Potential Techniques for Conversion of Lignocellulosic Biomass into Biofuels

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Abstract
Lignin has been found as a naturally available aromatic resource for biofuel production. Reduced reliance on fossil fuels and replacement with a green and environmentally friendly strategy are currently one of the most pressing challenges. There has been significant growth in energy consumption, necessitating the transition to an alternative energy source. The current renewable energy source has significant biofuel production potential. It is critical to discuss the process parameters for pinpointing lignin content as part of the technology development process. Biofuel production possesses various challenges that need to be addressed. In this research, we precisely discussed the numerous lignin conversion mechanisms that can boost the biofuel output. Catalytic deoxygenation is a fuel promotion process that decreases the oxygen content, which causes instability and corrosion. SiO2, ZrO2, CeO2, TiO2, and Al2O3 are used in catalytic deoxygenation to produce biofuel. The use of chosen Al2O3-TiO2 metal oxide catalysts is critical in biofuel production. To obtain hemicellulose levels, two-step pretreatments with alkali and acids are used. The constraints, challenges, industrial perspectives, and future outlooks for developing cost-effective, energy-efficient, and environmentally friendly procedures for the long-term valorization of lignocellulosic materials were examined in the conclusion.

Keywords: Agriculture; Lignin; Renewable Energy Resource; Biofuel; Environment.

Introduction
The process of turning biomass-derived leftovers and feedstock into high-value-added end products is one of the fascinating issues in the world today. There is rapid global climate change resulting in global warming. Since 1750, CO2 levels in the atmosphere have risen rapidly, reaching roughly 43% [1]. The CO2 production rate reached 0.85 ppm yr−1 from 1960 to 1969, whereas it was observed at around 2.28 ppm yr−1 from 2008 to 2017. This sudden drastic variability in climate was noticed due to overdependence on non-renewable energy. Because of the increasing CO2 level, the average global surface temperature has risen to around 0.86°C [2]. Climate change has an increasing impact on both established and developing nations, resulting in alarming environmental challenges such as warmer oceans, less snow, and rising sea levels. Globally, primary energy is consumed at a rate of about 82% from various types of fuels. The transport sector is dependent on fuel such as gasoline, up to 58% [3-4]. A growing reliance on renewable fuels may result in a reduction in supplies. Efforts should be made to develop alternative fuels
with effective properties such as sustainability and high calorific value.

Biofuels have become essential to consumers due to their adaptability and potential to replace traditional fossil fuels [5]. In the recent past, bio-fuels have secured a position as a sustainable fuel source. This biofuel can be used by industries to connect their environmentally favorable characteristics. Agriculture waste and biomass account for around 75% of renewable energy. According to a research contribution, global bio-energy use in 2015 was equal to coal consumption. The direct combustion of biomass is the most serious environmental issue. Furthermore, different biochemical processes can be used to produce different liquid biofuels [6-7]. In this regard, the major technologies to manufacture ethyl alcohol from sugar, starch, and bio-oil from vegetable oils have got contemporary scientists focused. These can be valuable for the transportation sector due to their low cost.

There is an urgent need to focus current efforts on specific applications of cellulose biomass and lignin [8]. The generation of bioethanol from lignocellulosic biomass is valuable. The traditional liquid fuels can be obtained from food crops of non-edible deposits and vegetable biomass. The decreased content of greenhouse gas emissions can be secured from renewable feedstock such as lignin. Furthermore, the production of the green chemical from lignocellulosic biomass is increasing due to their environmental-friendly features [9].

Biomass is dominantly comprised of cellulose (42–80%), hemicellulose (15–32%), and lignin (10–28%) [10]. Cellulose is insoluble in water due to its molecular weight and semi-crystalline polysaccharide. While, hemicellulose has a low molecular weight and multicomponent polysaccharide structure with various functional groups that consist of acetyl and methyl, glucuronic, cinnamic, and galacturonic acids [11]. However, lignin is composed of aromatic rings, which are polymeric chains connected with β-O-4 ether and C–O and C–C linkages. The amount of lignin in biomass varies depending on whether the biomass is soft or hard and the other characteristics of the biomass [12]. The cellulose, hemicellulose and rigid lignin structures stop the rapid decay and dissolution of biomass. Lignin works as a “glue” to make bonded fibrous cellulosic material [13].

Effective biomass preparation tends to increase cellulose porosity and surface area. Its crystallinity reduces, resulting in thermochemical changes and bio-digestibility to produce biochemicals and biofuels. There are physical, chemical, and biological pretreatment steps are implemented to get a better yield of lignocellulosic biomass-linked fuels [14]. Mechanical comminution, microwave pre-treatment, ultrasound, and nano-thermal plasma are some of the physical pre-treatment technologies that have been clarified. With diverse processes such as sieving, grinding, and milling, mechanical comminution changes lignocellulosic structure. These procedures alter the physical environment in a known way as size reduction [15]. Microwave pre-treatment includes the ultrasound and non-thermal plasma processes, both of which cause damage and a reduction in fossil fuels. Climate change, green chemicals, and bioenergy are all elements that have raised worries about the expansion of fossil fuels. These are derived from biomass and have recently gained much attention from scientists and policymakers. Heat processes enable the acquisition of improved biofuel generation, as well as their relative conversion to useful biofuel and chemical products from waste. Some of the processes that can be used are pyrolysis/alcoholics, hydrothermal liquefaction, gasification, and carbonization [16-22].
With acid-catalyzed hydrolysis and a method that works at a temperature of 100–250°C for bioenergy generation, there has been a significant stride forward. Glucose, 5-hydroxymethylfurfural (HMF), and levulinic acid (LA) have all been linked to a possible impact on chemical synthesis and platform development. The hemicellulose and cellulose can alter the xylose and furfural. On the other hand, cellulose can be hydrolyzed to form glucose, HMF, and LA. The hydrolysis of biomass produces lignin as the solid residues. Furfural and glucose are obtained and used to make biofuel additives. On the other hand, these solid leftovers can be used to generate heat and biofuel. For example, a platform for the manufacture of methyl tetrahydrofuran, ethylfurfuryl, ethyl-tetrahydrofurfuryl ethers, valerate esters, and other C10–C15 oil can be developed.

Furthermore, the enhanced products can be used to substitute gasoline. Glucose is used to make bioethanol and is a primary component of oxygenated gasoline. HMF may be converted into low oxygenate diesel fuels in the C9-C11 range. 1-ethoxynonane, C13–C15 hydrocarbons, and LA, for example, can establish a chemical bridge between biomass and oil. It’s been touted as a promising feedstock to produce liquid fuel. The hydrogenation of LA to valerolactone can be created there. As a result, it produces liquid alkenes with a high carbon content [23]. Hence, LA may be altered to a group of valerate esters, methyl, ethyl, and propylvalerate, by using gasoline as an additive. Only renewable biofuels, such as HMF and LA, can be used to improve biofuel. LA and HMF can be combined to produce resins, polymers, and chemical intermediates. Cosmetics, pharmaceuticals, pesticides, and fungicides require LA to be manufactured. The biomass hydrolysis technique can be used to create formic acid. As a result, it might make formaldehyde, medicinal plasticizers, and textiles. As a result, it has been determined that the hydrogen donor tendency of Formic acid has a durable effect on the hydrogenation of LA to produce fuel chemicals [24].

**Potential Techniques for Lignin Conversion Challenges in manufacturing bio-fuels**

Using sodium hydroxide (NaOH) and organic acid (Formic acid/Acetic acid) Quaternary ammonium compounds (OAT) processing, waste rice straw (RS) is degraded to remove lignin [25]. With acidic and alkaline techniques, this fractionation leads to the recovery of lignin components. UV spectroscopy and FTIR methods are being used to characterize the lignin structure [26]. The total phenolic content of the lignin components is also determined. The XRD technique is used to compare the surface properties of treated and untreated rice straw [27]. There has been progressed in meeting the problem of producing lignin as biomass in biorefineries [28].

**Rice straw fractionation process**

Organic acid (Formic acid/Acetic acid) OAT and alkaline sodium hydroxide treatment (SHT) were used to produce lignin from waste rice straw (RS). According to the fractionation technique, the dissolution of biomass in OAT and SHT is 45.9% and 40.7%, respectively. The OAT approach yielded 108 mg/g of RS of lignin, and the SHT technique yielded 140 mg/g of RS of lignin. The findings show that the OAT methodology can produce more lignin yield with more efficiency than other methods. When compared to OAT, the fact that SHT yields hydrolyzed lignin is also elaborated. As a result, the OAT approach yields a faster biomass dissolving rate than the SHT method. These hypotheses could be crucial in terms of organic acid penetration, which is the source of cellulose and...
hemicellulose solubilization during the delignification process. With relative lignin extraction, this orientation has proven to be effective [29].

**Biomass Characterization**

**SEM results of pulps and rice straw**

The SEM results confirmed a theory that the RS surface is secure, clean, and smooth, as indicated by surface morphology, as illustrated in Fig. 1 [29]. The reason for this is that lignin has the ability to cover the fibre surface. The finding reveals that the fibre surface has been damaged, and holes have been discovered near cellulose fibres due to the separation of lignin from the fibre surface employing alkaline SHT. The OAT biomass provides a smooth surface. It goes on to say that the OAT approach was used to accomplish the full separation of wax and lignin from biomass. [30-32].

**XRD and FTIR characterization of rice straw for surface analysis**

The authors discovered three XRD patterns of RS, each with two peaks at 21° and 14°, as shown in Fig. 2. It shows a dense biomass area with both crystalline and amorphous structures. This study found that 73% of big sugar crystals were obtained, compared to 59% for raw sugar [32]. In contrast to SHT-RS (44% versus 37%), OAT-RS shows a complete separation of lignin, extractives, and hemicelluloses in an acidic media, as evidenced by a high crystallinity index.

![Figure 1. Illustration of three different FE-SEM images of UT-RS (A), SHT-RS (B), and OAT-RS (C) [32]](image)

![Figure 2. Illustration of XRD of biomass components (A), Illustration of FTIR analysis of biomass components (B), adopted from Manilla et al. [32]](image)

On the other hand, previous research studies have found no evidence of a high crystallinity index. The variation at the RS surface can be seen in the FTIR spectrum (Fig 2). Absorption spectra obtained with UT-
RS, 3444 cm\(^{-1}\) with SHT, and 3450 cm\(^{-1}\) with OAT reveal discrepancies induced by lignin and its constituents dissolution at 3339 cm\(^{-1}\), 3444 cm\(^{-1}\), and 3450 cm\(^{-1}\), respectively. The most important findings from rice straw surface treatments with alkaline sodium hydroxide treatment show that weak lignin peaks at 1599, 1499, and 1399 cm\(^{-1}\) are present.

**Characterization of C1s and O1s spectrums**

Which has obtained a high-valued RS XPS spectrum analysis using a scanned model. As shown in Fig. 3, the presence of three components (C1-C3) peaks between 291 and 281 eV. Carbon-hydrogen (C-H) groups are represented by a C1 peak in the relationship. The aliphatic and aromatic carbons in RS biomass were used to extract the lignin. In SHT-RS and OAT-RS, the C1 peak decreases from 72.9 to 52.9%. This is because the delignification process separates the lignin. As a result, the C-O connected to C2 and C-O connected to C3 peaks grow. From SHT and OAT processings, the second C2 peak increases by 20% to 36.2% and 40.1%, respectively. SHT-RS was discovered to be made up of lignin and cellulose components. The OAT-RS surface, on the other hand, can maintain superior cellulose continuity. In comparison to the SHT procedure, the acquired results show that the OAT process can enhance the biomass surface [33-35].

![Figure 3. Illustration of large resolution XPS C1s spectrum of UT-RS (A), SHT-RS (B), and OAT-RS (C) [36]](image-url)
The primary findings of the O1s spectrum have revealed that the components of O1 have been reduced. With the completion of the OAT process, oxygen levels tend to rise. The high content biomass from SHT-RS processing causes the SHT-RS and O1 peaks to become larger and the O2 peak to become smaller compared to untreated RS. Two peaks from 519 and 529 eV were discovered in RS O1s spectra. Because lignin is so abundant, the O1 peak was discovered to have a linear relationship to (O–C=O) bonds. As shown in Fig. 4 [37], the O2 peak interacts with (C–O–), which has a relationship with hemicelluloses and cellulose biomass.

![Figure 4](image-url)
Lignin Application and Synthetic Approaches to Produce Biofuels from Lignocellulosic Biomass

Lignin can always be utilized as a starting point for a variety of commercial applications, including high-value lignin derivatives, both before and after chemical modifications. Lignin-based compounds can be employed as fuels, chemical reagents, and polymers in general.

These approaches have forecasted a sustainable target development for the upcoming future. It can be realized that liquid biofuels have paramount importance, and their production can be acquired from an efficient and commercial process-making technique. There is making a trend for lignocellulosic biomass conversion into fuels. Thus, it demonstrates a novel synthetic approach dependent on the bio-catalyst system process technique [39]. A novel process for hydrotreatment of lignin sample is developed employing only Fe-limonite catalyst, at which surfactant is not used for changing the surface chemistry [40]. There is obtained a total yield of up to 41 wt%. It comprises alkylphenols and aromatics. Further, it can be utilized for the production of liquid fuels. For instance, there is a synthesized Jet-fuel (high octane number) range product from single softwood lignin incorporating metals which are Fe, Ni, Cu, and Zn, with Ru on HY zeolite catalysts [41]. The obtained overall hydrocarbon products up to 26-33 wt%. There is a reduction in gaseous molecules’ production. Hence, the one-step HDO has emerged as a proficient approach to synthesizing hydrocarbon fuels. The lignin ratio’s high residence time and catalyst content are forced to optimize less productivity. There are characterized by biofuel from variation in biomass material under rough conditions. It can be optimized to a high

Value by treating hydrodeoxygenation (HDO) with hydrogen gas and catalysts. There is an increase in product quality in comparison to conventional biofuels. Furthermore, recent work on HDO catalysts to upgrade lignin-based bio-fuels is focused on metal-based catalysts [42]. There has been measured an up-gradation from fast pyrolysis lignin vapors by conventional hydrotreating catalysts HZSM-5 [39]. To conclude, these bio-process synthesis techniques evolved with the action of lignin and phenolic assets from biomass. This alternative has raised a horizon to generating hydrocarbons by using flow reactors. It can upgrade the energy and mass values at the process chain [43-45].

![Figure 5. Industrial Applications of Lignin](image)

**Chemical Looping Gasification of Lignin**

Chemical looping gasification (CLG) has evolved as a feasible technology to generate without air. It has a high effect with an innovative scheme for separating hot gas from gasified biomass. As the lignin is produced in biorefineries as waste material. There are investigated of lignin as a resource with the help of oxygen carriers that are CaFe$_2$O$_4$, CaMn$_2$O$_4$, BaFe$_2$O$_4$, and BaMn$_2$O$_4$. BaFe$_2$O$_4$ is capable of gasifying the lignin and displays good regeneration too. The results now showed a high ability for regeneration after the process completion and vice versa. It is also noticed that with the addition of CO$_2$, the production of CO increases, gets reverse caused by the reverse Boudouard reaction.
which is \((C + CO_2 = 2CO)\). Further, it was accelerated with biomass conversion and specific process kinetics of the gasification [47].

**\(CO_2\) Gasification of lignin without an oxygen carrier**

The \(CO_2\) is used as a medium for lignin gasification under 50°C to 900°C (ramp rate of 10°C/min) in various \(CO_2\) concentrations (0–10% \(CO_2/He\)). There are two stages of reaction: the first of the pyrolysis process at 50–670°C. It has presented the comparison curves of derivative thermogravimetry (DTG) with temperature and reaction time. There was no change in lignin’s first pyrolysis stage, which demonstrates the \(CO_2\) environments have no effect at thermal pyrolysis temperature of 150–670°C. Furthermore, the weight varies caused of the gasification reaction, which increases \(CO_2\) at temperature > 700 °C. The findings reveal that charcoal has been produced after the separation of water and volatile components. The second stage consists of a gasification reaction, it includes the charcoal and fixed carbon that are combined to react. As the \(CO_2\) gasification process was completed, the remaining left was ash as residue. Consequently, gasification gas \(CO_2\) addition is efficient for carbon conversion and relative syngas generation [46].

Demonstrated a comparison between produced gas after the completion of the lignin gasification process at variable concentrations of \(CO_2\). The traced CO at low temperature and low space-time < 80 min. A high production rate of CO was observed at production at reaction time >80min. It is confirmed from the procured analysis that the addition of \(CO_2\) is vital to change biomass char into the useful product as CO. There is also noticed reforming by measuring the peaks of \(H_2\) at 900°C. As a result, the generation of \(H_2\), \(CH_4\) gases, and \(H_2O\) was raised as biomass pyrolysis increased. The \(CO_2\) gasification gas displays a paramount effect for gasifying lignin to generate unique synthesis products. The low-temperature range acts as \(CO_2\) for the separation of tar removal. A high temperature facilitates \(CO_2\) to gasify lignin char for the generation of CO. These results indicate that hydrogen and carbon elements in lignin can do the complete CO. Hence, there was attained maximum synthesis gas production from the gasification of lignin.

**Figure 6. Illustration of TGA and DTG profiles that include lignin content with variable values of \(CO_2\) measured, adapted from[46]**
Conclusion

The review work depicts the most up-to-date understanding of current developments in lignin-based biomass conversion. The creation of reaction systems and the identification of new catalysts are critical. As a result, it predicts a guarantee for increasing the usefulness and selectivity of lignin-based biomass. There were two methods for valuing biomass at the time. It is possible to achieve this by integrating by-products from a related process. To begin, one strategy has a promising effect by producing a large volume of products. The second group of factors includes those that have the potential to meet production demand in the near future. The chemical processing of biomass influences the production of pulp and paper. The revenue generated from hemicellulose and cellulose components serves as a standard for producing renewable oil from wood as a substrate. Technically, lignin is widely available in the paper, and the pulp sector has been presented as the fact that postulates concerning valorization should be lined up. Finally, it works to convert lignin-based biomass components into usable fuel. However, with the tax benefits, the net income gained from paper and pulp is lower than the revenue amount generated from bio-oil production. The most important issue is maintaining a long-term culture for producing good renewable biofuels. It has been proved that using biofuel in transportation can increase the energy sector in a variety of ways. Because the transportation sector is made up of organized vehicles, their use contributes to public electrification. The idea mentioned above has led to the conclusion that renewable bio-based fuels and chemicals are unquestionably guiding research for safe, cost-effective, and clean fuel production.

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Conflict of Interest

The authors declare no conflict of interest.

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