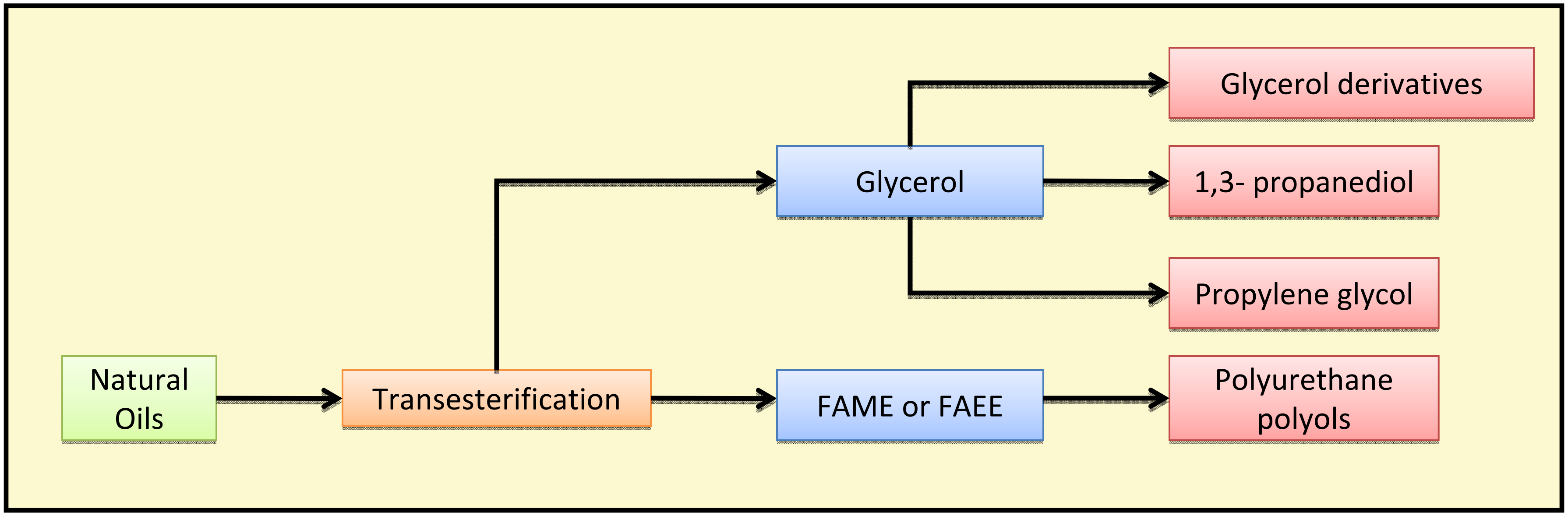
Biomass Processes

The following biomass conversion processes are considered for integration into the chemical complex superstructure:

- Fermentation
- Anaerobic digestion
- Transesterification
- Gasification
- Direct conversion of plant oils

Pretreatment of biomass is necessary before any of the biomass conversion processes.

Transesterification



– Transesterification process is the treatment of vegetable oil with an alcohol and a catalyst to produce esters and glycerol.

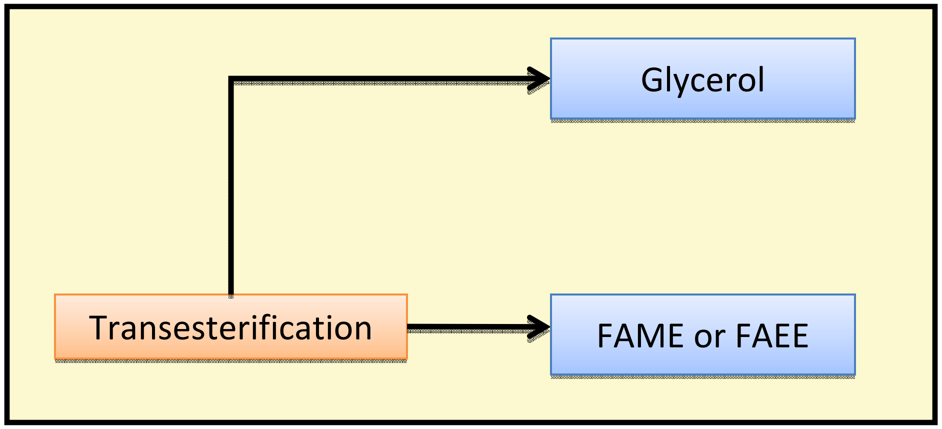
– Methanol or ethanol is used as alcohol for fatty acid methyl or ethyl esters (FAME/FAEE).

– These esters can be transformed to chemicals.

– Glycerol is produced ~ 10% by weight in the process.

– Glycerol can be introduced to the propylene chain

HYSYS Design of Transesterification



Transesterification	
Thermodynamic model	UNIQUAC
Reactants	Methanol Soybean Oil
Catalyst	1.78% (w/w) Sodium Methylate in methanol
Products	Methyl Ester Glycerol
Temperature	60°C
Methyl Ester Purification	
Wash agents	Water HCl
Glycerol Recovery and Purification	
Purification Agents	NaOH Water HCl

- The design is divided into three sections
  - Transesterification reaction
  - Methyl ester purification
  - Glycerol recovery and purification
- 10 million gallons per year [1] of Fatty Acid Methyl Ester (FAME) produced
- FAME is utilized in manufacture of polymers
- Glycerol is used in manufacture of propylene glycol
- Further work includes evaluation in feedstock changes, e.g. Algae oil

[1] *Design based on Super-Pro Designer model obtained from M.J. Haas et al., Bioresource Technology 97 (2006) 671-678*

HYSYS Design of Transesterification

Material Balance

Inlet Material Streams	Mass Flow (kg/hr)	Outlet Material Streams	Mass Flow (kg/hr)
Methanol	612	FAME	4260
Catalyst	133	Glycerol	393
Soybean oil	4250	Water	349
HCL	345	Sodium-chloride	177
Water (wash)	166	Methanol	223
NaOH	21		

Energy Balance

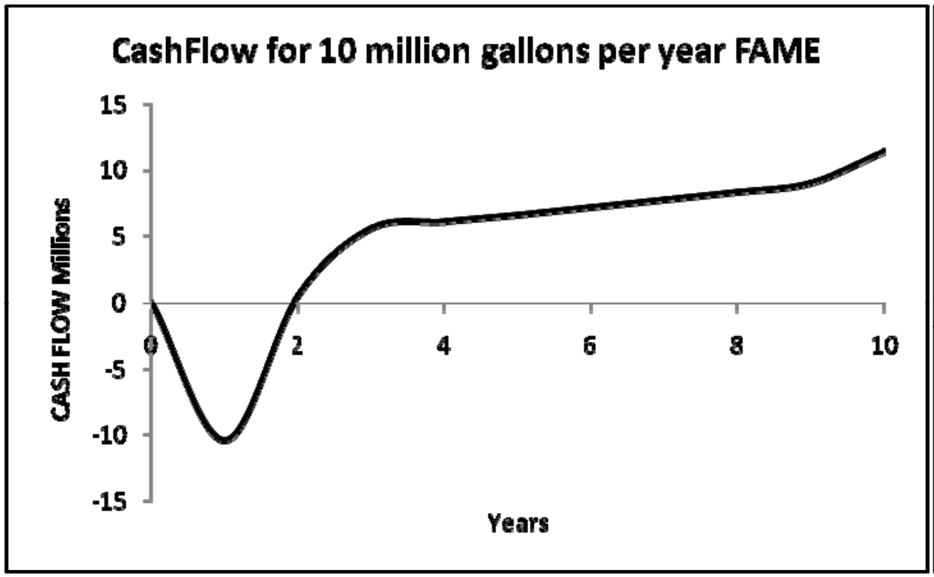
	Energy Flow (kJ/hr)	Type	Required (kg/hr)
Energy Required	25×10^5	HP Steam 47 bar, 260°C	1,500
Energy Liberated	40×10^5	Cooling water	47,900

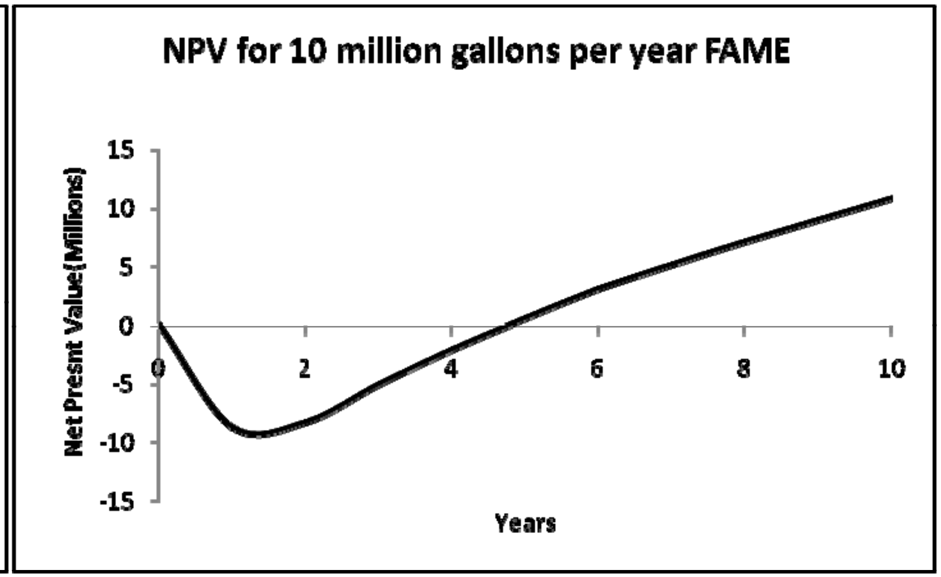
ICARUS Process Evaluator Economic Analysis of Transesterification

Economic Analysis		
Economic Life	10	Years
Plant Capacity	9,277,000	GALLONS/Year Methyl Ester @ 3.000 USD/GALLONS
Total Project Capital Cost	6,795,000	USD
Total Operating Cost	21,000,000	USD/Year
Total Raw Materials Cost	18,000,000	USD/Year
Total Utilities Cost	128,000	USD/Year
Total Product Sales	28,000,000	USD/Year
Desired Rate of Return	20	Percent/Year
Net Present Value	12,000,000	USD
P.O. Period	4.75	Year

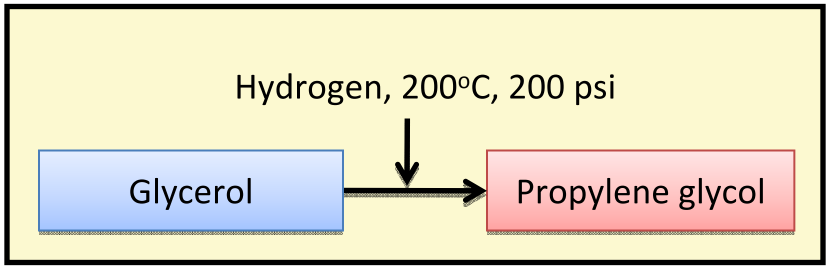
Cash Flow and Net Present Value

Time	0	1	2	3	4	5	6	7	8	9	10
CF (CashFlow for Project) Cost/Period ($ 10^6)	0	-10.41	0.58	5.65	6.14	6.66	7.21	7.79	8.42	9.09	11.49
NPV (Net Present Value) Cost/Period ($ 10^6)	0	-8.68	-8.27	-5.00	-2.04	0.64	3.05	5.23	7.19	8.95	10.81





HYSYS Design of Propylene Glycol



- The design is based on a low pressure (200 psi) and temperature (200°C) process for hydrogenation of glycerol to propylene glycol [1]
- 65,000 metric ton of propylene glycol is produced per year[2]

Hydrogenolysis	
Thermodynamic model	UNIQUAC
Reactants	Glycerol Hydrogen
Catalyst	Copper Chromite
Products	Propylene Glycol Water
Temperature	200°C
Pressure	200 psi

[1] *Design based on experimental results from* Dasari, M. A. et al. 2005, A*pplied Catalysis, A: General*, Vol. 281, p. 225-231.
[2] *Capacity based on Ashland/Cargill joint venture of process converting glycerol to propylene glycol*

HYSYS Design of Propylene Glycol

Material Balance

Inlet Material Streams	Mass Flow (kg/hr)	Outlet Material Streams	Mass Flow (kg/hr)
Glycerol	20,300	Propylene Glycol	9,130
Hydrogen	242	Water Vapor	3,150
Catalyst	1,060	Unreacted glycerol	9,210
Water	991		

Energy Balance

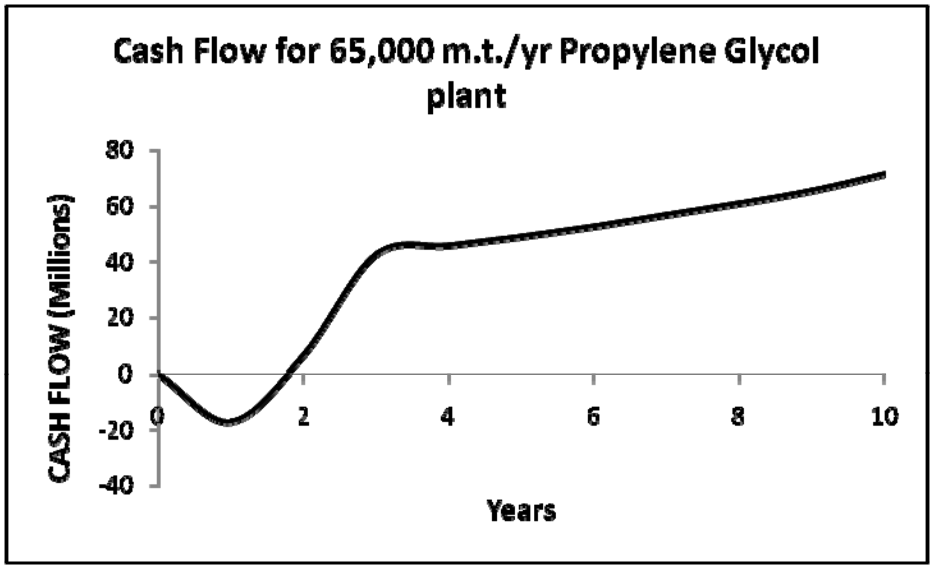
	Energy Flow (kJ/hr)	Type	Required (kg/hr)
Energy Required	302×10^5	HP Steam 47 bar, 260°C	18,200
Energy Liberated	276×10^5	Cooling water	330,000

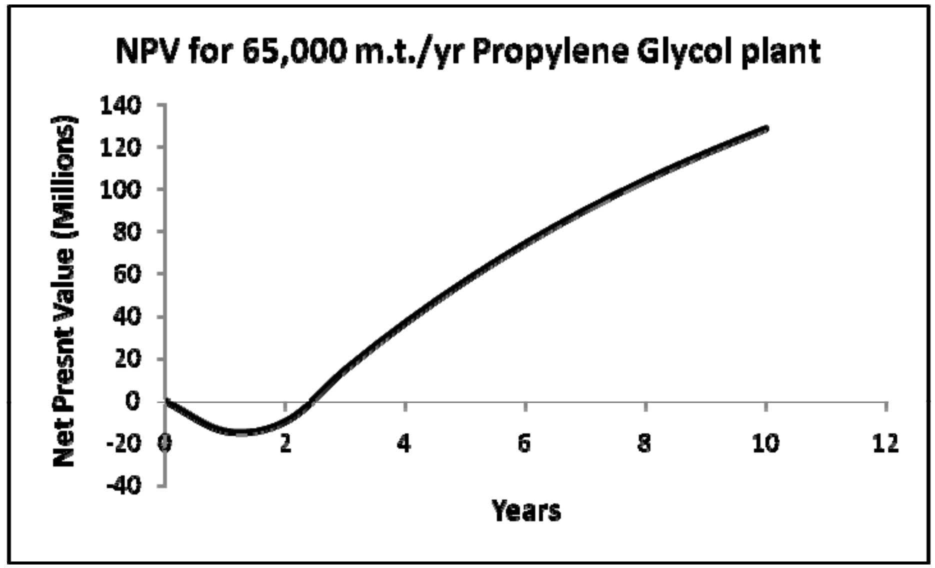
ICARUS Process Evaluator Economic Analysis of Propylene Glycol

Economic Analysis		
Project Duration	10	Years
Plant Capacity	145,000,000	LB/Year propylene glycol @ 0.815 USD/LB
Total Project Capital Cost	5,180,000	USD
Total Operating Cost	113,000,000	USD/Year
Total Raw Materials Cost	102,000,000	USD/Year
Total Utilities Cost	1,540,000	USD/Year
Total Product Sales	169,000,000	USD/Year
Desired Rate of Return	20	Percent/Year
Net Present Value	602,000,000	USD
P.O. Period	2.38	Year

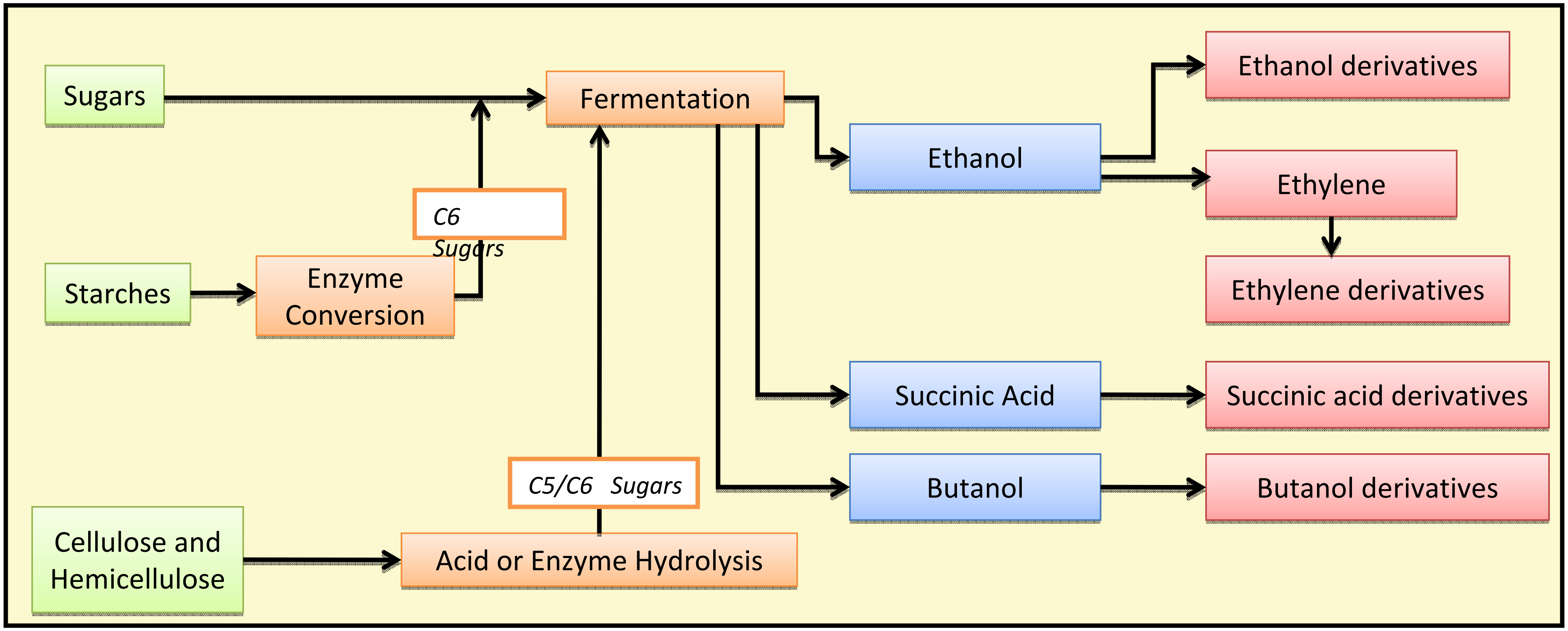
Cash Flow and Net Present Value

Time	0	1	2	3	4	5	6	7	8	9	10
CF (CashFlow for Project) Cost/Period ($ 10^6)	0	-16.98	7.03	42.39	45.65	49.09	52.77	56.66	60.79	65.18	71.12
NPV (Net Present Value) Cost/Period ($ 10^6)	0	-14.15	-9.27	15.25	37.27	57.00	74,.67	90.48	104.62	117.25	128.74





Fermentation



Fermentation is the enzyme-catalyzed transformation of an organic compound.

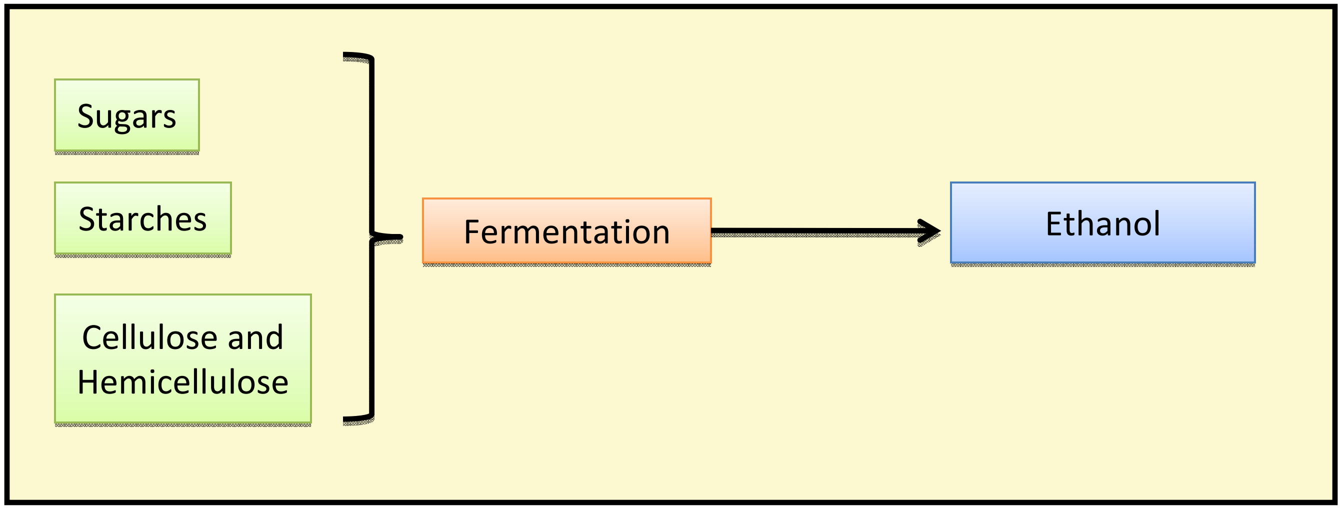
Fermentation enzymes react with hexose and pentose to form products.

Enzyme selection determines product :-

- *Saccharomyces Cervisiae* (C6), *Escherichia coli* (C5 & C6), *Zymomonas mobilis* (C6)– Ethanol
- Engineered *Eschericia coli, A. succiniciproducens* – Succinic Acid
- Engineeried microorganism - Butanol
- Lactic Acid Producing Bacteria (LAB) – Lactic Acid

Ethanol from fermentation can be converted to ethylene and introduced into the ethylene chain.

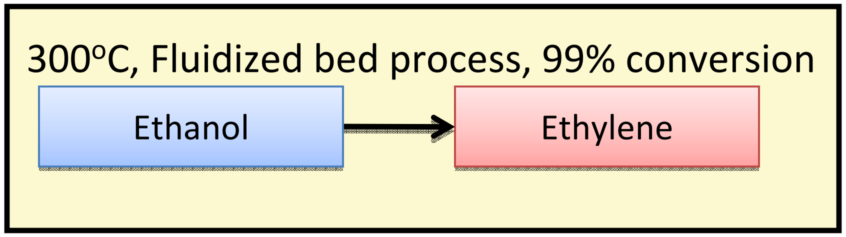
Design of Fermentation



- The design is based on NREL's[1] lignocellulosic biomass to ethanol process design which converts 2000 m.t./day of corn stover.
- Use of different feedstock are being evaluated.

[1] *Design based on results from* Aden A. et al., NREL/TP-510-32438, National Renewable Energy Laboratory, Golden, CO, (June 2002)

HYSYS design of Ethylene



- Design is based on dehydrogenation of ethanol to ethylene[1]
- The capacity of the plant is based on a 200,000 m.t./yr ethylene production facility proposed by Braskem in Brazil[2]

Dehydrogenation	
Thermodynamic model	UNIQUAC
Reactants	Ethanol
Catalyst	Activated silica-alumina
Products	Ethylene Water
Temperature	300°C

[1] *Design based on process described by* Wells, G. M., 1999, *Handbook of Petrochemicals and Processes*, Sec. Ed., Pg 207-208
[2] *Capacity based on Braskem proposed ethanol to ethylene plant in Brazil http://www.braskem.com.br/*

HYSYS design of Ethylene

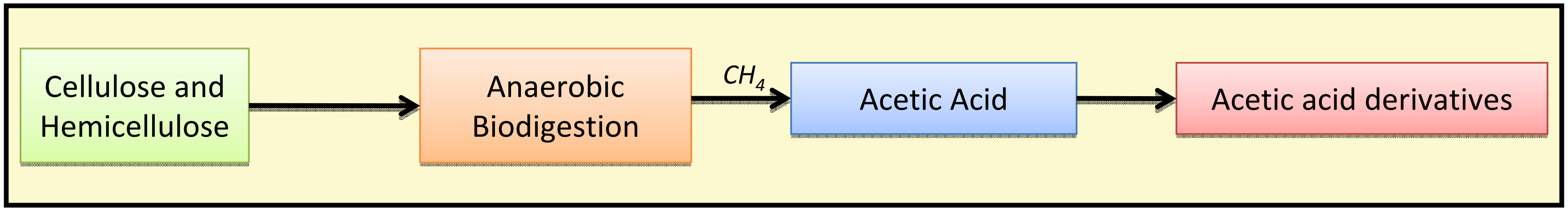
Material Balance

Inlet Material Streams	Mass Flow (kg/hr)	Outlet Material Streams	Mass Flow (kg/hr)
Ethanol	46,000	Ethylene	28,000
Water (wash)	9,000	Water	28,000

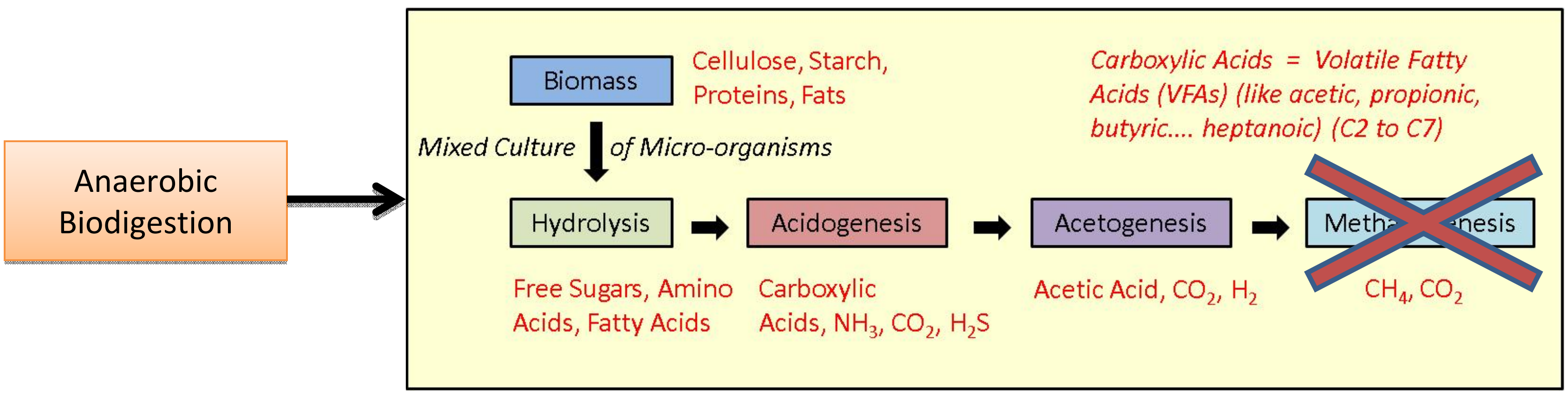
Energy Balance

	Energy Flow (kJ/hr)	Type	Required (kg/hr)
Energy Required	1,139 x 10^5	HP Steam 47 bar, 260^oC	69,000
Energy Liberated	650 x 10^5	Cooling water	778,000

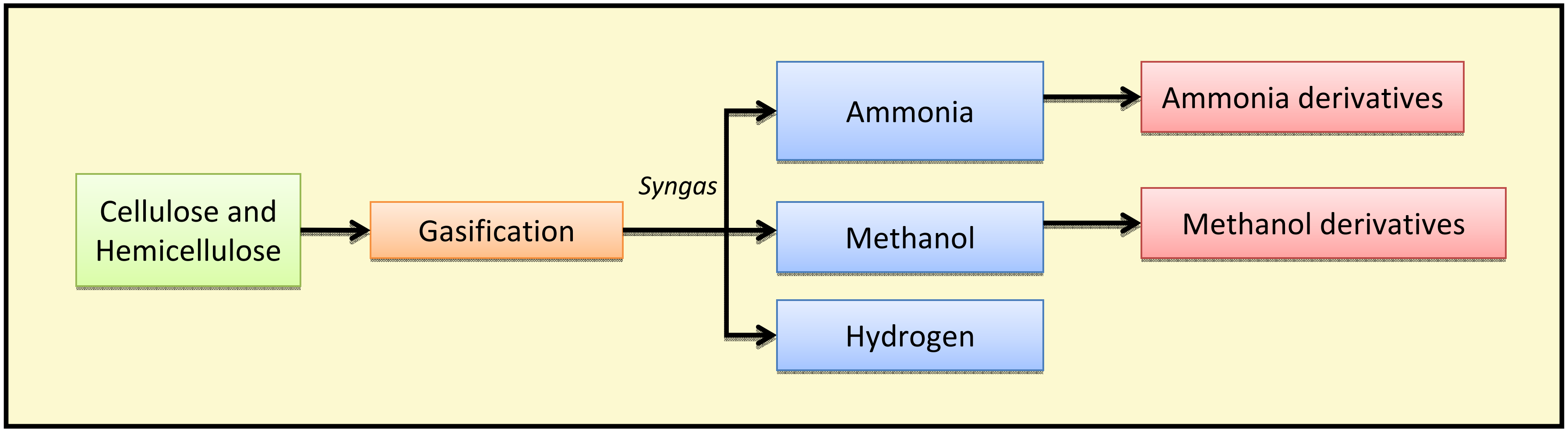
Anaerobic Digestion



- Anaerobic digestion of biomass is the treatment of biomass with a mixed culture of bacteria in absence of oxygen to produce methane (biogas) and carbon dioxide.
- Four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis
- **MixAlco** process – Inhibits fourth stage of methane production using iodoform (CHI_3) or bromoform ($CHBr_3$). Reduces cost of process by using mixed culture of bacteria from cattle rumen. Produces mixed alcohols, carboxylic acids and ketones.



Gasification



- Biomass can be gasified to produce of syngas
- Syngas can be converted to chemicals like methanol, ammonia and hydrogen

Industry Perspective

Ethylene and Propylene are basic building blocks for polymers and chemical intermediates

Approximately 1% of global energy market and 3% of global oil and gas market is used as chemical feedstock

½ of the energy and ¾ mass of the chemical feedstock is retained in the end product

1

How Might Biofuels Impact the Chemical Industry?

William F. Banholzer, Keith J. Watson and Mark E. Jones
The Dow Chemical Co.

The chemical industry is a critically important contributor to modern society, providing the raw materials for a staggering 70,000 products ranging from the chlorine used to purify water to the light-

Considering the range of possibilities and constraints, a major transformation of the chemical industry's current capital structure ...cades.

...ts — a dramatic ...chemical industry ...al feedstocks to- ...hly unlikely to be ...xt few decades.

...ls

...opylene serve as ...locks from which ...chemical inter- ...today (6). Both of ...are produced by

30/10/2007 19:23:00

2

Braskem confirms investment to produce 200 kton/year of green polyethylene

Strategic clients are already receiving samples of the product made 100% from renewable raw materials

Braskem, the Brazilian petrochemical company that leads the thermoplastic resins market in Latin America, today confirmed their project for the ...tion plant for polyethylene made from sugar can... ...s at the end of 2009 and with a capacity of 200 ...news was officially relayed by José Carlos ...o is in Germany to take part in the K 2007 ...gest international event for the petrochemical

Ashland / Cargill license technology from Davy Process Technology Ltd. for planned JV
Technology to produce propylene glycol (PG) from glycerin

3

7/9/2007

COVINGTON, Ky., MINNEAPOLIS – Ashland Inc. (NYSE:ASH) and Cargill today announced they have entered into a technology licensing agreement with Davy Process Technology Ltd., a Johnson Matthey Company, on behalf of the joint venture the companies intend to form. The basis of the agreement is a highly efficient vapor-phase hydrogenation technology for use in converting glycerin to propylene glycol (PG).

1 CEP, March 2008, Pg S7-S14
2 http://www.braskem.com.br/site/portal_braskem/en/sala_de_imprensa/sala_de_imprensa_detalhes_6970.aspx
3 http://www.ashland.com/press_room/news_detail.asp?s=1543

Industries in Louisiana

- Petrochemical complex in the lower Mississippi River Corridor
  - Dow
  - DuPont
  - BASF
  - Shell
  - Exxon
  - Monsanto
  - IMC-Agrico
  - Union Carbide

  …. and others

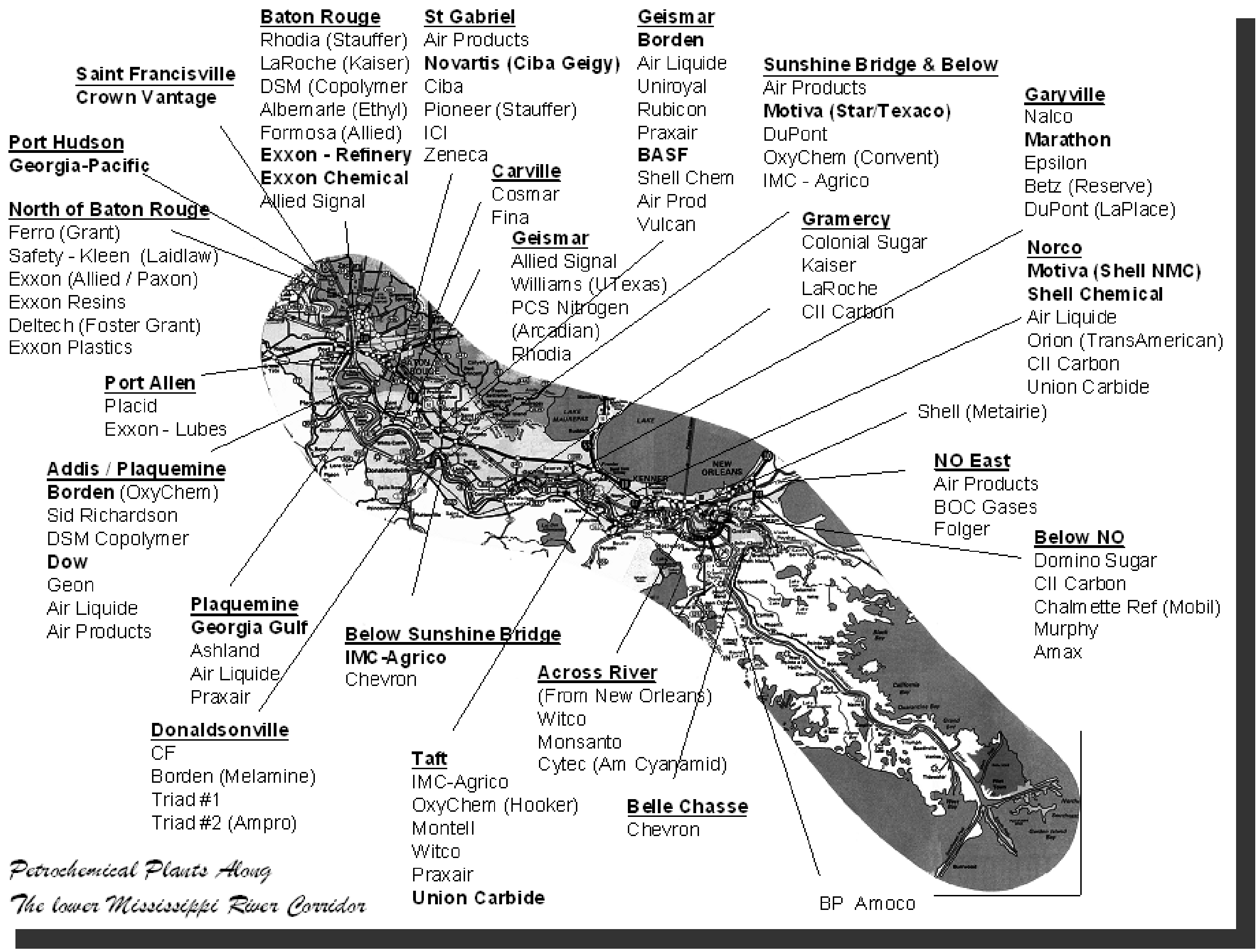
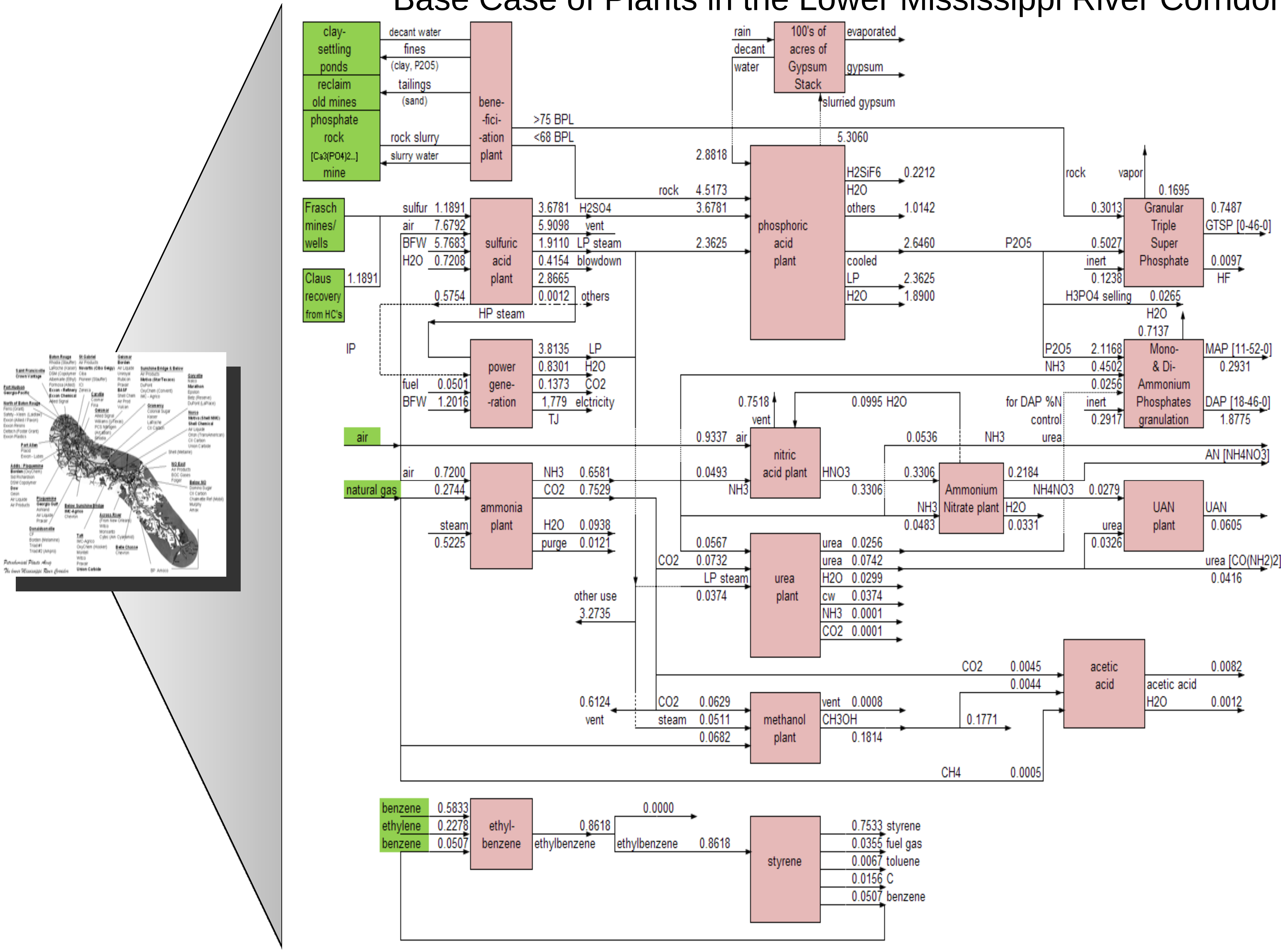
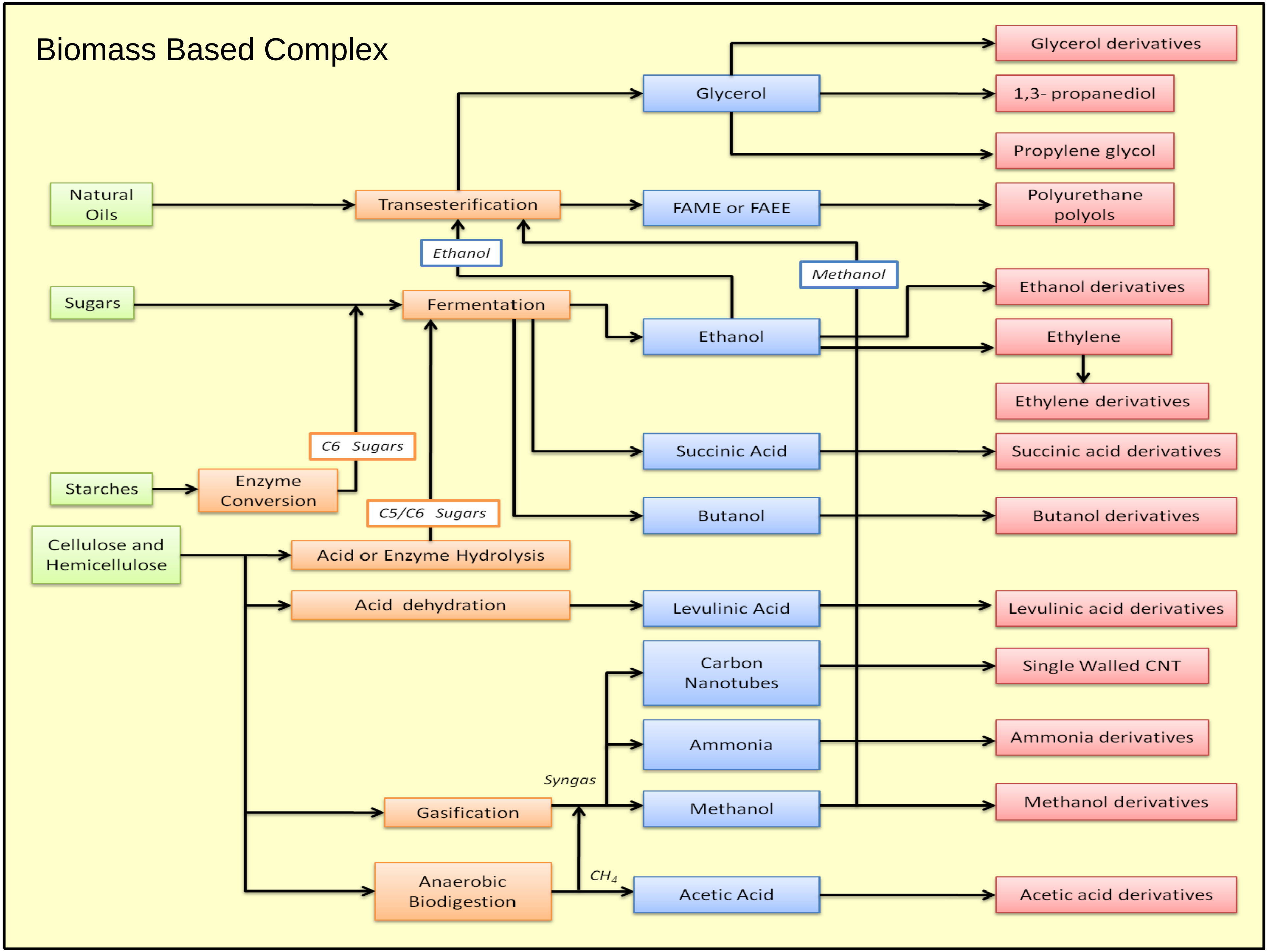


Photo: Peterson, 2000

Base Case of Plants in the Lower Mississippi River Corridor




Biomass Based Complex
Natural Oils
Sugars
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Acid or Enzyme Hydrolysis
Acid dehydration
Gasification
Anaerobic Biodigestion
Ethanol
Methanol
C6 Sugars
C5/C6 Sugars
Syngas
CH_4
Glycerol
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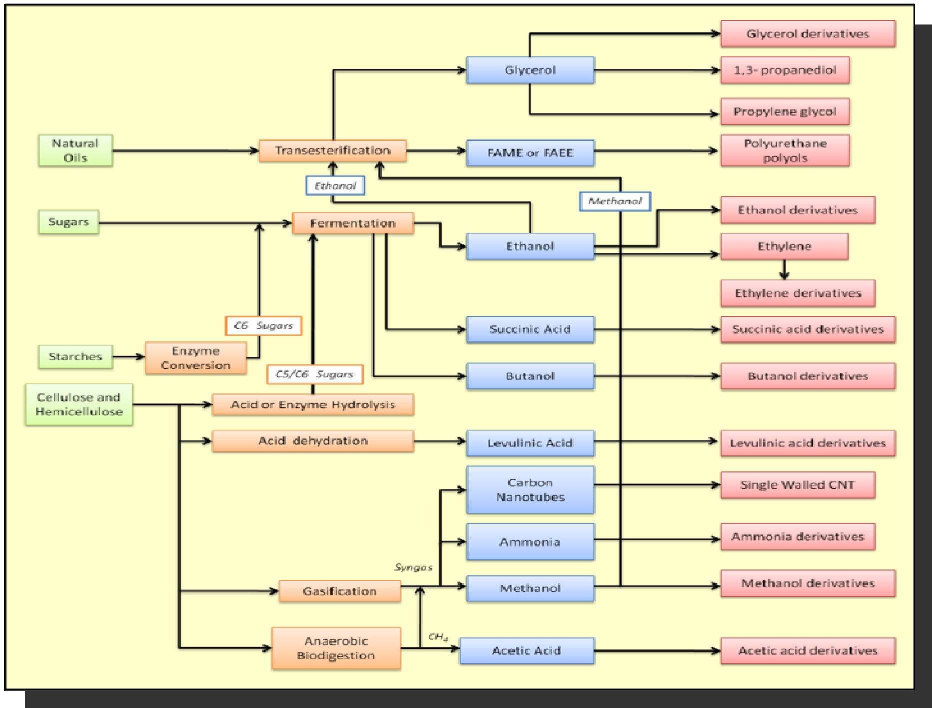
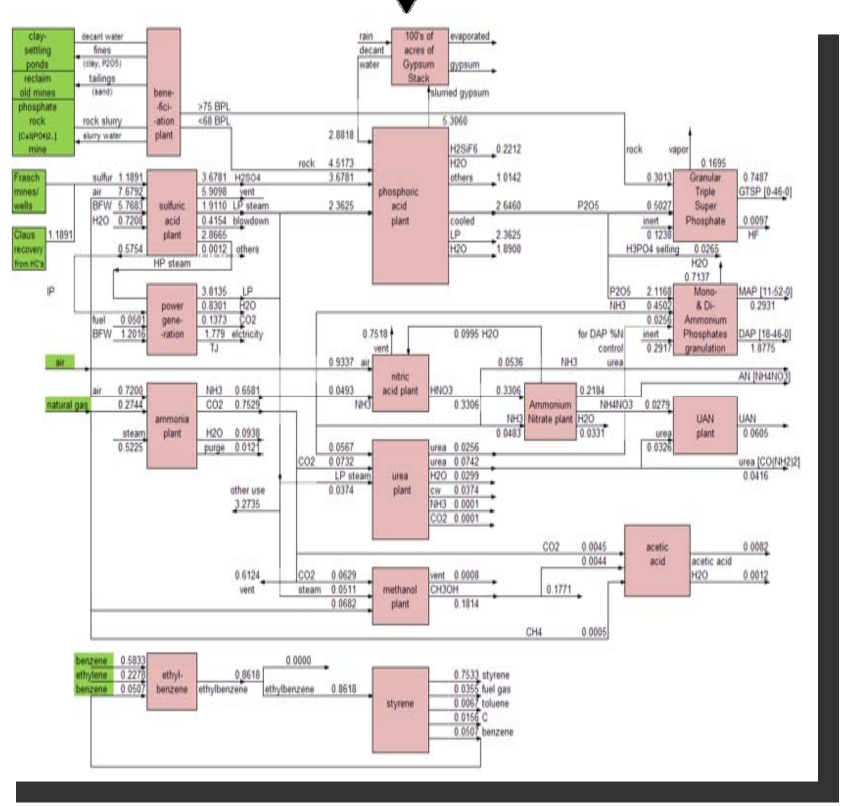
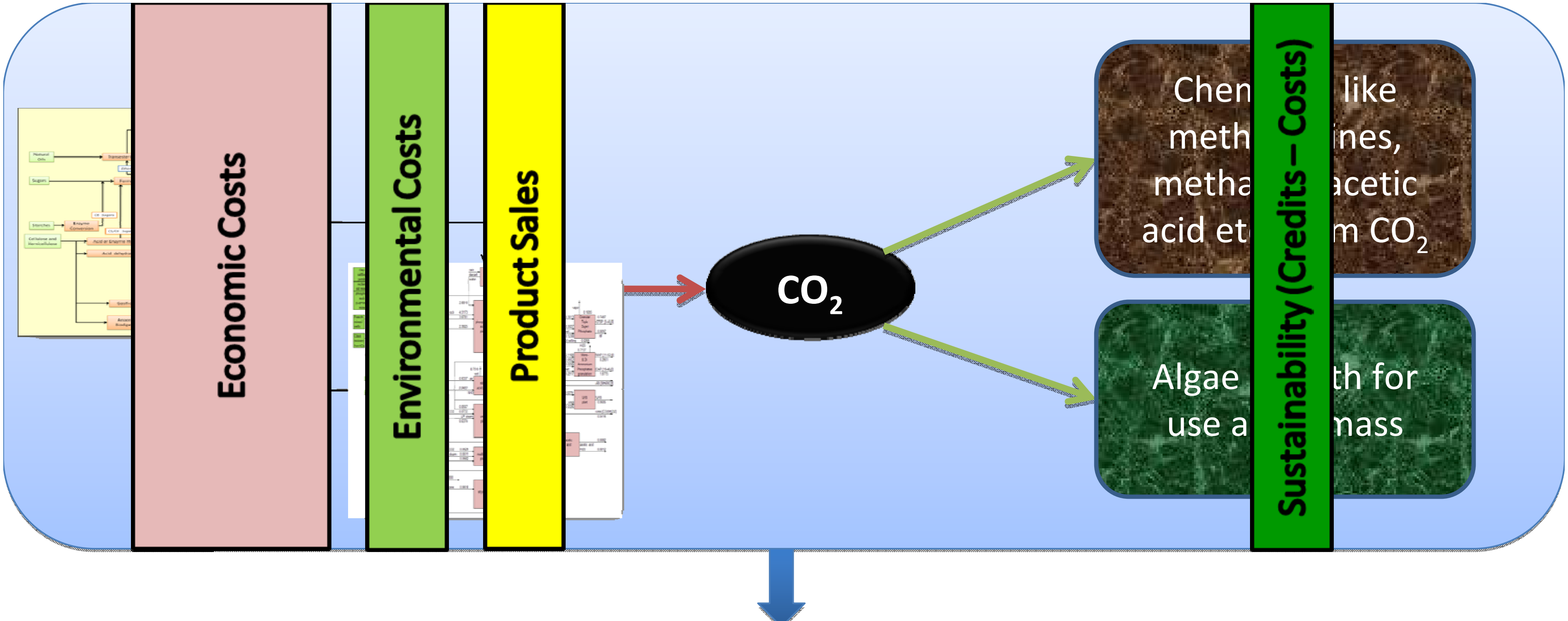
Integrated Chemical Production Complex







Multicriteria Optimization Problem

Maximize: $w_1 P + w_2 S$

$$P = \Sigma\text{Product Sales} - \Sigma\text{Economic Costs} - \Sigma\text{Environmental Costs}$$

$$S = \Sigma\text{Sustainability (Credits} - \text{Costs)}$$

$$w_1 + w_2 = 1$$

Subject to:

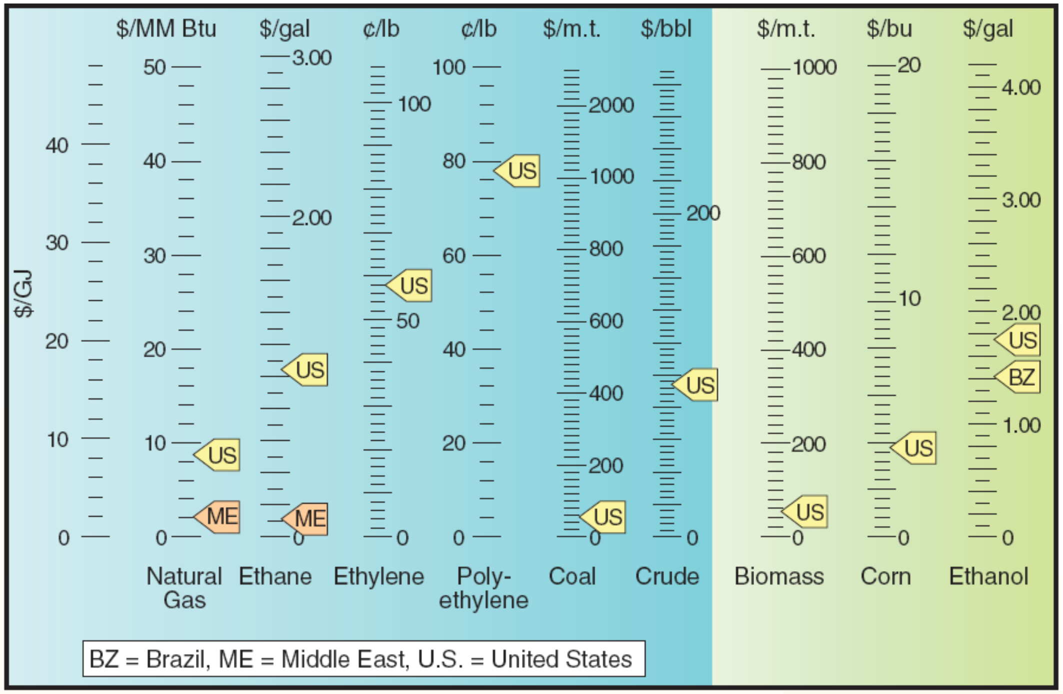
Multiplant material and energy balance

Product demand

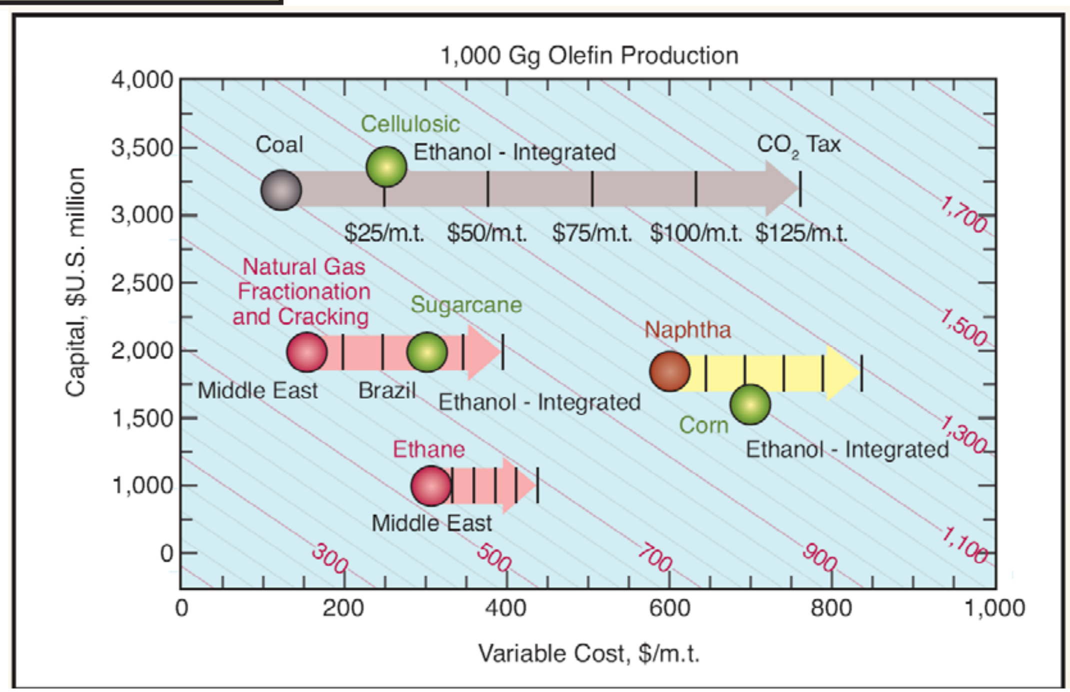
Raw material availability

Plant capacities

Costs in the Triple Bottom line



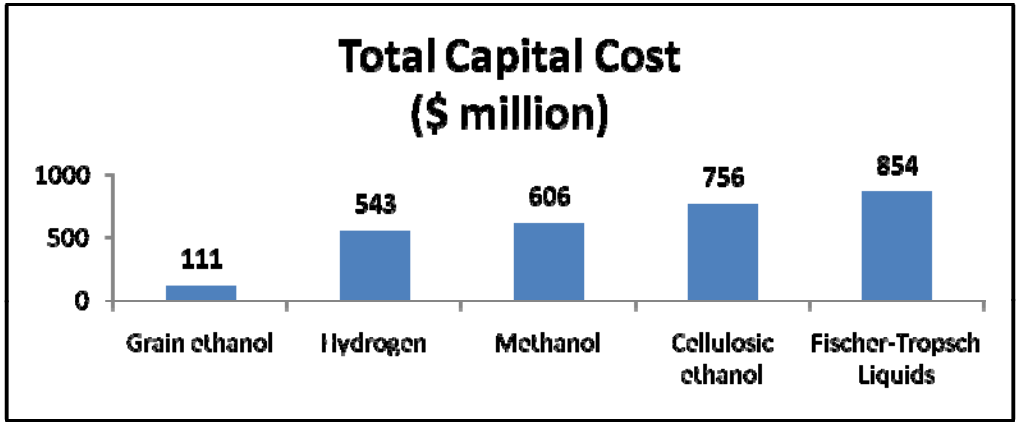
Relative Price per unit energy of various feedstocks and products, quoted in their traditional units and calibrated to $/GJ

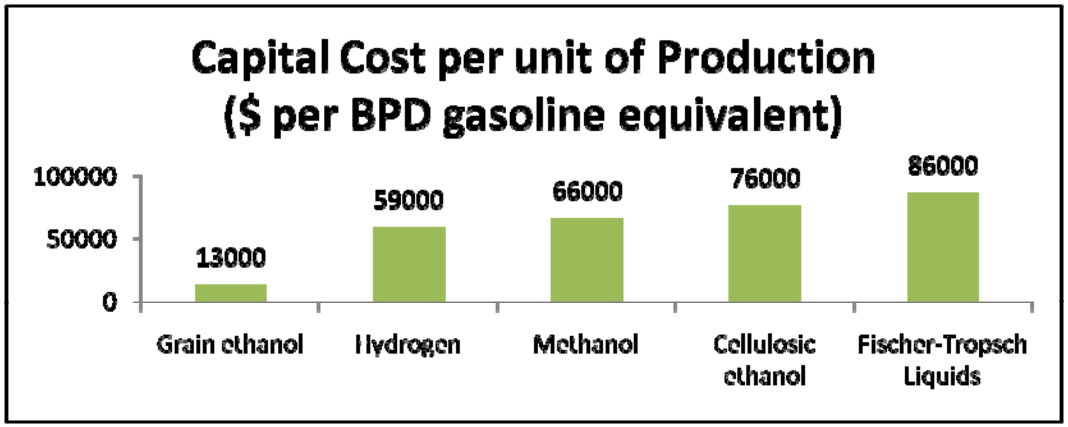


Contour plot of production cost plus return on investment as a function of capital and variable costs (based on 1000Gg/year of olefin production)

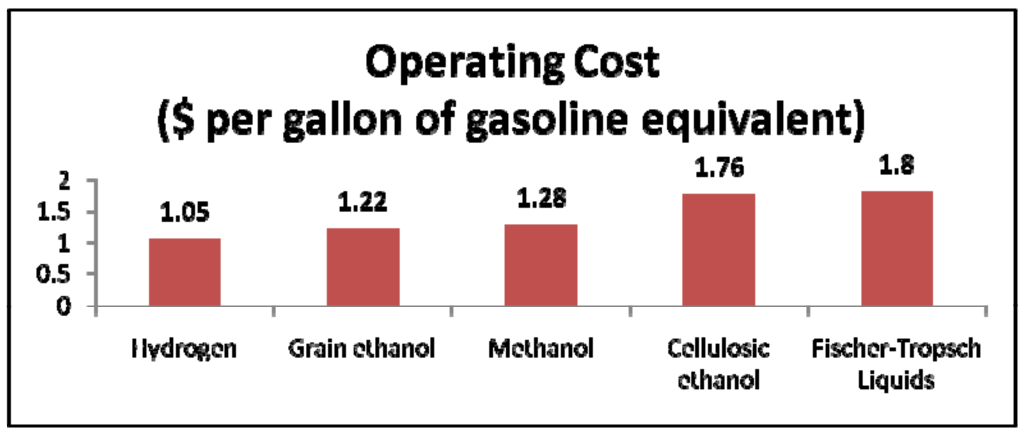
CEP, March 2008, Pg S7-S14

Costs in the Triple Bottom line





Capital and operating costs for 150 million gallons per year (MMGPY) of gasoline equivalent plants, 2005 dollars



Biofpr, 1:49-56 (2007)

Costs in the Triple Bottom line

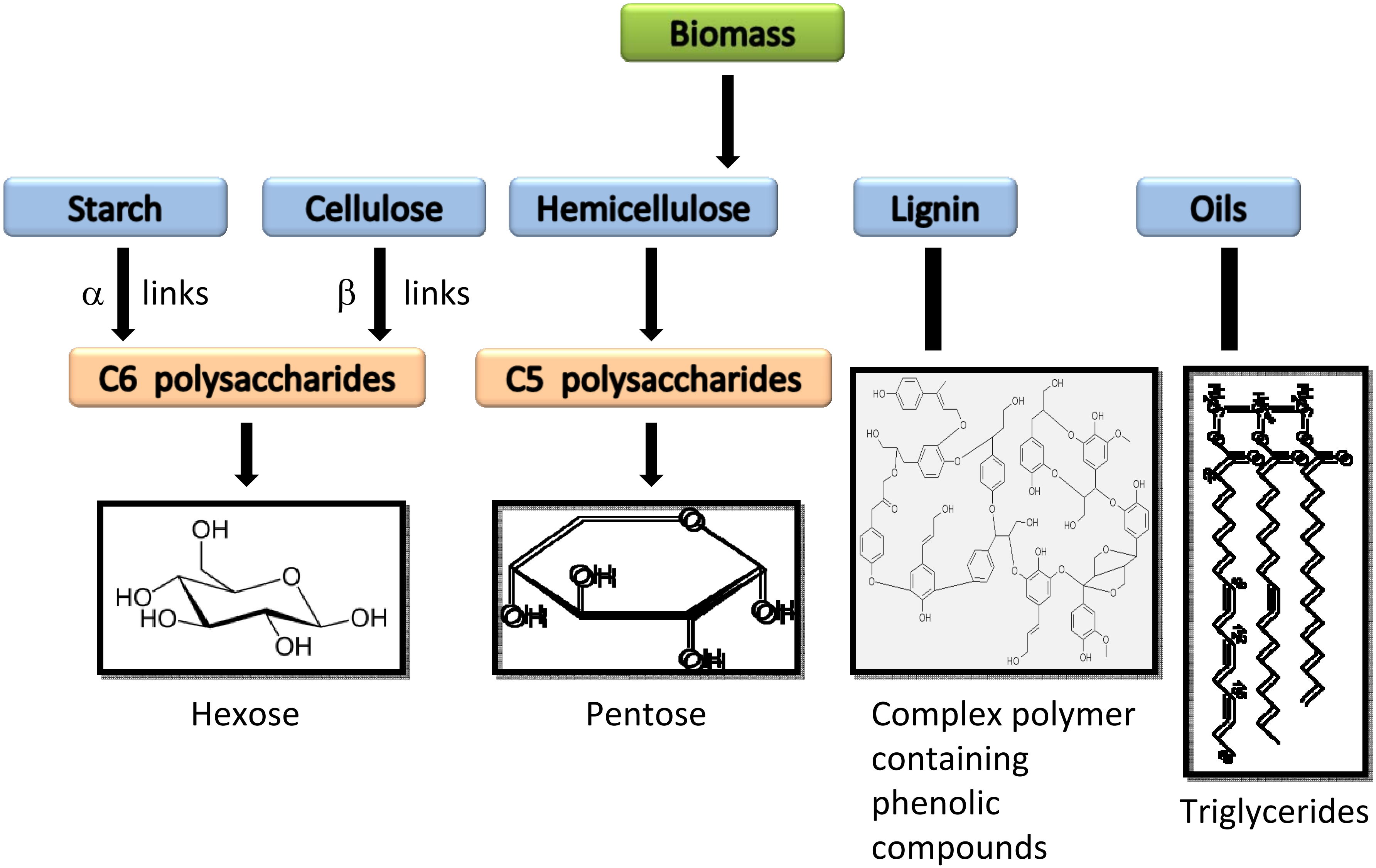
- Environmental costs
  - AIChE/TCA report [1] lists environmental costs as approximately 20% of total manufacturing cost and raw material as 30% of manufacturing costs (data provided by Amoco, DuPont and Novartis).
  - Environmental cost estimated as 67% of raw material cost.

- Sustainable costs
  - Sustainable costs were estimated from results given for power generation in AIChE/TCA report [1].
  - Alternate methods to estimate sustainable costs are being evaluated.

Component	Sustainable Cost ($/m.t.)
Carbon Dioxide	3.25
NO_x	1,030
SO_x	192

[1] *Constable, D. et al., "Total Cost Assessment Methodology; Internal Managerial Decision Making Tool", AIChE, ISBN 0-8169-0807-9, July ,1999.*

Biomass Components



Feedstock

- Algae
  - Consumes CO_2 in a continuous process using exhaust from power plant (40% CO_2 and 86 % NO)
  - Can be separated into oil and carbohydrates
  - High oil density yields production rate of **15,000 gallons/acre** compared to 60 gallons/acre for soybeans
  - Water used can be recycled and waste water can be used as compared to oilseed crops' high water demand
  - High growth rates, can be harvested daily

•Use Algae to consume CO_2 from chemical production processes
•Algae becomes feedstock for the production of oil and carbohydrates for chemicals

Photo: National Geographic, October 2007

Feedstock

— Vertical Algae Reactor fed continuously with atmospheric CO_2

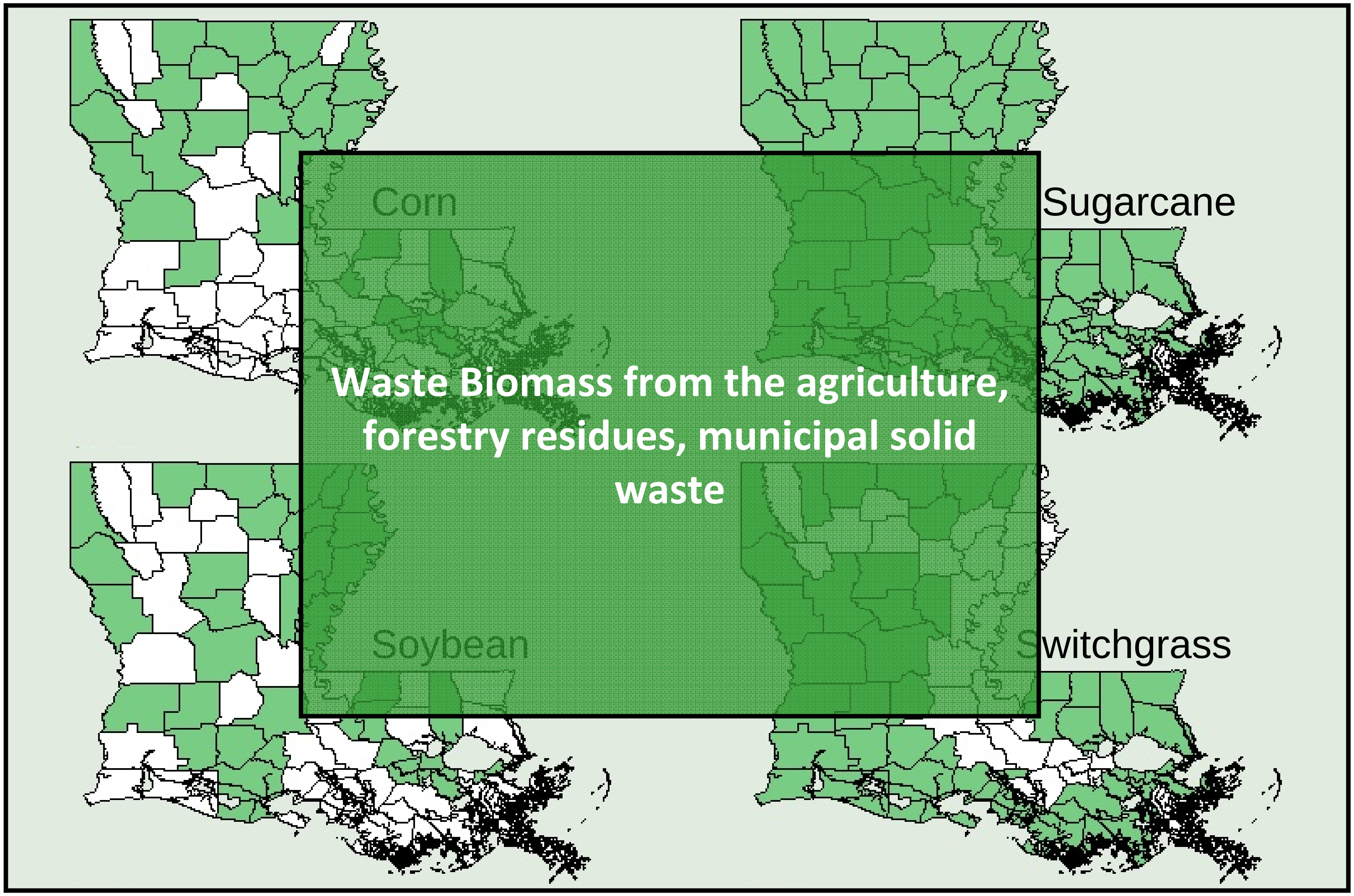
— **16 times** growing volume in the same area is achieved in these vertical reactors as opposed to algal ponds

— Closed system ensures optimal growth and reduces harmful external influences

— Oil extraction from algae is the costliest step in the process

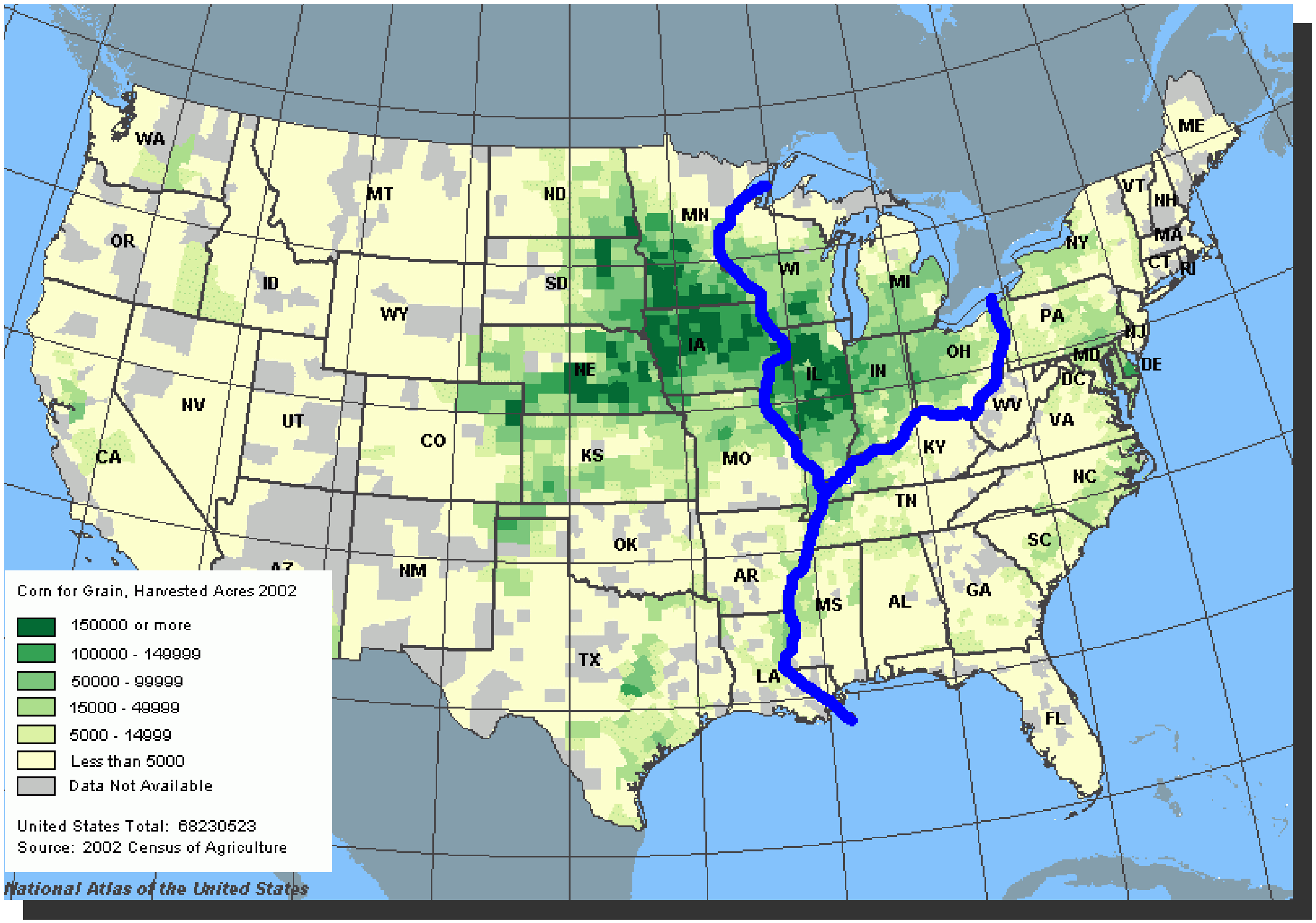
Photo: FUEL | 4th Quarter 2007

Feedstock in Louisiana



http://plants.usda.gov/

Transportation to Gulf Coast



Waterways from the midwestern states can provide excellent transport for biomass feedstock to the Gulf Coast.

Industries in the Lower Mississippi River Corridor can receive the feedstock and convert to chemicals.

Map created from http://nationalatlas.gov/

Summary

- Extend the Chemical Production Complex in the Lower Mississippi River Corridor to include:
  - Biomass based chemical production complex
  - CO_2 utilization from the complex
- Obtain the relations for the above chemical plants:
  - Availability of raw materials
  - Demand for product
  - Plant capacities
  - Material and energy balance equations
- Assign Triple Bottomline costs:
  - Economic costs
  - Environmental costs
  - Sustainable credits and costs

Summary

- Define Multicriteria Optimization Problem with constraints
- Use Mixed Integer Non Linear Programming Global Optimization and Local Optimization Solvers to obtain Pareto optimal solutions of the problem below.
  - GAMS/BARON - Global Optimizer
  - GAMS/DICOPT - Local Optimizer

$$\mathbf{w_1 P + w_2 S}$$

$$\mathbf{P = \Sigma Product\ Sales - \Sigma Economic\ Costs - \Sigma Environmental\ Costs}$$

$$\mathbf{S = \Sigma Sustainability\ (Credits - Costs)}$$

$$\mathbf{w_1 + w_2 = 1}$$

- Use Monte Carlo Analysis to determine sensitivity of the optimal solution.
- Follow the procedure to include plants in the Gulf Coast Region (Texas, Louisiana, Mississippi, Alabama)
- Methodology can be applied to other chemical complexes of the world.

Questions

Comments

Research White Paper and Presentation available at www.mpri.lsu.edu