

LIGNIN VALORIZATION AND GENERATION OF PRECIPITATED LIGNIN : A SUSTAINABLE ROUTE FOR CIRCULAR ECONOMY IN THE CONTEXT OF THE INDIAN PULP AND PAPER INDUSTRY



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Abstract:

Indian pulp and paper industry has great potential to produce high-value-added products with pulp and paper as the major product. Currently, there is an increased interest towards 2G ethanol using LCB among researchers and Government, which is a great opportunity for pulp and paper industry to contribute significantly to achieve the set target by government. Paper industry has its potential to utilize the pulp which is a rich source of cellulose, and hemicellulose for generation of bioethanol using fermentation technology. Whereas, leftover lignin can be a good source for production of value-added chemicals. Lignin, the second largest lignocellulosic biomass (LCB), is the most promising biopolymer for sustainable production of lignin-based new compounds. Therefore, extracting lignin from black liquor that is always in excess/unused without affecting steam generation operation in large integrated paper mills can be used as solid biofuel. In this context, a cost-effective method applied to reduce the load on the recovery boiler in terms of calorific value, high value precipitated lignin known (at pH 2-11) is recovered. The lignin precipitated at pH 2 is known as Klason lignin (KL), and their various properties are studied in detail. WBL precipitated from 13-9 pH using CO₂ / sulphuric acid can

be used as green biofuel in lime kiln. Further, sulphuric method applied for pH reduction was performed using 6 M H₂SO₄ for obtaining Klason lignin. This KL contains various types of useful aromatic compounds, which were characterized and confirmed using FTIR and GC-MS. The obtained compound has potential applications for medical and industrial purposes and can significantly contribute to a circular economy. Therefore, in the present study, various useful compounds from Klason lignin were produced from mixed hardwood pulp and their present market values with their suitable applications are discussed in detail.

Keywords: : Lignocellulosic biomass, precipitated lignin, Klason lignin, lignin valorization

1. Introduction:

In the current time, the Indian pulp and paper market is valued at \$11.48 Billion and expected to grow to \$31.41 Billion by 2029 as per the report of 2022 edition of Paperex, India. The significant increase in the demand and production of paper domestically and its export would generate opportunity for researcher to develop some value added products along with paper products. In India, paper is produced from various lignocellulosic biomass (LCB) such as Eucalyptus, Poplar, Bamboo, and straws (wheat and rice), etc. The LCB has a potential to generate sustainable renewable, recyclable, environment friendly, and cost-effective materials.

In LCB, lignin accounts for ~25% (w/w) total, constituting second largest available renewable resource on the earth. In this context, pulp and paper industry is the major producers of lignin, but it majorly uses the lignin for steam production. However, in the present situation, only ~2% of total lignin is utilized annually to produce valuable chemicals [1]. Cao et al. elaborated about lignin owing to its recalcitrant nature, high energy demand, and monomer accessibility is the biggest challenge. In the recent years, there have been a very high research interest in lignin valorization and its diverse range of applications. In this context, various techniques for treatment of black liquor for recovering lignin have been anticipated such as chemical coagulation [2], alkali recycling [3], adsorption of organic pollutants [4] and acidification [3].

Alkaline recovery process and acid precipitation are the best-known available methods for alkali recovery and lignin removal respectively [5]. Therefore, a suitably selected method can precipitate the valuable lignin from a small amount of unutilized black liquor. Which can be a better solution to develop lignin-valorized products without affecting the steam generation demand. The use of lignin as a feedstock for the production of valuable compounds will be helpful in reducing carbon credits, and significantly contribute in the field of value-added product synthesis.

To date, chemical precipitation methods are accepted worldwide, thus the use of acidic treatment is the economical way for industry to separate out lignin. The addition of CO₂ to WBL produces a unique type of lignin which has similar characteristics to lignoboost at pH 9, which have very high calorific value and can be used in lime kiln [6]. This technique provides energy surplus Kraft pulp mill to separate valuable lignin feedstock. Further, tailoring of lignin and its hydrolysis can give more valuable compounds.

Due to lack of available information and downstream processing methods to separate valuable compounds from WBL are still under research. Therefore, in this paper chemical precipitation of lignin with the generation of valuable compounds and their uses are discussed in detail. Sub-pipeline of WBL into its precipitation can help in reducing load to recovery boilers and could be helpful for sustainably reducing environment load.

2. Material and Methods

Concentrated sulphuric acid purchased from Sigma Aldrich (St. Louis, MO), filter paper (Whatman grade 1)

2.1 Preparation of different type of lignin

2.1.1 Preparation of alkaline lignin

Precipitation of lignin was carried out by sufficient amount of CO₂ or 6 M sulphuric acid supplied to WBL to achieve pH 9 at 60°C. Further, coagulation was achieved using gentle mixing at

50 °C [7]. Higher heating value of lignin was determined using bomb calorimeter, and solid content was checked at 105 °C, till constant weight was achieved.

2.1.2 Preparation of Klason lignin

Using Theliander et al. method the Klason lignin preparation was carried out as described [8]. Weak black liquor (15% w/v) obtained from kraft pulping process (Star Paper Mill Limited, India), 200 g of WBL sample was weighed in the 500 mL reagents bottle, further precipitation was done with 72% (v/v) sulphuric acid (drop wise to the WBL) and pH was adjusted to 2 ± 0.1. Further, 84 mL of deionized water was mixed with WBL sample in reagent bottle and autoclaved (121 °C, 15 psi for one hour). After completion of hydrolysis, residual insoluble solids were filtered using Whatman filter paper. Residue was thoroughly washed with distilled water and the remaining lignin is referred to as Klason lignin. Which is further dried at 70 °C, till constant weight was achieved.

2.2 Lignin precipitation yield calculation

Yield of precipitated lignin =

$$\frac{(\text{Lignin in black liquor} - \text{Lignin in filtrate}) \times 100}{\text{Lignin in black liquor}}$$

2.3 Characterization of Klason lignin

2.3.1 FTIR spectroscopy

The recovered Klason lignin, after hydrolysis in autoclave, was characterized by FTIR spectroscopy, The FTIR spectra were studied between 4000 cm⁻¹ to 600 cm⁻¹ wave number using Perkin Elmer spectrometer. Dried Klason lignin was powdered and used for FTIR analysis

2.3.2 GC-MS analysis

The Klason lignin residue was dried and subjected to derivatization protocol. This method added 10 µL pyridine and 100 µL dioxane followed by 50 µL N, O- Bis (trimethylsilyl) trifluoroacetamide-Trimethylsilylation (BSTFA-TMS) addition. It was heated at 60 °C for 15 minutes with shaking condition. 1 µL sample was injected in GC with conditions given by Raj et al. [9]. The GC-MS of the Klason lignin and its degradation intermediates analysis was done using Agilent GC (Model 7890 A)-MS (model no. 5975C) [10]. The low molecular weight compounds of Klason lignin were analyzed by TMS derivative method [9]. In this GC-MS method, 2 mL sample was injected in a splitless mode in DB-5 MS column (30 m length *0.25 mm ID * 1 mm thickness). The oven temperature kept at 75 °C for 1 minute, then increased to 310 °C at a rate of 10 °C/min and kept constant at 310 °C for 20 minutes. The auxiliary heater temperature was kept at 300 °C, and the injector temperature was at 250 °C with helium as a carrier gas at a flow rate of 1.5 mL/min.

3 Results and discussion

Precipitation of Kraft lignin and its characterization can give more insights into lignin to form its valorize products. Recently, researchers have gained significant attention on lignin to solve the puzzle of the complex and diverse molecular structure of lignin. In the present study, it is observed that the varying ionic concentration of black liquor yields various types of phenolic compounds of lignin with their unique properties. But, it can be extracted from black liquor by reducing its ionic strength.

In the first experiment, the lignin precipitation was done by CO_2 or 6 M sulphuric acid to reduce the pH from 13 to 9 and to obtain CO_2 precipitated lignin $66.5 \pm 1.7\%$ and acid

precipitated lignin $75.9 \pm 2\%$ of initial WBL. The obtained CO_2 precipitated lignin has shown higher calorific value than the acid precipitated lignin by 1.35 MJ/kg. But both the precipitated lignins have higher calorific value than the WBL. Whereas, it is nearly equal to coal listed in Table 1. Thus, a high calorific value of 25.1–26.45 MJ/kg can be a better alternative to reduce coal consumption and directly use it as greenbiofuel and reduce fuel consumption costs. In the integrated kraft mill, this on-site generated precipitated lignin can be used in lime kiln operations and significantly contribute to the circular economy. Due to low ionic strength and higher cost of CO_2 , sulphuric acid precipitation technique was used for Klason lignin precipitation. In future, for lowering pH, a combinatorial method of CO_2 and sulphuric acid can be used.

Table 1: Characteristics of WBL, CO_2 treated lignin, sulphuric acid precipitated lignin, and coal

Parameters	WBL	Sulphuric acid treated lignin	CO_2 treated lignin	Coal [11]
Total solids (%)	15	72	70	95
pH	<13	9	9	Not applicable
Residual active alkali (%)	3.2	Not applicable	Not applicable	Not applicable
Calorific value (MJ/kg)	11.5	25.1	26.45	28

3.1 Klason lignin precipitation

In this experiment, recovery of lignin from WBL was done by the precipitation method using 72% (v/v) sulphuric acid (pH 13–9), and pH 9–2. From Figure 1, it is observed that the phenolic group present on lignin get precipitated out at their isoelectric point [12]. In the present study, decreasing pH from 13 to 9 precipitates out $75.9 \pm 1.33\%$ (w/w) in case of sulphuric acid treated lignin from initial WBL taken. Further, decreasing pH from 11 to the neutral, most of the lignin $8 \pm 0.5\%$ (w/w) were precipitated out in case of sulphuric acid treated lignin. To obtain Klason lignin, pH was reduced to 2 resulting in maximum lignin removal $89.7 \pm 1.6\%$ (w/w). This study clearly indicates that higher ionic strength results in precipitation of lignin. In the previously reported study, WBL obtained from softwood pulping under ionic strength of 20% resulted in 85% (w/w) precipitation of lignin at 45°C , pH 9.5 [13]. From the various reported studies, the insolubility of lignin in aqueous phase is the major problem for its valorization. Some advanced system were already developed to solubilize lignin from LCB in organic solvents and ionic liquids. Lignin valorization using organic solvent and ionic liquids technique attracted significant attention due to lignin's easy solubility in an organic solvent/aqueous-organic phase compared to the aqueous phase. Commercially, Organosolv process is used for lignin extraction, which uses a broad range of organic solvents such as acetone, dimethylformamide (DMF), dimethyl sulfoxide

(DMSO), dioxane, methanol, ethanol, ethyl acetate, and pyridine at 30–80% (v/v) for removal of lignin from various LCB. But use of organic solvent is avoided due to higher cost and their harmful impact on environment. Ionic liquids are the green solvents which are composed of ionic species and found in liquid form at room temperature [14]. The special properties of ionic liquid (density, hydrophobicity, melting point, miscibility, and viscosity) can suitably be tuned as per the reaction system [15]. Though, ionic liquid system is sustainable but requires high input cost for removal of lignin from ionic liquid. Therefore, in this study acidic chemical treatment method is adapted for obtaining lignin.

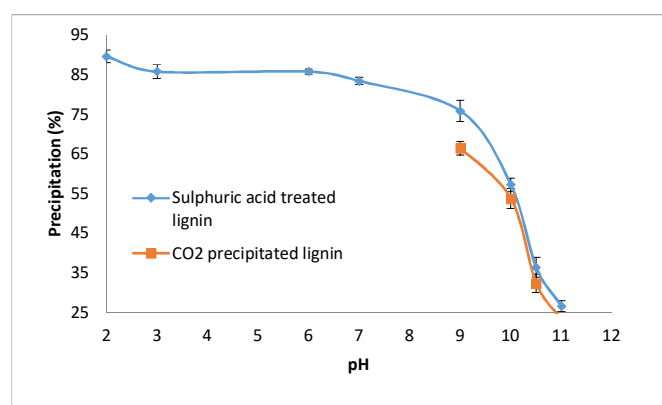


Figure 1: Precipitation of hardwood Kraft lignin from WBL at different pH (11 to 9 done by 6 M H_2SO_4 / CO_2 and further reduction done by 6 M H_2SO_4 at 60°C)

3.2 FTIR characterization

After precipitation of lignin at pH 2, it was autoclaved (121 °C for 1.1 kg/cm², for 1 hour) for thermal hydrolysis. KL was successively underwent degradation of higher molecular weight lignin into lower molecular weight of lignin. The FTIR transmittance analysis shown in Figure 2 at 3394 cm⁻¹, showed O-H stretching and confirmed the presence of the alcoholic group. While, 1601 cm⁻¹ showed strong C=C stretching of α - β unsaturated ketone, 1514 and 1457 cm⁻¹ showed stretching of C-H bond showed presence of higher alkanes, thus these compounds are originated from presence of hemicellulose and cellulose compounds of LCB. Whereas, at 1425 cm⁻¹ O-H bending of carboxylic acid groups is shown. At 1210 cm⁻¹ showed strong C-O stretching of alkyl aryl ether. 1111 cm⁻¹ showed strong C-O stretch and showed formation of aliphatic ether. From previously reported study, they found similar type of peaks in their FTIR analysis at 1600, 1510, and 1425 cm⁻¹, and 1270cm⁻¹ as syringyl lignin, 1330 as guaicyl lignin [16]. It is not possible to determine the exact structure using FTIR but we clearly observe some prominent peaks to infer the formation of new compounds. For getting some detail insight of the story, GC-MS was performed.

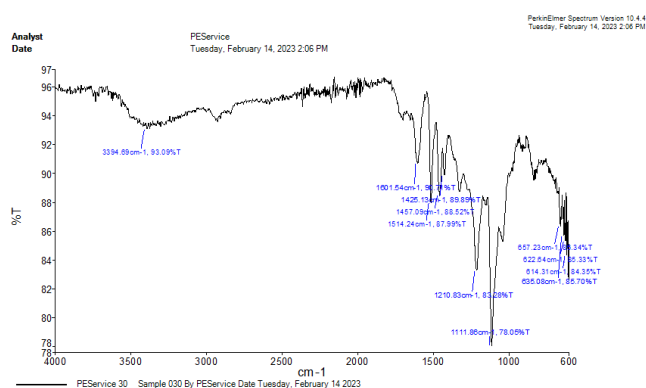


Figure 2: FTIR of hydrolyzed Klason lignin

3.4 GC-MS characterization of Klason lignin

GC-MS study of hydrolyzed Klason lignin showed (in Figure 3), that the highest molecular weight lignin can be converted into useful products (Table 2). Formation of new products can be explained by opening of ring, and couple reactions and production of free radicals. It has been observed that C6-C30 carbon chain compounds were formed due to hydrolysis of KL. The hydrolyzed Klason lignin compounds have several applications in the field of medicine, cosmetic compounds, flavoring agents, surfactants, composition of paints and plastics. Formation of majority of acid soluble lignin can be easily seen in Table 2. The formation of fatty acid methyl esters (C14-C17) can be explained on the basis of possible conversion of these acidic groups via transesterification reaction by utilizing alcoholic group formed during hydrolysis of KL. The major

reactive groups present in lignin are the aromatic and phenolic hydroxyl groups which have proven potential applications in various industries as given in Table 2. The previously reported study converted KL to precursors (propanoic acid, hexadecanoic acid, 1,5 pentanediyl ester, docosone, hexadecanoic acid, etc.) of biodiesel or advanced biofuels at room temperature and atmosphere pressure [17].

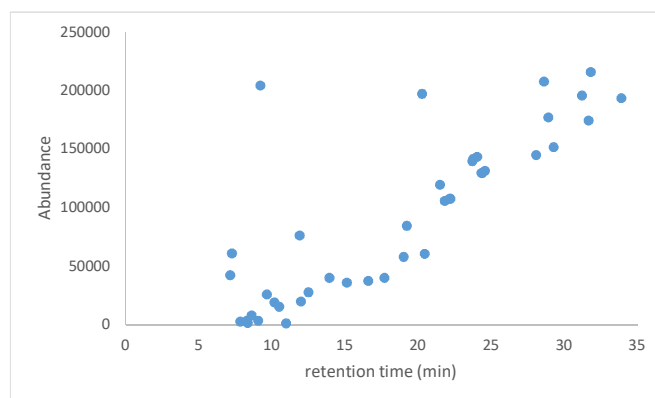


Figure 3: GC-MS chromatogram of hydrolyzed Klason lignin

4 Cost increment for setting new lignin precipitation technology

The direct operating cost includes the chemicals (CO₂ and H₂SO₄), and a minor cost of steam consumption. The primary requirement of CO₂ increases the operating cost (Rs 23/m³ of CO₂). But this can be reduced by diverting in-house CO₂ produced from lime kiln by approximately 50% [6]. Further, the high cost is borne by H₂SO₄ (Rs 5/kg) for further processing of lignoboost in to Klason lignin to more valuable compounds of lignin.

5 Conclusions

This study gives an idea about precipitation technique which can achieve up-to 90% (w/w) lignin recovery from hardwood Kraft WBL. Approximately 66-75% (w/w) lignin was obtained using CO₂ and sulphuric acid precipitation at pH 9 which can be directly used in integrated Kraft pulping mill as a green biofuel. In the present scenario, lignin business is increasing worldwide due to already-developed lignoboost [13] and lignoforce technology [7]. But present method produces almost equal characteristics of precipitated lignin as lignoboost and lignoforce. These methods give sustainable and economically viable ways to kraft pulping paper mills. Further, developing downstream process of degraded higher molecular weight Klason lignin into valuable compounds can generate more revenue to paper industry (confirmed by FTIR and GC-MS). In addition, more characterization methods of WBL gives more insights for converting lignin into valorized products. These compounds, having various applications

Table2: GC-MS profile of Klason lignin formed from this study

Retention time (min)	Compound	Number of carbons	Uses
7.8267	Phenol	C6	Precursors of plastics and various drugs
12.4973	Phenol, 2,6-dimethoxy-	C8	Syringol gives smoky aroma
15.1245	Apocynin	C9	Acetovanillone used for treating edema, heart problem, and asthma
16.6044	Benzoic acid, 4-hydroxy-3-methoxy-	C8	Vanillic acid used as flavoring agent
19.2384	Tetradecanoic acid	C14	Myristic acid
20.4604	Benzoic acid, 4-hydroxy-3,5-dimethoxy-	C9	Syringic acid well known for anti-oxidant, antimicrobial, anti-cancer and anti-diabetic properties
21.4922	Hexadecanoic acid, methyl ester	C17	Methyl palmitate used for cosmetic, flavor and fragrance agent
21.8249	Palmitoleic acid	C16	Anti-inflammatory and improves insulin sensitivity
22.144	n-Hexadecanoic acid	C16	Palmitic acid has various applications in surfactant, food and various medicinal applications
23.6986	9,12-Octadecadienoic acid, methyl ester	C18	Linoleic acid has applications as surfactant, oil paints, varnishes, etc.
24.0448	Heptadecanoic acid, 16-methyl-, methyl ester	C17	Margaric acid used as mosquito repellent
24.3502	cis-13-Octadecenoic acid	C-18	Isomer of steric acid
24.3978	cis-Vaccenic acid	C-18	Found in milk (omega 7 fatty acid)
24.5811	Octadecanoic acid	C-18	Stearic acid (used for cosmetics, detergents, lubricants, softening and releasing agent)
28.0704	Dehydroabietic acid	C-20	Used in lacquers, varnishes, and soaps
28.9258	Docosanoic acid	C22	Behenic acid used for hair conditioners, moisturizers and lubricants, etc.
29.2652	1-Docosene	C22	Metabolite observed in cancer metabolism
31.2204	Tetracosanoic acid	C23	Lignoceric acid known as wood tar
31.6548	Cyclotetracosane	C23	Cyclic product of lignoceric acid
31.8245	Squalene	C30	Triterpenoid used for steroid formation for medicinal use
33.8951	1-Hexacosene	C26	Used of cosmetics purpose of skin conditioning

in medicine, paint, developing nanoparticles, and food industries, can significantly contribute to circular economy. These valorized products need to be separated using various downstream processing and can be further valorized using chemical and/or biological catalysis to form more valuable compounds. Therefore, the formation of valorized products or intermediates from a small part of surplus WBL can generate revenue without affecting the steam generation and can be a significant achievement for paper industry. Thus the bridge between the research and paper industry can give valuable and sustainable solutions.

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