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Biomass-based energy fuel through biochemical routes: A review

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Abstract

Energy demand is increasing continuously due to rapid growth in population and industrialization development. The development of energy sources is not keeping pace with spiraling consumption. Even developed countries are not able to compensate even after increasing the energy production multifold. The major energy demand is provided from the conventional energy sources such as coal, oil, natural gas, etc. Two major problems, which every country is facing with these conventional fuels, are depletion of fossil fuels and deterioration of environment.

The present review article aims to highlight various biochemical processes for conversion of biomass into biological hydrogen gas and ethanol. The present discussion focuses on hydrogen production through various routes viz. fermentative, photosynthesis and biological water gas shift reaction. In addition, emphasis has been laid on ethanol as biomass-based energy fuel. The discussion has been focused on the technology for ethanol production from various biomass sources such as molasses, lignocellulosic feedstock and starch. Various biochemical processes and their major steps involved during the ethanol production from biomass have been discussed in detail.

Keywords: Hydrogen; Ethanol; Biomass; Biochemical

Contents

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1. Introduction

As energy demand is increasing continuously due to speedy development in population and industrialization, the development of energy sources is not keeping pace with spiraling consumption. Developed countries are also finding it difficult to compensate even after increasing the energy production multifold due to growth pressure.

The major energy demand is compensated from conventional energy sources such as coal, oil, natural gas, etc. Two major problems, which every country is facing with these conventional fuels are as follows:

(i) These energy sources are at the verge of getting extinct. World's oil reserves are estimated to get depleted by 2050.
(ii) Energy extraction from these conventional fuels causes pollution. It is well known that SO_2 emission produced by burning fossil fuels is the major cause of acid rain. Globally, increase in emissions rates of greenhouse gases, i.e., CO_2 present a threat to the world climate. As an estimate in the year 2000, over 20 million metric tons of CO_2 were expected to be released in the atmosphere every year [1,2]. If this trend continues, some extreme natural calamities are expected such as excessive rainfall and consequent floods, droughts and local imbalances.

Presently, there is utmost need of alternative energy resources which are cheap, renewable and do not cause pollution. Therefore, attention is being given to alternate and renewable sources such as solar, wind, thermal, hydroelectric, biomass, etc.

Biomass is a carbon neutral resource in its life cycle and the primary contributor of greenhouse effect. Biomass is the fourth largest source of energy in the world after coal, petroleum and natural gas, providing about 14% of the world's primary energy consumption. Renewable biomass is being considered as an important energy resource all over the world. Biomass is used to meet a variety of energy needs, including generating electricity, fueling vehicles and providing process heat for industries [3,4]. Among all the renewable sources of energy, biomass is unique as it effectively stores solar energy. It is the only renewable source of carbon that can be converted into convenient solid, liquid and gaseous fuels through different conversion processes [5].

2. Biomass

2.1. Introduction

Biomass comprises all the living matter present on earth. It is derived from growing plants including algae, trees and crops or from animal manure [4]. The biomass resources are the organic matters in which the solar energy is stored in chemical bonds. It generally consists of carbon, hydrogen, oxygen and nitrogen. Sulfur is also present in minor proportions. Some biomass also consists significant amounts of inorganic species. Plants, via photosynthesis, produce carbohydrates which form the building blocks of biomass [6].

2.2. Importance of biomass

Biomass has always been a major source of energy for mankind from ancient times. Presently, it contributes around 10–14% of the world's energy supply [1]. Biomass can be converted into three main types of products:

- electrical/heat energy,
- fuel for transport sector and
- feedstock for chemicals.

Traditionally, biomass had been utilized through direct combustion. Burning biomass produces pollutants including dust and the acid rain gases such as sulfur dioxide and nitrogen oxides but the sulfur dioxide produced is 90% less than that is produced by burning coal. The quantities of atmospheric pollution produced are insignificant compared to other pollution sources. Biomass usage as a source of energy is of interest due to the following envisaged benefits:

- Biomass is a renewable, potentially sustainable and relatively environmentally friendly source of energy.
- A huge array of diverse materials, frequently stereochemically defined, are available from the biomass giving the user many new structural features to exploit [7].
- Increased use of biomass would extend the lifetime of diminishing crude oil supplies.
- Biomass fuels have negligible sulfur content and, therefore, do not contribute to sulfur dioxide emissions that cause acid rain.
- The combustion of biomass produces less ash than coal combustion and the ash produced can be used as a soil additive on farms, etc.

- The combustion of agricultural and forestry residues and municipal solid wastes (MSW) for energy production is an effective use of waste products that reduces the significant problem of waste disposal, particularly in municipal areas.
- Biomass is a domestic resource which is not subject to world price fluctuations or the supply uncertainties as of imported fuels.
- Biomass provides a clean, renewable energy source that could improve our environment, economy and energy securities [8,9].
- Biomass usage could be a way to prevent more carbon dioxide production in the atmosphere as it does not increase the atmospheric carbon dioxide level.

Biomass can be used in many ways to obtain energy. Most of the biomass energy is consumed in domestic purposes and by wood-related industries. It is burned by direct combustion to produce steam that drives the turbine/generator to produce electricity. Gasifiers are used to convert biomass into a combustible gas which is then used to drive a high efficiency, combined cycle gas turbine.

Biomass is converted to pyrolysis oil by heating. Pyrolysis oil is easier to store and transport than solid biomass material and is burned like petroleum to generate electricity.

2.3. Resources of biomass

Biomass can be obtained from various sources. These categories are mentioned below.

Wastes: This category comprises wastes from agricultural production, process waste from agro industries, crop residues, etc.

Standing forests: This comprises various intermediate products and residual wastes of different nature.

Energy crops: This energy crop includes various edible and non-edible crops.

Biomass resources that can be used for energy production cover a wide range of materials which can be categorized in two ways, namely, modern biomass and traditional biomass. Modern biomass usually involves large-scale uses and aims to substitute for conventional energy sources. Traditional biomass is generally confined to developing countries and small-scale uses [6,9].

2.4. Land availability

The major factor that determines the availability of land for biomass production is the demand of land for food production. According to an estimate made by Sudha and Ravindranath using the FAO/IIASA classification, an assessment has been made for land availability for biomass production under the agro ecological regions (AEZ) in India [10]. The types of land available are dry semi-arid, moist semi-arid, sub-humid, humid, marginal moist semi-arid, sub-humid and humid, naturally flooded land (fluvisols and gleysols), marginal fluvisols and gleysols, NS-crop and forest land not suitable for crops. An estimate of the land potentially available for biomass production in India is given in Table 1.

2.5. Biomass components

The importance of particular type of biomass depends on the chemical and physical properties of the large molecules from which it is made. The chemical structure and major organic components in biomass are important in the development of processes for producing derived fuel and chemicals. Biomass contains varying amounts of cellulose, hemicellulose, lignin and a small amount of extractive [4].

Cellulose is a glucose polymer containing linear chains of (1,4)-D-glucopyranose units, in which the units are linked 1–4 in the alpha configuration, with an average molecular weight of around 100,000. Alpha cellulose is a polysaccharide having the general formulae ($C_6H_{10}O_5$). Hemicelluloses are complex polysaccharides that exist in association with cellulose in the cell wall. It is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methlyglucoronic and galaturonic acids, with an average molecular weight of $<30{,}000$. Lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of the certain biomass, especially woody species, and are often adjacent to cellulose fibers to form a lignocellulosic complex [11].

In biomass, cellulose is generally the largest fraction, about 40–50% by weight and hemicellulose about 20–40% [9,12]. For example, the sugarcane bagasse contains cellulose (40–50%), hemicellulose (20–30%), lignin (20–25%) and ash (1.5–3.0%).

2.6. Energy in biomass

Biomass is the fourth largest primary energy resource in the world after coal and crude oil. The amount of biomass that a plant produces depends mainly on the amount of solar energy the plant receives and the amount it can store as carbohydrates. Plants use 0.1% of solar radiation for the process of photosynthesis:

$$CO_2 + H_2O + \text{light} \xrightarrow{\text{Chlorophyll}} (CH_2O) + O_2.$$

Through photosynthesis, and with the help of CO_2, water and chlorophyll, the carbohydrate substance is produced, that makes up the bulk tissues. It contains a proportion of the solar energy trapped in their chemical bonds. It is these chemical bonds which broken by any means, produces the carbohydrates [8,9,13].

Biomass with their heating values can be viewed in Table 2.

Table 1
Estimates of availability of land for biomass production in India

Author/source	Category	Area of land available, (Mha)
Degraded land quoted in Planning Commission (1992–1997)	Degraded forest	36
	Degraded non-forest	94
Degraded non-forest	Cultivated land	13
Land available for tree planting	Strips and boundaries	2
	Uncultivated, degraded land	33
	Degraded forest land	36
Kapoor (1992): Land available for tree planting	Agricultural land	45
	Forest land	28
	Pasture land	7
	Fallow land (long and short)	25
	Urban land	1
Ministry of Agriculture (1992)	Forest land with $<10\%$ tree crown cover	11
	Grazing land	12
	Tree groves	3
	Culturable land	15
	Old fallow	11
	Current fallow	14
Sudha (1996)	Cultivable land under agro ecological zones	26.1
	Land not suitable for cultivation	13.6
	Pasture land	2.9
NRSA (1995)	Forest degraded land	16.27
	Waste land	38.11
	Other category	11.07

3. Biomass conversion processes

Biomass can be converted into useful forms of energy using a number of different processes. Choice of conversion process depends on the type, property and quantity of biomass feedstock, the desired form of the energy, i.e., end-use requirements, environmental standards, economic conditions and project-specific factors. Biomass can be converted into three main products: power/heat generation, transportation fuels and chemical feedstock [8,9,13,14].

There are various types of conversion processes for converting biomass into biomass-based energy fuel. Biochemical conversion is one among the few which provide environment friendly direction for obtaining energy fuel from biomass.

3.1. Biological hydrogen production

According to recent literature, hydrogen will be an important energy carrier in the near future [15,16]. Instead of fossil fuel, hydrogen production from biomass has to be employed as it is sustainable and renewable. All processes of biological hydrogen production are dependent on the presence of hydrogen-producing enzymes [17]. It is hypothetically possible that the quantity or inherent activity of these enzymes could limit the overall process. It was found that all the enzymes contain complex metalloclusters as active sites and that the active sites of the enzyme units are synthesized in a complex process involving auxiliary enzymes and protein maturation steps. Three enzymes that were found to carry out these reactions are nitrogenase, Fe-hydrogenase and NiFe hydrogenase.

Table 2
Biomass with heating values

Biomass	Residue yield ($t\,ha^{-1}$)	Heating value ($MJ\,dry\,kg^{-1}$)
Wheat straw	2.97	17.9
Rice straw	4.52	16.8
Almond branches	6.21	18.4
Olive kernels	64.0	18.9
Ptolemais lignite	–	16.9
Forest residue	–	19.5
Hazelnut shell	–	15.43
Safflower seeds	–	23.86
Rapeseed	–	26.7
Cotton seed residue	–	16.9

3.1.1. Fermentative hydrogen production

In dark fermentation, anaerobic bacteria and some microalgae, such as green algae on carbohydrate-rich substrates, can produce hydrogen in a dark environment. Hydrogen can be produced by dark, anaerobic bacterial growth on carbohydrate rich substrates giving organic fermentation end products, hydrogen and carbon dioxide. Pure cultures found to produce hydrogen from carbohydrates include species of *Enterobactor*, *Bacillus* and

Clostridium. The pure substrates used include glucose, starch and cellulose. Process conditions including inoculums have a significant effect on hydrogen yield as they influence the fermentation end products.

Carbohydrates are the preferred organic carbon source for hydrogen production. Glucose in biomass gives a yield of 4 mol of hydrogen per glucose when acetic acid is the by-product [17,18]:

$$C_6H_{12}O_6 + 2H_2O_2 \rightarrow 2CH_3COOH + 2CO_2 + 4H_2,$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2.$$

Anaerobic fermentation in dark by heterotrophic bacteria can be explained by the following process:

$$\text{Biomass} \rightarrow \text{Carbohydrate} \overset{\text{Dark fermentation}}{\longrightarrow} \text{Organic acids} \overset{\text{Hydrogenease}}{\longrightarrow} H_2 + CO_2.$$

Hydrogen production from energy crops and waste-employing hyperthermophilic microorganisms can be seen in Fig. 1. Fig. 2 shows the microbial fermentation using a fixed bed reactor [19].

3.1.2. Photosynthesis process

Photosynthesis reaction during hydrogen production in light by algae, purple sulfur and non-sulfur bacteria is

$$H_2O + CO_2 \underset{\text{Hydrogenase and nitogenase}}{\overset{\text{Sunlight}}{\longrightarrow}} \text{Carbohydrates} + H_2 + O_2.$$

Many phototropic organisms such as purple bacteria, green bacteria, Cyanobacteria and several algae can produce hydrogen with the aid of solar energy. Microalgae, such as green algae and Cyanobacteria, absorb light energy and generate electrons. The electrons are then transferred to ferredoxin (FD) using the solar energy absorbed by photo-system. However, the mechanism varies from organism to organism but the main steps are similar to those of photosynthesis shown in Scheme 1.

Some strains like *Rhodopseudomonas capsulata* produce hydrogen during irradiation in the presence of organic compounds such as maleate, succinate, etc. Cyanobacteria (B-G algae) represent the most numerous groups of phototropic procaryotes that can produce hydrogen. Table 3 shows hydrogen production by some bacteria.

However, direct biophotolysis is sensitive to oxygen and thus difficult to sustain hydrogen production. The indirect biophotolysis can overcome the problem by producing hydrogen and oxygen at different stages to resolve the issue of oxygen sensitivity.

Major limitations to practical application of bio-hydrogen systems is the uncoordinated R&D effort to link the amount of hydrogen and the rate of hydrogen required by the standard Proton Exchange Membrane Fuel Cell (PEMFC), a highly efficient hydrogen-linked transportation fuel system.

In a recent study, it has been estimated that the flow rate of hydrogen required to 1.5 kW size of PEM fuel cells is 36 mol or 866 SL per hour. The comparison of hydrogen synthesis rate among the potential bio-hydrogen processes indicates that photosynthesis-based hydrogen production rate is highly inefficient to supply enough hydrogen to power 1 kW PEMFC on a continuous basis [20]. A better process route has been developed to overcome the problem.

3.1.3. Hydrogen production by biological water gas shift reaction

It is a new route to hydrogen production via the biological water-gas shift reaction (BWGS). Certain photo-heterotrophic bacteria, such as *Rubrivivax gelatinosus* are capable of performing water gas shift reaction at ambient temperature and atmospheric pressure. These

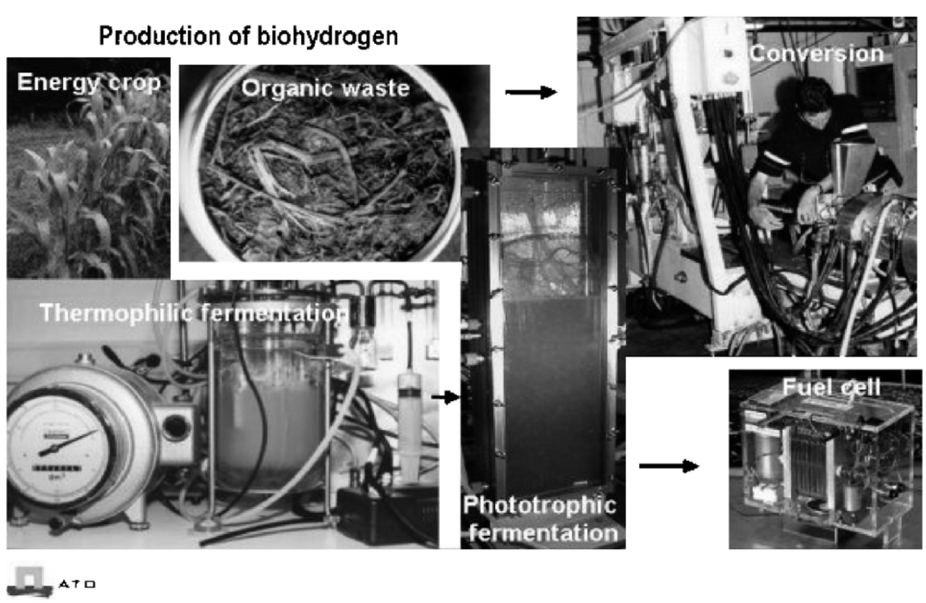


Fig. 1. Showing several disciplines which are aimed at the production, the processing and the conversion of biomass to hydrogen (Wageningen University Netherlands bio-hydrogen project).

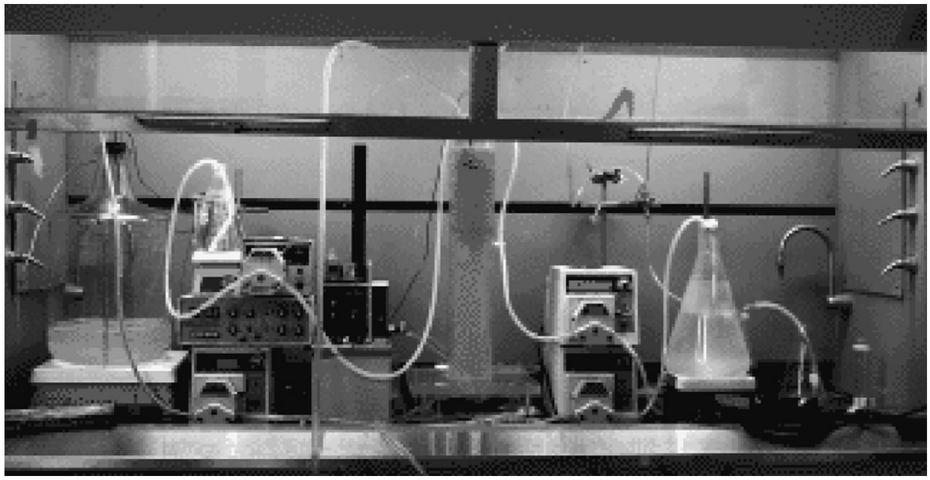
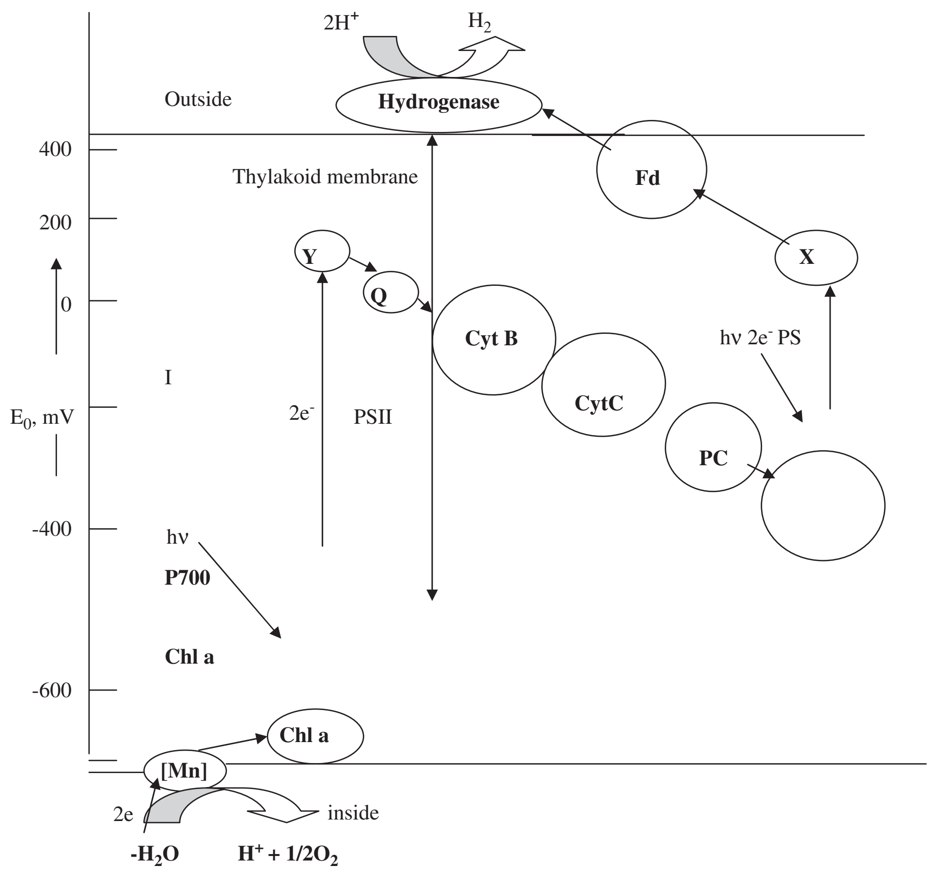


Fig. 2. Microbial fermentative process using a fluidized bed reactor.



Scheme 1. Photosynthetic process for hydrogen production: PC, plastocyanins; [Mn], manganese; Fd, ferredoxin; PSI and PSII, photosystems I & II; Y and X, primary CH acceptors of PSI & PSII; Chl, chlorophyll; Q, plastoquinone; Cyt B and Cyt C, cytochrome B and cytochrome C.

bacteria can survive in the dark by using CO as the sole carbon source to generate adenosine triphosphate (ATP) coupling the oxidation of CO with the reduction of H+ to H_2:

$$\text{Biomass} \rightarrow CO(g) + H_2O(l) \rightarrow CO_2 + H_2(g), \quad \Delta G^\circ = -20\,\text{kJ mol}^{-1}.$$

The purple non-sulfur bacteria perform CO–water gas shift reaction in darkness' converting 100% CO into near-stoichiometric amount of hydrogen. It also able to utilize CO in the presence of other organic substrates. The biomass available in nature can easily be converted to water gas (CO and H_2O) by thermo-chemical conversion.

Table 3
Hydrogen production by some bacteria

Phototropic microorganisms	H_2 evolution per hour per gram dry biomass	
	ML	Mmol
Purple bacteria		
Rhodospirillum rubrum	146	6.5
Rhodopseudomonas palustris A	54	2.8
Rh. Capsulata SL	130–150	5.8–6.7
Rh. Capsulata B 10	300–500	13.4
Rh. Capsulata L B 2	178	7.9
Thiocapsa roseopersicina	13	0.6
Cyanobacteria		
Anabaena cylindrica B 629	5–40	0.2–2.0
An.variabilis	32	1.3
Spirulina platensis	9	0.4
Green algae		
Chlamydomonas reinhardii 137 C	45	2.0
Chl. Moevussii ICC 97	8	0.4

The studies have indicated that 1 kg of cells can produce 1 kg of hydrogen per day in a bubble column or trickling bed bioreactor. Hydrogen synthesis rate by Biowater gas-shift reaction was reported as $96\,\mathrm{mmol\,H_2\,L^{-1}\,h^{-1}}$ as compared to $20–50\,\mathrm{mmol\,H_2\,L^{-1}\,h^{-1}}$ by dark anaerobic fermentation process. It has been estimated that the processing cost of hydrogen production by Biowater-gas shift process would be $\$3.4\,\mathrm{kg^{-1}}$ as compared to other biological processing cost at around $\$\ 12–20\,\mathrm{kg^{-1}}$.

3.2. Ethanol as biofuel from biomass

The history of ethanol as a fuel dates back to the early days of the automobile era. However, cheap petrol (gasoline) quickly replaced ethanol as the fuel of choice, and it was during the late 1970s, when the Brazilian government launched their "Proalcool" Programme, that ethanol made a comeback to the market place. Today, fuel ethanol accounts for roughly two-thirds of world ethyl alcohol production.

Ethanol is a comparative cleaner burning fuel with high octane and fuel-extending properties. Although blending of ethanol with petrol enhances the volatility of the mixture, on the contrary, ethanol reduces the carbon monoxide emission from vehicles. The use of petrol blended with 20–24% ethanol is a standard practice in Brazil. Therefore, it is highly desirable for a country like India to use ethanol–petrol blend as transportation fuel to save valuable foreign exchange in importing crude oil as well as in reducing the environmental pollution caused by the vehicular emission.

Ethanol production and its utility in the world scenario are shown in Fig. 3. India produces 1.3 billion liters of ethanol from cane molasses against an installed capacity of 3.2 billion liters currently. Besides a substantial consumption for portable purposes, nearly 50% of total ethanol production is also used as a feedstock for the chemical industry in India. The detailed data are given in Table 4. The market size of the alcohol-based chemical industry in India is about US$1.2 billion. Growth in world ethanol production crucially depends on the development of the fuel-alcohol market. Spurred on by the Brazilian "Proalcool" Programme and the US Gasohol scheme, output jumped in the early 1980s, and growth continued at very strong rates up to the mid-1990s. In 1998, fuel-alcohol production fell sharply due to the crisis in the Brazilian alcohol sector, which was not compensated for by the record output in the US.

Requirement of ethanol in the first phase of the programs on 5% blending in petrol in India, was 3.45 billion liters a year, which could have gone up to 5.00 billion liters had the program been introduced throughout the country. Due to non-availability of enough molasses in India, it is not possible to meet the requirements. So there is need to switch over to other biomass sources for ethanol production. Some of the important biomass, which can be used successfully for the production of ethanol, are listed in Table 5.

Few varieties of biomass are not available throughout the year, thereby affecting the productivity. Fig. 4 shows the comparison of production of ethanol from different biomass per year and per harvest (Fig. 5).

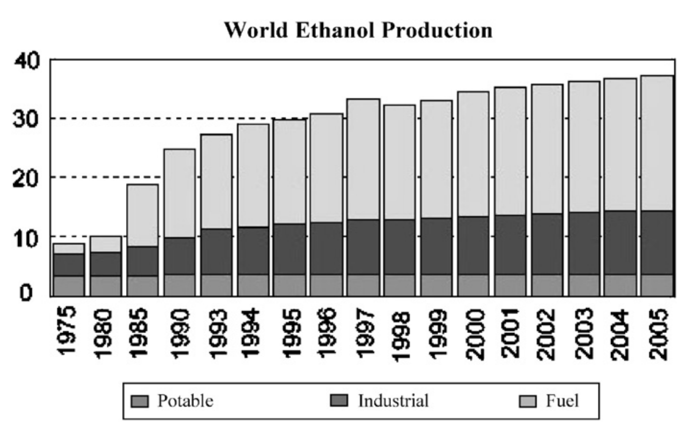


Fig. 3. Ethanol production and utility.

Table 4
Ethanol availability per year

Year	Sugar	Molasses	Ethanol (billion liters)	
	MMT	MMT	Potential	Actual
1998–99	15.5	7.1	1.59	1.30
1999–00	18.2	8.0	1.80	1.38
2000–01	18.8	8.5	1.98	1.40
2004–05	12.5	5.8	2.0	1.14
2005–06	24.7	11.3	2.54	2.30

Table 5
Potential biomass for ethanol production

Biomass source	Composition of biomass (wt%, dry basis)				
	Sugars	Cellulose	Hemicellulose	Lignin	Others
Bagasse	3	38	27	20	12
Molasses	61	–	–	–	39
Sugarcane prepared	43	22	15	11	9
Sugarcane leaves	–	36	21	16	27
Sugarcane whole	33	25	17	12	13
Napier grass	–	32	20	9	39
Sugarcane hybrids	28	37	14	15	6
Sweet sorghum	34	36	16	10	3
Eucalyptus grandis	–	38	13	37	12
Eucalyptus saligna	–	45	12	25	18
Leucaena leucocephala	–	43	14	25	18
Municipal solid waste	–	33	9	17	41
Newspaper	–	62	16	21	1

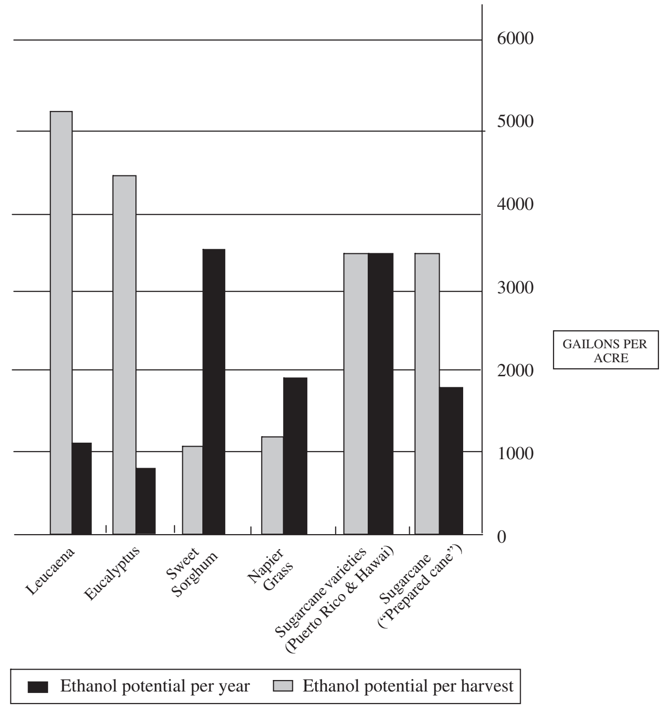


Fig. 4. Ethanol production per year and per harvest.

3.2.1. *Biomass to ethanol: technology*

There are many options available at each of the steps of ethanol production from biomass. Several government laboratories, academic institutions and private sector companies have devised various techniques to accomplish each of the steps required to process the biomass to ethanol. Because of the relatively high cost of gasoline in India (as compared to international price), opportunities to produce biomass year round, and the potential of land becoming available due to the stagnant of the sugar industry, India has gained the attention of several of these organizations.

There are different technological options available for the techno-economically feasible process for ethanol production from biomass. The options at each step of the biomass-to-ethanol processes are illustrated in Fig. 6. Nevertheless, combination of appropriate option at each step of the entire ''Systems'' would provide successful technology for biomass-to-ethanol production.

3.2.2. *Ethanol from molasses*

Production of ethanol from molasses requires three major steps:

(1) hydrolysis,
(2) fermentation and
(3) ethanol recovery.

3.2.2.1. *Hydrolysis*

3.2.2.1.1. Enzymatic hydrolysis of lignocellulosic waste. Microbial degradation of lignocellulosic waste and the downstream products resulting from it is accomplished by a concerted action of several enzymes, the most prominent of which are the cellulases. For microorganisms to hydrolyze and metabolize, insoluble cellulose, extracellular cellulases must be produced which are either free or cell associated. Three major types of cellulase activities are recognized [21,22]:

(1) Endoglucanases (1,4-β-D-glucanohydrolases)
(2) Exoglucanases
  (a) Cellodextrinases (1,4-β-D-glucan glucanohydrolases)
  (b) Cellobiohydrolases (1-β-D-glucan cellobiohydrolases)
(3) β-Glucosidases (β-glucoside glucohydrolases)

Endoglucanases cut at random at internal amorphous sites in the cellulose polysaccharide chain generating oligosaccharides of various lengths and consequently shorter chains appear. Exoglucanases act in a processive manner on the reducing and non-reducing ends of the cellulose chains liberating either glucose (glucanohydrolases) or cellobiose (cellobiohydrolase) as major products. Exoglucanases can also act on microcrystalline cellulose peeling of cellulose chains from the microcrystalline structure [23]. β-Glucosidases hydrolyze soluble cellodextrins and cellobiose to glucose. The cellulase system of *Trichoderma reesei* consists of at least two exoglucanases, five endoglucanases and two β-glucosidases.

Cellulase enzyme is commercially available from other manufacturers such as Valley Research Inc. under the trade name, *Validase TR Concentrate*, and *Cellulase 4000*; costs of their product ranges from \$33–48 kg in 25 K lots with the enzyme activity of 30,000 unit g^{-1}.

3.2.2.1.2. Concentrated acid hydrolysis process. This process is based on concentrated acid de-crystallization of cellulose followed by dilute acid hydrolysis to sugars at

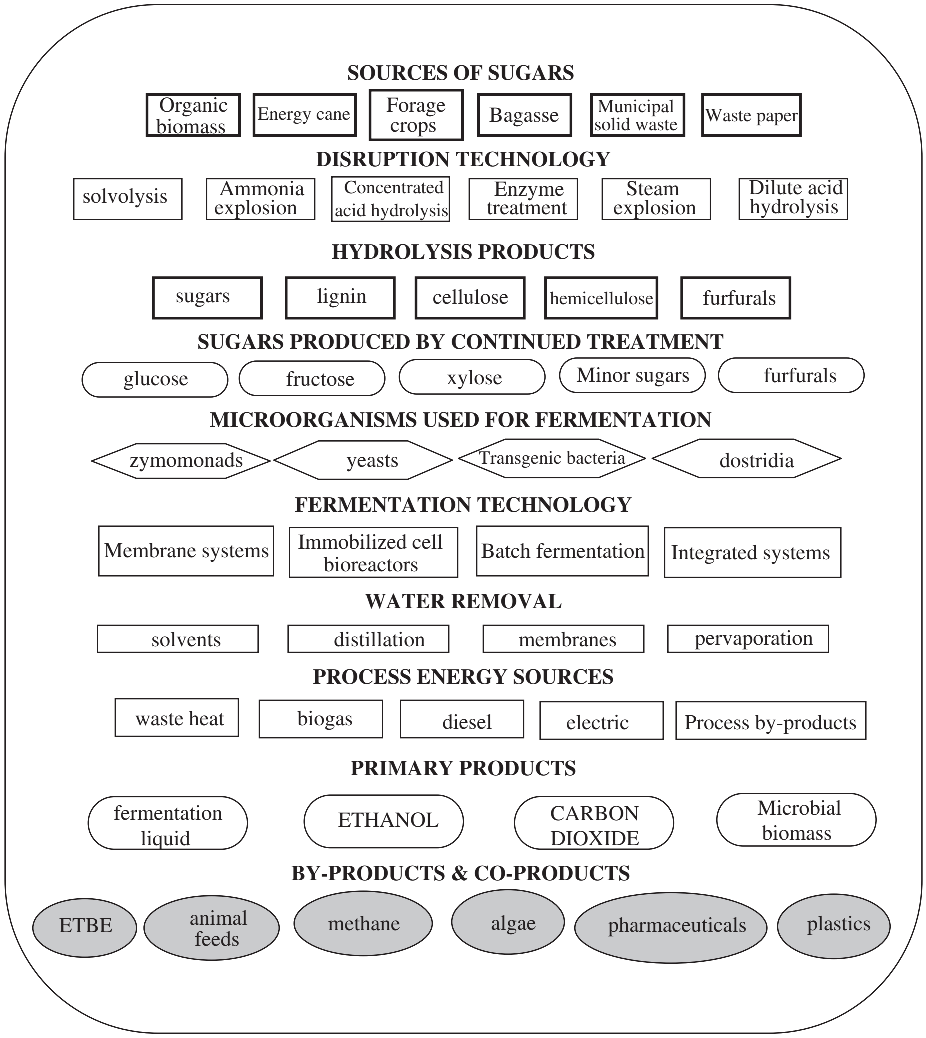


Fig. 5. Different steps of biomass to ethanol.

near 85–90% theoretical yields. Separation of acid from sugars, acid recovery and acid re-concentration are critical unit operations [24,25]. Fermentation converts sugars to ethanol as in Fig. 6.

3.2.2.1.3. Dilute acid hydrolysis. The dilute acid hydrolysis process is one of the oldest, simplest and most efficient methods of producing ethanol from biomass. Dilute acid is used to hydrolyze the biomass to sugars. The first stage uses 0.7% sulfuric acid at 190 °C to hydrolyze the hemicelluloses present in the biomass. The second stage is optimized to yield the more resistant cellulose fraction. This is achieved by using 0.4% sulfuric acid at 215 °C. The liquid hydrolates are then neutralized and toxic compounds are removed before fermentation of sugar solution to ethanol [26,27].

3.2.2.2. Fermentation processes. Different fermentation processes are

- batch processes,
- semi-continuous processes and
- continuous processes.

3.2.2.3. Ethanol recovery. Ethanol concentration and purification is an expensive step in industrial alcohol production as distillation is a large energy consumer. The use of bioethanol as a liquid fuel has been questioned on the basis of that the energy required for distillation is equal to the total combustion energy of the alcohol product. Further, new processes now under development may improve distillation or replace it entirely with more efficient separation processes [28,29].

3.2.3. Ethanol production from other lingo-cellulosic feedstock

3.2.3.1. Simultaneous saccharification and fermentation. This technology is largely associated with the research and development program of the National Renewable Energy Laboratory (NREL) in Golden, CO. The processes consist of four major steps that may be combined in a variety of ways:

(1) pre-treatment,
(2) enzyme production,
(3) hydrolysis and
(4) fermentation.

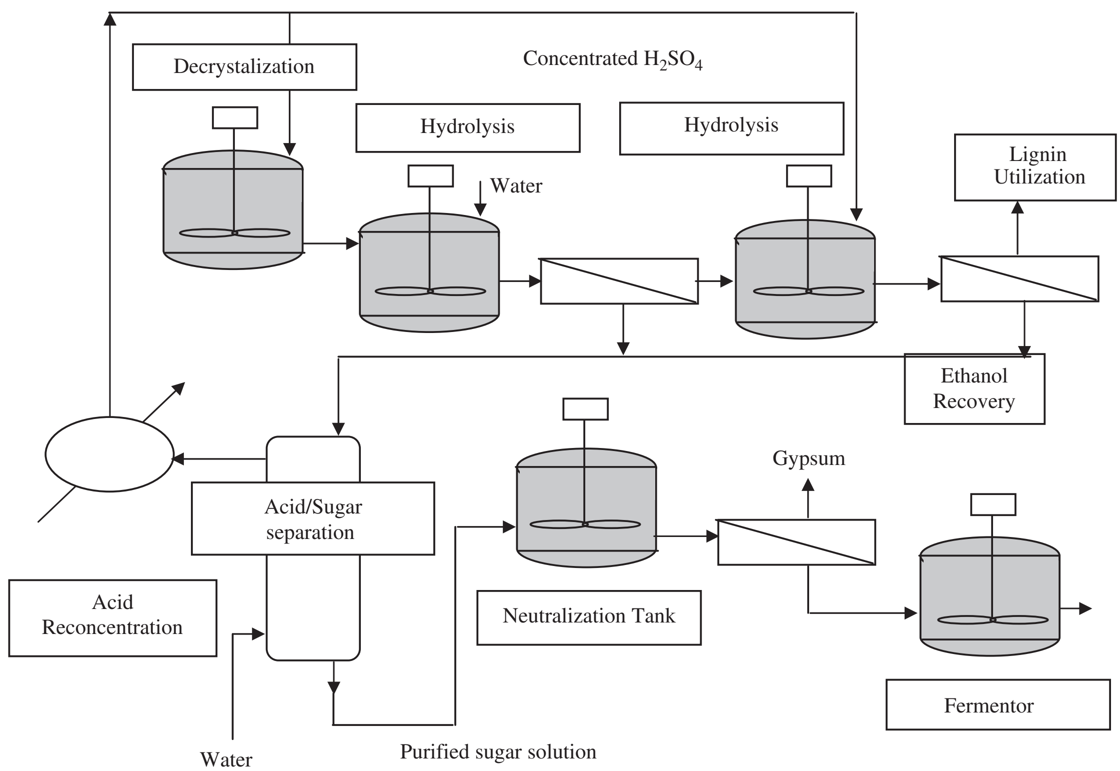


Fig. 6. Concentrated acid hydrolysis.

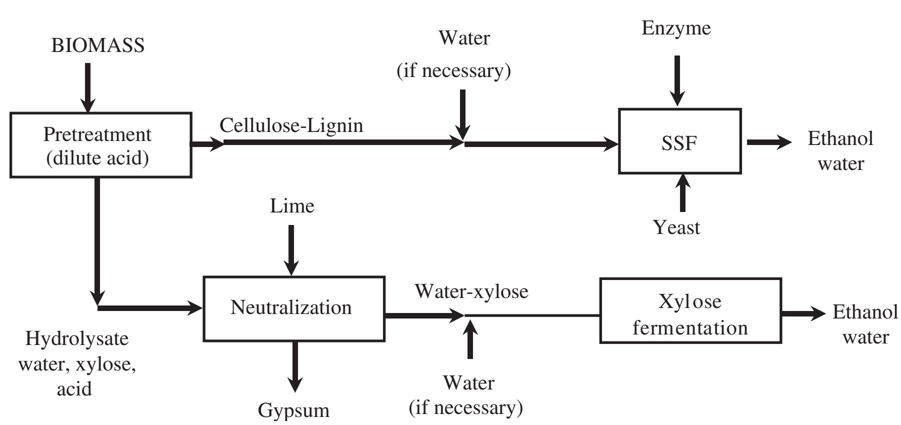


Fig. 7. SSF process developed by NREL.

The key to increasing the digestibility of lignocelluloses lies in increasing the cellulose surface area that is accessible to enzymes. By carrying out a pre-hydrolysis (dilute 1.1% sulfuric acid at 160 °C for 10 min) the hemicellulose fraction is removed (93% of the xylan is hydrolyzed resulting in fully digestible cellulose pulp) enlarging pore size and thus opening the structure to attack by enzymes. In the SSF process, enzymes that break down cellulose are produced separately by the fungus *T. reesei*. Yeast and the enzymes are added to the remaining material where the enzymes digest the cellulose to produce glucose. Glucose is then fermented by yeast or other microorganisms to produce ethanol as shown in Fig. 7.

The unique aspect of the NREL approach is that the microorganisms and the enzymes are present in the same system [30].

3.2.3.2. Simultaneous saccharification and vacuum recycling. IIT Delhi developed a process involving SSF followed by removal of ethanol by vacuum distillation. Details of the process are shown in Fig. 8. The SSF reactor is coupled to a settler and a flash vessel operated in conjunction with a vapor recompression system. The operation was programmed to work between two discrete steps, namely, (i) vacuum to remove the bulk of the ethanol produced and (ii) feeding of fresh lots of cellulose equivalent to the ethanol removed. The average concentration of ethanol obtained in the fermented product is 12.4 wt% and ethanol productivity of 4.4 g L $^{-1}$ h^{-1}.

3.2.3.3. Acid disruption and transgenic microorganism fermentation (Quadrex process). Bioenergy International, L.C., a subsidiary of Quadrex Corporation, posesses the exclusive worldwide license for a constructed set of genes that when inserted into a microorganism has the ability to ferment both pentose (5-carbon sugars) and hexose (6-carbon sugars) [31,32]. The detail of this process is shown in Fig. 9.

3.2.4. Bio-ethanol production from starch

Corn and cassava as the most potential starch-based feedstocks so far have been used for the production of ethanol. Ethanol production from corn-starch has been developed by DOE and NREL in USA whereas cassava-based ethanol production has been reported in Thailand. To produce ethanol, starch is initially converted to fermentable sugars, namely, glucose by the enzymatic process. The sugars are then fermented to ethanol by suitable ethanologens, similar to fermentation of cane sugar or molasses.

Two technologies are available for the conversion of corn or cassava chips to fermentable sugars:

(1) Wet-milling process
(2) Dry-grinding process [33].

4. Conclusions

As biomass is a potentially reliable and renewable energy resource, biomass-based energy fuel is being considered as

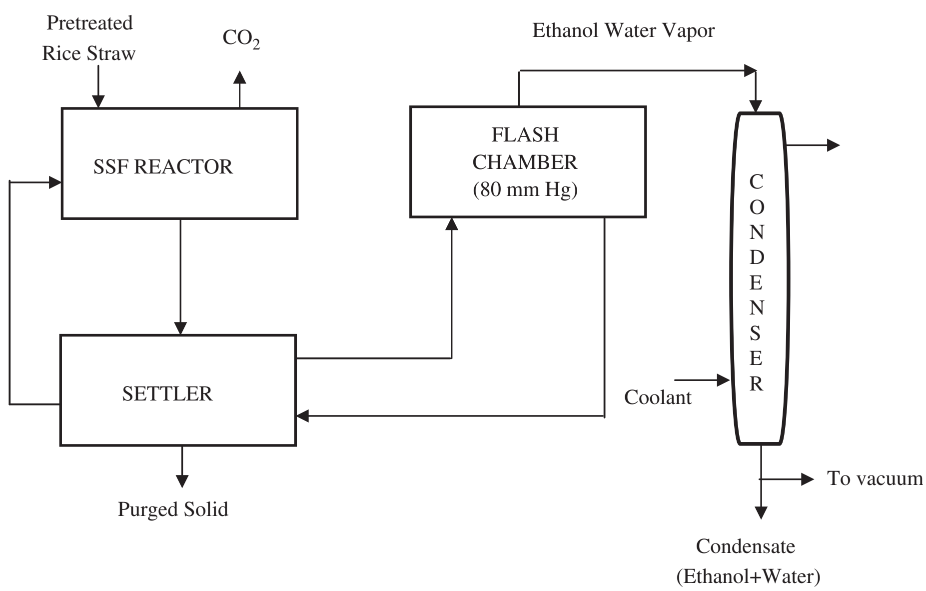


Fig. 8. Ethanol by SSF and vacuum recycling.

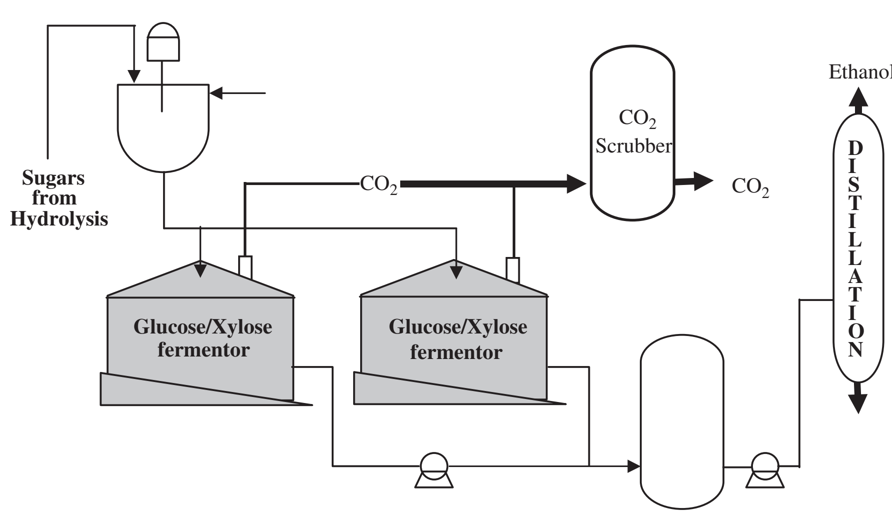


Fig. 9. Acid disruption and GM ethanologens.

one of the most promising energy carrier of the future generation. India has resources to meet the demand by using various agricultural products or residues such as sugarcane juice, molasses, bagasse, sweet sorghum, cassava and energy biomass. Various studies have been carried out aiming at the production of new generation biofuel through different routes.

Considering hydrogen production from biomass through biochemical routes, dark fermentation is more versatile than photosynthesis process as there is high energy demand for the use of nitrogenase enzyme, low solar energy conversion efficiency and substantial land requirement for anaerobic photo-bioreactors. However, hydrogen production rate is higher by biological water gas-shift reaction than dark fermentation process using bubble column or trickling bed bio-reactor consequently decreasing the hydrogen production cost as compared to other biological processes.

Fuel ethanol requirement in India for the transportation sector has been projected around 12 billion liters per annum by 2007 considering 10% blending to petrol and diesel. The most critical element for the success of bio-ethanol technology is the availability of celluloses at a nominal cost. Major R&D effort is required to produce cellulase with high yield and productivity. Alternatively, thermo-tolerant high activity liquefying and saccharifying enzymes (α-amylase and glucoamylase) would be required for the development of cost-effective starch-based ethanol production in India.

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