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A Review: Chemical and Biological Pretreatment Techniques for Optimized Bioethanol Production

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ABSTRACT

Overwhelming the recalcitrance of lignocellulosic biomass is a vital step in biofuel production. The recalcitrance is a result of the crystalline nature of the lignin bound to the hemicelluloses leading to rigidity of the biomass. The pretreatment is necessary to subdue the recalcitrance, separate the cellulose, hemicelluloses from the lignin to expose the surface area of the biomass and enhance solubilization of the hemicelluloses to release sugars. It was reported that pretreatment with acid on rice straws gave 90.8% sugar and with ammonia resulted to 96% sugar yield. Ammonia pretreatment of Bermuda grass with ammonia yielded 19.7% and 22.93% respectively. This paper reviewed different techniques to identify their merit and demerit with respect to hydrolysis and fermentation. Also, look into promising techniques that help to produce high quality biofuel, minimize the volume of feedstock utilize. The problems of these techniques will also be reviewed based on the enzymatic reaction, inhibitors formation, and action on the equipments.

Keywords: Biofuel, Pretreatment chemicals, Lignocellulosic biomass, Inhibitors, Enzymatic.

I. INTRODUCTION

The goal of pretreatment is to produce biofuel and chemicals from biomass to replace the gasoline by 2030 (US DOE). The potential of biomass is to obtain energy and valuable chemicals resulting from its availability, low cost, and environmental friendly. Energy production from cellulosic biomass have zero greenhouse gas emission and a sustainable renewable (Muhammad and Saha, 2020).

One of the key step in processing biomass to fuel and chemicals is to depolymerize the cellulose for high quality ethanol by enzymatic hydrolysis. The cost of enzymes to convert cellulose and hemicelluloses to sugar for fermentation process will be higher compare to starch hydrolysis to glucose. The cost of the enzymes, requires a way of reducing its cost in bioprocessing of biomass to fuels and chemicals. The major challenges of wide acceptance of biomass for biofuel is low cost of technology to subdue the recalcitrance of the materials (Zafar,2020).

Lignocellulose composed of cellulose, hemicelluloses and lignin, extracts, pectin, and other inorganic materials. The cellulose is a portion of the lignocellulosic biomass constitutes 30 – 50 % with linear chains of homopolymers linked by β- (1-4) glycosidic bond (Kumar *et al.*,2017). Celluolse is more susceptible to enzymatic degradation in its non-crystalline form. It is packed into microfibrils, stabilized by hydrogen bond (Tursi, 2019) and attached by hemicelluloses and polymers of sugars.It does not dissolves in water except at extreme pH. Cellulose has various properties and used as resources such as fibres, fuels, chemicals etc (Jedvert and Heinze, 2017).

The hemicellulose consist of 25 - 40 % made up chains of ylogucan (Sharama *et al*.,2020). A branched polysaccharides of low molecular weight than cellulose with sugar residues carrying different bonds. It readily decomposed into monosaccharides as a result of low degree of polymerization. They are bound with hydrogen and weak forces and are soluble in alkali solvents.

Lignin an amorphous polymer constitutes about 15-30% of the biomass , containing p-coumaryl, coniferyl, and sinapyl (Devi et al., 2021) . This is bound to hemicelluloses resulting the rigidity of the biomass, resistance against microbial attack and prevent enzymatic hydrolysis. It does not take part in fermentation processses but is used in biorefineries as fuels, paper production and to produce value product such as vanillin , benzoquinone and carboxylic acid (Garlpati et al., 2020). The lignin can also be converted to bio-oil, methanol and syngas by thermal depolymerization process. However, reductive ploymerization process produces alkozyphenols, benzyl phenols, catechols and methoxy phenols (Yogalakshmi *et al.*, 2022).

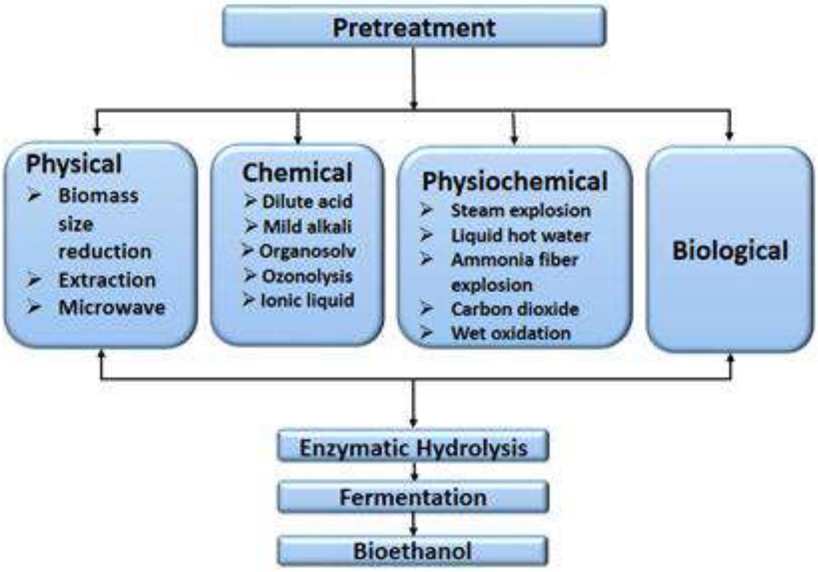

Fig 1 : Pretreatment Methods of lignocellulosic biomass

II. PRETREATMENT TECHNIQUES

This is the process of changing the properties, structural and composition of lignocellulosic biomass to enhance enzymatic hydrolysis for conversion to biofuel (Amin et al., 2017). It exposes the surface area of the cellulose and makes it susceptible to microbial degradation (An et al., 2015). Hence, pretreatment disrupt the cellulose crystals, remove the lignin to improve the solubilization of the biomass.

Pretreatment of biomass is followed by enzymatic hydrolysis to produce sugars and fermentation proceed to yield biofuel (Zhang et al., 2023). Pretreatment is very important prior to enzymatic hydrolysis and fermentation. Cellulose and hemicelluloses are broking down to simple sugar either by enzyme or acid hydrolysis. However, there has been search for microbes capable to ferment glucose and xylose to useful chemicals (Bhurat et al., 2023).

An effective pretreatment should be cost effective, minimize formation of inhibitory compounds, and improve the percentage of cellulose degradation for hydrolysis (Sun and Cheng, 2002).

a. Goals of Pretreatment

The goal of pretreatment is to enhance reaction of cellulose and hemicelluloses to increase sugar yield. This involves solubilization of cellulose, prevention of degradation of sugars from hemicelluloses and minimise formation of inhibitors. Moreso, ability to recover lignin for conversion into valuable products, minimize heat and provide cost effective of the equipment

Table 1 : Significance for various treatment of biomass (Alvira et al., 2010)

Common pretreatment	Main Objectives
Physical pretreatment (comminution)	reduce biomass size, Increase surface area
Acid pretreatment	Solubility of the hemicellulose
Alkaline pretreatment	Delignification
Thermal pretreatment	Mechanically – separation of fibers due to explosive decompression

Microwave-assisted-alkaline pretreatment	Improve the effect of alkaline pretreatment (delignification)
Biological Pretretment	Degrade lignin and hemicelluloses

Pretreatment can be categorize into physical, chemical, physiochemical and biological. Physical pretreatment involves breakdown of biomass sizes and crystallinity by milling, grinding or chopping and the energy required depend on the sizes of the biomass. Biological pretreatment involves the use of microorganism mostly fungi to degrade lignin and hemicelluloses and the cellulose unaffected (Zhang et al.,2023). The process required mild condition, low cost and low rate of hydrolysis. Effort is on in combining this method with other pretreatment and developing a new hybridized microorganism for rapid hydrolysis (Zhang et al., 2023).

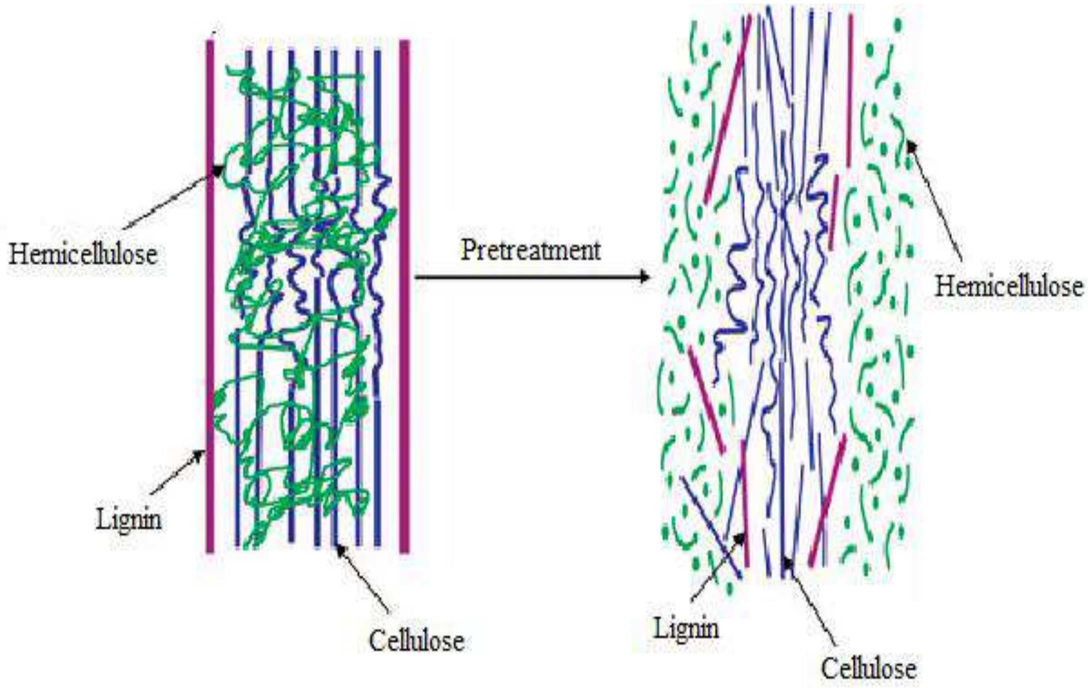

Fig 2 : Pretreatment of lignocellulosic biomass

b. Chemical Pretreatment

This pretreatment aims at disrupting the cell plant to yield sugars and convert it to biofuel and other valuable products (Oyedeji et al., 2020).

Acid

This involves the use of concentrated and dilute acid to break the lignin structure of the biomass. Acid pretreatment does not have much effect on lignin but only on the polysaccharides. However, it makes the enzymes more accessible to the cellulose. The drawback is formation and cost of inhibitors removal (Rezania *et al*., 2020). Concentrated acid is corrosive, increase production cost, and also produce unwanted products from cellulose degradation. Dilute acid requires to increase in rate of reaction, and can be improved by raising the temperature of the process. Hence, less inhibitors is formed and low yield of sugar.

Weak acid such as dicarboxylic acid is better as it is less toxic to microorganism than the concentrated acid. Other weak acid such as organic acids for the pretreatment purposes and cellulose degradation which does not hamper glycolysis. The main advantage is production of less amount of inhibitors and no odour is produced.

For example, tetraoxosulphate vi acid for pretreatment of switch grass (Digmanet al., 2010), yield high sugar concentration. Dilute acid at higher temperature lead to formation of furfural as inhibitors. This process results into the disruption of intermolecular forces of hemicelluloses. Li *et al.,* (2019), implores using acid such as trioxonitrate v acid at a temperature condition on the biomass, break the hemicelluloses thus increasing the biomass porosity. However, it requires adequate materials, corrosion of reactors. Wang et al., (2013), sugar is maximize using a two stage dilute tetraoxosulphate vi process, 15% of tetraoxosulphate vi acid on Bermuda grass and rye straw yield 19.71% and 22.93% reducing sugars. Saha et al., (2020), reported 76% of sugar yield on acid wheat straw and on rice hull 60% of sugar is obtained. Marzialatti et al., (2008) utilize tetraoxosulphate vi acid, trioxonitrate v acid and trioxophosphate acid to enhance 75% yield of sugar and inhibitor such as furfural, hydroxylmethylfurfural are produced.

Alkaline Treatment

This type of treatment is very effective for solubilization of cellulose . The main advantage is that it can be recovered. However, this pretreatment is less productive for hard wood. The Alkaline solutions are mostly for delignification and make the hemicelluloses and cellulose available for hydrolysis. This method removes lignin without reduction in carbohydrate content and improves enzymatic hydrolysis. . The main setback is time consuming (Razenia et al., 2020).

This involves the use of hydroxide of sodium, potassium, calcium, and ammonia to degrade polymers resulting in structural alteration of cellulose, hemicelluloses and lignin (Cheng et al., 2010). The disruption of the lignin enhance accessibility of enzyme to cellulose and hemicelluloses. Sun and Cooker (Lynd et al., 1999), shows that 60% of lignin is removed, 80% of hemicelluloses on using 15% sodium hydroxide on wheat straw. Zhao et al., (2010), give rise to 26% of lignin removal using calcium hydroxide. The advantage of using alkaline is that it is costlier. Alkaline can be combine with wet oxidation, steam explosion, ammonia fibre explosion for improved sugar yield of sugar from switch grass.

Solvent Pretreatment

This method uses organic solvents such as alcohol, esters, amine, propionoic acid, Phenols, formaldehyde etc (Das *et al.,* 2021). This method is mostly used because it can disrupt and separate biomass lignin, cellulose, and hemicelluloses with high purity. The method is expensive and thus making it not economically viable. (Joy and Krishna, 2020).

The method using Organosolv

This requires solvents like acetone, alcohol, with inorganic acid such as (HCI, H_2SO_4). Phosphoric acid and some salts are used as catalyst (Borand and Karaosmanongn, 2018) to eliminate the lignin, hemicellulose , and increase surface area . This method is very effective but the disadvantages is that it leads to corrosion, neutralization and removal of solvent. However, high energy consumption, high combustion, makes the method to take place at a regulated condition (Borand and Karaosmanogln, 2018).

Ionic liquids

These are salts of ammonium, disodium, phosphonium, pyridinium, pyrrolidinium, and sulfonium which are used to open the cellulose and its conversion to glucose. The main challenges of using ionic liquids includes high price, production of much waste, difficulty to recover the solvent, much energy is needed and non-toxic (Asim *et al.,* 2019).

This involves dissolving biomass in solvent at room temperature for a period of time. The biomass is precipitated before enzymatic hydrolysis. It reduces degree of polymerization, and structure of lignin, hemicelluloses altered. Nguyen et al., (2010) result in 97% conversion of cellulose to glucose. Lenzing et al., (2007) obtained over 99% of solvent recovery at low temperature.

Method of Deep Eutectic Solvent

This is a recent pretreatment method, composed of different liquids at temperature lower than 100^0 C to form an eutectic mixture linked with hydrogen bond. There is low cost of synthetic technology and biodegradability. Deep eutectic solvent is less expensive and produces few toxic compounds. It is biodegradable and easily recovered. (Yoon *et al.,* 2022).

Method of using Natural Deep Eutectic Solvents

Organic acid have been converted into the different eutectic solvents which are less expensive, easy to produce, eco-friendly and biodegradable. Lignocellulosic feedstock pretreatment with NADES reagent is highly specific for lignin solubilization and production of high purity lignin from agricultural waste (Kumar *et al*., 2019). The method has the ability to extract natural products, but has a drawback of high viscosity.

Oxidative pretreatment

This type of pretreatment is oxidation and several reactions occur during the process which leads to delignification, and exposing the biomass surface area (Den *et al.*, 2018). Disadvantages of this pretreatment is that the hemicellulose is damaged, making it unavailable for fermentation.

This utilizes oxygen as oxidants to biomass disruption at low and high temperature. The low temperature is hydrolysis reaction while the high temperature is oxidation reaction. During wet oxidation, lignin is decomposed into water, carbon dioxide, carboxylic acid. Amount of lignin removed from 50% to 70% depending on the types of biomass. For bagass, 80% of lignin resulted to 57% conversion to sugar yield. Combining wet oxidation with other pretreatment reduces formation of inhibitors and other by-products. Georgiera et al., (2008) obtain 75% cellulose conversion to yield 68% ethanol yield.

Ozonolysis

This process utilizes ozone to break lignocelluloses biomass lignin without affecting its composition (Kumar *et al.,* 2019). The merit is that the reaction take place at ambient temperature. The inhibitors produced is carboxylic acid which can be removed easily. The technique is very expensive due of high costs of the oxidant (Dey *et al*., 2020).

SPOR Pretreatment

SPOR pretreatment is a method used for the effective biomass pretreatment (Xu *et al.*, 2019). This involves treating with sulphite of metals and using disk miller. This open the biomass, thus produces less inhibitors. It is versatile, efficient and simple. It reduces energy consumption and can easily convert biomass to glucose.

c. Biological Pretreatment

Despite the harsh, cost , energy consumption, and generation of fermenting inhibitors of chemical pretreatment, biological method is mild and environmental friendliness. It requires the use of microorganism, mainly fungi to degrade the lignin anaerobically (Rafeenia et al., 2018). The parameters affecting the treatment are varieties of microbes, size of biomass, and process conditions (Usmani et al., 2021). The advantages are low energy input, zero chemicals, minimal inhibitors and environmentally friendliness. The major drawback is that it required large space, the reaction is slow to monitor the growth of microorganism and its activities (Ummalyma *et al.*, 2019).

III. Strategies for Pretreatment Techniques for Optimized Bioethanol Production

The pretreatment required much energy for biomass processes, for effective and low cost bioethanol, the pretreatment process must be optimized (Rajesh et al., 2021). However, a pretreatment with low energy consumption must be adopted so that the bioethanol production will be economical, feasible for a greener future (Karitha et al., 2023). Thus, the development of a concept on technologies in the biorefinery for effective valorization of all the components of the lignocellulosic biomass for cost effective bioethanol (Gandam et al., 2022). This development will make bioethanol process more economically sustainable.

There is need for adoption of use of integrated enzymes production technology, low cost of raw materials as a source of enzyme synthesis through bioengineering in biological pretreatment (Malik et al., 2022). Thus, the synthesis will require minimal operation cost, low biomass, as well as less use or zero utilization of chemicals, would help in the development of low -cost bioethanol. Moreso, utilization of less toxic chemicals is an innovative integration process that lowers the overall cost of production

In addition, there are some problem that emanate in the course of production process which has not being addressed such as formation of inhibitors, reduce efficiency of the hydrolysis , production and cost of waste disposal, low fermentation efficiency, high energy requirement, and chemical usage should be put into consideration for effective and low-cost optimized bioethanol production.

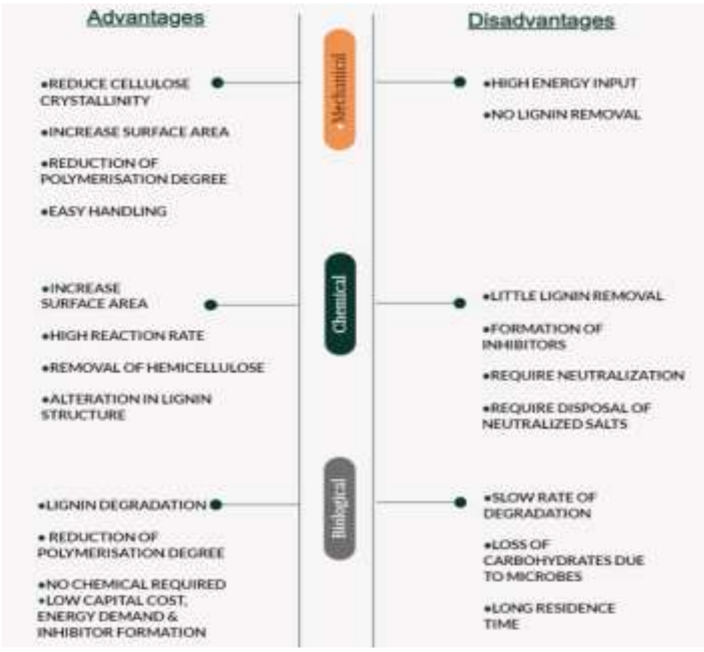

Figure 3: Advantages and disadvantages of various pre-treatment procedures

Combination of biological pretreatment with other techniques enhances high yield of biofuel and added value chemicals. Biological-alkaline enhances delignification of biomas, reduces the chemical used , lowering the time and temperature. Thus, reduce the operation cost (Si *et al*., 2019). This results may lead to high loss of carbohydrate content. Biological-acid pretreatment improves the solubility of the hemicelluloses, decrease toxic compounds. Thus, it increases sugar yield as well as ethanol production (Yan *et al*., 2018). Biological-oxidative implores using white-fungi and oxidizing reagent e.g hydrogen peroxide on the biomass. This shortens the time and increase biomass delignification with no inhibitors produced. Thus, high sugar yield and very effective. which results in higher sugar yield (Paudel *et al*., 2017).

Biological-organosolv pretreatment is basically for wood waste. This enhance increase in sugar production and large amount of biomass component (Xie *et al*., 2017). Biological-Liquid hot water method enhances high glucose yield owing to enzyme activity (Li *et al.*, 2022) Biological-steam explosion pretreatment increases the sugar yields compared to the steam explosion. This combination raise the energy use , costs of the process and removes the toxic compound in the biomass. The combined pretreatment methods are very efficient and cost effective (Leonard *et al*., 2021). However, there are further improvement on step to reduce the limitations of utilization of biomass and making the production of bioethanol more sustainable (Ho *et al.,* 2019).

IV. CONCLUSION

Lignocellulosic biomass is a potential feedstock for sustainable energy generation due to its abundance, low cost and eco-friendly. The use of chemical pretreatment to enhance biomass delignification is relatively high for enzymatic hydrolysis. It is simple, cheap, and have a good yield but large adverse effect on the environment. Although, biological technologies are friendly, low energy consumption, zero chemicals but the reaction is slow and specific. Combination of chemical and biological pretreatment have been reported to obtain high yield of sugars and quality biofuel. It is a better combination option to obtain clean biofuel and reduce production cost.

References

Amin,F.R., Khalid, H., Zhao, H., Rahman, S., Zhang, R; Liu, G; (2017) Pretreatment method of lignocellulosic biomass for anaerobic digestion.

Asim, A.M.; Uroos, M.; Naz, S.; Sultan, M.; Griffin, G.; Muhammad, N.; Khan, A.S (2019). Acidic Ionic Liquids: Promising and Cost-Effective Solvents for Processing of Lignocellulosic Biomass. *J. Mol. Liq.287*, 110943.

Chen, J.; Zhang, B.; Luo, L.; Zhang, F.; Yi, Y.; Shan, Y.; Liu, B.; Zhou, Y.; Wang, X.; Lü, X. (2021). A Review on Recycling Techniques for Bioethanol Production from Lignocellulosic Biomass. *Renew. Sustain. Energy Rev. 149*, 111370.

Das, N.; Jena, P.K.; Padhi, D.; Kumar Mohanty, M.; Sahoo, G. A (2021). Comprehensive Review of Characterization, Pretreatment and Its Applications on Different Lignocellulosic Biomass for Bioethanol Production. *Biomass Conv. Bioref. 82*, 1–25.

Den, W.; Sharma, V.K.; Lee, M.; Nadadur, G.; Varma, R.S. (2018). Lignocellulosic Biomass Transformations via Greener Oxidative Pretreatment Processes: Access to Energy and Value-Added Chemicals. *Front. Chem.*, *6*, 141.

Dey, P.; Pal, P.; Kevin, J.D.; Das, D.B. (2020). Lignocellulosic Bioethanol Production: Prospects of Emerging Membrane Technologies to Improve the Process—A Critical Review. *Rev. Chem. Eng. 36*, 333–367.

Gandam, P.K., Chinta, M.L., Pabbathi, N.N.P., Baadhe, R.R., Sharma, M., Thakur, V. K (2022). Second-generation bioethanol production from corncob-a comprehensive review on pretreatment and bioconversion strategies, including techno-economic and life cycle prespective. Ind Crops Production. 186:115245.

Ho, M.C.; Ong, V.Z.; Wu, T.Y (2019). Potential Use of Alkaline Hydrogen Peroxide in Lignocellulosic Biomass Pretreatment and Valorization—A Review. *Renew. Sustain. Energy Rev. 112*, 75–86.

Karitha, S., Gondi, R., Kannah, R.Y., Kumar, G., Rajesh, B.J (2023). A review on current advances in the energy and cost effective pretreatment of algae bioconversion enhancement in liquefaction and biofuel recovery. Bioresour Technol. 369:128383.

Kumar V. and Kataria R., (2019). Bioethanol Production from Lignocellulose Waste: A Comparative Study Between First and Second Generation Substrate, Acta Scientific Microbiology, 2, 25-8.

Li, X.; Shi, Y.; Kong, W.; Wei, J.; Song, W.; Wang, S (2022). Improving Enzymatic Hydrolysis of Lignocellulosic Biomass by BioCoordinated Physicochemical Pretreatment—A Review. *Energy Rep. 8*, 696–709.

Liu, Y.; Cruz-Morales, P.; Zargar, A.; Belcher, M.S.; Pang, B.; Englund, E.; Dan, Q.; Yin, K.; Keasling, J.D (2021). Biofuels for a Sustainable Future. *Cell* **,** *184*, 1636–1647.

Malik, k., Sharma, P., Yang, Y., Zhang, P., Zhang, L., Xing, X (2022). Lignocellulosic biomass for bioethanol: Insight into the advanced pretreatment and fermentation approaches. Ind Crops Prod. 188:115569.

Muhammad, M. L; and Saha, B.(2022) Recent Adraneen in Greener and energy efficient Alkene Expoxidation processes. Energies, 15(8).

Rajesh Bann, J., Porrnina Devi, Y., Yukesh Kannah, R., Kavitha, S., Klim, S.H., Munoz, R (2021). A review on energy and cost effective phase separated pretreatment of biomas. Water Resour, 198:117169.

Rezania, S.; Oryani, B.; Cho, J.; Talaiekhozani, A.; Sabbagh, F.; Hashemi, B.; Rupani, P.F.; Mohammadi, A.A. Different Pretreatment Technologies of Lignocellulosic Biomass for Bioethanol Production: An Overview. *Energy* **2020**, *199*, 117457.

Saha K, Maharana A, Sikder J, Chakraborty S, Curcio S, Drioli E (2019) Continuous production of bioethanol from sugarcane bagasse and downstream purification using membrane integrated bioreactor. Catal Today 331:68–77.

Sharma, B.; Larroche, C.; Dussap, C.-G. Comprehensive Assessment of 2G Bioethanol Production. *Bioresour. Technol.* **2020**, *313*, 123630.

Sharma, B; Larroche, C., Dussap, C-G. (2022) Comprehensive Assesement of 2G Bioethanol Soccol, C.R, Brar, S.k, Faulds, C., Ramos, L.P., Eds

Toor M, Kumar SS, Malyan SK, Bishnoi NR, Mathimani T, Rajendran K, Pugazhendhi A (2020) An overview on bioethanol production from lignocellulosic feedstocks. Chemosphere 242:125080.

Ummalyma, S.B.; Supriya, R.D.; Sindhu, R.; Binod, P.; Nair, R.B.; Pandey, A.; Gnansounou, E. (2019) Biological Pretreatment of Lignocellulosic Biomass—Current Trends and Future Perspectives. In *Second and Third Generation of Feedstocks*; Basile, A., Dalena, F., Eds.; Elsevier: Amsterdam, The Netherlands, pp. 197–212.

Xie, C.; Gong, W.; Yang, Q.; Zhu, Z.; Yan, L.; Hu, Z.; Peng, Y (2017) White-Rot Fungi Pretreatment Combined with Alkaline/Oxidative Pretreatment to Improve Enzymatic Saccharification of Industrial Hemp. *Bioresour. Technol. 243*, 188–195.

Yogalakshmi KN, Sivashanmugam P, Kavitha S, Kannah Y, Varjani S, AdishKumar S, Kumar G (2022) Lignocellulosic biomass-based pyrolysis: a comprehensive review. Chemosphere 286(2):131824.

Zhang, Y, Li, T, Shen, Y; Wang, L, Zhang, H; Qian, H; Qi, X; (2020). Extrusion followed by altresound as chemical free pretreatment method to enhance emzymatic hydrolysis of rice hull for fermentable sugar production. Ind Crops prod 149; 112356