Butanol scoping study:
opportunities and threats for developing countries

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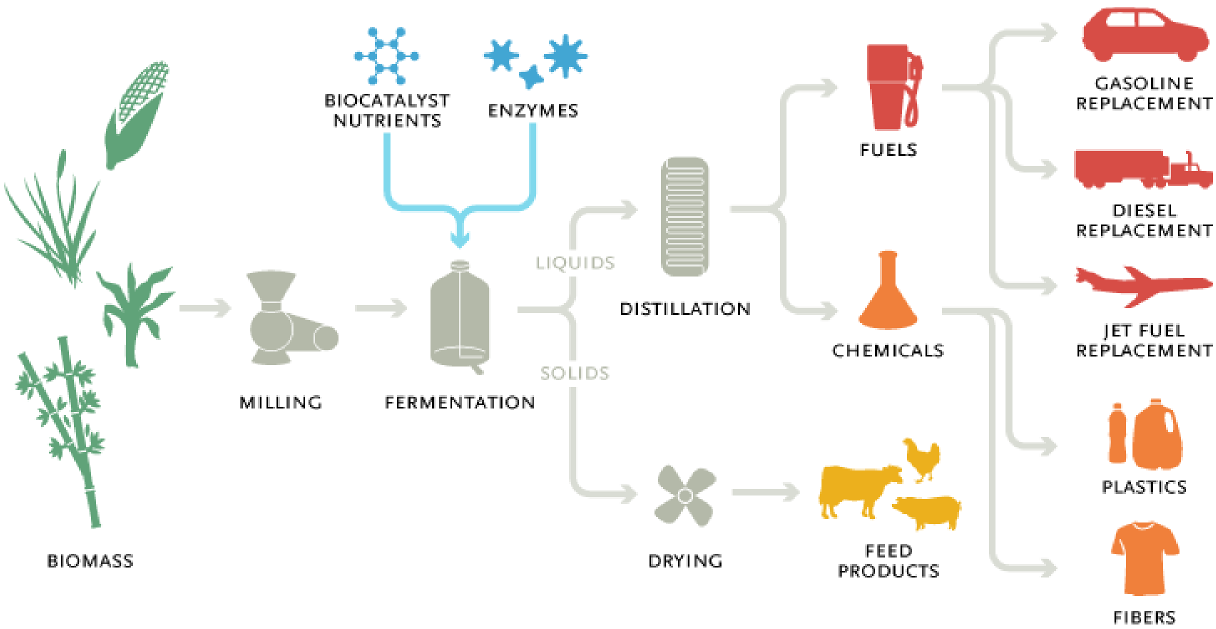


Butanol fermentation from biomass

Content

1. Introduction

Due to increasing oil demand and unpredictable climate changes related to CO2 emissions, interest grows in producing sustainable fuels from primary and particularly secondary generation biomass sources. Production capacity, infrastructures and the current use of bioethanol as a transportation fuel has grown considerably in Brazil, China, US, Scandinavia and other countries. Ethanol, however, has some serious limitations related to its polar character.
Butanol, can overcome most of these drawbacks though its physical, chemical and thermal properties: 1) higher energy density, 2) better diesel miscibility, 3) lower vapor pressure, that are more compatible with conventional fuels such as gasoline and diesel.

Table 1: Comparison of properties of n-butanol, ethanol and gasoline.

	n-Butanol	Ethanol	Gasoline
Specific Gravity @ 60°F	0.814	0.794	0.720-0.775
Heating Value, MJ/L	26.9-27.0	21.1-21.7	32.2-32.9
Research Octane Number (RON)	94*	106-130*	95
Motor Octane Number (MON)	80—81*	89-103*	85
RVP of 5% and 10%			
Alcohol/Gasoline Blends, psi	6.476.4*	31720*	_t
Oxygen, wt.%	21.6	34.7	<2.7
Water Solubility at 25°C, %	9.1	100.0	<0.01

* Gasoline blend values of the alcohol octane numbers and vapor pressures.

RON: Research Octane Number, MON: Motor Octane Number. The higher the octane number, the more pressure the fuel needs to combust. This is desirable, as the goal is to prevent actual explosions, and instead to create controlled ignition of the fuel.

2. Overview different pathways for butanol production

Basically there are three primary routes:
1) Fermentation of carbohydrates (1st of 2nd generation biomass) to biobutanol, using *Clostridium beijerinckii* or *acetobutylicum* strains (improvements by Blaschek/Tetravitae and

DuPont-BP commercialization plans or ButylFuel/EEI's "Dual Immobilized Reactors with Continuous Recovery" (DIRCM™) process, using two separate Clostridium strains

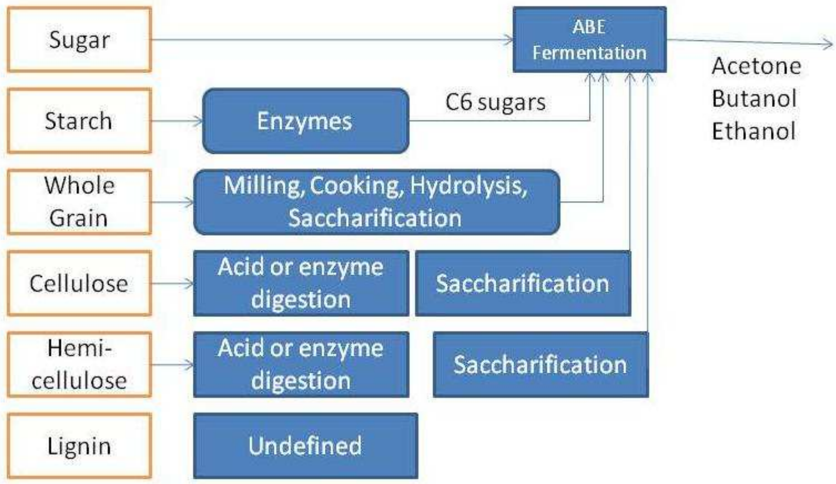


Figure 1: Fermentation (left) and gasification right).

Clostridium acetobutylicum is a chemo-organotroph. It obtains energy via substrate phosphorylation by fermentation. Substrates are organic molecules which act as electron donor and acceptor. C. acetobutylicum requires a carbohydrate source capable of undergoing fermentation to survive. In addition, C. acetobutylicum is an obligate anaerobe. It can only survive hours in an aerobic environment before undergoing sporulation as a means to survive.
C. acetobutylicum is able to use a number of different fermentable carbohydrates as an energy, as well as carbon, source. Considerable research has been invested into metabolic pathways of Clostridium acetobutylicum in order to improve industrial fermentation operations. The metabolic pathways which produce acetone, butanol, ethanol (ABE), acetate and butyrate: are all based upon acetyl-CoA. In addition to these products, CO_2 and H_2 are produced.

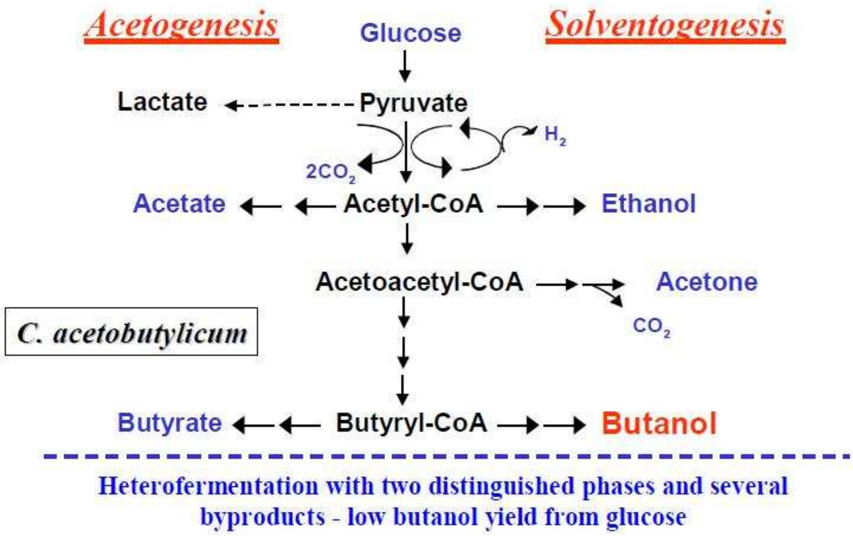
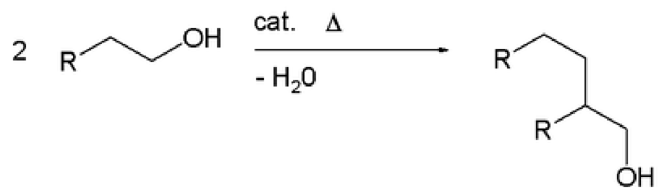


Figure 2: ABE fermentation pathways (Acetogenesis and Solventogenesis) of C. acetobutylicum.

2) Potential technology for dehydrating bioethanol to butanol by the Guerbet reaction using Japanese Sangi's hydroxyapatite (HAP) or other catalyst systems

The Guerbet reaction, named after Marcel Guerbet (1861–1938), is an organic reaction converting a primary aliphatic alcohol into its β-alkylated dimer alcohol with loss of one equivalent of water. This reaction requires a catalyst and elevated temperatures.



3) Gasification of cellulosic biomass to make syngas, to produce biobutanol catalytically

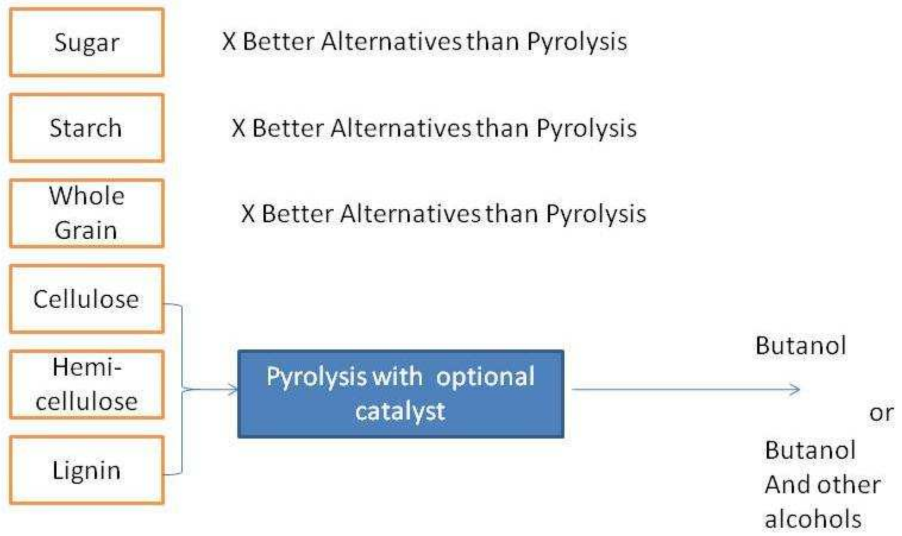


Figure 3: Gasification process .

3. Global feed stocks

From economic point of view activities are focused on applying agricultural waste streams (straw, leaves, grass, wood, spoiled grain and fruits) for the production of butanol. Other potential (new) sources of plant biomass are micro-algae, as the production only needs light and CO2. Some algae strains contain a relatively high percentage of sugars in dry matter, such as Chlorella (30-40%).

Table 2: Feedstock and biobutanol production - years to commercialization

Feedstock	Fermentation	Pyrolysis
Sugarcane Juice, Corn Kernels (Sugar source)	0-2 years	N/A
Sugar beet, Sorgum (complex sugar)	0-2 years	N/A
Miscanthus, Switch grass (cellulosic technology)	2-4 years	1-3 years
Wood waste, Crop waste, Poplar tree	2-4 years	1-3 years
Algae biomass	2-4 years	N/A
Food processing waste, household waste	4-6 years	1-3 years

4. Production and separation technologies

Distillation is energetically and economically unfeasible, as the maximum concentration of butanol and butanol fermentation broth is 3% by weight and as butanol has a higher boiling point than water. Currently other separation processes such as adsorption, membrane pertraction, extraction, pervaporation, reverse osmosis or "gas stripping" are studied. Pervaporation, can be interesting in this respect as it allows separation and concentration of butanol during a single process step.

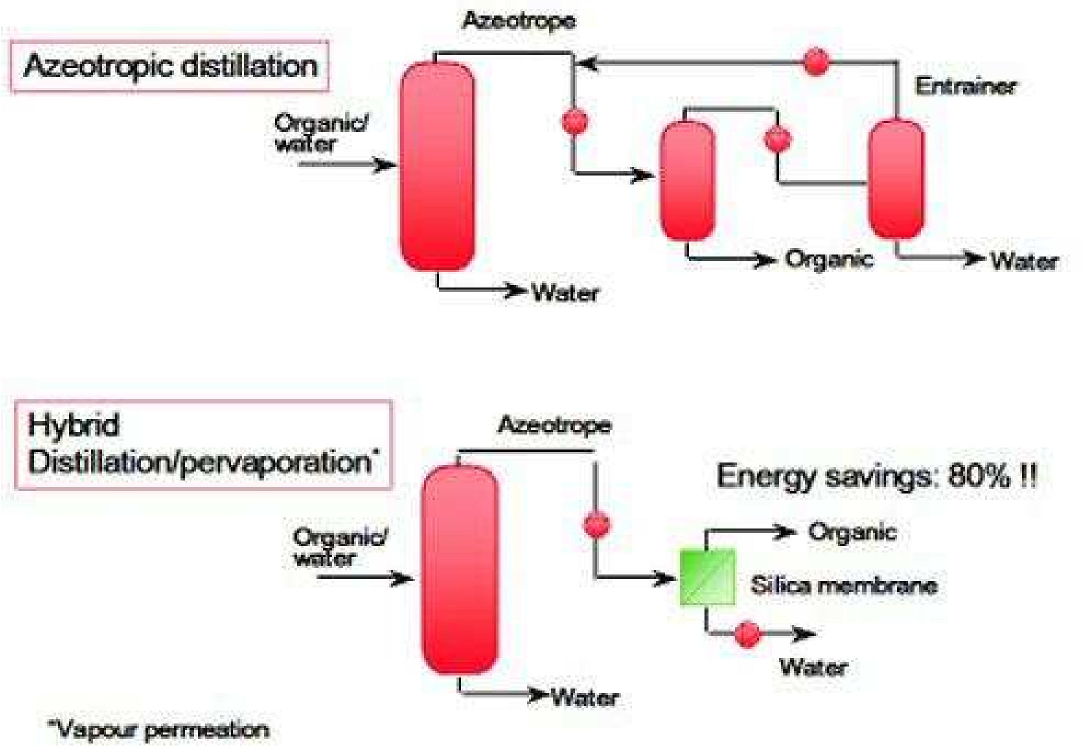


Figure 4: Comparison of 2 methods, distillation and pervaporation, for in situ butanol removal from bioreactor outlet

Potential applications of pervaporation:
- Distillation/pervaporation (breaking the azeotrope)
- Reaction and pervaporation (in situ removal of liberated water during the reaction)
- Low temperature dehydration (for heat-sensitive molecules)

Table 3: Separation performance of the silica membrane (pervaporation) in various model solvent/water systems

Solvent	**F (◦C)**	**P (mbar)**	**F,H2O (wt.%)**	**P,H2O (wt.%)**	**α process**	**Flux (kg/m2/h)**
Methanol	60	13	10.5	71.69	20	0.39
Ethanol	70	12	11.0	95.26	160	2.00
Isopropylalcohol	75	13	9.8	95.33	190	2.55
n-Butanol	75	16	9.4	97.20	340	4.14

5. Process economic aspects

The relative production costs for biobutanol was compared for 6 cases:
1: ABE fermentation of wood chips,
2: Improved ABE fermentation of corn,
3: DIRCR-process with immobilized catalysts,
4: Guerbet catalysis from ethanol (ethanol production costs not calculated),
5: Thermochemical route – gasification,
6: Oxo synthesis petrochemical route (as comparison) by Nexant.

Process economy improvement is possible on utilities (power, water, etc), fixed (rents, salaries of permanent employees and depreciation) and capital-related (purchase of land, buildings, construction and equipment) costs. Costs are based on process estimations.

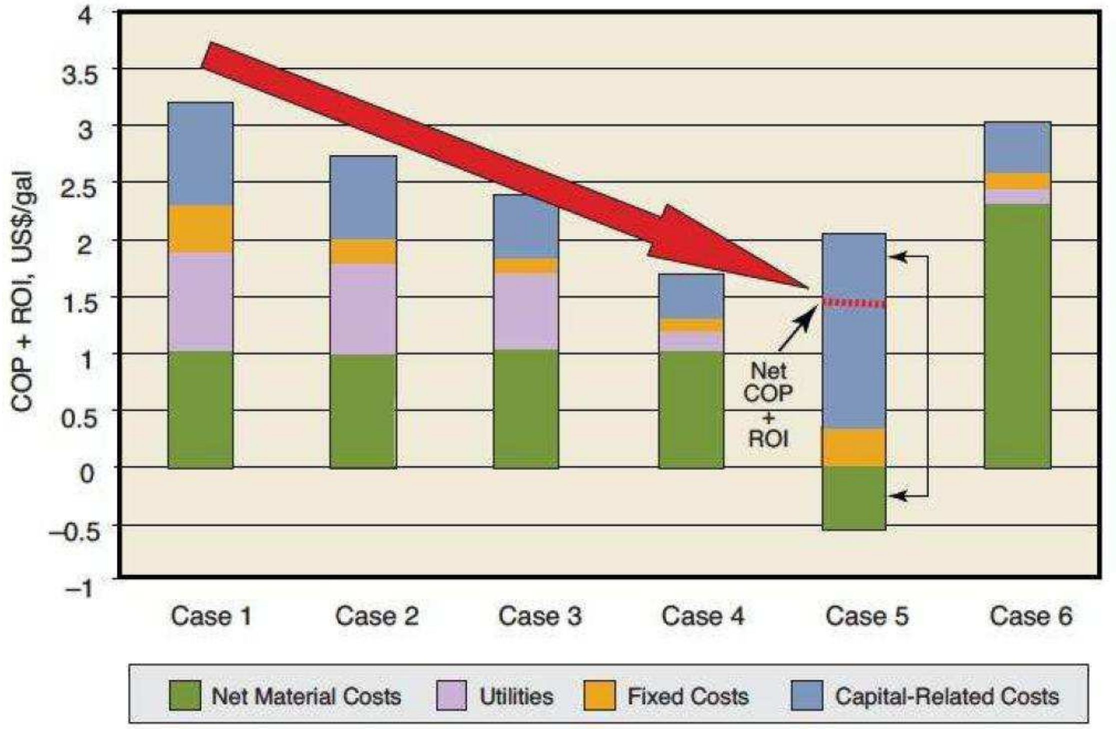


Figure 5: Relative production costs for biobutanol for 6 cases. 1 $/Gallon = 0,2 €/l (2011).

6. Industries involved in the subject

Currently pilot- or plant scale butanol production is being researched and even commercialized by many private and public entities globally, such as Sovert (UK based company focused on n-butanol production via fermentation), Butamax (Joint venture: BP and Dupont, Process utilizes the fermentation of corn), Gevo (Receiving funding from Cargill and Total, Plans to modify existing ethanol plants for butanol production from corn, sugar, and beets), Cathay Industrial Biotech (Facility for biobutanol production via fermentation located in Jilin Province of Northeast China), Cobalt Technologies (Butanol produced via a continuous fermentation process from wood pulp and sugar beets), Green Biologics, Butyl Fuel LLC (Operates a pilot facility to produce n-butanol via fermentation), Plantaonix (Use photosynthetic microorganisms known as PhytoConverters), W2 Energy (Uses an altered pyrolysis system which converts biomass into syngas), ZeaChem, Energy Quest, ButalcoGmBH (Employs modified yeasts for butanol production from lignocellulose), Laxmi Organics, NexantChemSystems (see below), Eastman Chemicals by purchasing Tetravitae Bioscience and METabolic Explorer (Process relies on the fermentation of various feedstocks and hemicelluloses). Source: www.biobutanol.com.

Technology program and fuel testing by Butamax

- the benefits of Biobutanol over alternative biofuel molecules is shown by Butamax, through an extensive program of technology development and fuel testing
- Biobutanol has been tested in real vehicles on real roads – covering more than 1.3 million
- vehicle road-miles. These tests have proven that biobutanol blended at a 16% volume into fuels does not impact vehicle performance.
- A commercial fuels trial confirmed the compatibility of butanol with existing fuel infrastructure and consumer satisfaction with the product.

7. SWOT-analysis

Strengths
- Fuel production from cheap biomass and waste streams.
- Butanol fits well in conventional fuel chain.
- Process economy can be further improved substantially.

Weaknesses
- No large scale production facilities operational yet.
- Clostridium is slow producer and sensitive for low butanol concentrations (>5%).
- In situ butanol removal technology is still under development.

Opportunities:
- High amounts of low cost feedstock available for conversion (bagasse, rice straw, empty fruit bunches, coffee/cocoa hulls, etc).
- Cheap local labour, facilities, land (for Developing Countries).
- Ambition of governments to become self-supporting.
- Mixing possibilities of butanol with petrol/diesel are better compared to ethanol.
- Estimated cost price butanol (2009/2010): 0,48 Euro/l (type Case3 conversion).
    - If any it would be in LAC and SE Asia.
    - Low temperature heat available: up to 95 °C.

Threats:
- Pre-treatment, production and separation technology still under development
- Local unskilled labour(for Developing Countries).
- No suitable hardware facilities available as separation technology can be expensive (for Developing Countries).
- Low local infrastructure biomass collection, transportation, storage, pre-treatment (for Developing Countries).

8. Conclusions and recommendations

<u>Main current technological issues:</u>
- Lignocellulose represent a potential substrate source for fermentation of ABE. Current fermentation processes are however optimised for starch, but not for lignocellulose as potential future feedstock. Production strains are not adjusted to utilize lignocellulose feed stocks.
- Strain improvement of Clostridium is important to increase ABE tolerance and butanol production levels as low yields of ABE produced during fermentation processing will toxicate Clostridium.
- In situ solvent removal results in increased ABE productivity, but cost effective downstream processing technology is not yet well developed. A promising method of biobutanol separation from the fermentation broth is the use of membrane systems.

<u>Future focus issues</u>
1. Genetic modification of *Clostridium acetobutylicum* and *Clostridium beijerinckii* to improve the spectrum of applicable feed stocks, ABE tolerance and production levels during fermentation.
2. Development of process technologies for in situ solvent removal during fermentation. Distillation processes are not applicable here.
3. Pretreatment of biomass from agricultural waste streams is an important step in order to be able to achieve substantial butanol conversion rates. This technology needs to be researched

further. Possible techniques are heat/steam, pH, mechanical treatment (extrusion, ball milling), novel treatments (pulsed electric fields).

9. Recommendations for FACT

- FACT should only become involved –if at all- in the field of butanol fermentation from lignocellulosic feedstocks in a consortium with national & local (industrial) partners. In this way FACT can join (ongoing) research projects in cooperation with technology partners such as Wageningen UR-Food & Biobased Research and ECN.
- FACT can join industrial initiatives and actively support research projects focused on scaling-up, demonstration, technology transfer and dissemination of results and progress to emerging markets. For these tasks FACT can acquire (joint) funding from available national and EU sources.

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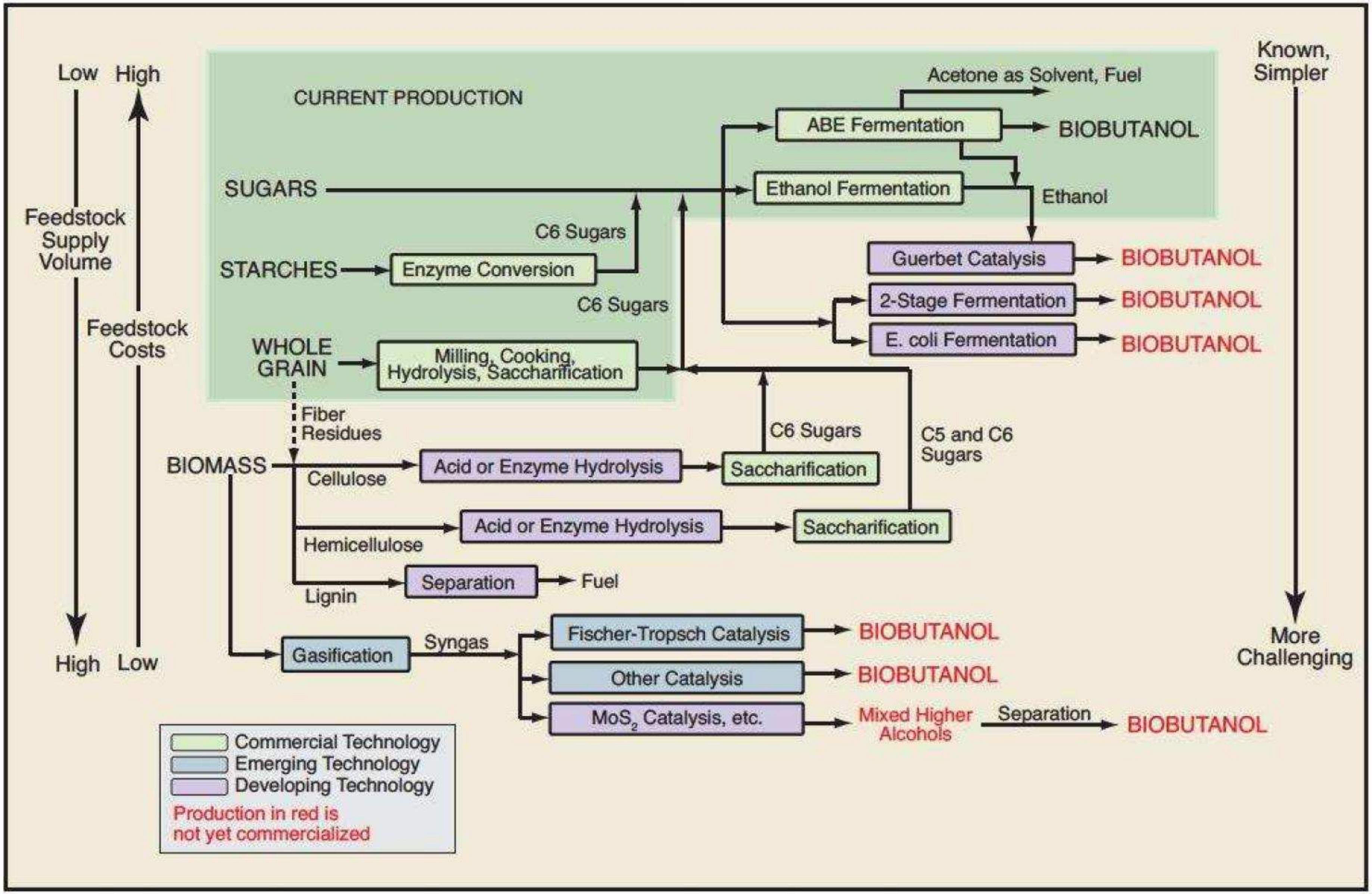
Low High
Feedstock Supply Volume
Feedstock Costs
High Low
CURRENT PRODUCTION
Acetone as Solvent, Fuel
ABE Fermentation
BIOBUTANOL
SUGARS
Ethanol Fermentation
Ethanol
C6 Sugars
STARCHES
Enzyme Conversion
Guerbet Catalysis
BIOBUTANOL
2-Stage Fermentation
BIOBUTANOL
C6 Sugars
E. coli Fermentation
BIOBUTANOL
WHOLE GRAIN
Milling, Cooking, Hydrolysis, Saccharification
Fiber Residues
C6 Sugars
C5 and C6 Sugars
BIOMASS
Cellulose
Acid or Enzyme Hydrolysis
Saccharification
Hemicellulose
Acid or Enzyme Hydrolysis
Saccharification
Lignin
Separation
Fuel
Gasification
Syngas
Fischer-Tropsch Catalysis
BIOBUTANOL
Other Catalysis
BIOBUTANOL
MoS_2 Catalysis, etc.
Mixed Higher Alcohols
Separation
BIOBUTANOL
Known, Simpler
More Challenging
Commercial Technology
Emerging Technology
Developing Technology
Production in red is not yet commercialized