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Review article

Bioalcohol as green energy - A review

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ABSTRACT

Bioethanol has now become a big industry and this industry seems to become much bigger in the near future. People regard bioethanol as renewable and sustainable new energy source, although some contraversies such as the rivalry of bioethanol for human food widely exist. Actually, bioethanol can also be a good source of basic raw materials. In early days, ethylene, the most important organic chemical raw material, was produced from dehydration of ethanol. Later, things reversed as petrochemical industry well developed after World War II, when industrial ethanol was mostly produced mainly via hydration of ethylene. Now that bioethanol has already become an important fuel blender, we should well expect that bioethanol should also be new resources for basic organic raw materials, as well as other more valuable fine and specialty chemicals, instead of merely a fuel blender. Nowadays, countless new bioethanol companies are setting up every day. It should lead to more research on bioethanol also as a starting raw chemical material.

1. Introduction

Biofuels are a wide range of fuels which are in some way derived from biomass. The term covers solid biomass, liquid fuels and variousbiogases [1]. Biofuels are gaining increased public and scientific attention, driven by factors such as oil price spikes, the need for increasedenergy security, and concern over greenhouse gas emissions from fossil fuels. Bioethanol is an alcohol made by fermenting the sugar components of plant materials and it is made mostly from sugar and starch crops. With advanced technology being developed, cellulosic biomass, such as trees and grasses, are also used as feedstocks for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the USA and in Brazil.

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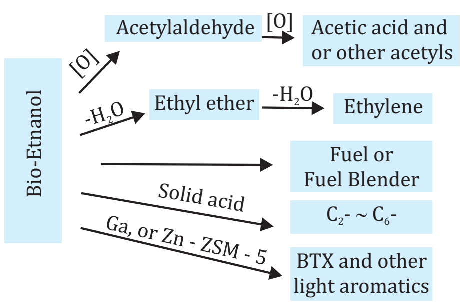
Biodiesel is made from vegetable oils, animal fats or recycled greases. Biodiesel can be used as a fuel for vehicles in its pure form, but it is usually used as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles. Biodiesel is produced from oils or fats using transesterification and is the most common biofuel in Europe. Biofuels provided 1.8% of the world's transport fuel in 2008. Investment into biofuels production capacity exceeded $4 billion worldwide in 2007 and is growing [2].

Figure-1. Feasible pathways for bioethanol



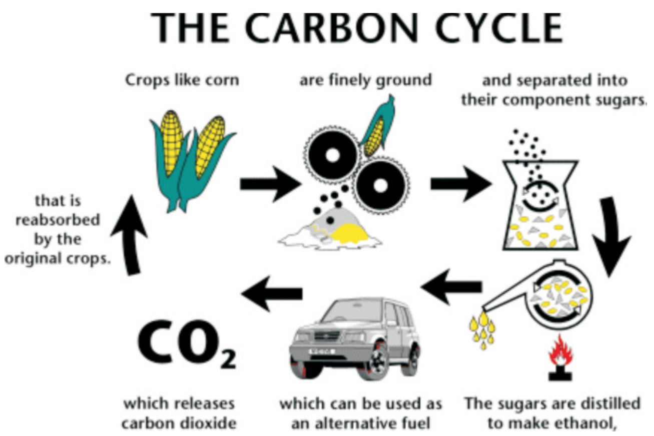
Feasible Pathways for Bioethanol to Basic Raw Materials

First generation biofuels
'First-generation biofuels' are biofuels made from sugar, starch, and vegetable oil.

1.Bioalcohols

Biologically produced alcohols, most commonly ethanol, and less commonly propanol and butanol, are produced by the action of microorganisms and enzymes through the fermentation of sugars or starches (easiest), or cellulose (which is more difficult). Biobutanol (also called biogasoline) is often claimed to provide a direct replacement for gasoline, because it can be used directly in a gasoline engine (in a similar way to biodiesel in diesel engines).
Ethanol fuel is the most common biofuel worldwide, particularly in Brazil. Alcohol fuels are produced by fermentation of sugars derived from wheat, corn, sugar beets, sugar cane, molasses and any sugar or starch that alcoholic beverages can be made from (like potato and fruit waste, etc.). The ethanol production methods used are enzyme digestion (to release sugars from stored starches), fermentation of the sugars,distillation and drying. The distillation process requires significant energy input for heat (often unsustainable natural gas fossil fuel, but cellulosic biomass such as bagasse, the waste left after sugar cane is pressed to extract its juice, can also be used more sustainably).

Figure-2. The carbon cycle



Ethanol can be used in petrol engines as a replacement for gasoline; it can be mixed with gasoline to any percentage. Most existing car petrol engines can run on blends of up to 15% bioethanol with petroleum/gasoline. Ethanol has a smaller energy density than gasoline, which means it takes more fuel (volume and mass) to produce the same amount of work. An advantage of ethanol (CH3CH2OH) is that it has a higher octane rating than ethanol-free gasoline available at roadside gas stations which allows an increase of an engine's compression ratio for increased thermal efficiency. In high altitude (thin air) locations, some states mandate a mix of gasoline and ethanol as a winter oxidizer to reduce atmospheric pollution emissions. Ethanol is also used to fuel bioethanol fireplaces. As they do not require a chimney and are "flueless", bio ethanol fires are extremely useful for new build homes and apartments without a flue [3].The downside to these fireplaces, is that the heat output is slightly less than electric and gas fires. In the current alcohol-from-corn production model in the United States, considering the total energy consumed by farm equipment, cultivation, planting, fertilizers, pesticides, herbicides, and fungicides made from petroleum, irrigation systems, harvesting, transport of feedstock to processing plants, fermentation, distillation, drying, transport to fuel terminals and retail pumps, and lower ethanol fuel energy content, the net energy content value added and delivered to consumers is very small. And, the net benefit does little to reduce un-sustainable imported oil and fossil fuels required to produce the ethanol [4]. Although ethanol-from-corn and other food stocks has implications both in terms of world food prices and limited, yet positive energy yield (in terms of energy delivered to customer/fossil fuels used), the technology has led to the development of cellulosic ethanol. According to a joint research agenda conducted through the U.S.

Department of Energy, the fossil energy ratios (FER) for cellulosic ethanol, corn ethanol, and gasoline are 10.3, 1.36, and 0.81, respectively [5-8]. Many car manufacturers are now producing flexible-fuel vehicles (FFV's), which can safely run on any combination of bioethanol and petrol, up to 100% bioethanol. They dynamically sense exhaust oxygen content, and adjust the engine's computer systems, spark, and fuel injection accordingly. This adds initial cost and ongoing increased vehicle maintenance. As with all vehicles, efficiency falls and pollution emissions increase when FFV system maintenance is needed (regardless of the fuel mix being used), but is not performed. FFV internal combustion engines are becoming increasingly complex, as are multiple-propulsion-system FFV hybrid vehicles, which impacts cost, maintenance,reliability, and useful lifetime longevity. Even dry ethanol has roughly one-third lower energy content per unit of volume compared to gasoline, so larger / heavier fuel tanks are required to travel the same distance, or more fuel stops are required. With large current unsustainable, non-scalable subsidies, ethanol fuel still costs much more per distance traveled than current high gasoline prices in the United States [9].

Methanol is currently produced from natural gas, a non-renewable fossil fuel. It can also be produced from biomass as biomethanol. The methanol economy is an interesting alternative to get to the hydrogen economy, compared to today's hydrogen production from natural gas. But this process is not the state-of-the-art clean solar thermal energy process, where hydrogen production is directly produced from water [10]. Butanol is formed by ABE fermentation (acetone, butanol, ethanol) and experimental modifications of the process show potentially high net energy gains with butanol as the only liquid product. Butanol will produce more energy and allegedly can be burned "straight" in existing gasoline engines (without modification to the engine or car) and is less corrosive and less water soluble than ethanol, and could be distributed via existing infrastructures [11]. DuPont and BP are working together to help develop Butanol. E. coli have also been successfully engineered to produce Butanol by hijacking their amino acid metabolism[12]. Fermentation is not the only route to forming biofuels or bioalcohols. One can obtain methanol, ethanol, butanol or mixed alcohol fuels through pyrolysis of biomass including agricultural waste or algal biomass. The most exciting of these pyrolysis alcoholic fuels is the pyrolysis biobutanol. The product can be made with limited water use and most places in the world.

Cellulosic ethanol is a biofuel produced from wood, grasses, or the non-edible parts of plants. It is a type of biofuel produced from lignocellulose, a structural material that comprises much of the mass of plants.Lignocellulose is composed mainly of cellulose, hemicellulose andlignin Cornstover, switchgrass, miscanthus, woodchips and the byproducts of lawn and tree maintenance are some of the more popular cellulosic materials for ethanol production. Production of ethanol from lignocellulose has the advantage of abundant and diverse raw material compared to sources like corn and cane sugars, but requires a greater amount of processing to make the sugar monomers available to the microorganisms that are typically used to produce ethanol by fermentation.

2.Biofuels for Transportation

Most cars and trucks on the road today are fueled by gasoline and diesel fuels. These fuels are produced from oil, which is a non-renewable fossil fuel. Non-renewable fuels depend on resources that will eventually run out. Renewable resources, in contrast, are constantly replenished and will never run out. Biomass is one type of renewable resource, which includes plants and organic wastes. Biomass Program researchers are studying how to convert biomass into liquid fuels for transportation, called biofuels. The use of biofuels will reduce pollution and reduce the United States' dependence on non-renewable oil. DOE's Biomass Program is focusing on bioethanol and biodiesel production. Other DOE research programs are looking at using biomass to produce other types of clean energy and fuels. For more information about bioenergy in general, link to Biomass Energy Basics.

Ethanol (ethyl alcohol), also known as grain alcohol, is the same 'alcohol' found in all alcoholic drinks.Bioethanol is simply ethanol that has been produced using biological materials (biomass) for feedstocks. Since it relies on sunlight and photosynthesis to contribute to the growth of that biomass (plants, grasses, corn, wheat, etc), bioethanol is a renewable fuel[13].

Glucose (a simple sugar) is created in the plant by photosynthesis.

$$\mathbf{6\ CO_2 + 6\ H_2O + light \rightarrow C_6H_{12}O6 + 6\ O_2}$$

During ethanol fermentation, glucose is decomposed into ethanol and carbon dioxide.

$$\mathbf{C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 + heat}$$

During combustion ethanol reacts with oxygen to produce carbon dioxide, water, and heat:

$$\mathbf{C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O + heat}$$

After doubling the combustion reaction because two molecules of ethanol are produced for each glucose molecule, and adding all three reactions together, there are equal numbers of each type of molecule on each side of the equation, and the net reaction for the overall production and consumption of ethanol is just: Light → heat

The heat of the combustion of ethanol is used to drive the piston in the engine by expanding heated gases. It can be said that sunlight is used to run the engine (as is the case with any renewable energy source, as sunlight is the only way energy enters the planet) [14].

Glucose itself is not the only substance in the plant that is fermented. The simple sugar fructose also undergoes fermentation. Three other compounds in the plant can be fermented after breaking them up by hydrolysis into the glucose or fructose molecules that compose them. Starch and cellulose are molecules that are strings of glucose molecules, and sucrose (ordinary table sugar) is a molecule of glucose bonded to a molecule of fructose. The energy to create fructose in the plant ultimately comes from the metabolism of glucose created by photosynthesis, and so sunlight also provides the energy generated by the fermentation of these other molecules.

Ethanol may also be produced industrially from ethene (ethylene). Addition of water to the double bond converts ethene to ethanol:

$$\mathbf{C2_{H4} + H_2O \rightarrow CH_3CH_2OH}$$

When ethanol is burned in the atmosphere rather than in pure oxygen, other chemical reactions occur with different components of the atmosphere such as nitrogen (N2). This leads to the production of nitrous oxides, a major air pollutant.

There are two ways of producing ethanol from cellulose:•

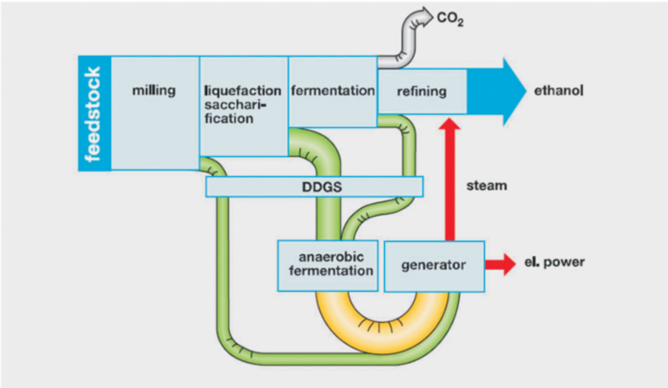
- Cellulolysis processes which consist of hydrolysis on pretreated lignocellulosic materials, using enzymes to break complex cellulose into simple sugars such as glucose and followed by fermentation and distillation.
- Gasification that transforms the lignocellulosic raw material into gaseous carbon monoxide and hydrogen. These gases can be converted to ethanol by fermentation or chemical catalysis.
  As is normal for pure ethanol production, these methods include distillationBioethanol
  Bioethanol is liquid, clear, colorless,biodegradable and havelow toxicity.

Bioethanol is an alcohol made by fermenting the sugar components of biomass. Today, it is made mostly from sugar and starch crops. With advanced technology being developed by the Biomass Program, cellulosic biomass, like trees and grasses, are also used as feedstocks for ethanol production. Ethanol can be used as a fuel for cars in its pure form, but it is usually used as a gasoline additive to increase octane.

3.Bioethanol Feedstocks

Biomass is material that comes from plants. Plants use the light energy from the sun to convert water and carbon dioxide to sugars that can be stored, through a process called photosynthesis. Organic waste is also considered to be biomass, because it began as plant matter. Researchers are studying how the sugars in the biomass can be converted to more usable forms of energy like electricity and fuels. Some plants, like sugar cane and sugar beets, store the energy as simple sugars. These are mostly used for food. Other plants store the energy as more complex sugars, called starches. These plants include grains like corn and are also used for food [15,16].

Figure-3: Bioethanol feedstocks



Another type of plant matter, called cellulosic biomass, is made up of very complex sugar polymers, and is not generally used as a food source. This type of biomass is under consideration as a feedstock for bioethanol production. Specific feedstocks under consideration include:

- Agricultural residues (leftover material from crops, such as the stalks, leaves, and husks of corn plants)
- Forestry wastes (chips and sawdust from lumber mills, dead trees, and tree branches)
- Municipal solid waste (household garbage and paper products)
- Food processing and other industrial wastes (black liquor, a paper manufacturing by-product)
- Energy crops (fast-growing trees and grasses) developed just for this purpose.
- Cellulose is the most common form of carbon in biomass, accounting for 40%-60% by weight of the biomass, depending on the biomass source. It is a complex sugar polymer, or polysaccharide, made from the six-carbon sugar, glucose. Its crystalline structure makes it resistant to hydrolysis, the chemical reaction that releases simple, fermentable sugars from a polysaccharide [17].
- Hemicellulose is also a major source of carbon in biomass, at levels of between 20% and 40% by weight. It is a complex polysaccharide made from a variety of five- and six-carbon sugars. It is relatively easy to hydrolyze into simple sugars but the sugars are difficult to ferment to ethanol.
- Lignin is a complex polymer, which provides structural integrity in plants. It makes up 10% to 24% by weight of biomass. It remains as residual material after the sugars in the biomass have been converted to ethanol. It contains a lot of energy and can be burned to produce steam and electricity for the biomass-to-ethanol process.

4.Bioethanol Production

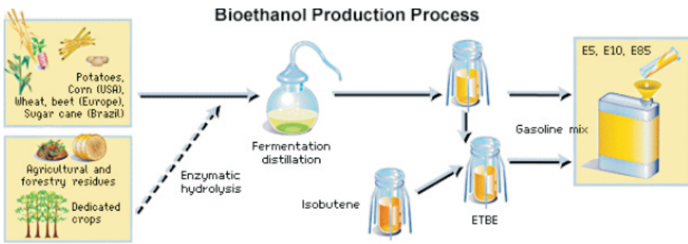
Bioethanol is made when biomass is converted to sugars, which are then fermented into ethanol. The process of hydrolysis seperates most of the water from ethanol, leaving an end product that is generally about 95% ethanol and 5% water.

Key Reactions

Two reactions are key to understanding how biomass is converted to bioethanol

- **Hydrolysis** is the chemical reaction that converts the complex polysaccharides in the raw feedstock to simple sugars. In the biomass-to-bioethanol process, acids and enzymes are used to catalyze this reaction.

Figure 4. Bioethanol production process



- **Fermentation** is a series of chemical reactions that convert sugars to ethanol. The fermentation reaction is caused by yeast or bacteria, which feed on the sugars. Ethanol and carbon dioxide are produced as the sugar is consumed. The simplified fermentation reaction equation for the 6-carbon sugar, glucose, is:

$$C_6H_{12}O_6 \rightarrow 2CH_3CH2_0H + 2CO_2$$

Glucose ethanol carbon dioxide

CO_2 Emissions: Combustion of bioethanol does release CO_2 into the atmosphere.

Process Description. The basic processes for converting sugar and starch crops are well-known and used commercially today. While these types of plants generally have a greater value as food sources than as fuel sources there are some exceptions to this. For example, Brazil uses its huge crops of sugar cane to produce fuel for its transportation needs. The current U.S. fuel ethanol industry is based primarily on the starch in the kernels of feed corn, America's largest agricultural crop [18].

Figure 5. Key reactionsof bioethanol

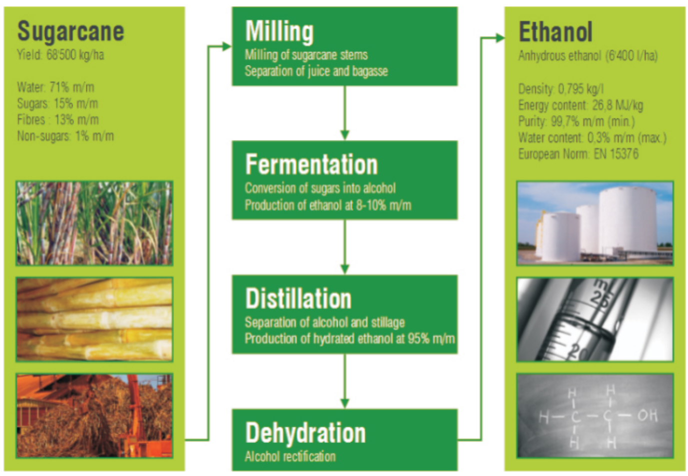
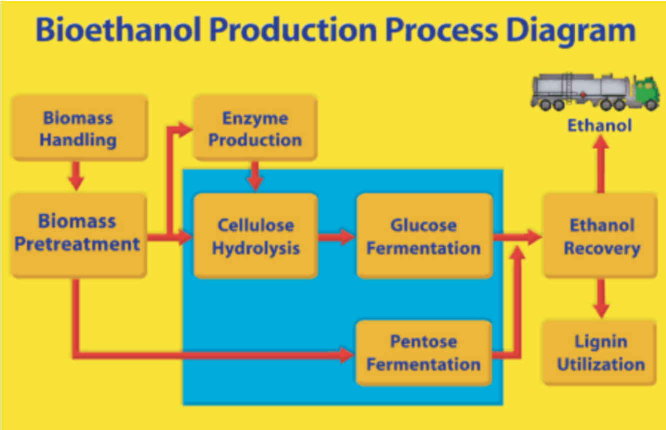


Figure 6.Bioethanol production process



- Biomass Handling. Biomass goes through a size-reduction step to make it easier to handle and to make the ethanol production process more efficient. For example, agricultural residues go through a grinding process and wood goes through a chipping process to achieve a uniform particle size.
- Biomass Pretreatment. In this step, the hemicellulose fraction of the biomass is broken down into simple sugars. A chemical reaction called hydrolysis occurs when dilute sulfuric acid is mixed with the biomass feedstock. In this hydrolysis reaction, the complex chains of sugars that make up the hemicellulose are broken, releasing simple sugars. The complex hemicellulose sugars are converted to a mix of soluble five-carbon sugars, xylose and arabinose, and soluble six-carbon sugars, mannose and galactose. A small portion of the cellulose is also converted to glucose in this step.
- Enzyme Production. The cellulase enzymes that are used to hydrolyze the cellulose fraction of the biomass are grown in this step. Alternatively the enzymes might be purchased from commercial enzyme companies.
- Cellulose Hydrolysis. In this step, the remaining cellulose is hydrolyzed to glucose. In this enzymatic hydrolysis reaction, cellulase enzymes are used to break the chains of sugars that make up the cellulose, releasing glucose. Cellulose hydrolysis is also called cellulose saccharification because it produces sugars.
- Glucose Fermentation. The glucose is converted to ethanol, through a process called fermentation. Fermentation is a series of chemical reactions that convert sugars to ethanol. The fermentation reaction is caused by yeast or bacteria, which feed on the sugars. As the sugars are consumed, ethanol and carbon dioxide are produced.
- Pentose Fermentation. The hemicellulose fraction of biomass is rich in five-carbon sugars, which are also called pentoses. Xylose is the most prevalent pentose released by the hemicellulose hydrolysis reaction. In this step, xylose is fermented using Zymomonas mobilis or other genetically engineered bacteria.
- Ethanol Recovery. The fermentation product from the glucose and pentose fermentation is called ethanol broth. In this step the ethanol is separated from the other components in the broth. A final dehydration step removes any remaining water from the ethanol.
- Lignin Utilization. Lignin and other byproducts of the biomass-to-ethanol process can be used to produce the electricity required for the ethanol production process. Burning lignin actually creates more energy than needed and selling electricity may help the process economics.

  Converting cellulosic biomass to ethanol is currently too expensive to be used on a commercial scale. So researchers are working to improve the efficiency and economics of the ethanol production process by focusing their efforts on the two most challenging steps:
- Cellulose hydrolysis. The crystalline structure of cellulose makes it difficult to hydrolyze to simple sugars, ready for fermentation. Researchers are developing enzymes that work together to efficiently break down cellulose. Read more about Enzymatic Hydrolysis.

  Pentose fermentation. While there are a variety of yeast and bacteria that will ferment six-carbon sugars, most cannot easily ferment five-carbon sugars, which limits ethanol production from cellulosic biomass. Researchers are using genetic engineering to design microorganisms that can efficiently ferment both five- and six-carbon sugars to ethanol at the same time.

5. Infrastructure

Bioethanol can use the existing road transport system for conventional fuels, but the corrosive capacity of bioethanol may prevent it from being able to use the pipeline system—a major drawback.

Compared to Gasoline

As a blended fuel, bioethanol reduces emissions of carbon monoxide a number of other pollutants by as much as 25% or more over conventional gasoline.

Advantages

Bioethanol is already compatible, in low blends, with existing gas engines.

Bioethanol is a high octane fuel with lower emissions.

Disadvantages

Bioethanol can be corrosive to metals such as aluminum.

Bioethanol may require the use of too much arable land (to grow the required crops) and too much energy input during production to justify it. As such, costs—financially, environmentally—are currently prohibitive.

6. The Future

The future of bioethanol lies directly with precisely what composes the biomass used in the production process. Many researchers believe its future is with cellulosic ethanol using biomass such as corn stover and switchgrass. As was already mentioned, compared to oil, ethylalcohol has a lower calorific value, low cetane number and a very low lubricating capacity. The inflammability and lubricating capacity can be adjusted almost perfectly by the use of suitable additives so that ethylalcohol can be used for diesel engines without any interference with the engine design. Suitable organic nitrate and nitrite-based addives which increase the cetane number are supplied by a number of producers. These are added into ethylalcohol in the amount of 4 to 12% pursuant to the producer´s recommendation.However, in the light of the low calorific value of ethylalcohol, it is necessary to modify the engine fuel system. To obtain the same range of travel from a vehicle using diesel fuel and ethylalcohol, the ethylalcohol fuel tank has to have 1.7 times bigger volume than the diesel one [19,20].

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