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A Current Scenario and Novel Approaches to Degrade the Lignocellulosic Biomass for the Production of Biodiesel

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Abstract

Biofuels derived from lignocellulose biomass are alternative options replacing fossil fuels in near future. Lignocellulose biomass consists of lignin, cellulose and hemicelluloses. These three elements form a complex network in lignocellulose biomass which is difficult to break by following traditional methods because of lignin. Pretreatment technologies makes possible to degrade the main barrier ie lignin.The possible pretreatment approaches are: organic solvent-water mixture, natural dyes, nanocatalyst, Ionic Liquids (ILs) treatments and combinational culture of bacterial strains i.e. Bacillus and Geobacillus species efficently produces biofuel via transesterification. Currently, the production of biofuels across the world has increased especially in U.S, India and other European countries. On account of following reasons: ecofriendly residues, less expensive and natural lubricant makes biofuels are better fuel for future generation. Furthermore, some important key policy actions have been discussed in article.

Keywords: Lignin; Combinational culture; Lignocellulose biomass degradation; Pretreatment approaches

Introduction

In recent years, the exploitation of renewable and sustainable energy sources is taking center place in the fields of science, research, media and politics [1]. Many renewable energy sources are available: atomic energy, wind and water but for future these are not better option for us due to non availability.

Energy demand is increasing day by day across the world mainly useful for transportation purposes has been attracted the attention of many countries therefore, the better fuel options for future i.e. "biofuels" instead of choosing the fossil fuels. In this respect, other two major key factors are: rising fuel prices and global warming.

What is biofuel?

Biofuels include fuel derived from biomass conversion and obtained from edible feed and other non edible feed stocks. Biofuels are classified into solid, liquid and gasesous fuels [2] on the basis of application and the type of biomass used. Solid fuel includes: wood, charcoal, liquid fuel: bioethanol, biodiesel and gaseous fuel: biohydrogen and methane.

Biofuel constitute the major source of energy for over half of the world's population, accounting for more than 90% of the energy consumption in poorly developing countries [3]. The biofuels currently offered in the market are essentially "first-generation technology" but their growth is limited by the less availability of agricultural resources and inhibited by the sustainability criteria imposed by current and future legislation (GHG emissions in the main). Nevertheless, biofuel market should continue to grow at least until 2015-2020, whilst we await the emergence of second-generation biofuels that use "non-food" resources [4].

The use of lignocellulose biomass should relieve the pressure on edible feed stocks usage and deliver more effective environmental benefits resulting in a more sustainable sectors ie biofuels production.

Several countries are looking for the most promising category of biofuels ie biodiesel

Importance of fuel: biodiesel

A. Biodiesel has been gaining its popularity in recent years and people became more environmentally aware. Because diesel is made from natural resources like animal fat and plant residue and improves environmental health.

B. Usuage of renewable energy sources for biofuel production which enhance the living standards of rural peoples. Biodiesel is used as a natural lubricant and increases engine life.

C. Large government subsidies and research dedicated to biofuel: biodiesel. Reducing the dependency on fossilized fuel by bioenergy "biodiesel". This directly links with economics of country.

Global market scenario of biodiesel: The cost of fossil fuels was raising to US$ 100 a barrel during the year 2007/2008 therefore, the search for future fuel has become an urgent issue of every country.

The global market is poised explosive growth especially in the sector of biodiesel production in near future. According to the reported data, in terms of consumption and production around 85% of global biofuel is contributed only by European countries viz. Germany, France, Italy and Argentina and rest of the world contribute only 8% and USA 7%. Other countries like U.S. is now ramping up its production rate at a much faster rate than Europe and Brazil and is expected to surpass European biodiesel production by the year 2015 [5]. Biodiesel replaces 20% of all on-road diesel by the year 2020 with the pursuit of second generation fuels. Indian government has made 'National Biofuel Policy' on 12 September 2009, [6] its aim is to meet 20% of India's diesel demand with fuel derived from plant derived biomass. It has advantage to replace the 20% of fossilized fuel in near future [7,8]. Therefore,

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government is aggressively pursuing steps for the production of second generation fuels and continously promoting research and development and investment on alternative non-food feedstocks such as grease tallow, jatropha, castor, algae and other renewable diesel resources.

What is lignocellulosic biomass?

Refers to plant biomass waste which consists of cellulose, hemicelluloses and lignin [9]. Lignocelluloses waste may be grouped into different categories such as wood residues, grasses, food industry residues, municipal solid wastes [10-12], agricultural residues (straw, stover, peelings, cobs, stalks, nutshells, seeds, bagasse) and domestic wastes (lignocelluloses garbage and sewage). These residual biomass oftenly used for energy production mainly deriving from non energy crops i.e. (Jatropa, Sunflower, Popular, Switch grass and Eucalyptus sp.) instead of using energy crops on account of following reason: the energy crops competes land and water with food crops, lignocellulose biomass abundance and renewability.

It promotes a great deal of interest of utilizing lignocellulose biomass from non energy feed stocks for biofuels production and recovery of many value-added products [13-15]. But it is quite difficult to produce biofuels from lignocellulose biomass due to the presence of hemicellulose which forms a complex cell wall network by cross-linking cellulose microfibrils with lignin [16] linked via carbon-carbon bond or ether bonds. This strong bonding forms a complex network in cell wall which inhibits the preharvesting processing and further processing of biomass.

Fundamental chemistry of plant cell wall constituents

Lignin {$C_{10}H_{11}O_{3.5}$}: Lignin is a phenolic crosslinked polymers which provide structural integrity to the cell wall as well as sealing of water-conducting systems and protect plants against degradation [17]. Lignin is a phenolic-polymer build up by oxidative coupling of three major phenyl propanoid units composed of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units that are present in different ratio [18]. The biosynthesis of lignin begins with the synthesis of cinnamic acid from the amino acid phenylalanine by Phenylalanine Ammonia Lyase (PAL) present in the cytosol [19] and forms a complex network of hemicelluloses-lignin but this complex network should be broken down by following advanced technologies for efficient biofuel production. lignin contribute of upto 15–35% of the dry weight of wood [20].

Cellulose {$CH_{1.67}O_{0.83}$}: Cellulose is pure organic polymer, consisting solely of units of anhydroglucose held together by β-(1,4)-glycosidic linkage and forms a giant straight-chain molecule [21]. Cellubiose as a repeating units for cellulose chains due to the presence of glycosidic linkage. It contribute around 50% of the dry weight of wood [20].

Hemicellulose {$CH_{1.64}O_{0.78}$}: Hemicelluloses or polyoses are present in wood and other plants [22]. Actually, nature of hemicelluloses is amorphous polysaccharides, such as xylans, galactoglucomannans, arabinogalactans, glucans and galactans [23]. Hemicelluloses, unlike cellulose, not only contain glucose units, but they are also composed of a number of different pentose and hexose monosaccharides. Hemicelluloses are derived mainly from chains of pentose sugars and act as the cement material holding together the cellulose micelles and fiber [24]. It contribute around 20–35% of the dry weight of wood [20].

Biomass (Feedstock)

The term biomass refers to nonfossilized and biodegradable organic material derived from plant, animal and microorganism [2]. In other words, biomass refers to wood, short rotation wood, agricultural waste, industrial waste.

Biomass includes waste from agriculture, forestry as well as the non-fossilized and biodegradable organic fractions of industrial and municipal solid wastes and gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic material. Biomass types only differs in terms of dry wt% i.e. (wt% of hemicelluloses, cellulose, lignin) and other extractive present in all woody biomass.

Bio-based materials require pretreatment by chemical, physical and biological means which is helpful to open up the complex branced network of lignin, hemicellulose and cellulose. Some basic pretreatment technologies are discussed here.

Selective Biofuel Pretreatment Technologies are as Follows

Usage of organic solvent and water

Organic solvent is used to digest the lignocellulosic biomass into three main constituents: Lignin, Hemicellulose and Cellulose. In this process, lignocellulosic biomass comes in contact with an organic solvent-water mixture in different wt% ratio of organic solvent and water (50-60 wt% of organic solvent and 50-40 wt% of water) at elevated temperature (temperature range approx. 100°C-200°C) and pressure (Pressure up to 1 atm–5 atm) for approx. 1 h. Hence, lignin is extracted out and pentose sugar hemicelluose and cellulose is hydrolysed, remaining solid residue is more easily accessible for enzymatic hydrolysis in the subsequent process step [25] for biofuel production. Other organic solvents are used for lignin decomposition: mixture of ethanol-water, dioxane-water, acetone-water and ether-water.

Combinational culture approach

It involves the inoculums preparation of lignin and hemicelluloses or cellulose and hemicelluloses or lignin and cellulose in a different combination ratio. Prepared inoculums is provided as substratte to the bacterial strains namely Bacillus species and Geobacillus species. Bacillus sp. i.e *B.cellulolystic* uses cellulose as substrate and Geobacillus sp. degrade the lignin. If both the bacterial species produces same metabolites i.e fatty acid after the consumption of sugar as substrate.

Fatty acid react with alcohol (ethanol or propanol) in the presence of waste cooking oil or catalyst e.g.: sodium oxide or potassium oxide. This process is known as transesterification reaction. Transesterification reaction produces a valuable bioproduct "biodiesel" and co-product "glycerol". The co-product glycerol is removed by following evaporation or froth floation technique or adding iron or magnesium oxide in the medium.

One of the big advantage of above stated approaches is that the main constituents of plant cell wall is fractioned fully i.e. lignin.

Natural dyes treatment

Dyes obtained from natural resources has the ability to digest lignocellulose biomass of up to 40–60%. After the treatment of biomass with natural dye breaks the main barrier of lignocellulose biomass ie lignin and release the sugar after further enzymatic hydrolysis.

Dyes obtained from family Lythraceae and Asteraceae. Scientific name: *Lawsonia inermis* (Heena) and Scientific name: *Eclipta alba* (Bhringraj or Bhengra). Sources of producing Black henna" powder is leafs which contain *p*-phenylenediamine (PPD). Due to presence of aromatic properties, dyes are capable to digest the lignocelluloses

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biomass. Heena Figure 1 [26] and Figure 2 Perenial Herb Bhringraj or Bhengra [27].

Ionic liquid technology

Ionic liquids (ILs) are group of organic salts i.e large organic cations and small inorganic anions exist as liquids at relatively low temperature (<100°C) to digest the lignocelulosic biomass for biofuel production. Recently, interest in ILs is due to following reasons: high thermo-stability, unique solvent properties, non-flammibility and non-detectable vapour pressure, increases the acessibilty of sugar components as well as effective fractionation of lignincellulosic biomass and comprehensive utilization of its sub components which can reduce the investment cost by shortening of protocol for the production of biodiesel.

This pretreatment technology effectively increase the saccharifaction rate and fermentable sugar yield [28]. For example: 1-H-3-methylimidazolium chloride an acidic ILs can effectively pretreat the wood chips of yellow pine under mild conditions for enzymatic saccharification at temperatures between 110–150°C for up to 5 h in the ionic liquid. After pretreatment with ionic liquid three fractions are collected; a cellulose rich fraction, lignin and an aqueous fraction. This treatment almost degrade the pentose sugar hemicelluloses and lignin as well as dissolve cell wall of the pine wood. This process occurrs more quickly at higher temperatures, significantly effectual for the degradation of cellulose fraction. The cellulose rich fraction was saccharified using cellulase isolated from fungus *Trichoderma viride*, after a longer pretreatment times at high temperature, resulting in higher glucose yields [29].

Figure 1: Bringraj or Bhengra (Perennial herb) depicts the Bringraj is a small herb which produces dyes (source of producing dye is leaf) which has aromatic properties, digest the lignocelluloses biomass into a more accessible form and further undergo processing to enzymatic hydrolysis.

Figure 2: Heena (Perennial shrub) This figure shows the picture of shrub (Heena) which produces dyes (source of producing dye is leaf), dyes digest the lignocellulose biomass of agricultural residues into more accessible form. Around 40-60% of lignocelluloses biomass is digested.

Microwave heating with catalyst technology

Maleic acid act as a catalyst in biomass conversion to deconstruct the hemicelluloses-lignin seal to pentose sugar at mild temperature approx. 100°C–200°C and depends on the temperature and no. of times of repated cycle of treatment. This is a two step process to first hydrolyze the hemicelluloses to furfural and then subsequently dehydrate xylose to furfural and this can be achieved at different equimolar concentration or higher concentration of maleic acid as compared to the intial xylose concentration [30].

Biomass conversion to biopower via nanocatalyst

A new type of technology has been developed known as nanocatalyst to improve the product quality and achieving optimal operating conditions. Nanocatalyst having high catalyltic activity and high surface to volume ratio makes it highly efficient overcome some limitations on heterogeneous catalysts for their application in biodiesel production from biomass [31].

Current Scenario of Biofuel Market-production Form (EIA-22M Monthly Biodiesel Production Survey in U.S.) [32]

The biodiesel production in U.S. was increased at a much faster rate in recent years. According to forum EIA, on March 2013 approx. 98 millon gallons production of biodiesel was achieved and expected to increase to 106 million gallons upto April 2013. This huge production of biodiesel came from 114 biodiesel plants with operable capacity of 2.2 billion gallons per year [33] which is located at the Midwest region (Petroleum Administration for Defense District 2) of U.S. it contributes approx. 66% of the world biodiesel production.

Sales

Sale of biodiesel is up to 79 million gallons which is sold as B100 (100% biodiesel) and additional 31 million gallons of biodiesel B100 sold as biodiesel blends [34].

Feedstocks

Soybean oil was the largest feed stock used for the biodiesel production and approx. 423 million pounds of soyabean oil. The next three largest biodiesel feedstocks are yellow grease (79 million pounds), corn oil (71 million pounds) and tallow (56 million pounds) [35].

According to biodiesel association of India, biodiesel is made from renewable resources such as Jatropha. Its constant consumption decreases our dependence on foreign oil and contributes to economy [36]. At present, India is focusing on the production rate and around

2 million tonnes of biodiesel from wild plant Jatropha oilseeds is produced to meet the demand of energy [37] by the year 2012.

Reduction of oil dependence cost

Today, about half of the oil we use is imported and our dependence will increase as we use domestic resources. Now, every one is fully dependent on oil derived from fossil or non renewable energy sources. Most of the world's oil reserves are concentrated in the Middle East, about two-thirds of them are controlled by Organization of the Petroleum Exporting Countries (OPEC) members.

High oil prices and price manipulation by OPEC effects an economy of developing countries like India. Approx. $1.9 trillion economic loss was occurred in 2004 to 2008 due to oil price shock followed by a collapse of market [38]. The problem of reducing the oil prices by finding an alternative fuel i.e biodiesel. This could reduce our petroleum usage of up to 25 billion gallons by the year 2030 and develop the new advanced vechicle technologies.

Current scenario of biofuel production in India [39]

Currently, India's position in global biofuel map is not very prominent and countributes only 1% of the global production. It will be estimated about 380 million litres of ethanol and 45 million litres of biodiesel [40] production in recent years. It is worth noticing that India is the second largest producer of sugarcane in the world but accounts for only about 1% of global ethanol production. Therefore, indian government is serious about this issue and now making a policy for the growth and improvement in this sector. The Government of India has approved the "National policy of biofuels" (Ministry of New and Renewable Energy) on December 24, 2009. Since then, considerable advancements have taken place in the direction of cultivation, production and use of biofuels. Under this policy, developments of bioenergy sector and following it have strengthened India's energy security by encouraging the use of renewable energy resources to supplement transport fuels and to stimulate rural development as well as create employment opportunities. It has addressed the global concern about containment of carbon emission through use of environmentally friendly biofuels.

Key policy of action [41] taken by Government of India in respect to biofuel production

Stability: Fuel should be stable which creates a long-term policy framework for bioenergy production.

Advancement and deployment: Providing continual funding programs for advanced biofuels research and development department and provide commercial deployment to the rural peoples which support research efforts on land availability mapping and biomass potential analysis.

Sustainability: Use of waste and agriculture crop residues or non energy crops to enhance its economic value which links our economic incentives which enhance the performance of biofuels and implement sound internationally aligned sustainability of biofuels.

International collobration: Promote the alignment of biofuels and other residue properties and engage in international collobration on capacity of building and technological transfer for biofuels.

Future Trends: Biodiesel

In near future, biofuels such as lignocellulosic biofuels, algal biofuels, electrofuels have bright future for next generations.

Today's scenario of the world's biofuel market has been growing at an accelerated pace in the last twenty years. This trend is expected to continue in the future due to increasing number of countries participation due to environmental, security reasons and hicke in price structure of fossilized fuels. Biofuels have the potential to meet more than a quarter of world demand as transportation fuels by 2050 [42] and become a major alternative fuel. Therefore, social awareness is needed to production and usage of biofuels as option of fossilized fuel like petroleum based fuel especially in developing countries like India in near future.

Therefore, Indian government is taking a following steps to encourage biofuel sector

A. The Indian government should take steps to set up nurseries for planting materials and seeds and regulating mechanism of cultivation.

B. Following better technology for efficient and cost effective production of biofuels.

C. The research should be continous with respect to factors such as ecofriendly and economical feed stocks.

D. Creating employment for local people and their participation in plantation and enhancement of women participation.

E. Doubts in land rights is also considered as an issue in development of wastelands for biofuel production and the government should follow the some of the measures from the success of biofuel in countries like Brazil.

Executive summary

- A new renewable energy technology "biofuel" emerges from the bioconversion of lignocelluloses biomass.
- A pretreatment technologies ie Ionic liquid treatment, organic solvent and water, microwave heating with catalyst technology, natural dyes treatment, nano catalyst and combinational culture of bacterial strains are utilized for the Lignocellulose biomass conversion into a more potential source of energy ie biofuels.
- Current scenario of biofuels market across the world and its importances which encourages the biofuel sector.

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