LIGNOCELLULOSE BIOMASS DELIGNIFICATION USING ACID HYDROTROPE AS GREEN SOLVENT: A MINI-REVIEW

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Efficient and cost-effective conversion of lignocellulosic biomass into usable forms of energy presents unique challenges. Lignocellulosic biomass, comprising cellulose, hemicelluloses, and lignin, necessitates advanced conversion technologies. Common commercial delignification techniques, including kraft pulping, sulfite pulping, acid hydrolysis, and organosolv pulping, often involve harsh conditions leading to structural changes in lignin and environmental impacts. To address these issues, acid hydrotropes have emerged as a promising method for lignin extraction. Acid hydrotropes, represented by p-toluenesulfonic acid (p-TsOH), enable the solubilization of hydrophobic substances like lignin. This mini-review provides an overview of various lignocellulose fractionation techniques and explores the acid hydrotrope approach. The mechanism behind acid hydrotropic fractionation is discussed, and its performance is evaluated. In conclusion, the review emphasizes the pivotal role of the acid hydrotrope approach in advancing lignocellulosic biomass conversion technology, promoting a sustainable and efficient bio-based economy.

Keywords: lignocellulose, delignification, lignin, acid hydrotrope, p-toluenesulfonic acid (p-TsOH)

INTRODUCTION

There has been a remarkable surge in global interest in renewable resources in recent years as researchers strive to address the pressing challenges of climate change and sustainable development.[1] Among the many renewable resources available, lignocellulosic biomass has emerged as a promising clean and sustainable energy source.[2] Lignocellulosic biomass is the non-edible plant material found in agricultural residues, forest residues, dedicated energy crops, and organic waste.[3] This abundant and widely available biomass resource holds tremendous potential for meeting energy demands, while minimizing the environmental impacts of traditional fossil fuel consumption. The growing interest in lignocellulosic biomass stems from several factors. Firstly, lignocellulosic biomass is considered a carbon-neutral energy source.[4] When it is utilized for energy production, the carbon dioxide released during combustion is offset by the carbon dioxide absorbed during the growth of the biomass feedstock. This feature makes lignocellulosic biomass a valuable tool in mitigating greenhouse gas emissions and combating climate change. Secondly, lignocellulosic biomass offers a sustainable alternative to finite fossil fuels, contributing to environmental degradation.[5] As an abundant and renewable resource, lignocellulosic biomass can provide a reliable energy supply, while reducing dependence on depleting fossil fuel reserves. Furthermore, its utilization can help mitigate other environmental issues, such as air pollution and water contamination associated with traditional energy sources.[6] Moreover, processing lignocellulosic biomass for energy production can create economic opportunities and stimulate rural development. Communities can generate income by establishing biomass supply chains through cultivation, harvesting, transportation, and conversion processes. This can contribute to the

creation of local jobs, poverty reduction, and increased economic resilience.[7]

Lignocellulosic biomass is composed of three primary macromolecular components, which are cellulose, hemicelluloses and lignin, all of which hold significant potential as building blocks for the production of biofuels, biochemicals, and biodegradable products.[8,9] Among these, lignin is the second most important polymer in the plant world, with distinctive properties.[9,10] Currently, lignin is predominantly generated as a by-product of the ethanol and paper industries, with an estimated annual global production of about 100 million tonnes and a market value of USD 732.7 million in 2015. This value is projected to increase by 2.2% annually, reaching $913.1 million by 2025.[11] Lignin is a linear polymer with branching points, chemically linked to hemicelluloses and cellulose.[12] It is an amorphous three-dimensional polymer composed of three primary units: syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units, interconnected by ether and C-C linkages.[13,14] Figure 1 shows the chemical structure of lignin. This polyphenolic structure of lignin makes it a promising source for various value-added products, including lignin-based carbon fibers, isocyanate binders, bio-dispersants, phenolic, and thermosetting resins.[15,16] However, the characteristics of the lignin contents would be expected to vary depending on the type of plant, weather, and growing conditions. Above all, the techniques employed for the extraction and separation play important roles in producing high yield and purity of lignin.[14,17]

Nonetheless, the efficient and cost-effective conversion of lignocellulosic biomass into usable forms of energy poses unique challenges. The complex structure of lignocellulosic biomass, consisting of cellulose, hemicelluloses and lignin, requires advanced conversion technologies and processes. Overcoming these challenges necessitates ongoing research and development efforts to optimize biomass conversion technologies, improve efficiency, and reduce costs. Delignification is a crucial step in the production of biofuels and other value-added products from lignocellulosic biomass. Currently, the most common commercial delignification techniques include kraft pulping,[18] sulfite pulping,[19] acid hydrolysis,[20] and organosolv pulping.[21] However, these processes involve severe conditions, such as high temperatures, pressures, and long extraction times, leading to considerable changes in the original lignin structure and resulting in high costs and environmental impact.[22,23]

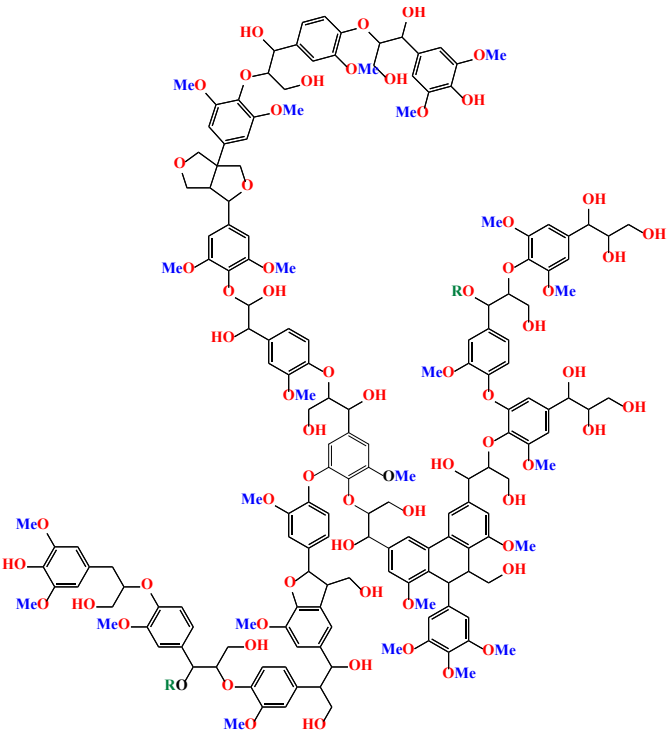

Figure 1**:** Chemical structure of lignin

In order to tackle these issues, acid hydrotropes have emerged as a promising method for lignin extraction. Acid hydrotropes are a class of chemicals that form micelles in aqueous solutions, enabling the solubilization of hydrophobic substances like lignin. Among these, p-toluenesulfonic acid (p-TsOH) has proven effective for delignifying various plant sources. Therefore, this mini-review provides an overview of several lignocellulose fractionation techniques, including alkali-based fractionation, ionic-liquid assisted fractionation, organosolv fractionation, and deep eutectic solvent fractionation. Subsequently, the acid hydrotrope approach is introduced, the mechanism behind acid hydrotropic fractionation of lignocelluloses is discussed, the performance in acid hydrotrope fractionation is evaluated, and the review concludes with final insights. This review aims to offer an analysis of these fractionation methods, with a particular emphasis on acid hydrotrope-based approaches, in order to advance lignocellulosic biomass conversion technology and promote a more sustainable and efficient bio-based economy.

COMMON FRACTIONATION METHODS OF LIGNOCELLULOSIC BIOMASS

An efficient fractionation of lignin, hemicelluloses and cellulose into their primary constituents is critical for optimal biomass utilization and the creation of inexpensive, resilient, and dependable biorefinery technologies.[24] Moreover, the fractionation process significantly influences the chemical reactivity of lignin, prompting extensive research efforts to uncover novel methods for extracting lignin from biomass. Alkali-based fractionation, ionic-liquid assisted fractionation, organosolv fractionation, deep eutectic solvent fractionation, and many more technologies have gradually evolved and received significant attention from industry and academia.[25] Figure 2 depicts a schematic representation of a few processes employed in the fractionation of lignin from lignocellulosic biomass.

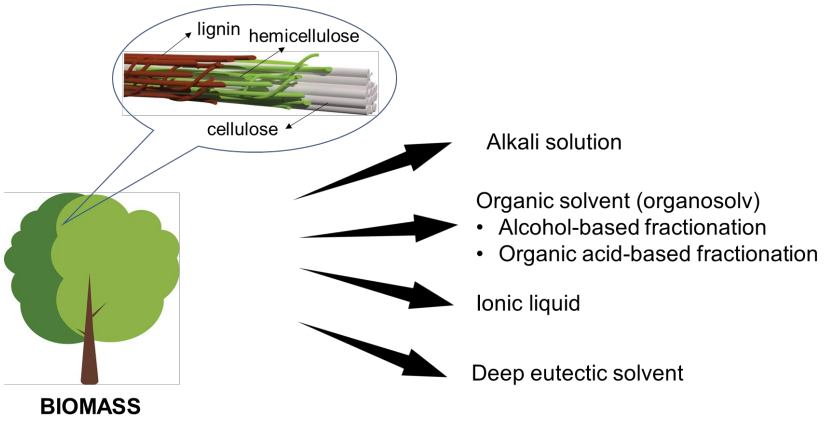

Figure 2: Schematic illustration of chemical pretreatment used to fractionate lignin from biomass

Alkali solution fractionation

Alkali-based fractionation is a common technique used in extracting lignin from lignocellulosic biomass. Delignification using alkaline reagents is extremely selective. It can be used to recover a significant portion of lignin with high purity.[26] In contrast to lignin produced by pulping processes, lignin produced by alkali-based fractionation contains no sulfur.[27] The utilization of an alkaline reagent breaks the hydrogen bond between hemicelluloses and cellulose molecules in lignocellulosic biomass. Besides, it also destroys the chemical bonding between lignin and hemicelluloses, resulting in the dissolution of lignin and hemicelluloses.[28] Another major reaction that takes place during alkali-based fractionation is the de-esterification of intermolecular ester bonds.[29] Various types of alkali, such as ammonia, sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrazine and many others, were used in the delignification of biomass.[25,26] Alkali reagents are less caustic than acidic reagents, and the fractionation can be performed under mild conditions and at atmospheric pressure.[30] Using this method may avoid the necessity for expensive materials and specialized designs to deal with corrosion and harsh reaction conditions. Furthermore, the

alkaline reagent used in the extraction process can also be recovered and used in the next fractionation process.[31] Up to now, much research has been reported regarding alkali-based fractionation.

Among various alkali solvents available, sodium hydroxide (NaOH) has received the most attention due to its role in breaking certain bonds during the delignification process. The first stage consists in breaking of the phenolic bonds α-O-4, β-O-4, β-O-5, and β-β in lignin, followed by breakage of the non-phenolic β-O-4 bonds and carbon-carbon bonds. These breakages will lead to the degradation of carbohydrates.[31] Asghar and co-workers reported that the utilization of a 2.5% concentration of NaOH resulted in 63.2% of lignin removal from wheat straw, where the fractionation process was performed under pressure and steam for 30 minutes. The delignification increased to 72.5% as a result of increasing the reaction time to 60 minutes.[32] Another research by Nadeem and co-workers found that the delignification of kallar grass increased with the increase in alkali concentration and soaking time. Maximum delignification (52%) was observed for kallar grass after it was treated with 2.5% NaOH concentration for 60 minutes.[33] The effect of potassium hydroxide (KOH) in biomass fractionation has also been investigated. Irfan and co-workers reported that maximum delignification of sugarcane bagasse (70.7%) was achieved with 2.5% KOH at autoclaving time of 45 min.[34]

In addition, alkaline hydrogen peroxide (AHP) fractionation is also widely used in the pretreatment process of biomass. According to da Costa Correia and co-workers, the fractionation of cashew apple bagasse using 4.3 vol% H_2O_2 for 6 h at 35 °C caused lignin solubilization up to 92.44%.[35] The degree of delignification dramatically increased from 16.5 to 80.2% when the concentration of H_2O_2 was increased from 0.645 to 4.3 vol% under the same solid loadings (10%) and conditions (35 °C, 24 hours, pH 11.5). Furthermore, it was also found that the maximum delignification significantly rose to 96.7% throughout 24 hours of pretreatment when a lower solid loading (5%) was used.

Ionic liquid assisted fractionation

Ionic liquids (ILs), also known as green solvents, have gained high interest due to their ability to dissolve lignin and cellulose under normal conditions.[36-38] Besides, they also have excellent properties, such as low volatility, high solvating power, and excellent chemical and thermal stability.[39-41] In comparison with many other organic solvents, ILs typically exhibit very low environmental impact due to their low volatility, low vapor pressure, high solvating power, non-toxic nature, unflammable and eco-friendly solvent characteristics. As a result, it is reasonable to anticipate that ILs will lower the price of solvent consumption and facilitate recycling.[42,43] Basically, ILs exist in the form of liquids at room temperature and are entirely made of ions, typically organic cations, such as derivatives of N, N-substituted imidazolium, N-substituted pyridinium, tetra-alkylated ammonium, and tetra-alkylated phosphonium, and either organic or inorganic anions.[37,44,45] Recently, various ILs, such as 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-ethyl-3-methylimidazolelium acetate ([C_2mim]-[OAc]), 1-allyl-3-methylimidazolium chloride ([Amim]Cl) and many others, have been used in lignocellulosic biomass fractionation.[24,46]

Lopes *et al*. (2013) performed fractionation of wheat straw using three types of ILs, which are 1-butyl-3-methylimidazolium hydrogensulfate ([bmim][HSO_4]), 1-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), and 1-butyl-3-methylimidazolium dicyanamide ([bmim][$N(CN)_2$]). It was reported that [bmim][SCN] gave the highest lignin solid fractionation (13 mg), followed by [bmim][$N(CN)_2$] with 10.1 mg and [bmim][HSO_4] with 7.1 mg. Their research concluded that the fractionation of wheat straw using ionic liquids (ILs) can be controlled, depending on the type of ILs used, highlighting the significant flexibility of the developed process.[46]

Sorn *et al*. (2019) found that the utilization of three different ILs resulted in different lignin removal. The results of a chemical composition analysis of lignocellulosic rice straw showed that significant lignin removal was achieved using 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) (41.01%) and 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim]HSO_4) (16.88%). The degree of lignin removal depends on the efficiency of IL absorption on the hydrophobic side of lignin. Further delignification was aided by the strong bonds between the C-O-C and C-C linkages that connect lignin to cellulose and hemicelluloses. The fractionation using [Bmim]Cl resulted in higher delignification compared to

[Bmim]HSO_4] caused by the lower surface tension of the material, which also increased the cavitation and caused the α-O-4 and β-O-4 linkages between the cellulose and lignin to break.[47]

Deep eutectic solvent (DES) fractionation

The employment of ionic liquid (ILs) in lignocellulose biomass fractionation encountered a few issues, caused by the high cost, poor recoverability, complex synthesis procedure, high viscosity, and high energy consumption in the fractionation process.[48-50] Therefore, a new fractionation method was introduced, where a deep eutectic solvent (DES) is utilized as an alternative to ILs. DESs are an emerging class of green solvents that have been gaining scientific interest due to their ability to remove lignin and hemicelluloses, as they can selectively solubilize large amounts of lignin and insignificant amounts of cellulose.[51] A DES is the combination of two or three ionic compounds that interact with each other by self-association, forming a eutectic mixture with a melting point lower than that of each compound.[52-54] The ionic compound in the mixture can be either a hydrogen bond donor (HBD) or a hydrogen bond acceptor (HBA), where they are combined through the hydrogen bond (H-bond) interaction, which is responsible for charge localization within the mixture and contributes to high interaction energy between the DES and lignin.[55,56]

DES fractionation is preferred over traditional kraft pulping and organosolv fractionation methods. Traditional kraft pulping generates sulfur-containing lignin, while organosolv fractionation requires a significant amount of organic solvent, which is unfavorable because of the volatility and flammability of most organosolv solvents.[57] In addition, DESs are often preferred to ILs due to their excellent properties, such as biocompatibility, biodegradability, low toxicity, and lower cost, as DESs are estimated to be 20% cheaper than ILs.[58-60]

Generally, DESs are categorized into four types based on the nature of the complexing agent. Type I DESs are made up of two compounds, which are metal halides (*e.g.*, aluminum chloride ($AlCl_3$), silver chloride (AgCl)) and quaternary ammonium salts (*e.g.*, choline chloride (ChCl)). However, due to the high melting points of non-hydrated metal halides, Type I DESs have not been applied in lignocellulose processing.[61] Type II DESs comprise hydrated metal halides (*e.g.*, $AlCl_3$, $ZnCl_2$) and quaternary ammonium salts, and, due to their inherent resistance to air and moisture, these chemicals are more suitable for industrial processes. Quaternary ammonium salts (ChCl) and different types of HBD, such as carboxylic acids, alcohols, and amides, are the main components of type III DESs. Type IV DESs comprise HBD, such as urea and inorganic transition metals.[62] Figure 3 shows the classification of DESs. Type III deep eutectic solvents (DESs) are the most researched and commonly used in biomass processing due to their favorable properties. These DESs are derived from non-toxic, biodegradable, low-cost starting materials and are straightforward to prepare, featuring low viscosity.[61,63-65]

DES delignification involves the breakage of two types of glycosidic bonds (C-O-C bonds) within the lignocellulose. The first bond breakage is inside the hemicelluloses and the other one is the breaking of the glycosidic bond between lignin and hemicelluloses.[66] Figure 4 shows an example of delignification mechanism using a DES (choline chloride–oxalic acid).

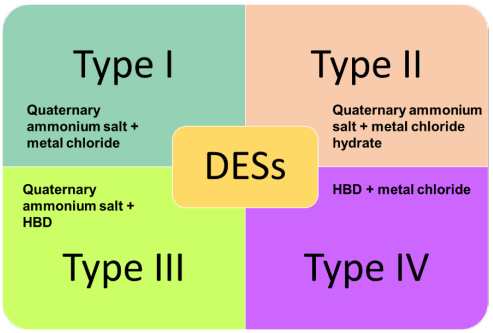

Figure 3: Classification of DESs

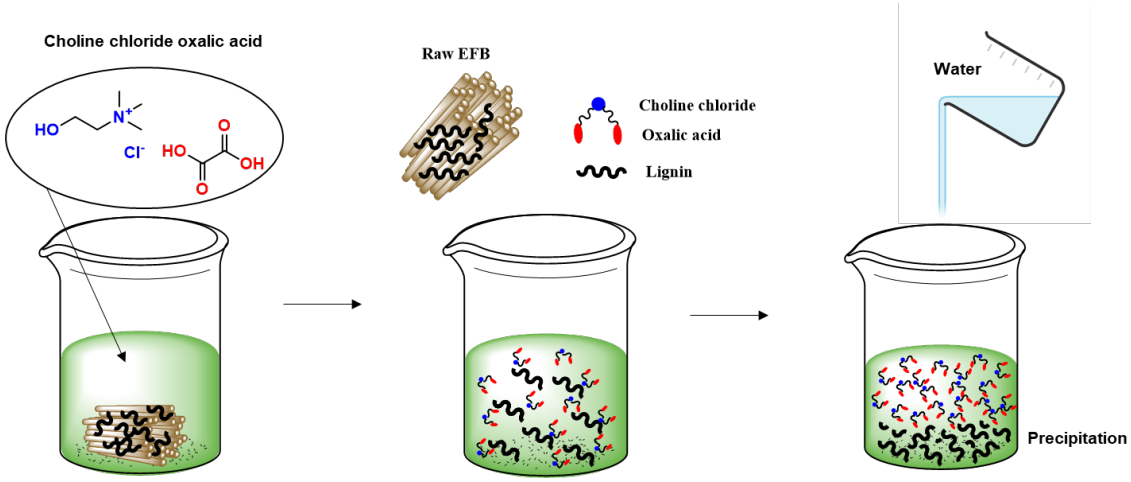

Figure 4: Delignification using DES (choline chloride and oxalic acid)

Choline chloride can act as hydrogen-bond donor (HBD), where it can interact with the lignin through hydrogen bonding.[67] The presence of the chloride anion, which is an active component of choline chloride, helps to disrupt the intermolecular hydrogen bonding network of biomass and facilitates the dissolution of lignin. On the other hand, oxalic acid acts as hydrogen-bond acceptor (HBA), where it can interact with the hydroxyl group in cellulose and lignin through hydrogen bonding.[61] This interaction weakens the intermolecular bond within the lignocellulose and facilitates the breakdown of lignin.

Li and co-workers performed the fractionation of bamboo (*Dendrocalamus yunnanicus*) using choline chloride and oxalic acid (ChCl:OA) at 80-120 °C for 4 hours. It was found that the lignin yield and delignification ratio increased with the increasing reaction temperature, where the maximum lignin yield of 50% was achieved at the reaction temperature of 120 °C. The high reaction temperature caused the hydrogen bond to break in the plant cell wall, allowing the lignin system to be broken down into small lignin fragments. Besides, they also reported that the extracted lignin is of high purity, of about 90%.[68] Additional research concerning biomass fractionation using deep eutectic solvents (DES) has been carried out by Tan *et al*.[69] In the study, lignin was extracted from empty fruit bunches (EFB) utilizing choline chloride:lactic acid (CC-LA) and glucose:lactic acid (GLUC-LA) as the primary solvents. The results revealed that CC-LA and GLUC-LA yielded lignin recovery rates of 50.6 wt% and 40.2 wt%, respectively, from the total lignin content present in the EFB.[69] CC-LA was found to be more efficient in delignifying the EFB compared to GLUC-LA.

Organosolv fractionation

Over the past few years, there has been a growing interest in the research and development of the organosolv process. This process has proven valuable in fully utilizing lignocellulose to generate various products, including high-quality lignin and digestible cellulose.[70] Organosolv fractionation is a promising biomass fractionation technique, wherein lignin from plant cell walls is dissolved in an organic solvent. A diverse range of organic solvents can be utilized in this process, primarily organic alcohols, organic acids, esters, and mixed solvents, with or without acid or alkaline catalysts.[71,72] The lignin obtained through organosolv fractionation exhibits low molecular weight and has no sulfur element, unlike impure lignin obtained by conventional pulping processes, such as the kraft and sulfite process.[25] Additionally, during organosolv fractionation, non-toxic reagent organic solvent can be recovered. Several organosolv fractionations based on extraction and isolation techniques have been made accessible up to this point. The two primary organosolv fractionations are based on organic acids and organic alcohols.[25] The most widely used alcohol-based fractionation is ethanol and methanol pulping. Meanwhile, formic and acetic acids are widely used in delignification for acid-based fractionation, followed by other organic solvents, such as dioxane, acetone, and methyl ethyl ketone. An interesting extension within the organosolv landscape is the incorporation of hydrotrope in biomass fractionation. Hydrotrope, categorized as organic-acid base fractionation, has gained attention for its potential to enhance lignin solubility in organic

solubility in organic solvents, thus facilitating the fractionation process.[25]

ACID HYDROTROPE APPROACH

An alternative approach employed in biomass delignification involves the utilization of compounds that enhance the solubility of hydrophobic substances, including lignin, within aqueous media. These compounds include a range of organic solvents, such as ethanol, ionic liquids, deep eutectic solvents, and hydrotropes. Hydrotropes, composed of sodium and potassium salts of benzoic and aryl sulfonic acids with a substituted alkyl group, exhibit a molecular configuration and characteristics similar to surfactants. However, unlike surfactants, hydrotropes do not form micelles due to their smaller hydrophobic structure. The amphiphilic nature of hydrotropes makes them well-suited for effectively reducing the surface tension of liquids and enhancing the solubility of lignin during the initial treatment phase.[73] An additional advantage of incorporating hydrotropes in the delignification process is the potential to precipitate lignin by diluting the hydrotrope solution with water. This resultant lignin can subsequently be utilized in the production of derivatives or polymers, while the hydrotrope solution, after concentration, can be recycled for lignocellulose pretreatment. This recycling ability significantly enhances the cost-effectiveness of the delignification process. The effectiveness of using solvents like hydrotropes, deep eutectic solvents, and ionic liquids in the delignification process depends on the specific type of biomass and the prevailing process conditions, especially the lignin composition.[31]

A hydrotrope can be described as an organic salt that plays a crucial role in significantly enhancing the solubility of hydrophobic chemical compounds when introduced into aqueous solutions.[74] Unlike pure hydrophilic compounds, hydrotropes possess a molecular structure that integrates both hydrophobic and hydrophilic elements, enabling them to interact effectively with a wide range of substances. Researchers investigating lignin extraction have explored various hydrotropes, including benzenesulfonates, maleic acid, sodium xylene sulfonate, sodium cumene sulphonate, alkyl benzene sulfonate, and p-toluenesulfonic acid.[75-79] Remarkably, hydrotropes exhibit distinct geometric characteristics, giving rise to divergent behaviors among their o-, m-, and p-isomers, which consequently influence their hydrotropic actions. These characteristics highlight the delicate balance of molecular forces intrinsic to hydrotropy.[74] Moreover, hydrotropes offer an intriguing advantage by providing highly selective separation processes for industrial mixtures that conventionally pose challenges for segregation. Each specific hydrotrope demonstrates a unique affinity for particular components within the mixture, facilitating the convenient recovery of the hydrotrope solution through controlled dilution with water. This selectivity presents opportunities for efficient reclamation and reuse of the hydrotrope solution, contributing not only to economic feasibility, but also to sustainable practices.

P-toluenesulfonic acid (p-TsOH) is emerging as a prominent acid hydrotrope, capturing significant attention within academia for its pivotal role in the exploration of lignocellulosic biomass fractionation. This class of acid hydrotropes exhibit a remarkable capability to enhance the solubility of hydrophobic compounds in aqueous environments, triggered by the attainment of the minimum hydrotrope concentration (MHC).[80] The MHC is a specific concentration level at which hydrotrope molecules start to come together and form clusters. This clustering creates a unique environment that has different characteristics compared to how hydrotropes behave in more diluted solutions.[74] The interaction dynamics involve weak van der Waals forces, including π–π attractive dipole-dipole interactions, through which hydrotropic molecules engage with less water-soluble counterparts.[81] Hydrotropes are notable for their unique combination of hydrophobic and hydrophilic properties, and the delicate equilibrium between these characteristics plays a pivotal role in governing their effectiveness in dissolving solutes such as lignin.[82]

Mechanism of acid hydrotropic fractionation of lignocelluloses

There are many types of mechanism in hydrotropic fractionation, such as self-aggregation, self-association, co-solvency, hetero-association, structure breaker and structure maker mechanism. The self-aggregation mechanism mainly depends on the amphiphilic features and the nature of the lignin. The balance apolarity between solute and hydrotrope acts as the driving force for the aggregation of a hydrotrope. The interaction of the apolar moiety of a hydrotrope

molecule with water is much weaker than a water-water hydrogen bond, causing the aggregation of hydrotrope molecules around a solute (lignin).[83] In accordance with this mechanism, it is understood that the introduction of an acid hydrotrope will catalyze the hydrolysis of ether or ester bonds in hemicelluloses and lignin carbohydrate complexes, resulting in the isolation of the lignin. After that, acid hydrotrope molecules will form an aggregate around the lignin through π–π (strong van der Walls forces) forces. CH–π interactions between hydrotrope and lignin molecules caused the separation and isolation of lignin from the plant cell wall matrix and the addition of water destroyed the aggregation resulting in lignin precipitation.[11,78,84] Apparently, the most commonly used hydrotropes are p-toluenesulfonic acid (p-TsOH) and maleic acid (MA) due to their richness in π electrons.[75,85] Figure 5 shows an example of the self-aggregation mechanism of p-TsOH.

Several researchers have reported the occurrence of hydrotrope self-association in aqueous conditions in recent years, with hydrotrope stacking being considered a type of self-association.[74,82,86] This fascinating phenomenon includes the aggregation of hydrotropic molecules in an aqueous environment, which results in the development of supramolecular structures via non-covalent interactions.[87] A high MHC value will enable the self-association of the hydrotrope to occur. Besides, the self-association of the hydrotrope with solutes also enables the formation of a micellar structure. A few hydrotropes that exhibit self-association and micelles forming ability are alkyl-benzene sulfonates, lower alkanoates, and alkyl sulfates. Malik and co-workers reported that the intercalation of the hydrotrope reduces the electrostatic repulsion between the heads of the solute, resulting in the formation of stable mixed micelles.[88]

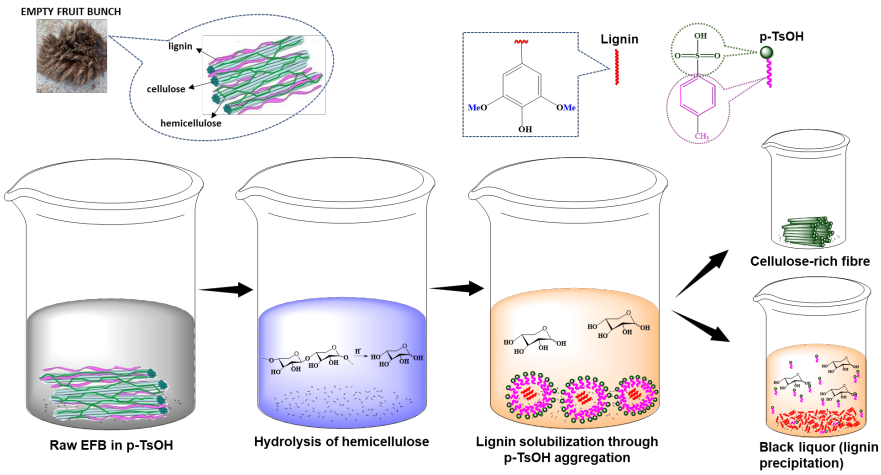

Figure 5: Delignification mechanism using p-TsOH

Performance of acid hydrotrope fractionation

There are a few crucial parameters that need to be considered in the delignification process, such as reaction time, reaction temperature, and acid hydrotrope concentration. Reaction time is a crucial parameter in any hydrotropic process due to the slow phenomena of hydrotropic solubilization, along with progressive aggregation.[78] Feng and co-workers stated that the increase in the reaction time would have a negative impact on the physico-chemical structure of biomass.[89] Therefore, a shorter reaction time was used in many studies of acid hydrotrope fractionation. High lignin removal in a brief period of time indicates excellent efficiency in the delignification process.

Another critical parameter that will affect the delignification is reaction temperature. The thermal energy will disturb the lignocellulose bonding, whereby hydrogen bonding between water molecules is destabilized during the aggregation of the hydrotrope molecules and higher temperature. This results in inadequate hydration and increased surface activity, causing more solute solubilization in the hydrotrope solutions.[90] There was quite a significant increase in biomass extractives with a temperature rise. A previous report mentioned that p-TsOH has

unparalleled performance in delignification at low temperatures.[75]

Recent studies on hydrotropic delignification used aromatic sulfonic salts to fractionate lignocellulosic biomass. In a study conducted by Chen and co-workers, the utilization of p-TsOH in the fractionation of wood resulted in more than 90% delignification at an acid concentration of 80% and a reaction temperature of 80 °C within 20 minutes.[75] Meanwhile, more than 57% delignification was accomplished with an acid concentration of 75% and a reaction temperature of 65 °C within 5 minutes. In both situations, more than 80% of cellulose was retained. This indicates that fractionation using p-TsOH is rapid and highly selective.[75] Another study by Wang and co-workers reported that fractionation using an aqueous p-TsOH solution on poplar wood dissolved 79.3% lignin at 90 °C in 60 minutes.[91] They also found that increasing the concentration of p-TsOH increased the dissolution of lignin and hemicelluloses. Besides, the glucan retention in water-insoluble solids (WISs) was maintained at roughly 90%, indicating remarkable selectivity in the solubilization of lignin and hemicelluloses, while the cellulose is preserved.[91] Recently, Su and co-workers used p-TsOH and maleic acid (MA) to treat switchgrass under mild conditions. It was found that fractionation using MA achieved more rapid and greater maximal dissolution of lignin (63%) compared to p-TsOH (55%). The increased concentration of both types of hydrotropes caused an improvement in lignin removal where the maximal lignin removal was achieved by MA and p-TsOH at concentration of 60 wt%.[92] This indicates that the hydrotrope concentration plays an important role in the delignification process. The same study also revealed that lignin dissolution increased with the increasing reaction temperature and time.

Another study on hydrotropes was conducted by Mikulski and Klosowski, where the lignin was extracted from three biomass sources, namely pine chips, beech chips and wheat straw, using sodium cumene sulfonate (NaCS) as hydrotrope solvent. It was reported that the highest lignin removal from pine chips, beech chips, and wheat straw was achieved using 10 wt% NaCS concentration, where 34.31%, 16.03%, and 12.88% of lignin was extracted respectively.[31] A recent study on hydrotropic pretreatment on rice straw by using sodium cumene sulfonate (NaCS) and sodium xylene sulfonate (Na-X) found that more than 50% of lignin was removed from NaCS pretreated rice straw, whereas for Na-X only 34% of lignin was removed. NaCS was found to be more efficient in delignifying the rice straw, as compared to Na-X.[78]

Korpinen and Fardim suggested that sodium xylene sulphonate (Na-XS) was a promising green solvent alternative for extraction of a lignin fraction that appeared to be pure enough to undergo further processing into new chemicals. Their research on hydrotropic treatment used Na-XS solution as a solvent to extract lignin from spruce and birch wood. The yield of extracted lignin was varied from 20% to 70%, depending on the type of biomass used and the variation of the Na-XS concentration.[77] Another similar research that used Na-XS in biomass fractionation was conducted by Ansari and Gaikar. The maximum delignification (85%) was achieved with 30% (w/w) Na-XS solutions. The delignification of bagasse by Na-XS increased with the increase of reaction time and temperature.[93] High fractionation temperatures significantly condensed dissolved lignin with low levels of ether-aryl β-O-4 linkages. It can be concluded that Na-XS based hydrotropic fractionation of lignocellulose biomass was effective.

CONCLUSION, OPPORTUNITIES AND PERSPECTIVES

In conclusion, acid hydrotrope fractionation emerges as a highly promising method in the pursuit of efficient lignin extraction from lignocellulosic biomass. The method's remarkable rapidity and selectivity, demonstrated by p-toluenesulfonic acid (p-TsOH) and other hydrotropes, render it an attractive choice for biomass processing. Throughout this review, we have discussed key parameters such as reaction time, temperature, and hydrotrope concentration, highlighting their significant impact on delignification efficiency. Studies have shown that p-TsOH can achieve over 90% delignification within minutes, while still preserving the cellulose content. Additionally, investigations into alternative hydrotropes, such as sodium cumene sulfonate (NaCS) and sodium xylene sulfonate (Na-X), have confirmed their effectiveness in removing lignin from various biomass sources. In a world that is actively pursuing sustainable solutions for biomass utilization, acid hydrotrope fractionation emerges as a promising approach, offering significant potential. Its unique ability to selectively remove lignin, while safeguarding cellulose, opens doors to diverse applications,

aligning perfectly with the global shift toward eco-friendly and efficient biomass conversion technologies.

Utilizing acid hydrotropes for lignocellulose biomass delignification represents a promising frontier in sustainable biorefinery processes. The inherent opportunities in this innovative approach lie in its potential to revolutionize traditional biomass processing methods. Acid hydrotropes offer a cost-effective and environmentally friendly alternative, addressing the escalating concerns over the ecological impact of conventional delignification techniques. The ability of acid hydrotropes to efficiently break down lignin, while preserving the cellulose and hemicellulose components, presents a valuable prospect for advancing the production of bio-based materials, chemicals, and biofuels. Moreover, the scalability and versatility of this method open avenues for integration into diverse industrial settings. Looking forward, the perspective of research in this domain extends to further optimization of delignification conditions, exploration of novel applications, and the development of integrated biorefinery strategies. Emphasizing these opportunities can catalyze transformative developments in lignocellulose biomass processing, contributing significantly to the sustainable and circular economy.

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