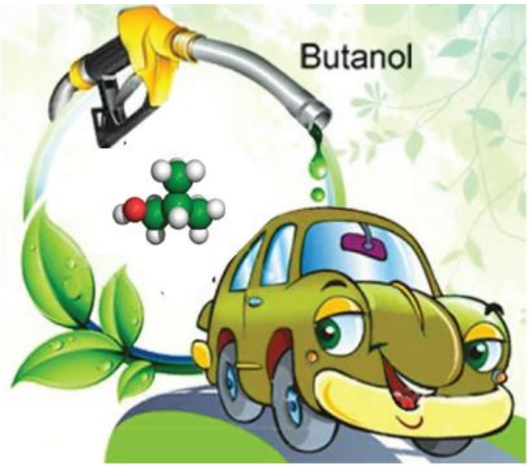
# LECTURE-17

# (BIOBUTANOL)

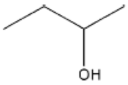
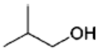
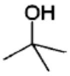


## ➢ INTRODUCTION

- Biobutanol is a 4-carbon alcohol (butyl alcohol, butanol) produced from the same feedstock source as bioethanol which include corn grain and other biomass.
- When we talk of the term 'biobutanol', means it has been produced by microbial source using any substrate or from biomass feedstocks.
- Butanol is colorless and flammable.
- It can be mixed with ethanol, ether and other organic solvent.
- It can be used as a solvent, in cosmetics, hydraulic fluids, detergent formulations, drugs, antibiotics, hormones and vitamins, as a chemical intermediate in the production of butyl acrylate and methacrylate, and additionally as an extract agent in the manufacture of pharmaceuticals.
- It's molecular formula is $C_4H_9OH$ and the carbon atoms can form either a straight-chain or a branched structure, resulting in isomers with distinct properties.
- The isomers are based on the location of the – OH group and carbon chain structure.
- The different structures, properties and main applications have been shown in **Table-1**.
- Although the properties of butanol isomers are somewhat different in octane number, boiling point, viscosity, etc., the main applications are similar in some aspects, such as being used as solvents, industrial cleaners, or gasoline additives.
- All these butanol isomers can be produced from fossil fuels by different methods, only *n*-butanol, a straight-chain molecule structure can be produced from biomass.
- In the present lecture, biobutanol produced from biomass feedstock is the topic of discussion.
- It is known that bioethanol as one of the biofuel has been applied in automobiles with gasoline in different blending proportions.
- Biobutanol is one of the new types of biofuel.
- Due to it's superior properties over other biofuel, it has continuously attracted the attention of researchers and industrialists throughout the world.

- Now biobutanol is seen as a potential option for fuel additive or a direct replacement for gasoline or diesel.

**Table 1.** Structures, Properties and Main Applications of N-Butanol, 2-Butanol, Iso-Butanol and Tert-Butanol

| | n-Butanol | 2-Butanol | iso-Butanol | tert-Butanol |
|---|---|---|---|---|
| Molecular structure |  |  |  |  |
| Density (g/cm3) | 0. 81 | 0. 806 | 0. 802 | 0. 789 |
| Boiling point(°C) | 118 | 99. 5 | 108 | 82. 4 |
| Melting point(°C) | -90 | -115 | -108 | 25-26 |
| Refractive index(n20D) | 1. 399 | 1. 3978 | 1. 3959 | 1. 3878 |
| Flash point(°C) | 35 | 22-27 | 28 | 11 |
| Motor octane number | 78 | 32 | 94 | 89 |
| Main applications | Solvents-for paints, resins, dyes, etc.<br>Plasticizers- improve a plastic material processes<br>Chemical intermediate -for butyl esters or butyl ethers, etc.<br>Cosmetics- including eye makeup, lipsticks, etc.<br>Gasoline additive | Solvent<br>Chemical intermediate- for butanone, etc.<br>Industrial cleaners -paint removers<br>Perfumes or in artificial flavors | Solvent and additive for paint<br>Gasoline additive<br>Industrial cleaners -paint removers<br>Ink ingredient | Solvent<br>Denaturant for ethanol<br>Industrial cleaners- paint removers<br>Gasoline additive for octane booster and oxygenate<br>Intermediate for MTBE, ETBE, TBHP, etc. |

- Fuel properties of conventional gasoline and biofuels used in the transportation sector are compared in **Table-2.**

**Table-2: Properties of Gasoline and Biofuels used in Transportation.**

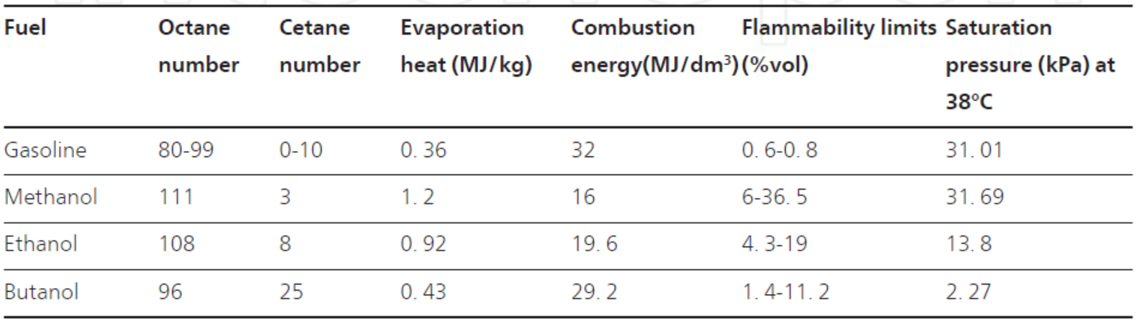
| Fuel property | Gasoline | (Bio)Butanol | (Bio)Ethanol | Biodiesel | Reference |
|---|---|---|---|---|---|
| Chemical structure | $C_4$ to $C_{12}$ | $CH_3CH_2CH_2CH_2OH$ | $CH_3CH_2OH$ | Methyl esters of $C_{12}$ to $C_{22}$ and fatty acids | (USDOE 2013) |
| Carbon ratio (%) | 86.3 | 64.9 | 52.2 | 77.6 | (GREET 2012) |
| Density (g L$^{-1}$) | 744.7 | 809.7 | 789.3 | 887.9 | (GREET 2012) |
| Feedstock | Crude oil | Sugars from *e.g.* corn, grains or agricultural waste, (cellulose) | Sugars from *e.g.* corn, grains or agricultural waste, (cellulose) | Fats and oils from *e.g.* animal fats, soy beans, cooking oil or rapeseed | (USDOE 2013) |
| Energy content (lower heating value, MJ kg$^{-1}$) | 32.4 | 27.8 | 21.3 | 33.3 | (GREET 2012) |
| RON[1] | 91–99 | 96 | 129 | - | (Lee *et al.* 2008a) |
| MON[2] | 81–89 | 78 | 102 | - | (Lee *et al.* 2008a) |

[1]Research octane number, [2]Motor octane number.

## ADVANTAGES OF BUTANOL AS FUEL

- Except the use of solvent, chemical intermediate and extract agent, butanol also can be used as fuel, which attracted people’s attention in recent years.
- Because of the good properties of high heating value, high viscosity, low volatility, high hydrophobicity, less corrosive, butanol has the potential of a good fuel.
- The properities of butanol and other fuels are compared in **Table-3**.

**Table-3: Properities of Butanol and other Fuels**



| Fuel | Octane number | Cetane number | Evaporation heat (MJ/kg) | Combustion energy(MJ/dm$^3$) | Flammability limits (%vol) | Saturation pressure (kPa) at 38°C |
|---|---|---|---|---|---|---|
| Gasoline | 80-99 | 0-10 | 0. 36 | 32 | 0. 6-0. 8 | 31. 01 |
| Methanol | 111 | 3 | 1. 2 | 16 | 6-36. 5 | 31. 69 |
| Ethanol | 108 | 8 | 0. 92 | 19. 6 | 4. 3-19 | 13. 8 |
| Butanol | 96 | 25 | 0. 43 | 29. 2 | 1. 4-11. 2 | 2. 27 |

- When ethanol is mixed with gasoline (less than 10%), there exists some disadvantages.
- Firstly, the heating value of ethanol is much less than gasoline.
- The fuel consumption increases if the engine is not retrofitted.
- Secondly, acetic acid is produced during the burning process of ethanol, which is corrosive to the engine.
- The preservative must be added when the ethanol proportion upper than 15%.
- Thirdly, ethanol is hydroscopic and the liquid phase separation may be occurring with high water proportion.
- Furthermore, ethanol as fuel cannot be preserved easily and it is more difficult in the process of allocation, storage, transition than that of gasoline.
- Compared with ethanol, butanol overcomes above disadvantages and it shows potential advantages.
- Butanol has higher energy content and higher burning efficiency, which can be used for longer distance.
- The air to fuel ratio and the energy content of butanol are closer to gasoline.
- Therefore, it can be easily mixed with gasoline in any proportion.
- It is less volatile and explosive, has higher flash point, and lower vapor pressure, which makes it safer to handle and can be shipped through existing fuel pipelines.
- In addition, butanol can be used directly or blended with gasoline or diesel without any vehicle retrofit.
- Actually, the first-time synthesis of biobutanol at laboratory level was reported by Pasteur in 1861 and the industrial synthesis of biobutanol was started during 1912–1914 by fermentation.
- However, before 2005, butanol was mainly used as solvent and precursor of other chemicals due to the product inhibition and low butanol productivity.
- To bring awareness to butanol’s potential as a renewable fuel, David Ramey drove his family car from Ohio to California on 100% butanol.

- And then, two giant companies DuPont and BP declared to finance development of a modernize production plant supported by research and development.
- The economy of biobutanol production also was revaluated.
- The research of a continuous fermentation pilot plant operating in Austria in the 1990s introduced new technologies and proved economic feasibility with agricultural waste potatoes.

## PRODUCTION METHODS OF BUTANOL

Butanol can be obtained using chemical technologies, such as Oxo-synthesis and aldol condensation. It is also possible to produce butanol in the process of fermentation by bacteria and butanol as one of the products called biobutanol. The most popular bacteria species used for fermentation is *Clostridium acetobutylicum*. Because the main products of this process containing acetone, butanol and ethanol, the fermentation is called ABE fermentation.

- **Chemical Process**
  - ✓ Butanol can be produced by chemical synthesis.
  - ✓ One process is Oxo-synthesis, which involves the reaction of propylene with carbon monoxide and hydrogen in the presence of cobalt or rhodium as the catalyst.
  - ✓ The mixture of n-butyraldehyde and isobutyraldehyde are obtained and then the mixture can be hydrogenated to the corresponding n-butanol and isobutyl alcohols .
  - ✓ The reactions are as following:

$$CH_3CH\text{-}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO + (CH_3)_2CHCHO \quad (1)$$

$$CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2OH \quad (2)$$

$$(CH_3)_2CHCHO + H_2 \rightarrow (CH_3)_2CHCH_2OH \quad (3)$$

  - ✓ When using cobalt as the catalyst, the reaction proceeds at 10~20MPa and 130~160 $^0$C, the products ratio of *n*-butyraldehyde and isobutyraldehyde is 3.
  - ✓ Rhodium as the catalyst used in industry since 1976 and the reaction processes at 0.7-3MPa and 80-120 $^0$C.
  - ✓ The products ratio of *n*-butyraldehyde and isobutyraldehyde can reach 8-16.
  - ✓ Another route is aldol condensation, which involves the reaction of condensation and dehydration from two molecules of acetic aldehyde.
  - ✓ And then, the product crotonaldehyde is transformed into *n*-butanol by hydrogenation at 180 $^0$C and 0.2 MPa.
  - ✓ The reaction is as following:

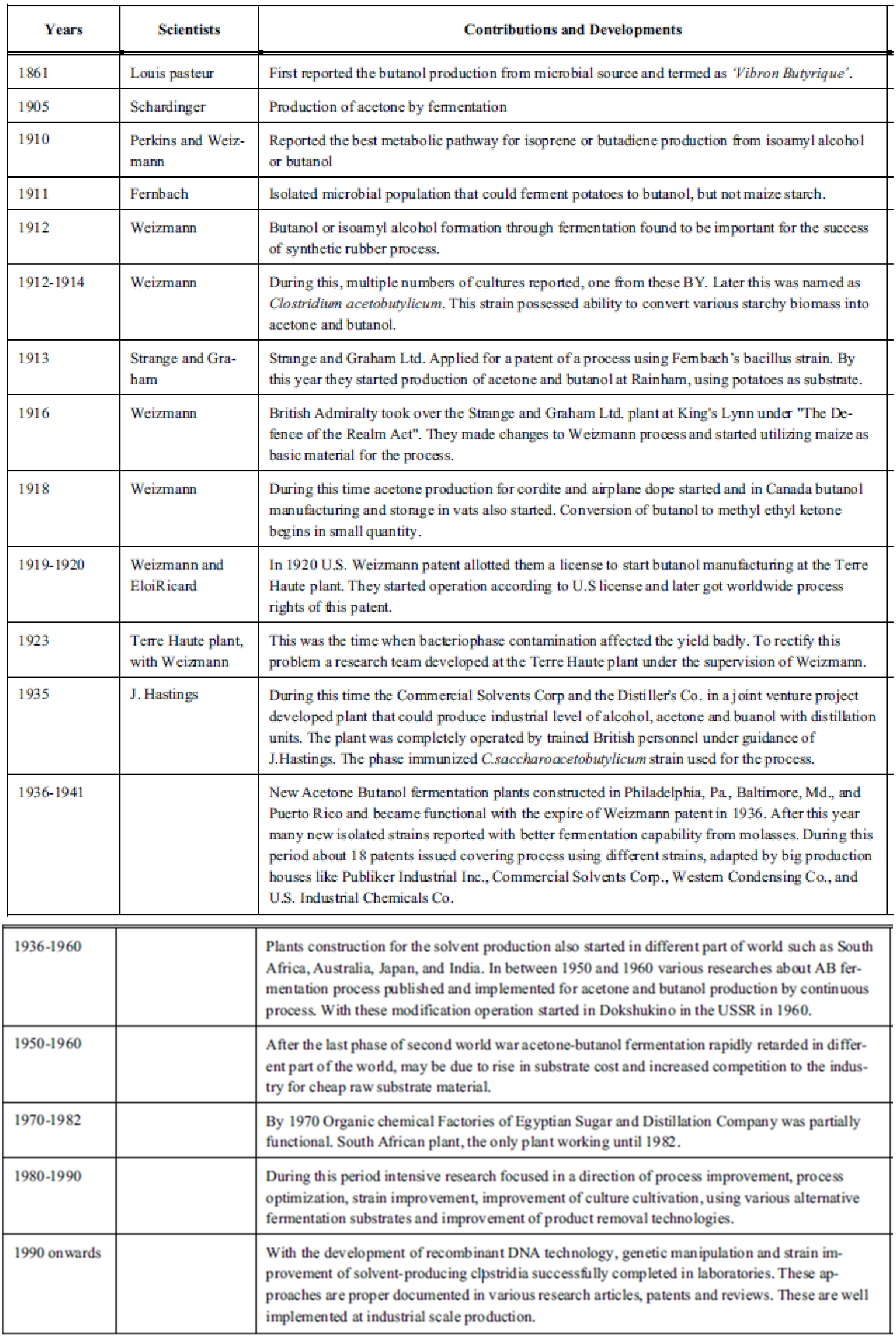
$$CH_3CH{=}CHCHO + 2H_2 \longrightarrow CH_3CH_2CH_2CH_2OH \quad (4)$$

  - ✓ Comparing the two processes, Oxo-synthesis route has the advantages of materials easily obtained, comparable moderate reaction conditions, enhanced ratio of n-butanol to isobutyl alcohol.
  - ✓ So, Oxo-synthesis process is the main industrial route for *n*-butanol production.
  - ✓ Note: There are also some other fossil oil derived raw materials such as ethylene, propylene and tri-ethyl-aluminium or carbon monoxide and hydrogen which are used in butanol production.

- **Biological Process**
  - ✓ Butanol can also be obtained from biological ways with the renewable resources by the microorganism through fermentation.
  - ✓ The *Clostridia* genus is very common for butanol synthesis under anaerobic conditions, and the fermentation products are often the mixture of butanol, acetone and ethanol.
  - ✓ The production of butanol by fermentation using lignocellulosic feedstocks is also known as ABE fermentation, i.e. acetone-butanol-ethanol fermentation.
  - ✓ Compared with the chemical method, biological route has the distinct advantages.
  - ✓ For example, it can utilize the renewable resources such as wheat straw, corn core, switch grass, etc. as feedstocks.
  - ✓ Biological process has high product selectivity, high security, less by-products.
  - ✓ Furthermore, the fermentation condition of butanol production is milder than that of chemical process and the products are easier to separate.

  - ✓ History of Biological Process for Manufacturing of Biobutanol
    - ○ Biological production of butanol under anaerobic conditions is typically referred to in literature as a part of 'ABE fermentation', since acetone, butanol and ethanol are usually produced simultaneously in this process.
    - ○ Louis Pasteur was the first to report about microbial butanol production in 1862.
    - ○ However, the first production utilizing the Weizmann process began only in 1913, aiming to produce acetone for rubber synthesis.
    - ○ Later in 1916, the first industrial-scale ABE fermentation began operation due to a high demand for acetone during World War I, and after the armistice in November 1918, most of the plants were shut down.
    - ○ Industrial ABE fermentation, however, kept expanding worldwide, facilitated by the usability of butanol as solvent.
    - ○ In 1945, two-thirds of the butanol and one tenth of the acetone in the U.S. were produced by ABE fermentation processes.
    - ○ However, their share in the total output declined rapidly during the 1950s mainly because of the acute competition with the expanding petrochemical industry and decreasing feedstock availability.
    - ○ ABE fermentation became popular again in the 1970s after the oil crisis, and it has since been gaining increasing interest owing to the advancements in Metabolic Flux Analysis, Metabolic Engineering, Gene KO Homologous Recombination, and Complete Genome Sequencing, holding promise of improved production yields and productivities for more economic microbial production processes.
    - ○ There are several excellent reviews covering the historical development of ABE fermentation in detail.
    - ○ The historical details of ABE fermentation has also been briefed in **Table-4**, given on the next page.

## Table-4: History and Development of ABE Fermentation.



| Years | Scientists | Contributions and Developments |
|---|---|---|
| 1861 | Louis pasteur | First reported the butanol production from microbial source and termed as *'Vibron Butyrique'*. |
| 1905 | Schardinger | Production of acetone by fermentation |
| 1910 | Perkins and Weizmann | Reported the best metabolic pathway for isoprene or butadiene production from isoamyl alcohol or butanol |
| 1911 | Fernbach | Isolated microbial population that could ferment potatoes to butanol, but not maize starch. |
| 1912 | Weizmann | Butanol or isoamyl alcohol formation through fermentation found to be important for the success of synthetic rubber process. |
| 1912-1914 | Weizmann | During this, multiple numbers of cultures reported, one from these BY. Later this was named as *Clostridium acetobutylicum*. This strain possessed ability to convert various starchy biomass into acetone and butanol. |
| 1913 | Strange and Graham | Strange and Graham Ltd. Applied for a patent of a process using Fernbach's bacillus strain. By this year they started production of acetone and butanol at Rainham, using potatoes as substrate. |
| 1916 | Weizmann | British Admiralty took over the Strange and Graham Ltd. plant at King's Lynn under "The Defence of the Realm Act". They made changes to Weizmann process and started utilizing maize as basic material for the process. |
| 1918 | Weizmann | During this time acetone production for cordite and airplane dope started and in Canada butanol manufacturing and storage in vats also started. Conversion of butanol to methyl ethyl ketone begins in small quantity. |
| 1919-1920 | Weizmann and EloiRicard | In 1920 U.S. Weizmann patent allotted them a license to start butanol manufacturing at the Terre Haute plant. They started operation according to U.S license and later got worldwide process rights of this patent. |
| 1923 | Terre Haute plant, with Weizmann | This was the time when bacteriophase contamination affected the yield badly. To rectify this problem a research team developed at the Terre Haute plant under the supervision of Weizmann. |
| 1935 | J. Hastings | During this time the Commercial Solvents Corp and the Distiller's Co. in a joint venture project developed plant that could produce industrial level of alcohol, acetone and buanol with distillation units. The plant was completely operated by trained British personnel under guidance of J.Hastings. The phase immunized *C.saccharoacetobutylicum* strain used for the process. |
| 1936-1941 |  | New Acetone Butanol fermentation plants constructed in Philadelphia, Pa., Baltimore, Md., and Puerto Rico and became functional with the expire of Weizmann patent in 1936. After this year many new isolated strains reported with better fermentation capability from molasses. During this period about 18 patents issued covering process using different strains, adapted by big production houses like Publiker Industrial Inc., Commercial Solvents Corp., Western Condensing Co., and U.S. Industrial Chemicals Co. |
| 1936-1960 |  | Plants construction for the solvent production also started in different part of world such as South Africa, Australia, Japan, and India. In between 1950 and 1960 various researches about AB fermentation process published and implemented for acetone and butanol production by continuous process. With these modification operation started in Dokshukino in the USSR in 1960. |
| 1950-1960 |  | After the last phase of second world war acetone-butanol fermentation rapidly retarded in different part of the world, may be due to rise in substrate cost and increased competition to the industry for cheap raw substrate material. |
| 1970-1982 |  | By 1970 Organic chemical Factories of Egyptian Sugar and Distillation Company was partially functional. South African plant, the only plant working until 1982. |
| 1980-1990 |  | During this period intensive research focused in a direction of process improvement, process optimization, strain improvement, improvement of culture cultivation, using various alternative fermentation substrates and improvement of product removal technologies. |
| 1990 onwards |  | With the development of recombinant DNA technology, genetic manipulation and strain improvement of solvent-producing clpstridia successfully completed in laboratories. These approaches are proper documented in various research articles, patents and reviews. These are well implemented at industrial scale production. |

## ➢ FERMENTATIVE BUTANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

A typical conversion process from lignocellulosic biomass to butanol involves three major steps: pretreatment, detoxification and fermentation. A representative schematic diagram of the process is shown in **Figure-1**.

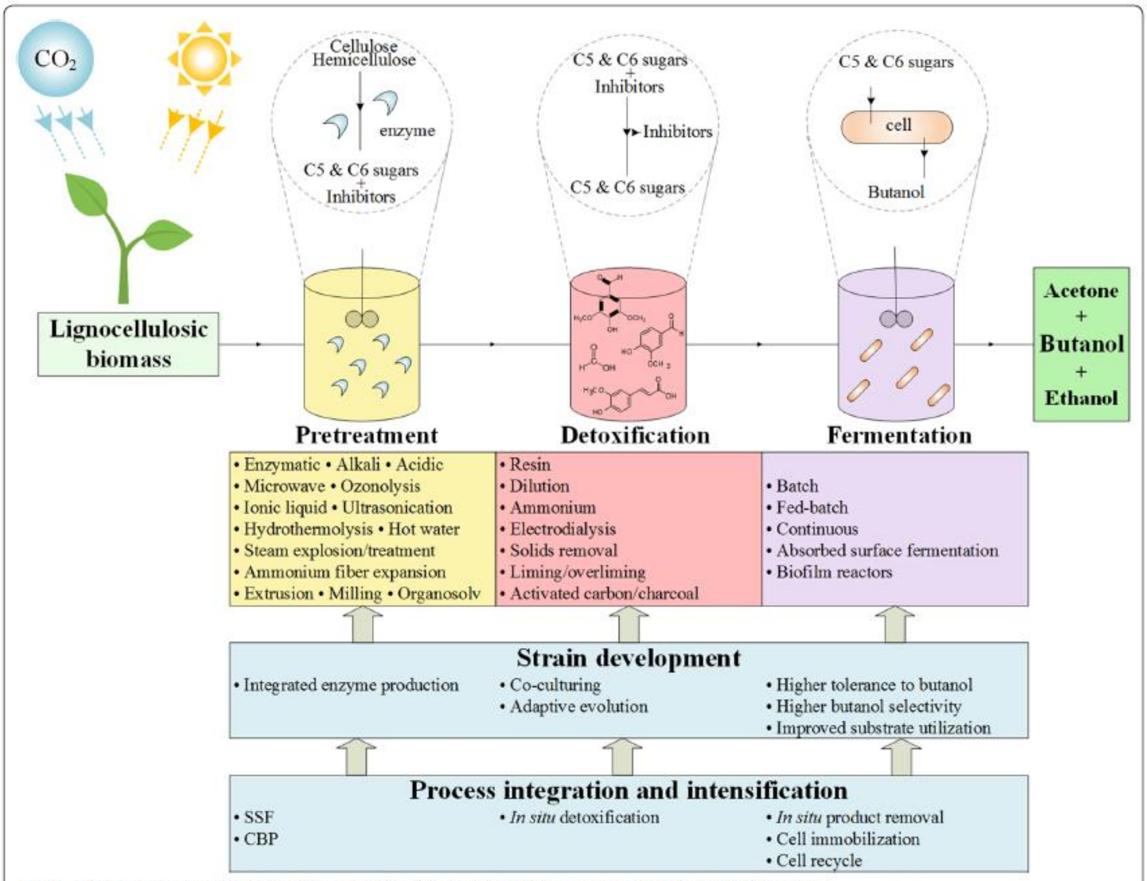


**Fig. 1** A representative schematic diagram of fermentative butanol production from lignocellulosic biomass

- **Pretreatment**
  - ✓ Lignocellulosic biomass is a favorable feedstock since it is the most abundant renewable biomass resource on the planet, and, compared to sugars from e.g. sugar cane or maize, it avoids direct fuel-versus-food competition.
  - ✓ Its main constituents are cellulose, hemicellulose and lignin.
  - ✓ The opening of the lignocellulosic biomass structure and the release of sugar content from hemicellulose and cellulose with other cross-linked units and the residual non-hydrolyzed raw feedstock is called pretreatment.
  - ✓ Conversion of biomass into its main constituents is referred to in literature as fractionation, which is sometimes used interchangeably with pretreatment, i.e. pretreatment is mentioned as a way of achieving biomass fractionation, or the term fractionation is used as (part of) a pretreatment method.
  - ✓ In the present study, for simplicity reasons we name all steps involved in the conversion of the feedstock to sugars as pretreatment though enzymatic hydrolysis of the polysaccharide fractions is often referred to as a step that is distinct from other pretreatment measures.

- Predominance of enzymatic hydrolysis in the pre-treatment methods in **Figure-2 (a)** shows its widespread application to produce fermentable sugars from lignocellulosic biomass.
- Milling/grinding, extrusion, microwave and ultrasonication are common physical pretreatment methods that open up the physical structure of lignocellulosic biomass.
- Physico-chemical methods such as steam explosion, steam treatment, hydrothermolysis, ammonium fiber expansion, and hot water treatment cause both the structure to unravel and a release of sugar monomers and dimers.
- Major chemical pretreatment methods are alkali, acidic, ozonolysis, ionic liquid and organosolv treatments.
- Enzymatic hydrolysis using suitable enzyme mixtures degrades polysaccharides such as cellulose and xylan to fermentable C6 and C5 sugar monomers, respectively.
- Typically, combinations of several of the above-mentioned pretreatment methods are employed depending on the feedstock.
- Operating conditions of pretreatment are crucial since a small change in the operating parameters can cause great differences in reduced sugar composition and concentration as well as inhibitory compounds, consequently negatively affecting enzymatic hydrolysis, fermentability and the cost of substrate.
- Therefore, it is crucial to examine the feasibility of any pretreatment method with respect to the generation of inhibitors, energy consumption, operating cost, and sugar yield.

**Figure-2: Common Pretreatment Methods (a), Detoxification Methods (b), Lignocellulosic Feedstocks (c), and *Clostridium Strains* (d) Used in Fermentative Butanol Production From Lignocellulosic Biomass**

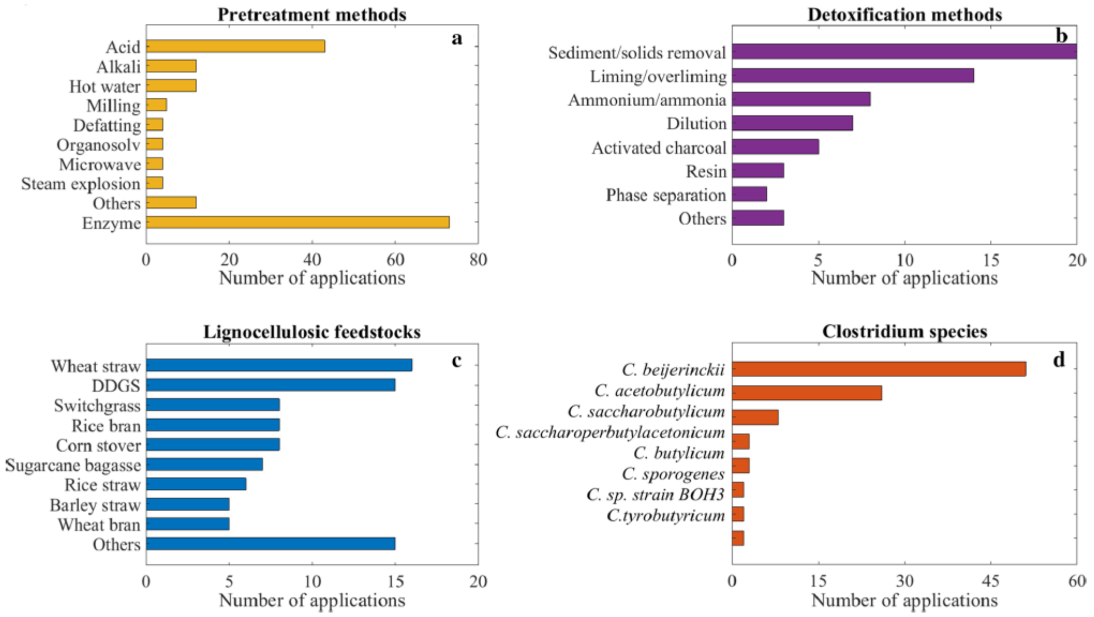


**Fig. 2** Common pretreatment methods (**a**), detoxification methods (**b**), lignocellulosic feedstocks (**c**), and Clostridium strains (**d**) used in fermentative butanol production from lignocellulosic biomass

- **Detoxification**
  - ✓ Compounds that are inhibitory to microorganisms and enzymes are often generated during pretreatment.
  - ✓ Cellulose and hemicellulose should ideally only yield sugar monomers such as glucose, xylose, and mannose.
  - ✓ However, severity of some pretreatment conditions converts those sugars into furfural, 5-hydroxymethyl furfural (HMF), formic acid, acetic acid, levulinic acid and salts, which can be inhibitory.
  - ✓ Partial decomposition of lignin generates inhibitory (poly)phenolic aromatic compounds such as *p*-coumaric acid, ferulic acid, syringe aldehyde, vanillic acid and vanillin.
  - ✓ Contrary to ethanol-producing microorganisms like the yeast *Saccharomyces cerevisiae*, furfural, HMF or acetic acid are not inhibitory to clostridial butanol producers at relatively low concentrations, rather they are reported to be stimulatory.
  - ✓ Another common compound generated during pretreatment of lignocellulosic biomass is formic acid.
  - ✓ It is found to be inhibitory to *C. acetobutylicum* at 0.5 g/l and 0.074 g/l (1 mM) inside the cell wall due to acid crash.
  - ✓ Therefore, if larger amounts of inhibitors are present after pretreatment, it is a necessity to remove these for a successful fermentation.
  - ✓ For this purpose, several detoxification methods such as electrodialysis, liming/overliming, activated carbon/charcoal, dilution, and resin treatments as depicted in **Figure-2 (b)** are applied.
  - ✓ Even though it is not specifically mentioned as a detoxification method, solid/sediment removal by filtration or centrifugation is also commonly applied to alleviate the inhibitory effects of the solids and undissolved lignin in the lignocellulosic hydrolysates.
  - ✓ It is important to note that the enzymes used in the hydrolysis step can be inhibited by the compounds mentioned above as well as their sugar yields, which can impose a limit to high substrate concentration.
  - ✓ Alternative lines of research currently target new pretreatment methods that are less prone to inhibitor formation (like organosolv or other low-temperature methods) and thus ideally do not require detoxification prior to fermentation, as well as increasing the inhibitor tolerance of fermentation strains e.g. by means of adaptive evolution.
- **Fermentation**
  - ✓ ABE fermentation is biphasic; first, acetic acid and butyric acid are produced in the acidogenesis phase, then the acids are re-assimilated to yield the solvents acetone, butanol and ethanol.
  - ✓ Batch fermentation is the most widely used method due to simple operation and low risk of contamination.
  - ✓ Low cell density can result in low productivity, and absorbed substrate fermentation and biofilm reactors have been applied to overcome this problem in batch processes.
  - ✓ Fed-batch mode is beneficial to tackle substrate inhibition by gradually adding the substrate, thus keeping the substrate concentration below toxic levels.

- ✓ However, fed-batch fermentation should still be accompanied by in situ product removal to alleviate product inhibition.
- ✓ Continuous fermentation (chemostat) has advantages over batch and fed-batch modes such as improved productivity.
- ✓ Multi-stage, immobilized cell, cell recycling and bleeding techniques have been applied to improve chemostat performance.

- **Strain Development**
  - ✓ Strain development refers to any modifications in the butanol production strain done by random mutagenesis and selection, like in adaptive laboratory evolution, or directed, rational and/or systems biology guided genetic modification employing metabolic engineering and synthetic biology to improve fermentation performance nby means of increased tolerance to toxic components, butanol selectivity and productivity, and improved substrate utilization and range.
  - ✓ In general, detoxification methods shown in **Figure-2 (b)** are used for removal of inhibitors present in the substrate and/or feedstock as described in "Detoxification" section.
  - ✓ Co-culturing with other species to eliminate toxic components such as oxygen in case of anaerobic fermentation is an alternative method.
  - ✓ Random mutagenesis and selection, and metabolic engineering have been applied for the same purpose.
  - ✓ Inhibition due to butanol accumulation is one of the greatest challenges.
  - ✓ Therefore, metabolic engineering and mutagenesis have been targeting this specific problem as well by developing strains with greater resistance to butanol toxicity.
  - ✓ A typical fermentative butanol production yields acetone and ethanol as well, which decreases the selectivity of the product of interest.
  - ✓ Metabolic engineering for disruption of acetone producing pathways, homo-butanol fermentation via chemical mutagenesis and metabolic engineering and conversion of acetone into isopropanol are among the strategies developed to address this issue.
  - ✓ Efficient utilization of the substrate is crucial to achieve a high butanol yield, thus improving fermentation performance.
  - ✓ Disrupting the genes responsible for *Carbon Catabolite Repression* and overexpression of genes responsible for xylose transport and catalytic enzymes (d-xylose isomerase, xylulokinase, and enzymes of PPP) are commonly followed approaches.
- **Process integration and intensification**
  - ✓ Process integration and intensification techniques are applied to obtain cost-effective fermentation processes.
  - ✓ Important process intensification approaches include (a) simultaneous saccharification and (co-) fermentation (SSF or SSCF) in which hydrolysis of polysaccharides present in (pre-treated) biomass is performed by externally produced and added hydrolytic enzyme mixes in situ with the simultaneous fermentation of the liberated sugars by a strain (or in the case of SSCF several strains with complementary sugar substrate spectrum) producing the product of choice, e.g. butanol, and (b) consolidated bioprocessing (CBP) in which the

saccharolytic enzymes are produced within the sugar fermenting culture e.g. by the target product producing strain itself or in co-culture with a partner strain specialized in enzyme production and secretion.

- ✓ Gas stripping, pervaporation, adsorption, liquid–liquid extraction, pertraction (membrane extraction), reverse osmosis and membrane distillation are in situ product removal methods used to alleviate inhibitory effects of butanol.
- ✓ Fermentation with integrated gas stripping has widely been studied, mostly in fed-batch mode, which showed improved butanol productivity.
- ✓ Cell immobilization and cell recycle are mostly integrated to fermenters operated in continuous mode to improve butanol productivity by preventing the loss of cell mass with the bleeding stream out from the fermenter.
- ✓ Process integration and intensification measures therefore play crucial roles in optimizing butanol fermentation processes for improved performance and economic competitiveness.

- **Another Process Flow Diagram which can be alternatively used is given below:**

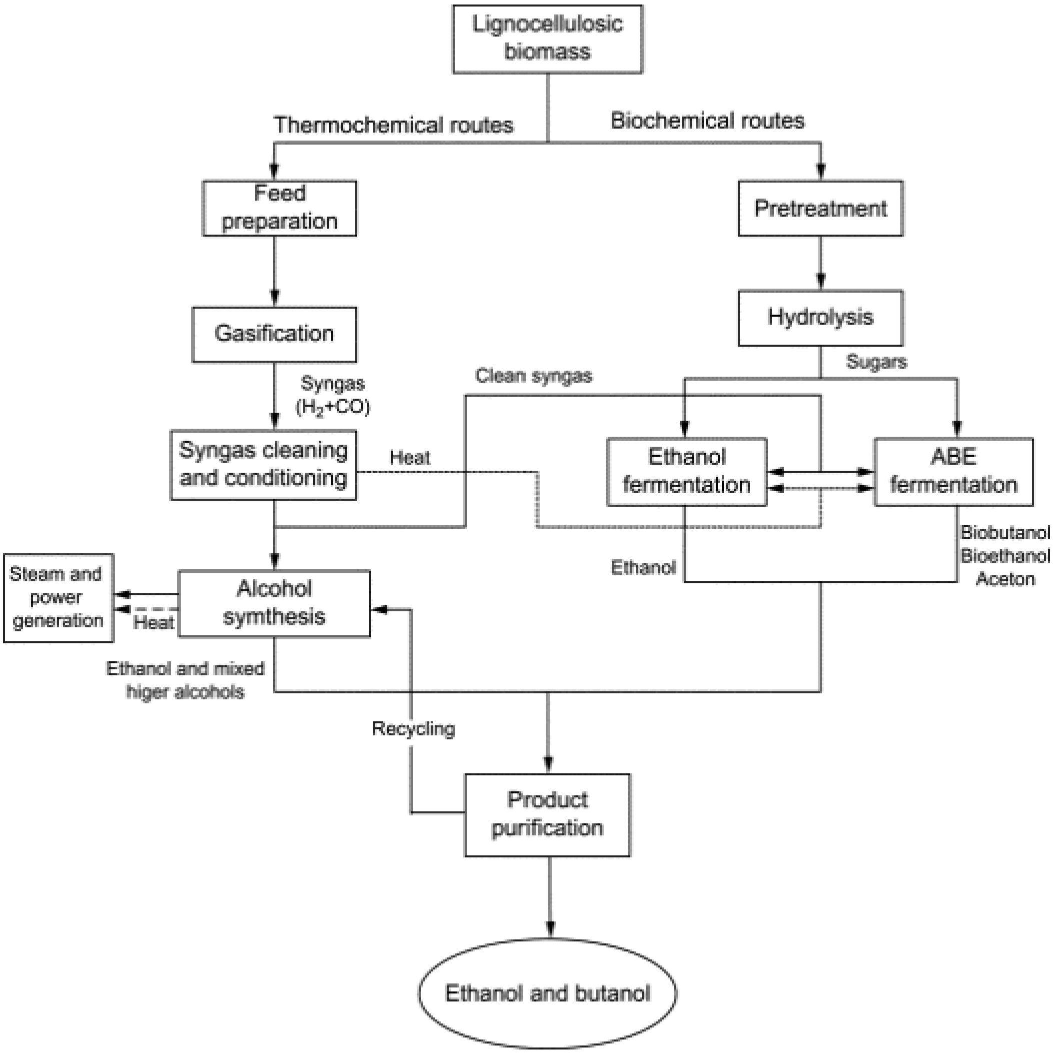


**Figure-3: Manufacture of ethanol and butanol from linocellulosic feedstocks.**

## ➢ CHALLENGES AND SOLUTION

- There are several challenges such as high substrate cost, solvent toxicity, low cell density and by-product formation that need to be addressed for sustainable and economical fermentative butanol production.
- These issues cause low butanol yield, titer, productivity and selectivity.
- Great efforts have been made to find cheap/free feedstock and cost efficient processing methods to overcome the high substrate cost problem, and several review papers address this issue in detail.
- Low solvent tolerance limits the butanol titer to maximum 2% dependent of the strain used, causing high downstream processing cost; therefore some reviews collected and discuss information on this specific challenge.
- Efficient separation of butanol from the fermentation mixture is another important topic with several reviews discussing particularly downstream processes for ABE fermentation.
- Strain improvement by metabolic engineering has an important role in optimizing butanol production.
- Main issues and possible solutions are summarized in **Table-5**.

**Table-5: Challenges and Solution for Butanol Production by Fermentation**

| **Challenges** | **Solutions** |
|---|---|
| Increased operating cost due to high raw material cost | Switching to cheaper and sustainable raw material such as lignocellulosic materials |
| High cost of recovery due to low yield, limited sugar loading | Development of improved microoraganisms with improved yield and/or butanol selectivity; Development of novel reactive separation processes |
| Capital and operating cost increases due to low volumetric productivity | Development of continuous fermentation processes for reduction in reaction time |
| Product recovery with conventional distillation is expensive and energy intensive | Development of low cost energy efficient methods for solvent purification and recovery. |
| High water usage is not sustainable and caused higher cost of effluent treatment. | Recycling the process water back through the fermentation. |
| Formation of undesirable or low value by-products | Engineering of respective knock-out or deletion strains |
| Culture degeneration | Avoid the excessive acidification of the culture. |
| Phage contamination | Good culture practices, proper sterilization, use of phage resistant strains |

## ➢ GLOBAL SCENARIO

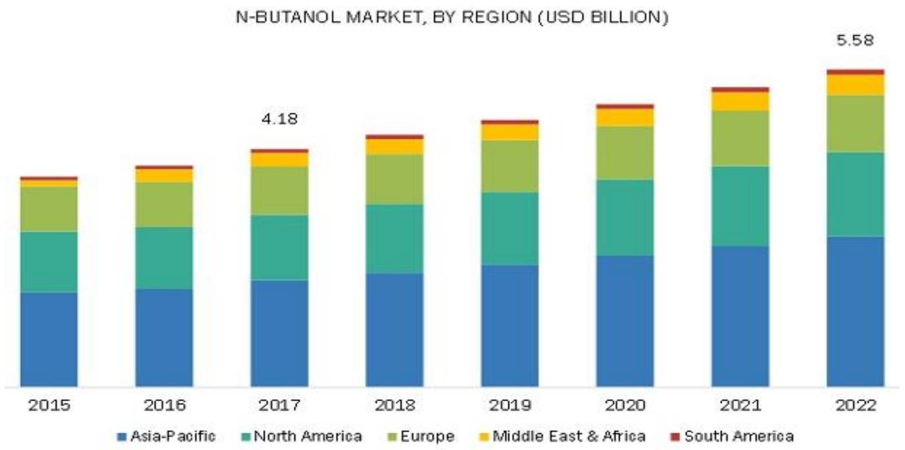
- **Global Bio-Butanol Market - Growth, Trends, and Forecast (2019 - 2024)**
  - ✓ Market Overview: The market for bio-butanol is expected to register a compound annual growth rate (CAGR) of 8. 36%, during the forecast period of 2019-2024. Major factors driving the market studied are the reduction of carbon emission to a great extent and gaining prominence as a building block for chemical manufacturing.

    Bio-butanol is generating interest as a potential green alternative to petroleum fuels. It is preferred as a superior automobile fuel, as compared to bioethanol, owing to its high energy content. Furthermore, it is less corrosive in nature, and can be blended with any concentration with gasoline (petrol). Moreover, bio-butanol has low vapor pressure, thus lower volatility and evaporative emissions. Bio-butanol also reduces greenhouse gas emissions, as it exhibits fewer emissions compared to other transport fuels. The United States and the European countries have started with fleet-testing of bio-butanol, in order to further promote the usage of bio-butanol. Growing number of cars on road and increasing sales of vehicles are expected to drive the market for motor fuel, which, in turn, may boost the market studied through the coming years.

The number of cars on the road is expected to rise by up to 2 billion, by 2050. According to OICA (Organisation Internationale des Constructeurs d'Automobiles, International Organization of Motor Vehicle Manufacturers) the total sales of all vehicles, including passenger and commercial, reached 96,804,390 million units, in 2017, from 93,905,634 million units, in 2016. This increase is leading to more usage of motor fuels in cars, which, in turn, may drive the market for bio-butanol as an alternative to transport fuel.

Asia-Pacific Region to Dominate the Market: In the Asia-Pacific region, China accounts for the largest market share in bio-butanol consumption. The country is the largest producer of paints and coatings in the Asia-Pacific region, with an estimated coating production of more than 15 million metric ton, which is expected to increase significantly in the near future. According to the China Adhesives and Tape Industry Association, the Chinese adhesive market grew by 7.5%, in terms of volume, and was valued at 7.887 million metric ton in 2017. The market grew further in 2018, and is expected to witness a positive trend through the forecast period. The increasing coatings, adhesive, and resin production is primarily supported by the growing construction, and infrastructural and automotive industries. China is promoting and undergoing urbanization, with a 60% target rate by 2020. The increased living spaces required in urban areas, resulting from urbanization, and the desire of middle-class urban residents to improve their living conditions are expected to have a profound effect on the housing market. Additionally, various paint manufacturers are expanding their product line, owing to the increasing demand for coatings. Major adhesive manufacturers are expanding their product line in India. The aforementioned factors are expected to drive the market growth, over the forecast period.

Competitive Landscape: The bio-butanol market is in the nascent stage and is apparently a consolidated one. Currently, Cathay Industrial Bio produces corn-based *n*-butanol for chemical applications at its biorefinery in Jilin Province, China. The company claimed to be the world’s largest bio-butanol producer, based on active production capacity, in 2017. The potential entrants to the market include Microvi Biotechnologies, Cobalt Technologies, and ButaNext.



Source: Investor Presentation, Secondary Literature, Expert Interviews, and MarketsandMarkets Analysis

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WHITE PAPER

TRANSPORTATION FUELS

# *Renewable Solution*

## ISOBUTANOL—A RENEWABLE SOLUTION FOR THE TRANSPORTATION FUELS VALUE CHAIN

### Executive Summary

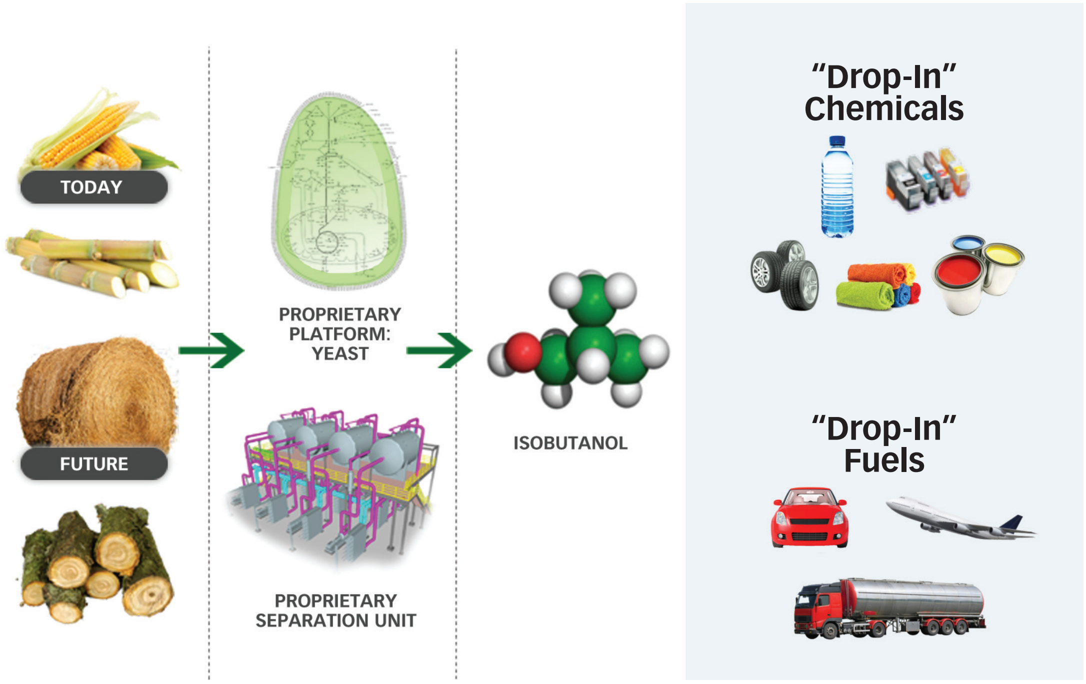
The demand for a clean, renewable biofuel increases as new benchmarks are legislated and increased pressure is placed on the petroleum industry to reduce America's dependence on imported fossil fuels for energy consumption.

Gevo®—a leader in next-generation biofuels—has developed and patented a cost-effective process, Gevo Integrated Fermentation Technology® (GIFT®), which converts fermentable sugars from sustainable feedstocks into isobutanol, a biobutanol product that provides solutions to many of the value chain issues highlighted by first-generation biofuels.

In this paper, you'll learn how isobutanol provides a renewable solution to improve the transportation fuels value chain.

### What You Will Learn:

» Isobutanol is a dynamic platform molecule.
» Isobutanol ships in pipeline systems.
» Isobutanol can address future regulatory issues now.
» Isobutanol mitigates end-user challenges.



# TRANSPORTATION FUELS

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WHITE PAPER

As the demand for renewable sources of fuels intensifies, it is imperative that the transportation fuels industry has the necessary solutions to optimize the value chain. Gevo's renewable isobutanol can potentially be applied across the entire transportation fuels industry and shipped through the pipeline, while complying with government regulations and mitigating end user issues.

To find out how isobutanol is the next-generation biofuel, contact us at:

**345 Inverness Drive South**
**Building C, Suite 310**
**Englewood, CO 80112**
**303-858-8358**

**www.gevo.com**

***Notice Regarding Forward-Looking Statements**
Certain statements in this document, including, without limitation, Gevo's ability to produce cellulosic isobutanol once biomass conversion technology is commercially available, may constitute "forward-looking statements" within the meaning of the Private Securities Litigation Reform Act of 1995. These forward-looking statements are made on the basis of the current beliefs, expectations and assumptions of the management of Gevo and are subject to significant risks and uncertainty. Investors are cautioned not to place undue reliance on any such forward-looking statements. All such forward-looking statements speak only as of the date they are made, and the Company undertakes no obligation to update or revise these statements, whether as a result of new information, future events or otherwise. For a further discussion of risks and uncertainties that could cause actual results to differ from those expressed in these forward-looking statements, as well as risks relating to the business of Gevo in general, see the risk disclosures under the section captioned "Risk Factors" in Gevo's final prospectus related to its initial public offering filed pursuant to Rule 424(b) under the Securities Act of 1933, as amended on February 9, 2011.

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# Butanol Evolves

## BACKGROUND ON BUTANOL

The use of butanols in gasoline goes back to the 1970s–'80s and has been approved under Section 211(f) of the Clean Air Act through the "Arconol," "DuPont" and "Octamix" waivers. At that time, tert-butyl-alcohol (TBA), a man-made material, was the prime butanol used, although research suggests that isobutanol was also being evaluated. These butanols were produced from petroleum processes: Both n-butanol and isobutanol were produced using the oxo process, and TBA was a by-product of the PO process.

Gevo has developed a proprietary biochemical pathway to produce renewable isobutanol, a four-carbon alcohol with many attributes that may aid the transportation fuels industry across its value chain. It is now being evaluated as a next-generation biofuel.

Isobutanol should not be confused with the other isomers in the butanol family (n-butanol, sec-butanol, tert-butyl-alcohol [TBA]). It is a naturally occurring material with a musky odor found in many essential oils, foods and beverages (brandy, cider, gin, coffee, cherries, raspberries, blackberries, grapes, apples, hop oil, bread and Cheddar cheese).

Today, Gevo has developed a renewable method to produce a 98+ percent–purity product using sugars from any available source. The initial plan is to convert existing U.S. cornstarch ethanol plants into isobutanol plants for a fraction of the cost to build new facilities. Gevo also plans to upgrade some of these facilities to produce an isobutanol that will be classified as an advanced biofuel as defined by EPA under the U.S. Energy Independence and Security Act (EISA), to allow cellulosic sugars to be used as a feedstock as they become cost competitive, and to allow multiple products to be generated.

## ISOBUTANOL IS A NEXT-GENERATION RENEWABLE FUEL AND A "BUILDING BLOCK" TO THE FUTURE FUELS VALUE CHAIN

To become a next-generation renewable fuel, it is paramount that the manufacture of a renewable product leverages existing infrastructure and extends the current fuels value chain. With the U.S. oil-and-gas downstream industry (inbound distribution, refining, outbound distribution and marketing) conservatively valued at over $500 billion, it would be inefficient to build an entirely new supply chain infrastructure to accommodate a renewable product industry valued at less than 10 percent of the downstream industry.

The optimal value chain for a transportation fuel, including renewables, might look like this [Figure 1]:

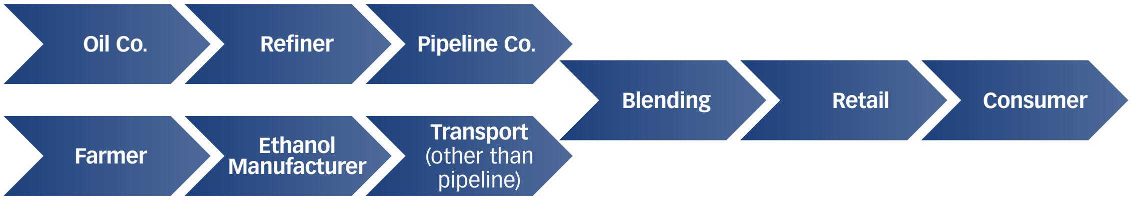
Figure 1

Feedstocks are shipped to a producer (refiner, blender or bio-refiner), where they are converted to a finished product, which is then cost-effectively shipped to market, and sold to the end user based on a specification that meets regulatory needs. Over time, as regulations have been introduced, the optimal value chain has remained intact.

With the advent of the Renewable Fuel Standard (RFS) and EISA, the value chain, using first-generation renewable products, has been changed; for example, ethanol enters the value chain at the terminal [Figure 1a], where it is either blended with a sub-octane gasoline product to produce the finished gasoline, or is added to a finished gasoline to produce a higher-octane product.

Figure 1a

**Existing Gasoline Value Chain**

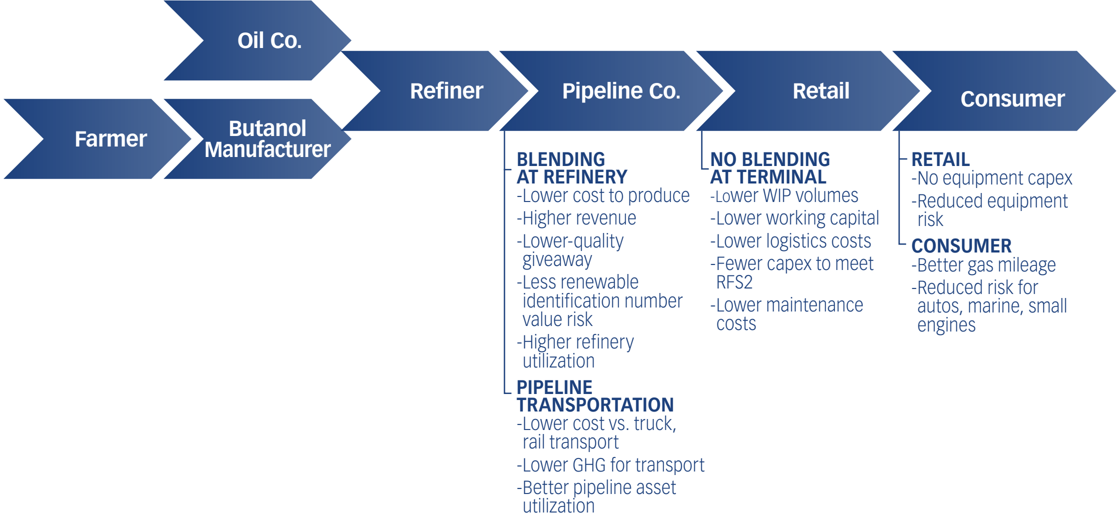


This inefficiency primarily stems from the inability of first-generation biofuels to be shipped in a pipeline, adding system cost(s) as additional capital is required at the terminals for blending these products. Additionally, giveaway costs increase as refiners no longer ship finished products but are held legally accountable for the finished-product specification. If the trend toward using first-generation biofuels grows, pipeline throughput volumes may decrease, giving rise to potential tariff increases on the remaining shippable products.

By analogy, isobutanol is today's "smartphone" to first-generation biofuels' "cell phone;" it can re-optimize the value chain with its ability to be shipped in pipelines, both inbound to and outbound from a refining/blending facility, as shown in Figure 1b. The versatility of isobutanol's properties as a blendstock for gasoline and its ability to be converted to other valuable products give the downstream industry great flexibility.

Figure 1b

**Projected Isobutanol Gasoline Value Chain**



**BLENDING AT REFINERY**
-Lower cost to produce
-Higher revenue
-Lower-quality giveaway
-Less renewable identification number value risk
-Higher refinery utilization

**PIPELINE TRANSPORTATION**
-Lower cost vs. truck, rail transport
-Lower GHG for transport
-Better pipeline asset utilization

**NO BLENDING AT TERMINAL**
-Lower WIP volumes
-Lower working capital
-Lower logistics costs
-Fewer capex to meet RFS2
-Lower maintenance costs

**RETAIL**
-No equipment capex
-Reduced equipment risk

**CONSUMER**
-Better gas mileage
-Reduced risk for autos, marine, small engines

# Dynamic Molecule

## ISOBUTANOL IS A DYNAMIC PLATFORM MOLECULE

Isobutanol is an ideal platform molecule, a more flexible and versatile renewable alternative to current biofuels. It can be used as a "drop in" gasoline blendstock; it converts readily to isobutylene, a precursor to a variety of transportation fuel products such as iso-octene (gasoline blendstock), iso-octane (alkylate—high-quality gasoline blendstock and/or avgas blendstock), iso-paraffinic kerosene (IPK, or renewable jet) and diesel. Isobutanol is not constrained to just the gasoline pool; hence, its value to a producer and/or purchaser is its flexibility.

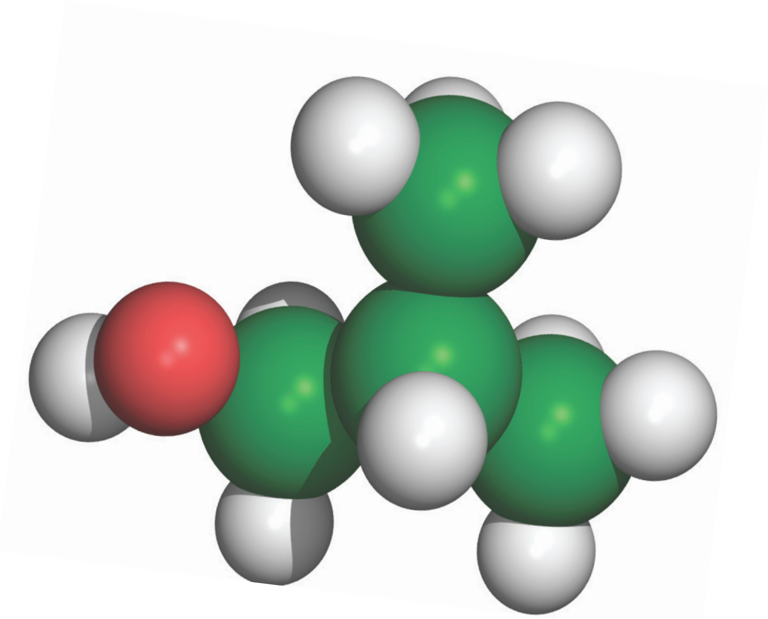
### Gasoline and Renewables

The oil embargoes of the 1970s drove the introduction of alternative, renewable feedstocks for the oil-and-gas industry. At the time, the EPA granted various waivers allowing methanol, ethanol, butanols and other materials into gasoline. By the 1990s, the Clean Air Act required gasoline to have an oxygenate added to improve urban air quality. Until 2005, there were two primary options: MTBE (produced by the refinery and optimally blended into the finished product) and ethanol (produced locally and blended into gasoline, not always optimally, at various distribution terminals).

With the creation of the Renewable Fuel Standard (RFS) and the elimination of MTBE as a viable blendstock in 2004, ethanol became the prime renewable material. Production increased dramatically. As more ethanol entered the market, its price decreased relative to gasoline and its usage increased. The 2007 Energy Independence and Security Act (EISA), which requires different categories of renewable fuels (based on greenhouse gas emission reductions), has also increased the volume obligation of a refiner or blender to use renewable products. In addition, as sulfur and benzene concentrations in gasoline have been addressed, it is anticipated that there will be continued efforts to lower ozone levels, with gasoline volatility being a key driver.

The first-generation renewable products have provided a good start to improving air quality and increasing energy independence, but may not provide an optimal economic solution across the value chain. Isobutanol, as the next-generation product, builds on the foundation and provides additional solutions to various challenges not met by first-generation products. Some of these include:

» Blend properties in gasoline
» Volatility
» Phase separation
» Energy content
» Blend wall



## Blend Properties in Gasoline

Isobutanol has several blend property advantages: low Reid Vapor Pressure (RVP), above-average octane, good energy content, low water solubility and low oxygen content [Figure 2].

Figure 2

| | ETHANOL | ISOBUTANOL |
|---|---|---|
| Blend RVP | 18–22 psi | 4.5–5.5 psi |
| Blend Octane | 112 | 102 |
| Energy Content (% of gasoline) | 65% | 82% |
| Water Solubility | Fully Miscible (100%) | Limited Miscibility (8.5%) |
| Oxygen Content | 35% | 22% |

## Volatility

As sulfur and benzene content in gasoline is limited by legislation, it is likely that efforts to control ozone, which have already increased, will continue to increase in the future.

A key tool used by state regulatory agencies for reducing ozone precursors in the air is through reduced volatility of gasoline as measured by RVP. As ethanol's RVP blend value is high (~18 psi for E10 blends), the base blendstock for oxygenated blending (BOB) must be low to accommodate this high-RVP material. This problem will be exacerbated as any ethanol blends less than 9 percent or greater than 10 percent currently do not qualify for a 1-psi waiver.

Isobutanol's low-blend value RVP (~5.0 psi for 12.5 percent–volume blends) [Figure 3] allows refiners to decrease costs by optimally blending additional lower-cost blendstocks (butane, pentane, NGLs, naphtha) and/or reducing the purchases of more costly low-RVP alkylate. For example, by using Baker and O'Brien's proprietary PRISM™ model [Figure 4] , a refinery serving a low-RVP gasoline market was able to eliminate alkylate purchases and significantly increase butane purchases by using isobutanol instead of ethanol.

Figure 3

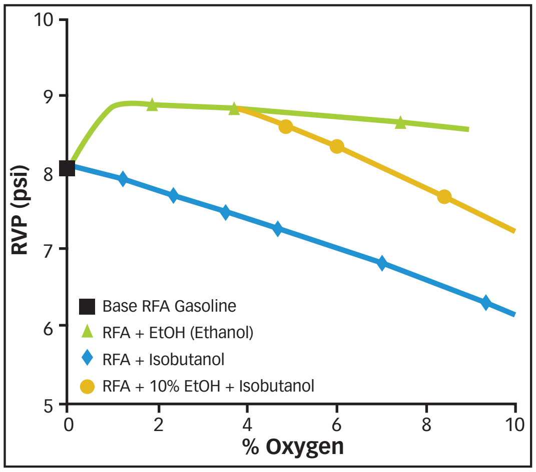
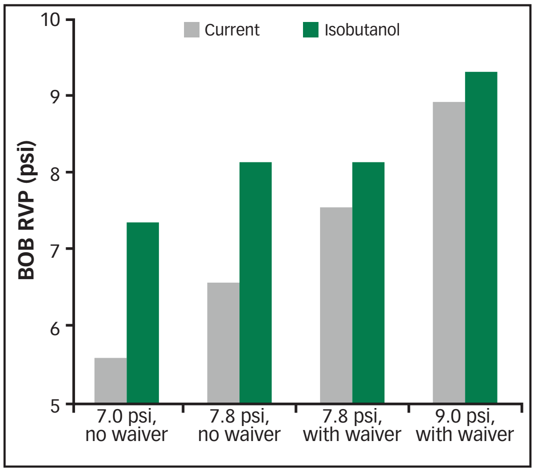


Figure 4



## Phase Separation

Because gasoline may come in contact with water, it is important that the blendstocks remain in the hydrocarbon phase and not migrate into the water. Ethanol, a highly polar material, will separate from the gasoline phase into the water phase, degrading the gasoline's octane. Isobutanol is less polar than ethanol, and tends to act like a hydrocarbon with very limited amounts moving from the gasoline phase to the water phase [Figure 5]. As a result, there is no dilution of the gasoline's octane value, and operational issues related to water content are reduced or eliminated.

Figure 5

Gasoline with 10% Water | Isobutanol-Blended Gasoline with 10% Water | Ethanol-Blended Gasoline with 10% Water

## Energy Content

Isobutanol has approximately 82 percent of the energy value of gasoline. Although every engine is different, higher energy content typically translates into greater fuel economy. In addition, per EISA, as isobutanol has 30 percent more energy than ethanol, its equivalence value (EV) is 1.3 [Figure 6], which translates into significantly more renewable identification numbers (RINs) being generated than ethanol.

Figure 6

| BIOFUEL | EQUIVALENCE VALUE (EV) |
|---|---|
| Ethanol | 1.0 |
| Isobutanol | 1.3 |
| Biodiesel (FAME) | 1.5 |
| Renewable Jet (Biojet, IPK) | 1.6* |
| Renewable Diesel | 1.7 |

*Estimate based on EISA formula.

## Blend Wall

Engine manufacturers are concerned about exceeding 3.5 percent–by-weight oxygen levels, and obligated parties need to generate even greater RINs. Isobutanol provides a solution to these needs. If isobutanol were used at E10 oxygen content levels (3.5 percent–by-weight oxygen), it would generate more than twice the RINs. Even at transitional "substantially similar" oxygen levels (2.7 percent– by-weight oxygen), isobutanol generates more RINs than either E10 or E15 [Figure 7].

Figure 7

| | OXYGEN CONTENT (%) | EV | RINS GENERATED PER 100 GALLONS FINISHED PRODUCT |
|---|---|---|---|
| 12.5% Isobutanol | 2.7 | 1.3 | 16.25 |
| 10% Ethanol | 3.5 | 1.0 | 10.00 |
| 16.1% Isobutanol | 3.5 | 1.3 | 20.93 |
| 15% Ethanol | 5.2 | 1.0 | 15.00 |

# Converting to Jet Fuel

## ISOBUTANOL CAN ALSO BE CONVERTED TO PRODUCE A RENEWABLE JET

According to the International Civil Aviation Organization (ICAO), environmental efficiency gains from technological and operational measures may not offset the overall emissions that are forecast to be generated by the expected growth in air traffic. As a result, the airline industry is evaluating sustainable alternative fuels to reduce its greenhouse gas (GHG) emissions profile, while improving local air quality. It is the ICAO's view that the development and use of sustainable alternative fuels may play an active role in improving the overall resource allocation and security of aviation fuels supply, perhaps by stabilizing fuel prices. A global framework has been established for sharing information on best practices and/or initiatives to allow sustainable alternative aviation fuels to be developed and brought to market.

## IPK/KEROSENE

Isobutanol is an ideal platform molecule to produce renewable iso-paraffinic kerosene (IPK), a blendstock for jet fuel. Through known technology, isobutanol can be readily converted to a mix of predominantly C12/C16 hydrocarbons [Figure 8].

Figure 8

**Bio-based IPK Jet**

Gevo's IPK offers several benefits:

- » Blend Rate—may be blended at up to a 1:1 ratio with petroleum jet.
- » Properties—very low freeze point (–80°C), high thermal oxidation stability, and meets ASTM distillation curve requirements.
- » Regulatory—using EISA's formula, the projected EV is approximately 1.6, which, at a blend rate of 50 percent, would generate 80 RINs per 100 gallons of finished product.
- » Tax Credit—it qualifies for a $1.00/gallon tax credit under IRS Title 26, Subtitle A, Chapter 1, Subchapter A, Part IV, Subpart D, Article 40A.f.3.
- » GHG—using renewable energy and/or improved feedstocks in the production process, it has the potential to significantly reduce GHG emissions.

# Distribution Versatility

## ISOBUTANOL CAN USE THE EXISTING PIPELINE DISTRIBUTION INFRASTRUCTURE

A key advantage for isobutanol to be adopted into the transportation fuels industry is its ability to be shipped in pipelines without negatively affecting the integrity, quality or operations of the pipeline system [Figure 9, below].

Pipelines are a key part of the value chain, and using the existing infrastructure to move product may provide significant advantages:

» There is value in blending at the refinery instead of at the terminal. According to a Solomon Associates presentation* finished fuel from a refinery appears to avoid giveaway costs estimated at $0.01 to $0.03 per gallon of finished gasoline.

» As ethanol volumes have grown, pipeline throughputs have fallen; with lower throughputs, tariffs on the remaining products may increase.

» Shipping material by pipeline is the most cost-effective manner to move liquid products compared to rail, barge and/or truck.

Isobutanol has the potential to be used in the existing pipeline system, both inbound and outbound, providing potential cost savings, flexibility and efficient access to end-user markets.

Figure 9

| | ETHANOL | | ISOBUTANOL | |
|---|---|---|---|---|
| **Integrity** | | | | |
| Stress Corrosion Cracking | Yes | | No | |
| Elastomeric Compatibility | Manageable | | Highly Compatible | |
| **Quality** | | | | |
| Oxygen Content in Gasoline | E10 | 3.5% | I12.5 | 2.7% |
| | E15 | 5.2% | I16.1 | 3.5% |
| Ship Neat Product | Qualified No | | Qualified Yes | |
| **Operations** | | | | |
| Blend Location | Terminal | | Refinery/Terminal | |
| Segregated Storage | Yes | | No | |

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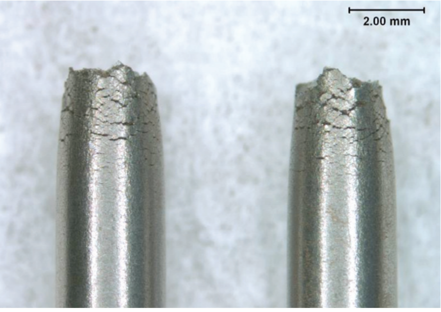
*Use of Ethanol in Conventional Gasoline Blending—A Look at U.S. Refiner Trends* by John Popielarczyk, October 2009, NPRA Q&A meeting.

## Integrity

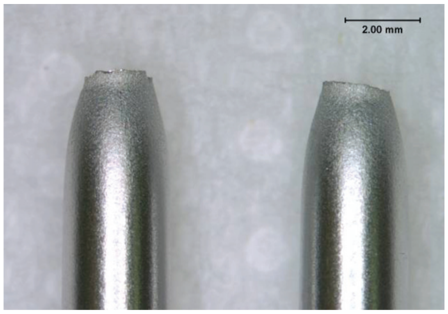
There are two key measures of integrity:

- » Stress corrosion cracking (SCC)
- » Elastomeric compatibility issues

Det Norske Veritas (DNV), a leading corrosion consultantcy that has done significant work on the distribution of ethanol-blended gasoline, has also evaluated isobutanol. Based on DNV's conclusions, carbon steel is susceptible to stress corrosion cracking (SCC) in fuel-grade ethanol; however, no SCC was noted in isobutanol-containing gasoline at concentrations of 12.5 percent and 50 percent, nor was any SCC found with neat isobutanol, as shown at right. In addition, several elastomeric materials were evaluated with respect to their compatibility with isobutanol and gasoline; the tested materials showed better performance in isobutanol than in gasoline.



Evidence of stress corrosion cracking



No stress corrosion cracking at 12.5% isobutanol

## Quality

Today, regulatory pathways exist for isobutanol to be used in gasoline at two volume levels, 12.5 percent under the EPA "substantially similar" ruling (2.7 percent by-weight oxygen content) and 16.1 percent under previous EPA waivers (DuPont, Octamix waivers allowing 3.5 percent by-weight oxygen content). Discussions with pipeline distribution companies have revolved around the shipping, handling and storage of three possible products: 12.5 percent and 16.1 percent by-volume isobutanol-containing gasoline and 100 percent neat isobutanol.

## Operations

In recent years, many terminals have increased capital spending to handle blending of ethanol. At the same time, the volume throughput of pipelines has been reduced by the amount of ethanol blended at the terminal. Isobutanol, shipped to a refinery, optimally blended to reduce giveaway cost(s), and then shipped as a finished product to end-user markets, would use the existing assets more cost-effectively.

# Regulations and RIN

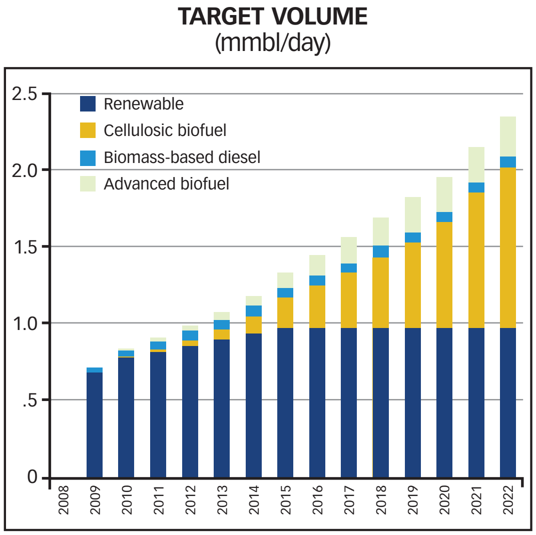
## ISOBUTANOL CAN ADDRESS FUTURE REGULATORY ISSUES NOW

A key driver for isobutanol that will influence its adoption into the transportation fuels industry is the impact that existing and potential regulations may have on guiding which renewable fuels become prominent. Key issues include total RIN volume needed, RIN generation, type of RIN generated, 1 psi waiver and ozone control.

### RIN Volume/Generation

EISA (or RFS2) set new volume targets for the industry; specifically, by 2022, 36 billion gallons per year (or about 2.4 million barrels per day) of renewable products are to be used [Figure 10]. To account for this volume, a renewable identification number (RIN) was established; using the concept of equivalence value (EV) [Figure 6, p. 5], which allows a multiplier based on energy content to be used, it is conceivable that the physical volume used by the transportation fuels industry is less than the EISA target volumes. For example, in Figure 11 (below), if 10 gallons of ethanol with an EV of 1.0 are used, 10 RINs are generated per 100 gallons of finished product. With isobutanol, if 12.5 gallons are used with an EV of 1.3, 16.25 RINs are generated per 100 gallons of finished product. The RINs generated are a function of the physical volume used multiplied by the EV of the renewable product.

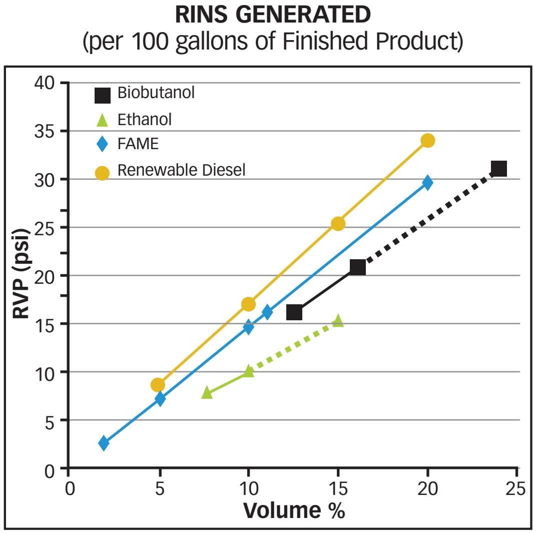
Figure 10



### "Advanced" RIN Capable

A key component of the EISA legislation was the introduction of RIN types: renewable and advanced. The advanced category, with a minimum hurdle of reducing GHG emissions by 50 percent, has the subsets of cellulosic, biomass-based diesel and "advanced other." The ultimate volume requirement for the renewable type was set at 15 billion gallons per year (BGY), and for the advanced type at 21 BGY. Although target volumes were set for the cellulosic and biomass-based diesel categories, EPA has the authority to adjust these totals annually, based on availability, but it cannot reduce the total advanced requirement. As such, there may be a growing need [Figures 12, 13, p. 10] for products that meet the "advanced other" category, or products that have 50 percent lower greenhouse gas emissions compared to gasoline.

Figure 11



## One psi Waiver

Another key driver of isobutanol adoption is a consistent standard with regard to volatility; for E10 blends, ethanol was granted a 1 psi waiver when the finished-product RVP was considered. If a state implementation plan (SIP) required a 9.0 psi RVP for conventionl gasoline, this specification would become 10 psi when using ethanol blends.

At present, only gasoline blends containing 9 percent to 10 percent ethanol are granted a 1 psi waiver. Hence, finished product with a 9.0 psi must have a base blendstock RVP substantially lower than 9.0 in order to accept higher ethanol blends, i.e., E15+.

With isobutanol, obligated parties have considerably greater formulation flexibility and might be able to go as high as 9.6 psi in their blendstock and still meet their Clean Air Act requirements without a waiver.

Figure 12

**PROJECTED RIN** (Gallons)
**VERSUS EISA NEEDS** (mmbl/day)

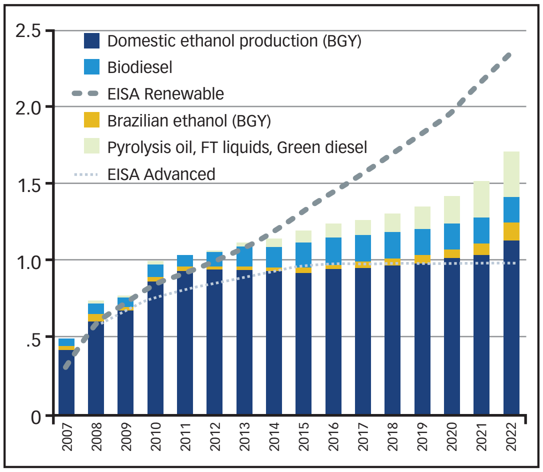
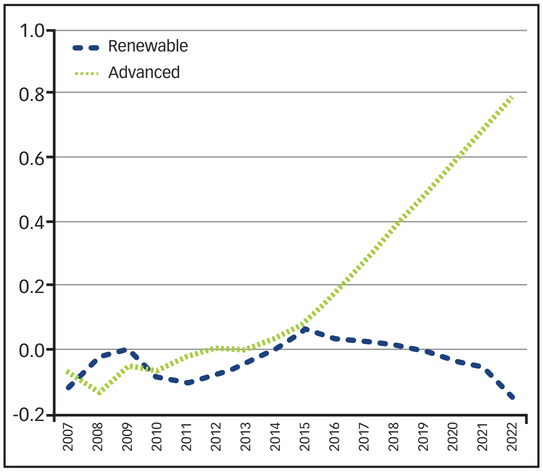


Figure 13

**PROJECTED UNDER-SUPPLY**
(mmbl/day)



NOTE: Per EISA, corn starch–derived ethanol plants are excluded from achieving an "advanced other" level. However, starch-derived isobutanol plants have the ability to achieve the advanced status. As the only currently available advanced products are FAME biodiesel (limited volumes) and Brazilian ethanol imports, isobutanol provides a secure alternative to meet this need.

## Ozone Control

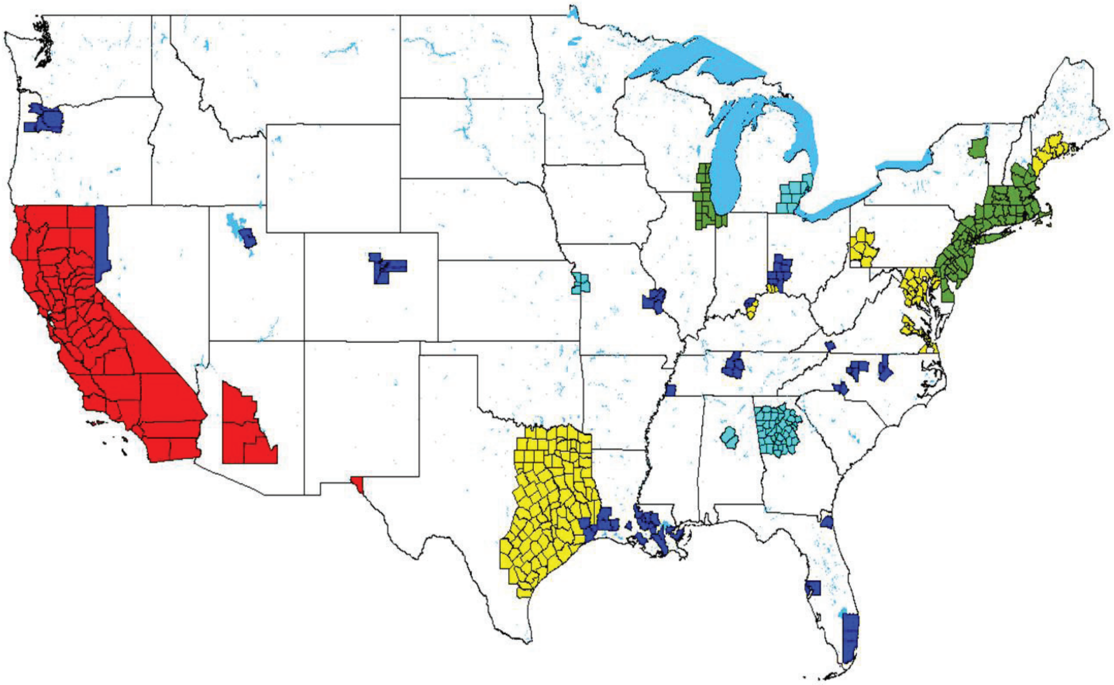
Ground-level ozone is harmful to breathe and damages crops, trees and other vegetation. Gasoline volatility is the key lever used by the states to control ozone precursors. There are already many markets requiring special RVP specifications [Figure 14]. If the EPA target for ozone is set at 75 ppb, it is estimated that over 300 counties nationwide will fall out of compliance. In addition, a U.S. EPA Scientific Advisory Board (SAB) has recommended that the ozone target be lowered (perhaps to 60–70 ppb), which would have a dramatic impact on most of the U.S. gasoline market. Isobutanol, with its low-blend volatility, provides obligated parties greater flexibility to meet both lower volatility (RVP) and renewable fuel obligations.

Figure 14

Increasing value ↑

| Market RVP Specification | Gasoline Market Size | Isobutanol Market Opportunity |
|---|---|---|
| PSI | BGPY | BGPY |
| 🔴 7.0 no waiver[1] | 18 | 2.2 |
| 🟡 7.8 no waiver | 16 | 1.9 |
| 🟢 9.0 no waiver | 18 | 2.2 |
| 🔵 7.0 waiver | 6 | 0.7 |
| ● 7.8 waiver | 11 | 1.3 |
| ○ 9.0 waiver | 72 | 8.6 |

[1] Waiver = 1 psi RVP waiver given to ethanol in many markets.



# Overcoming Concerns

## ISOBUTANOL MITIGATES END-USER ISSUES

The concept of energy independence was established with the introduction of first-generation renewable fuels. However, in trying to increase the use of these products, several significant constraints must be addressed relative to the various end users: certification of storage tank/dispensing equipment, equipment operational concerns, product liability issues for convenience store operators, fuel mileage/maintenance issues and American pride/innovation. Isobutanol can address these concerns as the next step in the evolution of American-produced biofuels.

### Fuel Dispenser Certification Concerns

Underwriters Laboratories (UL) establishes the safety requirements and testing procedures for automotive fuel dispenser systems (UL 87) and certifies new products to ensure they meet material compatibility, adhere to fire safety codes, and are consistent with related products. Although UL has certified certain dispensers for ethanol volumes greater than 10 percent, most existing dispensers used by convenience store operators were only tested and approved for 10 percent blends. The cost of replacing the dispensers is uneconomical for the operator. Isobutanol's initial use would be at EPA gasoline "substantially similar" levels eliminating the need to replace or certify fuel dispensers.

### Consumer Labeling/Product Liability Concerns

EPA has given qualified approval for the sale of E15 blends for use in car model years 2001 and newer, and discussions are under way to determine an appropriate label to be displayed on the dispenser to ensure that the consumer uses the appropriate fuel for their car. Unfortunately, per EISA and its current legal framework, the liability to ensure that the consumer uses the right fuel is placed on the convenience store operator. Many operators find this risk to be too high to consider selling ethanol blends above 10 percent. Again, as isobutanol's initial use would be at EPA "substantially similar" levels, it would be considered the same as a conventional petroleum product.

### Operational Concerns

The use of ethanol in gasoline has been encumbered by operational issues. In addition to its phase separation issues, it is a fairly strong solvent that tends to dislodge dirt/sludge from the dispensing equipment, causing dispenser filter problems and gasket leaking. Isobutanol is not as potent a solvent as ethanol, and based on preliminary discussions with dispenser equipment suppliers, is not expected to have the same issues as ethanol.

## Price and Energy Content Concerns

Consumers tell us that although price remains a key driver of fuel purchase decisions, product performance as a reason for choosing a gasoline brand is increasing. Consumers are keeping their vehicles longer and taking better care of them; rethinking what goes in the tank is becoming more important. Any product that reduces fuel mileage and/or may increase maintenance costs will be avoided if there is a better alternative. Isobutanol has higher energy density than ethanol, and tests are being conducted to quantify this potential benefit to fleet operators and the general motoring public. Qualitatively, gasoline marketers are looking for ways to differentiate themselves, and having a fuel that is renewable but not ethanol is of high interest.

## Marine and Small-Engine Concerns

For specialized uses, such as small-engine and/or marine fleet engines, it is paramount to have a fuel that does not cause operational safety issues and can meet EPA emission targets. As the amount of oxygen content in a fuel increases, the operating temperature of that engine increases, potentially causing undue wear and increased emissions. This is an issue with engines that do not have sophisticated instrumentation. In addition, safety issues have been highlighted, relative to higher idle speeds and unintentional clutch engagement.

The National Marine Manufacturers Association (NMMA), the Outdoor Power Equipment Institute (OPEI) and many of their member companies are evaluating isobutanol as a possible alternative to ethanol to help reduce emissions and eliminate phase separation issues. For example, BRP US Inc. recently conducted a study that found butanol-containing gasoline produced less greenhouse gas emissions and had less engine enleanment than ethanol-blended gasoline.

## Summary

The petroleum industry needs to focus on innovation to meet future environmental regulations, achieve energy independence and mitigate end-user issues. Isobutanol is an ideal platform molecule to address these issues while benefiting the transportation fuels industry value chain.

Isobutanol may provide environmentally favorable options for the transportation fuels industry to position its products facilities and manufacturing processes to meet increasingly stringent regulatory policies and industry standards.

## THE AUTHORS

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Dr. Christopher Ryan is the executive vice president of business development at Gevo. He started his tenure at Gevo in 2009 with more than 15 years of strategic leadership, business development, and research and product development in bio-based materials. Most recently, Dr. Ryan was chief operating officer and chief technology officer for NatureWorks, LLC, which he cofounded in 1997. While at NatureWorks, Dr. Ryan was involved in the development and commercialization of the company's new bio-based polymer from lab-scale production through the introduction and growth of PLA through its $300 million world-scale production facility. He also spent four years working in corporate R&D for HB Fuller, a specialty chemicals company.

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Dave Munz joined Gevo in early 2008 and has been focused on placing isobutanol and/or its derivatives in the transportation fuels industry. His background includes business development, pricing, and/or sales and marketing positions with DuPont (U.S. and UK), Conoco (upstream and downstream, U.S. and UK) and CountryMark. Over the past several years, Mr. Munz's focus has been on renewable fuels and their efficient integration across the value chain within the oil-and-gas industry.

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