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REVIEW

Choice of Pretreatment Technology for Sustainable Production of Bioethanol from Lignocellulosic Biomass: Bottle Necks and Recommendations

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Abstract

Sustainable and renewable resources are inevitable factors for biofuel production to meet the energy and transportation fuel demand of a nation. The urge in meeting the energy demand can be achieved by intensified research on agricultural and waste biomass utilization. In recent days, advanced agricultural practice throughout the world generates surplus biomass residues and this can be utilized through aggressive pretreatment technology for bioethanol production. Bioethanol production from food crops was having some ethical issues on cost and availability of potential sources. It has been anticipated that the lignocellulosic biomass to bioethanol transformation process contains several challenges and bottlenecks. Selection of an appropriate of pretreatment technology for individual lignocellulosic biomass decides the economic feasibility of biofuel production process. Scientists from different countries were working on the development of biofuel production in sustainable manner, but the technology abides only at a demonstration level due to lack of process intensification. Recent advancements in processing and conversion of biomass dealt with integration of conventional pretreatment principles to vanquish the bottleneck issues faced in development of sustainable biofuel production technology. This paper reviews the development of intensified pretreatment technologies with their current status and advancements. Several key processes and recommendations for cost-effective and eco-friendly pretreatment technologies were also discussed in details.

Keywords Lignocellulosic biomass valorization · Bottlenecks · Economic feasibility · Intensified pretreatment technology · Hybrid pretreatment technologies

Introduction

Energy is an essential sector for the development of socio-economic status of a country. Heavy depletion of fossil fuel and its environmental issues triggers high demand for biofuels in the global market. Biofuel production from lignocellulosic biomass (LCB) residues would be a promising way to keep the energy security of a country. Both developed and developing countries significantly contributing to the biofuel research for cost effective and eco-friendly bio-fuel production technology. Though, the energy equivalent of ethanol is 68% lower than the gasoline fuel with high octane content, the carbon emission rate of ethanol has made it to become a potential alternative to fossil fuel [1]. Mass balance of CO_2 utilization and emission by bioethanol blend is less compared to fossil fuels, i.e. bioethanol blend improves manual recycling of CO_2 with negligible emission rate into the atmosphere [2]. Utilization of edible crops for bioethanol production creates societal issues related to the availability and price hike of food crops [3]. Hence, the surplus agro-industrial residues would be an alternative resource for the second generation bioethanol production which are treated as waste in most cases.

More than 64 countries have been involved in various active programmes to utilize bio-ethanol as a primary fuel source. Ethanol blending varies from one country to another as low as 5% (E5) to 100% (E100). The world ethanol consumption rised to 100 billion liters in 2014 from 74 billion liters in 2009. Several nations have been implemented the

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bioethanol blending program in gasoline fuels. For example, china fixed a target of 10% ethanol blending by 2020, US fixed the bioethanol production target of 164 billion liters per year for blending and India fixed the target of 20% biofuel blending by 2017. Though we have a surplus agricultural residues the policy is still under execution due to lack of sustainable process technology and notable technologies are under demonstration level [4].

Valorization of lignocellulosic biomass (LCB) as bioethanol involves preprocessing and pretreatment steps to enhance the accessibility of hydrolytic enzymes. Pretreatment process will generate substantially more lignin as byproduct from lignocellulose, therefore various research activities have been carried out to convert them as value-added products in a sustainable way [5]. The exposed cellulosic polymers will be hydrolyzed to simple sugar moiety by the action of complex cellulolytic enzymes. This process accompanies one-third of the overall production cost. Numerous strategies for biofuel production process have been examined so far to vanquish the obstacles faced in sustainable production technology such as generation of inhibitor compounds [6], enzyme cost and reusability [7] and recycling of spent pretreatment liquor comprising of residual chemicals [8].

Energy input for biofuel production process depends on the type of biomass feedstock used such as molasses, Straw and corn stover. However, in most of the production process, high energy input have been spent to yield a lower energy product, which significantly influence in the overall production cost. This can be compensated through byproduct valorization integrated with bioethanol production. An innovative and intensified biorefinery technology must be developed for effective utilization of multiple substrates in a single processing system. This review paper provides a deep insights on global biomass availability, advanced pretreatment technology in biofuel production, bottlenecks and challenges in biofuel production and potentials of process intensification on sustainable biofuel production.

Compendium on Availability of Lignocellulosic Resources

Biomass based energy is an inevitable factor for energy in most of the countries due to lack of fossil fuel resources with them. They rely on agricultural residues such as rice straw, baggasse, stover and other crops. Secured and consistent biomass availability is one of the important key prerequisites for advanced biorefinery processes. The primary skeleton of lignocellulosic biomass consists structural polymers: cellulose ($C_6H_{10}O_5$), hemicelluloses such as xylan ($C_5H_8O_4$) and lignin [$C_9H_{10}O_3(OCH_3)$]n. Lignocellulosic biomasses are versatile resources providing not only biofuels, but they are also capable producing value added chemicals and industry related products [9]. Regional analysis of biomass availability is a prerequisite to estimate the economical feasibility at suitable location for a biofuel industry [10].

Agricultural Lignocellulosic Residues

Globally rice and wheat farming occupies 379 Mha and it has contributed to an increased production per capita in the irrigated lands. In general agricultural practices, the harvested wheat and rice straw will be left over in the fields. These residues are used for animal feed and for several other purposes such as thatching material for houses and fuel. In recent days mechanized harvesting activity releases enormous straw residues which farmers prefer to burn in-situ else the residues would interfere with tillage and seeding of next session crops [11]. Burning of crop residues should be avoided because it leads to serious environmental and health hazards such as air pollution, accelerated losses of soil organic matter (SOM) and reduces fertility by vanishing soil microbial activity [12]. Burning of residual biomass in mass level leads to increased respiratory problems and irritation in eyes due to the smoke [13].

As per OECD-FAO’s recent statistical analysis for 2017–2026 details the world cereal production was estimated to be 2563 Mt and annual wheat and rice production is 742 and 495 Mt subsequently [14]. Rice and wheat production is considerably increasing in their average production levels. The production of other Coarse Cereals is estimated to be 301 Mt. Residue to product ratio for agricultural practices have been reported in the range of 0.416–1.875 in parts of Thailand and other Southeast Asian countries [15]. Hence, they can be utilized for the purpose of biofuel production. The generation of agricultural residue is based on the variety of crop and region, it is estimated that 50–80% of the residues were collected from the harvested land. The statistical results of OCED-FAO agricultural outlook 2017–2026, depicts the annual residues of wheat and rice crop produced subsequently would have been 1336 and 891 Mt approximately in 2017 throughout the world. These residues constitute a major part of total biomass residues produced annually through agricultural practices and they are vital source of energy for domestic as well as industrial purposes. Wheat and Barley production in Turkey is estimated at 19.5 and 7.0 Mt respectively for 2017–2018. Wheat and rapeseed production in Australia is estimated as 23.5 and 3.2 Mt respectively for the year 2017–2018. Corn cultivation in Vietnam and Argentina is estimated at 5.6 and 42.0 Mt respectively for the year 2017–2018. The report from Foreign Agricultural Services (FAS) and World Agricultural Supply and Demand Estimates (WASDE) explain the global scenario of each crop production every year. Food crop residue such as Jowar, Bajra, Maize, Ragi, Barley, Gram and Sugarcane are also occupies a unique position in Asian countries, the residual biomass can also be used for the biofuel production. Indian Ministry of Agriculture, in post-harvest of sunflower article issued on 2005 reported that India occupies unique position in oilseed crop production in the world, especially sunflower seed is one of the most important oilseed crop cultivated in India. This accounts for 4.77% (1250 thousand MT) of total world production of sunflower in 2004. Silver leaf sunflower is a drought resistant wild species that produces larger, more solid stems and grows up to 4.5 m tall [16]. Post harvesting practices were not concentrating much on the residue collection. Many researchers were focusing on to utilize those residues as potential source for the biofuel production.

Forest and Wood Processing Residues

Woody biomass from forest and wood processing areas can be used as feedstock for biofuels production, and has several advantages over the other feedstocks: its use does not affect food availability or price, and the transformation into biofuel can have a more favorable energy balance. Forest residues consist of branches, leaves, lops, tops, damaged or unwanted stem wood of a tree which remains in the forests. Woody biomasses are broadly classified into two categories like softwoods or hardwoods. Gymnosperm trees are considered as softwoods because they possess lower densities and grow faster than hard wood [17]. Angiosperm trees are considered as hardwoods and they are mostly deciduous [18]. In Sweden there is a notable recovery of residues in the form of wood chips (bulk density about 300 kg/m^3) for industrial and domestic applications. The use of processed wood residues for power generation through burning will not only improves value of the residues but also deprive a part of the population [19]. As per FAO report most of the wood processing mills were considering the waste generated during sawmilling operation as a troublesome by-product and disposed as landfill or incinerated in burners. The energy produced by burning wood residues [17–23 MJ/kg (dry weight)] [20] is less compared to the energy produced by oil or gas (43.5 MJ/kg). In whole tree processing only 28% becomes lumber and the remaining being discarded as residues. Potential residues generated during raw wood processing are shown in Table 1 [21]. The major advantages of woody feedstock over the agricultural residues are high packing density, lower pentose sugar content and minimal ash content [18, 22]. The world's total biomass resource in forests amounts to 420 billion tonnes, of which more than 40% is located in South America. Estimates by FAO (2000) show that global production and use of wood fuel and round wood reached about 3300 (10^6) m^3 in 1999. Biomass from forest and wood processing industrial production are the good sources for second generation bioethanol production.

Table 1 Potential Residues from forest and wood industries [21]

Wood product and residues	Portion (%)
Top, branches and foliage	23.0
Stump	10.0
Saw dust	5.0
Slabs, edgings and off-cuts	17.0
Saw dust and fines	7.5
Various losses	4.0
Bark	5.5
Saw timber	28.0
Total	100.0

Food Industrial Residues

Globally, food production to feed a growing population is believed to double in the next era. Large volumes of solid and liquid residues are generated from the food processing industries. According to U.S. Department of Agriculture (USDA), 55% of the total food loss is contributed by fresh and processed fruits and vegetables, fluid dairy products, and meat. The remaining 45% loss of food is from grain products, caloric sweeteners, fats and oils and other foods. Annually, ~ 1.3 billion metric tons of food waste is generated worldwide which is estimated to increase in connection with growing population. Lignocellulosic food residues are mainly generated from alcoholic beverage industry, Saladin or malt filtration waste, fruity squeezed cake and rotten fruit in wine production. Sectoral report of India Brand Equity Foundation on July 2015 declares that the Indian food industries are facing huge growth and increasing its contribution in global food requirement every year. Food industries accounting for 32% of the India's total market [23]. Grain processing industries has generated 24 kilotons of waste, in which 90% of waste is dumped and remaining 10% is used for animal feed. Sugar industry generates different types of waste at different stages like sugar beet leaves and peals correspond to 142–400 kilotons/year, sugar beet cake corresponds to 240 kilotons/year, Molasses correspond to 30 kilotons/year. Sugarcane residues has a great potential as a cellulosic biomass for bio-ethanol production in the country due to its surplus availability. The waste generated from citrus fruit industries were estimated to be 21 million tons per annum, in which 7.13 million tons are being produced in Indian food processing industries as per Food and Agriculture Organization (FAO) of the United Nations. High fermentable sugar content and low lignin content of citrus peel can be a suitable feedstock for bioethanol production in future [24]. Along with this, starch based food such as noodle contributes significant amount of waste generation in Korea. In South Korea 2.1 kilotons of noodle residues were disposed as waste in 2011. For instance, in other developing countries like china, major cities Taipei and Seoul are producing 182 and 767 kilotons/year of food wastes respectively. In Brazil, US, India, China, Korea, and in many other countries plenty of food wastes are available. Thus, the future research can be focused on available food industrial lignocellulosic waste materials for the production of second generation Biofuels.

Other Lignocellulosic Biomass

The cellulosic fraction of the municipal solid waste (MSW) can be a potential source for the bioethanol production due to their availability, but handling of MSW presents some challenges. It is an inexpensive source of organic biomass and this includes domestic and industrial waste. A maximum potential production of 30 metrictons of ethanol could be achieved from 50% of the 180 million tons of MSW currently produced annually in Mediterranean countries [25].

Oil palm industries occupies significant place in island like Indonesia. The waste from oil palm industries, such as oil palm empty fruit bunches or frond, mesocarp fiber, and oil palm trunk which were obtained from milling and refining activities. In palm oil processing only 10% of the total dry matter was converted to oil, remaining 90% being oil palm biomass which can be utilized for the biofuel production. Based on recent survey, palm oil products reached a sum of 25.64 million tonnes [26].

Processing of Lignocellulosic Biomass for Bioethanol Production

Production of second generation biofuel requires continuous availability of LCB throughout the year. Long time exposure of lignocellulosic biomass into the environment has led to loss of fiber content by natural processes. Thus, it is an important consideration to process the biomass with adequate storage measures. Biomass processing unit should be applicable to large quantities of biomass as well as for range of biomasses like hard wood to straw residues [27]. Generally, transformation of LCB to bioethanol comprises of three important stages: (i) pretreatment, (ii) saccharification and (iii) fermentation of sugars to ethanol [28]. The bottleneck issues and recommendations for sustainable production of biofuels from various sources are listed in Table 2.

Pretreatment of Lignocellulosic Biomass

Recovery of fermentable sugars from LCB is an energy intensive process and far more difficult than first generation feedstocks [27]. In this stage, energy consumption, chemicals, and other requirements account for approximately 33% of the total production cost [39]. Pretreatment is a necessary step to alter some structural characteristics of lignocellulose, without losing glucan and xylan content [40]. The extent lignin deformation and cellulose recovery depend upon the choice of pretreatment technique used [41]. Deconstruction of biomass can be done by mechanical, physicochemical, chemical or biological methods [40–47]. In recent days, there are a lot of techniques have been developed to circumvent the bottlenecks in pretreatment process, but still, they are in demonstration level due to lack of process intensification. In this study, we will be discussing the advanced pretreatment technologies to overcome the problems encountered in the conventional methodologies and choice of pretreatment technology for the sustainable production bioethanol. A detailed flow diagram on advanced pretreatment technology over the conventional technology has been represented in Fig. 1.

Factors Influencing the Choice of Pretreatment Technology

Selection of pretreatment process for industrial scale bioethanol production is depending on the following factors: (i) nature of lignocellulosic biomass, (ii) heterogeneity of lignin polymer, (iii) generation toxic Inhibitor compounds, (iv) higher energy requirement to yield a lower energy product, (v) recycling of chemicals used and (vi) waste management [48]. Several factors were considered while choosing an effective pretreatment technology to circumvent the problems faced in lignocellulosic ethanol production [22]. A comprehensive overviews of lignocellulose pretreatment technologies are represented in Table 3.

Nature of Lignocellulosic Biomass Nature of a lignocellulosic biomass is an important consideration while choosing a feasible pretreatment process to recover high fermentable sugar. In recent days, research and development activities have been focused on lignocellulosic feedstocks from agricultural, forest residues and municipal wastes for bioethanol production. Agricultural residues like rice straw, wheat straw and corn stalk containing more hemicellulose than woody biomass (~ 25–35%) [61]. Bio-waste streams such as municipal solid waste, packaging waste, household waste, market waste and food processing waste can also be used as biomass for bioethanol production. However, woody biomass residues with negligible ash content and high density facilitates mass transportation of biomass to production site [22]. Structural characteristics of each biomass decide the

Table 2 Bottlenecks and recommendations for sustainable bioethanol production

S. no.	Bottlenecks	Causes	Recommendation	References
1.	Availability of Feed stock	Consistent availability of feed stock throughout the year is most important for sustainable bioethanol production. This requires vast availability of agricultural land. Supply from long distance influence in the cost of biomass	To produce second-generation biofuels, considerable amounts of biomass have to be supplied. This will require analysis of existing and potential biomass resources around the production site before start-up of large-scale production. Range of feed stock should be analyzed for their suitability in under same process condition (saccharification, fermentation, etc.). Commercial bioethanol plants require large quantities of biomass (up to 600,000 tons/year)	[29]
2.	Pretreatment design	Due to higher process design and considerations in conventional pretreatment contributes major cost (32–35%) of ethanol production. Dilute acid, dilute alkali, steam explosion and hot water treatments are considerably increase the energy consumption and electricity requirement during pretreatment Poor pretreatment design will leads to decomposition of fermentable sugar and produces more inhibitory compounds	A sustainable as well as renewable power plant design should be improved with the core focus on reducing the energy consumption and toxic compound generation. This will results in increased hydrolytic efficiency and reduced costs Hybrid pretreatment technology can be developed by combining an efficient unit operation from Physical, Chemical or Biological process. This can utilize low energy with higher efficiency	[30]
3.	Enzyme cost and reusability	Cellulases and hemicellulases used in the production of cellulosic ethanol are more expensive compared to the first generation counterparts Enzymes cost comprise a significant portion of *20–40%* for cellulosic ethanol production. maize grain ethanol production cost 2.64–5.28$, cellulosic ethanol production cost 79.25$ Enzyme reusability is another factor deciding the cost of technology. Enzymes were washed away with the effluent after saccharification process	Complex enzyme sources are required for range of biomass. It is vital to develop a pretreatment technology which increases the hydrolytic efficiency with negligible loss of cellulose content Technology with potential enzyme recycling system will address the issues regarding cost factors in biofuel production	[7]
4.	Solute concentration (sugars)	Ethanol production from hydrolysates with low sugar content is associated with a high operating cost due to a more expensive distillation process and generates more waste water	Hydrolysate must be concentrated before fermentation process by various unit operations and detoxified before fermentation Increasing solute concentration will result in high ethanol titer and reduced downstream processing cost	[31]
5.	Growth inhibition and toxic compounds	Inhibitors generation in pretreatment process will negatively influence the growth of ethanol fermenting microorganisms. Inhibitors like phenolic compounds, aromatics, aliphatic acids, furan aldehydes, inorganic ions, and bio-alcohols inhibit the growth metabolism of microbes	Certain pretreatment condition liberates fermentation inhibitors such as hydroxyl methyl furfural (HMF), methyl furfurans, phenolic etc., This will negatively influence the growth of alcohol fermenting microorganisms	[32]
6.	Post saccharification process	Saccharification of sugar polymers are achieved in short time, it is difficult to control the reaction due to high reaction temperature. This leads to several problems, such as the generation of fermentation inhibitors, decrease in sugar yield due to the decomposition of sugars. Furthermore, the costs for recycling or treating the acid used are expensive Detoxification is must before going to fermentation, if not ethanol production will be reduced by inhibitor compounds	Appropriate pretreatment technology which makes enzymes more accessible to cellulose is essential .it helps in reducing the enzyme loading and costs. Advanced hydrolytic process must be developed to control the reaction condition and to prevent the inhibitor compound formation. Immobilized enzyme hydrolysis could be used for controlled reaction	[33]

Table 2 (continued)

S. no.	Bottlenecks	Causes	Recommendation	References
7.	Product inhibition	The concentration of ethanol produced during fermentation above the critical level will inhibit further product formation. Above this concentration of ethanol will trigger the feedback inhibition process which induces the production of alcohol dehydrogenase (ADH) enzyme	S. cerevisiae growth was inhibited by butanol concentration in range of 1–2% (v/v), but it is able to withstand in higher concentrations of ethanol. In high-gravity alcoholic fermentations, *S.cerevisiae* produces ethanol concentrations of 17% (v/v) or higher. Ethanol tolerant microbes must be used in fermentation process	[34]
8.	Genetic instability of foreign genes	Instability of *S.cerevisiae* genes in *E.coli* cells after few generations. Lack of efficiency to promote foreign genes leads to poor ethanol yield	GMO's must be analysed by plasmid stability studies. Modifying the pathway by inhibiting or silencing the genes responsible for enzyme production. ADH inhibition to increase the ethanol yield	[35]
9.	Metabolic pathway energy imbalance	Changes made in metabolic pathway will negatively influence in the growth and metabolic flux balance of a microbe. Metabolic engineering of an organism may have imbalanced energy elements (ATP, NADP, and NADPH) in their metabolism. Growth might be inhibited by this action	Understanding the preliminary knowledge about pathways, enzymes, and their kinetics in metabolic pathways is must before engineering microbe. Pathways that trigger the optimal reprogramming can be identified and transferred to another strain. Material balance and Energy balance should be studied before application. Thus, we should consider the energy balance of metabolic pathway like (ATP, NADP, and NADPH)	[36]
10.	Lack of resources	Fermentation of ethanol requires huge amount of water. This is necessary for washing plants and seeds and for evaporative cooling. However, they show the biggest impact on local *water availability* stems. Crops such as sugar cane, Rice and maize have relatively high water requirements and are best suited to high-rainfall areas, unless they can be irrigated. Three quarters of the Rice production in India. A typical ethanol factory producing 50 m gallons of biofuels per year requires about 500 gallons of water, corresponding to about 4 gallons of water per gallon of biofuel	Treated effluent water can be reused for other purposes with a suitable treatment. Plant should be constructed with availability of resources as per requirement like water resource and biomass supply chain. It is estimated that a typical plant requires 860 l of water to produce one liter of ethanol. However, in the United States only 5–15% of the water required for corn comes from irrigation while the other 85–95% comes from natural rainfall	[22]
11.	Health Hazardous	Introduction of GMO into large-scale fermentation operations opens up the possibility of spread in environment and risks to public health. Likewise, industrial operations using antibiotics to control microbial contaminants in fermenter or as strain markers. This would generate and release antibiotic resistant organisms and offer another potential environmental public health risk	GMO's control during fermentation process is necessary to ensure environmental protection. Microbial risk assessment (MRA) modeling is an emerging systematic and science-based method generally used to provide a qualitative and quantitative evaluation. This gives the probability of occurrence of adverse health effects originating from microbial hazard contamination in food products	[37, 38]

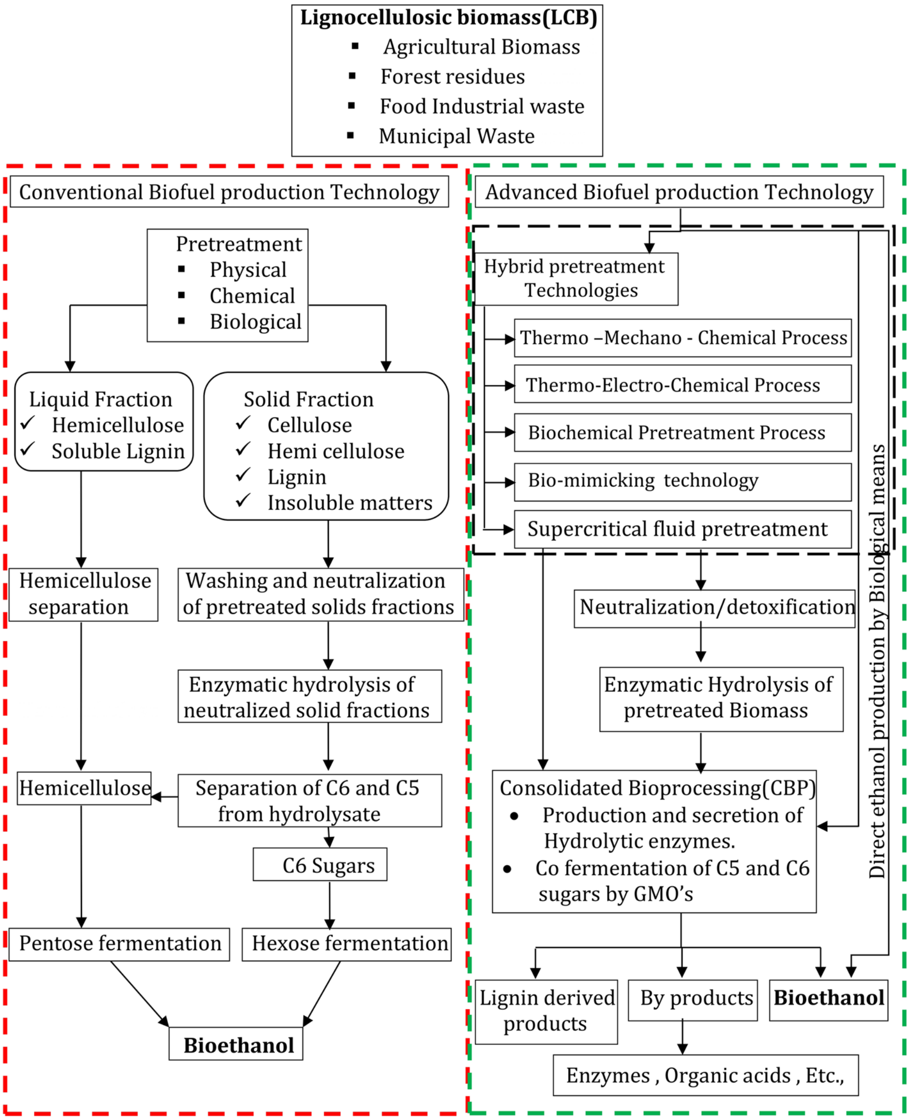


Fig. 1 Schematic representation of advanced pretreatment technology for sustainable production of second generation bioethanol

type of pretreatment required. Currently, biomass plays most important source of renewable energy and the only renewable source of carbon. According to IEA Statistics, 2008, it can provide for about 13% of total energy consumption worldwide. The major part of biomass produced every year remains underexploited. Catalyzed steam-explosion by 3% (w/w) sulfur dioxide (SO_2) on corn stover yields approximately 96% glucose and 86% xylose [62]. Besides, AFEX pretreatment on corn stover limits the formation of inhibitors when compared to other techniques [63]. Dilute acid Pretreatment of softwood have been reported that only 40% of enzymatic cellulose conversion [64]. This technology could not be employed with economic aspects for sustainable production. The selection of biomass should be based on clean, cheap, available in large quantities throughout the year, are independent of geographical location, plus it should be carbon rich and renewable and finally it should not compete with any other essential sources needed by human beings. So that selection of appropriate pretreatment technology for specific biomass is an important prerequisite for sustainable production technology.

Generation of Inhibitor Compounds Toxic inhibitor formation is a critical state during chemical and thermo-chemical pretreatment of biomass. Presence of inhibitors per level of recovered sugar is an important consideration while evaluating the pretreatment efficiency. Inhibitors present in sugar hydrolysate will negatively influence the ethanol productivity during fermentation and affect the cell growth [65]. In sulfite pretreatment, formed inhibitor level was low when compared to dilute acid pretreatment because of alkaline pH environment caused by sulfite ions [66]. Sugar recovery during thermo-chemical pretreatment is often low due to the decomposition of pentose to furfurals and other fer-

Table 3 Feasibility studies on various pretreatment technology for sustainable bioethanol production

S. no.	Pretreatment technology	Capital cost	Toxic compound generation	Sugar recovery	Solid loading capacity	Applicability to range of biomass	Pilot scale operation	Remarks	References
1.	Liquid hot	L	L	61.4% glucose	10–12%	No	Yes	High water consumption and energy input	[49]
2.	Organosolv	H	H	90.1%	16%	Yes	Yes	Pressure maintenance is required for low boiling point solvent pretreatment	[50]
3.	Wet Oxidation	H	L	96%	6–8%	No	–	Reduced water use by skipping pretreated solid wash step	[51]
4.	Ozonolysis	H	Negligible	88.6%	5–7%	Yes	No	Oxygen and Electricity cost around 0.135 €/kg of ozone generated	[52]
5.	Co_2 explosion	H	Negligible	< 80%	20–28%	Yes	Yes	Easy recovery of Co_2. Pressure maintenance leads to increase in pretreatment cost	[53]
6.	Steam explosion	H	H(sugar decomposition)	90.2%	L	Yes	Yes	Steam generation contributes major cost. High efficiency in sugar recovery	[54]
7.	AFXE	H	L	96%	20%	No	–	Poor efficiency in biomass with high lignin content. 99% of ammonia recovery after pretreatment	[55]
8.	Ionic liquids	H	L	83.7% total sugar and 96% glucose	20–40%	Yes	–	Cost of ILs is very high and researchers working on biodegradable ILs	[56]
9.	Popping pretreatment	H/L	Negligible	87.2%	15%	No	No	Steam generation in popping pretreatment process increases the capital cost	[44]

Table 3 (continued)

S. no.	Pretreatment technology	Capital cost	Toxic compound generation	Sugar recovery	Solid loading capacity	Applicability to range of biomass	Pilot scale operation	Remarks	References
10.	Hydrodynamic cavitation	L	–	85%	Upto 12%	No	No	Cost effective treatment. High energy density can be produced in small area	[57]
11.	Extrusion pretreatment	L	L	88 to 92%	20–25%	Yes	Yes	Improved hydrolysis efficiency. Combination of pretreatment with this can enhance the sugar recovery	[58]
12.	Biological pretreatment	L	L	70–90%	50–70%	Yes	No	No capital cost required and time consumption is the only drawback. It is an Effective delignification process	[59]
13.	Microwave irradiation	H	L	73–89%		Yes	Yes	Increases sugar recovery by 17 times higher than conventional heating process	[60]

mentation inhibitors. In addition to the common inhibitor, compounds such as hydroxymethyl furfural (HMF) and phenolic compounds, glycolaldehyde have been reported as an important inhibitory compound found in lignocellulosic hydrolysates [67]. Toxic inhibitors become more significant as its concentration increases with increase of solid loadings. The effect of inhibitor compounds can be controlled by supplementation of activated charcoal to biomass hydrolysates [68]. Pretreatments like concentrated acid, Lime, SO_2 steam and ammonia-recycle-percolation were rejected by Consortium of Applied Fundamentals and Innovation (CAFI) due to toxic by-product formation and higher operating cost associated with it [69].

Recovery of Fermentable Sugar An efficient chemical or thermal conversion of LCB facilitates maximum recovery of holocellulose and significant increase in the reducing sugars yield without any loss [70]. LCB can be comminuted by a combination of mechanical process such as chipping, grinding and milling to increase the surface area. Pretreatment of wheat straw with Na_2CO_3 results in 96% of cellulose recovery and 70% of hemicellulose yield [71]. However, in case of acid pretreatment, most of the pentose sugars were converted as inhibitory compounds. It is critical parameter to maintain the solid loading in hydrolysis process. High solid loading in saccharification process leads to poor enzyme efficiency and hence, drop in yield of reducing sugars (g sugar/g biomass) [56, 72]. To maximize the recovery of sugar after pretreatment, researchers have developed a two-step pretreatment for LCB. Initial step is carried out at low temperature to solubilize the sugar polymers and then subjected to second step in which temperature is maintained above 210 °C. This is advantageous in terms of improved sugar yield and notable increase in ethanol yield during fermentation [43]. Though, 80% of the theoretical yield was achieved at the expense of increased thermal energy with a two stage process, but the overall production cost would be doubled at the same time [73]. Thus, the yield of sugar negatively impacts the economic feasibility of process [74]. An intensified pretreatment methodology must be developed to reduce the production cost by reducing the energy consumption and inhibitor formation.

Techno-Economic Feasibility Studies The techno-economic feasibility assessment of newly developed pretreatment technology should be carried in order to ensure its sustainability [58]. However, the feasibility study on recovery and reuse of components in each pretreatment is very difficult due to different underlying assumptions [75]. The techno economic feasibility study of each pretreatment technology will give an information about the capital investment and efficiency of the technology in large scale (Table 3). Comparison of glucose and xylose proportions from various pretreatment hydrolysate liquor (yield range from 85 to 100%) is also required for evaluation of feasibility of technology [76]. While adapting a new technology, it is necessary to concentrate on the key factors such as feedstock potential, pretreatment efficiency, hydrolysis rate and fermentation for techno-economic feasibility [77]. A typical pretreatment stage in biofuel production contributes about 30–32% of overall cost. This can be reduced by evaluating the efficiency of a suitable pretreatment process for a biomass prior to their application. Table 3 represents the techno-economic feasibility of different pretreatment technologies with respect to their applicability and sugar yield. This detailed overview on different pretreatment technology would be helpful while choosing a pretreatment technology for particular biomass. Among all the discussed pretreatment technologies, chemical and thermal utilization require high capital cost as well as intensified process conditions to achieve high yield. Though, the sugar recovery from thermo-chemical pretreatments reached 83–96%, the production cost are not feasible for their large scale application. In case of wet oxidation pretreatment the sugar recovery is very high, but it is limited to a specific biomass. Thus, the application of pretreatment to a range of biomass is also an important consideration for large scale development.

Most of the pretreatment strategies are developed to improve accessibility of carbohydrate polymers by destructing the lignin barrier, but they were not considering much on the residual compounds generated during acid hydrolysis or steam explosion. They are threats our environment, they must be addressed before discharging into environment. Some of the pretreatment technologies such as concentrated acid, SO_2 steam and lime were rejected by Consortium of Applied Fundamentals and Innovation (CAFI) due to their higher toxic by-product generation during process. This can be vanquished by valorizing the by-products present in pretreatment hydrolysate through proper methodologies and also this would reduce the overall production cost. Besides, successful pretreatment process the technology should be feasible for the economic viability at commercial level.

Advanced Pretreatment Technologies

Efficiency of various technologies for biomass pretreatment has been investigated tediously for last few decades. Conventional methodologies include biological, physical, chemical and physico-chemical pretreatment lacks the techno-economic feasibility. This is because consumption a conventional pretreatment require different form of energy and chemicals during pretreatment and resultant process efficiency is very low [8]. Chemical pretreatment generates more inhibitory compounds during hydrolysis and the hydrolysate need to be neutralized prior to hydrolysis process [78]. Upon considering the above discussed issues, researchers have developed some hybrid pretreatment technologies by combining basic principles of conventional technologies to lower the energy consumption for an efficient pretreatment process [43]. Combination of different principles have been represented in Fig. 2. Hybrid pretreatment technologies have been designed in such a way to overcome the difficulties faced in the conventional pretreatment process.

Thermo-Mechanical–Chemical (TMC) Pretreatment

Chemical pretreatment is the most experimented technique till date and therefore extensively used for delignification of lignocellulosic materials. Conventional methodologies include: acid and alkali based hydrolysis approaches were employed in past era but, now it is advanced with combination of principles [79]. Thermo-mechanical–chemical pretreatment proceeds in three different phases, all these were conducted in a mechanical way by twin-screw extruder. The pretreatment is initiated by alkaline method followed by neutralization phase and then saccharification begins with addition of enzymes at impregnation phase. This process is suitable for high dry cellulosic matter content (> 20%). This offers continuous operation of LCB processing and enhancing the accessibility of enzyme cocktail into the cellulose by bio-extrusion phenomenon. This hybrid technology is advantageous in terms of (i) low temperature operation, (ii) minimal energy consumption, (iii) low liquid/solid ratio, (iv) fast and tedious operating condition and (v) applicable to wide of range biomass [40]. The combination of chemical and thermal principles in a dilute acid medium at low temperature can efficiently deconstruct certain components, especially hemicelluloses present in the cell wall material. This combination of extrusion and dilute acid was successfully tested on rice straw. In case

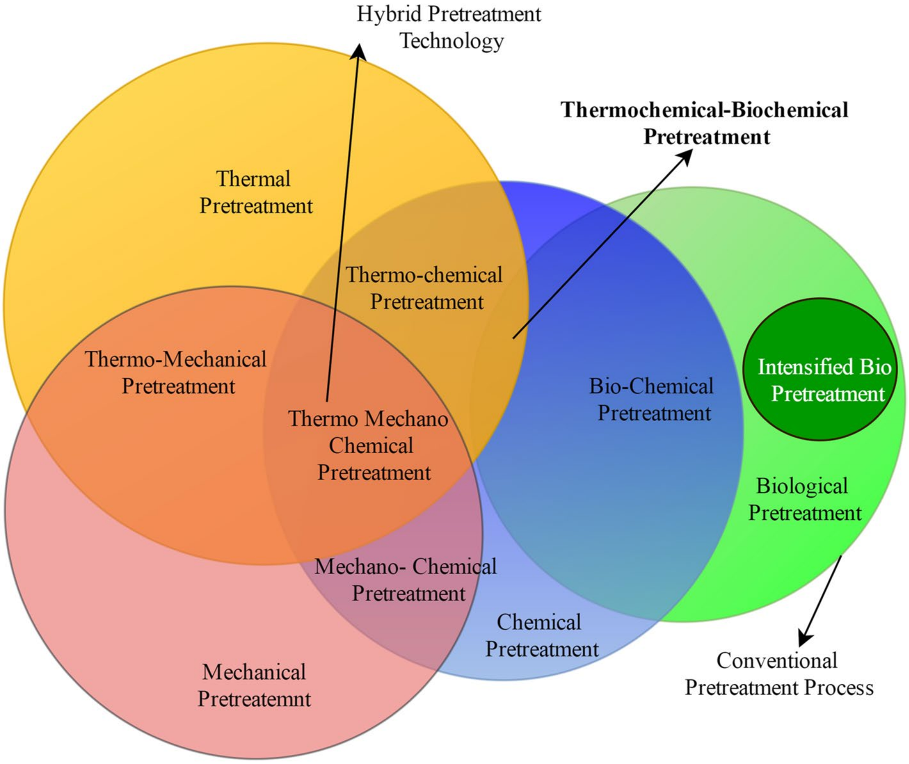


Fig. 2 Schematic representation of evolution of hybrid pretreatment technologies from conventional technologies

of, thermochemical pretreatment the straw digestibility was achieved only 35%, but in TMC with acid showed improved digestibility up to 42–50% and also the digestibility further improved to 89% with alkaline combination [80]. In TMC, capital investment and equipment design would be the limiting factors for commercial scale development. However, this can be compensated by valorization of byproducts from pretreatment.

Supercritical Fluid Extrusion (SC) The supercritical fluid extrusion has been carried out by forcing the penetration of supercritical fluids (SC) inside the cellulosic biomass (Stage 1) and subsequent explosion of SC fluid inside the biomass (Stage 2). In the two stage process, bonds between sugar polymer and lignin inside the biomass were broken. Supercritical fluid extrusion improved accessibility of biomass surface area to enzymatic hydrolysis and thus liberating high amount of sugars [81]. SC fluid extrusion pretreatment can be performed in different range of temperature from 35 to 85 °C under pressurized condition (120 atm) and facilitate recovery of sugars without decomposition. Advantage of supercritical(SC) fluid treatment are: (i) application of inexpensive fluid for pretreatment, (ii) utilizing non-toxic compounds, (iii) SC fluids can be stored in any form (solid, liquid or gas) and (iv) prevents degradation of sugars [53, 82]. Serna et al. [83], reported reduction of the lignin content in paddy straw was about 90.6% with 75% moisture content in biomass with SC-CO_2 treatment. Hence, supercritical fluid extrusion is an efficient and ecofriendly technology with an advantage of carbon dioxide recycling.

Thermo–Electro-Chemical Pretreatment

In recent days, thermal pretreatment involves direct application of an electromagnetic field in the core of biomass kept in the chemical medium. The microwaves inducing the physical or chemical reactions on heated object for deconstruction of bonds between aromatic polymer (lignin) and sugar polymers (cellulose and hemicellulose) [84]. This method combines both chemical and physical principles to break the recalcitrance of LCB with lower energy consumption. Microwave treatment with sensitizers has a powerful and selective delignification capability. The H_2O_2-activated ammonium molybdate system energized by microwave radiation is an example for thermo–electro-chemical process [85]. Pretreatment with NaOH and H_2SO_4 for Miscanthus under different temperatures (130–200 °C) showed effective results in sugar recovery. However, the yields of reducing sugars increased up to 180 °C and then declined with further increase in temperature. In this pretreatment, exposure time and temperature of microwave are the important consideration to ensure maximum sugar recovery [60]. Microwave pretreatment in mild acid concentration for 5 min incubation time released hemicellulose about 84–100 and 75% yield of reducing sugars in Norway *spruce* [86]. This technology employs microwave irradiation on biomass (corn straw and rice husk) immersed in the aqueous medium such as water, aqueous glycerol or alkaline glycerol. Among these highest sugar yield was obtained in corn straw and rice husk immersed in alkaline glycerol medium that has not been previously reported.

Verma et al. [85], reported that the carbon materials are good absorbers of microwave energy. Thus reducing the processing time, cost and energy demand to manipulate the hydrothermal environment required for pretreatment. The reducing sugar released by microwave assisted treatment is 17 times higher than the conventional heating technology in short time. In recent days, microwave irradiation is coupled with ionic liquids for efficient hydrolysis. This is an attractive hybrid technology in which application of cationic or anionic liquids (ILs) solubilized the biomass. Swatloski et al. [87], assessed the dissolution of biomass in ILs containing cations and a range of anions, including Cl^-, Br^-, SCN^-, $[PF6]^-$ and $[BF4]^-$. The result showed 25% of cellulose have been dissolved in 1-butyl-3-methylimidazolium with Cl^- after microwave heating for 3–5 s. This dissolution property of ILs have been considered for an effective biomass pretreatment. To develop a sustainable pretreatment technology with this phenomenon, researchers should investigate their effect on range of biomass. In microwave technology, sugar recovery can be optimized by altering the temperature or medium of pretreatment process. Thus, microwave assisted pretreatment in glycerol medium would be an efficient technology for effective dissolution of biomass [88].

Popping Pretreatment

Recently, new pretreatment technologies were developed to recover more sugars from complex LCB, among these popping pretreatment attracts much due to their process efficiency [89]. Popping technology was developed by combining the mechanical force from sudden explosion and certain chemical reactions. It has been carried out in very simple system consisting a direct burner and a rotary reactor without steam generator. This is advantageous over the other technologies with high saccharification efficiency and high sugar yield [90].

Wi et al. [44], investigated the effect of popping pretreatment on rice straw, which showed that the conversion efficiency of cellulose to glucose was significantly improved prior to the enzymatic hydrolysis. Under, optimized enzyme hydrolysis condition (15% substrate loading, w/v) the sugar recovery was achieved about 0.394 g/g biomass in 48 h. This is significantly high when compared to the result obtained from non-pretreated rice straw (0.270 g/g biomass). Chemical composition of the control and processed rice straw was found to be similar after pretreatment, which indicated that there is no toxic inhibitors generated during the pretreatment. Although the surface area of pretreated rice straw increased by two fold over the control rice straw and this improved the penetration rate of hydrolytic enzymes into the core of biomass. Thus, enzymatic hydrolysis rate would be improved popping pretreatment without any byproduct formation.

Bio-Mimetic Pretreatment

Bio-mimetic pretreatment technology has been conducted in-vivo or in-vitro to speed up the delignification process using specific biological reaction without employing microorganisms. This is utilizing very low energy during the process to mimetic biological reaction. Though it is economically feasible technology, it is poorly investigated by researchers. White-rot fungi is degrading the LCB by initiating the generation of hydroxyl radicals through Fenton chemistry. The same phenomenon has been used here in-vivo to deconstruct the lignin layer [91].

The Fenton reaction is an oxidative process in which iron as an electron donor, donates an electron to hydrogen peroxide. This inducing the formation of hydroxyl radical and the concomitant decomposition of H_2O_2 [90–94]. Solution phase Fenton chemistry has the potential to breakdown lignin layer effectively thereby enhancing the sugar recovery. Process conditions for this technique will vary according to the type of biomass used [92]. However, biomass treatment with high concentrations of iron and hydrogen peroxide would degrade the sugars and decrease radical scavenging. In connection to this, the rate of lignin degradation would be decreased by preventing the ferric ion reduction and further hydroxyl radical formation [93]. Hence, it is very important to optimize the concentrations of hydrogen peroxide and iron for each biomass pretreatment to improve their delignification efficiency. Bio-mimicking technology will reduce the cost and time of pretreatment process with great techno-economically feasibility. Lignin degradation have been reported as high in biomimetic technology when compared to other technologies under limited conditions [95]. To develop an effective bio-mimetic technology, there is a need for more research on biological reactions through in-vivo and in-vitro studies. The economic evaluation of typical pretreatment technology have been represented in Fig. 3.

Intensive Biological Pretreatment Technology (IBPT)

Biological pretreatment is an ecofriendly strategy which has been considered as an art of nature decaying mechanism. There are various strategies investigated so far in biological method for LCB pretreatment. They are: anaerobic digestion, micro aerobic treatment and aerobic digestion by various saprophytic fungus, bacteria and actinomycetes [96].

Intensified biological pretreatment (IBPT) employs microorganisms for the direct recovery of sugars from biomass in a cost efficient and ecofriendly way. Thermophilic digestion of organic matter is an efficient method under certain condition such as in low oxygen level, but the rate of hydrolysis is very high. Fu et al. [96], reported the thermophilic micro-anaerobic pretreatment (TMP) process not only reducing the lag phase time but also improves the hydrolytic efficiency through effective delignification. Cellulosic structure of corn straw has been partly disrupted and crystallinity index were also decreased during TMP process. Upon effective deconstruction of crystalline structure hydrolytic enzymes penetrates into the biomass and improves the hydrolysis rate.

LCB pretreatment with white rot fungi is an ecofriendly methodology with negligible power requirement and effluent generation. They are widely investigated for their main sources of peroxidases and laccase enzymes. Manganese stimulates selective delignification property of *Irpex lacteus*, which has led to increased level of glucose conversion under shorter pretreatment time. This is an innovative strategy, wherein the metal ions were added to biological pretreatment medium thereby improving the efficiency of delignification [59]. Inhibitor mediated Pretreatment strategy have been investigated by Ravikumar et al. [97], in which the grape leaves were used as a cellulase inhibitor to improve cellulose yield. Effective pretreatment strategy is always necessary to remove the surrounding lignin matrix prior to the enzymatic hydrolysis. Pretreatment of paddy straw by Pleurotus florida showed 49% of lignin degradation, whereas grape leaves mediated pretreatment process resulted 99% lignin degradation. This method not only explores a pathway to utilizing solid agro waste with high loading capacity, but also results in a valuable byproduct generation such as edible mushrooms and inhibitor compounds. This kind of pretreatment technology can be investigated more in details to reduce the cost and to recover maximum sugars with valuable by products.

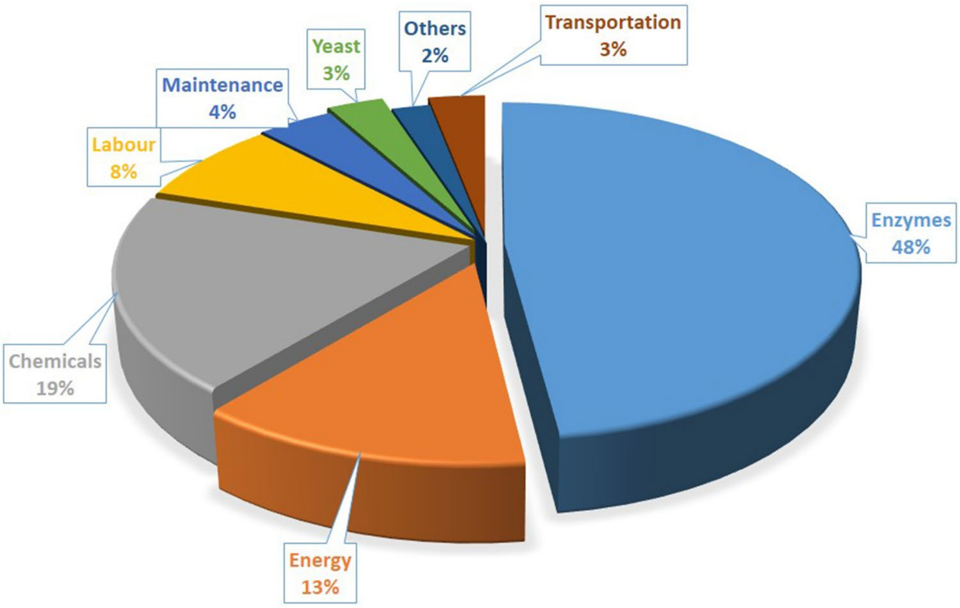
Consolidated bioprocessing (CBP) is an emerging approach with lot of advantages over the conventional biological pretreatment process. Globally, many researchers are working in the development of CBP for the biofuel production from LCB. But, the technology is still inefficient while considering for large scale operation with respect to saccharification rate and low ethanol yield. This technology combines two important unit operations such as saccharification and fermentation together to reduce the time and energy consumption. In recent days, co-culturing of different microbes on biomass as like natural environment has been conducted for the effective biodegradation of lignin [98]. In a single reactor system, co-culturing is an effective bioprocessing phenomenon because of the symbiotic relationship between the cellulose hydrolyzing microbes and sugar fermenting microbes. Park et al. [99], conducted an experiment on bioethanol production directly from cellulose through CBP approach using *Acremonium cellulolyticus* C-1 and *Saccharomyces cerevisiae* in a single reactor. The CBP experiment was carried out in 500 ml Erlenmeyer flask scale and the resultant ethanol concentration and yield were 8.7 and 46.3 g/l respectively. In 3 l fermenter 300 g of substrate was used and the resultant ethanol concentration and yield were 9.5 and 35.1 g/l respectively. Hence, it proved that the single reactor system is a reproducible process with varying concentration of biomass and this could be scaled-up for bioconversion of cellulose to ethanol in large scale. There are lot of advantages found in biological pretreatment process over the other chemical and physical process, but it is lacking the sustainability by long time duration. Hence, there is a need for more research on development of high cellulose recovery strategy and reducing the time consumption during pretreatment for a sustainable production technology.

Conclusion

Sustainable production of bioethanol requires intensive pretreatment technology for effective recovery of fermentable sugars without decomposition. Choice of pretreatment technology contributes a vital role in the cost evaluation process of whole technology, because they contributes about 30–35% of overall production cost. However, Most of the conventional technology involves application of unique principle for biomass pretreatment with lot of disadvantages such as quantity of chemicals, process cost, generation of inhibitor compounds and energy consumption.

Choosing an advanced pretreatment technology will improve the economic feasibility and recovery of sugars without inhibitors. As the evolution of advanced pretreatment technology continues to meet the fuel demand in furious way, it is necessary to figure out the bottleneck issues relevant to environmental impact and economical assessment. It is vital to analyze the pros and cons of each pretreatment technology before scale up for industrial application. Techno economic assessment will give a rough estimate on capital cost and the final fuel cost in commercial scale production. Many research findings are still in pilot scale level and demonstration plant level due to lack of detailed studies on these factors. Thus feasibility assessment studies on pretreatment process is vital for the development of sustainable technology. Although vast information about the bottle necks in biofuel technology have been reported in Table 2. While Table 3 summarizes the feasibility studies on various pretreatment technology with respect to sugar recovery and applicability to large scale level.

Fig. 3 Economic evaluation of pretreatment process



This study was focused on developing the sustainable pretreatment technology and improving sugar yield by combining different conventional approaches. Combination of various pretreatment principles has led to development of a hybrid technology to circumvent the problems faced in conventional pretreatment. Figure 2 shows the combination of different principles and development of hybrid technology. Among the different pretreatment methods, Intensified biological pretreatment and thermo–mechano-chemical are recently the most effective and feasible technologies for sustainable production of biofuels.

Twin screw extruder with supercritical fluid showed attractive results in sugar recovery. Since the technology is very efficient, pressure maintenance is the only bottleneck issue hindering the scale up with significant level of power consumption. This could be vanquished by researching more on the unit process requiring more energy. In microwave assisted pretreatment coupled with ionic liquids showed fruitful results in sugar recovery. But economically it is not feasible in terms of capital cost.

Biological pretreatment is an economically viable technology. However pretreatment process is very slow when compared to physical and chemical process. Power requirement is negligible due to absence of multimode equipment usage. Many researchers were working on the consolidated Bioprocessing approach to circumvent the pretreatment time issues. Actinomycetes, bacteria and yeast were engineered in such a way to exploit them in advanced bioethanol production process. Thus, development of hybrid pretreatment technology will address the bottleneck issues faced in the sustainable development of bioethanol production.

The choice of pretreatment technology at the fundamental level, a techno economic feasibility and sugar recovery are receiving more attention for development of sustainable biofuel production technology. The information given in this literature should be considered while developing a sustainable and efficient biomass conversion technology.

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