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PRE-TREATMENT AND VALUE-ADDED PRODUCTS OF LIGNOCELLULOSIC WASTE: A REVIEW

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Abstract

This paper showcases advances over the last decade in the pretreatment and conversion of Lignocellulosic Wastes (LCWs) to value-added products. Physical, chemical, physicochemical and biological pretreatments are covered, as well as conversion to reducing sugars, bioethanol and biocomposites. Current barriers to usage of LCWs in industry mainly consist of economic costs due to either expensive chemicals/enzymes or high energy requirements. There are also barriers formed by the production of toxic byproducts or the use of toxic chemicals in pretreatments. However, much research is being focussed on the field which doubtless provides much hope for further progress towards the mainstream use of LCWs in industry.

Key words: Lignocellulosic Wastes, Value-added products, Pretreatments.

Introduction

Lignocellulosic Wastes (LCWs) are plant waste materials composed of cellulose, hemicellulose and lignin. LCW can come in a plethora of forms, including grass, paper, wood residues, agricultural residues, industrial food residues and many others. These crops provide a valuable alternative in many areas to dedicated energy crops, which consume much of the farming area that is desperately requires for agricultural food production. Using wastes instead of crops such as sugarcane and grasses is viewed as an important alternative that will help prevent globally rising food prices and ensure that there is less land conflict between growing for fuels and farming for food products.

Lignocellulosic biomass is generally discarded as waste in industrial agricultural processes, but its value has been under intense review for some time. Uses found for LCW include as enzymes, reducing sugars, bioplastics, biofuels, resins, biosorbents and many others. The primary obstacle to the usage of LCW has been the strong linkage of chains via hydrogen bonds (in cellulose and hemicellulose) or ester linkages (in lignin). However, techniques for pretreatment have been developing over the last decade that could potentially make this degradation an easier process and open the gates to more prolific use of LCWs in industry and other areas where they may be useful.

This paper serves as a general update to the review published in the African Journal of Biotechnology by Godliving Y.S. Mtui in 2009 on the same subject (Mtui, 2009). In the below sections, the various pretreatment proceses and their effects on the separation of the complex components of various lignocellulosic sources are discussed. Fig. 1. shows Flow chart diagram of pretreatment processes.

Physical Pretreatment

Mechanical Pretreatment:

Mechanical pretreatment serves to compress LCW. While this does not separate the linkage between chains in the components of LCW, this greatly increases the rates of reaction for other pretreatment processes, such as physical and chemical ones, due to the greatly increased surface areas. One type of process for this is milling, which can fall into different categories, including hammer milling, centrifugal milling, ball milling, stirred milling, and the multi-cracker system. All of these have been shown to increase the surface area of LCW for further processing.

A significant limitation of mechanical pretreatment is the high energy requirement. One way this can be countered is by using chemical agents, such as the ionic

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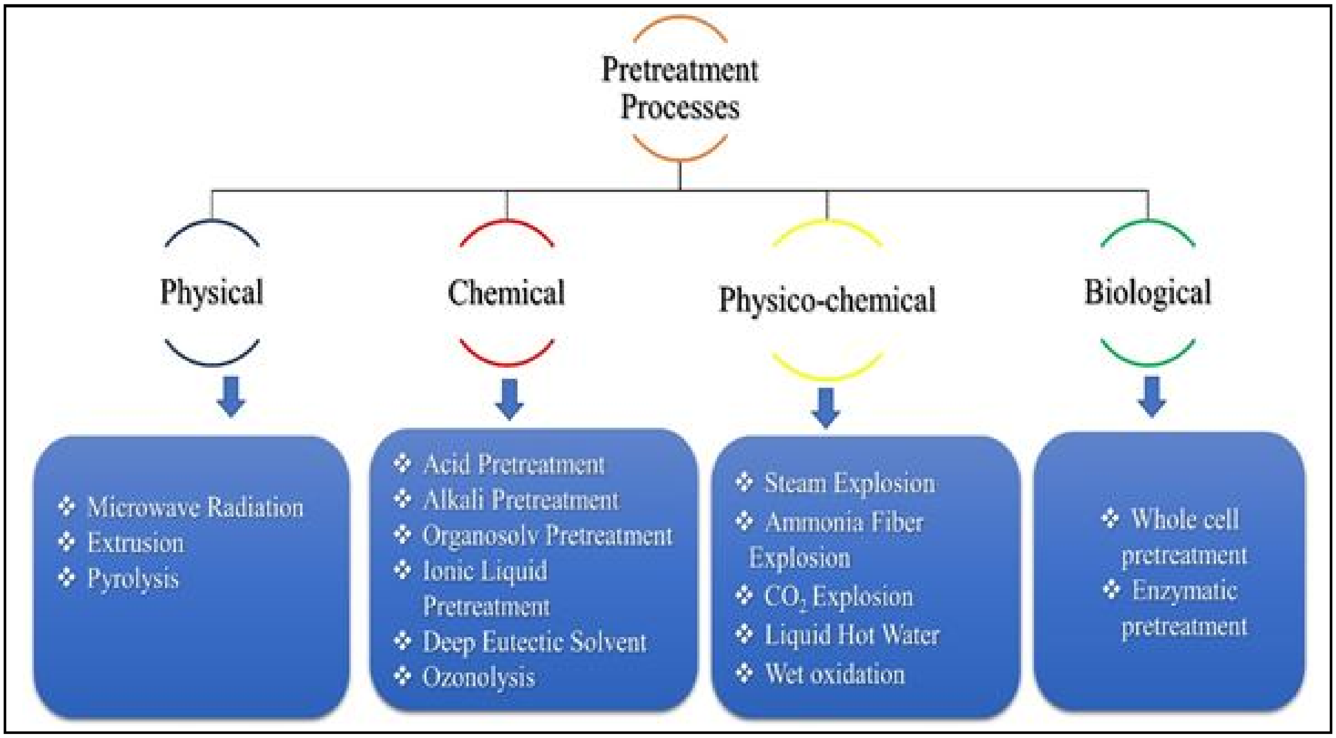

Fig. 1: Pretreatmnet process of Lignocellulosic Waste

liquid solvent. Observations following such treatment include greater disruption of cellulosic crystalline structure, higher glucose content in the product and a decrease in the degree of polymerisation of all the components. The table below adopted from review of Kamarludin *et al.,* 2014.

Microwave Radiation/Microwave-Assisted Size reduction:

Used on plant material, Microwave Radiation offers a short processing time, increased heating capacity, relatively low energy requirements and ease of operation. An appropriate temperature for the process falls in the range of 150-250°C (Li *et al.*, 2016). As with milling, microwave radiation can be used in conjunction with other pretreatment methods to increase yield. For instance, microwave radiation in conjunction with alkaline treatment on delignified hardwood kraft pulp significantly fractures the structure and increases the cellulose yield to 93.05% (Liu *et al.*, 2018). Microwave treatment in conjunction with ionic liquid treatment also yields 78.7% glucose from *Crotalaria juncea* fibers at 160°C after only 47 minutes (Paul & Dutta, 2018). Microwave radiation has been repeatedly confirmed to be a robust addition to the list of pretreatment methods for extracting fermentable sugars from LCWs.

Extrusion:

Extrusion functions by passing LCWs through a barrel using either one or two (twin) rotating screws under a high temperature (>300°C). The combined effect of the spinning screws and the high temperature results in high disruption of the recalcitrant structure of the LCW, exposing a greater surface area for enzymatic hydrolysis. Factors such as speed and duration of processing affect the yield of sugar. Alkalis such as sodium hydroxide can be added to break ester linkages and cause solubilisation in lignin and hemicelluloses, with low degradation of carbohydrates. Screw speed, temperature and compression ratios required for maximum sugar yields vary between plants (Baruah *et al.*, 2018).

Pyrolysis:

Pyrolysis is performed for production of bio oil from LCWs. It utilises temperatures of 500-800°C without any oxidising agents. Pyrolysis can be split into fast and slow pyrolysis. Biomass characteristics, reaction parameters and type of pyrolysis can affect the type of products formed. Pyrolysis has an energy-rich high-value output, including liquid products such as polar hydrocarbons, ash and water. A favourable form of pyrolysis is microwave-assisted for better efficiency.

A milder form of pyrolysis is torrefaction, which is carried out at a temperature of 200-300°C. Dry torrefaction is carried out in an inert atmosphere while wet torrefaction takes place in a pressurised vessel of water (1-250 mPa). Both processes yield partially decomposed products, such as biochar and hydro-char (Chen *et al.*, 2018).

Table 1: Studies of mechanical pretreatments on different lignocelluloses as well as the results of each.

Biomass Type	Grinder Type	Results	Ref
Grass feed, straw and stalk	Hammer mills	-Higher bulk density of biomass -Higher surface area of LB	(Tabil *et al.*, 2011)
-	Stirred mill	-Higher disc speed, higher the grinding rate-Larger the grinding media, larger the energy consumption -Bigger the grinding media, lower the ratio of total input power and impact energy	(Jayasundara *et al.*, 2012)
Wheat straw	Centrifugal and ball milling	-Higher surface area lower energy consumption and particle size	(Barakat *et al.*, 2014)
Wheat & barley straw, corn stoves etc	Hammer mill	-The mill screen size negatively correlated to specific energy consumption -Higher the content of moisture, larger the specific energy consumption -Greater the screen openings, greater the mean particle diameter of the grinds	(Mani *et al.*, 2004)
Wheat, maize & soybean	Multi-cracker system	-Disc speed, disc type, gap between the grinding discs and type of materials affected the mean particle size	(Thomas et al., 2012)

Chemical Pretreatment:

Acid Pretreatment

Acids can break down glucosidic bonds between cellulose and hemicellulose, and can break down the polymer chains into sugar monomer units. Inorganic acids (nitric (Kim *et al.*, 2015), sulfuric (Kärcher *et al.*, 2015), hydrochloric (Zu *et al.*, 2014), phosphoric (Nair *et al.*, 2015) and organic acids, formic (Du *et al.*, 2016), maleic (Jung *et al.*, 2015), oxalic (Jeong & Lee, 2016) are used in the process. The process can either involve concentrated acids (30-70%) and low temperatures (<100°C) or dilute acids at high temperatures (0.1-10%, 100-250°C).

Operational costs are high for acidic pretreatment as they can be toxic and corrosive. Additionally, they can cause unwanted degradation of cellulose into inhibitory products (furfurals, 5-hydroxymthylfurfural, phenolic acids, aldehydes). Sulfuric acid, the most commonly used for this process, produces a wealth of inhibitory products, but it has been seen that organic acids such as maleic and oxalic acid produce fewer such products and thus require less washing and detoxification after the process is complete. Maleic produces a higher concentration of xylose and glucose than oxalic acid. More research is required into the potential benefits of organic acids over mineral acids.

Alkali Pretreatment

Alkali pretreatment serves to cleave ester linkages between hemicellulose and lignin chains, resulting in the solubilisation of lignin. Alkali treatment also swells the structure of LCW, disrupting the crystalline structure and decreasing polymerisation. This also increases internal surface area for enzymatic action.

The four alkalis that can be used are hydroxides of sodium, potassium, ammonium and calcium. Sodium is the most effective in the process (Kim *et al.,* 2016) and thus the most commonly used, but calcium can be used at a lower cost than any of the others. 1% NaOH at room temperature for 3 hours increased methane yield by more than 34% after alkali pretreatment according to one study, due to decreased lignin and helicellulose content (Shetty *et al.,* 2017). The pretreatment also has little effect on the cellulose content.

Alkali pretreatment is a very effective pretreatment method, but presents issues for recovery after pretreatment. Its use is ideal on low-lignin-content LCWs.

Organosolv Pretreatment

Organosolv pretreatment uses organic solvents (ethanol, methanol, ethylene glycol, acetone etc.) that break down internal bonds between lignin and hemicellulose, leaving behind a relatively pure residue of cellulose. The process increases the pore width and surface area of the cellulose for enzymatic action (Zhang *et al.,* 2016).

This is typically done in the presence of inorganic acids, bases and a catalyst that can improve delignification rates or lower the temperature required to operate (the catalyst is often a salt (Borand and Karaosmanoðlu, 2018).

Organosolv has some disadvantages. These include the organic solvents themselves being very expensive. Fortunately, this can be countered as the solvents are easy to recover, bar the recovery still being relatively energy-intensive. The flammability also requires a very controlled environment to ensure safety (Borand and Karaosmanoðlu, 2018).. Overall, organosolv is a promising pretreatment bar having many issues. Using it in conjunction with other pretreatments (such as milling) can increase its efficacy further).

Ionic Liquid Pretreatment

Ionic Liquids (ILs) are solutions of ions, where the solvent has a low melting point (<100°C) and the solution has a high thermal stability. Typically, the cation used is a large organic one, while the anion is small and can be either inorganic or organic (Yoo *et al.*, 2017). This method works by interfering with hydrogen bonding in LCW, leading to disruption of the structure and thus an increase in surface area for enzymatic action. The charge delocalisation of the anion and the structure of the cation can significantly influence the ionic liquid properties. Temperature and the duration of exposure also contribute to the interaction between the ionic liquid and organic matter.

Deep Eutectic Solvent

A similar pretreatment to IL is deep eutectic solvent pretreatment. The solvent in this process is defined by the following:

Cat^+X^-zY

Where Cat^+ is a cation such as sulfonium, ammonium or phosphonium and X^- is a Lewis base. This complex interacts with z number of Y molecules. While the method by which these solvents interact is similar to IL, the solvents themselves are very different and as such require a different category as a pretreatment.

Ozonolysis

The use of ozone in pretreatment primarily serves to decrease lignin content in LCW as it nearly-negligibly affects hemicellulose and cellulose. Ozonolysis is heavily affected by the moisture content of the LCW, functioning best at low moisture levels. Ozonolysis additionally does not produce toxic byproducts for downstream processing, although some inhibitory products are made that must be removed, many of which are aromatic (Travaini *et al.*, 2013).

The current barrier to widespread usage of ozonolysis is the large concentrations of ozone required, which is prohibitively expensive for large-scale industrial processes. Thus, research must still be done on how to produce ozone more cheaply.

Physicochemical Pretreatment

Steam Explosion

Steam explosion involves exposing LCW to steam under a pressure of 0.7-4.8MPa. The steam at a temperature of 160-260°C penetrates the substrate structure, resulting in some hydrolysis of glycosidic bonds and leading to the term 'autohydrolysis'. This is also contributed to by the formation of organic acids during the process, which are already involved in a chemical pretreatment and are known to be effective at breaking down the LCW structure and aid in hydrolysis. Following this, pressure is rapidly decreased to atmospheric pressure, resulting in an 'explosive' decompression which cleaves fibers and hemicellulose-lignin bonds.

The ideal outcome of steam explosion is achieved with either a high temperature and short residence time, or a lower temperature and a longer residence time. A significant factor that makes this pretreatment technique valuable to industry is the high energy efficiency and high output of sugars (steam requires only 30% of the energy that mechanical methods utilise to produce LCW particles of the same size (Kim, 2018). However, the high thermal energy involved leads to the production of a variety of inhibitory products.

Ammonia Fiber Explosion (AFEX)

Liquid ammonia is involved in multiple pretreatments such as Soaking Aqueous Ammonia and Ammonia Recycle Percolation. AFEX involves heating ('cooking') liquid ammonia with LCW in a ratio of approximately 1:1 at anywhere from 60-100°C, with an added pressure of 3MPa. After 5-45 minutes of cooking (some papers have this range as 5-30 minutes (Shirkavand *et al.*, 2016), while another review put this at 5-45 minutes (Aftab *et al.*, 2019), pressure is rapidly released, leading to explosive decompression of LCW fibers, similar to steam explosion.

Ammonia is easily recovered afterwards due to its volatility. The optimal conditions for AFEX are still under investigation however. It appears that AFEX is much more effective with low-lignin-content LCWs, as AFEX is largely ineffective and solubilising hemicellulose and lignin. One study found that a mixing ratio of 5:1 of ammonia to biomass was optimal, 70% moisture content and 170°C were optimal conditions for enhanced enzymatic digestion of corn stover. They also found that presoaking the stover increased delignification from 15.74 to 24.07% (Zhao *et al.*, 2014).

The primary advantage of this method is the lack of any substantial amounts of inhibitory products. While ammonia is expensive to produce, it can be re-obtained and recycled easily to be used again.

CO_2 Explosion

In an effort to devise a pretreatment that was cheaper than AFEX and needed a lower temperature than steam explosion, CO_2 explosion involves passing gaseous CO_2 through a high-pressure cylinder, compressing past its critical point to make it behave as a solvent (the gas is termed subcritical) (Rostagno *et al.*, 2015). Once dissolved in water, the CO_2 hydrolyses hemicellulose and lignin as it is converted to carbonic acid. Once pressure is released, the structure of LCW is shattered similarly to AFEX and steam explosion.

Soybean hull pretreated with CO_2 explosion resulted in a 97% sugar yield after enzymatic hydrolysis, showing the effectiveness of CO_2 explosion at increasing surface area for enzyme action (Islam *et al.,* 2017). CO_2 explosion is also promising due to low temperatures requires and the cheapness of CO_2. However, the pressure cylinder must be able to withstand a pressure of around 8MPa, which requires a very significant economic input and factors as the primary obstacle for this pretreatment method.

Liquid Hot Water (LHW)

Similar to steam explosion, LHW employs H_2O under a high pressure to help break the structure of LCWs. However, the pressure in this process is used to maintain the liquid state of this water, and the maintenance of this pressure means that no rapid decompression is required later in the process. The pressure (up to 5MPa) involved is to prevent evaporation of water at the temperatures requires (170-260°C). LHW hydrolyses hemicellulose, detaching acetyl groups, and removes lignin. This makes cellulose very accessible to enzymes in later processing. To avoid the formation of inhibitory products and the degradation of sugars, LHW is carried out at a pH of 4-7 (Li *et al.,* 2014).

The advantages of LHW include a lack of catalysts and chemicals. The formation of toxic products is virtually non-existent and the low temperature and cheap solvent reduce costs. However, the significant drawback is the large amount of water used, which required a large sum of energy in downstream processing.

Wet oxidation

Wet oxidation involves treating LCW at a temperature of >120°C and a pressure of 0.5-2MPa for 30 minutes utilising oxygen/air and hydrogen peroxide/water (Varga *et al.,* 2003). At the high temperatures involved (170°C and above), water behaves as an acid, releasing more hydrogen ions as the temperature and thus reducing the pH. This results in the hydrolysis of hemicellulose and thus the production of pentose monomers. The process also results in the oxidation of lignin, while cellulose is less affected than either of these. Addition of catalysts such as sodium carbonate or alkaline peroxides can reduce both the temperature required for the pretreatment as well as the number of inhibitory products formed (furfurals and furfuraldehydes). However, the production of these products in any case is less than that for LHW and steam explosion pretreatment. Unfortunately, the most significant barrier for this method to reach industrial levels is the expense of hydrogen peroxide and the high flammability of oxygen.

Biological Pretreatment

Biological pretreatment employs the use of microbial enzymes to remove lignin and sometimes hemicellulose. It presents a low-cost and environmentally-friendly alternative to the other pretreatment methods. Methods can generally be divided into whole cell and enzymatic pretreatment.

Whole cell pretreatment

Whole cell pretreatment utilises cells of organisms such as fungi. A common example is white-rot fungi, as they decompose lignin with minimal effect on cellulose. However, large lignin polymers present issues to these fungi as the carbon-carbon bonds are challenging for them to break down. Another disadvantage is the requirement for a long residence time, along with a low efficiency. The table below from another review details some organisms that have been studied for whole cell pretreatment and the conditions used.

Enzymatic pretreatment

Enzymatic pretreatment solely uses enzymes isolated from organisms that produce them, often coming from bacteria, fungi and insects. The two families of enzymes used are laccases (phenol oxidase) and peroxidases (lignin peroxidase, versatile peroxidase and manganese peroxidase) (Zámocký *et al.,* 2014).

Laccases are multicopper enzymes that catalyse the oxidation of the phenolic structures in lignin (Heap *et al.,* 2014). They are produced by both bacteria and fungi and can greatly increase yields in saccharification and hydrolysis treatments. They can decompose both toxic and non-toxic substrates, leading to their use in textiles, food processing, wood processing, pharmaceutics and the chemical industry.

Lignin peroxidase is an H_2O_2-dependent heme glycoprotein that can be obtained from white-rot fungi. Manganese peroxidase is also a heme glycoprotein, but the key difference is that lignin peroxidase oxidises non-phenolic lignin, while manganese peroxidase oxidises phenolic rings. Versatile peroxidase can do both functions, being able to oxidise Mn^{2+} to Mn^{3+} as well as non-phenolic parts of lignin. These three enzymes can be used in conjunction. The table below from another review lists the effect of enzymatic pretreatments on different lignocelluloses.

Value-Added Products:

Reducing Sugars

In the chain of products required to make value-added products, reducing sugars are the first step, requiring hydrolysis of the hemicellulose and cellulose chains to give monosaccharides such as glucose, galactose, xylose, mannose, arabinose and others. These compounds can be further fermented into products such as biofuels.

Singh *et al.,* (2011) used concentrated acid, AAT and acid hydrolysis and dilute acid pretreatment with enzymatic hydrolysis. AAT and acid hydrolysis had the highest yield of 0.569g per gram of initial biomass, but further investigation of the enzymatic pathway as there was lower levels of toxic byproducts released. The method proved that Kans grass is a promising candidate for bioethanol production with high release of monomers and minimal release of toxic substances. Moraïs *et al.,* designed a cellulosome composed of cellulases and xylanases from *Thermobifida fusca*. The artificial cellulosome heralded 33-42% the efficiency of natural cellulosomes from *Clostridium thermocellum*, meaning more research is required into the manufacture of cellulosomes to reduce recalcitrance of lignocellulose (Moraïs *et al.,* 2012). Yu *et al.,* 2018 used a modified Fenton pretreatment with $FeCl_3$ to yield a 94% recovery of soluble monomeric carbohydrates (glucose, xylose). The process could be carried out at a slightly lower efficiency with Fe_3O_4. While the process presents a more eco-friendly treatment method than previously, energy requirements still present a significant challenge in obtaining reducing sugars. Another barrier to enzymatic hydrolysis is the high cost of cellulases, making the process economically difficult despite the low price of feedstock. This presents an economic issue additionally for fermentation of the sugars to biofuels such as bioethanol (Liu *et al.,* 2019).

Biofuels

With energy crises emerging globally and concern arising over carbon emissions, biofuels are an important topic to look into. LCW can be converted into a wide assortment of fuels that can render fuel usage carbon-neutral while avoiding conventional issues caused by sugarcane and other crops that take up space typically used for food crops. Biofuels like bioethanol are typically obtained through the fermentation of reducing sugars obtained from pretreatment and enzymatic/chemical hydrolysis.

Separate hydrolysis and co-fermentation (SHCF) involves cellulose being completely hydrolysed into beta-glucose before being fermented to ethanol. This can happen at temperatures around 50°C, the result of which is making fermentation impossible to carry out at the same time; *Saccharomyces cerevisiae* used in fermentation can only operate below 35°C. Separating lignin from the resulting mash produces a hydrolysate that can have increased HG fermentation ethanol titers. Microbial contamination is one issue with SHFC, but the method is still being explored in industry. Glucose accumulation also can cause some inhibition of beta-glucosidase, but supplementary beta-glucosidase at low prices could be an economic solution to this.

Saccharification coupled with co-fermentation (SCCF) can be used with starch-based feedstock. For use with LCB, this process was carried out as a modified version of SSCF, although Liu *et al.,* (2019) [39] claims this would be better classified as SCCF as the hydrolysis and fermentation are not actually simultaneous. This process has a high ethanol yield due to the lack of inhibition in hydrolytic activity, but the lower temperatures required (<35°C) result in a significantly compromised rate. Additionally, lignin cannot be removed prior to fermentation, so the extra mixing is required, making HG fermentation difficult and recovery of ethanol more expensive. A more blended approach is required to make the process more economically feasible for LCWs.

S. cerevisiae is the yeast responsible for fermenting hexose sugars into ethanol. However, it is known that many of the primary products of hydrolysis include pentose sugars such as xylose and arabinose from hemicellulose chains. Thus, engineered microbes are required for fully efficient metabolism of the reducing sugars. Other microbes such as *Z. mobilis* are being researched as alternatives to GM *S. cerevisiae*, but the limitations of the microbe, such as the range of sugars it can digest, limit its application to the fermentation process at an industrial level at the moment (Liu *et al.,* 2019).

Bioplastics

Global crises are emerging surrounding the use of plastics that do not biodegrade. With large masses of human industrial waste congregating in oceans and other ecosystems, initiatives to find biodegradable polymers are in high demand. LCWs provide an avenue to create bioplastics that present many benefits over regular hydrocarbon plastics taken from fossil fuels such as crude oil and natural gas.

Lignin is a major component being investigated for its use in bioplastics. As reinforcement, its relatively polar nature (from many hydroxyl groups) results in poor miscibility with most polymers. Lignin added to starch plastics can have varying effects depending on the amount and molecular weight added. 10% lignin has been indicated to be an optimal level, but more research is required on the topic. Adding 10-30 wt% of lignin to protein-lignin bioplastics increases the Young's Modulus greatly. PLA with added lignin has interactions between carboxyl and hydroxyl groups through hydrogen bonding has increased Young's modulus but a decreased tensile strength due to inconsistent distribution of lignin within the bioplastic structure. The tensile strength decreases in PLA-lignin bioplastics with increasing lignin content for this reason.In general, modified lignin with a lower polydispersity perform better in bioplastics, but cost-benefit analyses must be taken into account as bioplastics should be cheaper than current plastics in use.

Lignocellulosic fibres have been more thoroughly explored as they are cheaper to obtain, especially in unmodified form. Lignocellulose presents issues in miscibility due to the large extent of hydrogen-bonding withing lignocellulosic fibres leaving little room for hydrogen bonding with other biopolymers through blending, deteriorating structural integrity of biocomposites formed. However, lignin-containing lignocellulosic fibres present a promising candidate for reinforcement of biocomposites. More research into these fibres could provide industry with a substantially useful plastic-alternative in the form of a biocomposite reinforced with lignocellulose (Yang *et al.,* 2019).

Technoeconomic Evaluation

LCWs have continued to show promise in their potential uses for products such as biofuels and biocomposites. Work is still required in various areas regarding pretreatment and processing of LCWs for these value-added products. Many types of milling and LHW are both prohibitively energy-intensive on an industrial scale. Processes such as AFEX and Organosolv utilise chemicals that are too expensive at the moment to be applied in industrial processing. Being aimed at lower-income countries where the presence of LCWs are plentiful from industrial agricultural processes already taking place, the need for these processes to be both cheaper and more effective than current alternatives is essential. This means future progress should strive to make technologies involved cheaper and faster. For the bioproduction of ethanol, much research must go into finding low-cost alternatives to the enzymes used in hydrolysis such as cellulases. More research is also required on finding the ideal microbe for fermentation due to the limitations on substrates *S. cervisidiae* can digest without engineering. The cost overall of producing cellulosic ethanol is less cost-effective than ethanol production from sugarcane and starch-based produce, let alone crude oil and natural gas. Biocomposites still require more research into making plastics with more regular structures, particularly looking into the uses of lignin in these products as reinforcement.

Conclusion

This paper has attempted to put together research from the last eleven years. Much research has been carried out into which pretreatment methods are best for each type of feedstock, and a plethora of value-added products are coming into focus. Much of the goal of research to take place in the future will be to find ways to make these processes both cost-effective and to form products that are better than the environmentally harmful products being used in modern society.

References

Aftab, M.N., I. Iqbal, F. Riaz, A. Karadag and M. Tabatabaei (2019). Different Pretreatment Methods of Lignocellulosic Biomass for Use in Biofuel Production. In *Biomass for Bioenergy-Recent Trends and Future Challenges*. IntechOpen.

Barakat, A., S. Chuetor, F. Monlau, A. Solhy and X. Rouau (2014). Eco-friendly dry chemo-mechanical pretreatments of lignocellulosic biomass: Impact on energy and yield of the enzymatic hydrolysis. *Applied Energy,* **113:** 97-105.

Baruah, J., B.K. Nath, R. Sharma, S. Kumar, R.C. Deka, D.C. Baruah and E. Kalita (2018). Recent trends in the pretreatment of lignocellulosic biomass for value-added products. *Frontiers in Energy Research*, **6:** 141.

Borand, M.N. and F. Karaosmanoðlu (2018). Effects of organosolv pretreatment conditions for lignocellulosic biomass in biorefinery applications: a review. *Journal of Renewable and Sustainable Energy,* **10:** 033104.

Che Kamarludin, S.N., M.S. Jainal, A. Azizan, N.S.M. Safaai and A.R. Mohamad Daud (2014). Mechanical pretreatment of lignocellulosic biomass for biofuel production. In *Applied Mechanics and Materials,* **625:** 838-841. Trans Tech Publications Ltd.

Chen, Z., M. Wang, Y. Ren, E. Jiang, Y. Jiang and W. Li (2018). February. Biomass torrefaction: A promising pretreatment technology for biomass utilization. In *IOP Conference Series: Earth and Environmental Science,* **113(1):** 012201.

Du, H., C. Liu, Y. Zhang, G. Yu, C. Si and B. Li (2016). Preparation and characterization of functional cellulose nanofibrils via formic acid hydrolysis pretreatment and the followed high-pressure homogenization. *Industrial Crops and Products,* **94:** 736-745.

Heap, L., A. Green, D. Brown, B. van Dongen and N. Turner (2014). Role of laccase as an enzymatic pretreatment method to improve lignocellulosic saccharification. *Catalysis Science and Technology,* **4:** 2251-2259.

Islam, S.M., Q. Li, A. Al Loman and L.K. Ju (2017). CO_2-H_2O based pretreatment and enzyme hydrolysis of soybean hulls. *Enzyme and Microbial Technology,* **106:** 18-27.

Jayasundara, C.T., R.Y. Yang and A.B. Yu (2012). Effect of the size of media on grinding performance in stirred mills. *Minerals Engineering*, **33:** 66-71.

Jeong, S.Y. and J.W. Lee (2016). Optimization of pretreatment condition for ethanol production from oxalic acid pretreated biomass by response surface methodology. *Industrial Crops and Products,* **79:** 1-6.

Jung, Y.H., H.M. Park and K.H. Kim (2015). Whole slurry saccharification and fermentation of maleic acid-pretreated rice straw for ethanol production. *Bioprocess and* *biosystems engineering,* **38:** 1639-1644.

Kärcher, M.A., Y. Iqbal, I. Lewandowski and T. Senn (2015). Comparing the performance of *Miscanthus x giganteus* and wheat straw biomass in sulfuric acid based pretreatment. *Bioresource Technology,* **180:** 360-364.

Kim, D. (2018). Physico-chemical conversion of lignocellulose: Inhibitor effects and detoxification strategies: A mini review. *Molecules,* **23:** 309.

Kim, I., Y.H. Seo, G.Y. Kim and J.I. Han (2015). Co-production of bioethanol and biodiesel from corn stover pretreated with nitric acid. *Fuel*., **143:** 285-289.

Kim, J.S., Y.Y. Lee and T.H. Kim (2016). A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. *Bioresource technology,* **199:** 42-48.

Li, H., Y. Qu, Y. Yang, S. Chang and J. Xu (2016). Microwave irradiation–A green and efficient way to pretreat biomass. *Bioresource technology,* **199:** 34-41.

Li, H.Q., W. Jiang, J.X. Jia and J. Xu (2014). pH pre-corrected liquid hot water pretreatment on corn stover with high hemicellulose recovery and low inhibitors formation. *Bioresource technology,* **153:** 292-299.

Liu, C.G., Y. Xiao, X.X. Xia, X.Q. Zhao, L. Peng, P. Srinophakun and F.W. Bai (2019). Cellulosic ethanol production: progress, challenges and strategies for solutions. *Biotechnology advances,* **37:** 491-504.

Liu, Y., B. Sun, X. Zheng, L. Yu and J. Li (2018). Integrated microwave and alkaline treatment for the separation between hemicelluloses and cellulose from cellulosic fibers. *Bioresource technology,* **247:** 859-863.

Mani, S., L.G. Tabil and S. Sokhansanj (2004). Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass and bioenergy,* **27(4):** 339-352.

Moraïs, S., E. Morag, Y. Barak, D. Goldman, Y. Hadar, R. Lamed, Y. Shoham, D.B. Wilson and E.A. Bayer (2012). Deconstruction of lignocellulose into soluble sugars by native and designer cellulosomes. *Mbio.,* **3(6):**.

Mtui, G.Y. (2009). Recent advances in pretreatment of lignocellulosic wastes and production of value added products. *African Journal of Biotechnology*, **8:** 8.

Nair, R.B., M. Lundin, T. Brandberg, P.R. Lennartsson and M.J. Taherzadeh (2015). Dilute phosphoric acid pretreatment of wheat bran for enzymatic hydrolysis and subsequent ethanol production by edible fungi *Neurospora intermedia*. *Industrial Crops and Products,* **69:** 314-323.

Paul, S. and A. Dutta (2018). Challenges and opportunities of lignocellulosic biomass for anaerobic digestion. *Resources, Conservation and Recycling*, **130:** 164-174.

Rostagno, M.A., J.M. Prado, A. Mudhoo, D.T. Santos, T. Forster–Carneiro and M.A.A. Meireles (2015). Subcritical and supercritical technology for the production of second generation bioethanol. *Critical Reviews in Biotechnology,* **35:** 302-312.

Shetty, D.J., P. Kshirsagar, S. Tapadia-Maheshwari, V. Lanjekar, S.K. Singh and P.K. Dhakephalkar (2017). Alkali pretreatment at ambient temperature: A promising method to enhance biomethanation of rice straw. *Bioresource technology,* **226:** 80-88.

Shirkavand, E., S. Baroutian, D.J. Gapes and B.R. Young (2016). Combination of fungal and physicochemical processes for lignocellulosic biomass pretreatment–A review. *Renewable and Sustainable Energy Reviews,* **54:** 217-234.

Singh, I.K., G. Chaudhary and R. Kataria (2011). Production of Reducing Sugars From Lignocellulosic Biomass For Fuel Ethanol Production. National Conference on Water, Energy and Biodiversity.

Tabil, L., P. Adapa and M. Kashaninejad (2011). Biomass feedstock pre-processing-part 1: pre-treatment. *Biofuel's Engineering Process Technology*, **18:** pp.411-439.

Thomas, M., M. Vrij, T. Zandstra and A.F.B. Van der Poel (2012). Grinding performance of wheat, maize and soybeans in a multicracker system. *Animal feed science and technology,* **175(3-4):** 182-192.

Travaini, R., M.D.M. Otero, M. Coca, R. Da-Silva and S. Bolado (2013). Sugarcane bagasse ozonolysis pretreatment: effect on enzymatic digestibility and inhibitory compound formation. *Bioresource technology,* **133:** 332-339.

Varga, E., A.S. Schmidt, K. Réczey and A.B. Thomsen (2003). Pretreatment of corn stover using wet oxidation to enhance enzymatic digestibility. *Applied biochemistry and biotechnology,* **104:** 37-50.

Yang, J., Y.C. Ching and C.H. Chuah (2019). Applications of lignocellulosic fibers and lignin in bioplastics: A review. *Polymers,* **11:** 751.

Yoo, C.G., Y. Pu and A.J. Ragauskas (2017). Ionic liquids: Promising green solvents for lignocellulosic biomass utilization. *Current Opinion in Green and Sustainable Chemistry,* **5:** 5-11.

Yu, H.T., B.Y. Chen, B.Y. Li, M.C. Tseng, C.C. Han and S.G. Shyu (2018). Efficient pretreatment of lignocellulosic biomass with high recovery of solid lignin and fermentable sugars using Fenton reaction in a mixed solvent. *Biotechnology for biofuels,* **11:** 287.

Zámocký, M., B. Gasselhuber, P.G. Furtmüller and C. Obinger (2014). Turning points in the evolution of peroxidase–catalase superfamily: molecular phylogeny of hybrid heme peroxidases. *Cellular and Molecular Life Sciences,* **71:** 4681-4696.

Zhang, K., Z. Pei and D. Wang (2016). Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemicals: a review. *Bioresource technology,* **199:** 21-33.

Zhao, C., W. Ding, F. Chen, C. Cheng and Q. Shao (2014). Effects of compositional changes of AFEX-treated and H-AFEX-treated corn stover on enzymatic digestibility. *Bioresource technology,* **155:** 34-40.

Zu, S., W.Z. Li, M. Zhang, Z. Li, Z. Wang, H. Jameel and H.M. Chang (2014). Pretreatment of corn stover for sugar production using dilute hydrochloric acid followed by lime. *Bioresource technology,* **152:** 364-370.