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BIO 2010

V Seminario
Latinoamericano y
del Caribe de
Biocombustibles

Technical characteristics and current status of butanol production and use as biofuel

C Machado

Outline

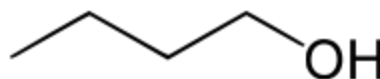
- ▶ **Butanol**
 - ▶ What is it
 - ▶ Current uses
 - ▶ Bio-butanol
 - ▶ **Production**
 - ▶ Past – Traditional ABE fermentation
 - ▶ Present – Production from oil
 - ▶ Future developments
 - ▶ **Butanol as a fuel**
 - ▶ **Final remarks**
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Butanol

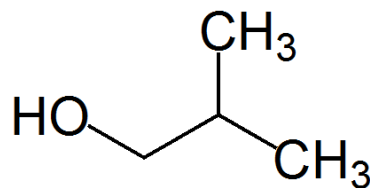
▶ Family of 4 Carbon Alcohols (C_4H_9OH)

▶ Isomers

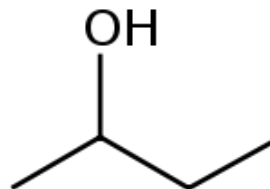
▶ normal(n)-butanol



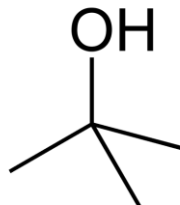
▶ iso(i)-butanol



▶ sec-butanol



▶ tert-butanol



n-Butanol

- ▶ Clear, colorless liquid that is flammable. Characteristic banana-like odor
 - ▶ Global market of 3M ton/year (market value over US\$4 billion)
 - ▶ Applications
 - ▶ Solvent – for paints, coatings, varnishes
 - ▶ Plasticizers – to improve how a plastic material processes
 - ▶ Coatings – as a solvent for a variety of applications,
 - ▶ Chemical intermediate or raw material – for other chemicals and plastics,
 - ▶ Textiles – as a swelling agent from coated fabric
 - ▶ Cosmetics –makeup, nail care products, shaving products
 - ▶ Drugs and antibiotics, hormones, and vitamins
 - ▶ Gasoline (as an additive) and brake fluid (formulation component)
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Isobutanol

- ▶ Colorless liquid with a sweet musty odor. Miscible with all common organic solvents (only slightly soluble in water)
 - ▶ Current market value of about US\$560 M/year
 - ▶ Uses:
 - ▶ Direct solvent – for surface coatings and adhesives
 - ▶ Chemical intermediate
 - ▶ Dispersing agent – cleaning preparations and floor polishes
 - ▶ Processing (extraction) solvent – flavor and fragrance manufacture, pharmaceutical, pesticide
 - ▶ Additive – in gasoline and deicing fluids
 - ▶ Flotation agent
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sec-Butanol

- ▶ Flammable, colorless liquid that is slightly soluble in water and completely miscible with polar organic solvent.
 - ▶ Uses:
 - ▶ Although some 2-butanol is used as a solvent, it is mainly converted to butanone ("MEK" - methyl ethyl ketone), important industrial solvent and found in many domestic cleaning agents and paint removers.
 - ▶ Volatile esters of 2-butanol have pleasant aromas and are used in small amounts as perfumes or in artificial flavors.
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tert-Butanol

- ▶ Clear liquid with a camphor-like odor. It is very soluble in water and miscible with ethanol and diethyl ether.
 - ▶ Tends to be a solid at room temperature (melting point slightly above 25 °C)
 - ▶ Uses
 - ▶ solvent
 - ▶ denaturant for ethanol,
 - ▶ ingredient in paint removers,
 - ▶ gasoline additive (octane booster; as an oxygenate)
 - ▶ intermediate in the synthesis of other chemical commodities such as MTBE, ETBE, TBHP, other flavors and perfumes.
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Properties & limits

Property	n-butanol	isobutanol	2-butanol	3-butanol
Density at 20°C (g/cm ³)	0.810	0.802	0.806	0.781
Boiling Point (°C)	118	108	99	82
Water Solubility (g/100mL)	7.7	8.0	12.5	Miscible
Flash point (°C)	35	28	24	11
MON	78	94		89

Bio-butanol

- ▶ Any of the isomers, produced from biomass
 - ▶ Which?
 - ▶ Butanol is the major natural product from ABE fermentation (known technology, low yields $\cong 15$ g/L)
 - ▶ Isobutanol – Can be produced in alcoholic fermentation (small amount). Some genetically microbial cells can produce it in higher yields (60 g/L)
 - ▶ Sec-butanol – Can't be directly produced by fermentation but fermentation produces 2,3-butanediol that is dehydrated to form MEK. Hydrogenation of MEK produces 2-butanol
 - ▶ Terc-butanol – not produced by any known biological route
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Butanol Production

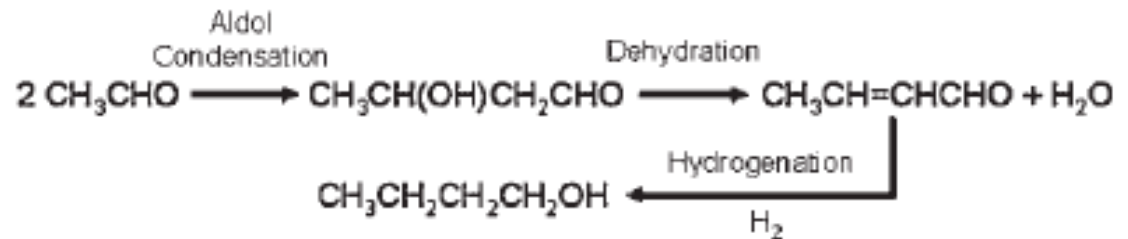
- ▶ Past – Bio-butanol
 - ▶ 1910 – 1950
 - ▶ ABE fermentation from molasses and starch
- ▶ Present – Petro-butanol
 - ▶ After 1950
- ▶ Future - Bio-butanol
 - ▶ biochemical routes
 - ▶ “new” ABE fermentation
 - ▶ other fermentative processes
 - ▶ thermochemical routes
 - ▶ gasification of biomass

ABE Fermentation

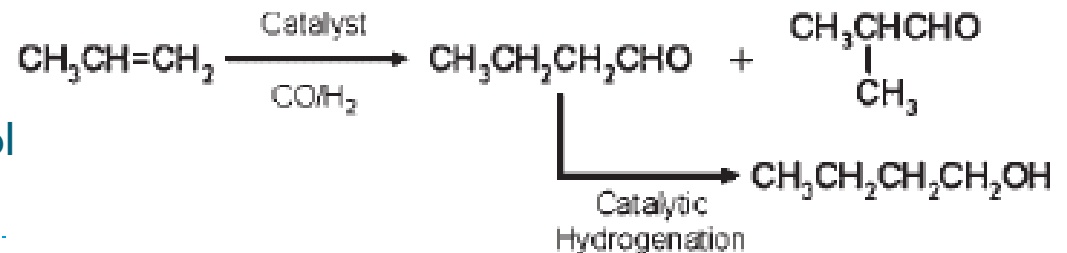
- ▶ First Industrial Fermentation Commercialized (1914)
 - ▶ Starchy raw material
 - ▶ *Clostridium acetobutylicum*
 - ▶ Use in WWI (Acetone for cordite - smokeless gunpowder)
 - ▶ Later butanol for butyl paint & coatings (1930's)
 - ▶ RAF planes flew on butanol during WWII
 - ▶ Petroleum based production becomes cheaper (1950s)
 - ▶ Problems
 - ▶ Toxicity to the bacteria
 - ▶ Low yield
 - ▶ Low concentration
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Butanol production from Oil

- ▶ Crotonaldehyde hydrogenation was the first process used.
 - ▶ Consists of aldol condensation, dehydration, and hydrogenation
- ▶ May again become important in the future
 - ▶ provides an alternative route from ethanol which can be produced from biomass.

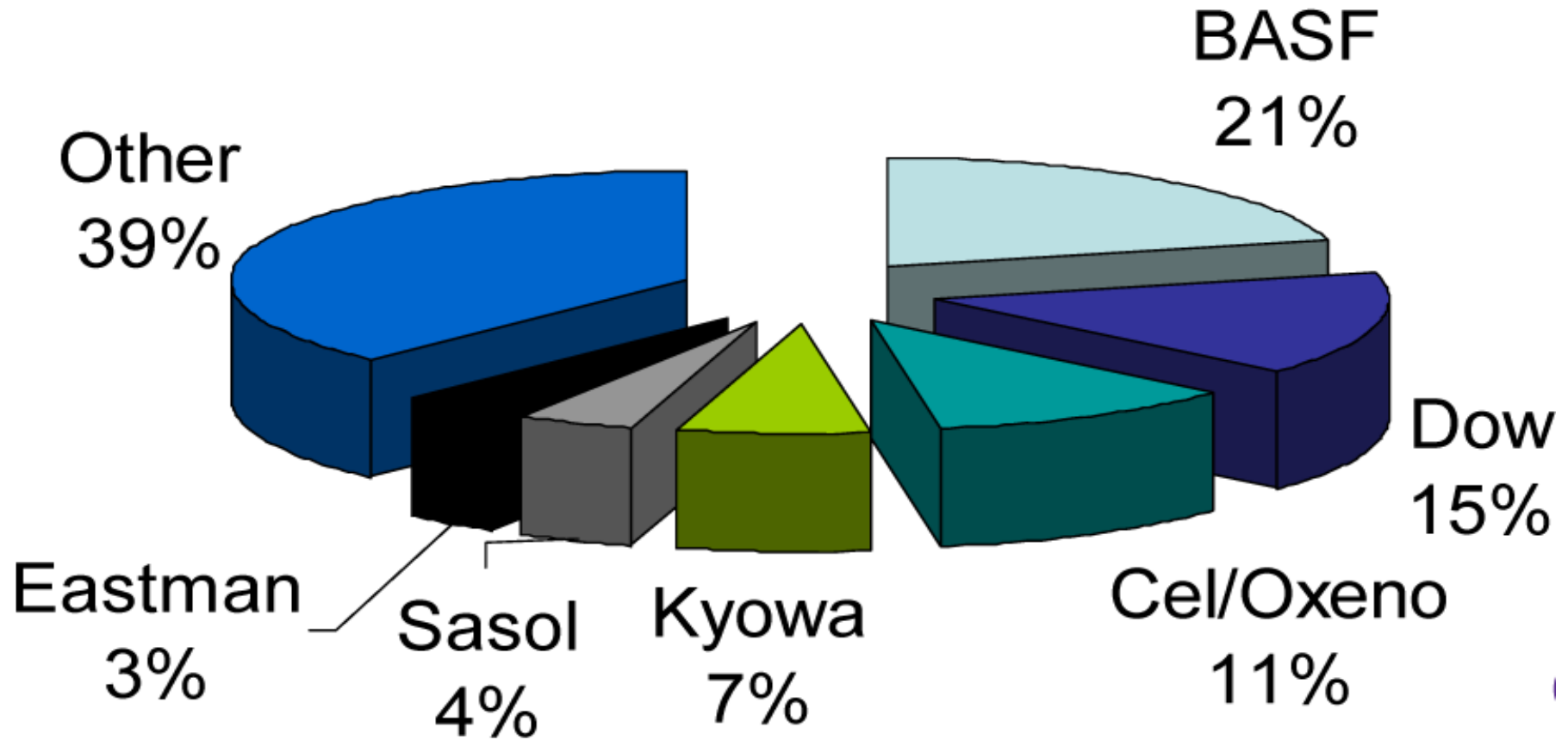


- ▶ Oxo-synthesis of propylene is the main process
 - ▶ process begins with propene, which is run through a hydroformylation reaction and reduced with hydrogen (usually with soluble cobalt or rhodium catalysts)



- ▶ mixture of butanol and isobutanol
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Current market share for n-Butanol

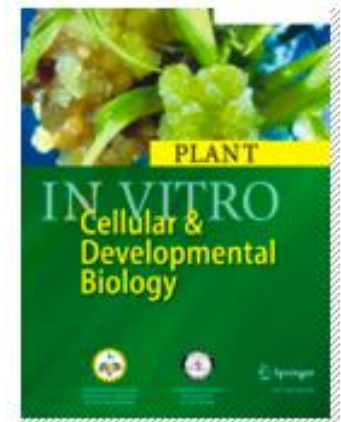


Economics of butanol production

- ▶ Several economic studies have been performed on the production of butanol (traditional ABE fermentation) from corn, whey permeate, and molasses
 - ▶ Is not economical when compared with butanol derived from the current petrochemical route
 - ▶ New developments in process technology for butanol production could allow for a significant reduction in the price of butanol.
 - ▶ Petrochemical industries gave capacity to reduce the price of butanol.
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The economics of current and future biofuels

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45MM gal/yr biofuel	Com ethanol	Sugarcane ethanol	Soybean diesel	Com butanol	Com stover ethanol (biochem)	Corn stover ethanol (thermochem)
Total production cost (\$M/yr)	\$74	\$58	\$121	\$88	\$64	\$58
Total project investment (\$M)	\$131	\$88	\$23	\$276	\$183	\$241
Production cost (\$/gal)	\$1.53	\$1.29	\$2.55	\$1.96	\$1.48	\$1.32
Energy density (BTU/gal)	76,330	76,330	119,550	99,837	76,330	76,330
Production cost with energy equivalent to gasoline (\$/gal)	\$2.33	\$1.95	\$2.48 equivalent to gasoline; \$2.74 equivalent to diesel	\$2.28	\$2.25	\$2.00

Corn to ethanol: US\$ 1.53/gal (0.40/L)

Corn to butanol: US\$ 1.96/gal (0.52/L)

Sugarcane to ethanol (Brasil): US\$ 1.29/gal (0.34/L)

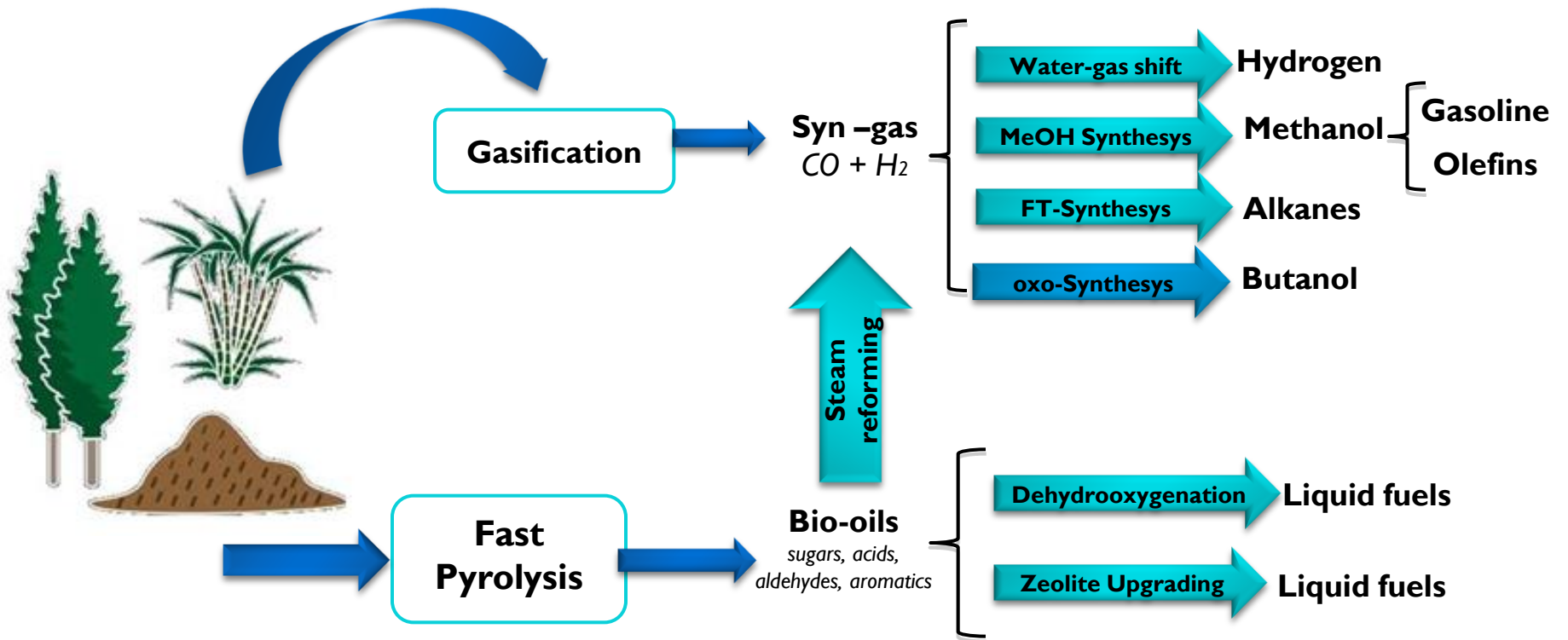
New developments in ABE Fermentation

- ▶ Genetic engineering for strain improvement
 - ▶ Higher yield, better tolerance to butanol
 - ▶ Use of different substrates
 - ▶ The clostridia secrete numerous enzymes that facilitate the breakdown of polymeric carbohydrates into monomer
 - ▶ This ability to utilize mixed sugars is of particular relevance for the use of inexpensive agricultural by-products and wastes as fermentation substrates (important factor influencing the cost of biobutanol production)
 - ▶ So far, the solventogenic clostridia have not been shown to directly utilize crystalline cellulose or lignocellulosic biomass as a carbon source, but this capacity is being explored
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New developments in ABE Fermentation

- ▶ **Advanced fermentation techniques**
 - ▶ In a biobutanol batch process, reactor productivity is limited to less than 0.50 g/L/h (low cell concentration, product inhibition)
 - ▶ The cell concentration inside the bioreactor can be increased
 - ▶ immobilization – reports of 15.8 g/L/h (Qureshi et al. 2005)
 - ▶ cell recycle – reports of 6.5 g/L/h (Ezeji et al. 2006)
 - ▶ **Recovery improvement**
 - ▶ Gas stripping
 - ▶ Liquid-liquid extraction
 - ▶ Perstraction
 - ▶ Pervaporation
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Thermochemical processes



Some industrial initiatives



Colorado based company. Genetically modified yeast, that produces only isobutanol from glucose . Lab results of 105 g/L of isobutanol (Glassner, 2009)

California based biofuel company has proprietary technologies in microbial physiology, strain development, fermentation. They use non modified *Clostridium* (ABE fermentation in a continuous process) to break down components of plant matter including cellulosic, hemicellulosic and starch.



There process is based on fermentation route of producing butanol using variety of feedstocks. They have recently announced commencement of commercialization of butanol with the name Butamax Advanced Biofuels which is planned to be operational in 2010 and the first commercial plant is expected to be operational by 2013.

Production of n-butanol with modified *Clostridium*. This patented technology claims to be able to produce 1.3 to 1.9 times more butanol (per weight of raw material)



UK-based company has developed their own thermophilic bacteria for rapid enzymatically release of fermentable sugar from biomass, this bacteria strains can also digest hemicellulose (5-carbon sugar) feed stocks. GBL's using genetic engineering has developed a strain to produce high yields of butanol and can tolerate close to 4% butanol concentration. Recently, GBL has announced signing agreement between GBL and Laxmi Organics, India for construction of commercial demonstrator for bio-butanol.



Syntec is a Canada based renewable energy company working on processes of biomass to alcohols (B2A). Right now they are working on development of catalyst for conversion of cellulosic biomass to pure isobutanol using thermochemical process. Syntec biofuel is focusing on utilizing wide range of biomass like, MSW, forestry and agriculture waste as a feedstock.

Illinois based company, uses of patented a mutant strain of *C. beijerinckii* to ABE fermentation with higher yields



With headquarters in Zug, Switzerland, genetically optimized yeasts enables increased yields in the production of biobutanol, using C5/C6 sugars for fermentation.

Based in Clermont-Ferrand, France, design high-performance microorganisms that can transform plant-derived raw materials into a flexible and competitive fermentation process for butanol production



Butanol vs. ethanol as a fuel

- ▶ Less hydrophilic
 - ▶ More compatible with oil infrastructure
 - ▶ Less corrosive
- ▶ Lower volatility
 - ▶ less explosive
- ▶ Has approximately 30% more energy accumulated per volume
- ▶ More compatible with installed base of autos (better mixing with gasoline)

Any issues?!!!

Final remarks

- ▶ What constitutes a good motor fuel?
 - ▶ a liquid,
 - ▶ highly combustible but not explosive,
 - ▶ something with a high energy to mass ratio,
 - ▶ stable on long-term storage,
 - ▶ transportable by pipeline and
 - ▶ inexpensive.
- ▶ It's very important to develop processes using non-food feedstock
- ▶ Car industry should take part of the process
 - ▶ Manufacturer's warranties essential

Wackett, 2008

Thank you!!!

