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Unlocking the Potential of Indian Agricultural Waste: Sustainable Pathways to Nanocellulose, Green Chemicals, and Biofuels

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ABSTRACT:

Cellulose, recognized for its inherent properties, recyclability, and availability, plays a pivotal role in contemporary sustainable technologies. This review provides an in-depth analysis of the extraction and utilization of cellulose, nanocellulose, and lignin-based materials, with a focus on rice straw as a key raw material. While the extraction of cellulose and lignin is technically feasible, synchronizing nanocellulose production and lignin-derived fuel synthesis presents notable challenges due to the distinct characteristics of these materials.This review synthesizes state-of-the-art methodologies for cellulose and lignin separation, emphasizing their applications in producing bio-based polymers and advanced materials. Additionally, the review highlights innovative approaches to functionalizing or deactivating lignin-based compounds, aiming to enhance their utility and scalability. Ongoing research seeks to optimize these processes, reducing costs and enhancing environmental benefits.The overarching objective of this review is to consolidate and present comprehensive insights into the extraction, processing, and applications of cellulose, nanocellulose, and lignin, paving the way for sustainable innovations that transform agricultural waste into economically viable and environmentally friendly resources.

Keywords: Crop residue, Rice straw , Cellulose, Nanocellulose , Lignin , Biofuels ,Biomass valorization ,

1) Introduction:

In recent years, there has been a growing emphasis on research and utilization of biomass due to its potential as a sustainable source for energy production and material development. Global policies increasingly mandate the replacement of fossil-based resources with bio-based alternatives to mitigate environmental impacts. Crop residues, the non-edible plant parts left after harvest, form a significant portion of agricultural waste. Major contributors to global crop residue production include barley, maize, rice, soybean, sugarcane, and wheat. Composed primarily of lignocellulosic fibers with high cellulose content, these residues are highly suitable as raw materials for industrial applications.Rice straw, a common agricultural byproduct, has minimal nutritional value and, when burned as a direct fuel source, generates large amounts of ash and harmful emissions. Nearly 90% of rice straw is burned on-site due to time constraints for decomposition between rice harvests and wheat sowing. This practice significantly impacts the environment, releasing harmful pollutants such as carbon dioxide (70%), methane (0.66%), carbon monoxide (7%), nitrous oxide (2.09%), and ash. Burning also depletes essential soil nutrients, such as carbon, nitrogen, phosphorus, and sulfur, while reducing microbial diversity, ultimately degrading soil fertility [1-7]. By halting the burning of rice straw, both soil health and air quality can be improved, making this a critical environmental priority.

Lignocellulosic biomass from agricultural and forestry residues represents a vast renewable resource for producing bio-based materials and energy alternatives. Rice straw, a major agricultural residue, generates 1–1.5 kg per kg of harvested rice grain, amounting to an annual production of 800–1,000 million tonnes globally, with Asia contributing 600–800 million tonnes. Rice straw can be utilized either through direct combustion or via separation and conversion of its components. Direct combustion is straightforward but inefficient, while indirect methods, such as pyrolysis to produce activated carbon or enzymatic hydrolysis for biofuel, offer higher efficiency. The primary components of rice straw include cellulose (32–47%), hemicellulose (19–27%), lignin (11–24%), and silica (7–20%).Research on cellulose, a critical natural polymer, focuses on developing microcrystalline cellulose, long fibers, microfibrils, nanocrystals, and nanofibrils. Cellulose, a fibrous and water-insoluble linear homopolymer of β-D-glucopyranose, is a key resource for producing sustainable materials. Its natural abundance and properties make it a preferred alternative to synthetic and mineral fibers. Cellulosic fibers offer advantages such as availability, biodegradability, biocompatibility, and high stiffness[8-12]. These fibers are also more elastic and flexible compared to glass and carbon fibers, making them suitable for composite reinforcement. Cellulose chains are organized into microfibrils by hydrogen bonds, embedded within an amorphous matrix containing hemicellulose and lignin. The release of cellulose requires pretreatment processes that disrupt the matrix, solubilizing hemicellulose and enhancing cellulose yield.

Pretreatment techniques, critical for biomass conversion, are categorized into physical, chemical, and biological methods. Chemical pretreatment, which removes lignin and hemicellulose to improve cellulose biodegradability, has been extensively studied. Common approaches include thermochemical processes like dilute acid treatment, ammonia explosion, and hydrothermal methods. Combining techniques often yields enhanced results.Cellulose-based

nanomaterials, such as nanocellulose, have gained significant attention for their versatile applications in industrial and biomedical fields. Nanocellulose offers advantages like low density, high tensile strength, minimal toxicity, and high aspect ratios. The hydroxyl groups in nanocellulose facilitate functionalization, enabling applications such as antimicrobial films, protective coatings, nanofillers in composites, filtration membranes, and substrates for electrochemical devices.Extensive research over the last two decades has focused on producing nanocellulose from natural sources, including rice straw, sugarcane bagasse, and wheat straw[13-18]. Rice straw has been used to produce cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) through methods like high-pressure homogenization, acid hydrolysis, and alkaline hydrolysis. CNCs and CNFs, categorized based on size and extraction methods, have shown great promise in various applications.

Lignin, a major organic component of pulping liquor, is precipitated using sulfuric acid during rice straw pulping. After separation and acidification of pulping fluid, lignin can be extracted and used as a feedstock for fine chemicals and biofuel production. Hydrogenation is a prominent technique for converting lignin into biofuel, although the phenolic components of lignin pose challenges to fully realizing its potential. Continued innovation in lignin processing holds promise for its effective utilization in renewable energy applications.Weather forecasting is the use of science and technology to forecast atmospheric conditions for a specific location and time. For millennia, people have sought to predict the weather informally, and systematically since the nineteenth century [19-21]. Weather predictions are created by gathering quantitative data on the current state of the atmosphere, land, and ocean, and then applying meteorology to project how the atmosphere will change at a certain location.

Weather forecasting is currently based on computer-based models that take many atmospheric aspects into account, rather than being estimated manually based on changes in barometric pressure, present weather conditions, and sky condition or cloud cover. Pattern recognition skills, teleconnections, knowledge of model performance, and understanding of model biases are still required for selecting the best potential forecast model on which to base the forecast.

The chaotic nature of the atmosphere, the massive computational power required to solve the equations that describe the atmosphere, land, and ocean, the error involved in measuring initial conditions, and an incomplete understanding of atmospheric and related processes all contribute to forecasting's inaccuracy. As a result, as the time difference between now and the time for which the forecast is being produced grows, projections become less accurate. The usage of ensembles and model consensus can help to reduce the error and increase the forecast's confidence level.

Weather forecasts have a wide range of applications. Weather warnings are crucial forecasts because they safeguard people and property. Agricultural forecasts based on temperature and precipitation are critical, and traders in commodities markets rely on them. Many people use weather forecasts to decide what to wear on a given day on a daily basis [22-27]. Because heavy rain, snow, and wind chill significantly limit outdoor activities, forecasts can be used to schedule activities around these phenomena, as well as to prepare ahead and survive them.

2) RICE STRAW TO MICROCRYSTALLINE CELLULOSE (MCC):

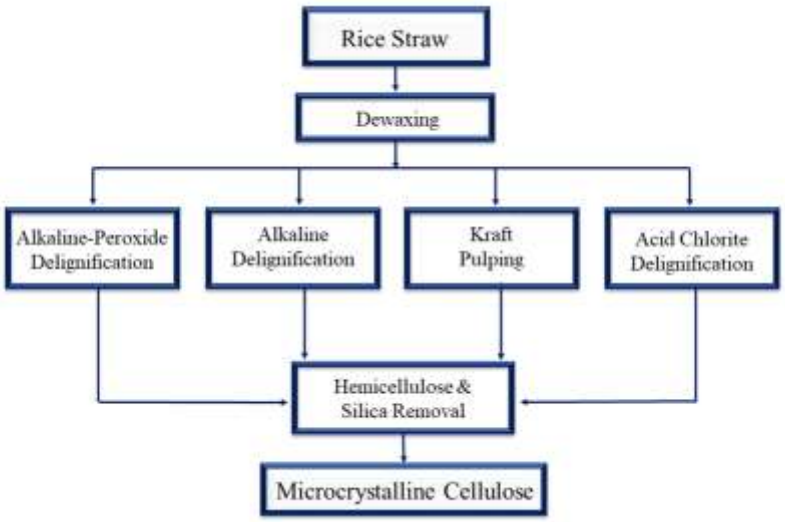

Figure 1:Process flowchart for the extraction of Microcrystalline Cellulose (MCC) from rice straw, outlining key steps such as dewaxing, delignification methods (Alkaline-Peroxide,Alkaline, Kraft Pulping, and Acid Chlorite), and subsequent hemicellulose and silica removal.

2.1 Dewaxing

Extraction of cellulosic content from rice straw required removal of wax, pigment and oils . Presence of wax layer at surface of rice straw decrease the permeability of water and organic solvent into the rice straw . For dewaxing, mainly Soxhlet apparatus were used. Soxhlet apparatus was developed by Franz Ritter von Soxhlet, German agriculture chemist in 1879 for determination of milk fat concentration in milk Some researcher also used hot water as wax and impurities removal agent. Soaking rice straw in hot water under constant stirring for 1hr removes wax and other impurities . In Soxhlet

apparatus, mixtures of organic solvent for varying duration were used by researcher. Toluene/ethanol mixture in the ratio of 2:1 volume by volume for 20hr . Toluene/ethanol mixture in the ratio of 2:1 volume by volume at 150℃ for 24hr [28-32]. Benzene/ethanol mixture in the ratio of 2:1 volume by volume at 90℃ for 12hr . Toluene/ethanol mixture in the ratio 2:3 volume by volume for 24hr .

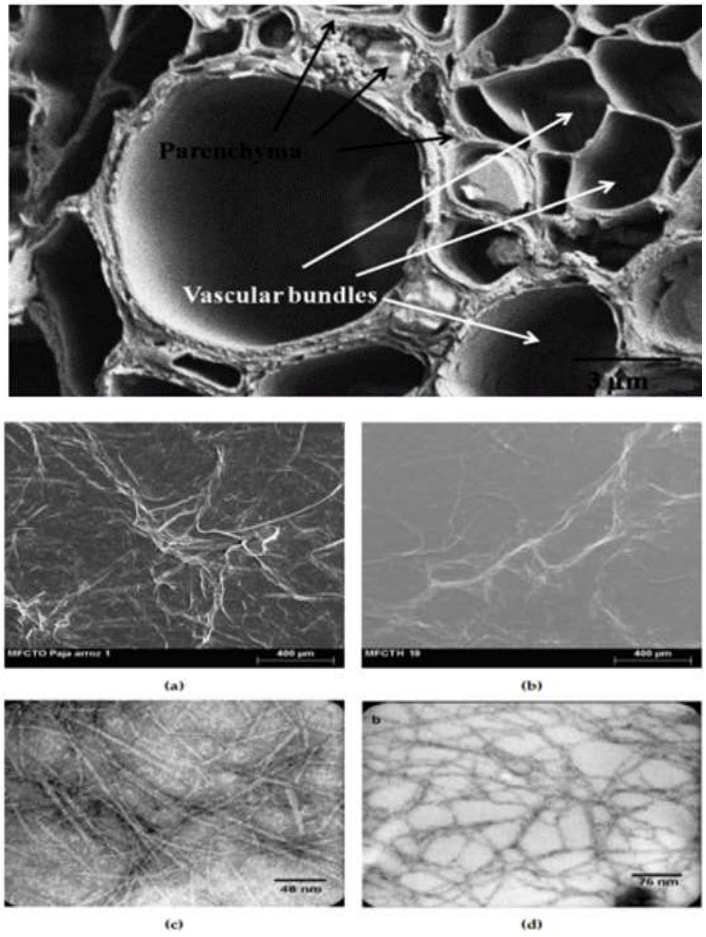

Figure 2: The SEM image of a rice straw cross-section (top) illustrates the structural composition, highlighting parenchyma cells and vascular bundles. The lower images include scanning electron micrographs of rice straw fibers (a) and eucalyptus fibers (b), show

2.1.2 Delignification

Rice straw is composed of mainly cellulose, hemicellulose and lignin in concentration of 42%, 24% and 20% respectively . Biomass delignification has variety of method. Kraft pulping is one among them. Kraft pulping is used to extract holocellulose from rice straw . Kraft process use sodium sulphide and sodium hydroxide for delignification. The dissolve lignin together with spent form a stream of black liquid known as weak black liquor. Kraft pulping is the most dominant pulping process in pulp and paper industry . Alkaline peroxide process is also effective for lignin removal. It also effectively removes hemicelluloses from rice straw . In alkaline peroxide process, solution of hydrogen peroxide in water is used for delignification. Sodium hydroxide used to provide alkaline medium for solution. Different researcher used different concentration of hydrogen peroxide and sodium hydroxide at different temperature for delignification. Patel et al obtain the maximum delignification of 62% of original lignin. They pretreated 2g of rice straw in 50ml of 1.5% (w/v) NaOH and 1% (v/v) H2O2 solution at 50℃ for 5h . Rice straw treated with 6% NaOH for 2 h at 60℃. The solid-to liquid ratio is maintained to 1:20. Followed by this, it is treated with 30% of H2O2 at 90℃ for 5 h. Solid-to-liquid ratio for this is 1:20 . Sun et al also able to remove 88.5% of original hemicellulose and 95.1% of original lignin. Certain amount of original cellulose (17.8%) is also removed. They first treated the dewaxed rice straw with 1% NaOH for 2h at 55℃[33-39]. Subsequently, they treated it with 5% H2O2 at 45℃ for 12h with pH 11.5 which is maintain by 4M NaOH . Sun et al able to show that sodium hydroxide alone is able to remove lignin from rice straw. As previous paper, they first treated dewaxed rice straw with 1% NaOH for 2h at 55℃. Analyses revealed nearly 60% of original lignin is removed in this first step . Alkali pretreatment has several advantages over other pretreatment techniques . It has good ability of removing lignin and cause very less degradation to carbohydrates . Washing doesn't require after alkali pretreatment. Addition of Alkali doesn't lead to any corrosion problem . Alkali pretreatment technique, unlike other pretreatment technique does not require high temperature and high pressure to operate . Alkali pretreatment can also be carried out at ambient condition. Time requires at ambient condition for alkali pretreatment is in hours or days . Parametric element that majorly affect the lignin extraction are sodium hydroxide concentration, reaction temperature and reaction rate . Different researcher varies this parametric element of alkali pretreatment. The dewaxed rice straw was treated with 4% NaOH solution for 5 min at 70℃. The solid to liquid ratio was maintained at 15 ml/g. After this process, the filtered material washed properly

and process repeat for the second time . In the ratio of 1g per 10ml of solution the dewaxed rice straw was treated in 12 wt% NaOH solution for 1 h at 121℃ . Rice straw without dewaxing treated with 6% NaOH solution for 2 h at 60℃. Rice husk was treated with 4% NaOH solution at reflux temperature for 2h . 50 g of rice straw was treated in 700ml of 10% weight by volume NaOH solution. This treatment was carried out for 2h at temperature range of 60-65℃ with occasional stirring . Lastly come acid-chlorite delignification of rice straw. Acid-chlorite pretreatment selectively remove lignin from rice straw. Only traces amount of xylan and glucan is also remove. In acid-chlorite delignification, aqueous solution of acetic acid and sodium chlorite used to dissolve lignin . Researchers used different-different methodology of acid-chlorite pretreatment. The dewaxed rice straw soaked for 5 h in 1.4 % NaClO2 solution at 70℃[40-45]. The pH of solution is maintained up to 3-4 by using glacial acetic acid . 50g of dewaxed rice straw stirred for 4h in solution of 5g of sodium chlorite and 5g of glacial acetic acid in 1L of distillate water. The temperature for stirring is 80℃. After this, the filtered material from solution washed properly. After washing, a second step of bleaching under the same chemical condition performed for 2h at room temperature

2.1.3. Silica and hemicellulose removal

Isolation of cellulose from rice straw required three step process including dewaxing, delignification and silica and hemicellulose removal. Last step of isolation of cellulose from rice straw is silica and hemicellulose removal. Conventional alkaline pretreatment was used for hemicellulose and silica removal mention in literature . Yuan et al uses this alkaline pretreatment for hemicellulose and silica removal from bamboo chips. With increase in pretreatment severity such as NaOH concentration and reaction temperature, all silica and up to 50% hemicellulose is removed without degrading cellulose and lignin Researcher use different method of this pretreatment. Delignified powder of rice straw is treated with the solution of 5% KOH at room temperature for 24 h. After this, it is treated again with the solution of 5% KOH for 2 h at 90℃ for complete removal of hemicellulose and silica . Delignified powder of rice straw is treated with 5% aqueous solution of KOH for 12 h at ambient room temperature for complete removal of hemicellulose and silica . In the ratio of 20ml/g liquid-to-solid, delignified powder is treated with 5% KOH at 70℃ for 24 h for hemicellulose and silica removal . After acid-chlorite delignification, silica content does not affect. Only lignin and hemicellulose is removed during acid-chlorite delignification. Base such as Na2CO3, NaOH and KOH used for desilication process . Hence, alkaline pretreatment is used for silica and remaining hemicellulose removal[46-52] . During alkaline delignification, silica is removed with lignin and hemicellulose. Alkaline delignification give solid residue is cellulosic content along with some amount of hemicelluloses . After alkaline delignification, bleaching pretreatment is used to obtain purified cellulose. Bleaching pretreatment used sodium chlorite/hypochlorite and glacial acetic acid. Researcher uses various method of bleaching pretreatment. The alkaline pretreated rice straw is treated with the solution of 5% wt acidified sodium chlorite for 90 min at 75℃. pH was ranges from 3-5 adjusted using 1M glacial acetic acid . Alkali pretreated rice straw is treated with mixture of 1.7% wt sodium chlorite and buffer solution of glacial acetic acid. The process is carried out for 4 h at reflux temperature (100-130℃)[53-59]. The process repeated for four times . Agustin et al treated the alkali pretreated rice straw with 1% v/v sodium hypochlorite solution. The pH of 5 is maintained using acetate buffer .

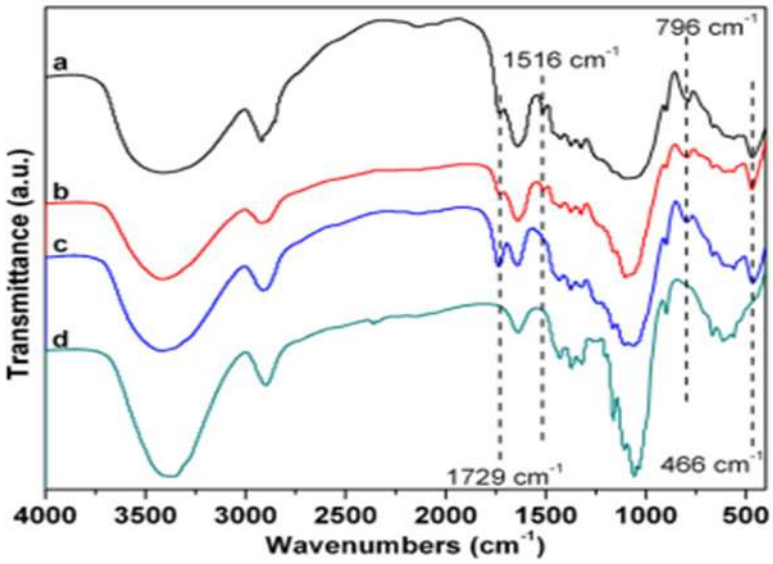

Figure 3:FTIR spectra of rice straw during isolation stages: (a) water washing, (b) dewaxing, (c) delignification, and (d) hemicellulose and silica removal, showing key transformations at 1729 cm^{-1}, 1516 cm^{-1}, 796 cm^{-1}, and 466 cm^{-1}.

3) MICROCRYSTALLINE CELLULOSE (MCC) TO CELLULOSE NANOCRYSTAL (CNC)

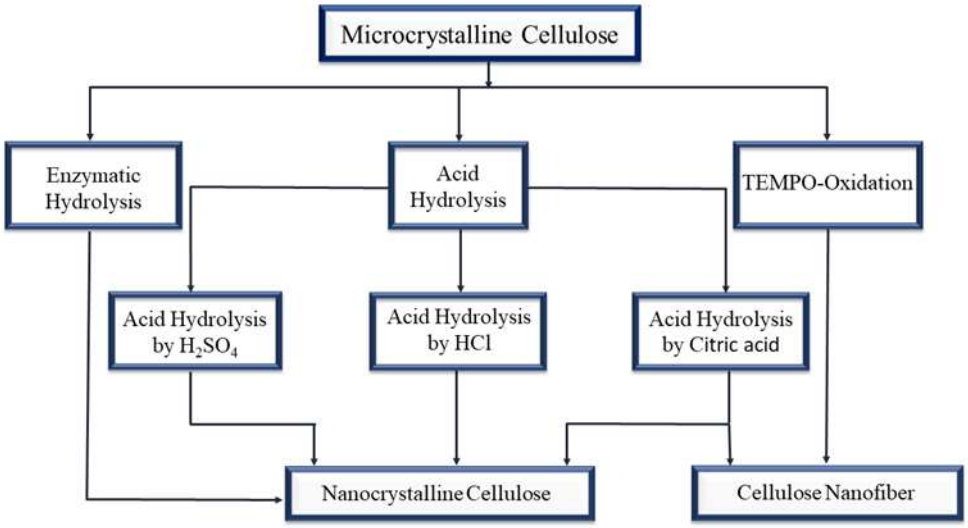

Figure 4: The chart outlines three primary pathways: Enzymatic Hydrolysis, Acid Hydrolysis (using H_2SO_4, HCl, or Citric Acid), and TEMPO-Oxidation. Acid hydrolysis produces Nanocrystalline Cellulose, while TEMPO-Oxidation generates Cellulose Nanofibers.

3.1 Method

Nanocelluloses are of three types; nanofibrillated cellulose (NFC), cellulose nanocrystals (CNC) and bacterial nanocellulose (BNC). Nanofibrillated cellulose also referred as microfibrillated cellulose (MFC), cellulose nanofibre (CNF) and nanofiberous cellulose or nanofibrillar cellulose (NFC). It is cellulose fibre that is flexible and web like twisted structure, long in length (up to several micrometers and having diameter in the range of 10-100 nm. It is obtain from purified cellulose using mechanical treatment preceded by pretreatment. Cellulose nanocrystal also known as, cellulose nanowhiskers, nanocrystalline cellulose, nanorod, nanoparticles, cellulose microcrystals and microcrystallites. It has needle-like form and nearly 90% crystalline cellulose moieties. Its length ranges from 100 to 1000 nm, and its average diameter is in the region of 3-35 nm. It is produced using acid hydrolysis or enzymatic hydrolysis of microcrystalline cellulose. Bacterial cellulose (BC), microbial cellulose, and bio-cellulose are other names for bacterial nanocellulose (BNC). It is produced by some anaerobic bacteria from sugars of low molecular weight (such as glucose, fructose, sucrose, arabinose, etc.). This nanocellulose synthesis is known as “bottom-up approach”. This nanocellulose is in the shape of twisted ribbon fibre. It has micrometer-long average lengths and average diameters of 20–100 nm (made up of nanofibre having diameter of 2-4 nm). This fibres is also highly crystalline (80-90%) and has high degree of polymerization (3000-9000). This nanocelluse is of high purity compare to other two nanocelluloses. Other polymer such as lignin, hemicelluloses and pectin are absent in it[60-66]. As these undesired polymers are not present in BNC, it is of high interest in biomedical field . As in this review paper, we only focused of formation of cellulose nanocrystal. Hence, we only discussed about acid hydrolysis and enzymatic hydrolysis in the further section

3.2 Acid hydrolysis

First preparation of cellulose nanocrystal was done by Rånby in 1949 using acid hydrolysis. Nickerson and Habrle was first to introduced this idea of acid hydrolysis for CNC extraction in 1947. The amorphous portion of the cellulose chain is removed using acid hydrolysis, which increases the crystallinity of the cellulose chain. Acid hydrolysis also cause the breaking of β-1,4-glycosidic linkages which cause reduction in size. Acid hydrolysis depends on mineral acid producing hydronium ions. Researcher mainly uses hydrochloric acid and sulphuric acid for acid hydrolysis. In addition to this, inorganic acids such nitric acid, phosphoric acid, hydrobromic acid, and tungstophosphoric acid are also utilised. For acid hydrolysis, organic acids such maleic acid, oxalic acid, benzenesulphonic acids, and p-toluenesulfonic acid are also utilised . Broadly acid hydrolysis can be categorized in two form; acid hydrolysis using sulphuric acid and acid hydrolysis using hydrochloric acid. Researcher used different method of acid hydrolysis using sulphuric acid for cellulose nanocrystal generation. Cellulose extracted from rice straw is treated with 64-65 wt% sulphuric acid for 30 or 45 min at 45℃[67-72]. The liquid-to-solid ratio is maintained at 8.75 ml/g . Cellulose from rice straw is stir in 58% sulphuric acid at 100 rpm for 3h at 45℃ . Thakur et al performed acid hydrolysis in concentration range of 45-75 wt% of sulphuric acid, temperature range of 30℃-50℃ and time period 1-3 h. An optimized process of acid hydrolysis, for which temperature is 30℃, concentration of H2SO4 is 75 wt% and time period is 5 h. It is predicted using central composite design . Cellulose extracted is treated with 10M sulphuric acid for 40 min under continuous stirring at 50℃. Cellulose content ranged from 4-6 wt% . Extracted cellulose is treated with 50% v/v sulphuric acid for 3 h at 30℃ under constant stirring. The liquid-to solid ratio is maintained at 10m/g . Researcher also used different method of acid hydrolysis using hydrochloric acid. Extracted cellulose from rice straw is hydrolyzed with 1M solution of hydrochloric acid. Cellulose stirred for 2 h at constant speed at 80 ± 5℃ . Akbar et al hydrolyzed the cellulose with hydrochloric acid at three different

concentration of 6, 8 and 10M. It is carried out for 70 min at 45℃ under strong magnetic stirring. The solid-to-liquid ratio is 1:20 g/ml . Kusmono et al repeat the previous process for CNC extraction with slight changes. At 6M concentration, process carried out for 70, 125 and 180 min. All other condition remains same. Optimal hydrolysis condition found at 6M hydrochloric acid concentration for 70 min at 45℃ [73-76].

3.3 Enzymatic hydrolysis

Group of multi-component enzymes system produces by microorganisms use for degradation of cellulose are known as cellulases . Cellulases usually comprised of three components; endoglucanases, cellobiohydralases and cellobiase or β-glucosidase . Unlike acid hydrolysis, enzymatic hydrolysis does not cause any surface modification of nanocelluloses due to attachment of sulfate group on hydroxyl group. This surface modified nanocelluloses also known as cellulose sulfate . Enzymatic hydrolysis generally produced spherically shaped nanocellulose . Cui et al were the first to prepare the rod-like cellulose nanocrystal using enzymatic hydrolysis . Several method of enzymatic hydrolysis is used by researcher for the production of cellulose nanocrystal from microcrystalline cellulose. Cui et al hydrolyzed 6 g of MCC with 3 ml of cellulase and 200 ml of acetate buffer solution (pH 4.8) at 50 ℃ for 72, 96 and 120 h. In every 12 h, dispersion is sonicate for 30 min and 60 min. For comparison, MCC is also treated without sonication. To eliminate particles larger than 1 m from the dispersion, centrifuge it at 1000g for 15 minutes. Further, resultant supernatant is centrifuge at 1400g to separate the NCC for 20 min. As the sonication time is increase, length of NCC is decrease[77-82]. Hence sonication is good tool for size control of NCC . Qian et al firstly pretreated 3 g of MCC with 90 ml of 1, 2, 5 and 10% (w/w) sulfuric acid with microwave heating at 300 W for 10 or 30 min at 95℃. At same concentration, same amount of MCC is heated with conventional oven at 95℃ for 30 min. After chilling, a 2:1 mixture of pretreated MCC and Aspergillus niger cellulase is added. The mixture kept under agitation for 72 or 144 h at 50℃. To further improve the NCC extraction yield, the suspension is sonicated for 30 minutes at 30°C after reaching ambient temperature. Highest yield of 84.4% is achieve for MCC pretreated with 5% sulfuric acid for 30 min with microwave heating and further enzymatic hydrolysis for 144 h. Without pretreatment it is less than 10% [83-85].

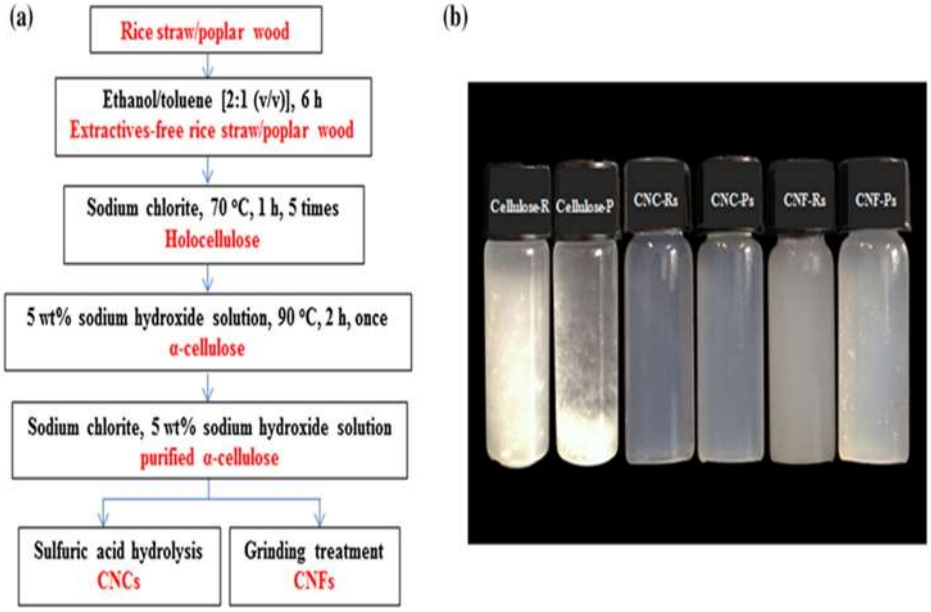

Figure 5: Process and outcomes of cellulose purification and nanocellulose preparation from rice straw and poplar wood. (a) The flowchart outlines the cellulose extraction process, including ethanol/toluene extraction, sodium chlorite treatment, and purification to produce α-cellulose, followed by nanocellulose preparation via sulfuric acid hydrolysis for CNCs (Cellulose Nanocrystals) and grinding for CNFs (Cellulose-Nanofibers). (b) Physical photographs of the resulting samples: cellulose, CNCs, and CNFs derived from rice straw (R) and poplar wood (P).

4) EXTRACTION OF LIGNIN FROM RICE STRAW

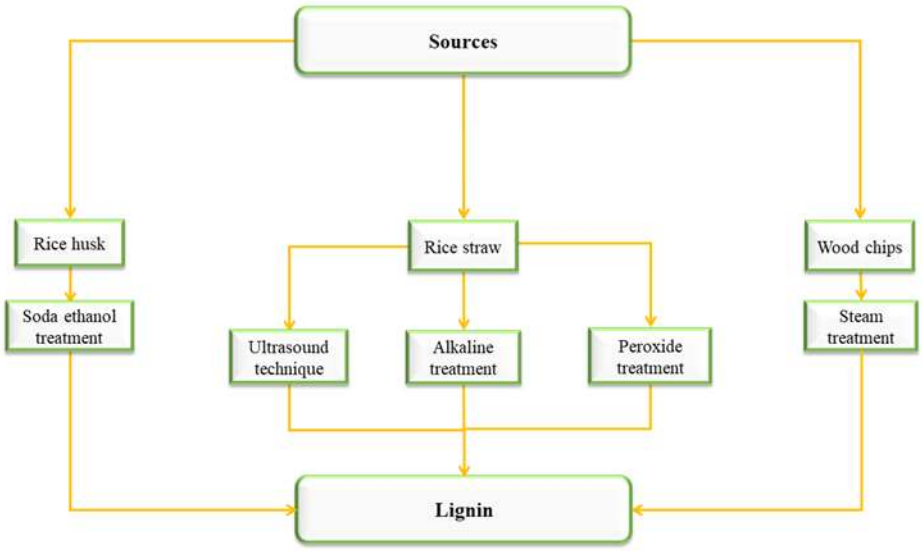

Figure 6:The flowchart illustrates the extraction of lignin from different sources such as rice husk, rice straw, and wood chips. Rice husk undergoes soda ethanol treatment, rice straw is treated using ultrasound, alkaline, and peroxide methods, while wood chips

Materials

Lignin extraction has been widely performed using the rice husk(coating on a seed or grain of rice)., usually sized to about 10*1 mm followed by water alcohol treatments. Rice straw and wood chips has also been proven to be effective for extraction of lignin followed by some effective pre-treatment methods like steam pretreatment a, alkaline peroxide treatments, with wet chemical methods treatment.

Rice straw to lignin

Rice straw is a by product which is produced during production of rice in large amount where its production is mostly greater then the production of rice itself. although the rice straw is a total waste to cultivators but still its is widely riched in silicon dioxide,k2o etc.1,2. If we see globally then around 800-1000 millions tons of rice straw is produced and only in the Asian countries itself the numbers are around 600-800 millions tons. Farmers mostly prefer to burn this rice straw waste rather than decomposing it properly which results in release of harmful gases such as oxides of sulphur and nitrogen 3,4.so this production of rice straw is considered to be serious issue leading to environmental pollution.

Rice straw is widely used for extraction of many substances present in it. It is mainly composed of cellulose (36.2), hemicellulose (23.5), lignin (15.6), ash (12.4) 5. Cellulose, a tough, fibrous, and water-insoluble polysaccharide that provides source for production of sustainable products for use in industry 6 3 .materials such as cellulose nanocrystals (CNCs) ,cellulose nanofibrils (CNFs),cellulose Nano whiskers (CNW),nanocrystalline cellulose (NCC) Nano fibrillated cellulose (NFC) micro fibril-lated cellulose (MFC) cellulose nanofibrils(CNFs) are derived from cellulose sources based on method of extraction 7[86-95]. These materials usually show properties like thermal stability, high specific elasticity, hydrophilicity, broad chemical-modification capacity, and the formation of versatile semicrystalline fibre morphologies, environmental friendliness, liquid-crystalline properties, stabilization of emulsions, rheological properties etc 8

Lignin is the most abundant bio polymeric polymer from biomass generated as a residue mostly from paper industries. due to its ability to be incorporated into biofuel and biolubricant formations it has been widely used as thickening agent.9 The conversion of lignin to biofuels have been widely researched because of its ability to be converted into adipic acids, polyhydroxyalkonates , alkanoic acids which leads to better production of transportation fluids[96-102]. 10 further many useful industrial substances like wood adhesives, bio-plastics, pharmaceuticals, fragrances, octane enhancers can also be developed by pyrolysis and valorisation of the lignin. 11

Application of ultrasound in producing lignin

Ultrasound assisted technique uses acoustic energy(disturbance of energy that passes through matter within the type of a wave) for extracting the various plant polysaccharides, diagnostic analysis and production of various nanoparticles. The principal behind the working of this ultrasound assisted extraction is the breaking of cell wall so that materials in cell could be flowed into the production channel which is performed by the producing pressure wave which results in deformation of cavity bubbles. The method leads to a greater transfer of the saccharides because of increase in the mass transfer rate due to breaking of the cell[103-109]. This ultrasound method lead to an increase in the efficiency as well as the process time as compared to the conventional method that are already in use for extracting the useful polysaccharides for industrial use..

[Vu el at,2017] reportedly used an ultrasound assisted extraction method for extracting the lignin. Sonic system SOMERSET with power of 500w was used for this purpose. Rice straw solution in basic aqueous medium was undeergone with irradiations after which the preciptation of the product of hydrolysis lead followed by alcohol bath lead to formation of a soluble compound as lignin.[Vu el at,2017] used TG-DTA,GC-MS, GPC(gel permeation chromatography) for detection of the lignin contents, analysing its various characteristics. The yield of the lignin increased with the radiation time reaching to nearly 84% as reported by [Vu el at,2017][110].

Alkaline treatment

Alkali pretreatment method is a very commonly used process for extracting the polysaccharides from biomass. This works on the principal of reducing the degree of polymerization and bond strength between lignin and the polymers. Mostly chemicals such as sodium hydroxide, ammonium hydroxides are used as agents for carrying out alkali pre treatment of biomass. The breaking of the ester linkages increases the solubilization of lignin. This method of extraction enables the decomposition of lignin to low molecular weight compounds. Ease of operation and low input cost are some important key factors in the vitability of this extraction method.

[Mishra el at, 2019] reportedly used sodium hydroxide treamnent and acid(mixture of formic acid, acetic acid) treatment for extraction of the lignin. preciptation of polymer from liquid was dispensed by dropwise addition of the acid. Characterization of the lignin from the sample was carried out using the UV-visible spectrophotometer, FTIR and NMR spectroscopy analysis[111-116]. As reported by [Mishra el at, 2019] the yield of extraction of lignin by the acid treatment method is more than the extraction by the alkaline treatment. This can be explained as a result of increase in rate of biomass dissolution due to effective delignification process.

Peroxide treatment

Peroxide treatment is a kind of oxidative delignification process that leads to the oxidation of the biomass. The use of peroxide in alkaline treatment prefers the delignification more over the other subtitutes which can be due to the breakeage and cleavage of the carbon bonds and the aryl ether bonds present in the lignin. Also due to the formation of the hydroperoxide anion (HOO-) reaction with carbonyl groups present in the lignin are further increased.This method further enhances the enzymatic coversion and also reduces the crystallinty of cellulose. The method provides a strong bleaching effect that reduces the amount of input cost and also lowers the loss of other useful products such as hemicellulose as compared to conventional methods.

[SUN el at,2000] as reportedly, isolated the alkali-soluble hemicelluloses by preciptation using NaOH solution in dewaxed rice straw. Further the preciptation of the lignin was carried out in high acidic medium and the solution was then mixed with aqueous hydrogen peroxide solution in basic medium.[SUN el at,2000] carried out the characterization of the lignin using high-performance liquid chromatography, array spectrophotometer, gel permeation chromatography[117-123]. the increase in solubilization and delignification process was due to the cleavages of ether bonds, and oxidation of aldehyde and ketonic groups.

Lignin extraction from other sources

Lignin can also be extracted from the other sources such as rice husk(hard protective coverings separated from the grains during milling process),wood chips. From past years many researches have been conducted on the lignocellulosic biomass as a source for alternative fuels. So these waste materials such as rice husk is the topic of concern for increasing its utility. Rice husk consists of around 18-19% lignin content and wood constitutes about 25% lignin. Many conventional methods such as acid- alkali treatments-pretreatments, steam treatment,organosolv haven been used for extracting the lignincellulose.

[Dagnino et al,2017] conducted the delignification of the rice husk using the soda ethanol treatment. Acid pre-treatment was conducted for rice husk followed by filtration and precipitation of the solution mixture. [Dagnino et al,2017] used NREL/TP-510-42618 method for characterization of the lignin. As stated by [Dagnino et al,2017] 52.7% of the liquid was obtained by the soda ethanol process[124-127]. [Tian et al,2017] carried out the steam pre-treatment of popalar wood chips followed by vaccum filtration and enzymatic hydrolysis. [Tian et al,2017] discussed various other post treatment methods such as DES, organosolv,soda post treatments.

4) DEPOLYMERIZATION OF LIGNIN

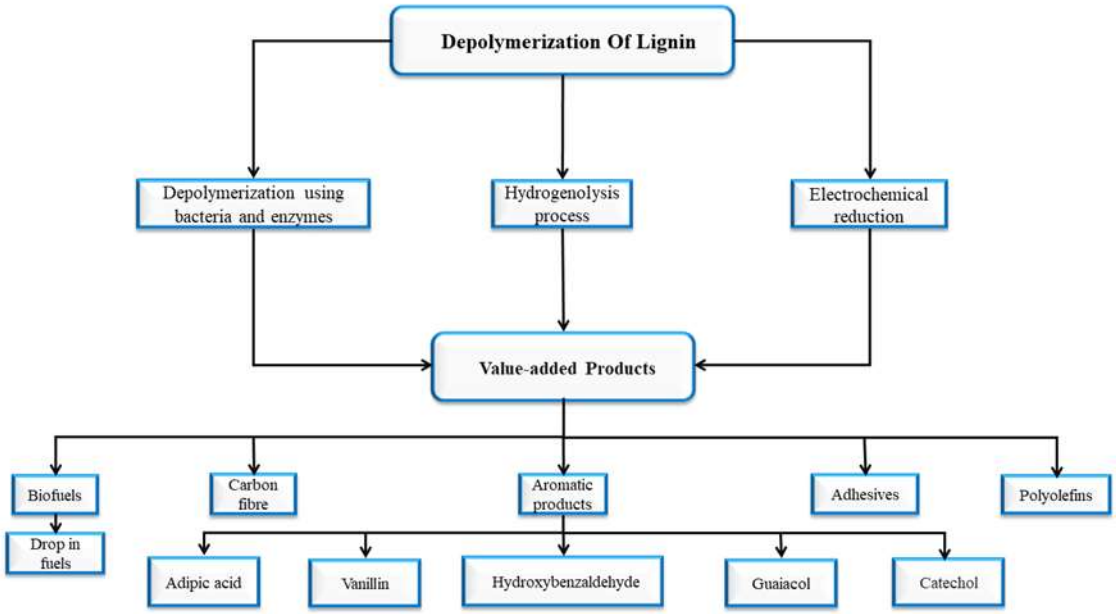

Figure 7:Pathways for lignin depolymerization and value-added product synthesis.

Biofuels production from the biomass sources has gained an huge importance in research areas due to its various advantages such as being a renewable source, non toxic,reduction in global warming due to the green house gases. Also the low input cost in production of biomass is the main key factor behind the utility of this source. Many researches have been conducted for converting these biomass to high value added chemicals so as to reduce the production and the consumptions of the petroleum based chemicals. Depolymerization methods have been widely used for production of the useful materials from sources such as lignin derived from the biomass.

Lignin structure consists of the phenylpropane units in macromolecular network,So the depolymerization is an sustainable method to converts lignin into monomer units for further applications. Depolymerization of lignin is many effected by the alpha and beta aryl ether linkages present in the structure. Studies stated that the cleavage of the b-o-4 linkages promoted the production of lower molecular weight products because these are dominant in lignin[128-134]. Many depolymerizations methods and treatments such as base catalyzed,acid catalyzed,ionic liquid-metal catalyzed treatments are widely used for lignin. Biochemical depolymerization using fungi was also performed for lignin. Oxidative and enzymatic cleavages of the lignin structure promoted the production of some aromatic products such as vanillin,hydroxybenzaldehyde.

Using Deep eutectic solvent in electrochemical media

[marino et al,2016] used the DES solvent with nickel as a catalyst for carrying out the depolymerization reaction. DES being recoverable an non toxic solvent increases the vitability of the reactions and is able to solubilize the lignin. [marino et al,2016] performed the recovery of lignin from DES in acidic medium and thereafter SEC analysis was conducted for lignin in basic medium for analysis of produced compounds . The conventional methods using nitrobenzene,alkaline solution for converting lignin to low molecular weight compounds are

Somewhat toxic and leads to over oxidation of product.this degrades the overall efficiency of the reaction. Electrochemical reduction process is a sustainable approach for performing catalytic cleavages and conversion of the compounds due to the involvement of only electrons as the reagents. The carbon-carbon bond cleavage and the production of the activated oxygen not only cleaves the lignin at room temperature but also increase the percent of hydroxide and carboxylic acid content[135-141]. Gas chromatography-mass spectrometry(GC-MS) performed by the [marino et al,2016] showed the production of phenolic compounds vanillin,guaiacol having good amount of yield during depolymerization reaction which also associates with data presented by [smith et al,2011].

Hydrogenolysis process

[wang et al,2013] performed the depolymerization of the lignin using the nickel carbon catalyst(consisting of nickel nitrate hexahydrate and activated carbon). The material was treated with alcohol mixture where its further process was carried out with catalyst in a reactor followed by characterization of the product using GC-MS instrument. The Ni/C catalyst successfully produced the monomeric phenols from the lignin where the alcohol mixture served as agent for breaking of the C-O-C bond. This reductive depolymerization mechanism is useful over other conventional methods due to easy catalyst separation. This method prevents the oxidation of the lignin to gases water mixture. Repolymerization of the lignin fragments and char(product of biomass pyrolysis) formation is also prevented by this mechanism as conversion of intermediate products to oligomers leads to decrease in the depolymerization reaction rate due to the coupling reaction.Depolymerization using the catalyst is very useful as different products from the lignin can be obtained[142-147]. The method shows much vitability in terms of the cost for regenerability and toxicity.

Depolymerization using bacteria and enzymes

Depolymerization of the lignocellulose by bio-catalysis is an environmental friendly process with less energy and cost input. The depolymerization by these bio compounds leads to cleavage of the β-aryl ether linkages in lignin where β-O-4 ether bond is most dominant linkage in lignin. Fungi,bacteria and microbial enzymes carry out the conversion and degradation of the lignin by the secretion of extracellular oxidases. Fungi mainly include white-rot,soft-rot and brown-rot fungi. P. chrysosporium, Pleurotus ostreatus, Gloeophyllum trabeum, Ascomycetes are some fungi that carry out the cleavage of lignin by production of oxidases and peroxidases enzymes.[zeng et al,2011] conducted biodegration og lignin by Phanerochaete chrysosporium that produced lignolytic enzymes such as esterases. The degradation was reported to be around 29-31%. (Ntougias et al., 2015) demonstrated that the Pleurotus strains could produce the value products such as protocatehuic and vanillin acid from lignin derived from wheat straw by the production of oxidoreductase chemical. Bacterial decomposition is highly tolerant to temperature,pH and limitations of oxygen by which different value added products from single phenols,xenobiotic substances can be produced. Sphingomonas, Pseudomonas, Actinobacteria, Proteobacteria, Streptomyces and Rhodoccocus are some bacteria types promoted for cleavage of lignin structure.[li et al,2017] demonstrated production of lipid from lignin derived from corn stover using Rhodococcus Strains via β-ketoadipate route by degrading lignin to aromatic intermediates[148-158]. 0.39g lipid per cell was stated to be produced as by the results of GC-MS and NMR spectroscopy.[zhang et al,2015] studied the combined effect of rhodococcus opacus strain(R. opacus PD630) cells and laccase for selective cleavage of different functional groups in lignin and cell growth.[lascar et al,2013] investigated S. viridosporus T7 for oxidative lignin biodegradation by producing peroxidase (ALiP-P3). Many studies have been conducted on the microbial enzymes for conducting out the depolymerization of lignin. Some of the major enzymes such as Lignin peroxidase (LiP), Dye-decolorizingPeroxidase, Manganese peroxidase, Laccase, Biphenyl bond cleavage enzyme release extracellular oxidases which leads to formation of free radicals that can cleave the lignin structure and can form unstable intermediate, which leads alkyl-aryl cleavage, and Cα-Cβ bonds cleavage. [wang et al,2015] conducted the lignin breakdown by Aspergillus oryzae in H2O2 hydrolysis.[Huang et al,2013] demonstrated the presence of the inducers like cu2+ that increases the intracellular laccase activity.

2.5. DROP IN FUELS PRODUCTION FROM LIGNIN

Lignocellulose has emerged as a great source for production of the transportation fuels. This study of lignin valorization and utilization holds a firm position in production of various fuels,chemicals and materials such as jet fuel,carbon fiber ,polyolefins,epoxies,adhesives etc . The hydrodeoxygenation (HDO) of lignin results in formation of non-condensable gases,water,char. Various hydrocarbons especially alkanes are produced from these lignin fragments by which value added products and biofuels can be created. Studies have also created pathways for reducing the need of external hydrogen for carrying out the hydrodeoxygenation during Biomass degradation. Hdo of lignin results in generation of C14-C20, C6 -C29 carbon chains and high octane fuel[159-162]. The catalytic process carried out for production of fuels are based on the reduction in O2 to carbon ratioand an growth in H/C ratio to attain most efficient gasoline residences and energythe density of the material.

[cao et al,2018] performed the hydrodeoxygenation of the lignin using a phosphidated Ni/SiO2 catalyst in a autoclave reactor followed by treatment with ethyl acetate. The catalyst was regenerated using the magnetic separation techniques . the aliphatic and aromatic hydrocarbon in Hdo of lignin ranged nearly 41% and 27% respectively with presence of some volatile products dihydro-p lignols, monolignols as detected by GC-MS analysis. [wang et al,2016] exemplified the use of Ni/Al-SBA-15, as a catalyst for HDO of lignin aromatic intermediates where the diphenyl ethers were converted to cyclic hexanes. The high acid sites in SBA-15 provides a better pathway for Ni to carry out the hydrogenation of aromatic ring and hydrogenolysis of C-O ether bond. [kouris et al,2021] investigated the production of 2-methoxy-4- propyl phenol from lignin for blending it with the diesel engine fuel. The resulted blended mixture lead to a lower emission of toxic gases because of complete oxidation of carbon in fuels. [omar et al,2020] demonstrated the use of Ru/C and Nb2O5 for the production of hexane hydrocarbons from dihydroeugenol (DHE)(lignin monomer)[163-171]. The ongoing researches are nowdays focusing on developing more efficient and cost effective catalysts for HDO like using the by products or catalyst base as hydrogen donors in a reaction. Drop in fuels have proven to have similar characteristics as conventional fuels which can reduce dependency on the crude based fuels and oils.

Conclusion

The sustainable valorization of agricultural waste, particularly rice straw, offers a transformative approach to addressing pressing environmental challenges while creating high-value products. This review underscores the immense potential of lignocellulosic biomass as a renewable resource for the production of nanocellulose, biofuels, and bio-based chemicals, presenting a compelling alternative to fossil-derived materials. Through comprehensive analyses of processes such as dewaxing, delignification, cellulose extraction, and lignin depolymerization, this study highlights advancements in technology that significantly enhance efficiency, scalability, and cost-effectiveness.Rice straw, a widely available agricultural residue, serves as a valuable feedstock due to its rich composition of cellulose, hemicellulose, and lignin. Its conversion into products such as microcrystalline cellulose, cellulose nanocrystals, and drop-in fuels offers a practical solution to agricultural waste management while mitigating the environmental impacts of open-field burning. The integration of advanced methods, including enzymatic and chemical hydrolysis, ultrasonic-assisted extraction, and innovative catalytic systems, has demonstrated the feasibility of achieving sustainable and economically viable outcomes.

Furthermore, the development of high-value chemicals such as vanillin, catechol, and adipic acid from lignin highlights its untapped potential for industrial applications. These processes contribute to the advancement of a circular bioeconomy, supporting global efforts to reduce greenhouse gas emissions, enhance soil health, and promote sustainable development.Future research should prioritize optimizing conversion technologies, enhancing process efficiencies, and exploring novel catalytic pathways to further improve product yields and cost competitiveness. By advancing the field of

lignocellulosic biomass valorization, this work contributes to shaping a sustainable future, aligning with global objectives for energy security, environmental preservation, and economic growth..

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