International Journal of Research in Biosciences Vol. 4 Issue 4, pp. (1-15), October 2015 Available online at http://www.ijrbs.in ISSN 2319-2844

Review Paper

## Bioethanol Production: Future Prospects from Non-traditional Sources in India

Tiwari Garima, Shivangi, <sup>\*</sup>Sharma Satyawati and Prasad Rajendra Centre for Rural Development and Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, INDIA

(Received January 17, 2015, Accepted August 9, 2015)

## Abstract

Production of fuels, especially bio-ethanol from lignocellulosic biomass, holds remarkable potential to meet the current energy demand as well as to mitigate greenhouse gas emissions for a sustainable clean environment. Present technologies to produce bioethanol largely depend on sugarcane and/or starch based food materials. The use of sugarcane and food grains to produce bio-ethanol has caused significant stress on food prices and food security. In this regard the non-edible biomass resources such as fruit waste, agriculture residues, oil cakes, Bamboo etc have been considered suitable for ethanol production. The process of ethanol production generally involves hydrolysis of lignocellulosic biomass to fermentable sugars followed by fermentation of such sugars to ethanol. To achieve fermentable levels of sugars from lignocellulosic biomass require relatively harsh pretreatment processes. The pretreatment process has pervasive impact on the overall operation because the process depends on the choice of lignocellulosic source, the size reduction via grinding, chemical treatment, acid hydrolysis, neutralization and fermentation. The present paper deals with the bioethanol production from different substrates. It reviews information about current practices and also suggests future prospects in India.

Keywords: Bioethanol, Lignocellulosic biomass, Non-traditional, Pretreatment.

## Introduction

Now a day's the world's present economy is highly dependent on various fossil energy sources such as oil, coal, gasoline, natural gas, etc. These are being used for the production of fuel, electricity and other goods. Due to excessive use of fossil fuels, mainly in urban areas, has resulted in depletion of their resources. The level of greenhouse gasses in the earth's atmosphere has drastically increased. In the present demand for renewable, sustainable sources of energy to overcome the burden on world energy crisis, bioethanol have presented exciting options. Bio-ethanol is one of the important alternatives being considered due to the easy adaptability of this fuel to existing engines, less greenhouse gas emissions and because this is a cleaner fuel with higher octane rating than gasoline <sup>[1,2]</sup>. Presently ethanol are blended with conventional gasoline in any proportion. Common blends include E10 (10% ethanol and 90% petroleum product) and E85 (85% ethanol and 15% conventional petroleum product).

Developing country, India has a positive outlook towards sustainable and renewable energy technologies and to supplement its energy requirements it is committed to the use of renewable sources. The country has a separate ministry for renewable energy which mainly focus on the development of biofuels along with other renewable energy sources. In the year 2003, the Planning Commission of the government of India brought out an extensive report on the development of biofuels <sup>[3]</sup> and bio-ethanol and biodiesel were identified as the principal biofuels to be developed for the nation. Elaborate policies were formulated for promoting both bio-ethanol and biodiesel and the time scheduled for enacting the development of biofuels and implementation of policies were defined.

Bioethanol is a produced from renewable sources of feed stock, such as wheat, sugar beet, corn, maize and sugarcane. Currently for bioethanol production, industries mainly uses sugarcane (Southern hemisphere) or cereal grain (Nothern Hemisphere) as feedstocks, but they have direct competition with food sector <sup>[1]</sup>. Although these are dominating feedstocks that are mostly used in today's market, but they are very expensive and affecting the overall cost of production. This indicates that new alternative, low-priced feedstocks are needed to reduce ethanol production costs <sup>[4]</sup>. The lignocellulosic biomass is a largest potential feedstock for ethanol production, which includes materials such as agricultural residues such as crop straws, rice straw, wheat straw, non-edible oil cakes, fruit waste, grasses, bamboo etc.<sup>[5]</sup>. These feedstocks could be an attractive alternative for bioethanol production and hence disposal of these residues <sup>[6]</sup>. Most important, thing is lignocellulosic biomass do not interfere with food security.

## Current status of fuel ethanol in India and its utilization

India is now a days showing interest towards use of ethanol as an automotive fuel. A tremendous contribution has been made by distilleries in India.They are using this surplus alcohol as a blending agent or an oxygenate in gasoline. The 5% ethanol-doped-petrol in vehicles now has been confirmed by Society for Indian Automobile Manufacturers (SIAM) . State Governments of major sugar producing States and the representatives of sugar/distillery industries also confirmed availability / capacity to produce ethanol. Government have set up an Expert Group headed by the Executive Director of the Centre for High Technology for examining various options of blending ethanol with petrol including use of ETBE in refineries and after considering the logistical and financial advantages, this Group has recommended blending of ethanol with petrol at supply locations (terminals / depots) of oil companies. In view of the above, Government have now with effect from 1-1-2003, started supplying 5% ethanol blended petrol in the following nine States and Four contiguous Union Territories: States & Union Territories 1. Andhra Pradesh 1. Damman and Diu 2. Goa 2. Dadra and Nagar Haveli 3. Gujrat 3. Chandigarh 4. Haryana 4. Pondicherry 5. Karnataka 6. Punjab 7. Maharashtra 8. Tamilnadu 9. Uttar Pradesh.

In the 2006 ethanol demand was 0.64 billion liters at 5% gasoline doping levels while the approximately about 1.5 billion liters will be required for 10% blending of entire gasoline sold in India .(Table 1). This demand will be projected to 2.2 billion liters in 2017. Indian alcohol industry is fairly mature with 295 distilleries established all across the country with an annual capacity of 3.2 billion liters. Major part of this produced alcohol is mainly used by the liquor industry and rest part going into chemical industry. According to a 2006 estimate, the total annual demand for alcohol in the country excluding fuel applications was about 1.3 billion litres which is about 40% of the installed capacity [7]. However, during the same year, the actual production of ethanol was only 1.69 billion litres which means the surplus availability was only 0.39 billion litres which was not sufficient to meet the fuel ethanol demand if the entire gasoline in the country had to be doped at 5% level.

Year	Motor gasoline demand/consumption (MMT)	Motor gasoline demand (billion litres)	Ethanol demand @ 5% blending (billion litres)	Ethanol demand @ 10% blending (billion litres)
2006	9.46	12.80	0.64	1.28
2007	10.47	14.17	0.71	1.42
2008	11.31	15.30	0.77	1.53
2017	16.41	22.21	1.11	2.22

Source: IEA's Energy Statistics of Non-OECD Countries [8]

#### Uses of Bioethanol

Bioethanol has mostly been used as a bio fuel for transport, as it is blended with petrol at 5% and in some countries at 10% level .Brazil was the first country where bioethanol fuelled car emerged on a large-scale. It is used as a oxygenating additive and has a high octane rating, which improves engine performance. Ethanol is also being used to formulate a blend with diesel fuel, known as "E-Diesel", and as a replacement for leaded aviation gasoline in small aircraft. Commonly it is used as a active constituent of fermented beverages, but it is also widely used as a solvent in chemical industries

because it can dissolve many organic compounds which are insoluble in water. It is used, for example, in cosmetics, many perfumes, colognes, mouthwash, aftershave lotions, soaps, shampoo, etc. A number of other chemicals such as ethyl esters, ethyl acetate, extractants, antifreeze and intermediates in the synthesis of various organic chemicals are formed by ethanol. If we talk about human consumption ethyl alcohol is always produced by fermentation of some suitable material to form beer, wine, or distilled spirits of various kinds <sup>[9]</sup>. It is also used by laboratories as disinfectants as it is able to kill bacteria (excluding spores), moulds and yeasts. Its versatility as a disinfectant varies from uses for skin hygiene, to applications in hospitals, dental practices and in the food and animal feed industry. Apart from these they are also used for the production of pills, extracts, tinctures and as a several other pharmaceutical applications <sup>[10]</sup>.



Figure 1: Various application of Bioethanol <sup>[9,10]</sup>

## Major sources of bioethanol

Edible feedstocks such as corn-starch and sugarcane molasses are commercially used for bioethanol production. The use of fuel ethanol has been quite successful in Brazil, where it is being produced at a very low cost by fermentation of sugarcane. In the United state, corn is the dominant biomass feedstock for production of ethanol, and in the European countries, straw and other agricultural wastes are the preferred biomass <sup>[12]</sup>.

Currently in India ethanol is produced from sugarcane molasses and corn starch (Table No.2). Molasses is a co-product in sugarcane production. The yield of molasses from crushed sugarcane ranges from 4 to 4.5% (Indian Sugar Mills Association). Alcohol is originally manufactured with a water content of 5-7% so it must first be dehydrated to create anhydrous ethanol, which is 99.5% ethanol <sup>[13]</sup>.Based on a statistics by All India Distillers Association for a one year period covering 65 distilleries in different parts of the nation, the average efficiency in production of molasses based ethanol is 85% and the amount of fermentable sugars in molasses is about 42% with a yield of 222 L of ethanol per ton of molasses <sup>[7]</sup>. According to the task force of 10th Five Year Plan in 2006-07 the production of ethanol was 2300.4 million liters while the industrial ,potable and other uses were 631.4,765.2 and 81.0 million liters respectively and the surplus availability was 822.8 which could barely supplement the demand of ethanol (1.28 billion litre at 10% blending level) <sup>[14]</sup>. The availability of surplus ethanol for fuel purpose from molasses is thus very limited and the fact remains that India's cane production can barely supplement the current demand of ethanol even at 5% blending. This indicates that, there is a considerable amount of interest should be focus on other non-traditional biomass for the production of bioethanol.

According to the biofuels annual data published by the United States Department of Agriculture (USDA), India has the potential of 2,171 million litre bioethnol production <sup>[16]</sup>, while Brazil is the largest producer of bioethanol with a potential of 6641 million litre <sup>[15]</sup>.

#### **Process of Bioethanol production**

Biochemical conversion of lignocellulosic materials through saccharification and fermentation is a major pathway for bioethanol production from biomass. Bioconversion of lignocellosics to bioethanol is difficult due to: (1) the resistant nature of biomass to breakdown, (2) the variety of sugars which are released when the hemicellulose and cellulose polymers are broken and the need to find or genetically engineer organisms to efficiently ferment these sugars, (3) costs for collection and storage of low density lignocellosic materials. Generic block diagram of bioethanol production from lignocellulose materials is given in Figure 2<sup>[17]</sup>. The basic process steps in producing bioethanol from lignocellulosic materials are: pretreatment, hydrolysis, fermentation and product separation/distillation.





## Pretreatment of biomass

The recalcitrance of lignocellulose is one of the major barriers to the economical production of bioethanol. Pretreatment remove the complexity of the substrate, breaks the bond between lignin, cellulose and hemicellulose and accessible them to hydrolytic enzymes for conversion to glucose <sup>[18]</sup>. The role of pretreatment on lignocellulosic material is depicted in Figure 3 <sup>[19]</sup>. If the pretreatment is not done properly enough the resultant residue is not easily break by cellulose enzyme and also if more severe, it causes production of toxic compounds such as furfural, hydroxyl furfural etc. which can create problem for the normal growth of fermenting microbes <sup>[20]</sup>. Pretreatment has been viewed as one of the most expensive processing steps within the conversion of biomass to fermentable sugar <sup>[21]</sup>. If extensive research will be done by research and development approaches then there is huge scope in lowering the cost of pretreatment process.

Pretreatment methods can be broadly classified into four groups:

- 1. Physical Employ the mechanical combination such as by a combination of chipping, grinding, and milling to reduce cellulose crystallinity or irradiation processes to change only the physical characteristics of biomass.
- 2. Chemical- The chemical processes employs acids (H<sub>2</sub>SO<sub>4</sub>, HCl, organic acids etc) or alkalis (NaOH, Na<sub>2</sub>CO<sub>3</sub>, Ca (OH)<sub>2</sub>, NH<sub>3</sub> etc) or ozone gas. The acid treatment typically shows the selectivity towards hydrolyzing the hemicelluloses components, whereas alkalis have better selectivity for the lignin and various uronic acid substitutions on hemicellulose that lower the accessibility of enzyme to the hemicellulose and cellulose <sup>[22,23]</sup>.

3. Biological- Microorganisms such as brown-, white- and soft-rot fungi are used in this treatment to degrade lignin and solubilize hemicellulose. White-rot fungi are the most effective biological pretreatment of lignocellulosic materials<sup>[24-26]</sup>.

Pretreatment process	Advantages	Limitations and disadvantages
Mechanical comminution Steam explosion	Reduces cellulose crystallinity Causes hemicellulose degradation and lignin transformation, cost- effective Destruction of a portion of the xylan fraction,incomplete disruption of the lignin-carbohydrate matrix, generation of compounds inhibitory to	Power consumption usually higher than inherent biomass energy Destruction of a portion of the xylan fraction,incomplete disruption of the lignin- carbohydrate matrix,generation of compounds inhibitory to microorganisms
AFEX (Ammonia fiber explosion)	Increases accessible surface area,removes lignin and hemicellulose to an extent,does not produce inhibitors for down-stream processes	Not efficient for biomass with high lignin content
CO <sub>2</sub> explosion	Increases accessible surface area, cost-effective, does not cause formation of inhibitory compounds	Does not modify lignin or hemicelluloses
Ozonolysis Acid hydrolysis	Reduces lignin content, does not produce toxic residues Hydrolyzes hemicellulose to xylose and other sugars, alters lignin structure	Large amount of ozone required, expensive High cost, equipment corrosion, formation of toxic substances
Alkaline hydrolysis	Removes hemicelluloses and lignin, increases accessible surface area	Long residence times required, irrecoverable salts formed and incorporated into biomass
Organosolv	Hydrolyzes lignin and hemicelluloses	Solvents need to be drained from the reactor,evaporated, condensed, and recycled, high cost
Pyrolysis Pulsed electrical field Ambient conditions, disrupts plant cells, Process needs more research	Produces gas and liquid products Pulsed electrical field Ambient conditions, disrupts plant cells, Process needs more research	High temperature, ash production Pulsed electrical field Ambient conditions, disrupts plant cells, Process needs more research
Biological	Simple equipment degrades lignin and hemicelluloses, low energy requirements	Rate of hydrolysis is very low

## Table 4: Various methods used for pretreatment

Source: [15,25]

## Hydrolysis

Hydrolysis is a process in which the carbohydrate polymers in lignocellulosic materials are converted to simple sugars before fermentation <sup>[24]</sup>. There are various methods for the hydrolysis of lignocellulosic materials have recently been described. The most commonly applied methods can be classified in two groups: chemical hydrolysis (dilute and concentrated acid hydrolysis) and enzymatic hydrolysis. There are some other hydrolysis methods in which no chemicals or enzymes are applied. For e.g., lignocelluloses may be hydrolyzed by gamma-ray or electron-beam irradiation, or microwave irradiation. However, those processes are commercially unimportant. By the hydrolyzed to xylose, mannose, acetic acid, galactose, and glucose are liberated. Whereas cellulose and lignin are hydrolyzed to glucose and phenolics respectively. Mainly propionic acids, acetic acid, hydroxy-1-propanone, hydroxy-1-butanone and 2-furfuraldeyde are formed due to degradation of xylan<sup>[28]</sup>.Due to high temperature and pressure xylose used to further degrade into furfural <sup>[29]</sup> while in case of hexose the main degradation product is 5-hydroxymethyl furfural (HMF)<sup>[30]</sup>. Both compounds affect the growth and metabolism of several microorganisms during metabolism <sup>[31]</sup>. Nirupama, B.et al. found protein and RNA synthesis inhibition in Candida tropical is due to furfural <sup>[32,33]</sup>.5-HMF was also found to be an inhibitor of ethanol production by Saccharomyces cerevisiae <sup>[32,33]</sup>.



Figure 3: Effect of pretreatment on lignocellulosic material, Source: [19]



**Figure 4:** Main degradation products occurring during hydrolysis of lignocellulosic material Source: <sup>[27]</sup>

## **Chemical hydrolysis**

In chemical hydrolysis lignocellulosic materials are exposed to a chemical for a period of time at a specific temperature, chemical concentration, substrate concentration and results in sugar monomers from cellulose and hemicellulose polymers <sup>[34]</sup>. In the chemical hydrolysis, the pretreatment and the hydrolysis may be carried out in a single step. Acids are predominantly used for chemical hydrolysis <sup>[28]</sup>. There are two basic types of acid hydrolysis processes: dilute acid and concentrated acid. Dilute acid hydrolysis is used from past so many years for converting cellulose to glucose. High temperature and pressure are required for this process and also has a reaction time in the range of seconds or minutes. Dilute acid process involves a solution of about 1%  $H_2SO_4$  concentration in a continuous flow reactor at a high temperature (about 488 K). Most dilute acid processes are limited to a sugar recovery efficiency of around 50% <sup>[35]</sup>. In comparison to dilute acid hydrolysis, concentrated acid hydrolysis leads to little sugar degradation and gives sugar yields approaching 100% <sup>[36]</sup>. The concentrated acid process offers more potential for cost reductions than the dilute acid process as it require lower temperature and less time. However, environment and corrosion problems and the high cost of acid consumption and recovery creating major problem for its economic success <sup>[36]</sup>.

## Enzymatic hydrolysis

Acid hydrolysis has a major disadvantage where the sugars are converted to degradation products like furfural, hydroxyl furfural. This degradation can be prevented by using enzymes favouring 100% selective conversion of cellulose to glucose. Enzymatic hydrolysis involves enzymes for the degradation of cellulose and hemicellulose <sup>[37]</sup>. Structural parameters of the substrate, such as lignin and hemicellulose content, surface area, and cellulose crystallinity hindered the enzymatic hydrolysis of cellulose and hemicellulose <sup>[38]</sup>. Enzyme hydrolysis is usually conducted at mild conditions (pH 4.8) and temperature (318–323 K) and does not have a corrosion problem, this leads to its low utility cost as compared to acid or alkaline hydrolysis <sup>[39]</sup>. The enzymatic hydrolysis has currently high yields (75–85%) and improvements are still projected (85-95%), as the research field is only a decade young <sup>[40]</sup>. Enzymatic hydrolysis uses carbohydrate degrading enzymes (Cellulases and hemicellulases) for hydrolyzation of lignocelluloses into fermentable sugars <sup>[41]</sup>. The mechanism of cellulase enzyme is given in figure 5.



Figure 5: Mode of action of cellulolytic enzymes <sup>[42]</sup>

Table 5: Relevant enz	ymatic activities for	enzymatic po	osthydrolysis	s of xylool	igosaccharides [43]

Enzyme	EC	Hydrolyzed linkage	Substrate	Main product
Endoxylanase	3.2.1.8	Internal b-1,4	Main chain	Oligomers
Exoxylanase	n.c.	Terminal b-1,4 (reducing end)	Main chain	Xylose, xylobiose
b-Xylosidase	3.2.1.37	Terminal b-1,4 (non-reducing end)	Oligomers	Xylose
Arabinosidase	3.2.1.55	-	Side groups	Arabinose
Glucoronisidase	3.2.1.139	-	Side groups	Methylglucuronic acids

\*n.c.: not yet classified

## Fermentation

Both six-carbon (hexoses) and five-carbon (pentose) sugars (if both cellulose and hemicellulose are hydrolyzed) are present in supernatant of enzymatic hydrolysis of lignocelluloses it also depend upon the lignocellulose source. Typically consists of glucose, xylose, arabinose, galactose, mannose, fucose, and rhamnose are present in the hydrolysate <sup>[41]</sup>.

The microorganisms should fulfil certain parameters in terms of their performance parameters and other requirements such as compatibility with existing products, processes and equipment for bioethanol fermentation.

The performance parameters of fermentation are: temperature range, pH range, alcohol tolerance, growth rate, productivity, osmotic tolerance, specificity, yield, genetic stability, and inhibitor tolerance. The characteristics required for an industrially suitable microorganism are summarized in Table 6.

Table 6: Important traits for bioethanol fermentation process,	Source: [44]

Trait	Requirement
Bioethanol yield	>90% of theoretical
Bioethanol tolerance	>40 gL <sup>- '</sup> h <sup>-1</sup>
Bioethanol productivity	>1 gL <sup>-1</sup> h <sup>-1</sup>
Able to grow in undiluted hydrolysates	Resistance to inhibitors

Now a days Saccharomyces cerevisiae and Zymomonas mobilis have been used for bioethanol fermentation. They have potential to ferment efficiently glucose into bioethanol, but are unable to ferment xylose <sup>[40,42,45,46,49]</sup>.Pichia stipitis, Candida shehatae, and Candida parapsilosis are natural xylose-fermenting yeasts and they can metabolize xylose via the action of xylose reductase (XR) and xylitol dehydrogenase (XDH) enzymes<sup>[45,48]</sup>.

S. cerevisiae most frequently used by industries for fermenting bioethanol in industrial processes because this is very robust and well suited to the fermentation of lignocellulosic hydrolysates .Bacteria, such as Z. Mobilis and Escherichia coli also gaining particular interest because the ability of rapid fermentation, which take less time (minutes) as compared to yeasts (hours<sup>) [48-51]</sup>. Z. mobilis, a Gram-negative bacterium, is well recognized for its ability to efficiently produce bioethanol at high rates from glucose, fructose and sucrose. Generally Z. Mobilis produce bioethanol more efficiently as compared to S. cerevisiae <sup>[52]</sup>. Thermophilic anaerobic bacteria have also been extensively examined for their potential as bioethanol producers. These bacteria include Thermoanaerobacterium saccharolyticum <sup>[53]</sup>, Thermoanaerobacter ethanolicus <sup>[54]</sup>, Clostridium thermocellum <sup>[55]</sup>.

## Potential of non-traditional sources for bioethanol production in india: Status and prospects

Sugarcane molasses is a primary feedstock for bio-ethanol in India. Sugarcane requires prime agricultural land, fertilizer and large quantities of irrigation water. Sugarcane expansion in India for bioethanol production will therefore most likely increase agricultural inputs and therefore cost of overall production will increase. As discussed above, if we increase agricultural inputs for biofuel crops they will begin to impact food prices. In addition, as India's biofuel program expands, the land space to large scale sugarcane cultivation will be going to increase. This may lead to a number of environmental problems such as land degradation, deforestation and water scarcity [56]. To prevent direct competition with sugar, in October of 2007 a ban on direct ethanol production from sugarcane juice was put (Cabinet Committee on Economic Affairs ). The price of sugar would increase due to diversion of sugarcane use from sugar production to biofuels. To avoid this competition, bioethanol production from non edible lignocellulosic biomass such as wheat straw, rice straw, non-edible oil cake, sorghum bicolor, Saccharum spontaneum, peels of fruits and vegetables would be a good alternative and gaining keen interest on this side. The structural composition of various types of non-traditional biomass is given in Table 8.

Substrate	Cellulose	Hemicellulose	Lignin	Ash	References
	(%)	(%)	(%)	(%)	
Rice straw	32-47	19-27	5-24	12.4	[26][57]
Wheat straw	35-45	20-30	8-15	10.1	[58][59]
Corn straw	42.6	21.3	8.2	4.3	[59]
Fruit peels	25-50	20-30	2-10	-	[60]
Grasses (Saccharum spontaneum, Pennisetum purpureum)	25–40	25–50	10– 30	-	[61]
Sorghum bicolour	35.87	26.04	7.52	0.7	[62]
Jatropha cake	15-20	15-20	-	3-5	[63]

#### Table 8: Biochemical composition of various types of non-traditional biomass

These biomass serve as a cheap and abundant feedstock and have potential to produce fuel bioethanol at reasonable costs (Table.9,10) for e.g. India is the third largest producer of Sorghum bicolor after USA and Nigeria with 7.15m tons <sup>[64]</sup>. Its growing period (about 4.0 months) and water requirement ( $8000 \text{ m}^3$  over two crops) <sup>[65]</sup> are 4 times lower than those of sugarcane (12-16 months and 36,000 m<sup>3</sup> of water crop<sup>-1</sup> respectively) (Table 9, 10). Its cultivation cost is also four times lower than that of sugarcane.

Сгор	Cost of cultivation (USD)	crop duration (month)	fertilizer requirement (N-P-K Kg/ ha)	Water requirement (m3)	Ethanol yield (liters ha-1)
Sorghum bicolour	217 crop <sup>-1</sup>	4	80-50-40	4000crop <sup>-1</sup>	4000 year <sup>-1</sup> over two
Sugarcane	1079 crop <sup>-1</sup>	12-16	250 to 400 -125-125	36000 crop <sup>-1</sup>	crops 6500 crop <sup>-1</sup> (b)

## Table.9. Sorghum bicolor vis-à-vis sugarcane, Source: [35, 67, 68]

In addition India is the world's second largest producer of fruits and vegetables. About 18 per cent of the country's fruits and vegetables, worth INR 133 billion, goes to waste annually because of the spillage, physiological decay, water loss, mechanical damage during harvesting, packaging and transportation lack of cold storage facilities <sup>[66]</sup>. Alternatives to such disposal methods could be the utilization of such cheap and renewable sources for bioethanol production.

The agro wastes could be the suitable feedstocks for bioethanol production due to their availability throughout the year. Worldwide production of these agro wastes is given in Table 10. For instance, approximately 600-900 million tons per year rice straw is produced globally <sup>[26]</sup>. Only a small portion of globally produced rice straw is used as animal feed, the rest is removed from the field by burning, a common practice all over the world, increasing air pollution and affecting human health <sup>[69,70]</sup>.

Table 9: Relative economics of ethanol	production from	different feedstocks	in India
--	-----------------	----------------------	----------

Parameter	Sweet sorghum	Sugarcane molasses	Sugarcane juice	Grains (pearl millet and broken rice)
Cost of raw material (`Rs. t <sup>-1</sup> )	801	3,000-5,000 <sup>1</sup>	1200 <sup>2</sup>	7,000 <sup>2</sup>
Total cost of production (Rs. t <sup>-1</sup> )	1,184	4,890-6,890	1690	9,400
Output of ethanol (liters)	45	270	70	400
Value of ethanol (Rs. t <sup>-1</sup> )	1,215	5,805	1505	8,600

1. Molasses prices have ranged between Rs.3000 and 5000 t-<sup>1</sup> during the last few years. Hence the profitability of producing ethanol from it is highly dependent on fluctuating molasses prices.

2. Data on other feedstock cost is for the year 2009. The price of feedstock (sugarcane and grains) has increased in recent years. Source: <sup>[71]</sup>

# Table 10: Quantities of agricultural waste (million tons) reportedly available for bioethanol Production

Agrowaste	Africa	Asia	Europe	America	Oceania
Rice straw	20.9	667.6	3.9	37.2	1.7
Wheat straw	5.34	145.20	132.59	62.64	8.57
Corn straw	0.00	33.90	28.61	140.86	0.24

Source: [72]

Approx 30% or more oil present in the seeds of Indian plants like Jatropha (Jatropha curcas), Mahua (Madhuca Indica), Karanja (Pongamia pinnata) and Neem (Mellia azadirachta)<sup>[73]</sup>. After expelling of oil from seeds the left over cake disposed in environment which simply goes waste <sup>[74]</sup>. Thus, efforts should be made to produce ethanol from them .Recently, Jatropha oilseed cake obtained as a by product from the oil extraction press <sup>[75]</sup> was reported to be rich in carbohydrates, fibers, water, and carbon content, along with low contents of hydrogen and oxygen, and it was utilized for the production of ethanol using acid hydrolysis treatment [76]. Another such kind of oil tree available in abundance is Karanja, belonging to the family Leguminosae, is a prominent species having nonedible oilseed. In India, about 1 million ha of lands are covered with this trees <sup>[77]</sup>. The yield of oilseed per tree is between 8 kg to 24 kg and has around has 30%–33% oil <sup>[78]</sup>. From the above discussion of *Pongamia* pinnata in India, it can be estimated that the production of biodiesel from this oilseed is going to increase in the near future and the residual waste will generate in huge quantities. Since the method for utilization of the oilseed residual waste for ethanol production is still a rare but sustainable approach, work in this area offers hope of new renewable raw material for ethanol-based industries. Due to their high growth rate and better reduction of carbon footprint compared to an equivalent area of woody plants, bamboos are also receiving a renewed interest among the available non-traditional feedstock <sup>[79]</sup>. Bamboos are a group of perennial evergreens belonging to the true grass family and enjoying wide distribution in India, especially in the north eastern region where it is an important resource with multiple applications<sup>[80]</sup>. In India 50% of the total area under bamboo growth is occupied by Dendrocalamus sp. India is the second largest producer of bamboo in the world with an annual production of about 32 million tons <sup>[81]</sup>. About 5.4 million tons of bamboo residues are generated in the country every year by the bamboo processing industries of which about 3.3 million tons remains as surplus. Compared to other feedstock, this biomass has high growth rate, easy harvesting characteristics, vegetative propagation, fast growth (can harvest three times a year) and also very high content of cellulose, hemicellulose [82-85], biogas [86] and other valuable products [87-88]. It can efficiently produce ethanol up to 800 gallons per acre. All these characteristics suggest that it could produce bioethanol in a promising way so that it can reduce energy crisis upto certain extent.

## Conclusion

India is a fast growing economy with an inherent increase in demand for energy. While keeping a huge population and limited energy resources in mind, the nation is looking for alternative renewable fuels to support the pace of growth. India is one among the largest producers of ethanol and currently all commercial ethanol production in the country uses molasses as feedstock. However, most of it is consumed for application in liquor and chemical industries and the surplus availability hardly fulfil the current demand created by a mandatory 5% blending of ethanol in gasoline implemented in several states. Once the law is implemented nationwide or if the blending ratio is increased, which the government is already planning to do the demand of ethanol will exceed at high level. Therefore, production of ethanol from other renewable resources such as agriculture residues, fruit waste, on-

edible oil cake etc is imperative for meeting this increased demand. These materials could prove as a cheap and abundant feedstock, and have potential to produce fuel bioethanol at reasonable costs.

#### References

- 1. Wheals A.E., Bassoc L.C., Alves D.M.G. and Amorimd H.V., Fuel ethanol after 25 years, Trends Biotechnol., 17 (12), 482–487, (1999)
- 2. Grad P., Biofuelling Brazil: An overview of the bioethanol success story in Brazil, Biofuels, 7 (3), 56–59, (2006)
- 3. Planning Commission, Report of the Committee on Development of Biofuels, (2003)
- 4. Adrados P., Choteborska B., Galbe P.M., and Zacchi G., Ethanol production from non-starch carbohydrates of wheat bran, Bioresource Technology, 96,843-850, (2005)
- 5. Kim S. and Dale B.E., Life cycle assessment of various cropping systems utilized for producing biofuels: bioethanol and biodiesel, Biomass & Bioenergy, 29, 426 439, (2005)
- 6. Wyman C., Handbook on bioethanol: production and utilization, Washington, DC: Taylor and Francis, (1996)
- 7. All India Distillers Association. http://www.aidaindia.org/public/AboutAida.php Website accessed ,(2006)
- 8. IEA., India Statistics, International Energy Agency www.iea.org/Textbase/ stats/countryresults.asp?COUNTRY\_CODE=IN&Submit=Submit,(2009)
- 9. Clark J., The direct hydration of alkenes, (2003)
- 10. www.cargill.co.in
- 11. www.celanesetcx.com
- 12. Raposo S., Pardao J.M., Diaz I., Costa M.E.L., Kinetic modelling of bioethanol production using agro-industrial by-products, Int. J. of Energy Env., 3(1), 8, (2009)
- 13. Kumar S. and Agrawal P.K., Alcohol The Viable Energy Substitute, All India Seminar on Ethanol and Co-generation, (2003)
- 14. Ethanol: Useful information and resources. http://www.ethanolindia.net/sugarind.html
- 15. Balat M. and Balat H.O., Progress in bioethanol processing, Prog Energy Combust Sci, 34:551-73, **(2008)**
- 16. Biofuels the fuel of future.http://biofuel.org.uk/asia.html
- 17. Cardona Alzate C.A. and Sanchez Toro O.J., Energy consumption analysis of integrated flow sheets for production of fuel ethanol from ligno-cellulosic biomass, Energy, 31: 2447–59, (2006)
- 18. Zhu J.Y., Wang G.S., Pan X.J., Gleisner R., The status of and key barriers in lignocellulosic ethanol production: a technological perspective. In: International conference on biomass energy technologies, Guangzhou, China, (2008)
- 19. Hsu T.A., Ladisch M.R., Tsao G.T., Alcohol from cellulose, Chem Technol, 10, 315–9, (1980)
- 20. Kodali B., Pogaku R., Pretreatment studies of rice bran for the effective production of cellulose, Electron J. Environ Agric, Food Chem., 5, 1253–64, **(2006)**

- 21. Zhang Y., Pan Z. and Zhang R., Overview of biomass pretreatment for cellulosic ethanol production, Int. J. Agric. Biol. Eng., (2),51–68,(2009)
- Silverstein R.A., Chen Y., Sharma-Shivappa R.R., Boyette M.D., Osborne J.A., comparison of chemical pretreatment methods for improving saccharification of cotton stalks, Bioresour. Technol., 98, 3000–11, (2008)
- 23. Han M., Moon S.K., Kim Y., Kim Y., Chung B., Choi G.W., Bioethanol production from ammonia percolated wheat straw, Biotechnol Bioprocess Eng., 14, 606–11,(2009)
- 24. Taherzadeh M.J., Karimi K., Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review, Int. J. Mol. Sci., 9, 1621–51,(2008)
- 25. Kumar P., Barrett D.M., Delwiche M.J., Stroeve P., Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production, Ind. Eng. Chem. Res., 48, 3713–29, (2009)
- 26. Karimi K., Kheradmandinia S. and Taherzadeh M.J., Conversion of rice straw by dilute acid hydrolysis, Biomass Bioenerg, 30, 247-253, (2006)
- 27. Demirbas A., Products from lignocellulosic materials via degradation processes, Energy Source A, 30, 27–37, (2008)
- Gullu D.E., Effect of catalyst on yield of liquid products from biomass via pyrolysis, Energy Source, 25, 753–65, (2003)
- 29. Dunlop A.P., Furfural formation and behaviour. Ind Eng Chem, 40, 204-9, (1948)
- 30. Ulbricht R.J., Sharon J., Thomas J., A review of 5-hydroxymethylfurfura HMF in parental solutions, Fundam. Appl. Toxicol., 4, 843–53, (1984)
- 31. Nirupama B., Rakesh B. and Viswanathan L., Enzyme Mierob. Technol., 3, 24-28, (1981)
- 32. Berta Sanchez and Juan Bautista, Effects of furfurai and 5-hydroxymethylfurfural on the fermentation of Saccharomyces cerevisiae and biomass production from Candida guilliermondii, Enzyme Microb. Technol., (10) (1988)
- 33. Nirupama B., Rakesh B. and Viswanathan L., Enzyme Mierob. Technol., (3), 24-28,(1981)
- 34. Taherzadeh M.J. and Karimi K., Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review, BioResources, 2, 472–99, (2007)
- 35. Badger P.C., Ethanol from cellulose: a general review. In: Janick J., Whipkey A., editors, Trends in new crops and new uses, Alexandria, VA: ASHS Press, (2002)
- 36. Yu Y., Lou X., Wu H., Some recent advances in hydrolysis of biomass in hotcompressed water and its comparisons with other hydrolysis methods, Energy Fuels ,22, 46–60,(2008)
- Pike P.W., Sengupta D., Hertwig T.A., Integrating biomass feedstocks into chemical production complexes using new and existing processes, Minerals Processing Research Institute, Louisiana State University, Baton Rouge, LA, (2008)
- Pan X., Gilkes N., Saddler J.N., Effect of acetyl groups on enzymatic hydrolysis of cellulosic substrates, Holzforschung, 60, 398–401, (2006)
- 39. Sun Y. and Cheng J., Hydrolysis of lignocellulosic materials for ethanol production: a review, Bioresour Technol., 83, 1–11, (2002)
- 40. Hamelinck C.N., Van Hooijdonk G., Faaij A.P.C., Ethanol from lignocellulosic biomass: technoeconomic performance in short-, middle- and long-term. Biomass Bioenergy, 28, 384–410, (2005)

- 41. Keshwani D.R., Cheng J.J., Switchgrass for bioethanol and other value-added applications: a review, Bioresour Technol., 100, 1515–23, (2009)
- 42. Kim S.H., Lime pretreatment and enzymatic hydrolysis of corn Stover. Doctoral dissertation, Texas A&M University, (2004)
- 43. Carvalheiro F., Duarte L.C., Girio F.M., Hemicellulose biorefineries: a review on biomass pretreatments, J Sci Ind Res ,67, 849–64,(2008)
- 44. Dien B.S., Cotta M.A., Jeffries T.W., Bacteria engineered for fuel ethanol production: current status, Appl Microbiol Biotechnol., 63,258–66, (2003)
- McMillan J.D., Pretreatment of lignocellulosic biomass. In: Himmel M.E., Baker J.O., Overend R.P., editors. Enzymatic conversion of biomass for fuel production. Washington, D.C., American Chemical Society, 292-323, (1993)
- 46. Talebnia F., Karakashev D., Angelidika I., Production of bioethanol from wheat straw: An overview on pretreatment, hydrolysis and fermentation, BioresTechnol., 101, 4744-53, (2010)
- 47. Gamage J., Howard L., Zisheng Z., Bioethanol production from lignocellulosic biomass, J. Biobased Mater. Bioenerg., 4, 3-11, (2010)
- 48. Zaldivar J., Nielsen J., Olsson L., Fuel ethanol production from lignocellulose: a challenge for metabolic engineering and process integration, Appl. Microbol. Biotechnol., 56,17-34,(2001)
- 49. Herrero A.A., End product inhibition in anaerobic fermentation. Trends. Biotechnol.,1, 49-53, (1983)
- 50. Zayed G. and Meyer O., The single-batch bioconversion of wheat straw toethanol employing the fungus Trichoderma viride and the yeast Pachysolentannophylus, Appl. Microbiol. Biotechnol., 45, 551-5, (1996)
- 51. Weber C., Boles E., Sugar-hungry yeast to boost biofuel production, Science News, Science Daily, 92, 881-2, (2010)
- 52. Gunasekaran P., Raj K.C., Ethanol fermentation technology Zymomonas mobilis, Curr Sci., 77, 56–68, (1999)
- 53. Zeikus J.G., Ben-Bassat A.H.L., Ng T.K., Lamed R.J., Thermophilic ethanol fermentation, Basic Life Sci., 18, 441-61,(1981)
- 54. Georgieva T., Mikkelsen M., Ahring B., Ethanol production from wet exploded wheat straw hydrolysate by thermophilic anaerobic bacterium Thermoanaerobacter BG1L1 in a continuous immobilized reactor ,Appl. Biochem. Biotechnol., 145, 99-110, (2008)
- 55. Shaw A.J., Jennery F.E., Adams M.W.W., Lynd L.R., End-product pathways in the xylose fermenting bacterium Thermoanaerobacterium saccharolyticum. Enzyme Microbiol Technol, 42, 453-8,(2008)
- 56. Food and Agriculture Organization, Crop Prospects and Food Situation. Website accessed January 2009. ftp://ftp.fao.org/docrep/fao/010/ai465e/ai465e00.pdf, (2008)
- 57. Lee J., Biological conversion of lignocellulosic biomass to ethanol, Journal of Biotechnology, 56, 1-24, (1997)
- Peiji G., Yinbo Q., Xin Z., Mingtian Z., Yongcheng D., Screening microbial strain for improving the nutritional value of wheat and corn straws as animal feed, Enzyme and Microbial Technology, 20,581-4,(1997)

- 59. Saha B.C., Iten L.B., Cotta M.A., Wu Y.V., Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol, Process Biochemistry, 40, 3693-700, (2005)
- 60. Arumugam R. and Manikandan M., Fermentation of Pretreated Hydrolyzates of Banana and Mango Fruit Wastes for Ethanol Production, Asian J. Exp. Biol. Sci., 2(2), 246-256, (2011)
- Scordia D., Cosentino S.L. and Jeffries T.W., Second generation bioethanol production from Saccharum spontaneum L. ssp. aegyptiacum (Willd.) Hack. Bioresource Technology, 101, 5358– 5365, (2010)
- 62. Cardoso W. S., Use of sorghum straw (Sorghum bicolor) for second generation ethanol production: pretreatment and enzymatic hydrolysis, Quim. Nova, 36(5), 623-627, (2003)
- 63. Prasad, R.B.N., Value Added By-products from Oilseed cakes, Indian Institute of Chemical Technology. (2008) Available at: http://www.competebioafrica.net/events/events2/seminar\_india/ppt/4-1-Prasad.pdf
- 64. Food and agricultural organization (FAO), Sorghum bicolour (L.) Moench. http://www.fao.org/ag/agp/agpc/doc/Gbase/DATA/pf000319.htm, (2007)
- 65. Soltani A. and Almodares A., Evaluation of the investments in sugar beet and sweet sorghum production, National Convention of Sugar Production from Agricultural Products, Shahid Chamran University, Alwaz, Iran, (1994)
- 66. Vision 2050 Report by Central Institute of Post-Harvest Engineering & Technology (CIPHET), (2013)
- 67. Rao Dayakar B, Ratnavathi C.V., Karthikeyan K., Biswas P.K, Rao S.S., Viyay Kumar B.S. and Seetharama N., Sweet sorghum cane for biofuel production: A SWOT analysis in Indian context, Hyderabad, Andhra Pradesh, India: National Research Center for Sorghum, 20, (2004)
- Reddy B.V.S., Ramesh S., Ashok Kumar A., Wani S.P., Ortiz R., Ceballos H. and Sreedevi T.K., Biofuel crops research for energy security and rural development in developing countries, Bioenergy Research, 1,248–258, (2008)
- 69. Wati L., Kumari S., Kundu B.S., Paddy straw as substrate for ethanol production, Indian Journal of Microbiology, 47, 26-9, (2007)
- 70. Chen Y., Sharma-Shivappa R.R., Chen C., Ensiling agricultural residues for bioethanol production, Applied Biochemistry and Biotechnology, 143, 80-92, (2007)
- Basavaraj G., Rao P.P., Reddy C.R., Kumar A.A., Rao P.S., and Reddy B.V.S., A Review of the National Biofuel Policy in India: A critique of the Need to Promote Alternative Feedstocks, Working Paper Series no. 34, (2012)
- 72. Kim S. and Dale B.E., Global potential bioethanol production from wasted crops and crop residues, Biomass and Bioenergy, 26, 361 375, (2004)
- 73. Padhi S.K. and Singh R.K., Non-edible oils as the potential source for the production of biodiesel in India: A review, J. Chem. Pharm. Res., 3(2), 39-49,(2011)
- 74. Subbarao P.M.V., A study on biogas generation from non-edible oil seed cakes: potential and prospects in India. In: Proceedings of 2nd Joint International Conference on "Sustainable Energy and Environment (SEE 2006)". Bangkok, Thailand, **(2006)**
- 75. Parawira W., Biodiesel production from *Jatropha curcas*: A review, Scientific Research and Essays, 5(14), 1796-1808,(2010)

- 76. Mishra M.S., Chandrashekhar B., Chatterjee T., Singh K., Production of bioethanol from Jatropha oilseed cakes via dilute acid hydrolysis and fermentation by *Saccharomyces cerevisae*, International Journal of Biotechnology Applications, 3(1), 41-47, (2011)
- 77. Kumar B.N.S., Phytochemistry and pharmacological studies of pongamia pinnata (Linn.) pierre, International Journal of Pharmaceutical Sciences Review and Research, 9(2), (2011)
- 78. Padhi S.K. and Singh R.K., Non-edible oils as the potential source for the production of biodiesel in India: A review, Journal of Chemical and Pharmaceutical Research, 3(2), 39-49, (2011)
- 79. Biswas S., Studies on bamboo distribution in north-eastern region of India, Indian Forester, 114 (9), 514–531, (1988)
- 80. Hunter I.R. and Jungi W., Bamboo biomass, an INBAR working paper, (2011)
- 81. Sukumaran R.K., Surender V.J., Sindhu R., Binod P., Janu K.U. and Sajna K.V., Lignocellulosic ethanol in India: Prospects, challenges and feedstock availability. Bioresource Technology, 101, 4826–4833, (2010)
- 82. Zhang X.Y., Yu H.B., Huang H.Y., Liu Y.X., Evaluation of biological pretreatment with white rot fungi for the enzymatic hydrolysis of bamboo culms, Int. Biodeter. Biodegr., 60, 159–164,(**2007**)
- Shimokawa T., Ishida M., Yoshida S.and Nojiri, M., Effects of growth stage on enzymatic saccharification and simultaneous saccharification and fermentation of bamboo shoots for bioethanol production, Bioresource Technology, 100, 6651–6654, (2009)
- 84. Yamashita Y., Shono M., Sasaki C. and Nakamura, Y., Alkaline peroxide pretreatment for efficient enzymatic saccharification of bamboo, Carbohyd. Polym., **79**, 914–920, **(2010)**
- 85. Sun Y. and Lin L., Hydrolysis behavior of bamboo fiber in formic acid reaction system, J. Agric. Food Chem., 58, 2253–2259, (2010)
- 86. Kobayashi F., Take H., Asada C. and Nakamura Y., Methane production from steam-exploded bamboo, J. Biosci. Bioeng., 97, 426–428, (2004)
- Asada C., Nakamura Y., Kobayashi F., Waste reduction system for production of useful materials from un-utilized bamboo using steam explosion followed by various conversion methods, Biochem. Eng. J., 23, 131–137, (2005)
- Yip J., Chen M.J., Szeto Y.S. and Yan S., Comparative study of liquefaction process and liquefied products from bamboo using different organic solvents, Bioresource Technology,100, 6674–6678, (2009)