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ORIGINAL ARTICLE

Hydrolysate as An Alternative Feedstock for Furfural Production

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ABSTRACT – Furfural has emerged as a value-added chemical product generated from hemicellulose-base biomass; in the context of hardwood, it is called biorefining. Several methods have been developed to produce furfural using both hydrothermal and catalytic processes. In this study, hydrolysate is used as feedstock to generate furfural by diluted sulfuric acid and aluminum chloride. Temperature and reaction time have been considered as valuable variables. Hydrolysate was charged with the acid catalyst for around 90 minutes at a certain temperature. The product was analyzed using the Fourier-transform index refractory and excess bromine method. The highest product of furfural for the non-catalyst process was 33.6 mg, which was achieved at 120°C for 90 minutes. As a comparison, diluted hydrochloric acid and aluminum chloride were applied. It shows that diluted acid solution by hydrochloric acid and $AlCl_3$ 1% were obtained at 44.2 mg and 47.3 mg, respectively. Overall, the diluted acid and aluminum chloride managed to increase furfural production from hydrolysate at a modest temperature.

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INTRODUCTION

Furfural demand has increased over the years since its potential for biofuel and biochemical resources. In addition, furfural is also one of the promising chemical platforms that is widely used in major industries such as plastic, pharmaceutical, and precursor for chemicals [1], [2]. Because of this, furfural demand has been predicted to reach around 954 million USD by 2030 [3]. Furfural is engendered from xylan and xylose, a pentoses structure from lignocellulose biomass. Therefore, biomass which contains hemicellulose has been utilized as furfural feedstock. The mechanism of xylose dehydration into furfural has been investigated for several years [4]–[6]. Previously, agricultural waste was preferred because of its pentosan content. Furfural is usually produced by batch and continuous processes, which are one- or two-step processes. Hemicellulose-rich biomass such as wheat straw, corncob, and sugarcane bagasse succeed in producing furfural [7]–[9].

Hydrolysate is one of the byproducts of dissolving pulp enriched with xylose content. Hydrolysate is liquid extracted from the prehydrolysis process in dissolving pulp. Prehydrolysis is a common and efficient method for generating dissolving pulp that is crucial for biorefining because it is necessary to fractionate lignocellulose. A previous report showed that hemicellulose was transferred into the hydrolysate, where xylo-oligomers were found predominantly during prehydrolysis higher than 150°C [10], [11]. Therefore, the hydrolysate liquor is enriched with hemicellulose fragments, acetic acid, and furfural [12], [13]. In biorefineries, introducing a xylan-rich substrate from the pulp and paper industry, the hydrolysate, as a feedstock material, can generate value-added chemicals, including furfural and acetic acid [7], [12], [14]–[16].

Several investigations have been carried out to produce furfural from biomass [3], [13], [17], [18]. Mineral acids such as sulfuric and hydrochloric acid have been utilized to generate furfural [19], [20]. They experimented with high temperatures (about 140–275 °C) and strong acidity concentrations (1–5.2 M). These conditions managed to elevate the furfural product and, at the same time, increase the dark-black suspension, which is denoted as humin [21]–[23]. Acid-based catalysts have been used to break down the macromolecule into small molecules, which caused severe product quality. However, low acid concentrations, especially by applying diluted acid solution through modest hydrolysis temperature, have not yet been fully investigated. It is interesting to look for more understanding regarding low acidity and temperature for producing furfural than the previous studies, which applied high temperature and acidity using hydrolysate from dissolving pulp production.

During these decades, Lewis acid has been reported that aluminum chloride ($AlCl_3$) works efficiently in water-based solvents which meet the condition of hydrolysate wood [24]–[26], [27]. This was also enhanced by other reports which mentioned that trivalent chloride from $AlCl_3$ managed to produce furfural from xylose well [25]. Triggered by the environmental aspects, the aim of our study focused on diluted acid solutions that might be interesting to explore based on their temperature and time of reaction to generate furfural from wood hydrolysate from dissolving pulp product. Therefore, lower acid concentration was applied in this study, together with $AlCl_3$, and also employed to compare the furfural production from hydrolysate.

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EXPERIMENTAL METHOD

Materials and Instruments

Wood chip from Acacia crassicarpa was used in the experiment to extract the hydrolysate as the feedstock. Sulfuric acid, hydrochloric acid, and aluminum chloride (AlCl3.6H2O) were applied as catalysts for furfural production. AlCl3.6H2O was purchased from Smart Lab and heated first before being used in the experiment. Levulinic acid in analytical grade was purchased from Sigma Aldrich and used without treatment.

Method and Procedure

Prehydrolysis stage

50 g oven-dried wood chips were subjected to a stainless steel reactor with 250 mL of distilled water and heated at 150 °C for 3 hours. Subsequently, it cooled, and the liquid, which was later named hydrolysate, was separated from wet wood after prehydrolysis. Next, approximately 180 mL of the liquor was extracted from the wood-liquor mixture, and the wet chips were subjected to a pulping process. Meanwhile, the hydrolysate was filtered and then placed in a 250 mL flask of glassware for hydrolysis to generate a furfural compound.

Furfural Production

Hydrolysate from the prehydrolysis stage was added with a catalyst charged to the flask and then heated to 80–150°C for 90 minutes. The procedure for furfural generation is shown in Figure 1. The concentration for diluted acid solution (HCl and H_2SO_4) was 0.5 M and $AlCl_3$ (range 1–5%). During the heating process, cool water (temperature range 5–10 °C) was loaded into the condenser to reduce the furfural vaporization. The product from the liquid and distillate were analyzed for furfural determination.

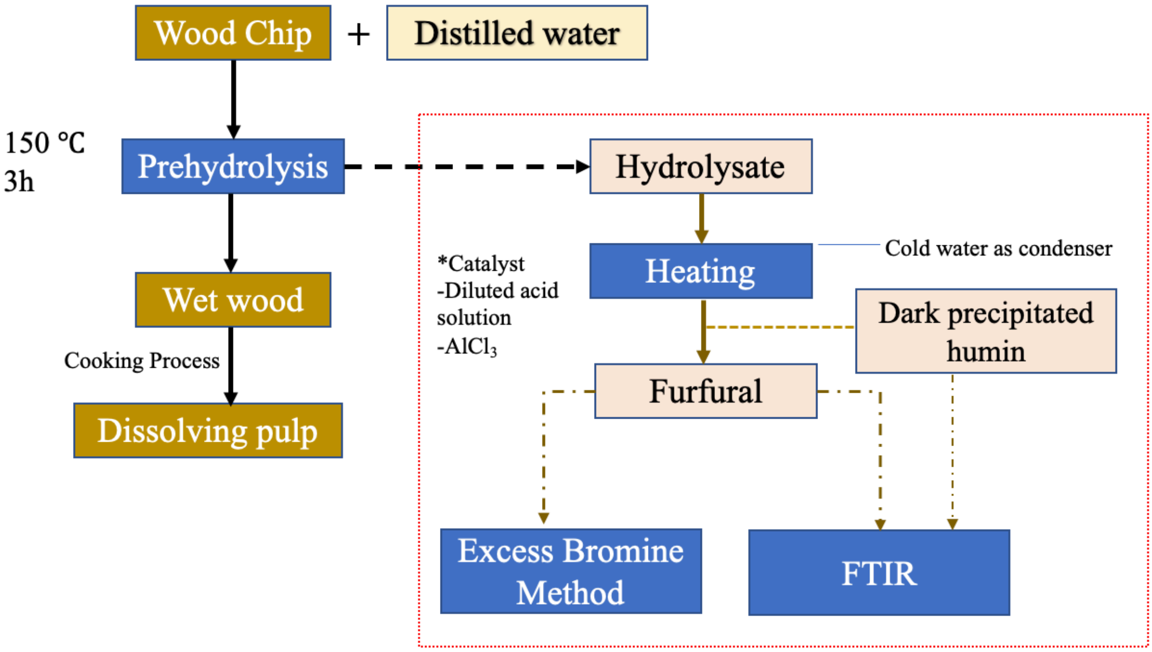

Figure 1. The scheme of furfural product

Analytical methods

The solid and liquid samples were analyzed by using Fourier-transform infrared spectroscopy (FTIR). The structure of furfural and levulinic acid was determined by using FTIR from PerkinElmer Frontier C90704 Spektrum IR version 10.6.1. Furfural was determined using Excess-Bromin methods, titrated with 0.1 N Sodium thiosulfate [28]. Another byproduct, levulinic acid, was determined by high-performance liquid chromatography (HPLC) with an Aminex HPX 87H column with a UV detector. The condition for the mobile phase was 5 mM sulfuric acid with a flow rate of 0.6 mL/min and a column temperature of 60°C.

RESULT AND DISCUSSION

The IR structure of hydrolysate was analyzed by Fourier-transform infrared spectroscopy (FTIR), as shown in Figure 2. Hydrolysate, without heating and after being treated with diluted acid, clearly showed different bands. The broad absorption peak can be seen at a range of 3400–3200 cm-1 for alcohol and phenolic groups in both hydrolysates. The strong C=C stretching around the 1616.42 for both figures indicates α-β unsaturated ketone. The stretching broad bond at 3400 was detected for O-H, and the small peak at 1259–1047 cm-1 is depicted as CO stretching, representing the carboxylic acid. Alcohol, O-H out of plane bend is observed in 690–750 cm-1 [29]. Figure 2 shows several levulinic acid structures for carboxylic acid when hydrolysate without heating and disappear after being treated with acid [17].

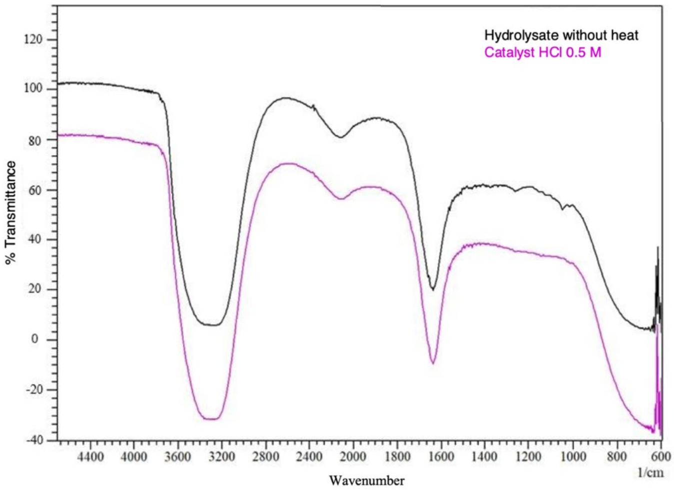

Figure 2. FTIR analysis of hydrolysate without heating and after treating with HCl 0.5 M

The influence of temperature in furfural production from wood hydrolysate without diluted acid solution and aluminum chloride ($AlCl_3$) is described in Figure 3. The non-catalyst experiment was conducted with ranging temperature from 80–150°C. The product of furfural (FUR) is slightly increased until the temperature is 120°C, then decreased when the temperature reaches 150°C. It was also found that at 150°C, a dark precipitate was formed, as seen in Figure 4. Figure 3 shows the highest yield was generated at 120°C for 90 minutes, around 33 mg. Therefore, a modest temperature around 80 to 120°C was applied to obtain reasonable furfural. The long reaction and high temperature caused this dark stick to precipitate, as shown in Figure 4, which is called a humin-like substance. It might formed by the side reactions and secondary conversion of pentose/hexoses compound as a result of depolymerization process [19], [23]. Since the reaction was conducted in the aqueous phase, it might trigger high selectivity of humins as it formed in the severe condition of the experiment. A similar condition was also reported by Yavorov et al.[19].

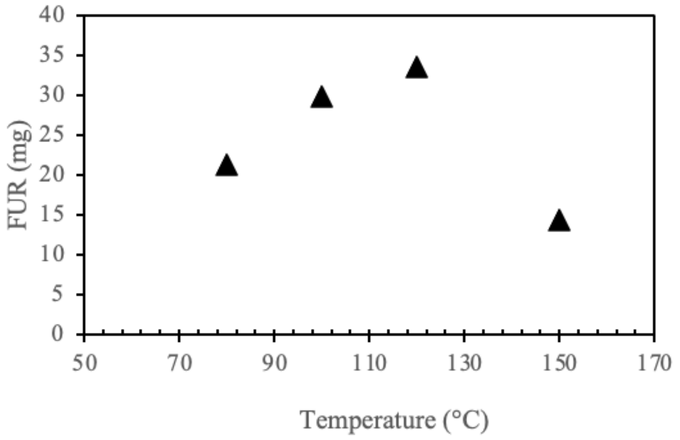

Figure 3. Furfural production at varied temperatures for 90 minutes without a catalyst

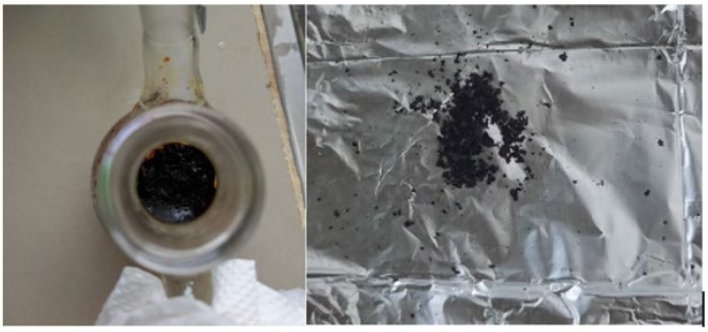

Figure 4. Dark precipitated (humin)

In relation to the temperature and time of reaction, diluted sulfuric acid was applied to increase the furfural products in a modest concentration. The results are depicted in Figure 5, where furfural production increases as the temperature rises. At low temperatures, the product slightly rises, around 7% by increment, then at 120°C reaches more than 85% than at 60°C. It can also be seen that the acid catalyst can boost the furfural product more than without the catalyst. However, aluminum chloride managed to improve furfural product at 100°C better than others. It mentioned that the high temperature (above 180°C) succeeded in giving high conversion to the xylose source, but the furfural product was low since another byproduct such as formaldehyde, levulinic acid, intermediate compound, and humin might formed [30]. On the other hand, AlCl3 utilization in the reaction was said that the metal cation from aluminum also accelerated the carbohydrate breakdown to their ionization potential in generating furfural [25]. This is depicted in Figure 6, where the highest furfural by AlCl3 was obtained at a lower temperature (100°C) than by diluted hydrochloric acid. Another study also mentioned that AlCl3 in the acid solution has a higher furfural selectivity at 100°C in the xylose solution compared to other metal chloride [31].

Figure 6 shows various concentrations of diluted hydrochloric acid for furfural generation. The furfural production was enhanced as the temperature increased, together with the upsurge in hydrochloric acid concentration. However, there is a decrease in the production of furfural at concentrations of more than 1%. The high concentration referred to more acidic conditions that affected the reaction. This is also reported by Delbecq et al. [4], who found that the highly acidic environment inhibited furfural production by at least half. On the other hand, the use of aluminum chloride can increase the furfural production of the diluted acid solution for each concentration. In Figure 6, it is seen that furfural by $AlCl_3$ dehydration is higher than diluted hydrochloric acid. The highest furfural was obtained at $AlCl_3$ dosages 1% at 100°C for 90 minutes.

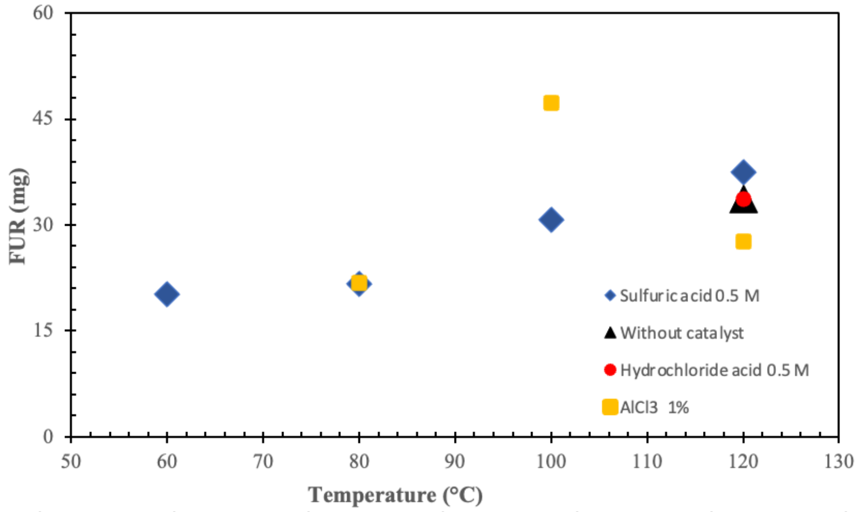

Figure 5. Diluted acid solution for generating furfural for 90 minutes

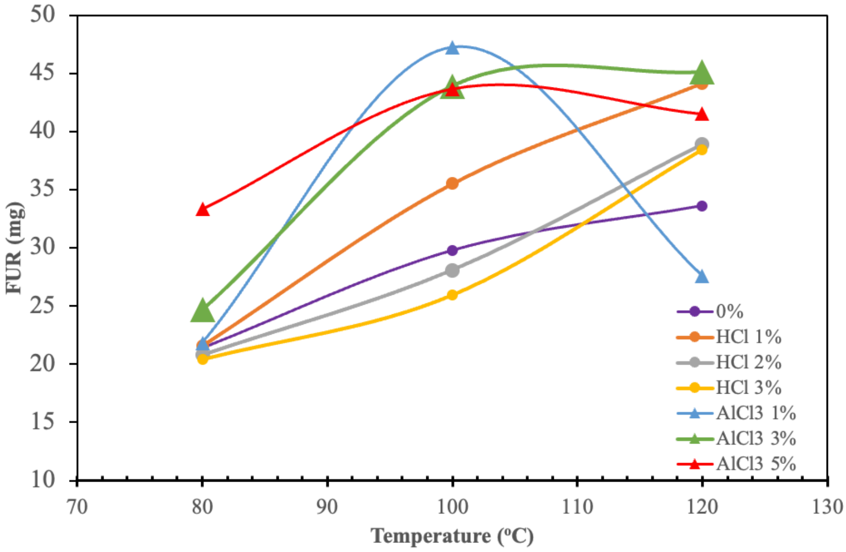

Figure 6. Varied concentrations of catalyst for hydrochloricacid and aluminum chloride for 90 minutes

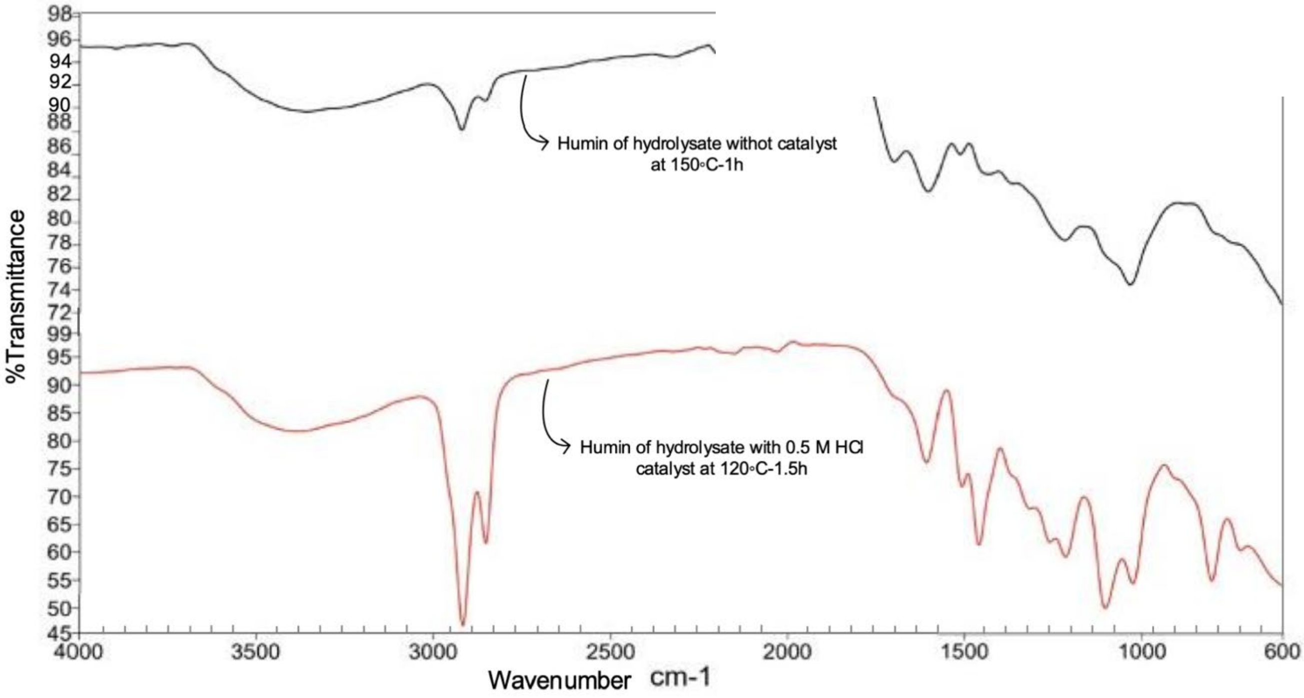

Figure 7. FTIR result for humin at temperature 120°C with 0.5 M HCl and 150°C without catalyst for 90 minutes

The humin traces from hydrolysate dehydration were analyzed and presented in Figure 7. It is described as an OH bond in the 3650–3250 cm^{-1}, and the sharp peak in 2935–2860 cm^{-1} indicated the aliphatic linear chain. A peak at 1700 cm^{-1} is observed as C=O stretch from acids, aldehydes, and ketones, and C-O at 1020 cm^{-1} stretches for furan ring deformation. It also shows C-H out-of-plane deformation at around 800 and 765 cm^{-1}, which can be referred to as substituted furans, and there is oscillation bound at 795 cm^{-1} for furan to both spectra. Interestingly, humin from hydrolysate with $AlCl_3$ has a weak peak in 750 cm^{-1} and 1460 cm^{-1} than humin generated from the acid solution. This peak is similar to the previous report, which investigated humin derived from fructose and glucose [32]–[34].

Hexoses and pentoses dehydration generated other derivatives such as 5-hydroxymethylfurfural, levulinic acid, formic acid, etc [35]. This study also investigated the possibility of byproduct formation; the concentration of levulinic acid can be depicted in Table 1. The absence of a catalyst triggered the high formation of byproducts, as seen in Table 1. However, diluted hydrochloric acid is indicated to suppress levulinic acid better than aluminum chloride.

Table 1. Hydrolysate dehydration heat for 90 minutes at 120°C

Catalyst	Furfural (mg)	Levulinic acid (ppm)
Without catalyst	33.6	3215.5
HCl 1%	44.2	1680.7
$AlCl_3$ 3%	45.1	3057.7

CONCLUSION

Furfural from wood hydrolysate has been produced in thermal and acid hydrolysis. A diluted acid catalyst under 4% was applied for the furfural production. Temperature and time become valuable parameters in generating furfural. During the non-catalyst process, the highest yield of furfural was obtained at 37 mg at 120°C for 90 minutes. Diluted sulfuric acid increases furfural up to 11% by increment compared to non-catalyst and diluted hydrochloride acid. High acid conditions have been proven to hinder furfural production. The aluminum chloride catalyst produced higher furfural than diluted hydrochloric acid. Humin is derived from hydrolysate with diluted acid at high temperatures and a long reaction time. Applying diluted acid solution and aluminum chloride at modest conditions has the potential to furfural production effectively.

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