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Current challenges and innovative developments in pretreatment of lignocellulosic residues for biofuel production: A review

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ABSTRACT

Lignocelluloses' pretreatment is targeted for the improvement of hydrolysis of their carbohydrates, i.e., cellulose and hemicelluloses. Modification of the hardheaded structure of lignocelluloses is a fundamental stair in biofuels and biochemicals production. The high crystalline configurations of cellulose embed with hemicelluloses and lignin, give rise to recalcitrance structure. Second-generation biofuel production processes, using lignocellulosic biomass as a feedstock, is based on a three-stage process, including pretreatment, enzymatic hydrolysis, and fermentation. The pretreatment stage is the most critical, influencing, costly stage. The perfect pretreatment process is designated to provide minimum cellulosic crystallinity with remarkable low lignin content as well as inhibitory compounds through a sustainable economical process. In the present review, advances in lignocellulosic pretreatment technologies for biofuels production are reviewed and critically discussed. The article further discusses the pros and cons of the various pretreatment methodologies as well as addresses the role and impact of different process parameters associated with the pretreatment process.

1. Introduction

In the present scenario, most fuels draining in haste along with a rise in demand is derived from exhaustible fossil resources. Generally, these fossil fuels have a finite stock, and their excessive usage contributing towards pollution and directly to green-house gases emission [1–3].To overcome these issues, a nonconventional fuel resource is required that makes less harm to ecology. Energy recovery from food and non-food crops is developing field and gaining much attraction as an alternative feedstock. The main attraction towards these biological residues is because of their fewer greenhouse gas emissions as the biofuel produced is carbon neutral. Lignocellulosic residues are very popular nowadays for commercial level biofuel production [4–6].Specifically, most of the produced energy extracted from Lignocellulosic biomass residues possess almost zero greenhouse gas emissions on the life cycle path [7–9].The major components of lignocellulosic biomass comprise of vegetation-based resources, i.e., crop wastes, that yield biofuel after pretreatment and biotechnological processes [2,10–12].The biomass mainly comprises of carbohydrates (i.e., cellulose and hemicelluloses) and lignin. Lignin creates a hurdle in biofuel production as it resists the interaction of enzymes with cellulosic structure during hydrolysis. Cellulose, hemicelluloses, and lignin compositions varied for different plants. The cellulose composition changes with change of biomass sources [13]. Biofuels can be utilized in a variety of forms, including fuels (biochar and torrified product), liquid fuels (long-chain alcohols, bioethanol, biodiesel, and biobutanol) and gas products (methane and hydrogen) [3,14].The most significant and under discussion fuel at current scenario is bioethanol. Bioethanol possesses very outstanding characteristics that enhance the octane number; research octane number (RON) and motor octane number (MON) of bioethanol. The introduction of bioethanol would help the smooth burning of gasoline in Compression ignition (CI) engines as it generates less black smoke with fewer NOx and hydrocarbons emissions [15].Biodiesel and biobutanol are blended with commercial gasoline without any difficulty and engine modification. Normally, the blends of B-10 and B-20 are commercially opted [16–18].

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Nomenclature

GHG	Green House Gases
RON	Research Octane Number
MON	Motor Octane Number
CI	Compression-Ignition
SHF	Simultaneous Hydrolysis and Fermentation
SSF	Simultaneous Saccharification and Fermentation
SSCF	Simultaneous Saccharification and Co-Fermentation
CBP	Consolidated Bioprocessing
HMF	5-hydroxymethylfurfural
AFEX	Ammonia Fiber Explosion
ARP	Ammonia Recycle Percolation
IL	Ionic Liquid
NMMO	N-methyl morpholine N-oxide
EM	Electromagnetic
SSB	Sweet Sorghum Bagasse
SEM	Scanning Electron Microscopy
EROI	Energy Return On Investment
MCC	Microcrystalline Cellulose
OEM	Original Equipment Manufacturer
MM	Milli Million

Fig. 1 comes up with a bigger and clear picture, which shows a versatile range of biofuels and chemicals with minimum or no process leftovers.

The synthesis of ethanol as a gasoline alternative using lignocelluloses displays a promising alternative for the biofuel manufacturing industry. As per International Energy Agency, the fuels originated from lignocellulosic residues are characterized as second-generation biofuels [19]. Second generation biofuels possess outstanding properties over conventional fuels and with passage of time better quality can be achieved. Furthermore, due to the presence of oxygenated compounds, the first generation biofuels possess low stability when applied to biochemical processes and can cause severe corrosion and damage to the internals of engines and gasoline storage facilities [20]. Normally, two methodologies are adopted for the synthesis of biofuels, including biochemical or thermo-chemical path. Major processes involved in the biochemical production of biofuels are biomass handling, biomass pretreatment, hydrolysis, and fermentation. However, thermochemical processes can convert both food and nonfood biomass to fuel products via pyrolysis and gasification [21–23]. Hybrid systems are also under research using combinations of thermochemical and biochemical technologies. In lieu with these approaches, a comprehensive assessment on biofuel synthesis and policies is reported recently [24].

In the recent scenarios, biochemical pathway for biofuel production from lignocelluloses is getting much attention towards a mature technology [25]. Above mentioned pathway for the second-generation biofuels production is modified with slight alterations in operations [19]. These modifications mostly comprises of change in process parameters like pH, temperature, and residence time. Additionally, chemical parameters include carbon source, nutrients, acid and alkaline hydrolysis agents, and phenolic inhibitors and sugars generated within the process are also manipulated. After efficient pretreatment of lignocellulosic material, hydrolysis is done to convert cellulose into glucose. Two methods of enzymatic hydrolysis i.e. Separated Hydrolysis and Fermentation (SHF) and Simultaneous Saccharification and Fermentation (SSF) were usually carried out. The process of separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) using amylase and glucoamylase are commonly employed. In the saccharification step of the SHF process, the enzymes are more likely to be inhibited due to inhibitors present in the hydrolysate than in SSF. Additionally, the overall operation of SHF is much more complicated than that of SSF with longer reaction time. On the other hand, SSF is a one-step fermentation method that is simpler to perform and utilized less energy. Fig. 2 shows the pathways from biomass to biofuel in simultaneous hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and simultaneous saccharification and co-fermentation (SSCF).The pretreatment applied to biomass utilizes about 20–30% of overall charges associated with biofuel production. Pretreatment is a costly operation with high energy needs to meet the requirements of downstream processes like SSF and SSCF [26].

Therefore, an efficient pretreatment process must equip with the following features;

(a) For the achievement of the highest process efficiency, the energy requirements must be at the minimum level without compromising the parameters for effective operations.

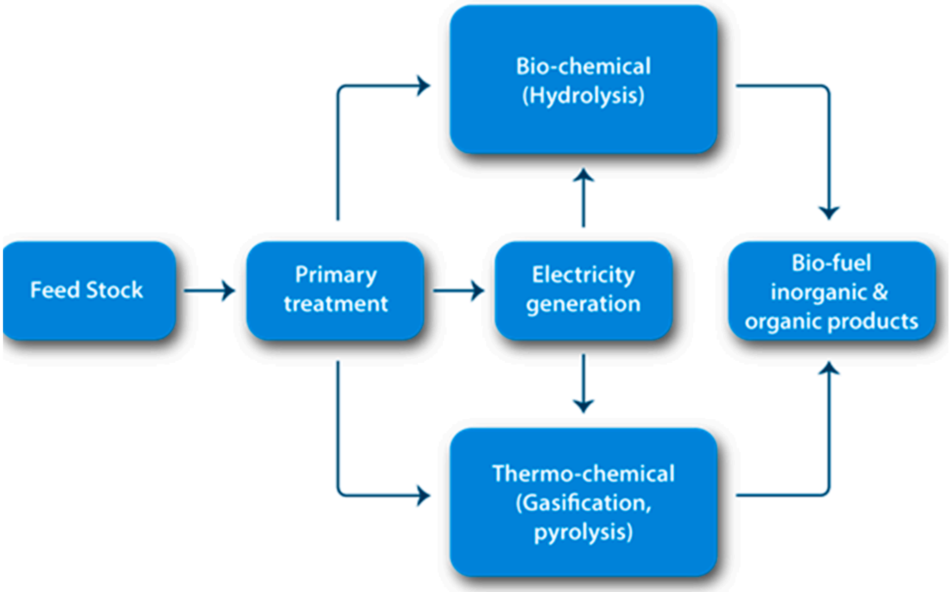

Fig. 1. Biofuel Platforms for biofuel production from lignocelluloses.

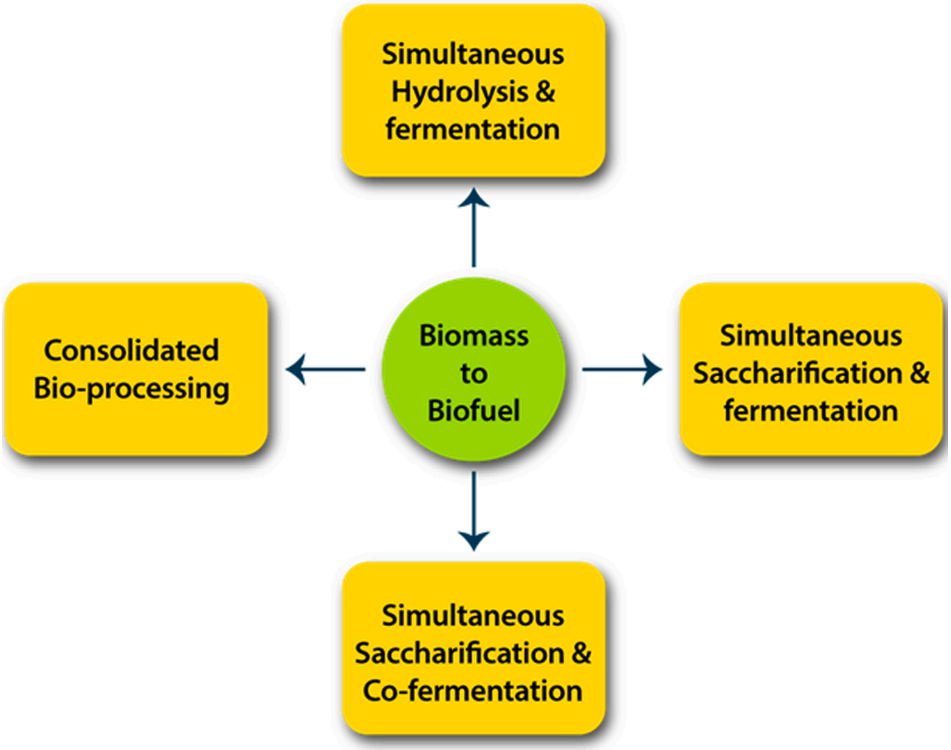

Fig. 2. Schematic of different path ways SHF, SSF, and SSCF.

(b) The design of pretreatment assures the minimum loss of sugar compounds particularly, C-5 compounds.
(c) Application of foreign chemicals must be avoided which acts as an inhibitor, which inactivates yeasts. Washing or additional neutralization steps should be applied prior to simultaneous hydrolysis and fermentation which increase operating and capital cost.
(d) For overall high process efficiency, the downstream operations must be synchronized with upstream pretreatment steps.
(e) Pre-concentration step of sugars might be necessary prior to downstream operations for overall process efficacy.
(f) The time duration of fermenting process is also accounted for efficient operations and directly linked with pretreatment phase. The optimum time duration is in between 3 and 4 days [26,27].

After pretreatment process, pretreated biomass residue is subjected to enzymatic hydrolysis or thermal degradation technique for biofuel synthesis and finally its recovery from final remains [28].Once the biofuel prepared further separation and purification processes were employed for enhancing the quality of fuel [29].

As per author information, there is no systematic review study reported yet regarding current challenges and latest developments in lignocellulosic biomass pre-treatment technologies. The aim of this study is to explore existing pretreatment technologies along with the technical pros and cons. In lieu with these investigations, new innovative schemes are suggested. The center of attention in this review is only the pretreatment technology and the technological impact towards commercial-scale biofuel production by addressing processes limitations. Each pretreatment technique is briefly explained with the latest growth and particular raw materials associated with it. Latest research outcomes are also presented with innovations required for further removal of bottlenecks in present technologies.

2. Pretreatment of lignocellulosic biomass

Lignocelluloses can be accounted for annual production of roughly 15–20 billion metric tons of biofuels worldwide. Table 1 depicts different compositions of lignocelluloses from a variety of sources.

The elementary part of pretreatment in biofuel synthesis has been acknowledged for years. It is the critical phase during the production of biofuels and adopted for delignification of biomass residues to break bounding created by lignin which hinders enzyme contact with celluloses. The cost factor and high residence time during processing make pretreatment a challenging task [31]. Lignocellulose biomass comprises of the compact structure due to the presence of lignin which holds cellulose and hemicellulose as shown in Fig. 3.

Several methods are available to minimize cost of energy and time. These methods are physical, biological, chemical, and physio-chemical pretreatments, as shown in Fig. 4**.** The pros and cons of various pretreatment technologies for lignocelluloses residues are depicted in Table 2.

Table 1
Different components of biomass on the weight basis [174].

Type of Biomass	Celluloses (%)	Hemicelluloses (%)	Lignin (%)
Spruce and Pine	40–45	25–30	30–60
Bagasse, Barley straw, Rice hulls, Wheat straw, Rice straw	35–50	25–50	15–25
Poplar &aspen	45–50	25–40	20–25
Paper &newspaper	40–55	25–40	20–25
Hardwood	20–25	45–50	20–25
Softwood	25–30	35–40	25–30
Oat straw	35–40	27–35	15–20
Corn cob	42–45	35–40	15–18
Corn stover	38–42	25–28	10–20
Municipal solid waste	30–45	10–20	5–10
Grasses	25–35	25–50	10–20
Miscanthus	35–40	20–25	20–25
Switch grass	10–20	20–45	15–35

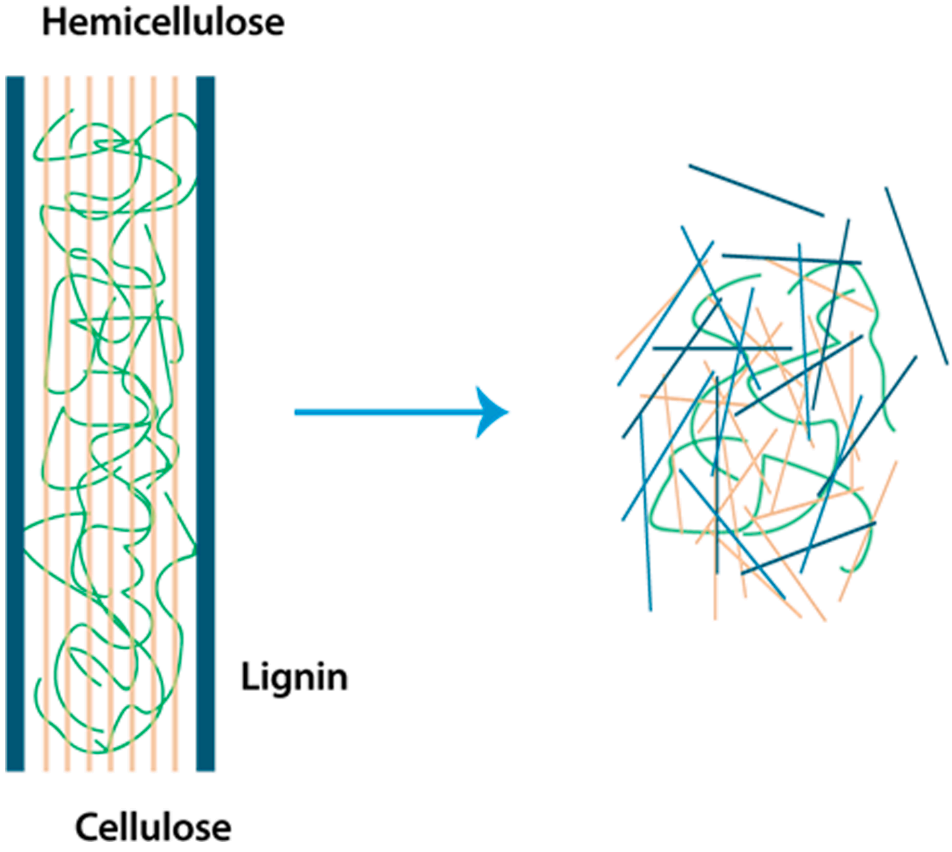

Fig. 3. Structure of Lignocellulosic Biomass [27].

2.1. *Physical pretreatment processes*

The core task behind physical process is to trim down the crystalline structure of cellulose as well as deterioration of lignin and hemicellulose.

2.1.1. *Size reduction*

Major size reduction processes, e.g., chipping, grinding, and milling, come under the umbrella of the physical pretreatment process. With the help of size reduction, the surface area of material is increased with decrease in the crystalline nature of cellulose. With the help of chippers, the biomass size is reduced and then grinders are used to further decrease the biomass size. The biomass particle size decreases to 10–30 mm after passing through chipping operation and reaches a value of 0.2–2 mm once it has been passed through comminution operation. Final required size of biomass decides the energy requirement for the crushing of raw material. Energy is also related to the nature of biomass. Hard biomass materials require more energy for crushing and grinding. Lastly, the method in the pretreatment of biomass residues comes with low-temperature torrefaction [33].The grinding capability of biomass residues enhances after passing through the torrefaction process which shows in the reduction of grinding energy. Torrified biomass possesses more surfaces to volume ratio thus improving enzymatic reactions during hydrolysis. Steam incorporated with microwave trimmed the biomass structure and reduced its crystallinity. Due to high-pressure energy stored in steam the particle size of biomass reduces with sudden depressurization of the system. Microwaves increase the temperature of biomass residue which helps in the reduction of crystalline nature of cellulose and enhances inner polymerization. Both of the above-mentioned methods are costly due to high energy requirement which makes them impractical for commercial applications [34].The energy costs associated with the milling biomass particles to such small sizes are likely to be high for low-profit-margins for high-volume industrial plants.

2.1.2. *Microwave irradiation pretreatment*

Microwaves comprise of non-ionizing electromagnetic radiations of 1 mm to 1 m wavelengths located in the range of 300–300000 MHz on electromagnetic spectrum that selectively transfer energy to diverse substances [35]. A recent study on lignocellulosic pretreatment performance using microwave radiation has been presented [36]. Presently, lignocellulosic biomass pretreatment assisted by microwave technologies with the use of appropriate catalysts is categorized into two broader categories namely (a) microwave-assisted solvolysis under moderate conditions of temperature (i.e. below 200 °C) to give commodity chemicals and (b) microwave-assisted pyrolysis at high temperature conditions (i.e. more than 400 °C) to transform biomass into biofuels. Microwave radiation has great advantages over conventional heating which include (a) accelerated rate of heat transfer and small time for reaction, (b) constant heating performance over the volume of the object of interest that could be selective as well, (c) energy efficiency and ease of operation, (d) formation of unwanted byproducts is suppressed due to little degradation. Additionally, hydrothermal pretreatment assisted by microwaves could also remove acetyl groups present in hemicellulose under the hot-spot effect of microwave irradiation [37]. In order to enhance better heat transfer for quick heating by microwaves, the low-quality biomass was supported with materials like charcoal, graphite, pyrites, and activated carbon [38]. These materials provide better results for breakage of solid parts present in biomass. Also, the existence of inorganic substances as well as moisture in biomass could greatly enhance their microwave absorption capacity thereby aggregating the microwave performance which rests on the dielectric properties of the organic matter (i.e., capacity to cache electromagnetic energy and to translate it into heat) [39].

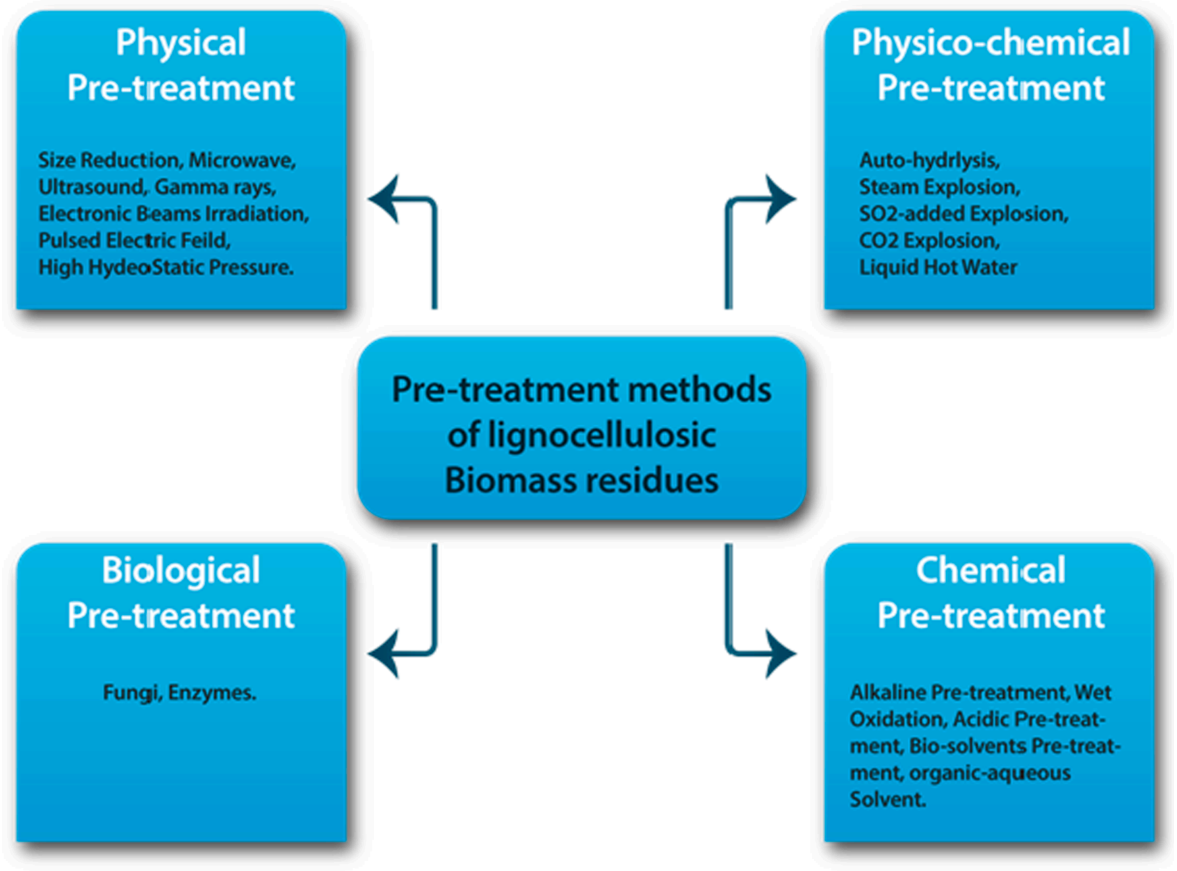

Fig. 4. Different Pretreatment Methods of Lignocellulosic Biomass [17].

While the traditional heating techniques of the biomass require particle size to be reduced in order to avoid higher temperature gradients by the application of indirect conduction of heat thereby adversely affecting the recovery of fermentable sugars via degradation of hemicellulose into humic acids or furfural [36]. The microwave-assisted solvolysis results in constant and rapid internal heating of the coarse biomass particles without any adverse effect on the plant fiber materials. Due to the application of lower temperatures in the range of ≤ 100 °C which ultimately enhances the subsequent enzymatic saccharification via the swelling and fermentation of the fibers [40]. A research study conducted by Choudhary et al. to analyze the pretreatment of sweet sorghum bagasse biomass via the application of microwave irradiation and reported total sugars recovery of about 65% when using 1 g SBB in 10 mL of water under the influence of 1000 W microwave energy for 4 min [41]. The sugar recovery from biomass was affected by lime addition, exposure time and water content. All these parameters were utilized to obtain maximum sugar content from biomass. Also the SEM images of degraded biomass supported the sugar results recovered during microwave pre-treatment. In another study carried out by Diaz et al. rice husk and corn straw were pretreated with glycerol assisted by microwave irradiation yielded distinct rupture of cell structure of plant as evident by SEM [42]. This technique was termed as the best pretreatment for the spent grain of breweries by another researcher in comparison to conventional chemical treatment methods (e.g., AFE, steam explosion, acid hydrolysis, ferric chloride pretreatment and Organosolv)[43]. Lowering of capital cost, significant improvements in efficient heating and ease of operation are among the advantages of lignocellulosic biomass pretreatment, assisted by microwave irradiation as established by Kostas[44].

Microwave-assisted pyrolysis of lignocellulosic biomass involves microwave radiation, as a pretreatment method, followed by the thermo-chemical pyrolysis of biomass. This technique could convert about 50% of biomass into synthesis-gas, while liquid product, i.e., bio-oil, obtained from fast-pyrolysis contains diverse phenolic compounds derived from lignin [45,46]. A study conducted by Huang et al. on comparison of heating rates of conventional pyrolysis and microwave-assisted pyrolysis methods reported a 42% higher heating rate by the later, indicating its superiority over the conventional technique due to less time required to achieve the desired temperature [35]. Kinetics of microwave-assisted biomass pretreatment were estimated by following first and second order reaction models [47].

2.1.3. *Ultrasound pretreatment*

The ultrasound pretreatment of lignocellulosic biomass using ultrasound frequencies in the span of 20 kHz to 1 MHz resulted into surface structure alterations and formation of oxidizing radicals which strike the matrix of lignocelluloses with the ability to form small cavitation bubbles via disruption of linkages present in lignin resulting into the bifurcation of structural polysaccharides and lignin fractions[48]. This is termed as a “potent green technology” for lignocelluloses biomass pretreatment. The bubble formed in the previous step grows in size so critically as to become unstable and suddenly collapses to give a pressure of around 1800 bar and temperatures of 1727–4727 °C [49]. Wood wastes of the forests were used by a researcher to produce commodity chemicals with the application of energetic ultrasonic waves of 400 W power and 20–100% amplitude, yielding a nine times shorter reaction time [49]. Another study identified a 90% removal of hemicellulose and lignin from sugarcane bagasse with the application of a 100 W ultrasound and 2 h of sonication time in distilled water maintained at a temperature of 55 °C wherein the ultrasound attacked the veracity of cell walls, slashing the linkages of ether, and enhancing extractability of hemicellulose [50].

Table 2
Pros and cons of various pretreatment technologies.

Pretreatment Technology	Pros	Cons
Mechanical grinding	• Destroy lignocelluloses structure • Crystalline nature diminishes • Enhances contact area for enzymatic reactions	• Energy Intensive process • Economical not viable
Irradiation	• Used as supporting pretreatment technology • Enlarge particle interfacial area • Boost sugars content	• Commercially not feasible • Slower reaction rates • Hazardous due to radiations
Alkaline Treatment	• Well-organized separation of lignin • No inhibitors generation	• Expensive Chemicals • Destruction of lignin
Acidic Treatment	• Higher sugars extraction • Solubilize hemicelluloses	• Higher acid cost • Reuse and Recycling • Corrosion Protection • Production of by-products
Ionic Solvents	• Higher processing capability • Ambient reaction condition	• High solvent cost • Need solvent recovery/ recycle
Steam Explosion	• Economical • Delignification and solubilize hemicelluloses • Higher sugars productivity	• Incomplete Hemicellulose Transformation • Cost of acid catalyst • Poisonous byproducts
Liquid Hot Water	• Easy partition of hemicelluloses • Required no catalyst	• Higher resources required (energy/water) • Hard material present after reaction
Ammonia Fiber Explosion	• Higher efficiency • Handle low lignin feedstock • Lower rates of inhibitor generation	• Recycle of ammonia • Poor effectiveness in terms of lignin concentration • Modify lignin configuration • Higher cost • Ammonia toxicity
Ammonia Recycle Percolation	• Greater than 90% lignin removal • Higher celluloses content subsequent to pretreatment	• Higher operating cost
Super Critical Technique	• Poor break down of sugars • Cheaper • Increases contact area (enzyme and celluloses)	• Higher energy cost (Elevated pressures) • Lignin and hemicelluloses unchanged
Organic-Aqueous Solvent	• Active celluloses • Solvent Recycling • No Catalyst is required	• Energy Intensive • Ethanol acted as inhibitor
Biological Pretreatment	• Lower energy consumption • Purity of cellulose	• Time consuming • Lower Reaction rates • Inhibitors cause deactivation

Enhancement in the degradation of lignin and rates of enzymatic saccharification could be achieved by alkali pretreatment of biomass assisted by ultrasound through the splitting of hydrogen bonds among lignocellulosic molecules. Nonetheless, the vibration energy of the ultrasound is insufficient to bring about any changes in the surface conformation of biomass particles [51]. In another study of biomass (pistachio & groundnut shells and coconut coir) delignification assisted by ultrasound, yielded about 80–100% increment compared to conventional alkaline pretreatment using 100 W ultrasound power for 70 min with 80% duty cycle and 0.5% biomass loading [52]. Furthermore, enzymatic hydrolysis assisted by ultrasound of same biomass produced around 2.4 times more yields of reducing sugar under optimized conditions i.e. 3% substrate loading (w/v), 0.08% cellulases loading (w/v), 60 W ultrasound power for 6.5 h and 70% duty cycle as compared to traditional alkaline hydrolysis. Besides, increased enzymatic digestibility was observed due to reduction in crystallinity of cellulose via acoustic cavitation.

In another study, ammonia pretreatment of biomass (sugarcane bagasse) assisted by ultrasound reported around 96% recovery of cellulose with ~ 58% delignification [53]. This technique also helped in conducting the pretreatment at moderate temperature, lowered crystallinity and reduced the formation of unwanted side products. Similarly, highest enzymatic hydrolysis sugar yields (57–81%) were reported by other researchers using diverse biomass feedstocks, e.g., corn stover, corn cob, and sorghum stalks, using 2 w/v% dilute ammonia, 90 W ultrasound power and 50 kHz frequency with sonication times of 2–4 h and temperatures of 50–70 °C [54]. In order to evaluate the kinetics of the ultrasonic biomass pre-treatment process, Yang et al. [55] investigated the kinetics of enzymatic hydrolysis of rice straw pre-treatment using bio-based ionic liquid in ultrasound. A reaction kinetic model was developed successfully to predict the design equations for the bioreactor.

2.1.4. *Combined microwave and ultrasonic pretreatment*

Accelerated biodegradability and hydrolysis were observed by coupling microwave and ultrasonic pretreatment of agricultural wastes (e.g. olive and grape pomaces) and wastewater sludge to produce biofuels due to reduced size, enhanced surface area, and increased availability of biomass constituents. This hybrid technique is found to be more productive than microwave alone due to selective degradation of lignin and waxes and removal of wax layer by microwave to expose more surface area for enzymatic action [56]. In the case of degradation of hemicelluloses, the brisk hydrolysis of hemicelluloses was observed by this hybrid technique via internal heating of the biomass [57]. Similarly, the high yield of xylose maize hydrolysate core was also observed by employing this technique for hydrothermal pretreatment of biomass (corn cobs) [58]. However, the combination of these strategies needs to be examined for a variety of biomass. The combination of these sequential treatments will fill the gaps by investigating the pretreatment of sequential use of ultrasound and microwave-assisted alkaline method for the fractionation of seed biomass [59,60].

2.1.5. *Gamma ray pretreatment*

Radio isotopes e.g. Cesium-137 and Cobalt-60 generate ionizing gamma-ray radiations that could easily penetrate the structure of lignocelluloses thereby breaking the crystalline regions of the cellulose and modifying the lignin; thus, have utility in the pretreatment of lignocellulosic biomass. Free radicals are formed by the breakdown of cellulose crystals which rapidly decay from the amorphous regions once the radiation has been terminated causing degradation of the biomass [61]. Bio-conversion efficiency of MCC using gamma radiations was studied by Liu et al. [62] in comparison to other pretreatment techniques (e.g. ILs, acidic treatments etc.) who reported 891 kGy as the optimum radiation dose. Various other researchers have demonstrated the augmented efficiency of enzymatic hydrolysis of lignocellulosic biomass using gamma irradiation. A sequence of alteration in physical as well as chemical properties of the rapeseed straw was observed upon gamma-ray irradiation at 1200 kGy thereby remodeling the carbohydrate-lignin linkages of the biomass, reducing the particle size, enhancing the surface area and lowering the thermal stability of organic matter [63].

2.1.6. *Electron beam (EB) irradiation pretreatment*

In this technique, disruption of polymer cell wall structure of the lignocellulosic biomass is carried out via free radical formation, chain scission or formation of cross-linkages, reduction in the degree of polymerization or de-crystallization with the help of accelerated beams of electrons generated from a linear accelerator in the form of ionizing radiations [64]. Mante et al. [65] reported an enhanced yield of phenolic compounds via de-polymerization of cellulose and hemicellulose structures of sugar maple upon irradiation of 1000 kGy EB. EB has a limitation that it is effective in de-polymerizing cellulose while other pretreatment techniques are required to hydrolyze lignin and hemicelluloses [66].

2.1.7. Pulsed electric field (PEF) pretreatment

This technique utilizes a simple device without any moving parts and equipped with 2 electrodes generating voltage pulses with the help of a 0.1–80 $kVcm^{-1}$ electric field to treat plant biomass for a petite time period of about 10^{-4}-10^{-2} sec. As a result, semi-permeability of the biomass is lost due to disruption of the biological membrane allowing transit of intra-cellular compounds to the surrounding solution [67] thereby facilitating the admission of hydrolytic enzymes across the pores of treated cell membrane. A research study [68] established that pretreatment of lignocellulosic biomass with 2,000 pulses at a field-strength of 10 $kVcm^{-1}$ could improve the fuel and chemical conversion via cellulose hydrolysis. De-lignification of lignocellulosic biomass could also be achieved via PEF; however, effects of PEF on the structure of lignocelluloses need to be explored further [69].

2.1.8. High hydrostatic pressure (HHP) pretreatment

This technique has been extensively used in the food industry for pasteurization of food products without deteriorating their quality. With technological innovations by the OEMs, capital and operating costs of this technology have been greatly reduced. HPP pretreatment of lignocellulosic biomass is performed by proportional distribution of pressure in all parts of the biomass which helps all structural reactions and changes involving a reduction in volume. Unlike temperature treatment, pressure treatment is independent of time or mass. It merely influences the hydrogen bonds leaving the covalent bonds intact thereby minimizing the processing time. Moreover, pressure also influences the activity of certain enzymes by changing their structure, changing reaction mechanism and modifying substrate physical properties [70]. A two-fold increase in hydrolytic performance of fungal cellulases has been reported by Albuquerque et al. [71] on coconut husk under the application of a pressure of 300 MPa for 30 min which ruptured the coconut fibers.

2.1.9. High-pressure homogenization (HPH) pretreatment

This technique employs a homogenizer to produce a consistent particle size distribution suspended in a liquid with the help of a pressure pump which forces the liquid across a definite valve to attain homogenization in order to rupture the cell wall and recover intra-cellular bio-products. A research study to pre-treat four different lignocellulosic biomass materials with HPH of 10 MPa, reported a high yield of reducing sugars via the reduction in particle size of biomass and increase in surface area for enzymatic hydrolysis [72]. HPH is a highly efficient yet simple and greener method to pre-treat lignocellulosic biomass [72,73].

2.2. Physicochemical pretreatment processes

2.2.1. Auto-hydrolysis

During auto-hydrolysis, the hydrolysis of hemicellulosic biomass takes place exclusive of major change in the structure of lignin and left behind cellulosic content in solid mass [74].Reactions that occurred during the hydrolysis of hemicelluloses require solvent media with elevated temperature ranges from 150 °C to 250 °C. De-polymerization of hemicelluloses occurs in the presence of aqueous solution resulting in the formation of various compounds starting from oligosaccharide and monosaccharide, along with a wider range of oxygenated compounds including furfural, acetic acid and HMF. After reaction, bottom remains contain lignin, celluloses and unreacted hemicelluloses [75,76].

2.2.2. Steam explosion

Steam explosion pretreatment technology is widely used nowadays which comes up with efficient results. Lignocelluloses residues structures are broken down using chemical and physical methods assisted by high temperature and pressure steam. From high pressure, sudden depressurization results in breakage of biomass structure which promotes easy access of enzymes to increase reaction rate of hydrolysis [77]. The large size of particles yields the best results and efficiency of the process to give the highest sugar content. Steam temperature ranging from 180 to 250 °C with the pressure of 10–20 bars and contact time of 2–10 min are required. Reduction in contact time and steam quality has been observed with changes in particle size of feed material. Fine particles required less stringent conditions [78,79]. In a research carried by Ballesteros et al. [80], saturated steam was applied to rupture the lignocellulosic structure of poplar, eucalyptus chips, and different additional raw materials. All the above-mentioned materials were treated at a temperature of 210 °C with different residence times. The highest residence time was reported for *Brassica carinata*, i.e., 8 min, whereas the lowest time was taken for sweet sorghum bagasse, i.e., 2 min. Ballesteros et al. [80], explained pretreatment with the steam broadly disrupted the biomass structure and solubilize the carbohydrates and reduced up to 75–90% of xylose content. Steam pretreatment process operated in batch as well as continuous operation without any interruption. Batch processes were cheaper, simpler and flexible for a wide range of biomass. Many different studies were conducted to check the effect of variables like catalysts, different shapes and sizes of particles and pressure on extractable sugar yield [81,82]. During the steam explosion, a small part of xylose damages and partial disorder of lignin structure limit this process. Inhibitor generation by this method harms the downstream operations [77]. The particle size of biomass affects the sugar recovery during the pretreatment process which reduces the overall efficiency of process [83].

2.2.3. SO_2-added steam explosion

With the addition of sulfur dioxide in steam during steam explosion, celluloses and hemicelluloses are recovered. Hemicelluloses sugar content increases by using acid. Adding inorganic acids upgrade enzyme hydrolysis reaction of solid biomass [84].

The researchers reported that the quantity of SO_2 injected with steam was depending upon nature of biomass. This amount varies from 1 to 5% for dry wood [85]. The research study revealed that for 1% of SO_2 at 200 °C, the overall process yield touches 95% of sugar content. The usage of SO_2 promotes high sugar content upon addition with steam and acting as an additive, which enhances the disruption of biomass structure. After pretreatment of biomass material like wood and spruce wood chips, the resulted product was simple to go through hydrolysis and fermentation process. Low concentration aqueous acid created problems in terms of the formation of inhibitors [86].The inhibitors produced during the fermentation process were inevitable while using acid-catalyzed explosion.

2.3. CO_2 explosion

Carbon dioxide is a byproduct obtained during fermenting the pretreated biomass. Another important feature of produced CO_2 is its usage as a de-carbonizing agent during energy generation.CO_2 structure was similar to water and ammonia molecules. Due to similarity in structure, CO_2 can easily break through the porous structure available in biomass. The carbon dioxide is released after penetration through biomass porous structure and demolishes the bonding present inside the biomass structure. Thus, the surface area is increased for enhancing the contact of enzymes with celluloses and hemicelluloses [87]. Another technique is using supercritical carbon dioxide for making biomass digestible. A study carried by Park et al. [88] using supercritical carbon dioxide with in-situ enzyme hydrolysis. The technique was performed at the very high pressure of 160 bar keeping the temperature at 500 °C with the retention time of 1.5 h. The overall conversion for the process reached a value of approximately 100%. The major limitation of this technology was its higher cost. On the other hand, Zheng et al. [89] suggested this technology extra efficient in terms of operational cost and low inhibitor formation in comparison with steam and acid explosion. The CO_2 explosion technology for lignocellulosic biomass offers less inhibitor formation which is favorable for downstream processes in biofuel synthesis [90].

2.3.1. *Liquid hot water (LHW) pretreatment*

In liquid hot water pretreatment, water in the liquid phase at high temperature and pressure was used to breakdown the celluloses and hemicelluloses structure that was bound by lignin. The pressure of water was kept high (up to 10 MPa) to maintain its liquid phase. The temperature of water varied from 160 °C to 240 °C with retention time depending upon the nature of biomass residue and the sugar content and its type. Normally the time ranges from minutes to a few hours. High temperature and pressure favor low retention time [91]. Sudden depressurization results in the destruction of biomass structure. The generation of inhibitors was also diminished using this pretreatment technique. The cellulose content is separated from hemicelluloses and lignin by the hot water which acted as an acid [92]. The products produced during the hot water pretreatment process are easily divided into two streams due to the formation of slurry containing the soluble hemicellulose and insoluble cellulose solid content [93]. The soluble hemicellulose contains mostly oligosaccharides that originated from hemicelluloses and lignin. The minor amount of cellulose is also present which is handled with the help of enzymes through enzymatic hydrolysis. The pH of the system is kept acidic during the process [94]. A research study that used 180 °C for 30 min gave the best results in terms of glucose yield and cost [91]. The prime objective of this technique is to decrease the cellulosic content in biomass feedstock and increase the hemicellulosic content. To achieve higher efficiency and stopping the production of inhibitors during the pretreatment process, some lignin content must be added with liquid part. This scheme also stops simple sugar generation during process. Low capital and operating costs are associated with this scheme of pretreatment as this process requires no add-ons to control corrosion and speed up the solubilization process. Final neutralizing step is not required at the end of pretreatment process. The only limitation of this technology is high pressure required to lower down the temperature, which increases the system running cost and makeup water cost also plays a part in the reduction of overall final efficiency of the process [95].

2.3.2. *Ammonia Fiber explosion (AFEX)*

Ammonia fiber explosion (AFEX) also known as freeze explosion is a technique similar to steam explosion where pure liquid ammonia is used at elevated pressure and low temperature to pre-treat the biomass residues. The biomass residue structure is disrupted by sudden decompression resulting in breakage of biomass inner structure. Low operating temperature (60 °C to 100 °C) of AFEX makes this process more economical in terms of energy and cost. The extent of disorder occurred in biomass is highly dependent upon ammonia temperature as it affects ammonia vaporizing ability in reaction vessel during decompression phase. The retention times for different biomass residues can vary from 5 to 30 min depending upon the nature of biomass and strength of ammonia used for pretreatment. Processing time increases when ammonia content is lower for pretreatment. Ammonia loading is very important which shows amount of ammonia per weight of dry feedstock. Normally, an equal amount of ammonia and biomass are used for achieving a higher degree of efficiency [96–98].

The presence of ammonia swells the biomass residues and breaks the bond between lignin and hemicellulose followed by hemicelluloses hydrolysis [98]. To make the process economical, ammonia recycling is very important after depressurization step. Handling of ammonia is also very critical due to its hazardous release in the environment. Another drawback of this technology is its inability to eliminate lignin and other oxygenated compounds from feedstock. The lignin causes hurdles by blocking the surface which reduces conversion of cellulases to cellulose [94]. Another disadvantage of ammonia process is that the product after pretreatment needs frequent washing with water to remove any ammonia contaminations. Generally, AFEX is applied to feedstock with low lignin content to achieve the best result. If the best possible conditions are achieved, ammonia process enhances the subsequent hydrolysis by enzymes [99].

2.3.3. *Ammonia Recycle Percolation*

Many authors combine ammonia recycle percolation (ARP) with AFEX technology; however, both technologies have diverse dissimilar properties. All these properties need to be addressed separately for achieving the best results and high yields. ARP uses ammonia ranging from 5 to 15% by weight which passes through fixed bed reactor containing bed of lignocellulosic residue at a volumetric flow rate of 5 mL/min. Temperature is maintained at 140 °C to 210 °C for high retention time which makes this process very costly [100]. Another method is known as low-liquid ARP (LLARP) utilizing lower flow rates of ammonia that is around 3.3 mL ammonia/g-feedstock. The retention time is maintained from 10 to 15 min. No significant decrease in efficiency is observed. This process is less energy intensive as compared to ARP [101]. The benefit behind using this technique over AFEX is its capability to handle and discard major portion of lignin (75–85%) and make around half of the hemicelluloses content soluble, whereas left behind higher quantity of cellulosic part at the same time [101]. By the selective action of ammonia, lignin decomposes along with hemicelluloses at the same time. But the time required for this process is very large. After conversion, the only thing present in the reaction tank is short chain celluloses with higher content of glucan [101]. The green plant material is mostly pre-treated with this method. A research study shows that around 60–80% lignin was pre-treated in case of feed of corn stover whereas for switchgrass, this value touches 65–85% [102]. Advantage of using this technique is that the generation of inhibitor compounds during process is suppressed. Due to this, excessive washing is not required after pretreatment step [103]. Many limitations are linked with this technology which creates a barrier for its commercialization including higher operating and capital cost along with high liquid flow rates. Continuous recycling and safe handling of solvent are also very critical in this technique. The concentration of celluloses to a higher value makes this technology worthwhile. On the other hand, more working is required to promote it towards commercialization [99].

2.4. *Chemical pretreatment processes*

2.4.1. *Alkaline pretreatment*

A pretreatment involving alkali comes from alkali and alkaline earth metals. These alkalis including sodium, potassium, calcium, and ammonium hydroxides are frequently used for the pretreatment of different herbaceous feedstocks. The power of alkali is its ability to degrade the esters and glucan chain present in biomass. Thus, modification is observed in the structure of lignin by the reduction in crystallinity of cellulosic structure. The alkali solutions also partially solubilize the hemicelluloses in it [104–106]. Strong and weak caustic solutions are widely used for a long time, to create disorderness in the configuration of biomass due to the presence of lignin which holds celluloses and hemicelluloses. With the help of sodium hydroxide, enzyme approachability becomes easy thus, downstream process occurs easily [107–110]. Calcium hydroxide is also very popular among researchers for chemical pretreatment of lignocellulosic residues. The biomass which was treated with this technology includes switch-grass, sugar cane bagasse, wheat and rice straw. A research study performed by Sun et al. [111] shows the efficiency in terms of strength of different alkali solutions by examining the lignin structure breakage and dissolubility of hemicelluloses in wheat straw. The best results were obtained when fixing the caustic percentage to a value of 1.5 at a temperature of 20 °C for 144 h. This method releases 60% of lignin along with 80% hemicelluloses. A case study performed by Zhao et al. [109] indicated the efficacy of sodium hydroxide for delignification of hardwood, wheat straw softwood and various grasses with low lignin percentage around 25%. Biogas yield also increases to a value of 37% on using strong caustic solution for corn stover as feed stock [110].

The temperature required for pretreatment during alkaline pretreatment technology is lesser as compared with other technologies using acid or other media. Atmospheric temperature condition is feasible for carrying out the reactions, but the residence time is high to process the feedstock. In alkaline process, the biomass is initially soaked in aqueous alkaline media and after intermixing at targeted temperature, the mixture is retained for specific time interval. A downstream neutralization process is a must to eliminate any carryover of lignin and oxygenated compounds (inhibitor). All these steps are a must requirement prior to hydrolysis in the presence of enzymes. A new scheme is adopted for the division of solid and liquid phases using CO_2 after the neutralizing step of lime. This method yields approximately 90% sugars recovery from rice straw as feedstock. The utilization of lime over other alkalis is its cheaper price for a specified amount of biomass residue. In 2005, the projected costs associated with lime pretreatment ranged from $70/ton hydrated lime whereas $270/ton fertilizer grade ammonia and $320/ton for 50 wt% NaOH and 45 wt% KOH [112]. The pretreatment process using lime requires more energy due to the separation step. Solid calcium carbonate is removed by passing CO_2 [113]. Carbon dioxide produced during fermentation can be recycled and used to generate calcium carbonate to decrease the operating cost of the whole process. The final separation of calcium carbonate from solid leftover makes the Park et al. [88] method unsuccessful towards commercialization due to excessive energy requirement. Zhao et al. [109] research work shows that glucose content can be increased by coupling alkali pretreatment with radiofrequency-based dielectric heating. This scheme promotes uniform heating across the whole feedstock. Large particle size material is also easily handled by this method. The radio waves assist in the breakage of lignin bonds which enhances the overall process efficiency. Ali et al. [114] used dilute alkali which enhances the biofuel yield up to 78%. Dilute alkali deforms the solid fraction present in pine wood. The efficacy of dilute alkali pretreatment is somewhat higher for small size particles feed than for hardwoods owing, in part, to the lower lignin content present in it.

2.4.2. *Wet oxidation*

Oxygen is used as an oxidizing media in the wet oxidation process. For wetting of biomass residue, water is frequently used. Two reactions take place simultaneously during wet oxidation process. One process occurs at low temperature and the other i.e. is oxidation requires high operating temperature [115]. Initially, the size reduction process takes place with drying of feedstock. The size of the particle reduces to 2 mm after that biomass is mixed with water. Additives like Na_2CO_3 are frequently added to decrease the production of compounds as side products. Pumping of air for oxidation is done till pressure is reached at 12 bars. The temperature of system is maintained at 195 °C for half an hour depending upon feed stock [116–118]. Wet oxidation is adopted to solubilize the hemicelluloses and removal of lignin [119]. Lignocelluloses biomass like straw, reed, and other food crops have a thick layer of wax constitute of silica and protein compounds which are washed away using this technique [120]. In this technology, lignin is converted into carbon dioxide, water and carboxylic acids [116,119]. The reaction process parameters are deciding factors for the efficiency of the process. Biomass type also plays a role in the conversion of solid biomass into its constituents. When sugar cane bagasse is pretreated with retention time of 15 min, around 50% of lignin is recovered, which results in an overall conversion of 60% of celluloses. This conversion is reduced when the same feedstock is applied to steam explosion technique [117]. The drawback of this process is that it facilitates more production of side products and inhibitors as compared to steam explosion. Most of these products contain oxygen in them like succinic acid, glycolic acid, formic acid, acetic acid, phenolic compounds, and furfural. All these compounds create problems like corrosion and catalyst poisoning on further chemical processes [121].

Also, oxygen presence reduces the heating value of the fuel. Combinations of other techniques with wet oxidation technology are also under consideration to enhance the overall yield of sugar compounds. Alkaline processes are combined with wet oxidation to decrease the generation of side products which later suppress production of inhibitors [120]. When wet oxidation is coupled with steam explosion, the technology is known as wet explosion. Georgieva et al. [122] carried out a research study by using wet explosion technology, in which the results showed 70% cellulose, 68% hemicelluloses conversions along with overall biofuel productivity of 68% through the SSF.

2.4.3. *Acidic pretreatment*

In acidic treatment for treating biomass residues, both weak and strong mineral acids are used. These acids are used either in concentrated form or as an aqueous solution. Mostly, sulfuric acid (H_2SO_4) is used in aqueous form for the pretreatment of different kinds of lignocellulosic residues. Pure sulfuric acid is initially diluted for furfural production by the conversion of hemicelluloses into sugar compounds which are ultimately converted to furfural [123]. Further research studies utilize hydrochloric acid (HCl) [124], phosphoric acid (H_3PO_4) [125,126], and nitric acid (HNO_3) [127] both in concentrated and aqueous form. The capabilities of acids to take out hemicelluloses from the bonded structure of lignin are widely used on commercial scale [125]. After acid pretreatment, washing and treatment with alkaline solution yields comparatively uncontaminated celluloses.

The process parameters for acidic pretreatment include acid quantity, temperature and residence time of reaction. The acid amount ranges from 0.2% to 2.5% weight by weight of lignocellulosic residue with continuous mixing using agitators and maintaining the temperature in the range of 130 °C and 210 °C. The residence time is kept in hours as reaction proceeds slowly. High temperature favors low residence time [128]. The plus point of using acidic pretreatment step is that no further downstream hydrolysis process is required. The lignocellulosic residues are hydrolyzed due to the presence of acid which results in fermented sugar compounds. In this way, operating cost is reduced by skipping one major step. During acidic pretreatment, no wastage of hemicelluloses and lignin occurs due to complete solubilization [129]. On the other hand, excessive water washing step is necessary prior to the fermentation process for removal of any oxidants or impurities [130]. The acidic and toxic characteristics of acids need coating with anticorrosion compounds to resist against the acid attack. An additional negative aspect of this pretreatment is the synthesis of fermented inhibition products like furfural and HMF which decrease the efficiency of overall process and create problem for downstream unit operations and processes [131]. The sugars quantity extracted during pretreatment process can be increased by applying two-step acidic pretreatment using aqueous sulfuric acid.

Sun and Cheng [131] carried out a research study using Bermuda grass and rye straw as feedstock. Two days later, with hydrolysis step in the presence of enzymes, the treated feedstock in the presence of dilute sulfuric acid, reduction was observed in total sugar content that was around 197.1 mg/g and 229.3 mg/g of dehydrated lignocellulosic residue. The form of acid, its strength, and process temperature and retention time in reaction vessel directly affects the product formed and quality of sugars extracted after the completion of the whole process. The overall goal of acidic pretreatment is to achieve high yield while minimizing the breakdown of sugars into decomposition products. The most favorable environment for performing the reaction and process depends upon the sugar which we want to produce. Furthermore, correct parameters are very essential to minimize the production of unwanted compounds which reduces the process efficiency and affects the product yield.

2.4.4. *Bio-Solvents pretreatment*

Due to environment friendly nature, green solvents also known as ionic solvents or liquids (IL) are gaining attention nowadays. The property of these liquids to soften a broad range of lignocellulosic residue makes them very popular. All these solvents come under the category of green chemistry. Ionic solvents composed of an anion smaller in size coupled with a big organic cation. This compound exists in liquid form at ambient conditions and possesses extremely small vapor pressure. By tuning of these liquids via tapping their anions and cations, a large diverse list of solvents can be made which are able to de-lignify a wide variety of lignocellulosic residues (corn stover, cotton, bagasse, switchgrass, wheat straw, and woods of different hardness).The lower vapor pressure of ionic liquids promotes their 100% recovery after the pretreatment process which makes this process very feasible. Thus, reductions in the cost of operation and capital costs are observed. Recycling of solvent is easy due to less vapor pressure. Another big advantage of this technique is that no harmful compounds are formed which makes their operation and handling much easier.

The research work carried out by Sun et al. [132] depicts different cellulosic solubilization ability of various ionic liquids. Good efficient ionic solvent possesses lower melting point along with lower viscosity and toxicity with higher thermal stability. Its solubilization power is much higher to cater harder feedstock easily. The origin and nature of biomass residue along with degree of polymerization in lignin structure affect the process using similar charge particles. Normally the temperature of the process is kept in between 90 °C and 130 °C with atmospheric pressure for a retention time of a few hours to days. After completion of pretreatment, excessive washing with fresh water is done to remove any entrained solvent before SSF. The anion of the IL forms hydrogen bonds with cellulose in a 1:1 ratio and breaks up the cellulose crystalline hydrogen bonded structure. This helps in making it more amorphous and accessible to enzymes for hydrolysis. The cellulose structure dissolved in ionic liquid without any destruction to polymeric chain. Much experimentation is performed which shows that the configuration of lignin and hemicelluloses remain unchanged when passing through ionic liquid pretreatment [133]. Dadi et al. [134] used two dissimilar ionic liquids 1-n-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazoliumchloride for pretreatment of biomass. After pre-treatment the pre-treated biomass goes through enzymatic hydrolysis for biofuel production. Wyman et al. [133] conducted a research study in which he suggested that the capacity of ionic liquid named as 1-ethyl-3-methylimidazolium acetate [Emim] Ac to dissolve the lignin was higher and showed very little affinity toward the cellulose content of maple wood flour. The ionic solvent showed selective action towards lignin and separated lignin from rest of the components of biomass residue. In this way, higher degree of separation was achieved which gave higher yield of celluloses for fermentation to produce biofuel. A research study was performed by Nguyen et al. [135] in which a mixture of ammonia with IL was used to conduct pretreatment of rice straw. The results revealed that 97% conversion was achieved from celluloses to sugar content. The ammonia and IL mixture was used 20 times with continuous recycling to reduce operating and capital costs. The drawback in the utilization of ionic liquids is that they deactivate the cellulases which reduce the yield of biofuel. Turner et al. [136] performed a study in which he used ionic liquid 1-butyl-3-methyl imidazolium chloride [Bmim]Cl and [Bmim]BF_4.The rate of hydrolysis reaction was very low due to the presence of higher amount of chloride ions. This high amount of chloride ions reduced the activity of enzyme, which in long term affected the reaction rate. The biggest limitation of this technique is that this deactivation is permanent. For this reason, all the ionic liquids need to be recovered to resume the activation of enzymes after pretreatment step. This can be done by employing a regenerator and separator which enhances the capital and operating cost. Another solvent that possesses the same properties like ionic liquid is N-methyl morpholine N-oxide (NMMO), which is also recognized as the Lyocell solvent. This solvent possesses both low vapor pressures along with higher dissolution capacity of celluloses. NMMO can be used as it is without any modification against a wide range of biomass feedstock. More than 99% of the solvent can be regenerated due to lower vapor pressure. NMMO is also non-hazardous with biodegradability property which makes it very popular nowadays [137]. The cellulose separated using NMMO shows higher rates of enzymatic hydrolysis reaction and the disruption rate of crystallinity was also on higher side [138]. Marzieh et al. [139] utilized recently developed morpholinium ionic liquid, 1-H-3-methylmorpholinium chloride ([HMMorph][Cl]) for pretreatment of hardwood birch (Betulapendula) and softwood spruce (Norway spruce). After that the pretreated wood was passed through enzymatic hydrolysis for synthesis of biofuel. The biofuel yield was enhanced up to 34.8% and 44.2% for hardwood and softwood spruce, respectively.

2.4.5. Organic-Aqueous solvent pretreatment

The main target behind organic solvent with some other aqueous liquid (such as methanol, ethanol, acetone, ethylene glycol, and tetra hydro furfuryl alcohol) as a blend to disrupt the lignocellulosic residue is to get the maximum amount of celluloses for downstream chemical processing using enzymes actions to convert sugars into biofuel. In organic solvent pretreatment step, the celluloses content remains active in solid phase. The solvent completely degrades lignin and hemicelluloses. The most selective organic compounds used for this reason are methanol, ethanol, acetone, ethylene glycol and tetrahydro furfural alcohol [140]. The rate of reaction was affected by presence of catalyst, whereas higher operating temperatures (160–200 °C) during pretreatment could decreases the amount of catalyst during operation [141]. Due to high boiling points, ethanol and methanol are more superior as compared to ethylene glycol and tetrahydro furfural alcohol. This also reduces the cost by continuous recycling of solvents [142]. The main disadvantage of this technology is continuous solvent recovery. This recovery process enhances the operating cost of the whole biofuel production. Moreover, ethanol acts as an inhibitor and needs to be removed completely. For this purpose, excessive washing is required to carry the solvent from pre-treated biomass residue. Distillation or liquid–liquid extraction is the simplest technique available for the recovery of solvents [143].

2.5. Biological pretreatment

Microorganism actions are used to disrupt the compact structure of biomass. Celluloses content of biomass withstands the microorganism actions whereas hemicelluloses and lignin easily degrade into its constituting components. Biological fungi (brown, white and soft rot) of different types are utilized frequently for this purpose. White rot fungi showed the best result for the lignocellulosic residue pretreatment. By using biological methods, the hydrolysis rate increases due to the increase in purity of celluloses [144]. Due to lower energy consumptions, biological processes are always under research and area of focus. Additionally, low or no additives are required, and ambient reaction parameters make this process more attractive. The only disadvantage associated with biological processes is their lower reaction rates. High residence times are required to process the feedstocks. By increase of temperature, the reaction activity is lost as microorganisms are unable to sustain high temperatures. Anaerobic digestion was applied along with ultrasonication to enhance the biofuel yield. Highest yield was obtained i.e. 69.5% when rice straw was pre-treated [145]. The key properties such as reduction in crystallinity, minimum inhibitor formation, lower amount of waste generation, higher yield with faster reaction rate with promising economic benefit of an effective pretreatment process are depicted in the Fig. 5.

Fig. 5: Key properties of an effective lignocellulosic biomass pretreatment process

The key parameters that differentiate the pre-treatment technologies are summarized in the Table 3 [94]. The surface area is observed an increase by incorporating all mentioned pre-treatment technologies however these technologies lacked to observe a decrease in crstallinity.

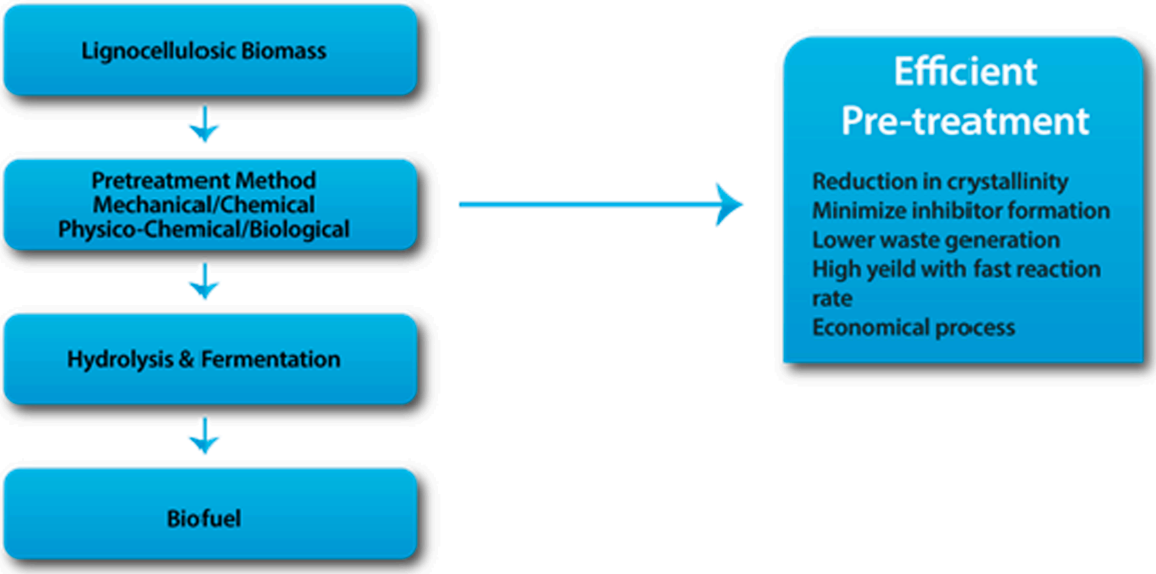

Fig. 5. Key properties of an effective lignocellulosic biomass pre-treatment process.

Table 3
Results of pretreatment on chemical and physical structure of biomass.

Pretreatment Technology	Surface Area	Crystallinity	Hemi-celluloses removal	Delignification
Steam Explosion	Increase	Decrease	Complete	Poor
LHW	Increase	Not. Detected	Complete	Poor
Acid Treatment	Increase	Decrease	Complete	Good
AFEX	Increase	Decrease	Not. Complete	Good
ARP	Increase	Decrease	Not. Complete	Good
Alkaline	Increase	Decrease	Not. Complete	Good
Ionic Liquids	Increase	Decrease	Not. Complete	Poor
Super-critical	Increase	Decrease	Complete	Poor
Organic-Aqueous	Increase	Decrease	Complete	Good
Biological	Increase	Decrease	Complete	Good

In terms of hemicellosic removal, all technologies showed major impact and completely removed except AFEX, ARP, alkaline and ionic-liquid methods. Steam explosion, LHW, ionic liquid and supercritical technologies were observed poor de-lignification characteristics in comparison to other pre-treatment technologies.

3. Current challenges and innovative method

3.1. Current challenges

The major challenges that arise in the field of pretreatment for biofuel productions from biomass residues are energy requirements and inhibitors production during pretreatment and downstream synthesis (Table 4).

Table 4
Byproducts and inhibitors generation during different pretreatment techniques for biomass.

Pretreatment Technique	Major Outcome	Chemical Usage	Inhibitor/By-product
Acidic Pretreatment	• Conversion of hemicelluloses to sugars	• Acids (H_2SO_4, HCl, H_3PO_4) • Acidic Gases (SO_2,CO_2)	• Aliphatic compound • Carboxylic acids • Phenolic compound • Furans
Steam Explosion	• Complete hemicellulosic solubilization	• CO_2/No other chemicals • No	• Acetic acid • Furans • Aldehydes • Ketones
Alkaline Pretreatment	• Separation of lignin and hemicelluloses	• Bases (NaOH, $Ca(OH)_2$, NH_3, KOH, NH_4OH)	• Acetic acid, • Hydroxyl acids, • Carboxylic acids, • Phenolic Compound
Wet Oxidation Method	• Lignin and hemicelluloses exclusion	• Oxidizing agents(H_2O_2, O_2 andO_3)	• Carboxylic acids • Furans • Phenolic Compounds
Biological Pretreatment	• Separation of lignin and hemicelluloses	• Enzymes (Lipases)	• Aliphatic Compounds
Green Solvents	• Solubilization of lignocelluloses residues	• Ionic liquid	• Mostly depend on solvent

The nature of feedstock is also very important which affects the energy needed for processing along with inhibitor generation. Continuous supply of lignocellulosic biomass residue is required for the continuous production of biofuel to meet frequent demand and minimize energy problems at plant site. Biomass residues are categorized into various different types, like energy plants, water bodies, forestry and agriculture crops. Municipal sewage sludge and waste also come under this category. Each type of these lignocellulosic residues shows potentials towards biofuel production in terms of yield, energy requirement, and minimization of inhibitors synthesis. Table 5 showed the prospective features which promote the feedstock selection. Mainly, biomass residues emerge as the biggest and leading source around the globe for biofuel synthesis with no greater requirement of agricultural fields or intervention in food crop nexus.

The energy requirements come up as a cost, which limits the pretreatment technologies towards successful commercialization. Many

Table 5
Prospective features of feedstock selection.

Type of Lignocelluloses Residue	Main leading attributes	Reference
Green grasses	• Higher productivity of herbaceous part • Greater celluloses content up to 35 % • Ease in harvesting • Green grasses show probability to reach more than 50 % as feedstock material. • Ethanol production touches to a value of around 160-460 liters/ton of biomass residue.	[175–177]
Marine plants	• No need of farmable land. • Only water bodies are required (Waste streams as well) • Extremely speed growth • Water purification capacity of these plants is additive advantage (e.g., phosphorus and arsenic) • Higher biomass production	[178,179]
Agriculture crop residue	• Ease of Availability • Controlling crop wastes and environment friendly • Reduces dependence on forestry wood • Quick harvesting and fast growth with frequent turnaround • Bioethanol productivity is 235–450 Liter/ton of agricultural biomass	[174,180,181]
Forestry plants and wastes	• Low ash formation in comparison to crops matter. • Ease in transporting due to denser biomass • Flexibility in growing • The bioethanol productivity ranges from 220–275 Liters/ton for softwood & 280–285 L/tons for hardwood.	[182–185]
Municipal wastes	• Conversion of Valorization of municipal wastes into bioethanol reduces both fuel crisis along with waste generation • The average generation of municipal waste materials is20.7 million tons/year for small towns and with 217 million tons/year for big cities. Biofuel average production is 154 L/ton of waste.	[114,139,145]

research studies were conducted which shows the cost of pretreatment steps employed to biomass for the production of biofuels such as the techno-economic study performed by Eggeman and Elander [146] for various pretreatment methodologies. Every pretreatment technique was applied to a model bio-refinery and then technical parameters and its economics were calculated. The technical parameters and economics were estimated by keeping the raw materials constant. Mass and energy calculations were performed and finally, the effect of pretreatment was evaluated on operational and fixed capital costs (Table 6**)**. The lower operational costs were compensated with high recovery and purification cost of catalysts and final biofuel yield. As a result, marginal variation in cost was observed for various types of pretreatment methods.

The formation of inhibitors during pre-treatment process creates lot of trouble during downstream hydrolysis and fermentation for biofuel synthesis. These undesired compounds such as furans, organic acids, phenolic compounds, lignocelluloses extractives, and other soluble mono-, oligomeric sugars combine with hydrolysis product. The generation of these inhibitors during pretreatment process is highly dependent on type of raw material, pretreatment technique and operating parameters of pre-treatment process [147–151].

Cara et al. [152] studied the generation of inhibitors during pretreatment of olive tree pruning using steam explosion. The temperature of the process kept in the range of 190–240 °C with sulfuric acid as a catalyst. When the temperature of process increases the inhibitors generation also increases as shown in Table below. Another research study was also conducted that observed the production of inhibitors during steam pretreated wheat straw and hardwood. The process parameters like temperature, residence time, substrate size, and sulfuric acid concentration affect the inhibitors formation as shown in the figure Table [153,154]. Many researchers identify that liquid hot water pretreatment method generates lot of inhibitors during pretreatment of high lignin biomass like hardwood, corn stover, and sugarcane bagasse. The inhibitors generated and process conditions of different studies are tabulated in the table below. When hardwood was pretreated using LHW at 15% (w/w, g dry solid/g total) with operating temperature of 195 ◦C for 10 min, the major inhibitors generated were phenolic (5.9 g/L) and xyloligomers (56 g/L) [155]. The Table 7 below represents many research studies indicating inhibitors formation during different pretreatment process.

3.2. Innovative methods

Fig. 6 shows possible advance strategies for lignocellosic biomass pre-treatment processes based on critical analysis of literature. These options are summarized below;

Use of supercritical carbon dioxide with in-situ enzyme hydrolysis could suppress inhibitor formation and enhance the overall conversion.

Coupling alkali pretreatment with radiofrequency-based dielectric heating could increase

glucose content.

4. Combinations of wet oxidation with other technologies such as alkaline processes could

decrease the generation of side products.

5. Coupling wet oxidation with steam explosion could enable handling of large particles of

biomass with high lignin content and hard material.

Table 6
Capital costs of different pretreatment technologies [146].

Pretreatment Methods	Pretreatment Permanent cost, $MM	StructureBreakage during pretreatment %	Total Capital Cost,$MM	Biofuel Yield, MMgallons/yr	Overall Cost,$/gal annually
No pretreatment	0	—	200.3	22.26	22.26
Acidic	25.0	64/36	208.6	56.1	3.72
Liquid Hot water	4.5	100/0	200.9	44.0	4.57
Ammonia Fiber Explosion	25.7	26/74	211.5	56.8	3.72
Ammonia Recycle Percolation Ammonia	28.3	25/75	210.9	46.3	4.56
Alkaline	22.3	19/81	163.6	48.9	3.35
Perfect Method	0	—	162.5	64.7	2.51

Table 7
Soluble inhibitory compounds generated from different physio-chemical pretreatment.

Method	Raw Material	Process Parameters	Inhibitors Produced g/L				References
			Phenols	Furans	Acetic Acid	Others	
Steam Explosion	Olive Tree Pruning (20%)	Temperature 190–240 ◦CResidence time 5 minSulfuric acid 0–2%	nm	0–3.2	0.4–4.2	Formic Acid, 0.8–1.8	[152]
Steam Explosion	Wheat Straw (30%)	Temperature 190–210 ◦CResidence time 2–10 minSulfuric acid 0.2%	nm	0.16–2.14	0.04–1.01	nm	[154]
Steam Explosion	Wood Chips (38–41%)	Temperature 180–210 ◦CResidence time 4–12 minSulfuric acid 0.25–0.5%	nm	0.5–3.2	Up to 7.5	nm	[153]
LHW	Maple Wood (23%)	Temperature 180–200 ◦CResidence time 24 min	1.3	4.1	13.1	Sugar oligomer 12.7, *xylo*-oligomers 11.2	[149]
LHW	Hardwood (15%)	Temperature 195 ◦CResidence time 10 min	5.9	0.7	2.5	Gluco-oligomers 3.4, *xylo*-oligomers 56, formic acid 1.9, bound acetyl 12.9	[155]
LHW	Sugar cane Bagasse	Temperature 180–200 ◦CResidence time 30 min	1.4–2.4	0.5–5.1	1.1–3.4	Gluco-oligomers 0.8, *xylo*-oligomers 6.5–12.5	[186]
LHW	Corn Stover	Temperature 190 ◦CResidence time 45 min	181–246 absorbance unit	0.74–8.37	2.01–2.8	Xylo-oligomers 9.71–21.7	[187]
AFEX	Poplar Wood	Temperature 180 ◦CMoisture ammonia 1:1, 2:1, and 3:1 w/w biomass	2.1 mg/g solids	8.6 µg/g solids	–	Aliphatic acid 1.8 µg/g solids	[188]

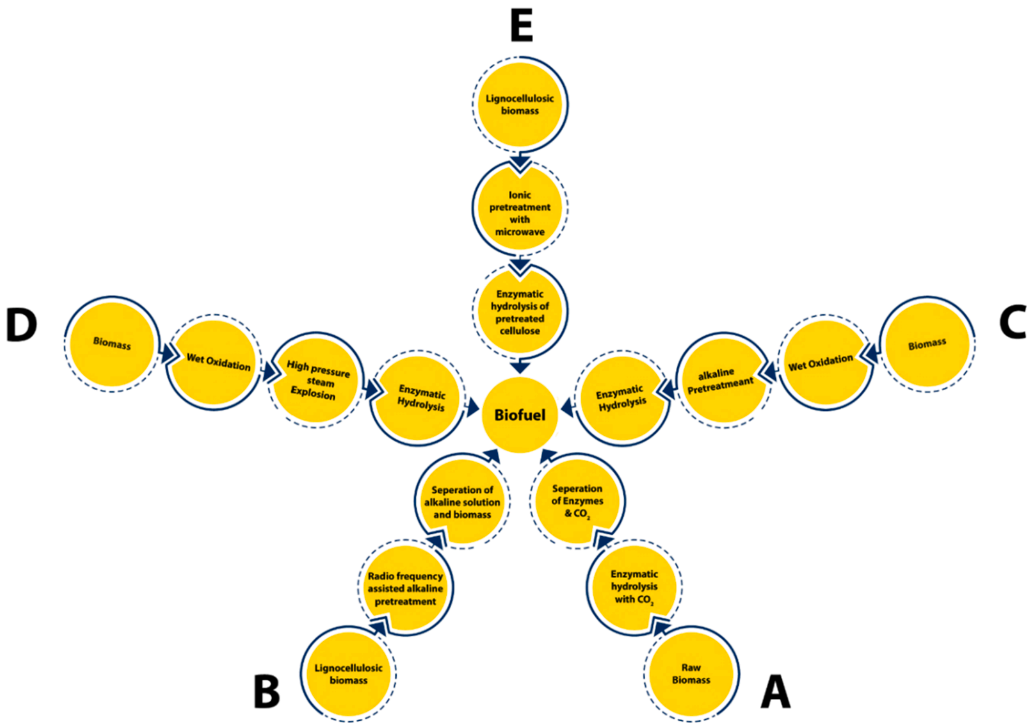

Fig. 6. Possible strategies for advance lignocellulosic pre-treatment, (A) supercritical carbon dioxide with in-situ enzyme hydrolysis, (B) Coupling alkali pretreatment with radiofrequency-based dielectric heating, (C) Combinations of wet oxidation with other technologies, (D) Coupling wet oxidation with steam explosion, (E) Ionic-liquid in combination with ultra-sound and microwave technologies.

6. Use of ionic liquid assisted by the dual energy of combined ultrasound and microwave

could enhance the efficiency of enzymatic hydrolysis of cellulose.

Fig. 6: Possible strategies for advance lignocellulosic pre-treatment, (A) supercritical carbon dioxide with in-situ enzyme hydrolysis, (B) Coupling alkali pretreatment with radiofrequency-based dielectric heating, (C) Combinations of wet oxidation with other technologies, (D) Coupling wet oxidation with steam explosion, (E) Ionic-liquid in combination with ultra-sound and microwave technologies.

6.1. Nano-biotechnological advancements in lignocellulosic biomass pretreatment

Nanotechnology is also gaining attention in the field of biofuel production [156,157]. Nanomaterials are used to facilitate the pretreatment of lignocellulosic biomass. Acid functionalized magnetic nanomaterials were efficiently applied for the pre-treatment of biomass. This magnetic nature of nano materials helps in ease of recovery with reuse [158,159]. Few research works have been conducted on pretreatment of biomass using magnetic nanomaterials to facilitate sugar extraction and promotes higher bio-fuel production **(**Table 8**)**.

Sulfonated magnetic carbonaceous acid nanoparticles were prepared

Table 8
Pre-treatment of lignocellulosic biomass using nanomaterials.

Feed Stock	Nano Materials	Yield (%)	References
Yellow Poplar saw dust	Poly ferrocenylsilane and AS nanoparticles	66& 61	[132]
Wheat Straw	Silica- propyl-sulfonic functionalized nanoparticles	90	[133]
Rice Straw	Cellulases immobilized magnetic nanoparticles	90	[134]
Agave atrovirens leaves	Chitosan-coated magnetic nanoparticles	80 after 15 cycles	[135]
Sugarcane bagasse	Iron oxide nanoparticles	72 after 24 h	[136]
Wheat Straw	Silica-protected cobalt-spinel ferrite nanoparticles	78	[137]

and tested for the hydrolysis of different biomass like jatropha, bagasse, and plukenetia hulls. After addition of these nanomaterials, significant levels of conversion have been achieved [160]. Additionally, sulfonic acid functionalized magnetic nanoparticles offers tremendous stability and significant catalytic activity during biofuel production [161]. New magnetic cross-linked cellulases aggregate (MCLCA) was synthesized and utilized for the conversion of lignocellulosic biomass. As Compared to the free cellulose immobilized cellulases gives more activity and considerably recycled up to six consecutive cycles for the hydrolysis of Lignocellulosic biomass. After that it still retain its activity up to 74% [162].

7. Limitations

Based on the critical analysis of the literature, all the mentioned technologies have their own benefits and limitations. These limitations are still lacked between novel findings and practical application of various pre-treatment technologies. Some recent investigations with their pre-treatment limitations are listed in the Table 9.

The key factors associated with the limitations for the pre-treatment of lignocellulosic biomass for biofuels can be highlighted as

a) Selection and continuous availability of raw materials
b) Efficient and reliable pre-treatment process
c) Capability to reduce cost i.e. apparatus, chemical cost, post-equipment and process control
d) Inhibit toxic compounds generated during pre-treatment process
e) Flexible and low-cost post-treatment process
f) Tackle and mitigate waste and environmental hazards associated with the pre-treatment process
g) Re-usability of the chemical/catalysts consumed during the process

8. Life cycle analysis of pretreatment technologies for lignocellulosic biomass.

Life cycle analysis is a method used to evaluate the environmental impact of any production process, irrespective of its aim of production. The life cycle analysis of any process involves the estimation of the various environmental impacts of it on the overall ecosystem. Four different principles of goal definition, inventory analysis, impact assessment and interpretation are done as under the umbrella of life cycle assessment [163]. This analysis covers the life cycle of any product or process encompassing extraction and processing of the raw materials, manufacturing, distribution, use, recycling, and final disposal. LCA is an environmental management tool applied to evaluate the life cycle of a product based on a framework given by ISO 14,040 and 14,044 [164]. For commercial scale processes for biofuel production, the cheaper and large amount of lignocellulosic biomass is utilized to meet growing demand of energy. The major parts of biofuel productions from lignocellulosic biomass comprises of three steps i.e. delignification, saccharification followed by fermentation [165]. The synthesis of renewable substances like biofuels offers a great source to reduce the carbon footprint associated with their usage along with lowering toxicity in the environment. Lignocellulosic biomass is considered to be carbon neutral, but on burning it releases few amounts of greenhouse gases during its life cycle. The steps involved during the life cycle analysis of biofuels include growth of feedstock followed by the conversion of biofuel and its transportation.

8.1. *Problems associated with biofuels synthesis*

Many wide range of lignocellulosic biomass are available and distributed as food based materials and non-food feedstock. These biofuels possess less harm in terms of greenhouse gases as compared to conventional fossil fuels utilized. On the other hand, few concerns are still present due to indirect emission associated with the plant growth as well as conversion of food land to land for fuel production. The major challenge in the biofuel synthesis is the pretreatment step which consumed huge amount of energy in terms of fossil fuel burning. Additionally, pretreatment processes utilized harsh chemicals that generate inhibitors during the process. Also, excessive washing is required during pretreatment of lignocellulosic biomass that generates a lot of waste that effect nearby water bodies. All these problems associated with pretreatment must be addressed [166,167]. The disadvantages of higher energy consumption during the process can be catered by using renewable energy sources as a substitute of fossil fuels.

8.2. *Life Cycle Analysis based solutions*

Many physical, chemical, physicochemical and biological pretreatment methods are available for delignification of biomass. An effective

Table 9
Few latest researcheson lignocelluloses biomass pretreatment processes with their limitationsfor biofuel production.

Raw Material	Method of Pretreatment	Conditions	Limitations	Year	Reference
Rice Husk	Acid & Alkali	80 °C for 2 h	Only hydrolyse the hemi-cellulose and lignin, post-treatment requires washing & drying of biomass	2020	[189]
Lignocellulosic biomass	Ionic liquids	80 °C to 170 °C for 3–8 h	Reaction kinetics is unexplored, High cost, low recyclability and viscous nature inhibit large scale adoption	2020	[190]
South African grass	Acid mine drainage	50 °C for 72 h with 100 RPM	Low glucose/ethanol concentrations from biomass pre-treated with AMD	2019	[191]
Barley straw	Nitrogen explosive decompression (NED)	50 °C for 72 h with 100 RPM	NED is more effective at lower temperature, hydrolysis efficiency is low, less effective for hemi-cellulosic dissolution	2019	[192]
Wheat straw and pearl millet	Biological (lignin-degrading fungi)	28 °C for 42 days	High cost & contamination due to longer time, loss of carbohydrates	2019	[193]
Corncobs, wheat straw	p-toluene sulfonic acid	80 °C for 10 min with 150 RPM	Low lignin recovery, recyclability & re-usability issues	2019	[194]
Spring wheat straw	Microwave	190 °C for 15 min	High energy demand, unknown effect of microwave irradation on biomass structure, lack of large scale facility	2018	[195]

pretreatment process enhances the substrate accessibility to obtain high yield of biofuels. A research study carried out on the Life cycle assessment of different pretreatment processes involving Liquid hot water (LHW), steam, dilute acid treatment and Organosolv. The results showed that LHW using pressurized deionized water for pretreatment was quite effective in reducing the Green House Gases and yields more sugar for fermentation to biofuel production [168]. Also the inhibitors and waste generated during the pretreatment process is minimum as compared to other processes [168]. Another research study showed that steam explosion of rice straw offered better yield in comparison with dilute acid, dilute alkali, hot water pretreatments. On the other hand, the results of energy yield show great potential as compared to conventional gasoline [169].

Candido and Gonçalves [170] conducted a research on sugarcane. The researchers found that the lignocellulosic biomass pretreated effectively by combining chemical (Acidic and Alkaline) and hydrothermal pretreatment methods together. The results were better in terms of sugar yield i.e. 86% but the environmental concern associated with the usage of chemical highlighted by life cycle assessment discourage the overall process. The research conducted by Smullen et al. [171] showed the environmental concerns associated with use of chemicals during pretreatment process. The methanol possesses least effect on the global warming, eutrophication, acidification, photochemical oxidation demand and marine and human ecotoxicity. Conversely, sodium hydroxide and sulfuric acid possesses severe effects to the surrounding environment and ecology [172]. A combination of chemical (alkaline peroxide) and mechanical pretreatment method followed by enzymatic hydrolysis of sugar cane bagasse reduces the energy consumption up to 65%. The resulted process also reduces waste and inhibitor generation as compared to the chemical pretreatment techniques [173].

9. Conclusions

Exhausting natural reserves of fossil fuels and a surge in global warming caused by the ruthless burning of these fuels had made it necessary to develop such energy sources, which are sustainable and eco-friendly to meet the energy demand of the world. Biofuels, especially bioethanol (the most suitable candidate to replace gasoline), is considered as the fuel of the future for quite some time. Lately, almost all the bioethanol production is dependent on either corn or sugarcane; however, these sources are not sufficient enough to meet the global energy demand. For the past two decades, the focus has been shifted to develop bioethanol from lignocellulosic biomass resources, which are not only available in abundance but also they have no competition with food or cultivated land. However, this route has some associated challenges; pretreatment being the major one of them as it alone is responsible for about 30% of the total cost of biofuel production. The commercialization of biofuels and implementation of biorefinery concept are, therefore, hindered due to the challenges being faced in the pretreatment of lignocellulosic biomass. The ultimate solution will be to use eco-efficient (in terms of cost, energy) green process technologies. A lot many traditional and innovative technologies for the pretreatment of lignocellulosic biomass have been explored which reveal high capital costs, the formation of inhibitors and unwanted side-products vis-à-vis unavailability of comparative efficiency of various process technologies as the major impediments. The need for techno-economic feasibility to ascertain the practicability of emerging innovative technologies lignocellulosic biomass pretreatment cannot be overlooked for successful implementation and commercialization of bio-refinery concept which necessitates further research work to be carried out in this field.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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