

SEPARATION OF LIGNIN FROM INDUSTRIAL PREHYDROLYSIS LIQUOR USING A SOLID ACID CATALYST

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ABSTRACT: The concept of a biorefinery has been introduced in the pulp and paper industry in order to improve the industry's profitability and competitiveness by generating new revenues from new products. Prehydrolysis liquor (PHL) produced from the Kraft based dissolving pulp production process contain monomeric sugars and oligomeric sugars, acids, degraded lignin, furfurals, and other dissolved low molecular weight extractable substances. Fractionation of dissolved organic compounds from the prehydrolysis liquor is of great economic significance, as the organic compounds are platform chemicals that can be used for the production of bio-based chemicals, materials, and products. The aim of the study was to separate acid soluble lignin from the prehydrolysis liquor during hydrolysis of oligomers using microwave-assisted solid acid catalyst treatment. HZSM-5 was used as a solid catalyst and microwave irradiation power, catalyst loading and reaction time were investigated as manipulated variables to determine the effect on lignin removal and monomeric sugar yield. Lignin characterization and quantification were done using UV, FTIR, and NMR analysis. HPLC was used to identify and quantify components in the PHL and reaction products. Approximately 90% of acid-soluble lignin, 70% of organic acid and 100% furfural could be removed from the PHL with relatively low sugar losses (< 2 wt. %). The results show that solid acid catalyst treatment was effective for not only removing lignin from the PHL but also most known fermentation inhibitors. Combining inhibitor removal, hydrolysis of residual oligomer fractions to fermentable sugars and recovery of platform chemicals in a single treatment step could not only significantly reduce the cost of second-generation ethanol production but also greatly improve the economic viability of forest-based bio-refineries such as paper and pulp mills.

Keywords: lignin, prehydrolysis liquor, solid acid catalyst, bio-refinery, separation

1 INTRODUCTION

Prehydrolysis liquor (PHL) is a byproduct of the kraft dissolving process. Prehydrolysis is an important step in the dissolving pulp production process during which most of hemicellulose and lignin are dissolved in water through depolymerisation and degradation (1, 2). Prehydrolysis liquor contains oligo- and mono sugars from hemicellulose, organic acids, furans derivatives and lignin fragments. Currently, PHL is considered to be waste stream due to the complexity and cost of recovering components from this stream. The hemicellulose saccharides dissolved in the PHL can be used for the production of chemicals, biomaterials and biofuels. Utilization of hemicellulose saccharides in prehydrolysis liquor (PHL) is essential for wood biomass biorefinery(1). Lignin presence is detrimental to the utilization of sugars and acetic acid present in the PHL. Lignin isolation in the PHL is the problem that remains unresolved and abstracts the utilization of hemicellulose in the liquor. The removal of lignin from the prehydrolysis liquor in colloidal or dissolved form is particularly important, because when filtration membranes are used to remove small organic substances such as acetic acid, furfural acid and hemicellulose, dissolved lignin can cause filtration membranes to foul and reduced membrane efficiency and durability(3). In addition, lignin is also an important inhibitor in fermentation, its removal can improve the fermentation products.

Lignin is a valuable source for renewable energy and biomaterials like plastics and adhesives. For value utilization, therefore, it is important to separate lignin and hemicellulose effectively in the prehydrolysis liquor. Lignin present in the prehydrolysis liquor has not been in contact with any chemical and has high purity. Once separated from the prehydrolysis liquor it can be used as a raw material for may value-added products like phenols, biofuels, plastics which can generate additional revenues to the kraft-based dissolving pulp mills. However, the

valorisation of lignin is challenging due to its heterogeneous structure and high reactivity of degraded fractions which are prone to polymerization (condensation) reactions. (4). A good fractionation method that is able to isolate lignin (high yields and high purity) from prehydrolysis liquor will be of benefit to the paper and pulp industry and biorefinery (1).

Various methods for lignin removal from PHL have been explored. The lignin removal can be achieved by membrane filtration(3, 5, 6), acidification (7-9), enzyme treatment, adsorption with lime(10, 11), activated carbon(12, 13) and flocculation with ionic polymers such as chitosan and cationic polyamide (CPAM) (14). Many combined processes have also been explored for lignin removal from PHL(15-17). It has been reported that approximately 46-61% of lignin from the PHL can be removed with laccase treatment due to the polymerization of the lignin caused by the laccase (18). In addition to laccase, horseradish peroxidase (HRP) enzyme has been reported to remove lignin or phenolic compounds from effluents through polymerization. It is believed through the addition of peroxide phenols are oxides to form radicals which spontaneously react to form larger molecular weight compounds.

The current methods for removing lignin from PHL suffers from low removal efficiency. Membrane separation has been used to separate hemicellulose and lignin from prehydrolysis liquor, but the main challenges of this process were blockage and fouling. The commercial membranes available for separation are often hydrophobic and are therefore highly susceptible to fouling by lignin and wood extractives. (19, 20). Koivula, Kallioinen (19), reported over 90% to permeate flux decrease within a few minutes when wood hydrolysate was fractionated using polysulfate ultrafiltration membrane. To enable an efficient separation for membrane filtration, pretreatment is carried out to reduce the fouling and the blockage problem. Removing lignin from PHL using adsorbents like activated carbon is also a viable way option but a challenge

is associated with recovering and the reuse of the adsorbent and further separation and utilization of the lignin removed. Once the lignin is adsorbed onto the activated carbon it cannot be recovered to be used as feedstock for chemicals. Other disadvantages associated with the mentioned lignin extraction method include high energy use and chemical requirements, low efficiency and high costs. Using inorganic adsorbents, especially zeolites has appeared to overcome the mentioned disadvantages. Solid acids catalyst (Zeolites) have received increasing attention for biomass conversion due to their non-toxicity, easy separation and high acidity strength. What makes solid acid catalyst attractive for the hydrolysis of hemicelluloses and lignin removal is that they are water-insoluble and can be easily filtered, reusable or recyclable and readily separable. Zeolites have been used as an adsorbent for removing phenols from wastewater (21). However, very few studies have investigated lignin removal from prehydrolysis liquor using zeolites. It is beneficial to use solid acid compared to the homogeneous catalyst, as they do not need neutralization, they can be easily separated from the products by filtration and they are non-corrosive which reduce operational cost (Jaing et al., 2016). This study will present a pretreatment method using a zeolite catalyst for lignin removal and hydrolysis of sugars. As the sugars are present in the PHL at low concentrations, monomeric sugar hydrolysis to oligomers will help improve separation. The aim of the study is to separate acid soluble lignin from the prehydrolysis liquor using microwave-assisted solid acid catalyst treatment. HZSM-5 is used as a solid catalyst and microwave irradiation power, catalyst loading and reaction time are the manipulated variables to determine the effect on lignin removal and monomeric sugar yield.

2 MATERIALS AND METHOD

2.1 Raw material, solid acid catalyst and chemicals

Industrial prehydrolysis liquor from kraft dissolving pulp mill was collected from pulp and paper company (pH 3.63). Proton exchange ZSM-5 zeolite catalyst with nominal Si/Al ratio of 15:1 was supplied by Riogen Catalysis for Chemicals and Energy.

Table I: PHL Composition

Components	Total Concentration g/L
Monomeric sugars	11.54
Oligomers	23.76
Acetic acid	9.12
Sugar alcohol	1.30
Lignin	6.8
furfural	3.69

2.2 Analysis of adsorbent

Characterization of the catalyst is necessary in order to understand the framework of the catalyst and assist in identifying any structural changes to the catalyst during pretreatment. The framework structure and the morphology of the solid acid catalyst were determined by several techniques. Scanning electron microscope (SEM) and Transmission electron microscope (TEM) were used to investigate the morphology of the catalytic material. Energy Dispersive Spectroscopy (EDS) was carried out to determine the chemical elements present in both catalysts. XRD and XRF were done for elemental composition and

crystal structure of the catalysts. FTIR was used to determine the functional group on the surface of the catalyst. The specific surface area and pore volume of the catalysts were measured by the nitrogen adsorption method (Micromeritics ASAP 2020). The catalysts were out-gassed at 423 K prior to the measurement and the Dubinin method was used to calculate the specific surface area (Faba et al., 2014.)

2.3 Solid acid treatment of PHL

Hydrolysis of the prehydrolysis liquor was performed in an industrial microwave (Anton Parr Multiwave Pro) PHL (40g) was mixed with a catalyst and the mixture was stirred and immediately transferred to the microwave reactor and irradiated under specific microwave power for an appropriate time. When the reaction was finished, the reactor was cooled down to the ambient temperature. The reaction mixture was separated into liquid and solid phases by centrifugation. The effect of catalyst loading (0,10,15,20,25,30 wt%) and reaction time (20,25 and 30 min) and lignin removal and fermentation sugar concentration was evaluated at a microwave power setting of 300,350, 400W. The experimental procedure followed is shown in Figure 1.

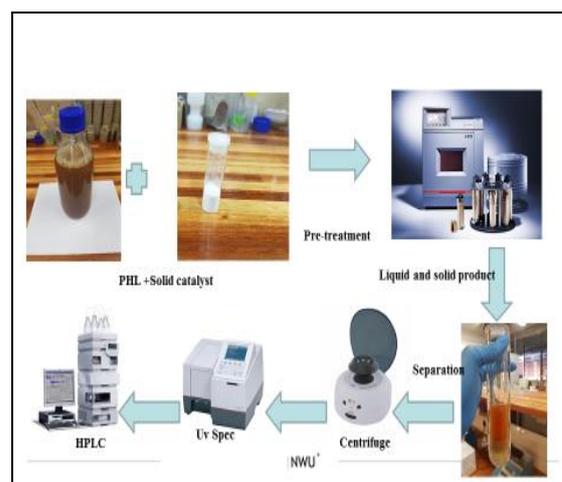


Figure 1: Experimental Procedure

2.4 Analysis methods

The liquid phase samples from the reaction mixture were quantitatively analysed by high-performance liquid chromatography (HPLC) to determine the concentration of sugars and acids. All samples were diluted appropriately with eluent (0.005M H₂SO₄) and filtered through a 0.2 µm filter. The HPLC was fitted with an Aminex HPX-87H column and the injection volume was 10 µL. The operating temperature was 55 °C. The mobile phase was 0.005 M of H₂SO₄ solution with a flow rate of 0.6 mL/min. The temperature detection cell in the RI detector was set at 55°C. Soluble lignin from the liquid phase was determined by UV spectrophotometry (Shimadzu UV min 1240) at a wavelength of 205 nm. PHL liquid phase samples were diluted with distilled water to acquired an absorbance between 0.2-1 and the solid phase of the samples was analysed by FTIR to determine the functional group changes during pretreatment. The wt% of acid-soluble lignin liquid was calculated using Eq1 and the wt% of lignin removed was calculated using Eq2.

$$\text{Acid Soluble Lignin} = \frac{(\text{Absorbance}) (\text{Dilution Factor})}{\epsilon (\text{Path length})} \text{ g/L} \quad (1)$$

Where: ϵ is the absorption coefficient with a value of 110 L/g/cm

$$\text{Wt. \% lignin removed} = \frac{W_o - W_t}{W_o} \times 100 \quad (2)$$

Where W_o the initial is mass of lignin in the PHL and W_t is the mass of lignin in the treated sample.

3 RESULTS AND DISCUSSION

3.1 Effect of catalyst loading

The effect of catalyst loading on the removal of soluble lignin from the PHL at the constant power setting of 400W

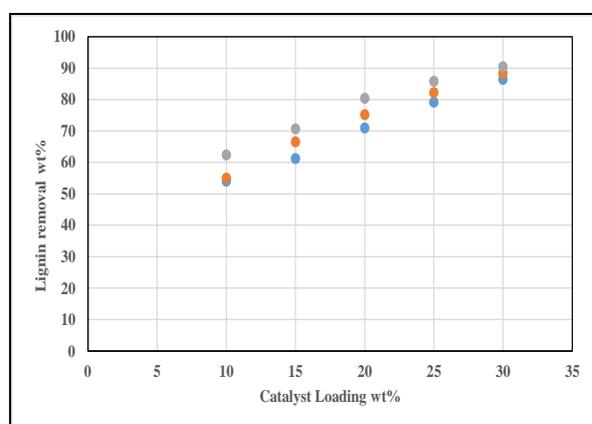


Figure 2: Effect of catalyst loading at different treatment time, \circ 20, \circ 25, and \circ 30 min.

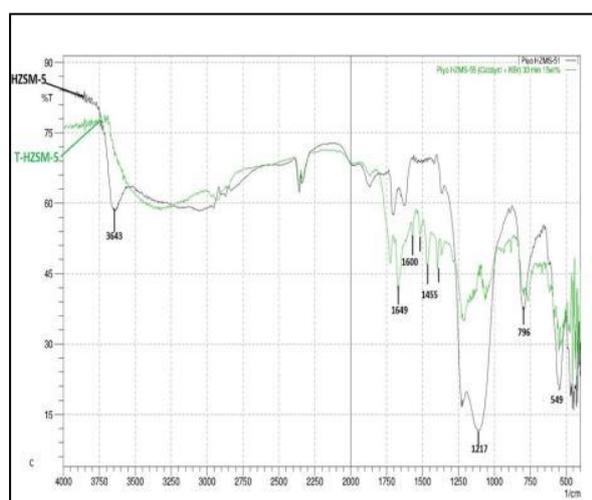


Figure 3: FTIR analysis

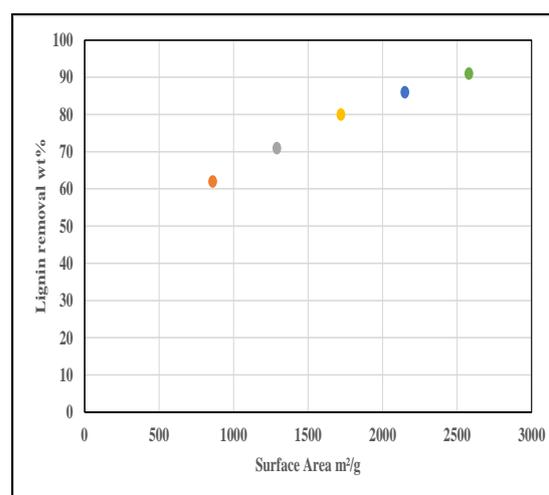


Figure 4: BET surface area and lignin removal wt%

The influence of pretreatment conditions on lignin removal such as catalyst loading, pretreatment time and microwave irradiation power was evaluated. The results from Figure 2, show the lignin removed from the prehydrolysis liquor increased from 50% to 90% with an increasing amount of solid catalyst from 10wt% to 30wt%. Increasing removal of lignin with more catalyst loading can be attributed to the increased surface area and availability of more active sites which result in more interaction of lignin with the catalyst. The higher removal of lignin with high catalyst loading can be explained by the results of the increase in surface area and active sites with increased catalyst loading and the adsorption of lignin to the solid acid catalyst (22).

According to Ranjan, Thust (23), zeolite with high silica content can adsorb phenolics more efficiently from biomass hydrolysate and are able to remove fermentation inhibitors like HMF and furfural (Ranjan et al., 2009). Zeolite when used as a solid additive, the zeolite may chemically or physically combine with lignin to form a lignin additive complex. To validate the adsorption of lignin to the zeolite catalyst, FTIR analysis was carried out, where the catalyst before and after treatment was compared (Figure 3). Removal of lignin with the increasing surface area was evaluated using BET analysis (Figure 4).

FTIR spectra of HZSM-5 before and after pretreatment were compared in order to validate structural changes on the catalyst (Figure 3). The FTIR spectra of HZSM-5 was taken in the range of 400-4000 cm^{-1} . It is known that the bands corresponding to OH bond vibration appear at wave number higher than 3200 cm^{-1} . HZSM-5 shows a single band around 3643 cm^{-1} , it has been reported that this band is assigned to vibration of -OH next to alumina and is associated with Bronsted acid sites in HZSM-5. The band around 3600 is a distinct band and the most characteristic of this type of zeolite (Goran Boskovic, 2011). However, after the pretreatment, the spectra show that the OH peak disappeared, which indicate treatment resulted in structural changes on the catalyst. The peaks at 549, 585 and 600 cm^{-1} are related and assigned to the double five rings of tetrahedral vibrations of HZSM-5 crystalline structure (24, 25). The spectra of HZSM-5 before treatment was compared to the spectra of HZSM-5 after pretreatment. HZSM-5 spectra after pretreatment show new peaks that appeared at (1700- 350 cm^{-1}) that

were not present before the treatment. The peak at 1600, 1510, 1455 and 816 cm^{-1} is assigned as the characteristic vibration of the benzene structures in lignin. The presence of the peaks on the catalyst confirms that the lignin removed from the PHL was adsorbed on the catalyst. In addition, the peak at 1649 is identified as stretching vibrations conjugated carbonyl groups, peak 1595 and 1510 cm^{-1} are related to vibration of aromatic rings and 1455 cm^{-1} is attributed to methoxyl groups. The peak at 816 cm^{-1} is considered to correspond to the characteristic of vibration of guaiacyl units(26). The peak located at 1330 cm^{-1} indicates the presence of syringly ring (S). In addition peak, 1116 cm^{-1} was present which is another signal characteristic of C-H bond in the aromatic rings for kraft lignin (Domínguez-Robles et al., 2017) All these mentioned peaks that are present on the catalyst is an indication of the presence of lignin groups adsorbed onto the HZSM-5 structure.

3.2 Effect of Microwave Power

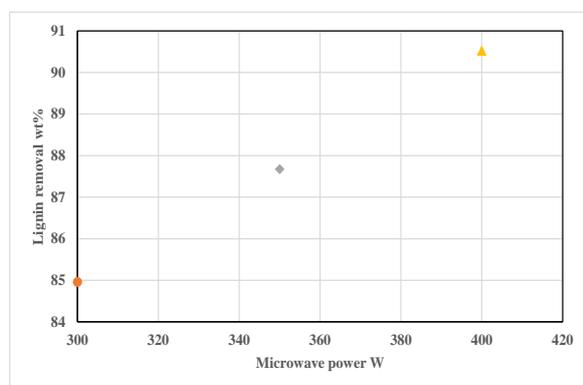


Figure 5: Effect of microwave power at 300, 350 and 400.

The experiments were carried out from 300, 350 and 400W using 30 min reaction time. Figure 5 shows the effect of microwave power on lignin removal. It can be seen that increasing microwave power output from 30W to 400W had the effect on amount of lignin removed from the PHL. Increasing power to 400W led to lignin removal of 90wt% compared to that of 50wt% at 300W. This suggests that the severe treatment conditions allowed more interaction between the catalyst and the lignin. The results show microwave irradiation can maximize the lignin removal from the PHL. The results of effect of microwave power on lignin removal were validated BET analysis. The BET results (Table2) show the surface area of the catalyst decreased in the increasing microwave radiation and increasing removal. The surface area and the pore volume of catalyst decreased compared to the catalyst before use, this is due to the accumulation of the lignin on the surface of the catalyst and blocking of the pore structure. HZSM-5 before pretreatment had a surface area of 395.9 m^2/g , the surface area decreases to 176.6, 148.7 and 214.9 m^2/g with increasing microwave radiation and increasing removal. The same trend was observed for the micropore volume. The micropore volume decreased from 0.0902 to 0.0418, 0.0331 and 0.0519 cm^3/g . The BET results suggest that catalyst pores were occluded by lignin after pretreatment. This finding supports the FTIR results which showed the presence of functional groups associated with lignin present on the surface after the pretreatment.

3.3 Lignin recovery from the catalyst

The recovered catalyst solid contain a quantity of lignin removed during the pretreatment. It is important to recover the lignin from the catalyst as the lignin can be used for the production of bio-products and the catalyst can be recycled and re-used. The lignin adsorbed can be removed by washing the catalyst. One or more washes are performed using a solvent to remove from the solid acid catalyst followed by water to displace the solvent and sugars from the solids (27).



Figure 6: Catalyst recovery, A filtrate after microwave pretreatment, B filtrate after NaOH washing, C solid acid catalyst after NaOH washing. D sample before the separation of the solid catalyst and recovered lignin.

Lignin from the prehydrolysis liquor was recovered using sodium hydroxide treatment. 0.2 M of sodium hydroxide solution was used to wash the catalyst after pretreatment. This led to a removal of lignin $\pm 100\%$ from the catalyst. Sodium hydroxide resulted in 90% lignin removal at pH 12.5. Alkaline treatment (desalination) is used as the treatment to increase the porosity and activity of zeolite. NaOH treatment creates more open mesopore in the micropore zeolite(28). Sodium treatment is commonly used in alkaline treatment which solubilizes and extracts lignin from the biomass by affecting the acetyl group in hemicellulose and linkages of lignin carbohydrates ester. This treatment does not disturb the structure of the lignin significantly. This may explain the successful recovery of 100% of the lignin adsorbed by the catalyst.

3.4 Fate of the Sugars

Table II: showing the sugars in the feed and after the treatment with a solid acid catalyst

	Feed (g)	Filtrate (g)
Total mono	0.885	0.307
Total Oligo	0.469	0.343
Total Sugars	1.354	0.650
Acetic acid	0.328	0.195

The results in table II, show that there was a loss of sugars during the pretreatment at 300W, 20min with the solid acid catalyst of 10wt%. Sugars decreased from 0.885g in the feed to 0.307 g in the filtrate. The loss of sugars suggests the sugars were converted to other products during the pretreatment or might have been adsorbed onto the catalyst along with the lignin and acetic acid.

4 CONCLUSIONS

Microwave-assisted solid acid catalyst treatment was used to separate acid soluble lignin from the prehydrolysis liquor. We have established that HZSM-5 solid acid catalyst can effectively remove the dissolved lignin from prehydrolysis liquor up to 90%. Soluble lignin was removed from PHL by adsorption. This was established by analysing the structure and morphological changes of the catalyst after the treatment, which confirmed the presence of the lignin functional groups on the catalyst

4.1 Acknowledgements

The authors gratefully acknowledge the financial support from and PAMSA and Sappi.

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