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Bioethanol from Lignocellulosic Wastes

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Abstract

Biofuels are derived from lingo cellulosic materials, which are why bioethanol is known as alternative fuel, which has many advantages in terms of energy efficiency, economically and environmental in comparison with bio-ethanol derived from starch or glucose. The optimum utilization of agricultural waste due to the recycling and the possibility of producing value added materials have many economic and ecological benefits. Ethanol is the most dominant type of biofuel that can be used either as an eat fuel or in the blended form with gasoline. Sugars, starches, lingo cellulosic materials, and more recently algal biomass are the main raw materials used for ethanol production. Among these raw materials, lingo cellulosic feed stocks are abundant and available at low price that make them suitable and potentially inexpensive feedstocks for the sustainable production of fuel ethanol. This Article covers different aspects of ethanol production including global market situation, various raw materials, status, and recent advances of the applied technologies, future perspective. Finally, technical challenges encountered in development of the biomass-based ethanol are presented and potential approaches to overcome these technical barriers and to improve the economy of the whole process such are presented and discussed in detail.

Keywords: Bio Fuel, Bio Ethanol, Lingocelluloscic

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1. Introduction

Energy security plays a critical role in the economy of both developed anddeveloping countries. Today, the major energy demand is supplied from conventional fossil fuels such as oil, coal, and natural gas. As global demand for energy continues to grow, the current price of fossil fuels is not likely to decrease. In addition, utilization of fossil fuels over the last few decades has drastically increased the level of greenhouse gasses (GHGs) in the atmosphere of our planet.

The negative impacts of fossil fuel on the environment and consequent global warming, rising demand for energy, The alternative fuels areexpected to be costeffective, produced from renewable feed stocks which areavailable worldwide, and must contribute to GHG reduction targets .Production of fuel ethanol from biomass seems to be an interesting alternative totraditional fossil fuel. Bioethanol can be utilized as a sole fuel in cars with dedicated engines or in fuel blends as an octane booster. Ethanol is currently produced from sugars, starches, and cellulosic materials. Cellulosic materials obtained from wood and agricultural residuals, municipal solid wastes, and energy crops represent the most abundant global source of biomass

These facts have motivated extensive research toward developing efficient technologies for conversion of lignocelluloses into sugar monomers to be used as feed stocks for fermentation to ethanol.

2. An Overview on Bioethanol Production

2.1 Global Market

world market

Because of the non-contamination of this fuel, and the interest of countries in having clean air, ethanol has been used as fuel. Ethanol, as a fuel, has created a very good market for cereal producers, and this market is increasing day by day due to the economic and environmental benefits of ethanol.

- Reduce carbon dioxide gas Reducing greenhouse gases and gases that damage the ozone layer.
- The lack of energy dependency and sufficient sources of energy production
- Reducing dependency on gasoline imports
- Make a job in both rural and urban settings

The idea of using ethanol as fuel dates back to the early twentieth century. In 1908 Henry Ford designed a machine that worked with ethanol, but by 1673, ethanol was not considered as fuel.

This year, crude oil increased and paid a lot of attention to fermentation operations for ethanol production. Some countries began to study and produce fuel using economic methods of raw materials. With the fall in oil prices, this decline was reduced to the fact that in 1979 another oil crisis arose. Since 1980, ethanol has been considered as a possible replacement fuel in many countries.

Ethanol production worldwide has drastically increased since the oil crises in 1970, And today, it is the most dominant biofuel. In 2012, three quarters of global biofuels market was for bioethanol, with the remaining quarter consisting of biodiesel sales. Global bioethanol production showed an upward trend over the last25 years with a sharp increase from 2000 to 2010.

product (GDP) in many countries. The market for beverage alcohol in most developed countries is stagnating or even declining, due to increased health awareness Global ethanol production by country or region, from 2007 to 2012, is represented in Fig. 1. Together, the USA and Brazil dominate the bioethanol market, accounting for 85 % of the world's ethanol production and 82 % of global consumption.

This makes the global fuel ethanol market very reliant on the markets of these two countries.

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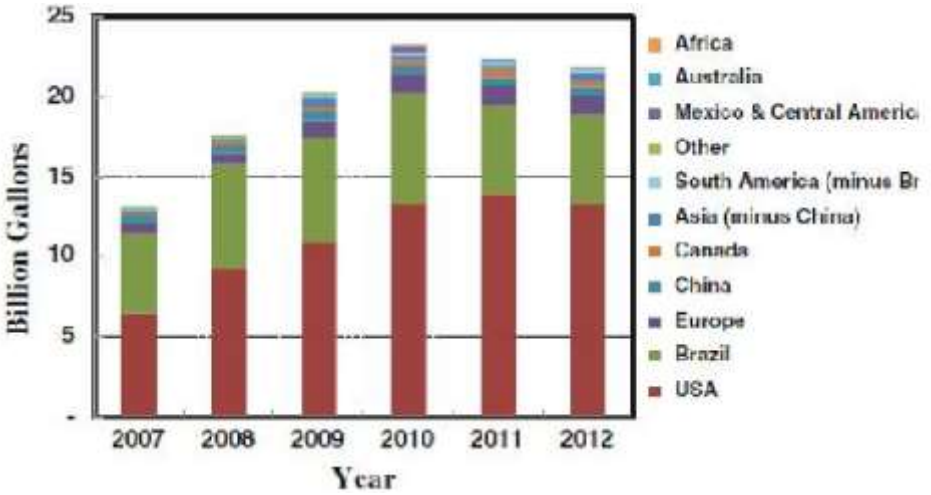

Fig1.Global ethanol production by the major producers

2.2. Bioethanol as a Fuel

Sustainable alternative fuels are nowadays in focus due to global warming caused by excessive emissions of CO2, rising prices of fossil fuels and unstable world oil market. Ethanol, also known as ethyl alcohol, can be used as a substitute for, as well as additive to, the traditional fossil fuels. Ethanol with the chemical formula C2H5OH is a flammable, clear, colorless, biodegradable, and slightly toxic chemical compound with acceptable odor. It can be produced either from petrochemical feed stocks by the acid-catalyzed hydration of ethane, or from biomass feed stocks through fermentation. On a global scale, synthetic ethanol accounts for about 5 % of total production, while the rest is produced from fermentation of biomass mainly sugar crops, i.e., cane and beet, and of grains (mainly corn).

Ethanol as a neat fuel or even in the blended form with gasoline has a long history as automotive fuel. As an automotive fuel, hydrous ethanol can be used as a substitute for gasoline in dedicated engines. Anhydrous ethanol, on the other hand, is an effective octane booster when mixed in blends of 5–30 % (by volume) with no engine modification requirement

2.3. Raw Materials for Ethanol Production

Ethanol can be theoretically produced from any material containing carbohydrates. This will lead us to three main groups of raw materials in nature, namely sugary, starchy, and non-food cellulosic materials. Nowadays, vast majority of ethanol is produced from sugar and starch; the former is mainly produced from sugarcane, beet, sweet sorghum, etc., and the latter comes from grains and root crops such as corn, wheat, and cassava. Technology for ethanol production from these materials is mature, and ethanol produced is referred to as first-generation ethanol (Fig2).

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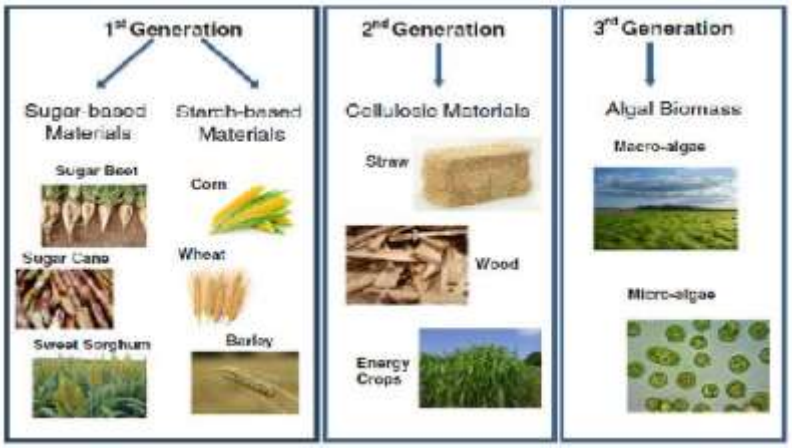

Fig. 2 Classification of raw materials used for bioethanol production

Lignocelluloses are complex mixtures of carbohydrate polymers, namely cellulose and hemicellulose, lignin, and a small amount of compounds known as extractives. Production of ethanol from lingo cellulosic materials, referred to as the second-generation ethanol (Fig2), has the advantage of abundant and diverse raw material availability compared to the current utilized resources. Besides, cellulosic ethanol can contribute to the reduced GHG emissions. However, due to structural complexity of lingo cellulosic materials, technology for the second-generation ethanol production requires more processing steps to make sugar monomers available to the microorganisms for fermentation.

Another class of non-food raw materials for biofuel production including bioethanol is algal biomass which has a very distinctive growth yield as compared with classical lingo cellulosic biomass. Algae include wide variety of photosynthetic organisms living in many diverse environments and present in all existing ecosystems on Earth. Cultivation of algae at seawater or industrial wastewater has been suggested as an interesting alternative solution for biofuels production. The biofuels produced from algal biomass are considered as the third- generation biofuels (Fig. 2). There are two different types of algae: microalgae and macro algae. The structure of some of the raw materials used in the second and third generation bioethanol is presented in (Table 1).

Table 1. Chemical composition of potential raw materials for the production of ethanol

Raw material	Cellulose	Hemicellulose	Lignin
Hardwood stem	40–50	24–40	18–25
Softwood stem	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Wheat straw	33–40	20–25	15–20
Rice straw	40	18	5.5
Leaves	15–20	80–85	0
Switch grass	30–50	10–40	5–20
Cotton, flax	80–95	5–20	0
Primary wastewater solids	8–15	NA	24–29
Paper	85–99	0	0–15
Newspaper	40–55	25–40	18–30
Algae (green)	20–40	20–50	0

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3 Conversion Pathways of Bioethanol

From Lignocellulosic feed stocks Biofuels production form lignocellulosic materials might be accomplished through two major pathways which are biochemical and thermochemical pathways. Through the first route, the biomass is fractionated to its main structural components, i.e., cellulose, hemicellulose, and lignin, and the carbohydrate polymers are then broken down into monomeric sugars. Therefore, this route mainly includes pretreatment and enzymatic hydrolysis of cellulose followed by fermentation of liberated sugars from both cellulose and hemicellulose to ethanol.

The latter which is an emerging technology includes heat treatment of biomass at different temperatures in presence or absence of an oxidizing agent. In this process, the biomasses converted to three main fractions: bio char (solid), bio oil (liquid), and a gas mixture known as syngas.

3.1 Biological Route

The technology of ethanol production through biological route consists of several steps and varies depending on the type of raw materials used. Overall, for ethanol production from cellulosic feed stocks, four major unit operations are required: pretreatment, hydrolysis, fermentation, and separation/ purification

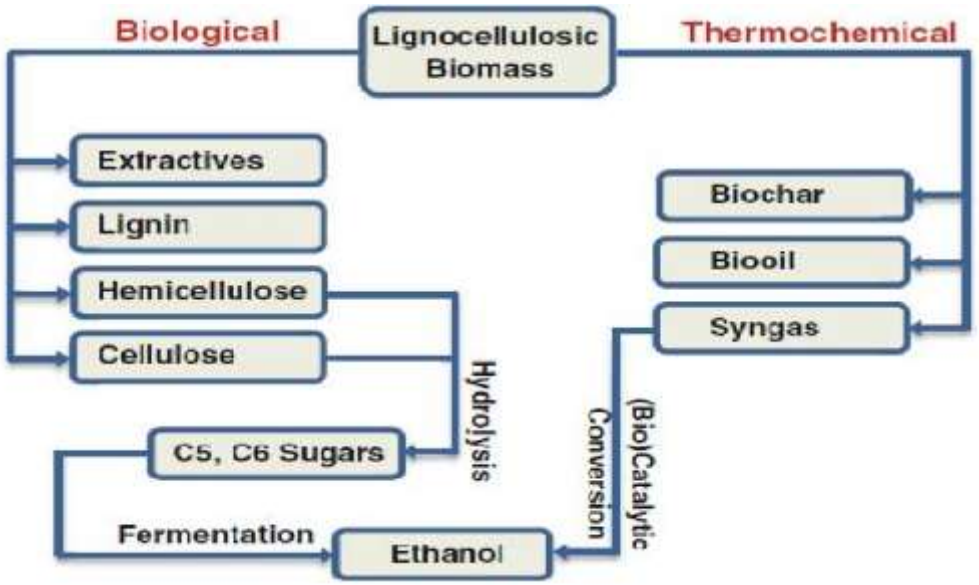

Fig. 3 Block diagram of lingo cellulosic biomass conversion routes to ethanol

3.1.1 Pretreatment

One of the main problems in application of cellulosic feed stocks as raw materials for ethanol production is resistance against enzymatic depolymerization. The carbohydrate polymers in lignocellulose are tightly bound to lignin mainly by hydrogen bonds as well as by some covalent bonds which make it a recalcitrant and inaccessible substrate for hydrolysis agents. The objective of pretreatment is therefore to increase the surface area and porosity of the substrate, reduce the crystallinity of cellulose, and disrupt the heterogeneous structure of cellulosic materials. This process makes the carbohydrate polymers accessible for depolymerization. The pretreatment results in an improved rate and yield of liberated sugars in hydrolysis step.

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3.1.2 Hydrolysis

Hydrolysis of cellulosic materials includes the processing steps that convert the carbohydrate polymers, e.g., cellulose and hemicellulose, into monomeric sugars. Cleavage of these polymers can be catalyzed enzymatically by cellulases or chemically by acids such as sulfuric acid.

- Enzymatic Hydrolysis

Hydrolysis of cellulosic materials can be catalyzed by a class of enzymes known as cellulases. These enzymes are mainly produced by fungi, bacteria, and protozoans that catalyze the cellulolysis or hydrolysis of cellulose.

- Acid Hydrolysis

Interest in wood hydrolysis dates back to 1819, when Braconnot discovered cellulose could be dissolved in concentrated acid solutions and converted to sugar. Acid hydrolysis can be performed with various types of acids including sulfuric, sulfurous, hydrochloric, phosphoric, nitric acid, etc.

3.1.3 Fermentation.

3.1.3.1. Fermentation operation

The Vigand Company carried out the fermentation process with yeast, so that the sweet mixture is taken up in the sugar curing unit and is fermentable under acidity, temperature and other things that are fully controlled. The sweet liquid that has been removed from the sugar process is mixed with yeast, which is carried out in fermentation tubes. Then the product is mixed. This action is performed in order to establish contact between sugar and yeast, at which time the temperature and temperature are fully controlled. The yeast converts the glucose molecule into two molecules of ethanol and two carbon dioxide molecules. The remaining carbon dioxide can be recycled and used in glass bottles for the beverage industry, or after entering the atmosphere after exposure to hazardous substances. The Vigand Company's Laboratory Fermentation Plan is available for testing at the Research and Development Center, which will test various inputs of various enzymes and yeasts, as well as both the step-by-step system in this pilot, in terms of process engineering.

3.1.3.2 Microorganisms

Microorganisms play a significant role in production of ethanol from renewable resources, and thus, selection of suitable strain is essential for the individual process. Ethanol production is much more challenging and difficult when cellulose based materials are to be used as raw materials. Unlike the starch-based materials, pretreatment and hydrolysis of lignocellulosic materials produce a mixture of pentose and hexose sugars along with other inhibiting compounds, causing many problems in the fermentation step. Therefore, capability of consuming both pentose and hexose sugars, high tolerance against substrate, ethanol as well as inhibiting compounds, high ethanol yield, and minimum nutrient requirements are the essential features of an ideal microorganism. (Fig. 5) shows ethanol producing microorganisms.

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Acinetobacter calcoaceticus	SmF	ND	0.46 U/ml	ND
Bacillus subtilis	SSF	2.8 IU/gds	9.6 IU/gds	ND
Bacillus pumilus	SmF	ND	1.9 U/ml	ND
Cellulomonas biazotea	SmF	7450 nkat/g	13,833 nkat/g	2850 nkat/g
Clostridium papyrosolvens	SmF	35 IU/ml	45 IU/ml	ND
Chaetomium globosum	SmF	1.4 U/ml	30.4 U/ml	9.8 U/ml
Streptomyces drozdowiczi	SmF	4.1 U/gds	595 U/L	ND
Thermomonospora sp	SmF	0.11 IU/ml	23 IU/ml	0.02 IU/ml
Thermoascus aurantiacus	SSF	4.4 U/gds	987 U/gds	48.8 U/gds
Neurospora crassa	SmF	1.33 U/ml	19.7 U/ml	0.58 U/ml
Thermotoga maritima	SmF	ND	ND	30 mU/ml
Trichoderma reesei	SmF	2.49 IU/ml	7.15 IU/ml	2.17 IU/ml
T. reesei RUT C 30	SmF	6.2 U/ml	54.2 U/ml	0.39 U/ml
T. species A 001	SmF	18 U/ml	167 U/ml	49 U/ml
T. reesei ZU 02	SmF	0.25 IU/ml	5.48 IU/ml	ND
T. viridae	SmF	0.88 U/ml	33.8 U/ml	0.33 U/ml
Penicillium funiculosum	SmF	1.4 IU/ml	4.55 IU/ml	9.29 IU/ml
Penicillium pinophilum	SmF	7 U/ml	65 U/ml	10 U/ml
P. janthinellum	SmF	0.55 U/ml	21.5 U/ml	2.31 U/ml
P. decumbens	SSF	20.4 IU/g	ND	ND
P. occitanis	SmF-Fed	23 IU/ml	21 IU/ml	ND
A. fumigatus IMI 248651	SmF	40 IU/ml	0.5 IU/ml	1.73 IU/ml
A. terreus	SSF	243 U/g	581 U/g	138 U/g
Fusarium oxysporum	SSF	304 U/g	ND	0.140 U/g

Figure 5 - Ethanol producer microorganisms

3.2 Thermochemical Route

Three main processes in thermochemical conversion of biomass to energy are direct combustion, gasification, and pyrolysis, among which gasification is considered the most efficient process. Gasification is the conversion of biomass, or any solid fuel such as coal and oil, into an energetic gas through partial oxidation at elevated temperatures (e.g., 750–800 °C). Air, oxygen, and steam are common oxidants used in this process. The gas, called synthesis gas or syngas in short, predominantly contains H2 and CO along with a mixture of other components including methane (CH4), small quantities of light hydrocarbons (CnHm), carbon dioxide (CO2), nitrogen (N2), and steam (H2O).

4. Summary and Future Prospects

Bioethanol can be produced from cellulosic-based feed stocks through the biological and thermochemical pathways. Both technologies need significant capital investment and consist of several sophisticated processing steps with higher operating costs compared with the first-generation ethanol. There is currently no clear commercial or technical advantage between the biological and thermochemical pathways. The overall economics of both conversion pathways are very similar, and they are more or less the same with respect to energy efficiency and environmental merit. Despite extensive technological advances over the last few decades, both technologies are still under continual development and evaluation and have significant technical and environmental barriers yet to be overcome. The high overall cost in biological route is because of some technological impediments encountered in all different steps of the process. Improving feedstock characteristics, more efficient pretreatment methods, and hydrolytic enzymes, and improving overall process integration are among the main challenges that need further development. The current leading pretreatment methods for lignocellulosic materials are capital-intensive. Economical comparison showed that there is little differentiation between studied pretreatment methods as for instance low-cost pretreatment reactors are counterbalanced by higher cost of catalyst and/or ethanol recovery. Development of less energy intensive and more effective pretreatment methods allowing lower enzymes consumption and minimal inhibitor formation consubstantially decrease the total cost of cellulosic ethanol. The next significant technical barrier is cost of enzymes which must be reduced by several folds through developing novel technologies for high solid handling and enhanced enzymes efficiency. Engineering the fermenting microorganisms to produce some or all of the cellulase enzymes in

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situ provides a complementary route to further reduce the enzyme cost Next challenge is need for more robust biocatalysts which must be resistant to inhibitors formed during the pretreatment, be able to utilize C-5 and C-6 sugars at high yields, secrete cellulase enzymes, and remain active under conditions that are near optimal for cellulase function (pH 5, 50 °C). Here, emerging integrated technologies such as SSCF and CBP could be successfully applied since they can create new prospects for reducing operation steps as well as overall cost of process.

Although not economically competitive yet, major cost reduction has been made in biological route, and to date, it can probably provide cheaper biofuels than thermochemical route. However, there are less technical barriers inthermo chemical route since much of the technology is already proven. In addition, it has the advantages of whole biomass conversion (including lignin) into syngas and significantly less freshwater consumption. Finally, the economy of lingo cellulosic ethanol could be significantly improved by integrating multiple product lines using bio refinery concept. Therefore, new technologies for efficient fractionation of various cellulosic feed stocks, novel processing methods, and conversion path to high-value materials and end products must be developed.

Colocation with existing infrastructure and facilities, such as power plants, pulp and paper mills, and existing ethanol plants, where various synergies can be achieved, create higher operational flexibility and new opportunities for further industrial development . Overall, the choice of the best technology for lignocellulose conversion to bioethanol could made based on the overall cost, environmental impacts, and energy efficiencies.

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