Quantifying Sustainable Development with Sustainable Costs in the Optimization of Chemical Production Complexes with New Plants for Carbon Nanotubes, Carbon Dioxide and Biochemicals

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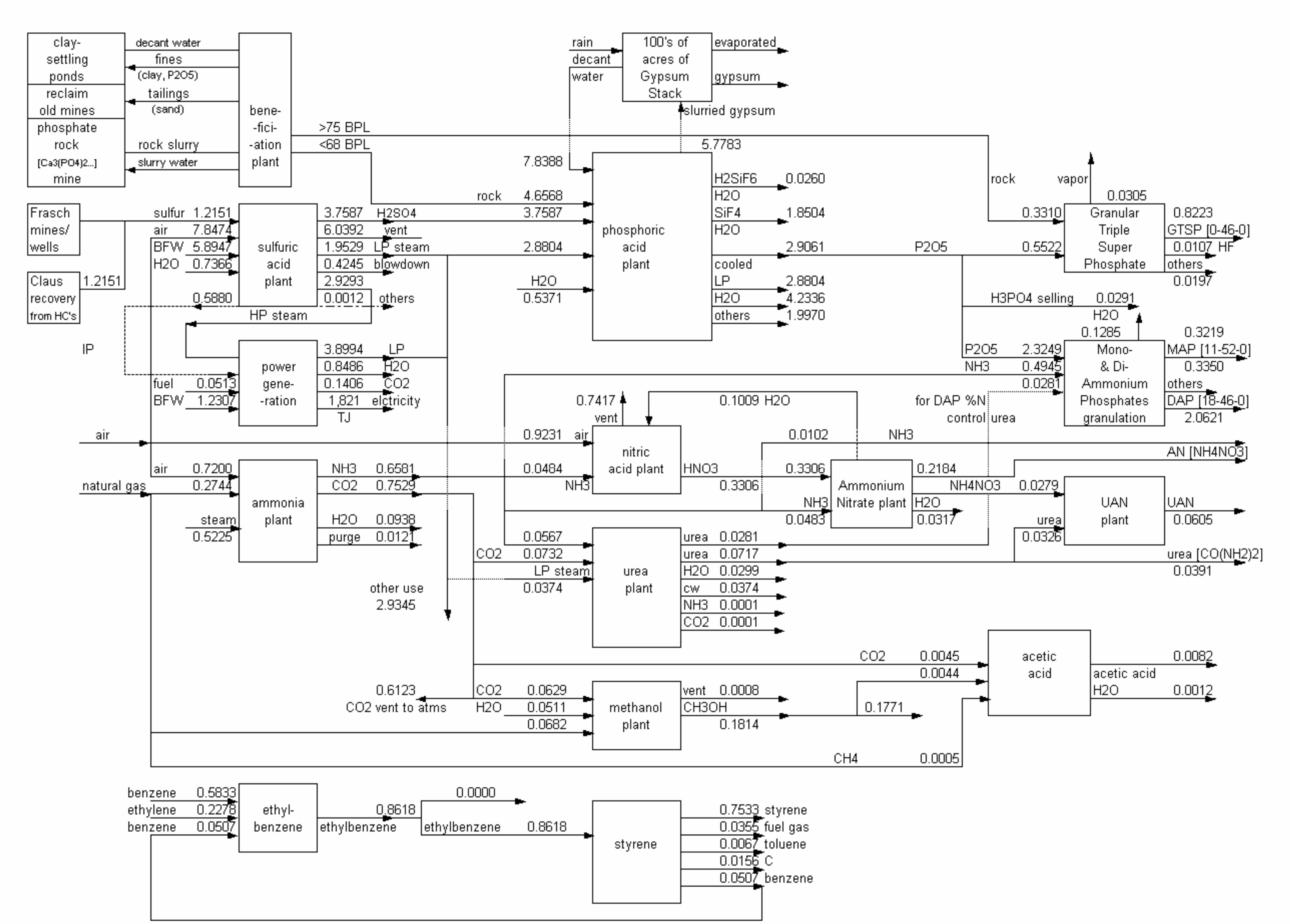
Introduction

- ► Industrial processes using biomass and carbon dioxide mitigate global warming
- ► Objectives are:
  - • Identify and design new industrial processes using biomass and carbon dioxide as raw materials
  - • Show how these processes are integrated into an existing chemical production complex
  - • Obtain the optimal configuration of plants in a chemical production complex using mixed integer nonlinear programming
- ► Demonstrate that these results are applicable to other chemical production complexes in the world

Base Case of Existing Plants



Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year

Optimal Configuration of Plants in a Chemical Production Complex

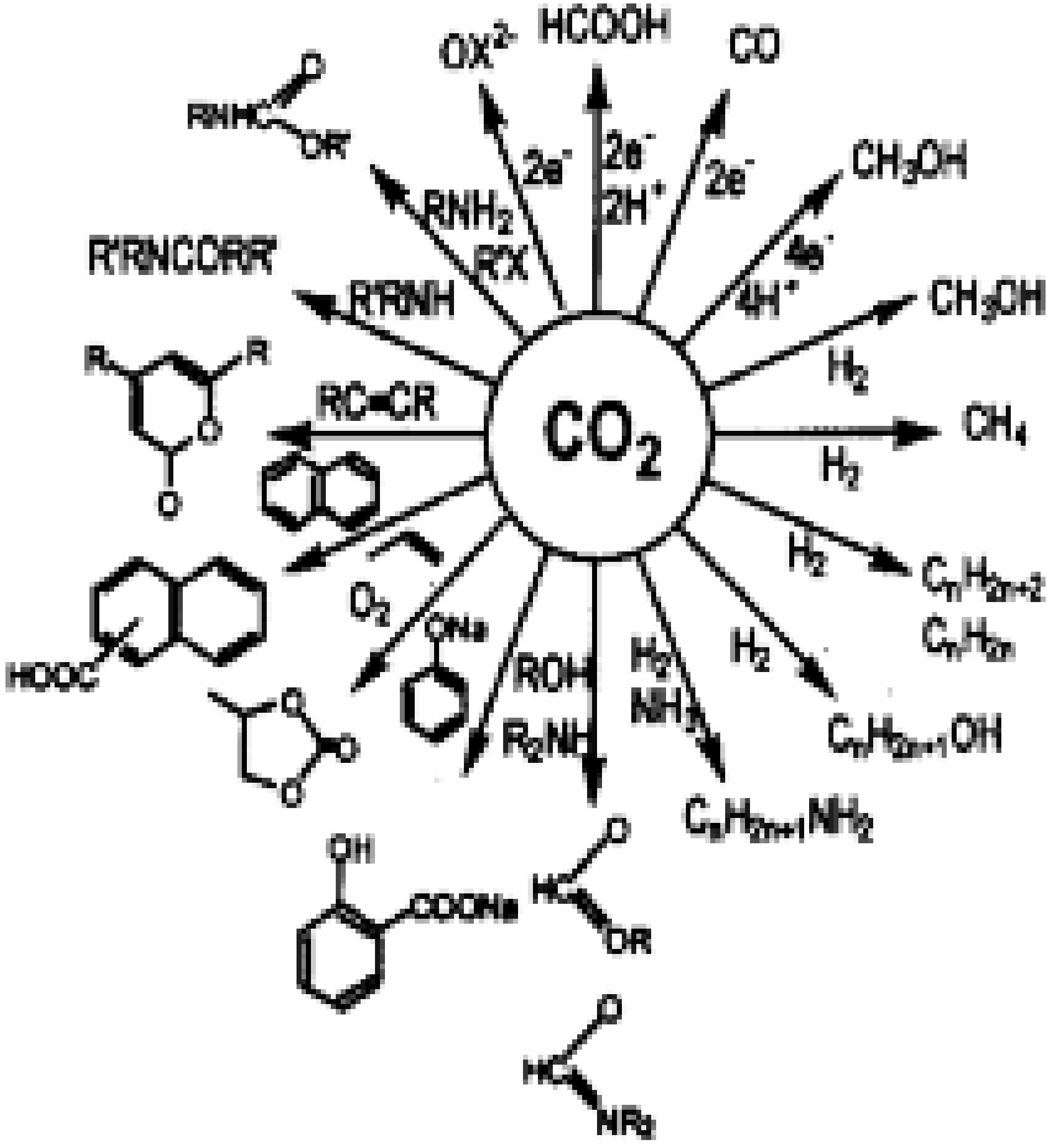
- ► Chemical Complex Analysis System.
  - ● Determines the optimum structure for a complex
  - ● Uses the triple bottom line as the objective function
  - ● Incorporates multi-criteria optimization for Pareto optimal solutions
  - ● Incorporates Monte Carlo simulation for sensitivity analysis of the optimal solutions

- ► Triple Bottom Line - economic, environmental, and sustainable costs
  - ● Economic and environmental cost to the company
  - ● Sustainable cost to society to repair damage to the environment from emissions within permitted regulations

- ► Life Cycle Analysis (LCA)
  - ● Comparative assessment of sustainability using eight impact categories.
  - ● Evaluates categories based on material and energy balances at stages of the life cycle from collecting raw material from earth and ending when all this material is returned to earth.

Carbon Dioxide as a Raw Material

- Intermediate of fine chemicals for the chemical industry
  -C(O)O-: Acids, esters, lactones
  -O-C(O)O-:Carbonates
  -NC(O)OR-: Carbamic esters
  -NCO: Isocyanates
  -N-C(O)-N: Ureas
- Use as a solvent
- Energy rich products
  CO, CH_3OH



From Creutz and Fujita, 2000

Methodology of Developing New Carbon Dioxide Processes

- Identify potentially new processes
- Simulate with HYSYS
- Estimate utilities required
- Evaluate value added economic analysis
- Select best processes based on value added economics
- Integrate new processes with existing ones to form a superstructure for optimization

New Processes Included in the Complex

Product	Synthesis Route	Value Added Profit (cents/kg)
Methanol	CO_2 hydrogenation	2.8
Methanol	CO_2 hydrogenation	3.3
Methanol	CO_2 hydrogenation	7.6
Methanol	CO_2 hydrogenation	5.9
Ethanol	CO_2 hydrogenation	33.1
Dimethyl Ether	CO_2 hydrogenation	69.6
Formic Acid	CO_2 hydrogenation	64.9
Acetic Acid	From CH_4 and CO_2	97.9
Styrene	Ethylbenzene dehydrogenation	10.9
Methylamines	From CO_2, H_2, and NH_3	124
Graphite	Reduction of CO_2	65.6
Synthesis Gas	Methane reforming	17.2
Propylene	Propane dehydrogenation	4.3
Propylene	Propane dehydrogenation with CO_2	2.5

Application of the Chemical Complex Analysis System to Chemical Complex in the Lower Mississippi River Corridor

- Base case
- Superstructure
- Optimal structure

Processes in the Superstructure

Plants in the Base Case

- Ammonia
- Nitric acid
- Ammonium nitrate
- Urea
- UAN
- Methanol
- Granular triple super phosphate
- MAP and DAP
- Sulfuric acid
- Phosphoric acid
- Acetic acid
- Ethylbenzene
- Styrene

Plants Added to form the Superstructure

- Acetic acid from CO_2 and CH_4
- Graphite and H_2
- Syngas from CO_2 and CH_4
- Propane dehydrogenation
- Propylene from propane and CO_2
- Styrene from ethylbenzene and CO_2
- Methanol from CO_2 and H_2 (4)
- Formic acid
- Methylamines
- Ethanol
- Dimethyl ether
- Electric furnace phosphoric acid
- HCl process for phosphoric acid
- SO_2 recovery from gypsum
- S and SO_2 recovery from gypsum

Triple Bottom Line

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

Triple Bottom Line = Profit - Σ Environmental Costs

+ Σ Sustainable (Credits – Costs)

Some of the Raw Material Costs, Product Prices and Sustainability Cost and Credits

Raw Materials	Cost ($/mt)
Natural gas	235
Phosphate rock	
Wet process	27
Electro-furnace	34
Haifa process	34
GTSP process	32
HCl	95
Sulfur	
Frasch	53
Claus	21

Sustainable Cost and Credits	Cost/Credit ($/mt)
Credit for CO2 consumption	6.50
Debit for CO2 production	3.25
Credit for HP Steam	11
Credit for IP Steam	7
Credit for gypsum consumption	5.0
Debit for gypsum production	2.5
Debit for NOx production	1,025
Debit for SO2 production	192

Products	Price ($/mt)
Ammonia	224
Methanol	271
Acetic acid	1,032
GTSP	132
MAP	166
DAP	179
NH4NO3	146
Urea	179
UAN	120
Phosphoric	496

Plants in the Optimal Structure from the Superstructure

Existing Plants in the Optimal Structure

Ammonia
Nitric acid
Ammonium nitrate
Urea
UAN
Methanol
Granular triple super phosphate (GTSP)
MAP and DAP
Contact process for Sulfuric acid
Wet process for phosphoric acid
Ethylbenzene
Styrene
Power generation

Existing Plants not in the Optimal Structure

Acetic acid

New Plants in the Optimal Structure

Formic acid
Acetic acid – new process
Methylamines (MMA and DMA)
Graphite
Hydrogen/synthesis gas
Propylene from CO_2
Propylene from propane dehydrogenation

New Plants not in the Optimal Structure

Methanol (Bonivardi)
Methanol (Jun)
Methanol (Ushikoshi)
Methanol (Nerlov and Chorkendorff)
Ethanol
Dimethyl ether
Styrene - new method
Electric furnace process for phosphoric acid
Haifa process for phosphoric acid
SO_2 recovery from gypsum waste
S and SO_2 recovery from gypsum waste

Triple Bottom Line Results
for the Base Case and Optimal Structure

	Base Case (million dollars/year)	Optimal Structure (million dollars/year)
Income from Sales	1,277	1,508
Economic Costs (Raw Materials and Utilities)	554	602
Raw Material Costs	542	577
Utility Costs	12	25
Environmental Cost (67% of Raw Material Cost)	362	385
Sustainable Credits (+)/Costs (-)	-18	-15
Triple Bottom Line	343	506

Life Cycle Assessment using TRACI

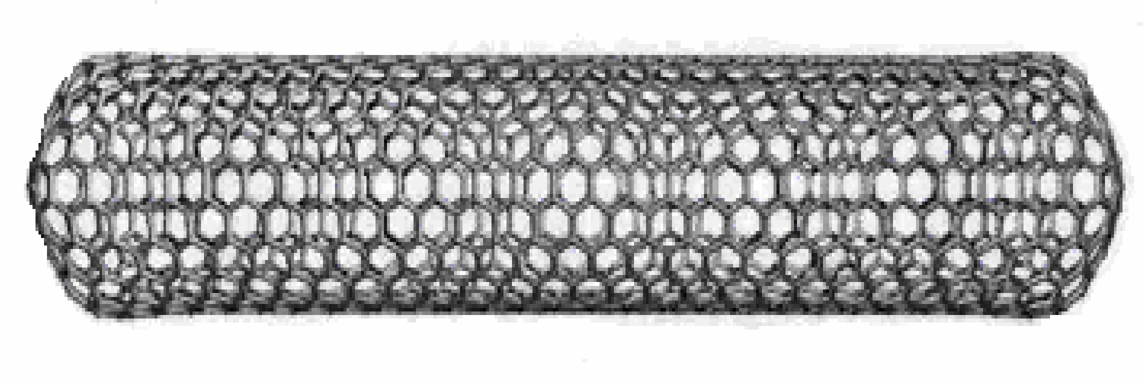
- **Comparative analysis was conducted on the base case and optimal configuration of plants in the chemical production complex using TRACI**
- **Scope is “Entry-to-Exit”**
  - **Classifies resources and releases into various impact categories**
  - **Characterization value quantifies the extent of harm stressor can cause**

- **Changes from the base case to the optimal configuration**
  - **Fossil fuel use increased by 75% from the increase is the energy use of the new plants added to consume excess carbon dioxide being released in the atmosphere.**
  - **Water use increased by a comparable amount**
  - **Global warming category decreased by 66% from base case because new processes consumed carbon dioxide**
  - **Small changes in acidification, water use, eutrophication, photochemical smog and human health.**

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.
- Challenge - production of purified carbon nanotubes in commercial quantities at affordable prices.

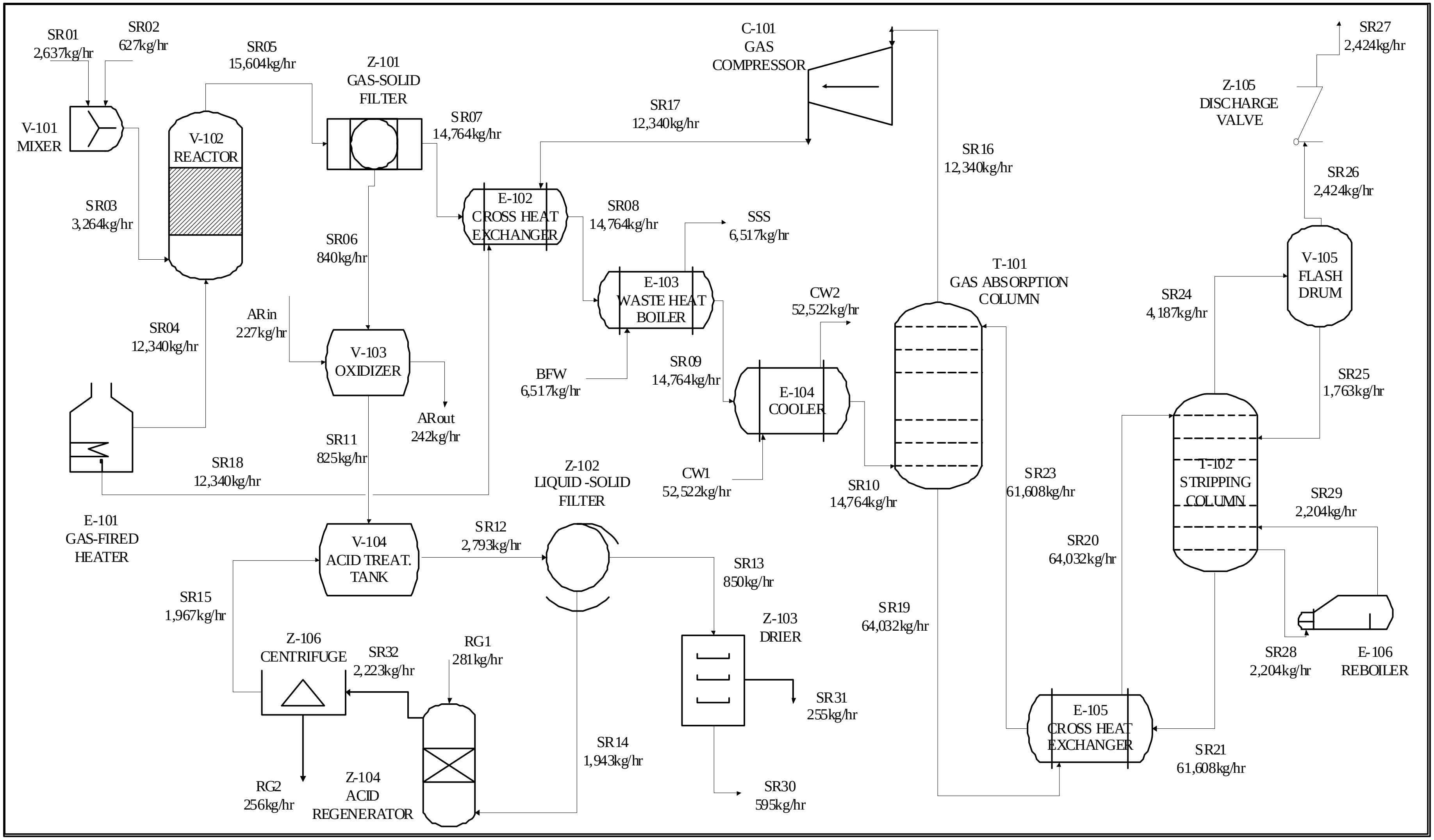
Market price is $100-$400/gm for purified nanotubes



Summary of Conceptual Designs 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 ^{o}C @ 450 psi	950 ^{o}C @ 150 psi
Selectivity to CNT	90%	80%
Purification	- Oxidation - Acid Treatment - Filtration	- Leaching - Froth Flotation - Acid Treatment
Production rate (kg/hr)	595	595

Flow Diagram of CNT-FBR Process



Summary of the Profitability Analysis for the Conceptual Designs of CNT Processes

Economic Analysis	CNT-PFR Process	CNT-FBR Process
Total Plant Costs	$4.6 million	$4.4 million
Total Product Costs	$186 million	$124 million
Annual Sales Revenue	$450 million	$450 million
Economic Price	$38/kg	$25/kg
Net Present Value (NPV)	$609 million	$753 million
Rate of Return (ROR)	37.4%	48.2%

Sustainable Chemical Plants using Biomass Feedstocks

Vision

- Convert existing plants to ones that are based on renewable resources requiring nonrenewable resource supplements

- Develop new plants using renewable resources which supply the needed goods and services of the current ones

Essential component of sustainable development

- Embodies the concept that sustainability is a path of continuous improvement, where products and services required by society are delivered with progressively less negative impact upon the Earth

- Consistent with sustainable development is defined as development which meets the needs of the present without sacrificing the ability of the future to meet its needs

Biomass Feedstock

- Virgin Biomass –
  - Specifically grown feedstock for food, animal feed, fuel or chemicals
  - Unit price set by usage as food or animal feed

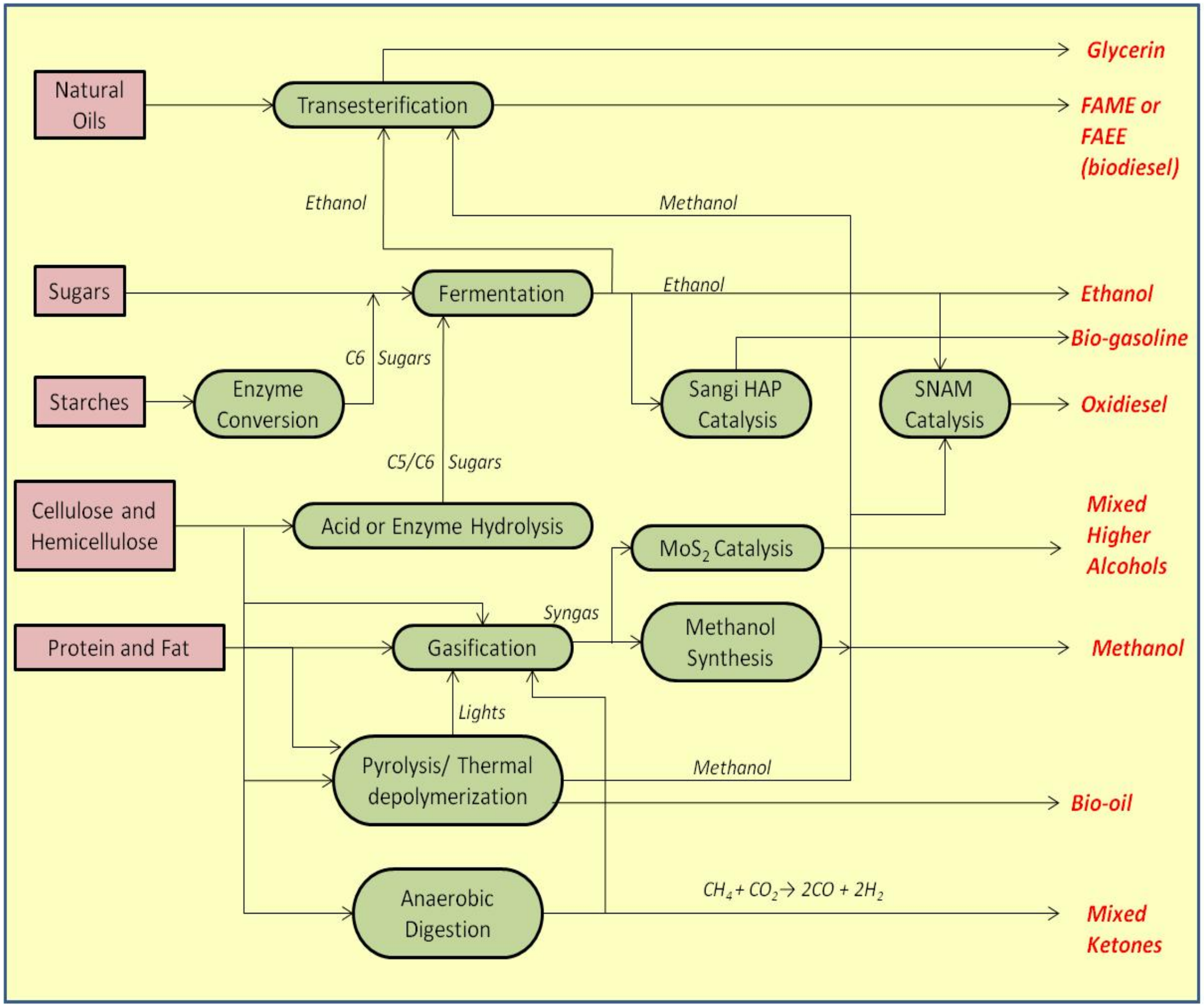
- Waste Biomass –
  - Typically agricultural residue, municipal solid waste, used cooking oils, fats and grease from animals etc.
  - Used as fuel
  - Unit price set by price of the fuel it replaces

- United States can provide about 1.0 billion dry tons of sustainable, collectable biomass and continue to meet food, feed and export demands. Corn led in annual production of grain crops in the U.S. with 330,000 tons per year in 2006.

Biomass Conversion Routes

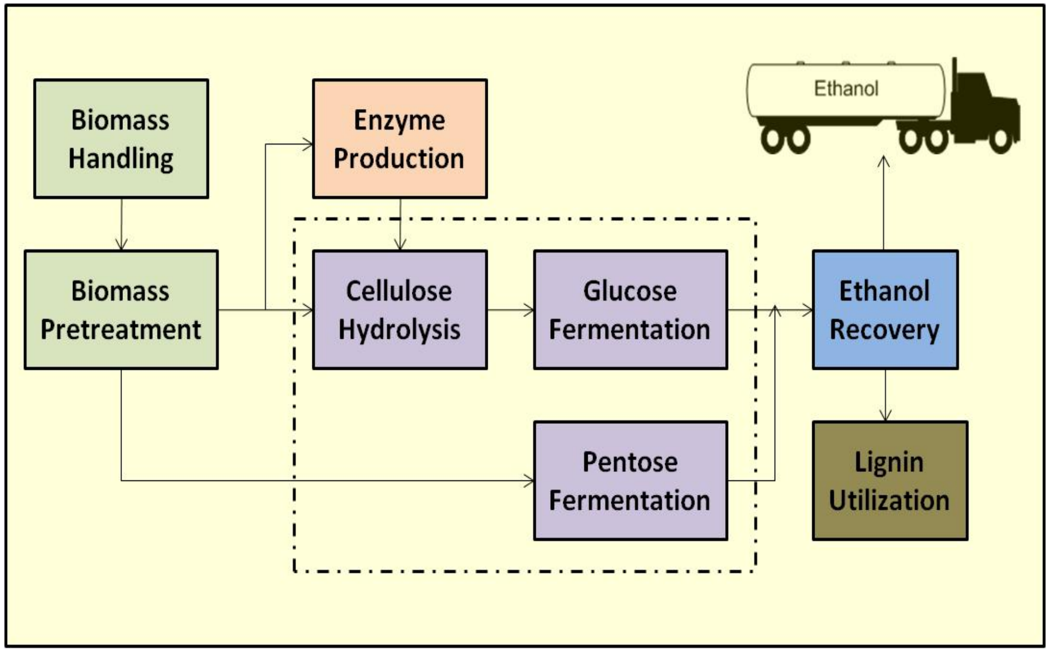
Common conversion routes for biomass include:

- **Fermentation**
- **Anaerobic digestion**
- **Transesterification**
- **Chemical conversion**
- **Gasification/Pyrolysis**
- **Liquefaction**



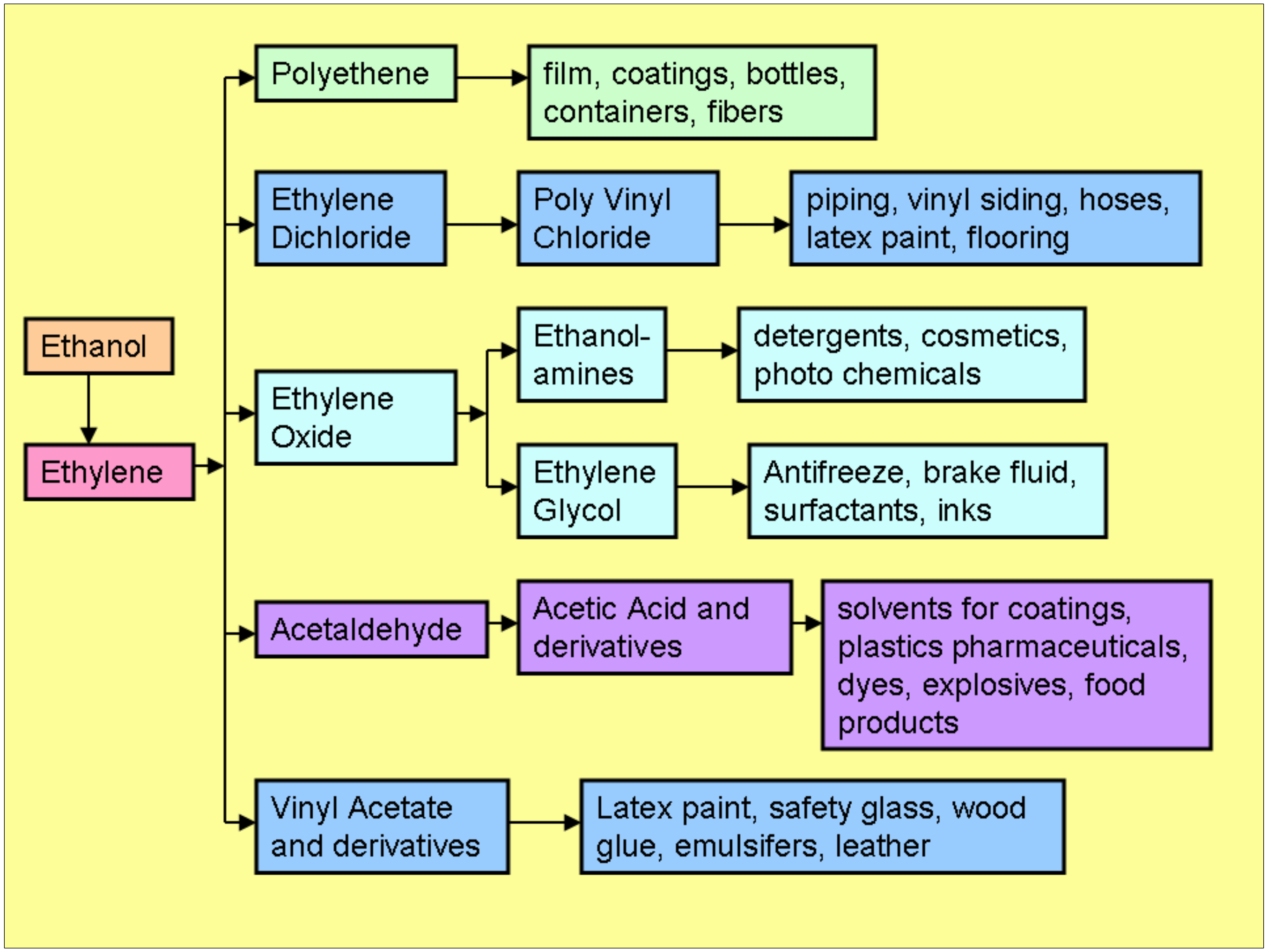
Chemicals from Fermentation

- **Fermentation is the enzyme-catalyzed transformation of an organic compound to release energy.**
- **Fermentation feedstock can be starch (corn), sugars (sugarcane) or cellulosic and lignocellulosic biomass (switchgrass, corn stover).**
- **Fermentation using different enzymes yield different products like succinic acid, butanol etc.**



U.S. produced 5.0 billion gallons of ethanol in 2006
Approximately 90% of U.S. ethanol is produced from corn
60% of the world's biobased ethanol is obtained from sugar cane in Brazil

Ethanol Product Chain

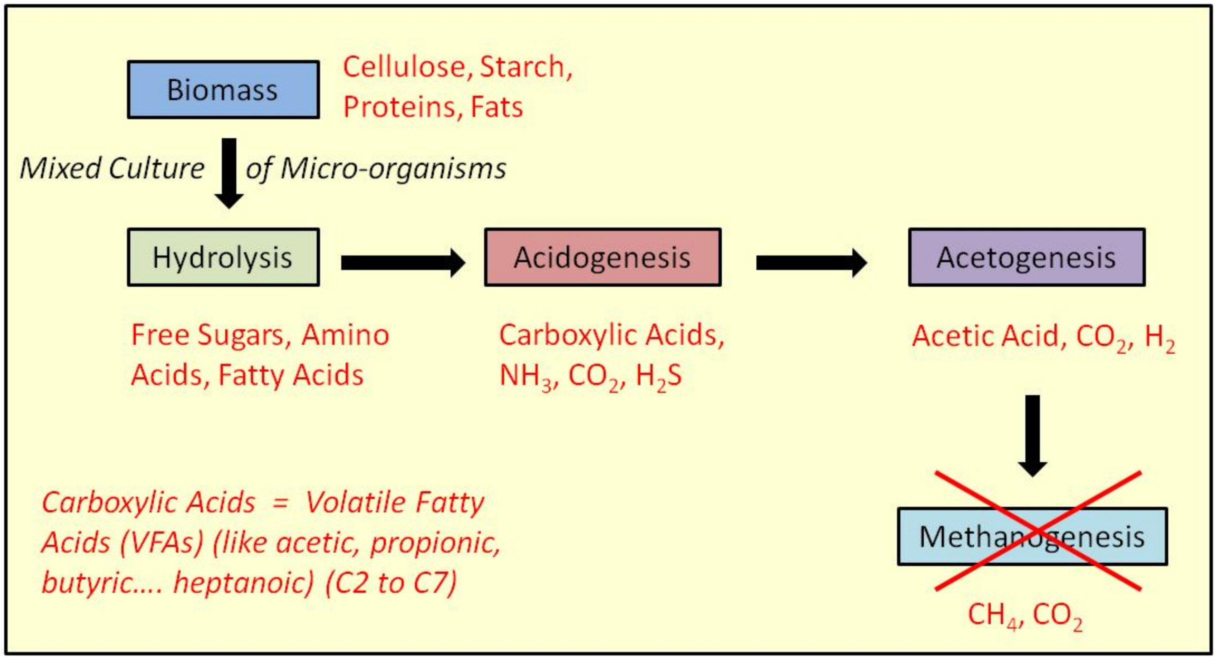


Ethanol can be the starting material for ethylene which is a major commodity chemical used to produce polyethylene, acetaldehyde etc.

Anaerobic Digestion of Mixed Biomass

Inhibition of the fourth stage of anaerobic digestion produces organic acids

Hydrolysis - Complex organic molecules are broken down into simple sugars, amino acids, and fatty acids with the addition of hydroxyl groups.
Acidogenesis - Volatile fatty acids (e.g., acetic, propionic, butyric, valeric) are formed along with ammonia, carbon dioxide and hydrogen sulfide.
Acetogenesis - Simple molecules from acidogenesis are further digested to produce carbon dioxide, hydrogen and organic acids (mainly acetic acid).
Methanogenesis - The organic acids are converted to methane, carbon dioxide and water.



Biomass

Cellulose, Starch,
Proteins, Fats

Mixed Culture of Micro-organisms

Hydrolysis

Free Sugars, Amino
Acids, Fatty Acids

Acidogenesis

Carboxylic Acids,
NH_3, CO_2, H_2S

Acetogenesis

Acetic Acid, CO_2, H_2

Methanogenesis

CH_4, CO_2

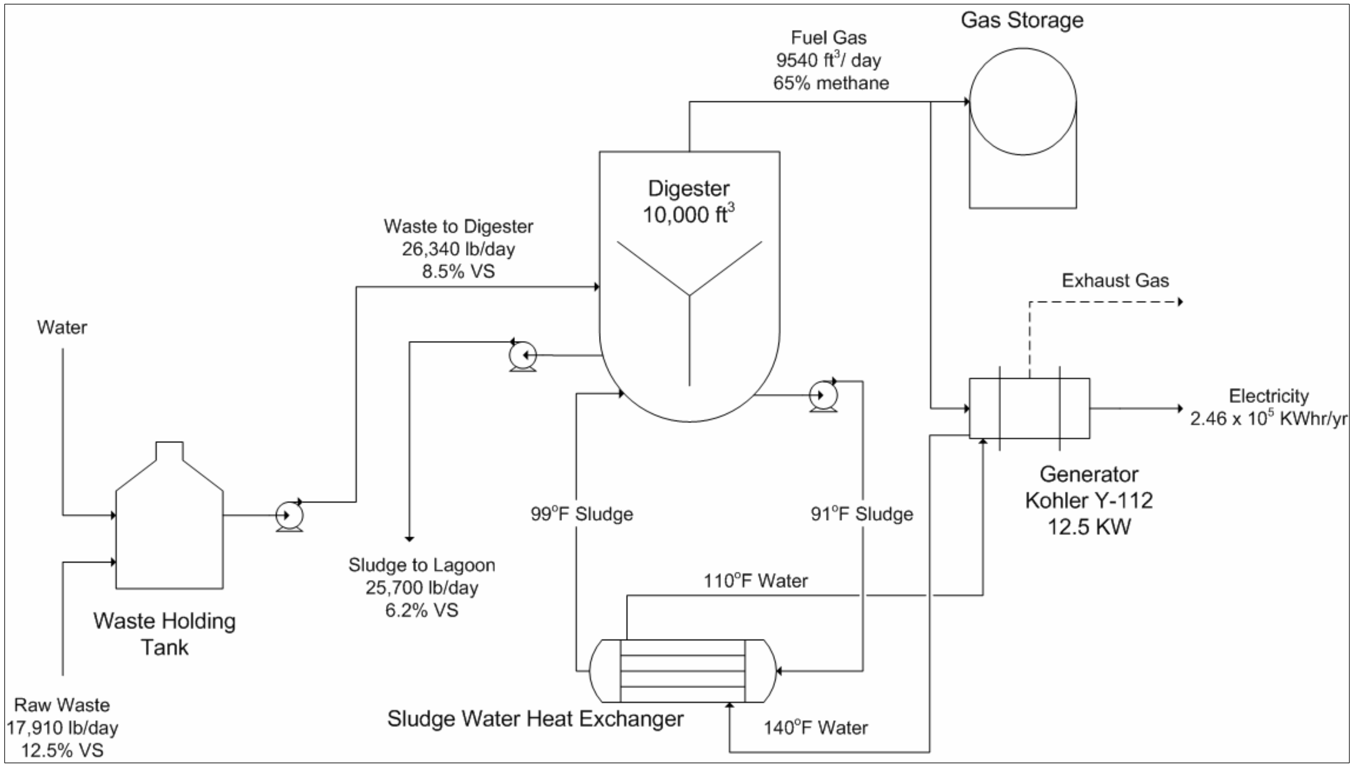
Carboxylic Acids = Volatile Fatty Acids (VFAs) (like acetic, propionic, butyric.... heptanoic) (C2 to C7)

The MixAlco process has a favorable return for producing acetone, diethyl ketone, and dipropyl ketone

Anaerobic Digestion of Animal Waste

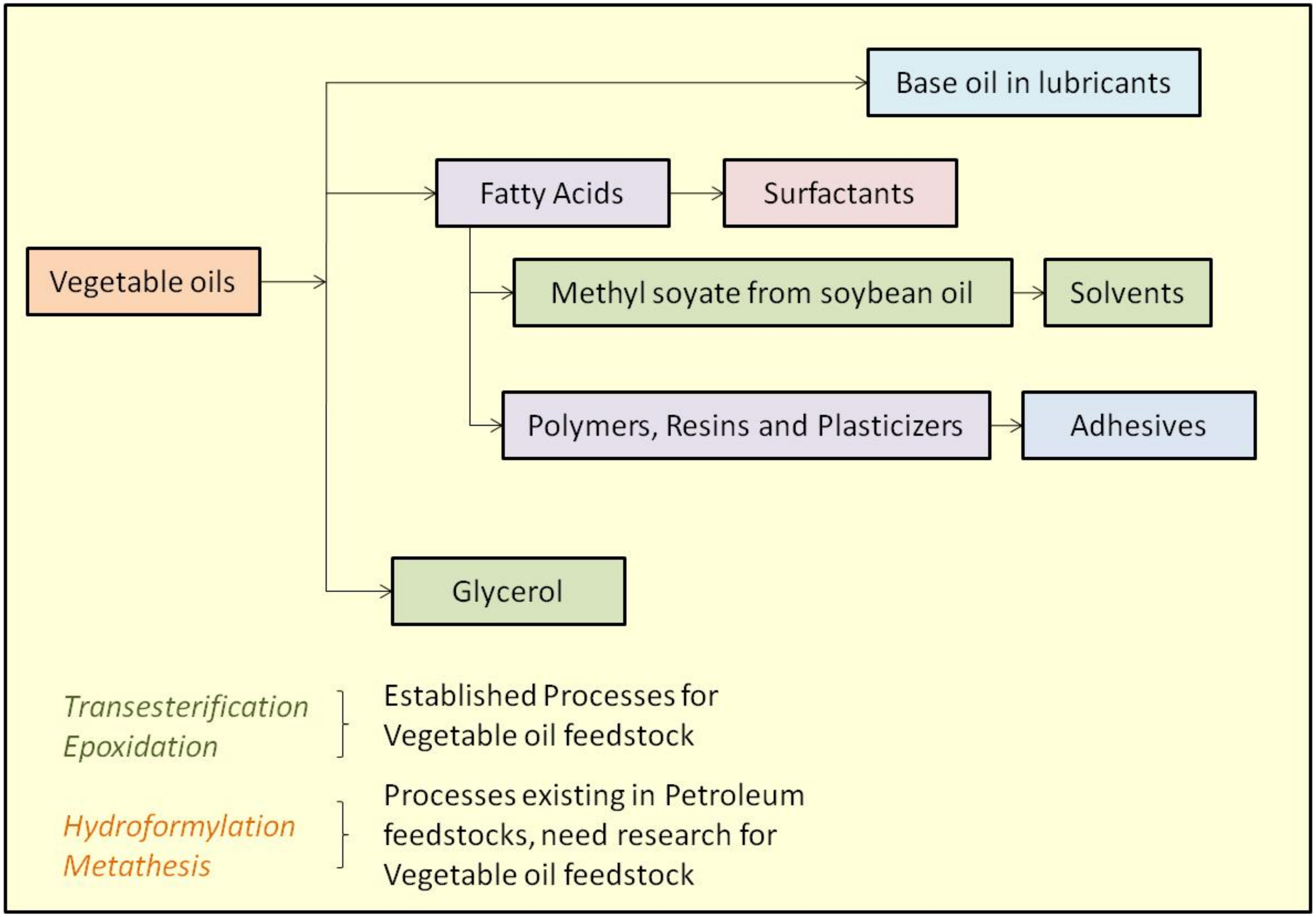
In this process flow diagram, anaerobic digestion of farm waste is used to produce electricity.

The fuel gas (commonly known as biogas) is a mixture of 65% methane and 35% carbon dioxide.



Chemicals from Vegetable oils

Vegetable oils can be directly used as base oil in lubricants or can be converted by transesterification to a wide variety of chemicals

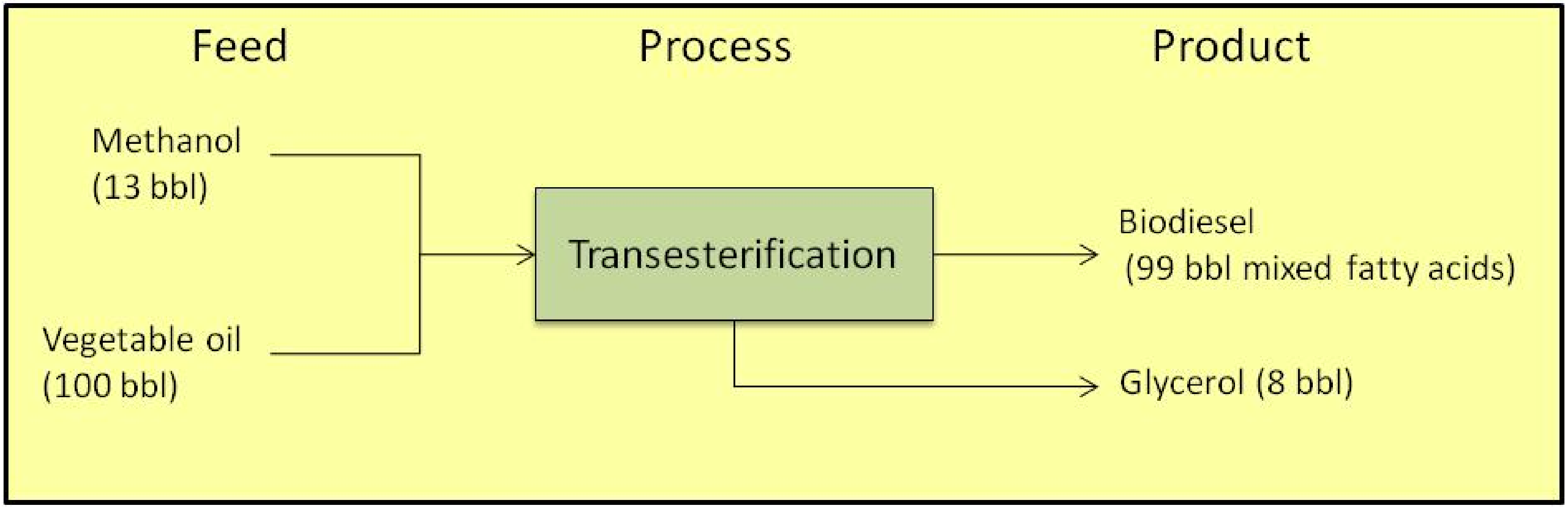


Chemicals from Transesterification

Transesterification process is the treatment of vegetable oil with an alcohol, acid or enzyme catalyst to produce esters and glycerol.

If methanol is used, then fatty acid methyl esters(FAME) are produced.

These esters have properties similar to diesel and can be used as fuel (biodiesel) or further transformed to chemicals.


Feed

Process

Product

Methanol
(13 bbl)

Vegetable oil
(100 bbl)

Transesterification

Biodiesel
(99 bbl mixed fatty acids)

Glycerol (8 bbl)

Utilization of Glycerol

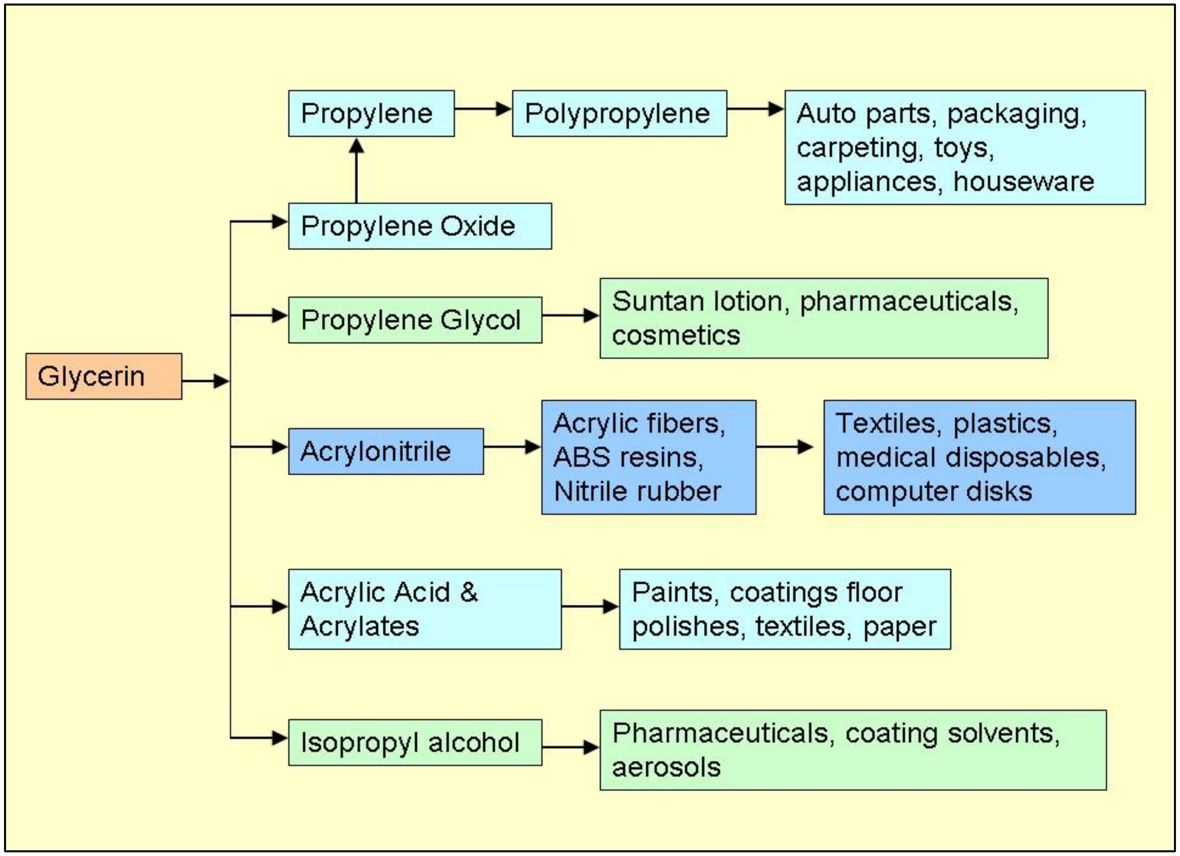
Glycerol or commonly known as glycerin is an byproduct of the transesterification process.

~10% by weight of glycerol is produced as a byproduct in transesterification process.

Glycerin can be used to manufacture numerous commodity chemicals such as propylene glycol.

Bio-PDO (1,3-propanediol) is a proprietary chemical produced from glycerol by DuPont.

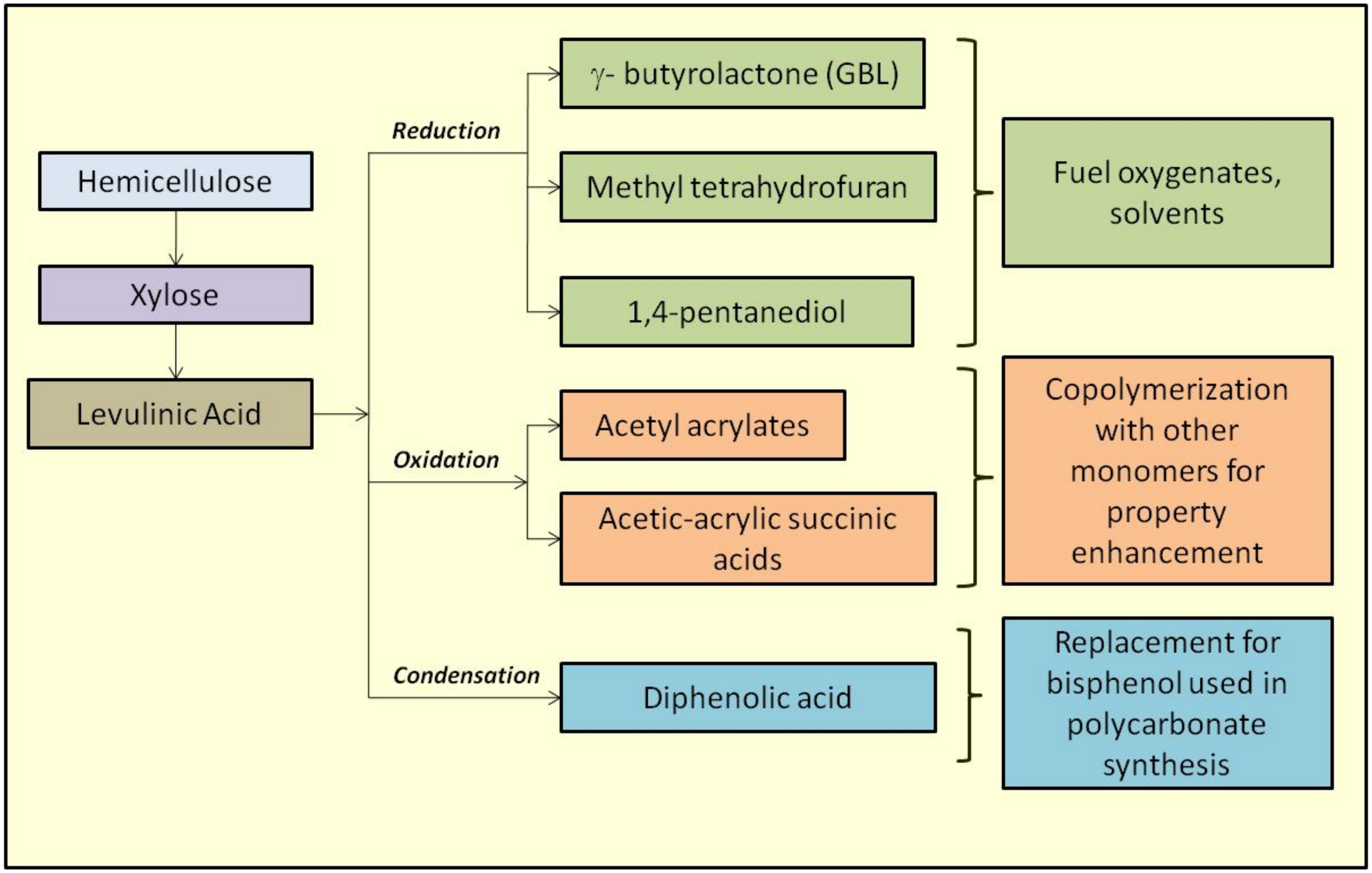
New low pressure and temperature (200 psi and 200°C) catalytic process for the hydrogenolysis of glycerol to propylene glycol has been reported.



Chemical Conversion of Biomass to Chemicals – Levulinic Acid

Levulinic acid can be produced from acid treatment of xylose.

It is a key intermediate for conversion to commodity chemicals by reduction, oxidation or condensation



Hemicellulose

Xylose

Levulinic Acid

Reduction

γ- butyrolactone (GBL)

Methyl tetrahydrofuran

1,4-pentanediol

Fuel oxygenates, solvents

Oxidation

Acetyl acrylates

Acetic-acrylic succinic acids

Copolymerization with other monomers for property enhancement

Condensation

Diphenolic acid

Replacement for bisphenol used in polycarbonate synthesis

Chemicals from Gasification

- **Biomass gasification is the conversion of biomass to synthesis gas (mixture of CO and H_2).**

- **“Syngas” is a starting point starting material for the manufacture of ammonia, methanol, urea and other important chemicals.**

- **Gasification can be in absence of oxygen (pyrolysis), in presence of oxygen (partial oxidation) and in presence of steam (steam reforming) :**

Pyrolysis: $C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$
Partial oxidation: $C_6H_{10}O_5 + O_2 \rightarrow 5CO + CO_2 + 5H_2$
Steam reforming: $C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2$

- **Synthesis gas is used in the chemical production complexes to produce ammonia and methanol**

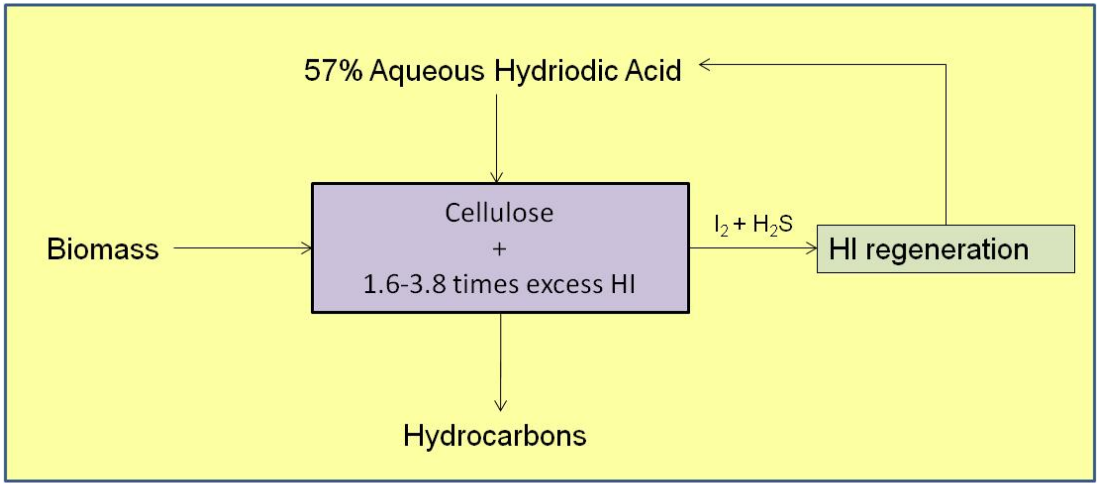
- **Nearly 12.2 billion pounds of methanol are produced annually in the USA . Methanol is converted to higher value chemicals such as formaldehyde (37%), methyl tertiary butyl ether (28%) and acetic acid (8%).**

Chemicals from Pyrolysis

- **Pyrolysis is the direct thermal decomposition of organic components of biomass in absence of oxygen to yield useful solid and liquid products and fuel gases.**
- **Slow, irreversible pyrolysis (conventional) include processes like carbonization, destructive distillation, dry distillation and retorting.**

Chemicals from Thermal Liquefaction

- **Thermal liquefaction is the direct chemical conversion of biomass to liquid fuels using a liquid medium (aqueous or non-aqueous).**
- **Hydriodic acid is used to convert biomass under low temperature and pressure to yield hydrocarbons.**



New Processes in the Chemical Complex

- **Two carbon nanototube processes – CNT-PFR and CNT FBR**

- **Biomass processes:**
  - **Fermentation process for corn to ethanol**
  - **Fermentation process for waste biomass (sugarcane bagasse) to ethanol**
  - **Conversion of ethanol to chemicals**
  - **Fermentation of sugar to succinic acid and derivatives**
  - **Anaerobic digestion to produce mixed ketones**
  - **Transesterification to produce FAME and FAEE**
  - **Conversion of glycerol to propylene glycol and other chemicals**
  - **Chemical conversion to levulinic acid and derivatives**
  - **Gasification to produce synthesis gas**
  - **Conversion of synthesis gas to ammonia, methanol and urea**
  - **Thermal liquefaction to produce hydrocarbons**

- **The optimum configuration of plants will be determined based on economic, environmental and sustainable costs using multicriteria optimization and Monte Carlo simulation**