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Production of Bio-Based Chemicals, Acetic Acid and Furfural, through Low-Acid Hydrothermal Fractionation of Pine Wood (*Pinus densiflora*) and Combustion Characteristics of the Residual Solid Fuel

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Abstract: Low-acid hydrothermal (LAH) fractionation conditions were optimized for the effective degradation of hemicellulose from pine wood (*Pinus densiflora*). The hemicellulosic sugar yield was maximized at 82.5% when the pine wood was fractionated at 190 °C, with 0.5 wt.% of sulfuric acid, and for 10 min. Consecutively, acidified heat treatment with zinc chloride and solvent extraction with ethyl acetate were carried out for the recovery of bio-based platform chemicals, such as furfural and acetic acid, from liquid hydrolysate through liquid–liquid extraction (LLE). Overall, 61.5% of xylose was decomposed into furfural, and the yield of acetic acid was 62.3% and furfural 66.1%. After LAH fractionation, 64.8% of the solid remained and was pelletized. The pellets showed excellent fuel characteristics, i.e., significant ash rejection (74.5%) and high calorific values (4770 kcal/kg), and the precursors of NO_x and SO_x also decreased by up to 60.0% and 71.4%, respectively.

Keywords: pretreatment; biofuel; bio-based chemicals; extraction; combustion



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1. Introduction

Lignocellulosic biomass is an abundant and renewable resource, replacing petrochemical resources by converting major constituents of biomass into high-value-added bio-based chemicals. This is critical for improving the energy structure, reducing environmental pollution, and progressively achieving carbon neutrality by 2050, which is the world's most urgent mission [1]. Until now, biomass has simply been used as a fuel for combustion or as a raw material for extracting biofuels (e.g., bioethanol). As biomass fractionation technology is developing, attention is being paid to the use of biomass components through fractionation [2–4]. To increase the economic feasibility of biomass use, first, relatively valuable components from biomass are fractionated through biomass fractionation, and then the residual solid is used as solid fuel, which is considered a reasonable method for replacing existing power generation from coal [5–7].

Biomass comprises three major components: cellulose, hemicellulose, and lignin. These components can be used as precursors and intermediates of biofuels and value-added chemicals that can partially replace petrochemicals. Therefore, numerous effective fractionation processes have been developed to use biomass more effectively and comprehensively [8–10]. If these three major components can be efficiently fractionated from biomass, the overall efficiency of the biorefining industry can be improved, in addition to improving economic feasibility to the point where it can replace the petrochemical industry. Although various processing methods can overcome the inherent limitations of materials, such as the recalcitrance of lignocellulosic biomass, it is essential to corroborate appropriate fractionation and specific component valorization [11–14].

Along with the development of bioethanol fueling technology, many studies have been conducted on the use of cellulose fractions by chemical catalytic processes or other physicochemical and thermochemical strategies [15–18]. However, due to its complex structure, relatively little research has been performed on the conversion of hemicellulose into fuels and chemicals. Within the lignocellulosic matrix, hemicellulose also exists as a branched sugar copolymer, predominantly xylose saccharide, surrounding the cellulose fibrils [19]. Hemicellulose can be used as a feedstock to produce many important chemicals, such as furfural of the furan family. Therefore, as a mid- to long-term goal, more research should be performed to explore promising pathways to convert hemicellulose into chemicals that can replace petrochemicals.

Hemicellulose is most easily fractionated from biomass and contains valuable active ingredients, which can be converted into a series of high-value products. Biomass fractionation, mainly by hot water, weak acid, and alkali, is an important step in extracting hemicellulosic components from biomass [20–22]. During hydrolysis pretreatment, acetic acid (AA) is produced by the cleavage of acetyl groups in hemicellulose. Subsequently, hemicellulosic sugars (a mixture of xylose, mannose, and galactose in hydrolysate, expressed as xmg, i.e., xylose + mannose + galactose) hydrolyzed under acidic conditions, mainly comprising xylose, are partially decomposed into furfural [23,24].

Acetic acid, an important chemical reagent, is produced by the wet oxidation of natural gas and is mainly used in pharmaceutical synthesis and the leather tanning and dyeing industries [25]. As global environmental awareness is increasing and the regulation of petroleum resources is becoming more stringent, changes are being made to biomass-derived acetic acid production. Processes based on renewable resources include the hydrothermal treatment of biomass and integrated production in pyrolysis oil plants [26,27]. Since the acid-catalyzed hydrothermal process is a promising process for producing bio-based chemicals from biomass, extensive research has been performed on converting biomass waste into chemicals through hydrothermal fractionation.

Furfural is one of the platform chemicals of interest that can be derived from renewable biomass and can therefore be converted into a variety of chemicals to replace petrochemicals [28,29]. Furfural serves as a precursor for jet- and diesel-fuel-range hydrocarbon production in the transportation sector and is therefore also used in the development of conversion technologies for the production of next-generation biofuels. In addition, in traditional chemical processes in various industries, furfural and its derivatives are strategically important chemicals that can be used as raw materials with high added value, such as adhesives, resins, and solvents. These include furfuryl alcohol, furan, and hydroxy methyl furfural [30–32].

Currently, furfural is produced by extracting xmg through acid-catalyzed hydrolysis and dehydration of the extracted pentose (mainly xylose) [33]. Mineral acids, such as sulfuric acid, are mainly used as catalysts in furfural production. However, this process has disadvantages, such as high neutralization process cost and high energy consumption [34]. The use of metal chlorides in furfural production can alleviate the disadvantages of using mineral acid catalysts, i.e., problems related to equipment corrosion due to a high acidic stream can be avoided and the xylose conversion reaction rate significantly improved. In addition, there are several reports on the production of furfural from biomass using solid acid catalysts [35,36].

Previously, we conducted various hydrothermal fractionation studies, such as extremely low-acid (ELA) [37], low-acid hydrothermal (LAH) [38,39], and acetic-acid-assisted hydrothermal (AAH) fractionation [40,41], for xmg recovery with low by-product formation from lignocellulosic biomass. In this study, a series of experiments was performed to maximize the recovery yield of xmg from pine wood biomass and to produce furfural for valorization of the fractionated hemicellulose-derived pentose sugar. In addition, an attempt was made to recover AA, which is unavoidably by-produced in the hydrothermal fractionation process, through liquid–liquid extraction (LLE). Finally, the biofuel combustion characteristics of the residual solids were investigated, and a material balance

analysis of pine wood fractionation was also conducted to suggest improvements for the comprehensive use of pine wood.

2. Materials and Methods

2.1. Feedstock Preparation

Pine wood (*Pinus densiflora*) chips were provided by the Forest Biomaterials Research Center, National Institute of Forest Science (Seoul, Korea). The chips were ground and screened using a laboratory blend mill (Blender 7012s; Waring Commercial, East bunker, IL, USA) and a US Standard sieve to obtain samples of uniform particle size (1.40–2.36 mm) for use in experiments. The particles were then air-dried for 24 h at 45 ± 5 °C. The average moisture content of the air-dried sawdust was 5.18% based on total weight.

2.2. Compositional Analysis of Raw and Fractionated Pine Wood

Raw pine wood, fractionated residual solids, and fractionated hydrolysate were quantitatively analyzed for their chemical composition following the NREL Laboratory Analytical Procedures: NREL/TP-510-42618 (structural carbohydrates and lignin) and 42,623 (sugars in liquid fraction) [42,43]. A series of procedures was followed to prepare samples, and the concentrations of carbohydrates and organic acids were measured using an HPLC system (LC-10A; Shimadzu Inc., Kyoto, Japan) equipped with an RI detector (RID-10A; Shimadzu Inc., Kyoto, Japan). The column used was an Aminex HPX-87H (300 mm by 7.8 mm; Bio-Rad Lab. Inc., Hercules, CA, USA), and HPLC analysis conditions were a column temperature of 60 °C and a mobile phase of 0.6 mL of 0.005 M H₂SO₄/min. Hemicellulose was expressed as the sum of three oligomeric sugars, xylan, mannan, and galactan, while fractionated hemicellulosic sugars were represented as the sum of the hydrolyzed sugars xylose, mannose, and galactose (xmg).

2.3. Low-Acid-Catalyzed Hydrothermal Fractionation

The bomb tubular reactor for the low-acid hydrothermal (LAH) fractionation was constructed with SS-316 stainless steel tubes (1.0 cm internal diameter (ID) by 20.0 cm length (L); 15.7 cm³ internal volume) and caps (Swagelok Cat. #SS-810-C). The reactor was designed to withstand the high-pressure atmosphere (>25 kg_f/cm³) formed during hydrothermal fractionation. A thermocouple probe (Omega.com[®], Cat. #HJMTSS-125-6) was installed inside the reactor to monitor the temperature changes among the reactants. The bomb tubular reactor was loaded with 0.50 g of oven-dried pine wood powder. The dry powder was added to the prepared fractionation media after taking into account the sulfuric acid concentration so that the solid-to-liquid ratio was 1:8. The reactor filled with biomass and fractionation media was immersed in the first bath set at 240 °C for quick preheating, where molten salt was used as a heating medium, so that the temperature inside the reactor could be rapidly increased. Then, the reactor was quickly transferred to a second bath set at a reaction temperature within the experimental range (140–190 °C), which used silicone oil as the heating medium. This approach allowed the reactants to reach the target temperature in about 1.5 min. In the reaction time setting, the reaction was believed to have started when the reactor was transferred to the second bath. After the reaction time according to the experimental design elapsed, the reactor was quickly transferred to a cooling water bath to stop the reaction.

2.4. Procedures for Converting Xylose into Furfural

Furfural production experiments were performed with xylose-rich hydrolysates obtained from LAH fractionation under optimized conditions. In our previous study, 0.73 M of ZnCl₂ was confirmed as an appropriate metal chloride concentration for furfural production from biomass hydrolysates [44,45]. ZnCl₂ solution was added to achieve a final concentration of 0.73 M of 10 mL hydrolysate. The reaction system was transferred to a molten salt bath at different temperatures for 30 min. After a pre-designed reaction time, the reaction was immediately terminated by quenching the reactor in an ice-water bath.

Samples were then diluted with ultrapure water, filtered with a 0.2 µm syringe filter, and then analyzed using HPLC. All experiments were performed in triplicate. Conversion of xylose and furfural yields of products were defined as follows:

$$\text{Xylose conversion (\%)} = (\text{moles of xylose reacted}) / (\text{moles of starting xylose}) \times 100$$

$$\text{Furfural yield (\%)} = (\text{moles of furfural produced}) / (\text{moles of starting xylose}) \times 100$$

2.5. Liquid–Liquid Extraction (LLE) Experiments for Acetic Acid Recovery

The organic and aqueous phases were mixed in proportion and then charged in a 15 mL conical tube according to the usual extraction method. LLE was carried out in a shaking water bath to maintain a constant temperature; the tubes were shaken vigorously for several seconds at intervals of 5 min. After 30 min, the samples were centrifuged at 4000 rpm for 4 min to promote phase separation and then a sample from the aqueous phase was recovered and analyzed [46,47]. To analyze the equilibrium distribution of acetic acid between the two phases, P_c was calculated as follows:

$$P_c = [\text{HAc}]_{\text{org}} / [\text{HAc}]_{\text{aq}}$$

where [HAc] is the acetic acid concentration and org and aq indicate the organic phase and the aqueous phase, respectively. Percentage extraction was used as a means to compare the extraction efficiencies, and percentage extraction was defined as the concentration of acetic acid removed from the aqueous phase into the organic phase, as follows:

$$\% \text{Extraction} = 1 - ([\text{HAc}]_{\text{remaining aq}}) / ([\text{HAc}]_{\text{initial aq}}) \times 100$$

2.6. Evaluation of the Combustion Reactivity of the Residual Solid Biofuel

To evaluate combustion reactivity, a thermogravimetric analyzer (TGA, Q500 TA model) was used. The TGA analysis temperature was 20–800 °C, and the heating rate was 10 °C/min. The combustion characteristics were evaluated in air. The combustibility of biomass fuel was evaluated using the combustion characteristic factor (S), defined as follows [48]:

$$S = (dw/dt)_{\text{max}} (dw/dt)_{\text{mean}} / T_i^2 T_f$$

where $(dw/dt)_{\text{max}}$ is the mass loss rate at the highest point, $(dw/dt)_{\text{mean}}$ is the average mass loss rate, and T_i and T_f are highest temperature peak at ignition and the burnout temperature, respectively.

3. Results

3.1. Chemical Compositions of Pine Wood Based on Oven-Dry Biomass

The chemical compositions of pine wood are presented in ODB weight percentages in Table 1. Based on the solid analysis of more than 10 replicates, the average percentages with standard deviations of cellulose (glucan), hemicellulose, extractives (soluble in water and alcohol), acid-soluble lignin (ASL), acid-insoluble lignin (AIL), the acetyl group, and ash are given. The composition of the carbohydrate group in pine wood was $41.1 \pm 0.3\%$ glucan, $12.5 \pm 0.2\%$ xylan, $3.1 \pm 0.2\%$ mannan, $1.1 \pm 0.1\%$ galactan, and $0.5 \pm 0.1\%$ arabinan. The lignin content of pine wood was $23.5 \pm 0.4\%$ acid-insoluble lignin (AIL) and $8.6 \pm 0.5\%$ acid-soluble lignin (ASL). The content of extractives was $5.8 \pm 0.1\%$ water and $1.3 \pm 0.1\%$ ethanol, in addition to $6.0 \pm 0.1\%$ of the acetyl group and $0.9 \pm 0.1\%$ of ash. A mass closure of 104.4% was finally reached with little experimental error.

Table 1. Initial composition of pine wood.

| Components (%) | | Dry Solids (<i>w/w</i> , %) |
|----------------|----------------|------------------------------|
| Carbohydrate | Glucan | 41.1 ± 0.28 |
| | Xylan | 12.5 ± 0.16 |
| | Mannan | 3.1 ± 0.15 |
| | Galactan | 1.1 ± 0.11 |
| | Arabinan | 0.5 ± 0.09 |
| Lignin | Acid Soluble | 8.6 ± 0.49 |
| | Acid insoluble | 23.5 ± 0.38 |
| Extractives | Water | 5.8 ± 0.13 |
| | Ethanol | 1.3 ± 0.09 |
| | Acetyl gr. | 6.0 ± 0.11 |
| | Ash | 0.9 ± 0.11 |
| Total | | 104.4 |

Note: The data in the table show the mean value ($n = 10$, SD: standard deviation). All numbers in the table are based on the oven-dry biomass.

3.2. Low-Acid-Catalyzed Hydrothermal Fractionation of Pine Wood

Acid-catalyzed hydrothermal fractionation was performed by changing one of three operating parameters: reaction temperature, reaction time, and acid concentration. Figure 1 summarizes the behaviors of products decomposed by thermochemical fractionation and the recovery of xylose and glucose from pine wood according to the change in the sulfuric acid concentration under fixed conditions (reaction temperature 180 °C and reaction time 30 min). The XMG yield increased with increasing fractionation severity at a low sulfuric acid concentration but significantly decreased at a higher sulfuric acid concentration. The maximum XMG (mainly xylan) yield was 61.37% when pine wood was fractionated at 180 °C with 0.25 wt.% sulfuric acid for 30 min. As the fractionation severity, i.e., the acid concentration, increased, the XMG yield significantly decreased because hemicellulose degrades into XMG, which is further excessively decomposed into furfural and formic acid under more severe fractionation conditions. The xylose yield was 51.19% at 0.5 wt.% sulfuric acid and sharply decreased to 9.99% at 0.75 wt.% sulfuric acid, indicating that the acid-catalyzed hydrothermal fractionation performance is sensitive to the acid concentration. In addition, a little glucose was released as a liquid hydrolysate due to the breakdown of cellulose during pine wood fractionation. When the sulfuric acid concentration was 0.5 wt.% or more, the concentrations of 5-HMF and levulinic acid, known as representative glucose decomposition, considerably increased.

Since the main goal of this fractionation process is the clean separation of XMG, the accompanying glucose release and over-decomposition of glucose are the main contributors to the loss of sugars from the solid residue as well as the lowering of the fractionated hydrolysate selectivity. Therefore, to achieve the goal of this study, we investigated low-acid-catalyzed fractionation, which is performed at a low sulfuric acid concentration of 0.5% or less. In addition, because the XMG yield was no longer high despite the increase in the sulfuric acid concentration and a decomposition reaction occurred, we believe that a reaction temperature higher than 180 °C should be applied to this fractionation.

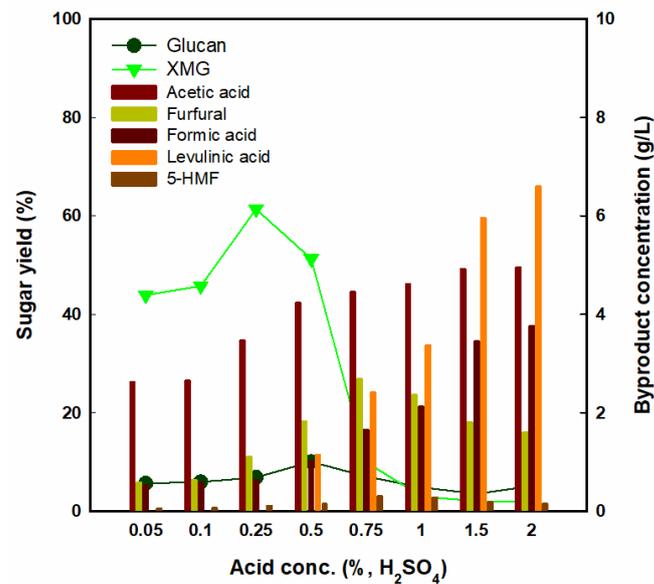


Figure 1. Hemicellulose (XMG) with glucan yield in the liquid hydrolysate and by-products production behaviors as function of acid concentration at the fractionation condition of 180 °C and 30 min.

Figure 2 shows changes in the glucan and XMG yields with reaction time when pine wood was fractionated at 0.1 (Figure 2a), 0.25 (Figure 2b), and 0.5 wt.% (Figure 2c) sulfuric acid at a solid-to-liquid ratio of 1:8 and a reaction temperature of 190 °C. In addition, the concentrations of acetic acid and furfural, which are products of xylose decomposition, were compared.

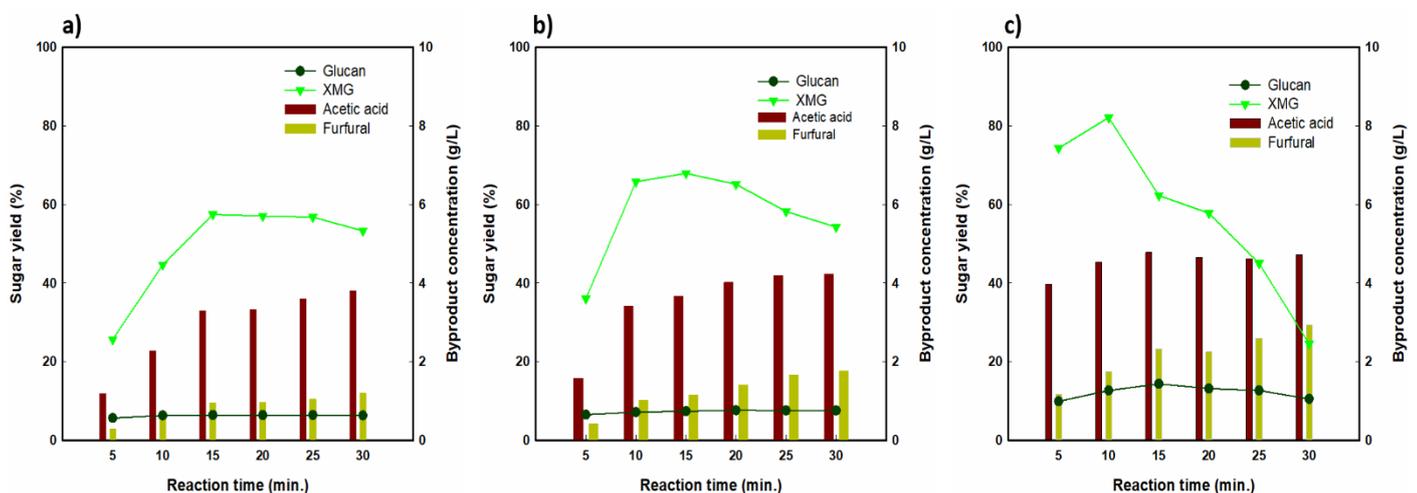


Figure 2. Changes in glucan and XMG yield and the concentrations of acetic acid and furfural with increasing the reaction time at 190 °C with 1:8 of solid/liquid ratio, (a) 0.1 wt.% of H₂SO₄, (b) 0.25 wt.% of H₂SO₄, and (c) 0.5 wt.% of H₂SO₄.

As shown in Figure 2a, when fractionation was carried out using 0.1 wt.% sulfuric acid, the XMG yield increased with the reaction time, reaching 57.5% at 15 min, but tended to decrease slightly at a reaction time longer than 15 min, indicating the over-decomposition of xylose. Glucose release was about 5%, with no significant difference as the reaction progressed, but the concentrations of the by-products furfural and acetic acid increased proportionally as the reaction progressed. In the case of furfural, a concentration of 1 g/L or more was confirmed after 25 min of reaction time. Figure 2b shows the change in the fractionation yield of XMG with time when fractionation was performed with 0.25 wt.% sulfuric acid with other conditions fixed, as described above. The XMG yield was relatively

high 65.8% after 10 min, a shorter reaction time than when fractionation was performed with 0.1 wt.% sulfuric acid, and the highest XMG yield of 67.9% was obtained at 15 min. As the reaction continued, the XMG yield decreased somewhat faster than in the case of 0.1 wt.% sulfuric acid. Glucose release was slightly higher than in the case of 0.1 wt.% sulfuric acid (6.5~7.6%), and with increasing temperature, more acetyl groups in hemicellulose were released into the fractionated hydrolysate. The acetic acid concentration increased after 10 min and exceeded 4 g/L or more after 20 min of fractionation. Furfural, a decomposed product, gradually increased with fractionation time, exceeding 1.0 g/L at 10 min and 1.77 g/L after 30 min of fractionation. When 0.5 wt.% sulfuric acid was used (Figure 2c), the fractionation was significantly different from when 0.1 and 0.25 wt.% sulfuric acid were used. After 5 min of fractionation, a high XMG yield of 74.3% was obtained, reaching the maximum of 82.1% in 10 min, after which there was a severe decrease as the reaction continued. Finally, after 30 min of fractionation, 24.6% of XMG was obtained, corresponding to about 30% of the maximum yield. Due to this XMG over-decomposition reaction, the furfural concentration in the hydrolysate steadily increased, showing a high concentration of 2.93 g/L after 30 min fractionation, indicating that a substantial amount of xylose was lost.

3.3. Mass Balance of Glucose and Xmg through LAH Fractionation

Changes in the composition of the solid residues and liquid hydrolysate after LAH fractionation of pine wood under optimal conditions obtained in the previous experiments: 190 °C, 0.5% (w/v) H₂SO₄, and 10 min., presented in Table 2. After the fractionation process, the remaining fractionated solids were 64.8% from raw pine wood. The glucan content in fractionated pine wood increased from 41.1% to 54.4%, which corresponded to 35.3% on the basis of the raw pine wood. That is, 14.1% of glucan was hydrolyzed during the LAH fractionation process, but only glucose corresponding to 3.5% of glucan was present in the fractionated hydrolysate, indicating that about 5.6% of glucan was over-decomposed into 5-HMF, levulinic acid, or an unknown substance. Meanwhile, the XMG contents in the solid residues decreased from 17.2% to 6.3%, which corresponded to 4.1% on the basis of the raw pine wood. That is, 73.8% of XMG was hydrolyzed to xmg, and 14.4% of xmg, which corresponds to 12.7% of XMG, was present in the fractionated hydrolysate, indicating that about 2.4% of xmg decomposed into products, such as furfural and formic acid. Glucan and XMG were retained in the fractionated pine wood at levels of 85.9% and 23.8%, respectively. Consequently, a xylose-rich hydrolysate was obtained. Consequently, a xylose-rich hydrolysate was obtained, and also residual solid rich in glucan and lignin (data are not shown), which can be used as an excellent biomass fuel, was obtained through LAH fractionation.

Table 2. Remaining solid and changes in sugar contents in the fractionated solid residue and liquid hydrolysate and mass closure for batch fractionation of pine wood under optimized conditions.

| Biomass | Fratctionation | Solid Remaining (%) | Solid (%) | | | Liquid (%) | | EMB ^b (%) | |
|------------------------|---------------------------|---------------------|-----------|------|------|------------|------|----------------------|--------|
| | | | Glucan | XMG | AIL | Glucose | xmg | Glucan | XMG |
| Pine wood ^a | Untreated | 100 | 41.1 | 17.2 | 35.4 | - | - | 94.4 | 97.6 |
| | Fractionated | 64.8 | 54.4 | 6.3 | 33.7 | 3.5 | 12.7 | (-5.6) | (-2.4) |
| | Fractionated ^c | | 35.3 | 4.1 | 21.8 | | | | |
| | Component Retention (%) | | | 85.9 | 23.8 | 61.5 | | | |

^a Pine wood was fractionated at the conditions; 190 °C of temperature 0.5% (w/v) of H₂SO₄, and 10 min. of reaction time. ^b Extraction mass balance (EMB) = $\frac{\sum C_{Li} + \sum C_{Si}}{\sum C_{Ri}}$; where C_i is the mass of each sugar component as C_{Li} determined through HPLC chromatography, the subscripts L, S, and R refer to the extracted liquid, fractionated solids, and raw straw fractions, respectively. ^c Analysis data is based on the oven dry untreated biomass.

3.4. Furfural Production with the Fractionated Hydrolysate at Optimized Conditions

The hydrolysate obtained from LAH fractionation under optimized conditions (maximizing xmg recovery) was also submitted to heat treatment with ZnCl_2 catalyst for furfural production. Based on the results of our previous experiments [49], we used 0.73 M of ZnCl_2 as a catalyst for the conversion of furfural by the dehydration of xmg. The experiments were performed in triplicate, and the average results are presented.

Figure 3a shows the decrease in xylose and furfural formation in the hydrolysate at various reaction temperatures (160, 170, and 180 °C). The formation of furfural increased for a certain period (30 min in this experiment) and then decreased, indicating that the harsher the reaction severity, the more the furfural decomposed. This is consistent with the findings of Köchermann et al., which they described as furfural resinification and furfural condensation as the decomposition of furfural under similar temperature conditions (160–200 °C) [50].

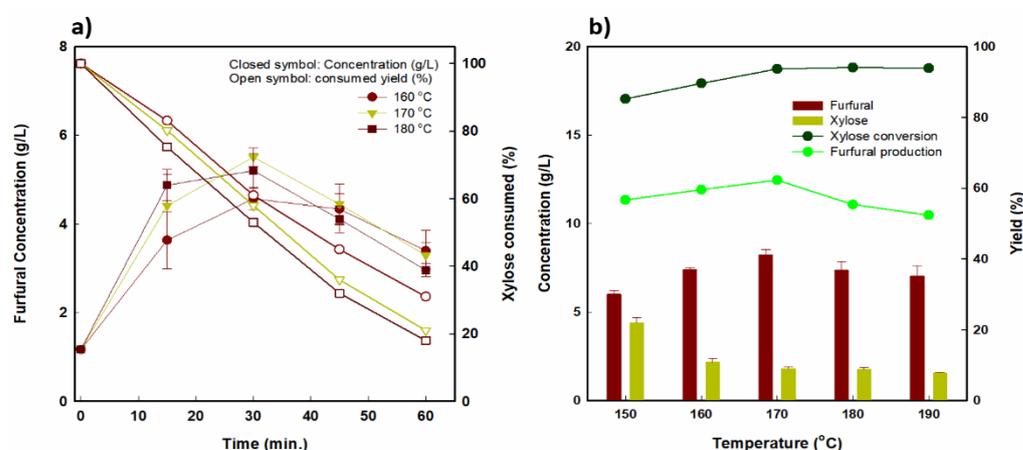


Figure 3. Furfural production and xmg consuming in the fractionated hydrolyzate with 0.73 M of ZnCl_2 , (a) with reaction time, (b) with reaction temperature.

Figure 3b shows the furfural yield, the xylose conversion yield, and the unreacted xylose at various reaction temperatures at a reaction time of 30 min with 0.73 M of ZnCl_2 . Furfural concentrations between 5.81 and 7.93 g/L were obtained, while the conversion of xylose into furfural was greater than 85% and the furfural yield did not exceed 62.3%. Hence, although most of the xylose is converted, part of the furfural formed is converted into other substances, which are not detectable, by side reactions such as condensation, cleavage, isomerization, resinization, and polymerization [37]. Consequently, it was possible to obtain 7.93 g/L of furfural, with the highest furfural yield of 62.3%, using ZnCl_2 catalyst at a concentration of 0.73 M at 170 °C. Under these conditions, 93.7% of the initial xylose was converted, leaving 1.82 g/L of unreacted xylose in the hydrolysate. In addition, 1.17 g/L of furfural present in the initial hydrolysate, which was produced in pine wood fractionation, was deducted from the yield or production calculation.

3.5. Acetic Acid Recovery from Fractionated Hydrolysate by Liquid–Liquid Extraction

Table 3 summarizes the extraction yields of acetic acid from hydrolysate as a function of the H/S ratio; that is, the ratio of fractionated hydrolysate to ethyl acetate. A low AA extraction yield (14.54% at 25 °C and 21.59% at 50 °C) was obtained at an H/S ratio of 1:1. At an H/S ratio of 1:2, the extraction yield of acetic acid increased to 55.73% (at 25 °C) and 58.59% (at 50 °C). When the H/S ratio was relatively large, the reaction temperature had some effect, but when the H/S ratio was small, the effect of the reaction temperature was not significant. The highest extraction yield of AA was obtained at an H/S ratio of 1:4. As the H/S ratio decreased, the extraction yield increased, but when the H/S ratio was 1:3 or less, there was no significant difference in yield. This finding is consistent with the results of Cebreiros et al. [51], who evaluated the effect of undissociation of acetic acid in the

region where the H/S ratio decreases. With an initial acetic acid concentration of 4.54 g/L in the hydrolysate, the amount of acetic acid recovered was 66.1% at an H/S ratio of 1:4 at room temperature (25 °C) (Table 3). Although this result fell short of the results of Park et al. [46], who investigated acetic acid recovery using ethyl acetate and obtained a high extraction yield of 93%, we believe the reason is the interfering action of other by-products in the fractionated hydrolysate.

Table 3. Recovery of acetic acid and furfural from liquid hydrolyzate using ethyl acetate as a extractant.

| Reaction Conditions | | | Acetic Acid Conc. (g/L) | | Partition Coefficient (P_c) | Extraction Yield (%) |
|--------------------------|------------------|-----------------------|-------------------------|-------------|---------------------------------|----------------------|
| Time (min.) ^a | Temperature (°C) | HS Ratio ^b | Aq. Phase | Org. Phase | | |
| 30 | 25 | 1:1 | 3.88 ± 0.32 | 0.66 ± 0.03 | 0.17 | 14.54 |
| | | 1:2 | 2.01 ± 0.18 | 2.53 ± 0.14 | 1.26 | 55.73 |
| | | 1:3 | 1.76 ± 0.06 | 2.78 ± 0.19 | 1.58 | 61.23 |
| | | 1:4 | 1.54 ± 0.06 | 3.00 ± 0.21 | 1.95 | 66.08 |
| | 50 | 1:1 | 3.56 ± 0.21 | 0.98 ± 0.13 | 0.28 | 21.59 |
| | | 1:2 | 1.88 ± 0.13 | 2.66 ± 0.23 | 1.41 | 58.59 |
| | | 1:3 | 1.64 ± 0.08 | 2.90 ± 0.32 | 1.77 | 63.88 |
| | | 1:4 | 1.61 ± 0.06 | 2.93 ± 0.24 | 1.82 | 64.54 |

* Initial acetic acid concentration of 4.54 g/L. ^a Shaken for 10 s at 5 min intervals for 30 min. reaction. ^b Hydrolyzate to solvent ratio.

A few studies have been conducted to recover acetic acid from biomass hydrolysates. Kim et al. [52] extracted only 33% of AA from barley straw hydrolysates using ethyl acetate. However, Kim et al. [39] reported acetic acid recovery of 62% and 83% from wood hydrolysates using TOPO and TAPO, respectively. According to Abrams and Prausnitz [53], if the AA concentration in the initial feed is high (more than 10 g/L), EA single solvent is not suitable to obtain an effective extraction yield and, thus, a co-solvent extraction strategy is required.

3.6. Combustion Reactivity Evaluation with Fractionated Residual Solid

Figure 4 shows the TG and DTG curves of the combustion process of raw pine wood and LAH-fractionated residual solid. In both, combustion of hemicellulose and cellulose substances started when the temperature exceeded 200 °C, but in the case of the LAH-fractionated solid, the peak at which the combustion reactivity improved was confirmed around 260–320 °C. In the case of biomass, carbon combustion, the last step, can be viewed as lignin combustion. Since neither sample extracted lignin, combustion was confirmed to have occurred at a similar temperature range of 400–450 °C. Compared with raw pine wood, in the case of the LAH-fractionated solid, a single combustion peak of glucose was seen as xylose was extracted through LAH fractionation. Table 4 shows the combustion characteristic factor (S) of raw and LAH-fractionated solids. The higher the calculated S value, the higher the combustion reactivity of the fuel [46]. The LAH-fractionated solid has a faster ignition temperature and a slower burnout temperature than raw pine wood. These results confirm that the weight reduction rate due to combustion is rapid because the LAH-fractionated solid has good reactivity. Compared with raw pine wood, the LAH-fractionated solid had an S value about eight times higher, so it is much more advantageous than raw pine wood in terms of fuel combustibility.

Table 4. Combustion characteristic factor (S) of raw and LHA fractionated solids.

| Sample | (dw/dt) _{max} (% min ⁻¹) | (dw/dt) _{mean} (% min ⁻¹) | T _i (°C) | T _f (°C) | S (10 ⁻⁷ min ⁻² °C ⁻³) |
|----------------------------|---|--|---------------------|---------------------|--|
| Raw pine wood | 5.99 | 0.51 | 315 | 483 | 0.64 |
| LAH fractionated pine wood | 22.12 | 1.14 | 305 | 507 | 5.35 |

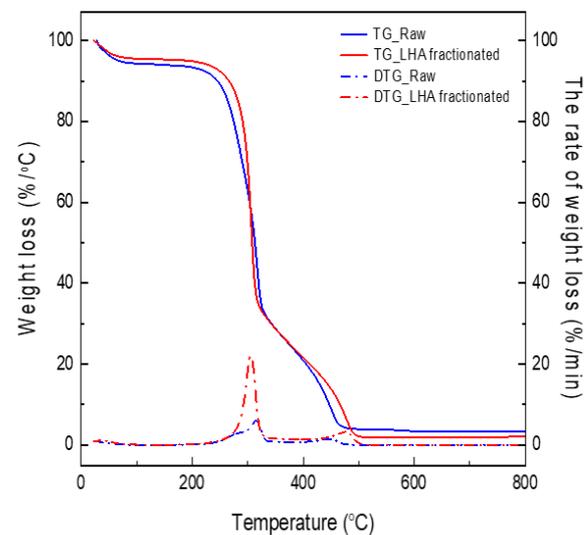


Figure 4. TG-DTG curves of raw and LHA fractionated pine wood.

3.7. Overall Mass Balance for Valorization of LAH Fractionated Pine Wood

Figure 5 displays a simplified flowchart with an overall mass balance of low-acid-catalyzed fractionation and the consecutive acidifying heating and liquid–liquid extraction performed to convert the substances contained in the fractionated hydrolysate into more valuable products. Under optimized LAH fractionation conditions, approximately 35.2% of the mass fraction was solubilized into liquid hydrolysate, which includes the breakdown of 76.2% of hemicellulose. The results indicate that 137 g of xylose and 54.5 g of acetic acid were recovered from 1000 g of raw pine wood. The xylose and acetic acid in the fractionated hydrolysate were used to produce 64 g of furfural and 38 g of acetic acid, which become platform chemicals for the biorefinery industry through a series of valorization processes. Through additional tests, such as combustion tests, 648 g of the residual solid, i.e., LAH-fractionated pine wood, was evaluated as a high-calorific-value (4770 kcal/kg) fuel compared with raw pine wood (3850 kcal/kg), with excellent fuel characteristics.

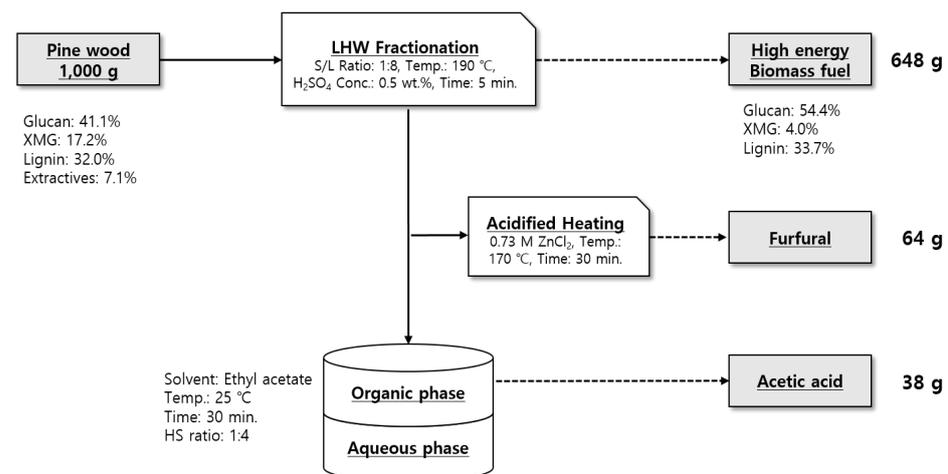


Figure 5. The simplified flowchart with an overall mass balance of products through LAH. Fractionation and consecutive valorization processes.

4. Conclusions

A low-acid catalytic hydrothermal fractionation process was evaluated for the solubilization of the hemicellulose in pine wood, resulting in effective generation of hemicellulosic sugar-rich hydrolysates and cellulose-rich solid residues. The fractionated solid can be effectively converted to ethanol, but it still requires further technological advances to

ensure economic competitiveness. This study confirmed that the solid residue, which is relatively low in hemicellulose, has excellent fuel properties and can be used in power generation fields. The hemicellulosic sugar in the liquid hydrolysates is used as a source of furfural production with a high production yield. These results strongly support the development and application of fractionation process for lignocellulosic biomass in order to maximize its potential utilization in the biorefinery field. However, in addition to the development of furfural production, a recycling method of $ZnCl_2$ should also be developed in future research.

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