Integrating Biotechnology and Nanotechnology into Sustainable Industrial Complexes

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Organization of Material

- Introduction to Sustainable Development
- Introduction to Biotechnology
  - Feedstock
  - Processes
  - Products
- Introduction to Nanotechnology
  - Carbon nanotubes
- Integration of biotechnology and nanotechnology in existing plant complex
- Research Direction

Carbon Dioxide

Annual average fossil carbon dioxide emissions:

1990s: 23.5 GtCO_2 (6.4 GtC) per year

2000–2005: 26.4 GtCO_2 (7.2 GtC) per year

Global atmospheric concentration:

650,000 years: 180-300 ppm

2005: 379 ppm

Annual carbon dioxide concentration growth-rate:

1960 – 2005 average: 1.4 ppm per year

1995 – 2005 average: 1.9 ppm per year

IPCC WGI Fourth Assessment Report, 2007

Global Warming
Radiative Forcing
Surface Climate
Temperature

Photo: National Geographic, October 2007

Sustainable Development

What can we do with the CO_2?

- Reduce its emission by increasing efficiency and conservation
- Carbon capture and storage
- Low carbon fuels
- Use renewable feedstock
- Utilize CO_2 to make chemicals

This introduces us to the concept of **"Sustainable Development"**

Development that meets the needs of the present without compromising the ability of future generations to meet their own needs – United Nations Department of Economics and Social Affairs, Division for Sustainable Development

Industries in Louisiana

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

  …. and others

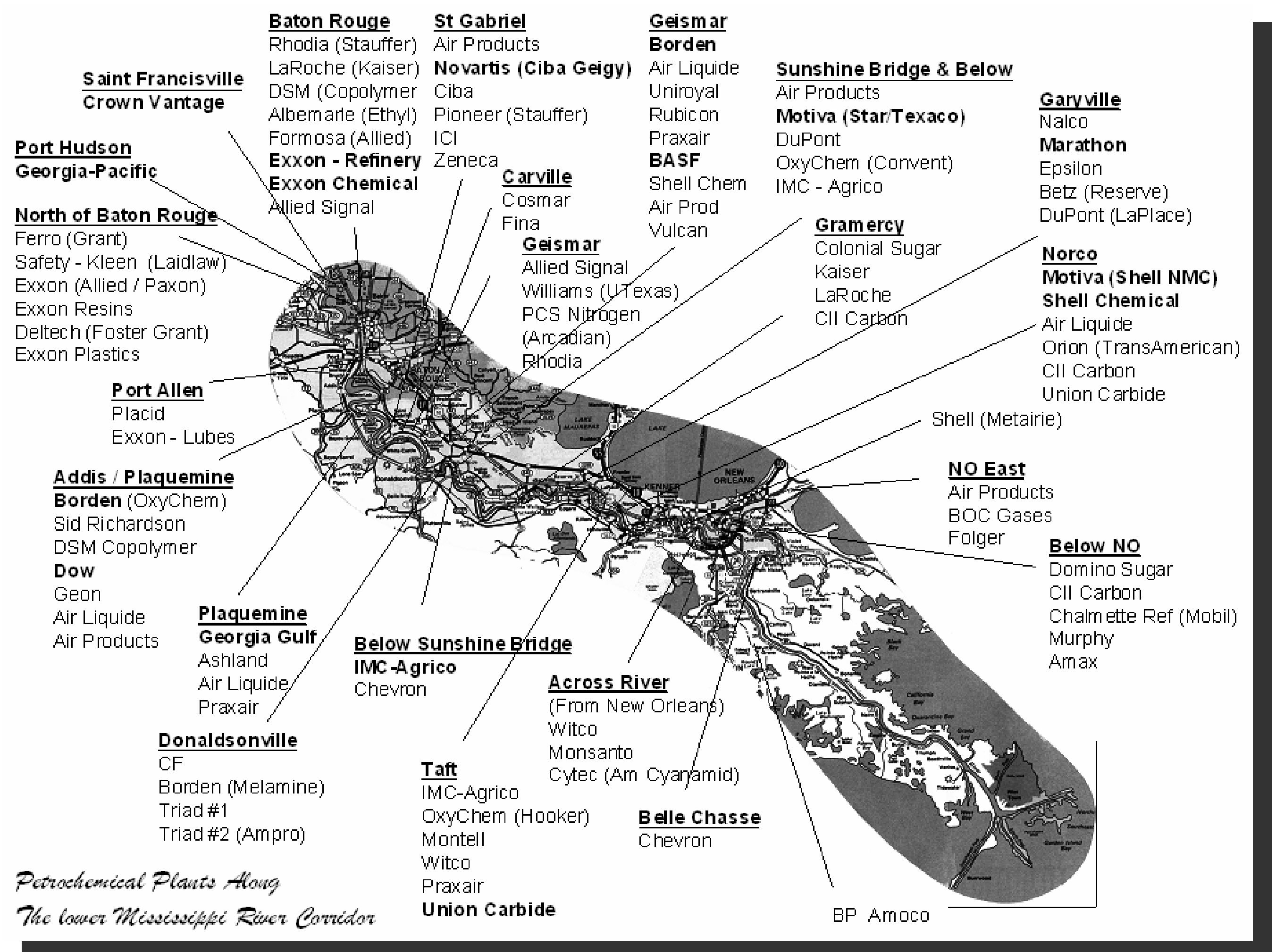


Photo: Peterson, 2000

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.

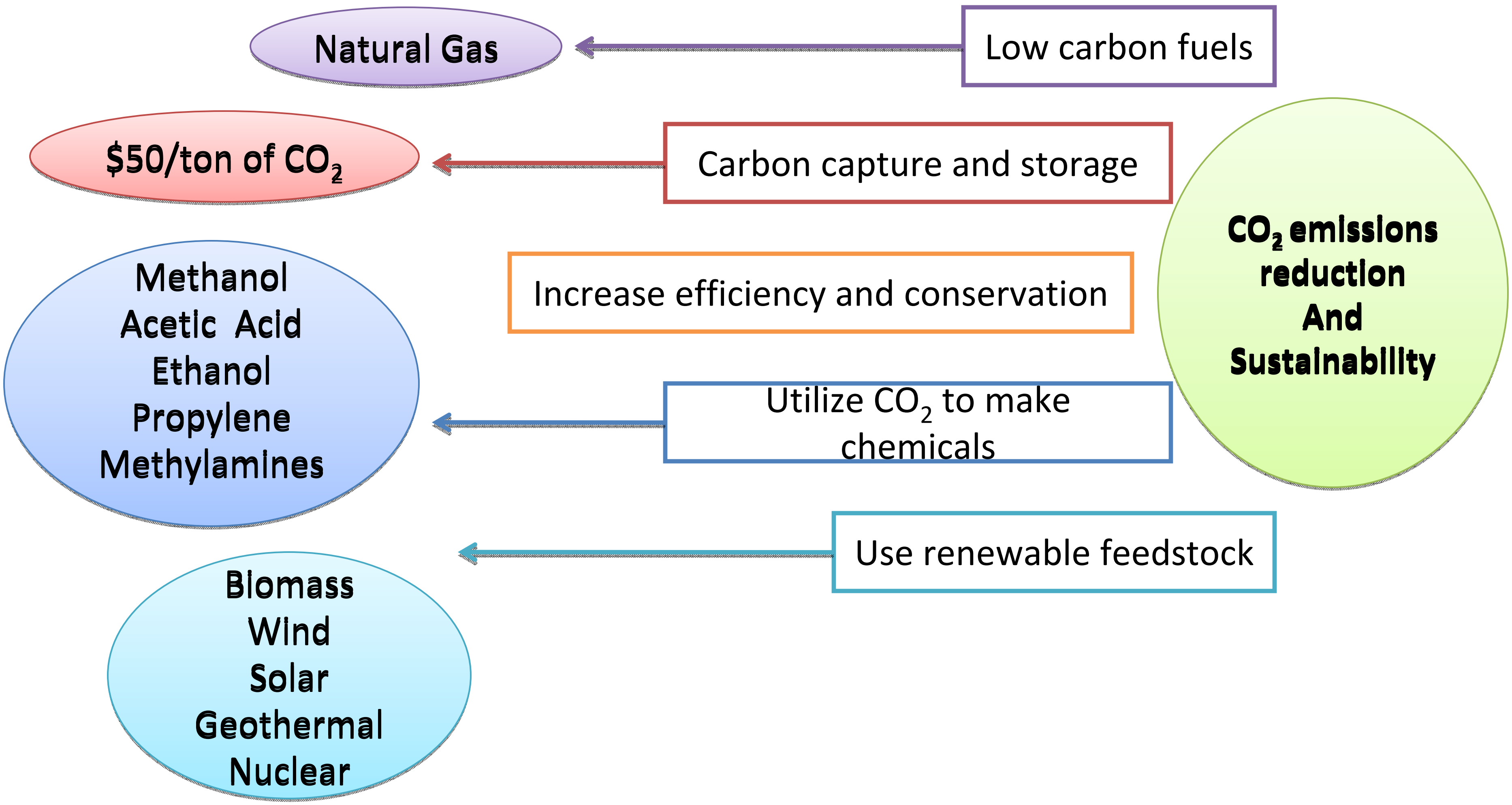
Profit = Σ Product Sales – Σ Raw Material Costs – Σ Energy Costs

- 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)

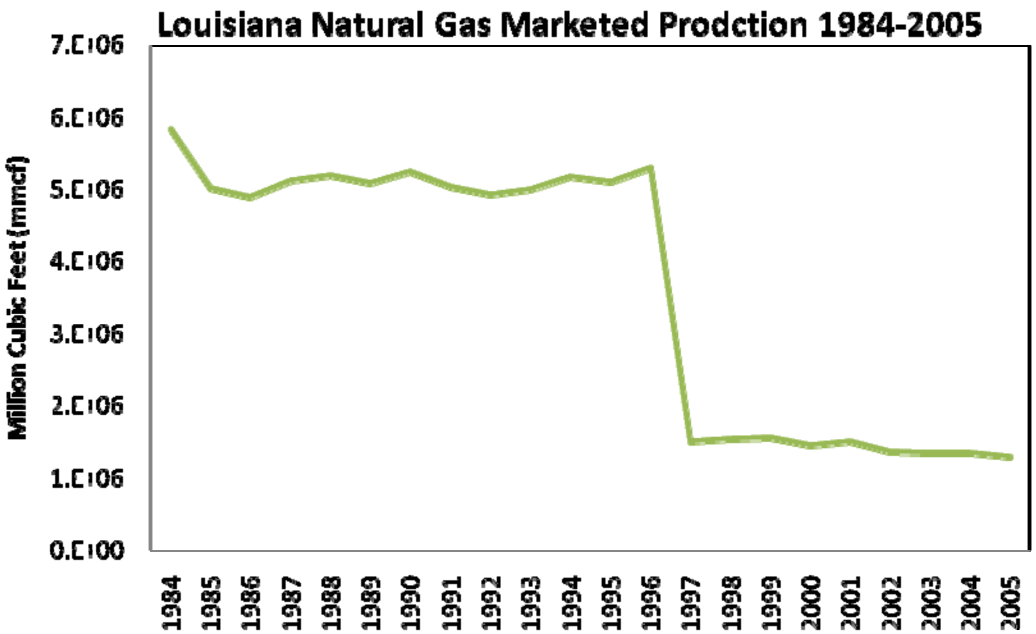
Triple Bottom Line = Σ Product Sales + Σ Sustainable Credits
– Σ Raw Material Costs – Σ Energy Costs
– Σ Environmental Costs – Σ Sustainable Costs

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

Achieving the Goal



Louisiana
Natural Gas Scenario



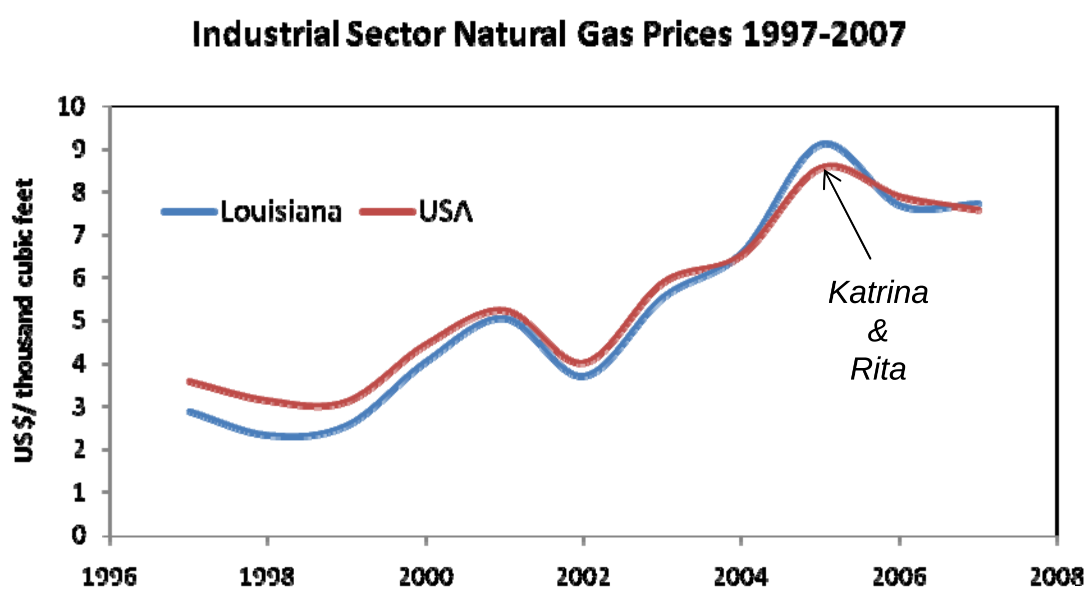
Profit = Σ Product Sales
– Σ **Raw Material Costs**
– Energy Costs

Louisiana Industries consumed 841,118 million cubic feet NG in 2006

80% increase in NG price from 2001 to 2005

Increases the cost of raw material

Results in plant shutdown or relocation

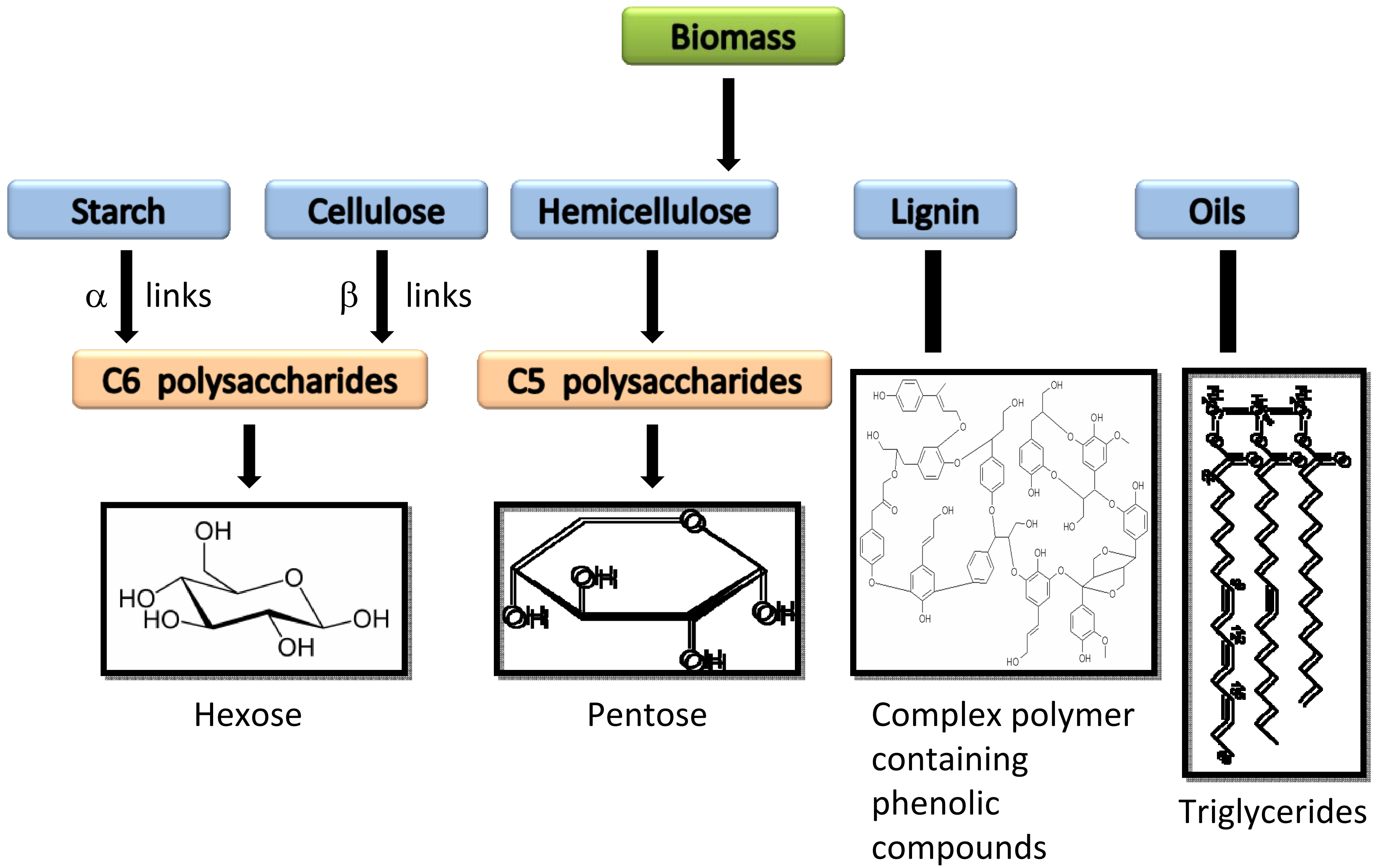


Source: EIA, 2007

Research Vision

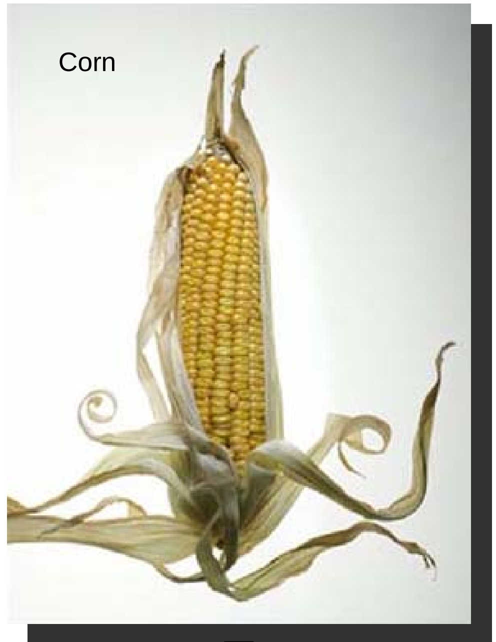
- Propose a **biomass based chemical industry** in the chemical production complex in the Gulf Coast Region and the Lower Mississippi River Corridor.
- Propose the production of **carbon nanotubes** in the complex.
- Utilize all **carbon dioxide** from all processes in the complex to make chemicals.
- 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

Components


Biomass
Starch
Cellulose
Hemicellulose
Lignin
Oils
α links
β links
C6 polysaccharides
C5 polysaccharides
Hexose
Pentose
Complex polymer containing phenolic compounds
Triglycerides

Feedstock

Oil



Starch → Sugar

Feedstock

Lignocellulosics

- Switchgrass
- Sugarcane Bagasse
- Corn Stover
- Agricultural residues

Separate and extract hexose and pentose

↑

Cellulose, Hemicellulose and Lignin

↑

Photo: LSU AgCenter, 2006; National Geographic, October 2007

Feedstock

Urban Wood Waste

Waste Biomass

- Municipal Solid Waste
- Animal Manures
- Food Processing Wastes
- Wood and residues from pulp and paper mills
- Logging residues

Sugarcane Bagasse

Logging Residue

Photo: LSU AgCenter, 2006

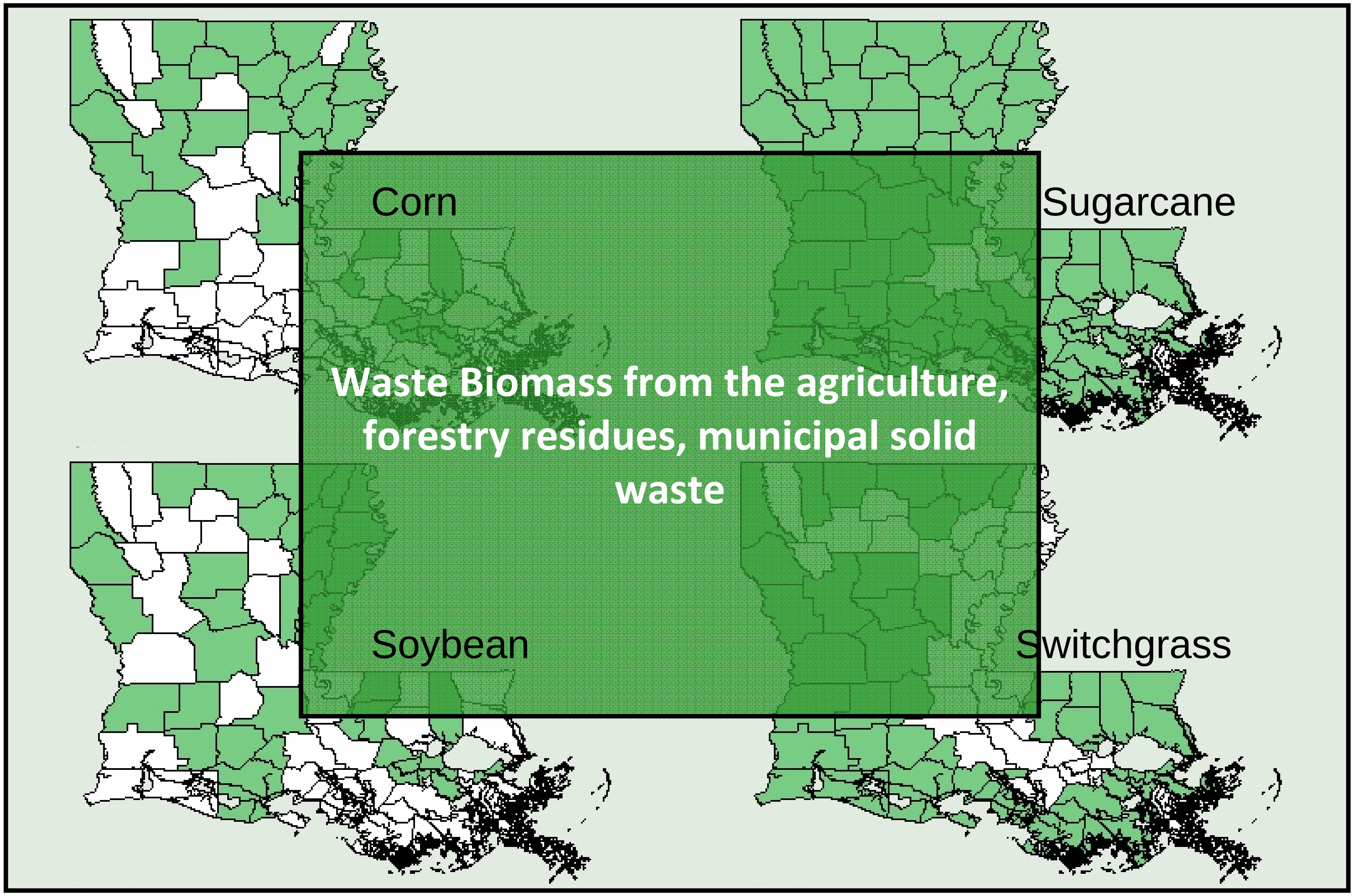
Feedstock

- 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 production processes
•Algae becomes feedstock for the production of oil and carbohydrates for chemicals

Photo: National Geographic, October 2007

Feedstock in Louisiana



http://plants.usda.gov/

Biomass Processes

The following biomass conversion processes are planned 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.

Process

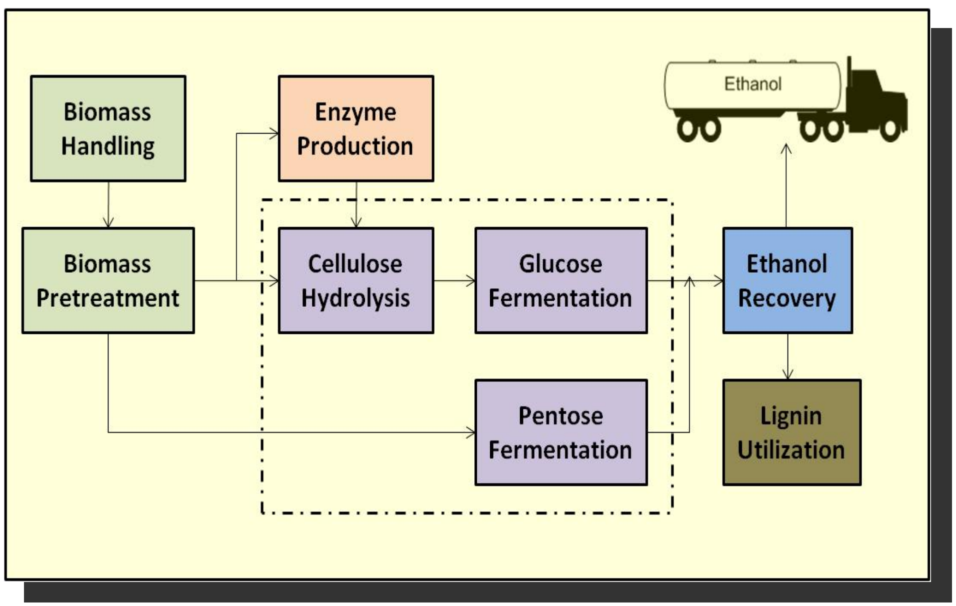
- Pretreatment
  - Physical size reduction – biomass is cut into pre-determined sizes for feeding into pretreatment reactors.
  - Hot wash – releases the complex structure of the biomass components releasing the cellulose, hemicellulose and lignin.
  - Acid hydrolysis – dissolves hemicellulose into pentose oligomers. Also forms degradation products under severe conditions.
  - Enzymatic hydrolysis – breaks down cellulose to C6 sugars (hexoses) and hemicellulose to C5 sugars by yeast or bacteria containing the enzyme (cellulase or hemicellulase).
  - Oil extraction – this process extracts oil from oil seeds for further processing

Breaks complex starch, cellulose and hemicellulose structures to glucose and pentose. Removes lignin from the process.

Process

Fermentation

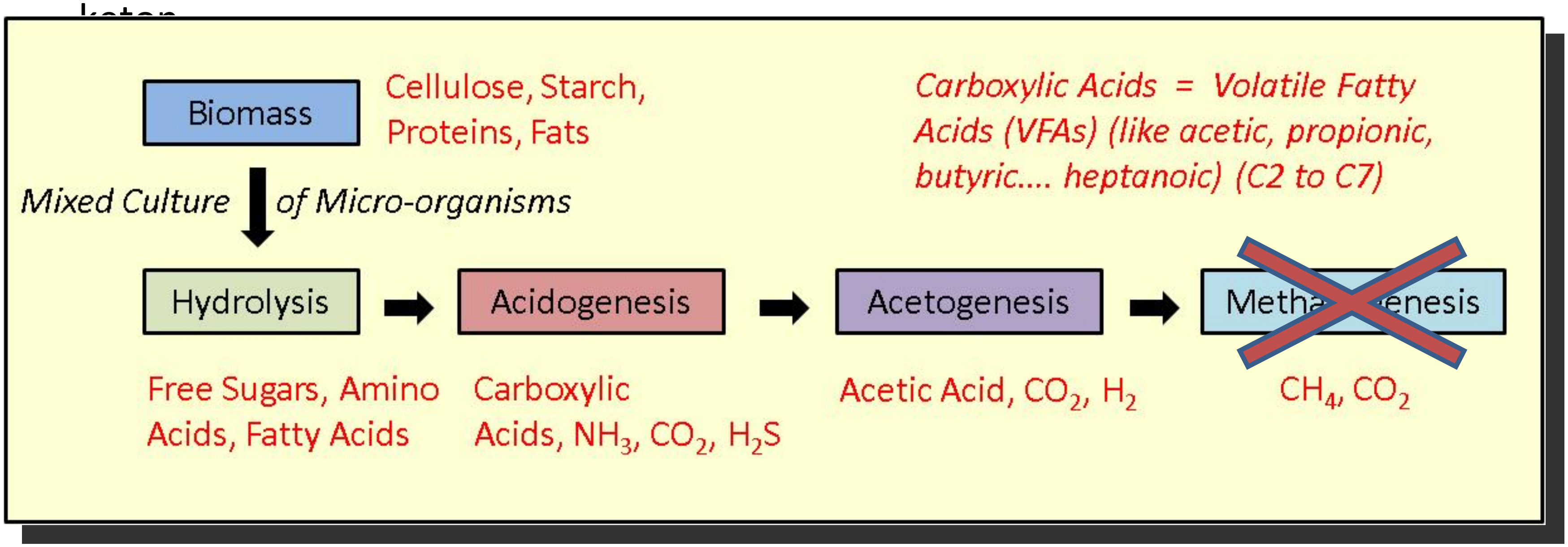
- Fermentation is the enzyme-catalyzed transformation of an organic compound.
- Fermentation enzymes react with hexose and pentose to form products.
- Enzyme selection determines product :-
  - *Saccharomyces Cervisiae* (C6), *Escherichia coli* (C5 & C6), *Zymomonas mobilis* (C6)– Ethanol
  - Engineered *Eschericia coli, A. succiniciproducens* – Succinic Acid
  - Engineeried microorganism - Butanol
  - Lactic Acid Producing Bacteria (LAB) – Lactic Acid



Process

Anaerobic Digestion

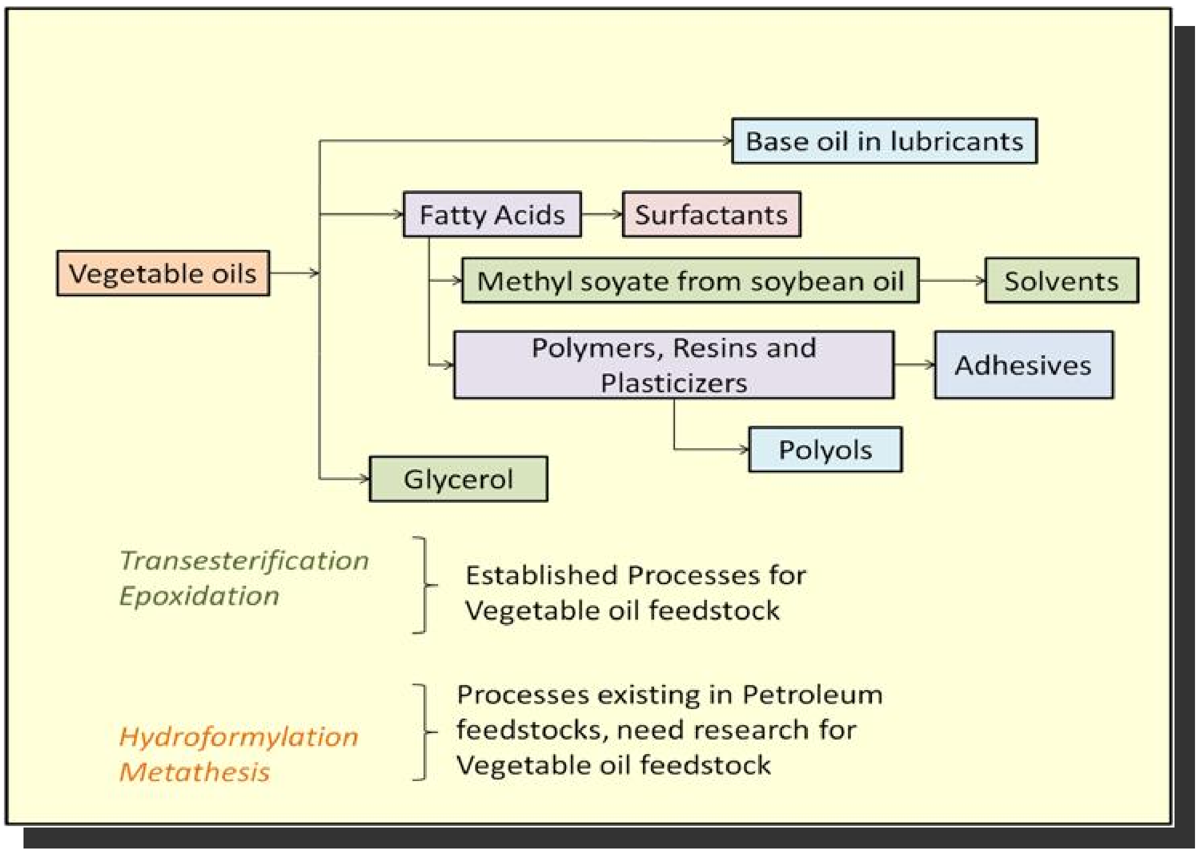
- Anaerobic digestion of biomass is the treatment of biomass with a mixed culture of bacteria in absence of oxygen to produce methane (biogas) and carbon dioxide.
- Four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis
- **MixAlco** process – Inhibits fourth stage of methane production 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 keton



Process

Direct Conversion of Plant Oils

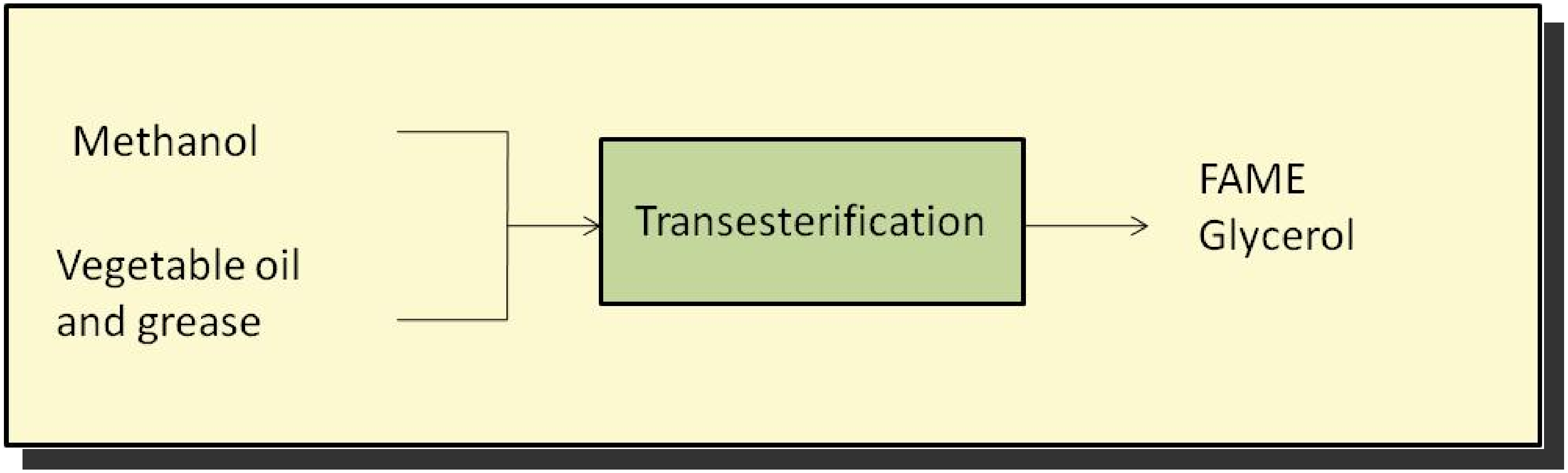
- Plant oils can undergo transesterification or epoxidation.
- Hydroformylation of methyl esters followed by hydrogenation gives monomer for polyols.



Process

Transesterification

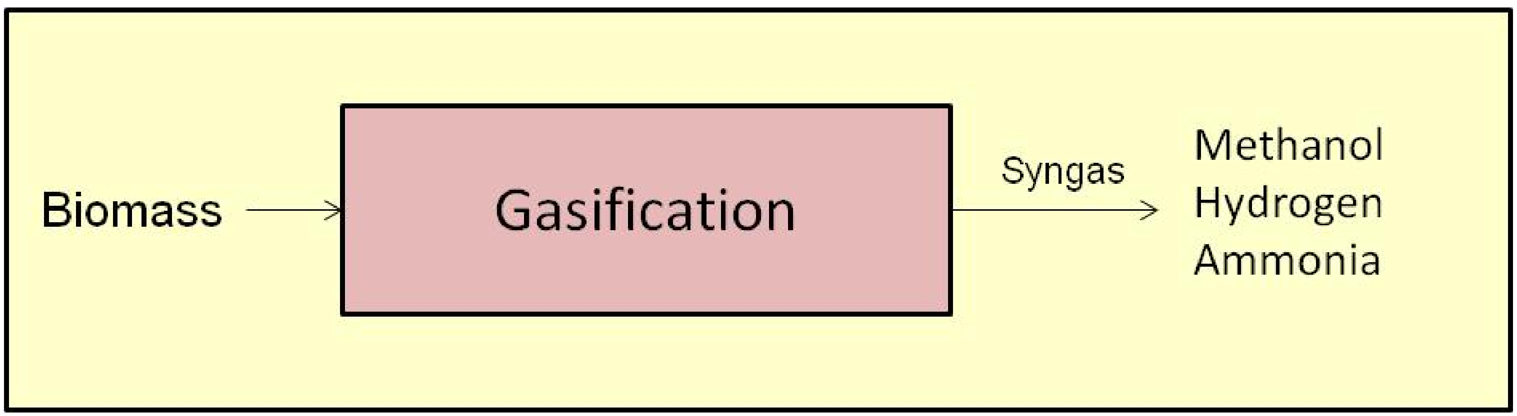
- Transesterification process is the treatment of vegetable oil with an alcohol and a catalyst to produce esters and glycerol.
- Methanol or ethanol is used as alcohol for fatty acid methyl or ethyl esters (FAME/FAEE).
- These esters can be transformed to chemicals.
- Glycerol is produced ~ 10% by weight in the process.
- Glycerol can be introduced to the propylene chain



Process

Gasification

- Production of syngas
- Syngas can be converted to chemicals like methanol, ammonia and hydrogen



Existing Products

HDPE

Tetrahydrofuran (THF)

Propylene Glycol

These are currently manufactured from petroleum and natural gas as feedstock.

These can be manufactured from biomass based feedstock.

Cellulose Acetate

PVA

Butanediol

Glycerol

New Products from Biomass

Dow VORALAST™

Zemea™ Pro-Cote®

Carbon Nanotubes

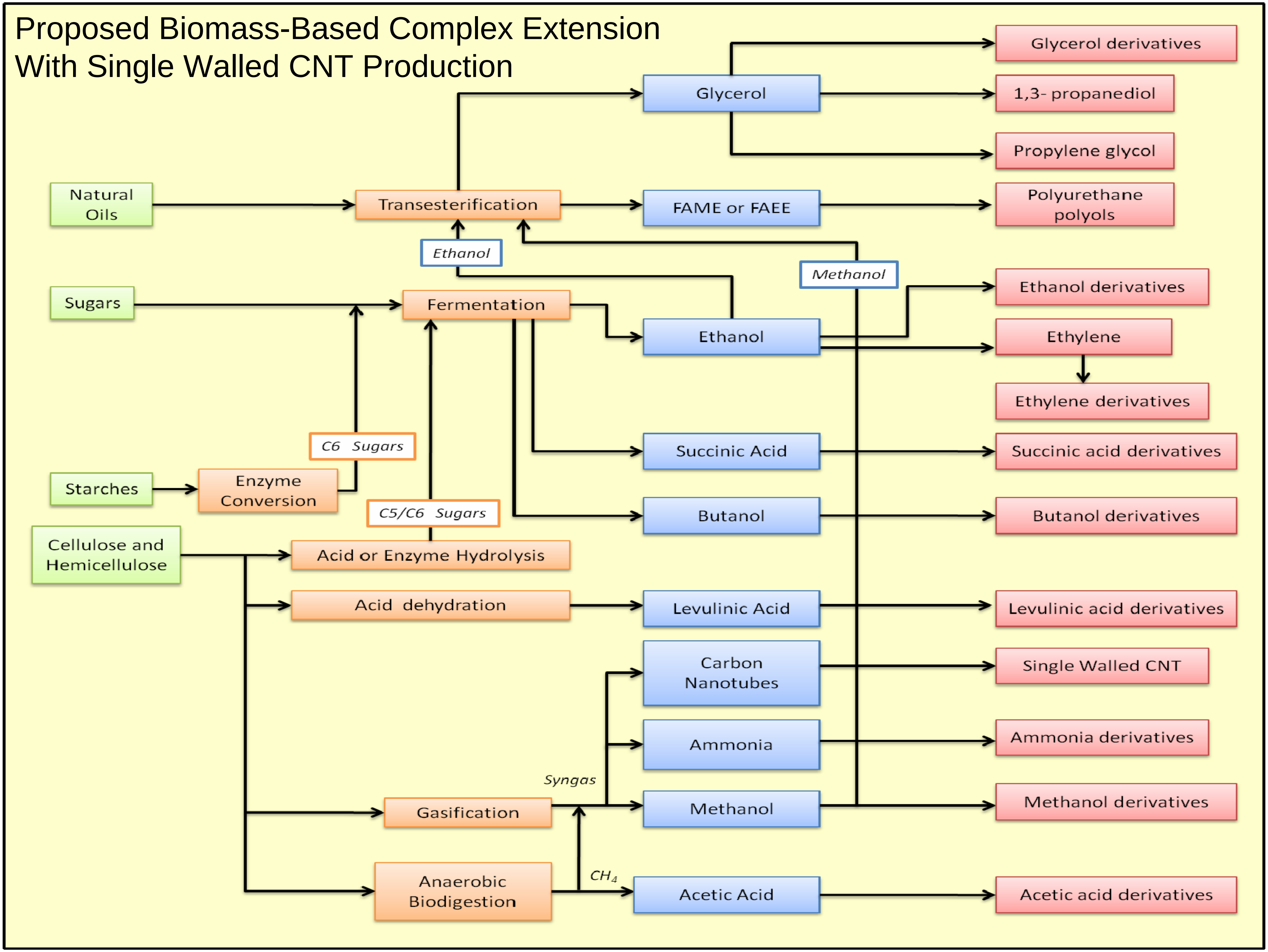
- Seamless cylindrical tubes, consisting of carbon atoms arranged in a regular hexagonal structure
- Consist of carbon filaments with nanoscale (10^{-9} m) diameter and micron scale (10^{-6} m) length.
- Considered as the ultimate engineering material because of their unique and distinct electronic, mechanical and material characteristics.

- Challenges
  - Production of purified carbon nanotubes in commercial quantities at affordable prices.
  - Equivalent quantity of carbon dioxide produced.
  - Market price is \$100-\$400/gm for purified nanotubes and \$1500-\$2000/gm for electronics grade CNT.
  - Bayer is building a **3,000 mt/yr** plant from a 60 mt/yr capacity to produce carbon nanotubes (Baytubes®)

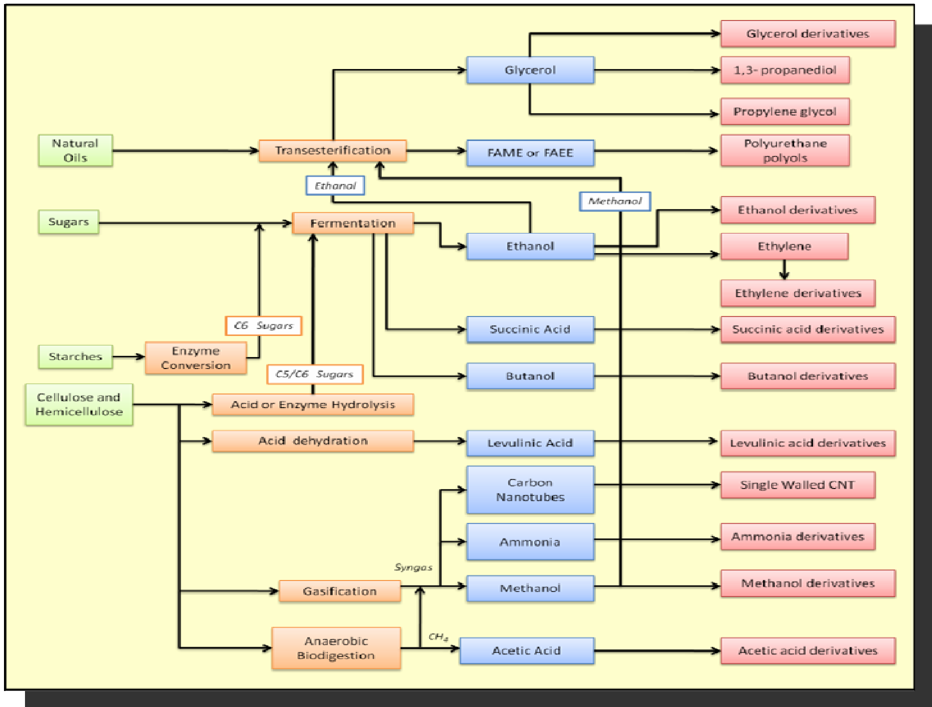
Conceptual Design of CNT Processes

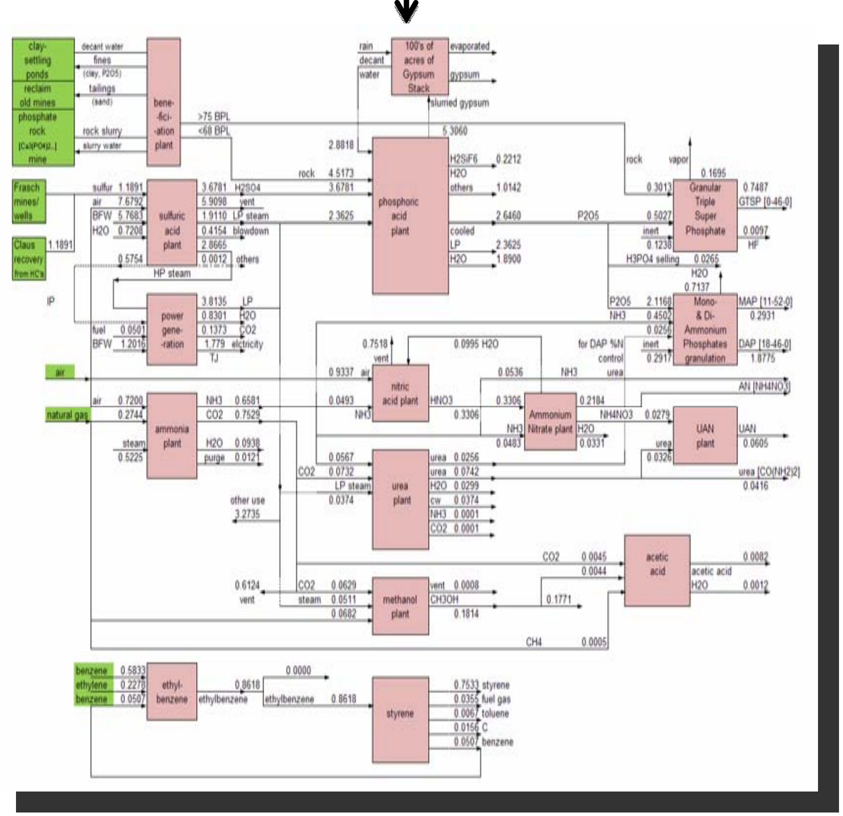
	CNT PFR Process	CNT-FBR Process
Catalyst	Fe	Co – Mo
	$Fe(CO)_5 \rightarrow Fe + 5CO$	Silica
Reactants	CO and $Fe(CO)_5$	CO
Reactor Type	Plug Flow Reactor	Fluidized Bed
Reactor Conditions	1050 ^oC @ 450 psi	950 ^oC @ 150 psi
Selectivity to CNT	90%	80%
Purification	- Oxidation - Acid Treatment - Filtration	- Leaching - Froth Flotation - Acid Treatment
Production rate (kg/hr)	595	595

Agboola, 2005

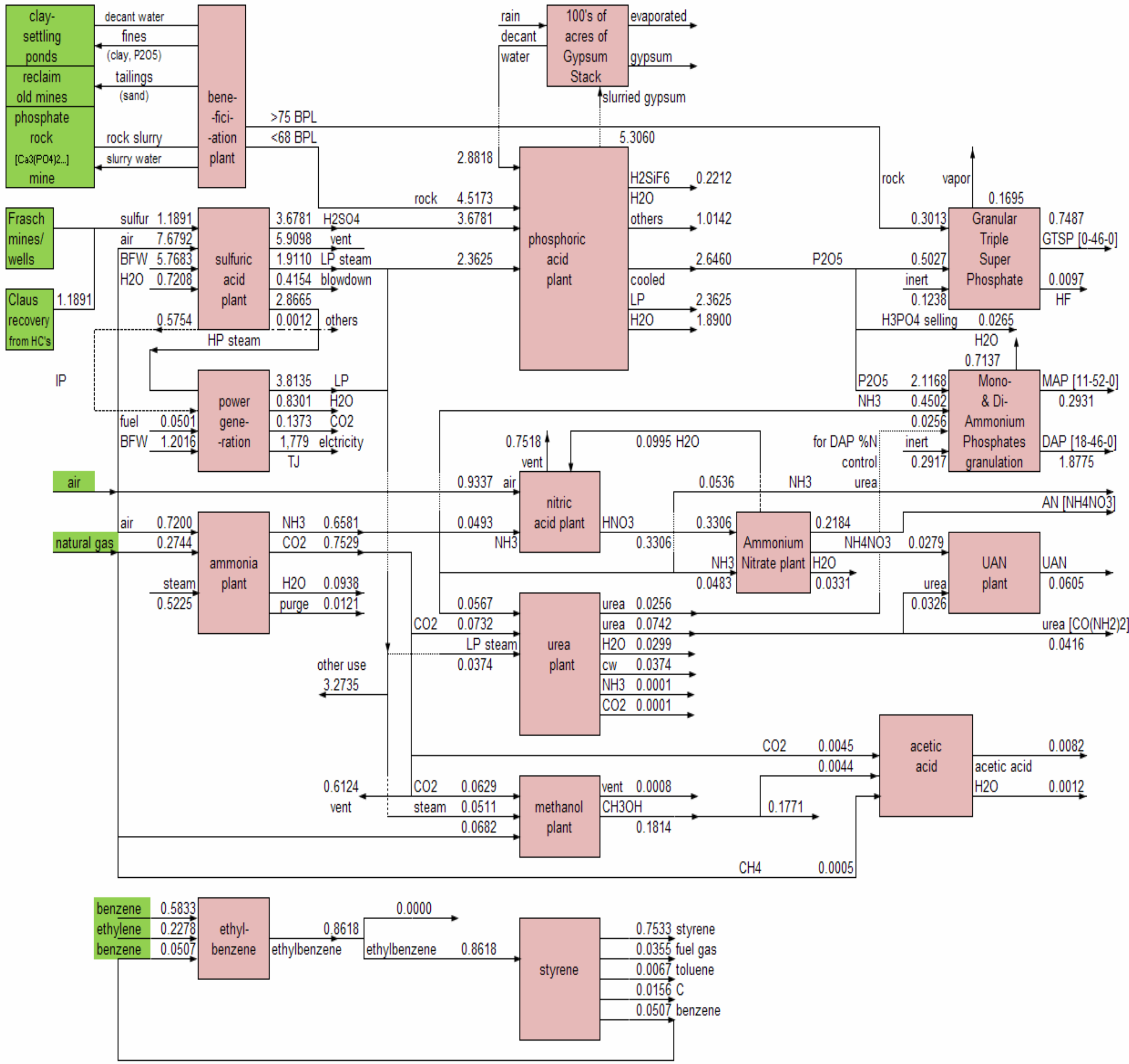

Proposed Biomass-Based Complex Extension
With Single Walled CNT Production
Natural Oils
Sugars
Starches
Cellulose and Hemicellulose
Transesterification
Fermentation
Enzyme Conversion
Acid or Enzyme Hydrolysis
Acid dehydration
Gasification
Anaerobic Biodigestion
Ethanol
Methanol
C6 Sugars
C5/C6 Sugars
Syngas
CH_4
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

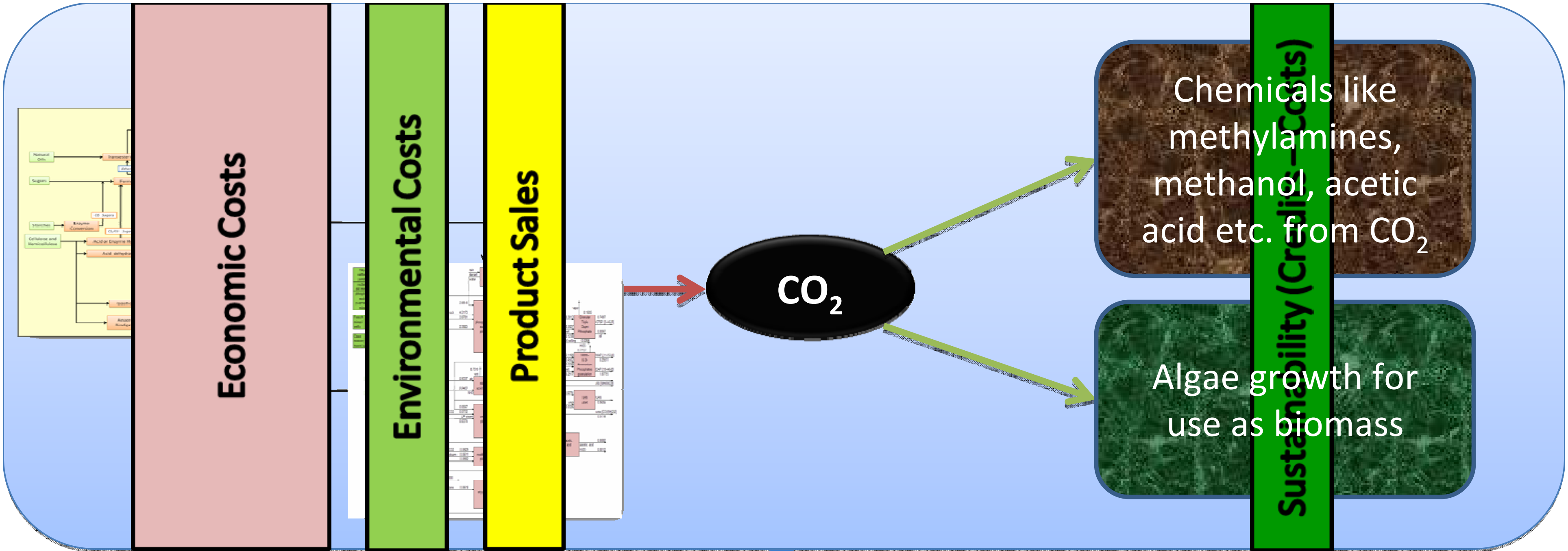
Integrated Chemical Production Complex





Base Case of Plants in the Lower Mississippi River Corridor





Multicriteria Optimization Problem

Maximize: w_1P+w_2S

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

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

$$w_1 + w_2 = 1$$

Subject to:

Multiplant material and energy balance

Product demand

Raw material availability

Plant capacities

Research Directions

Extend the Chemical Production Complex in the Lower Mississippi River Corridor to include:

- Biomass based chemical production complex
- Carbon Nanotube production in the 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

Research Directions

- 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

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

P = ΣProduct Sales – ΣEconomic Costs – ΣEnvironmental Costs

S = ΣSustainability (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