ISSN: 2394-1391

Review Article

Indian Journal of Biology
Volume 6 Number 1, January - June 2019
DOI: http://dx.doi.org/10.21088/ijb.2394.1391.6119.6

Potential of Lignocellulosics in Biothanol Production to Mitigate Energy Crisis

Pratyush Ghosh[1], Sayantan Dutta[2], A.K. Panigrahi[3]

How to cite this article:
Pratyush Ghosh, Sayantan Dutta, A.K. Panigrahi. Potential of Lignocellulosics in Biothanol Production to Mitigate Energy Crisis. Indian J Biol. 2019;6(1):31-36.

Abstract

Ethanol is a simple alcoholic compound having high octane number. It is an oxygenated fuel. Bioethanol is ethanol that is derived exclusively from plant starch or cellulose as a byproduct of fermentation. The mixing of ethanol into petroleum base automobile fuels decreases the release of green-house gas emissions. Moreover ethanol is safer than common additive MTBE. Combustion of bioethanol results in cleaner emissions. The bioethanol from cellulosic feed stock is classified as second generation biofuel. Lignocellulosic biomass composed of different carbohydrate polymers (cellulose & hemicellulose), lignin, and small fraction of extractable acid, salt, minerals etc. It is the biodegradable portion of products, wastes, organic residues from agriculture and agroindustry, forestry and wood industry. Lignocellulosic biomass has been projected to be one of the main sources of economically alternative bioethanol production. Lignocellulosics can be obtained from corn stover, sugarcane bagasse, wheat straw, rice straw, oat hull, rice hull cotton stalk, parts of *Lantana camara*, water hyacinth etc. Bioethanol production based on lignocellulosic biomass requires multistep complex conversion technology. Milling, pretreatment, enzymatic hydrolysis, fermentation and distillation steps are involved. Genetically engineered strains of *Zymomonasmobilis*, *S. cerevisiae* are widely used. *P. stiptis* and *Candida shehataehaving* the ability of fermenting both hexose (glucose) and pentose (xylose) sugars to ethanol. Second generation bioethanol production fulfills the delusive gap of first generation bioethanol production from non-edible renewable feed stock. Production of bioethanol from lignocellulosics still requires considerable R &D before reaching the commercial production stage.

Keywords: Ethanol; Renewable energy; Bioethanol; Lignocellulosics; Fermentation.

Introduction

Commensurate with the Population growth and industrialization, energy consumption and requirements has increased steadily. To meet this energy demand crude oil is proven to be the major resources. World's dependency on fossil fuel has resulted in many unfavourable effects including diminishing crude oil reserve, deteriorating air quality, global warming, unpredictable weather changes etc. As a substitute of fossil fuel like gasoline ethanol, a renewable energy source

Author's Affiliation: [1]Assistant Professor, Department of Zoology, Chandernagore College, Chandannagar, Hooghly, West Bengal 712136, India. [2]Postgraduate Student, Department of Zoology, University of Burdwan, Golapbag, Burdwan, West Bengal 713104, India. [3]Ecotoxicology and Fisheries and Aquaculture Extension Laboratory & Head, Department of Zoology, University of Kalyani, Kalyani, West Bengal 741235, India.

Corresponding Author: Pratyush Ghosh, Assistant Professor, Department of Zoology, Chandernagore College, Chandannagar, Hooghly, West Bengal 712136, India.

E-mail: pratyushghosh60@gmail.com

Received on 22.05.2019, **Accepted on** 19.06.2019

is getting attraction these days. Ethanol, an oxygenated fuel having high octane (MON:90 and RON:109) value like that of petroleum based fuels. Ethanol is best known to run combustion engines at higher compression ratio thereby provides better performance (Wheals et al., 1999). Efficient mixing of ethanol into petroleum-based automobile fuels can concomitantly decrease petroleum usage and greenhouse gas emissions. Moreover, ethanol can be a safer alternative to the common additive, methyl tertiary butyl ether (MTBE), in gasoline. Toxic MTBE is awell-known contaminant in ground water (Wang et al., 1999). So, ethanol can be a safer substitute to alleviate the problems associated with the increasing energy demands across the world as well as a solution for an extent of 85% reduction in greenhouse gas emissions (Perlack et al., 2005).

Bioethanol, a form of quasi-renewable energy, can be produced from agricultural feedstocks. It can be made from very ordinary crops such as potato, sugarcane, cassava and corn etc. The usefulness of bioethanol in replacing gasoline is not beyond debate. Concerns about its production and use in relation to increased food prices as the large amount of cultivable land required for crops, especially from corn gain attention. Recent advancements with cellulosic ethanol production may soothe some of these concerns (Kinver and Mark, 2006). Cellulosic ethanol is a promising alternative as cellulose fibers, a ubiquitous component in plant cells walls, that can be used to produce ethanol (O.R. Inderwildi and D.A. King 2009). According to the International Energy Agency, cellulosic ethanol may play paramount role in the future (World energy outlook, 2015). Ethanol can be produced either from petroleum based products or from biomass. Most of the ethanol is producing from renewable resources this day. Although currently most of the ethanol produced from renewable resources mainly coming from sugarcane and starchy grains, meaningful efforts are being made to use lignocellulosic biomass as a source material for ethanol production (almost 50% of all biomass in the biosphere) such as agriculture residues (Bothast and Saha, 1997). Production of ethanol at very low cost from lignocellulosic biomass, are quite promising due to technological advancement in recent years.

Bioethanol production from starch enriched feed stocks such as potato, corn and sugarcane etc., are considered first generation process. It has already been developed. The long-term viability of this process is questionable as it will require significant amounts of arable land and consequently significant hike in food prices which will ultimately lead to food insecurity (Mitchell, 2008). First generation ethanol production process can not sufficiently meet the demand of global energy needs as estimates pointing out. As a result, second generation bioethanol production is gaining momentum. There are sufficient supplies of lignocellulosic materials. The production of bio-ethanol from lignocellulosic biomass [wheat straw,cornstover, sugarcane bagasse, rice hull, rice straw, oat hull and cotton stalk; crops such as Alfa Alfa and switch grass, various weeds such as *Saccharumspontaneum, Eichhorniacrassipes, Lantana camara* etc.] has become one of the best alternatives, because of their widespread abundance and relatively cheap cost of their procurement.

Lignocellulosic Biomass

Composition

High abundance, minimum cost and non-competitiveness with foodstuffs make Lignocellulosic biomass a promising resource for the production of bioethanol. Lignocellulosic biomass comprised of Cellulose, lignin and hemicellulose. Among them, Cellulose is the major component of lignocellulosic biomass, its concentration ranges from 40 to 50% of dry weight. Cellulose is a homopolysaccharide consisting of several hundred to more than ten thousand (β-1,4) linked D-glucose units. Cellulose binds tightly with lignin and hemicellulose. Efficient hydrolysis of cellulose needs lignin component separation to make cellulose more accessible to the enzymes (Selvi et al., 2009). The enzymatic hydrolysis of cellulose (cellulolysis and saccharification) is influenced by several factors, viz., degree of crystallinity, degree of polymerization, structural composition and availability of surface area etc. (Qi et al., 2009). For enhanced enzymatic saccharification of lignocellulosics efficient pretreatment is required. Monomeric sugars released after enzymatic saccharification can be converted into bioethanol. Hemicellulose concentration in lignocellulosic biomass is 25 to 35%. It is easily hydrolysable to produce fermentable sugars (Saha et al., 2007). Hemicellulose is a hetero polysaccharide comprising of pentoses (D-xylose and D-arabinose), hexoses (D-mannose, D-glucose and D-galactose) and sugar acids. Softwood hemicellulose mainly bears mannose as a major constituent whereas hardwoods mainly possessXylans (Balan et al., 2009). Lignin is the third major component of lignocellulosic biomass and its concentration ranges for 20 to 35%. It is a complex polymer of phenyl propane (p-coumaryl, coniferyl and sinapyl alcohol). Lignin a cementing agent acts as an impenetrable barrier for enzymatic attack according to Howard et al. (2003). It provides plants with the structural support and impermeability. It also confers resistance against oxidative stress and microbial attack. These properties of lignin may be associated with amorphous nature, optical inactivity and water insolubility of it. The later properties also make it tough to degrade (Fengel and Wegener, 1984).

Sources

Sources of lignocellulosic biomass can be categorized as primary sources that includes crops and secondary sources includes residuals of production process such as straws, rice husks, baggase and tertiary sources as organic fraction of municipal solid wastes. (Fischer and Schrattenholzer, 2001). Agro-industrial biomass residues are byproducts of agriculture including coconut shell, rice straw, cotton stalk etc. (Demirbas et al. 2009). Forestry residues include wood chips, bark and saw dust. (Werther et al. 2000). Woody raw materials have long latency period and flexible harvesting times. Woody raw materials possess more lignin than agricultural biomass and have less ash content (Zhu and Pan, 2010). Agricultural residues are getting more reliance than woody stocks as they are more environment friendly than later one (Kim and Dale, 2005).

Lignocellulosics to Bioethanol conversion

Lignocellulosic biomass can be converted into ethanol via two major approaches –Thermochemical and biochemical approaches (Demirbas, 2007). Thermochemical approaches includes gasification of biomass first at high temperature (at 800°C) which has given rise to production of syngases. Then syngases are converted to ethanol and water by using microorganisms like *Clostridimljungdahlii*. Subsequently ethanol are separated through distillation (Mu D et al., 2010). Biochemical conversion includes pretreatment step that can be mechanical, chemical or biological. This pretreatment step enhances surface area to optimize cellulose accessibility to cellulose. (Young and Wyman, 2008). Pretreatment stage is followed by acid or enzymatic hydrolysis often known as cellulolysis. It results in production of fermentable monomeric reducing sugar (Saccharification). Fermentation is the next step, involving conversion of reducing sugar to ethanol using yeast or bacterial fermentation. Produced ethanol are then purified via distillation (Mc Millan, 1994).

Use of genetic engineering in bioethanol production

Fermentative microorganisms have to be thermos tolerant. Biological treatment steps involving fungi which require high temperature and low pH such as basidiomycetes. As fungi act slowly, Enhancement in ethanol production requires production of potential lignocellulolytic fungi by mutagenesis, gene expression and co-culturing (Dashtban et al., 2009). Some genera of fungus (*Candida, Dekkera, Pichia* etc.) produce low ethanol and acetic acid which again acts as an inhibitor of fermentative yeast (Basilio et al., 2008). Some groups of bacteria can efficiently convert monomeric sugars to ethanol as *Zymomonasmobilis*. These bacteria are more vulnerable to inhibition than fermentative yeast (*S. cerevisiae)* (Chen, 2009). Simultaneous saccharification and fermentation (SSF) and simultaneous saccharification and combined fermentation (SSCombF) are cost effective as they reduce end product inhibition (Ho et al.,1998). The genetic modification of conventional *S. cerevisiae* strain is gaining attention as they are more optimally adapted to bioethanol production (Lilly et al., 2009). CBP combines hydrolysis and fermentation in a single reactor by utilizing genetically modified microoraganism that are capable of producing celluase enzyme (Lynd et al., 2005). *S. cerevisiae*, can also be genetically modified to express cellulolytic and hemicellulolytic heterologous enzymes. These type of modifications can be achieved through reassembling of all existing components of mimicellulosome on yeast's membrane surface from the thermophilic microoraganism C. *cellulolyticum* via a chimeric protein scaffold expression under PGK 1 regulation. The successful functionality of cellulosomein of *S. cerevisiae* and dockerin and cohesion of *C. cellulolyticim* proved that this genetic engineering based on minicellulosome model can be an attractive option for CBP process (Zyl et al., 2007).

Bio-ethanol production in world: an overview

Several countries throughout the world, have initiated new alternatives for gasoline from renewable feedstock (Goldemberg et al., 2007). In the North American hemisphere, bioethanol extraction has been done from starch based sources such as corn, while in the South American hemisphere, biofuel has been largely produced from sugars including sugarcane and sugarbeets (Wheals et al. 1999). While European countries are taking extensive efforts to increase their 5% worldwide bioethanol production (Gnansounou et al., 2010), biodiesel produced in Europe primarily in Germany and France are substantial. They account for approximately 56% of the global biodisel production (EU, 2009). Although, most of the remaining countries in the world collectively account for only 5% of the global bioethanol production, China, Thailand as well as India are continuing to invest significantly in agricultural biotechnology sector and trying to be emerging as potential biofuel producers (Swart et al., 2008). In the U.S., biofuel-derived from corn has emerged as one of the primary raw materials for bioethanol production (DOE biomass 2009). According to the renewable fuels association statistics, the production of bioethanol was historically unparalleled in the U.S. by year 2009 capacity reaching 41.26 billion litres and representing 55% of the worldwide production. In the year 2010 corn-based ethanol operating productions generated a total of 12. 82 billion gallons (48.52 billion litres) with the largest nameplate capacity (28%) followed by Nebraska (13%) (Nebraska 2009). The world population is estimated to increases from 6.7 billion to 8 billion by 2030 (USCB, 2008). On the other side, global crude oil production is anticipated to decline from 25 billion barrels to 5 billion barrels by 2050 according to Campbell and Laherree (1998). Thus the energy demands of future are likely to play a key role in geo-political economics. Given this reality, nations throughout the world are now investing in alternative sources of energy, including bioethanol. The pioneer countries in bioethanol production are Brazil and the USA (as shown in Table 1). USA is the world's largest producer of bioethanol (Carere et al., 2008). Asian countries are altogether accounting for about 14% of world's bioethanol production.

Table 1: Leading bioethanol producers in the world

Country/group of countries	Ethanol produced in: Million liters	Ethanol produced in: MTOE
1. Brazil	19000	10.44
2. Canada	1000	0.55
3. China	1840	1.01
4. India	400	0.22
5. USA	26500	14.55
6. European Union	2253	1.24
7. Others	1017	0.56
8. World (Total)	52000	28.57

*Source: Data from OECD-FAOA glink-Casimo database (2007).
MTOE: Million tons of oil equivalents

Bio-ethanol as a renewable energy source

Renewable energy is energy that is obtained from renewable resources, are naturally replenished on a human timescale, such as sunlight, wind, rain, tides, waves, and geothermal heat (Ellaban et al., 2014). Renewable energy often provides energy in four important areas: electricity generation, air and water heating/cooling, transportation, and rural (off-grid) energy services (REN 21, 2010). Based on REN21's 2016 report, renewables contributed 19.2% to humans' global energy consumption and 23.7% to their generation of electricity in 2014 and 2015, respectively. This energy consumption is splitted as 8.9% coming from traditional biomass, 4.2% as heat energy, 2.2% is electricity from wind, solar, geothermal, and biomass 3.9% from hydro- electricity.

MTBE (Methyl tert-butyl ether) is an oxygenates (Fischer et al., 2005) and is a fuel additive that can raise the octane number. This water soluble chemical is a possible human carcinogenic (Belpoggi et al., 1995). To increase the octane number of the fuel, it should be substituted for other oxygenated substances. Presently, ethanol as an oxygenous biomass fuel is regarded as a most suitable substitute to MTBE for its biodegradable, low toxicity, persistence and regenerative feature(Cassada et al., 2000).

The United States gasoline supply is an ethanol blend and the importance of ethanol use is expected to increasety related health issues. Ethanol may be produced from many high energy crops such as sweet sorghum, corn, wheat, barely, sugar cane, sugar beet, cassava, sweet potato and etc. (Drapcho et al., 2008).

Conclusion

Focus on Lignocellulosic biomass as one of the main resources for economically attractive bioethanol production getting attention today. Agricultural wastes are renewable, less costly and abundantly available in nature. Agricultural wastes do not demand separate land, water, and energy requirements. They have no food value as well. For economically feasible bioethanol production, several hindrances are to be overcome.These refer to the four major aspects which are feedstock, conversion technology, hydrolysis process, and fermentation configuration. With regard to feedstock major obstacles are cost, supply, harvesting and handling. Conversion technology faces problems associated with biomass processing, proper and cost effective pretreatment technology to liberate cellulose and hemicellulose from their complex with lignin. To achieve an efficient process for depolymerization of cellulose and hemicellulose to produce fermentable monomers with high concentration is the main challenge for hydrolysis process. In this case enzymatic hydrolysis may be the most potent alternative process for saccharification of complex polymer. To optimize the enzymatic hydrolysis process, several efforts have been made to reduce the cost of cellulase enzyme. Lastly in case of fermentation, the challenges involve xylose and glucose co-fermentation, and the use of recombinant microbial strains. In conclusion it may be said that to solve the technology bottle necks of the conversion process, novel science and efficient technology are to be applied, so that production of bioethanol from agricultural wastes may be effectively developed and optimized in the near future.

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