Place of Biochemicals in Viable Biorefinery Operations

Petroleum Refining and Petrochemicals as a Model

IEA Bioenergy Workshop
Biofuels and Bioenergy: Challenges and Opportunities

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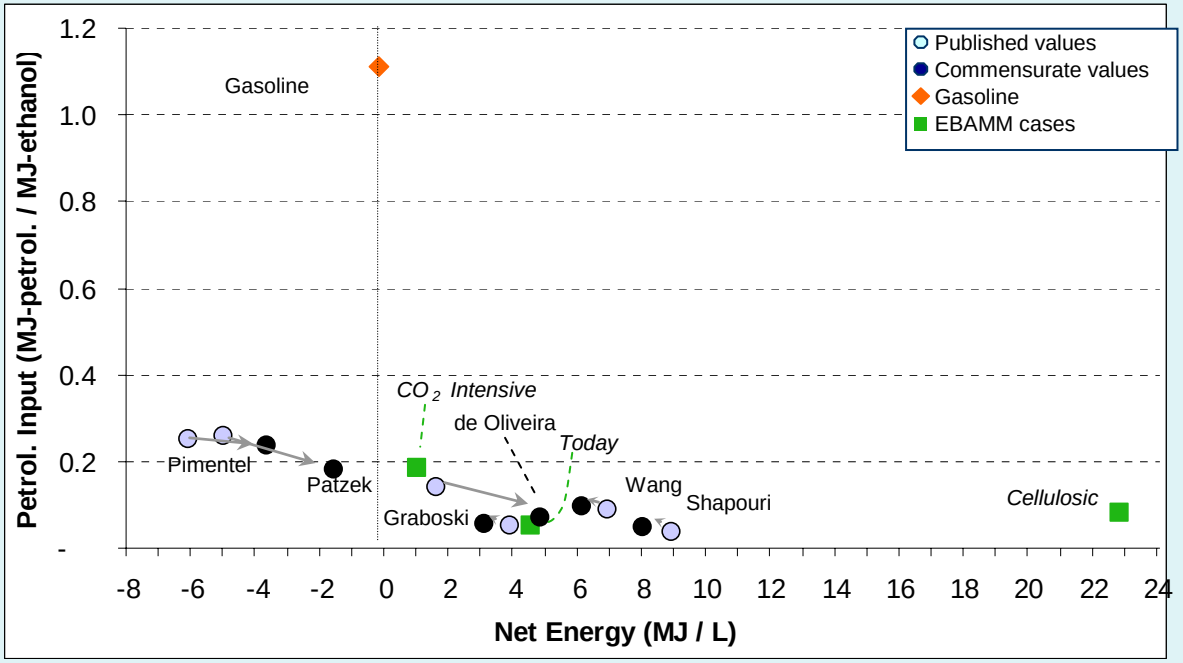
Impact of Bioproducts to Ethanol



Source: Alexander E. Farrell, Richard J. Plevin, Brian T. Turner, Andrew D. Jones, Michael O'Hare, Daniel M. Kammen, Jan 2006, VOL 311, SCIENCE

Two Refining Approach

- Corn wet milling/refining
  - (horizontal integration)
- Petroleum refining/petrochemicals plant
  - (vertical integration)

Petroleum Industry Timeline

1858 Abraham Gesner, M.D. Patented the extraction of lamp fuel from aphalt rock and named kerosene.

1859 Colonel Drake, Discovered petroleum near Titusville, Pensilylvania.

1860 Petroleum started to be distilled and cracked to produce kerosene.

Kerosene for lamps was the mainstay of the newfound petroleum industry.

1880 Over one hundred house fires were attributed to kerosene lamps.

1900 Until 1900's gasoline was a by-product of kerosene production from crude-oil and not an immediately useful one.

There was no significant demand for gasoline.

1920 The first petrochemical, isopropyl alcohol (75 tons/yr) manufactured on an industrial scale by Standard Oil of New Jersey.

1940 Establishment of petrochemical plants.

Most of the petroleum companies (some notable exceptions: Standard Oil of New Jersey and Shell) neglected petrochemicals and sold thei roff gases to chemical companies.

1964 World's aggregated petroleum production was about 8.4 bbl of which the fields in the United States were producing approximately 33%.

2000 Individual petrochemicals now number more than 4000 and many of them produced in large volume.

Petroleum supplies the feedstocks for more than 80% of produced organic chemicals.

Today etyhlene serves as a proxy to the overall petrochemical industry. North American annual production capacity is around 80 billion lb.

Birth of Petrochemicals

- Petrochemicals long neglected by the petroleum companies.
- Early thinking and planning of petroleum managers did not process along the chemical lines
- Several chemical companies took the lead.
- Joint ventures between chemical and petroleum companies
- Several larger petrochemical companies organized their own petrochemicals devision seperately from their oil refineries.

Refining and Petrochemicals Plants

- The basic materials supplied by petroleum refineries or natural gas plants are liquid petroleum gases, gases from cracking process, liquid distillate C4-C9, and distillates from special cracking processes and cyclic fractions of aromatics
- Such mixtures are separated in into their constituents in petroleum refineries
- Such feedstock are converted to petrochemicals by chemical conversions in petrochemical complexes.

Refining and Petrochemicals Plants

Refinery Products

(Gallons per Barrel)

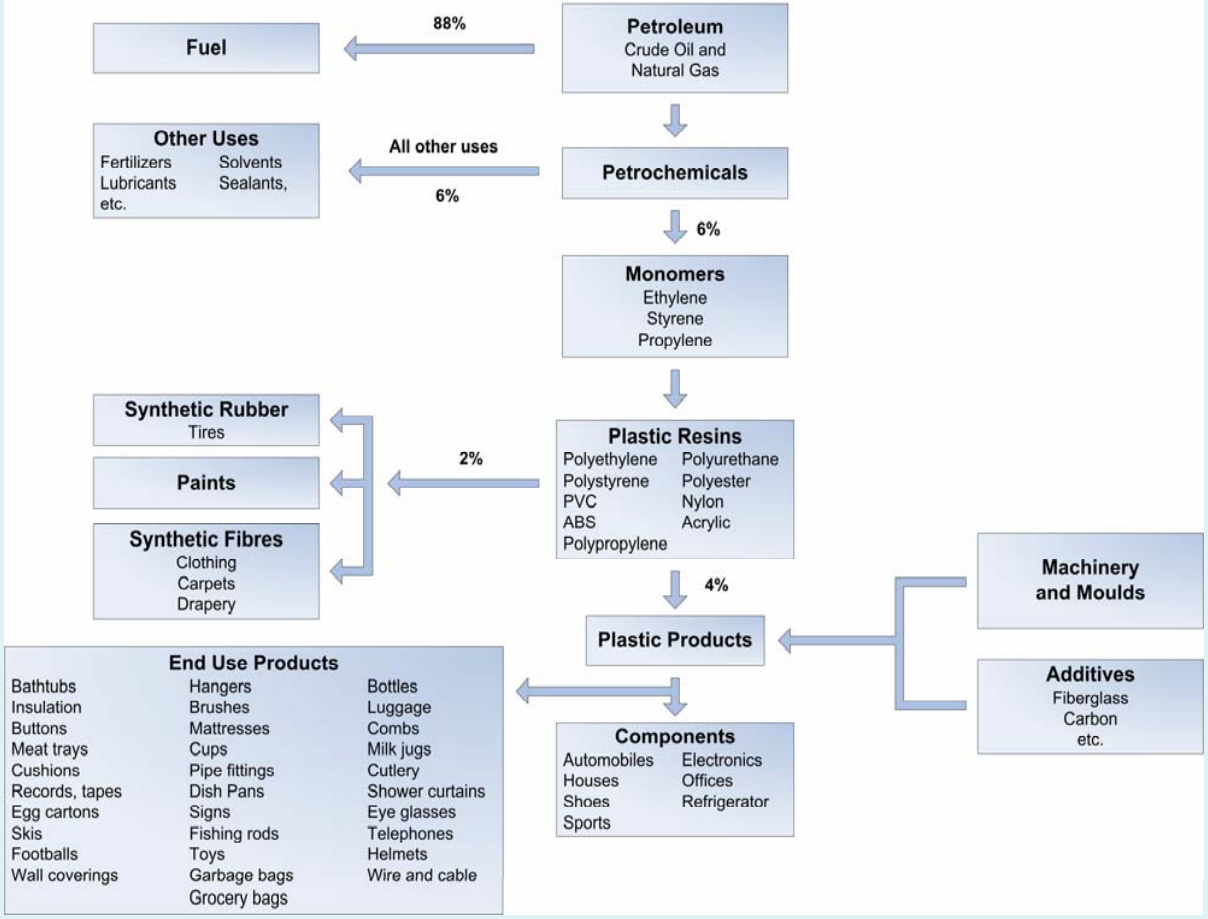
- gasoline 19.4
- diesel & home heating oil 9.7
- kerosene-type jet fuel 4.3
- residual fuel oil 1.9
- liquefied refinery gases 1.9
- still gas 1.8
- coke 2.0
- asphalt and road oil 1.4
- petrochemical feedstock 1.1
- lubricants 0.5
- kerosene 0.2
- other 0.4

Petrochemicals

(Only 3% oil and gas output is used in petrochemicals and plastics) Currently US annual ethylene production is around 65 billion lb, and used in the production of 132 bilion lb of organic chemicals and 110 billion lb of

- Olefins
  - Ethylene
  - Propylene
  - Butylene
  - Butadiene
- Aromatics
  - Benzene
  - Toluene
  - Xylene

Use of Petroleum Resources



Today's Petrochemical Industry

- No new significant inventions in the past 40 years. The petrochemical industry did not invent a new molecule in the last 40 years of any significance.
- The production technologies, consumption patterns and costs have reached a maturity stage with less and less innovation.
- Most of the new innovations in the last two decades are focused on: (1) value enhancement of existing products and /or (2) value capture by traversing the distribution channel
- The wide fluctuations between crude & natural gas ratio in terms of $value per BTU have taken an important role, because of its dependence on gas crackers and lack of naphtha cracking capacity.

Two points of view – Petroleum

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FUEL MIND

- Immediate profits
- Is methodical, will not be rushed
- Concentrates on fuels
- Is accustomed to large cash flow, big expenditures
- Produces at highest possible rate
- Build the biggest facility
- Prefers to increase amount of main products

CHEMICAL MIND

- Long term approach
- Values timing, moves rapidly
- Believes in diversification
- Combines smaller cash flow with long range investments
- Takes calculated risks on forecasts of greater demand
- Tailor to meet present and estimated future needs
- Prefers to increase the number of products

Source: Chemical Process Industries, Shreve, Third Ed., McGraw Hill, 1967

Two points of view – Biomass

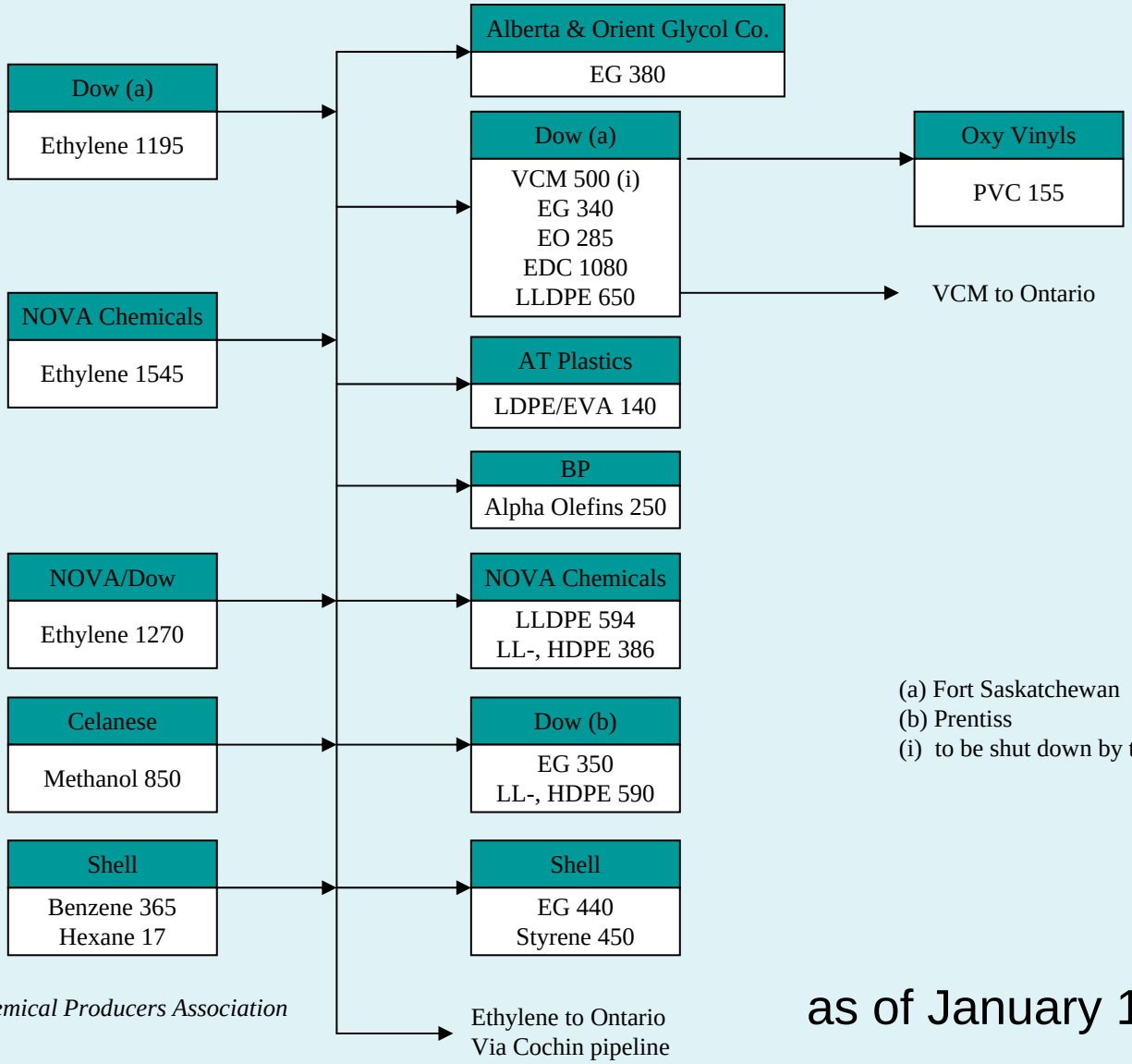
BIOFUEL MIND

- Immediate profits
- Is methodical, will not be rushed
- Concentrates on bioethanol
- Is accustomed to large cash flow, big expenditures
- Produces at highest possible rate
- Build the biggest facility
- Prefers to increase amount of main products

CHEMICAL MIND

- Has to have long term approach
- Has to move rapidly
- Has to offer diversified products
- Has to combine smaller cash flow with long range investments
- Has to take calculated risks on forecasts of greater demand
- Has to tailor to meet present and estimated future needs
- Has to increase the number of products

Alberta's Chemicals to Polymers Product Flow (kt)



(a) Fort Saskatchewan
(b) Prentiss
(i) to be shut down by the end of 2005

Source: Canadian Chemical Producers Association

as of January 1, 2004

Scale Comparison

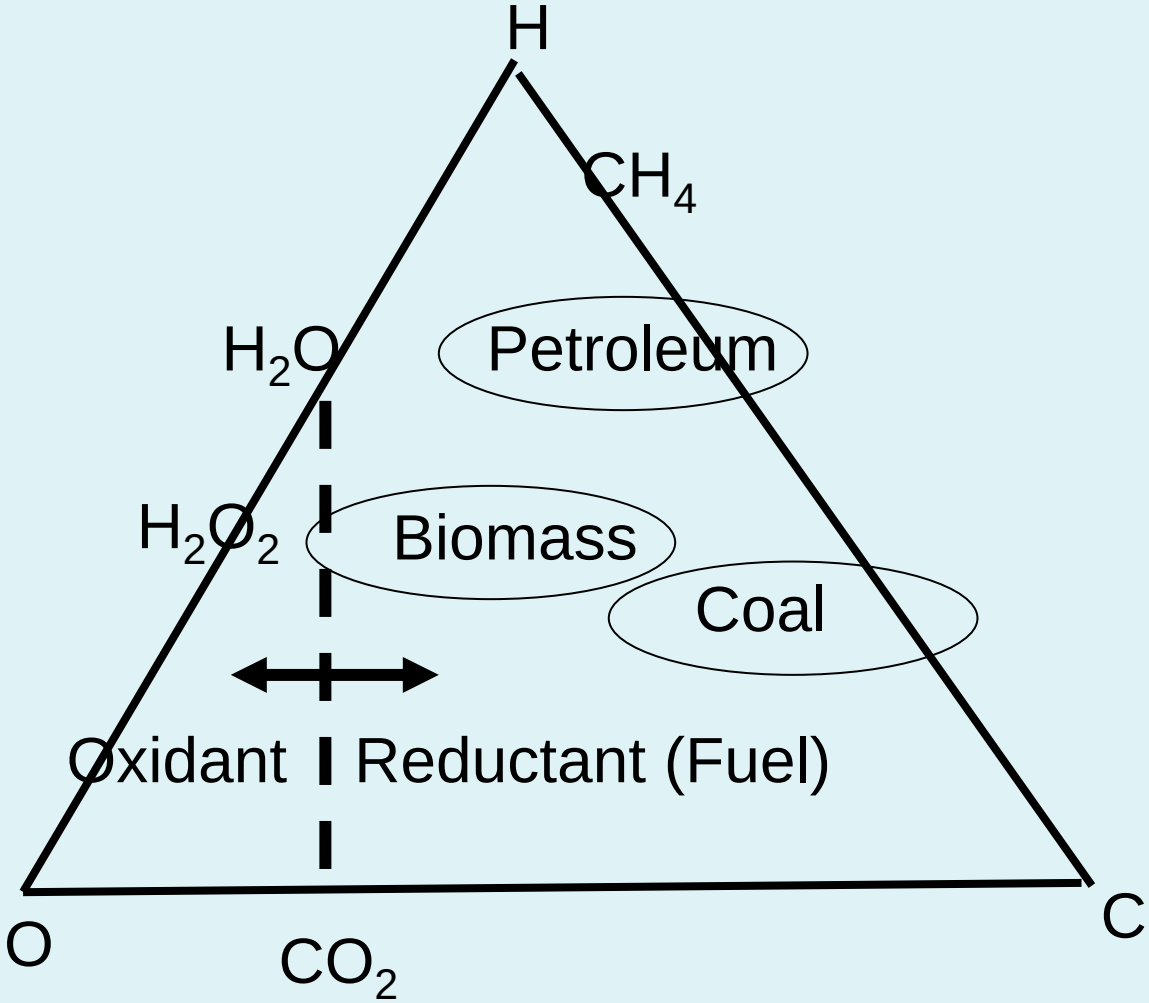
- Capacity of a full scale biorefinery: 3,250 dry kt/year [1]
- Produces: 300 MMgal ethanol/year [1]
- Overall ethanol conversion: 25% (85 gal ethanol/dry ton
- Typical ethylene plant 1,000 kt/year

[1] *Lynd, L.R., Wyman, C., Laser, M., Johnson, D., Landucci, R., "Strategis Biorefinery Analysis: Analysis of Biorefineries", NREL/SR 510-35578.*

Comparison of Resources: Oil vs. Biomass

Oil	***Biomass***
Simpler structure	Complex structure
Mostly low molecular mass	Mostly high molecular mass
Hydrocarbons C_nH_{2n+2}	Carbohydrates $C_n(H_2O)_n$
Hydrophobic	Hydrophilic
Devoid of oxygen and lacking functional groups	Overfunctionalized with hydroxyl groups

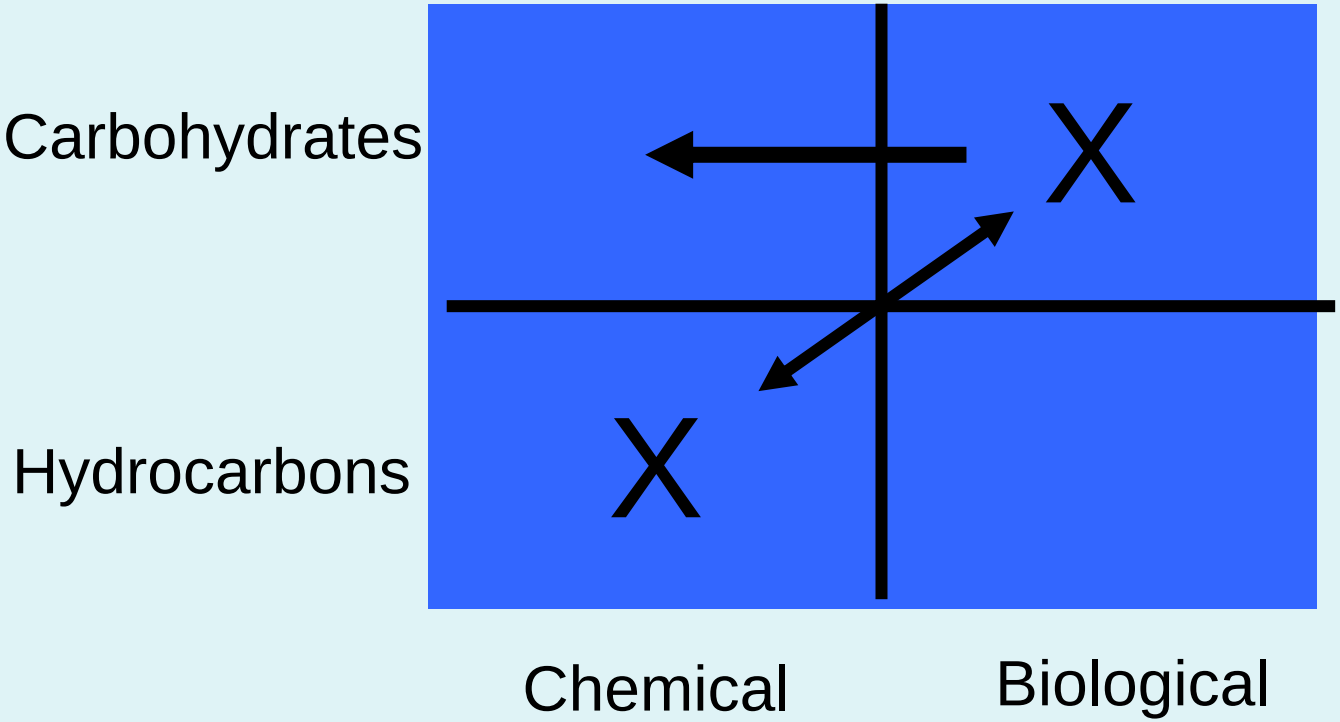
CHO Diagram of Various Substances



Some Examples of Unit Processes

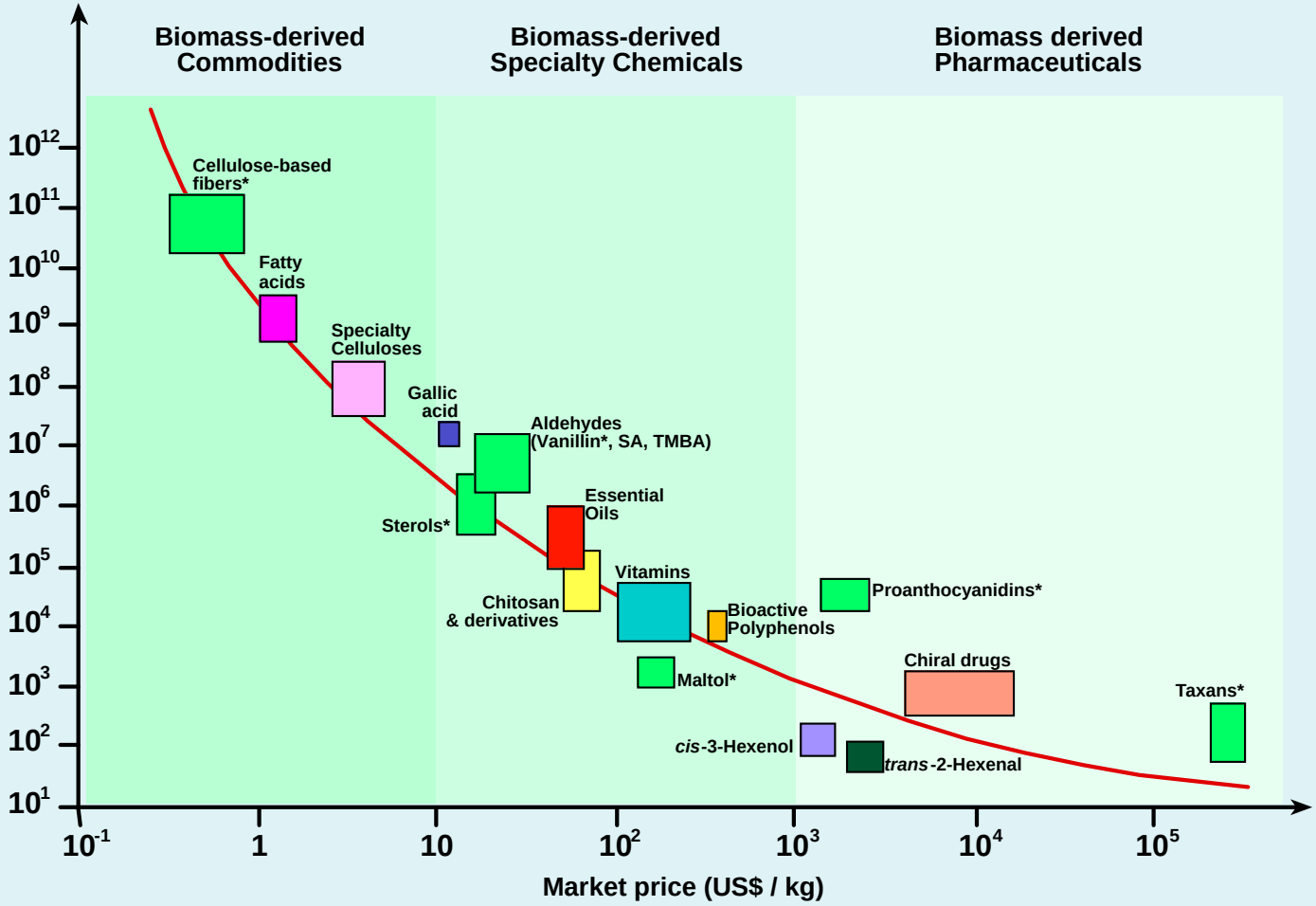
Unit Process	Description	Hydrocarbons	Carbohydrates
Oxidation/ Dehydrogenation	Increase oxygen content or decrease hydrogen content	Etyhlene oxide form etyhlene	
Reduction/ Hydrogenation	Decrease oxygen or increase hydrogen		Xylitol from xylose
Hydrolysis	Reaction with water to decompose the original reactants	Ethylene glycol from ethylene oxide	Glucose from cellulose (enzymatic or acid catalyst)
Carbonylation	Introduce carbon monoxide	Aldehydes and ketones	
Acetylation	Introduce an acetyl group into OH group of organic molecule	Acetic anhydride	Cellulose acetate

Conversion Methods



Place of Biochemicals

Market size / price for co-products derived from biomass



Source: Esteban Chornet, Thermochemical Strategies for Biofuels, Green Chemicals, Polymeric Biomaterials and Biofuels, Bio-Refineries Workshop, Novemner 2006, Edmonton

Renewables vs. Petrochemicals

	World Capacity (MM t/y)	Price ($/kg)
PETROCHEMICALS		
Ethylene	85	625
Propylene	45	225
Benzene	23	310
Isopropanol	2	500
Caprolactam	2	2500
RENEWABLES		
Cellulose	320	500
Sugar	140	435
Starch	55	500
Ethanol	26	875
Glutamic Acid	1	2500

Biochemicals

$$AC = DP * AV * KS$$

AC: Acceptance of Change

DP: Dissatisfaction with Presence

AV: Attractiveness of Vision

KS: Knowledge of Steps for Transition

Needs for Viable Biochemical Industry

- R&D in bioconversion technology
- R&D in chemical processes
  - Reaction media
  - Catalysts technology
  - Reaction at interfaces
- Integration with olefinics (petrochemicals)