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Effects of Sugars and Degradation Products Derived from Lignocellulosic Biomass on Maleic Acid Production

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Abstract: In this study, maleic acid was produced from xylose contained in a hydrolysate generated by oxalic acid pretreatment of yellow poplar (*Liriodendron tulipifera*), and the factors that influenced maleic acid production were evaluated. Furfural was obtained from the hydrolysate using H₂SO₄ as a catalyst, depending on combined severity factors (CSFs). Furfural production increased as the H₂SO₄ concentration increased. Furfural yield (46.70%), xylose conversion (70.95%), and xylo-oligomer conversion (75.47%) from the hydrolysate were high at CSF 1.92 with 1.64% H₂SO₄. However, the furfural concentration was slightly increased at 1.64% H₂SO₄ to 7.10 g/L at CSF 1.89, compared with that at CSF 1.92. Maleic acid was produced from the hydrolysate (CSF 1.92 and 1.64% H₂SO₄) at a yield of 91.44%. Maleic acid production was slightly better when formic acid and acetic acid were included in the hydrolysate than when furfural was included alone (79.94% vs. 78.82%). Based on the results, the xylose obtained from yellow poplar can be proposed as a new substitute for fossil fuel-derived raw materials.

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1. Introduction

A biorefinery that could produce biofuels and bio-based chemicals through the biological and chemical conversion of lignocellulosic biomass is a promising idea that could help offset the depletion of fossil fuels and the effects of climate change. Lignocellulosic biomass mainly consists of cellulose, hemicellulose, and lignin, which are not easily decomposed. Therefore, the efficient utilization of lignocellulosic biomass requires physical, chemical, and/or biological pretreatment [1]. Among such methods, high efficiency has been achieved using acid catalysts [2–4]. Sugars and various degradation products, such as organic acid, furfural, 5-hydroxymethylfurfural (HMF), and phenolic compounds, are simultaneously produced during pretreatment [5]. The sugars can be used to produce bioenergy and bio-based products, while the degradation products inhibit subsequent processing (enzymatic hydrolysis and fermentation).

Among the degradation products, furfural is one of the top 12 value-added products defined by the U.S. Department of Energy, and it is a precursor that can be applied to the fuel, plastic, cosmetic, and pharmaceutical industries [6–8]. Lignocellulosic biomass, such as that comprising corn and sugar cane, is the raw material for furfural production, and 250,000 tons of furfural are produced annually through hemicellulose hydrolysis to xylose and xylose dehydration to furfural using acid catalysts [9,10]. Furfural is used as a precursor for maleic acid production in which HMF or furfural is the starting material derived from glucose or xylose [11]. Maleic acid is an intermediate of chemical synthesis that is widely applied in medicines, pesticides, and foods [12]. Maleic acid cannot be produced biochemically, and it is industrially derived from the oxidation of butane, butadiene, or

benzene at high temperatures, with catalysts such as vanadium oxides or vanadium-phosphorous [12,13]. To produce about 2 million tons of maleic acid per year, bio-based and eco-friendly feedstock must be developed, and a cost-effective process is required [8]. Maleic acid is presently chemically synthesized from furfural in response to excessive fossil fuel consumption. Maleic acid is produced based on chemical oxidation using a catalyst and electrochemical oxidation. In particular, maleic acid is usually produced by oxidation using H_2O_2 [14]. This process can increase the maleic acid yield to 70% by the selective oxidation of furfural when H_2O_2 is combined with a catalyst and titanium silicalite-1, and to 60% when combined with betaine hydrochloride [14,15].

However, the process is problematic owing to catalyst reuse and complex reaction conditions at high temperatures and pressure [8]. Lignocellulosic biomass has received attention for producing valuable organic acids, such as formic, acetic, maleic, and succinic acids [16]. Most studies have produced maleic acid via the hydrolysis of hemicellulose/cellulose into xylose/glucose. A few studies have applied hydrolysates generated by dilute acid pretreatment of lignocellulosic biomass [17–19]. Maleic acid production using hydrolysate derived from lignocellulosic biomass, which contains an abundance of monosaccharides, can be regarded as a new eco-friendly process.

The reaction pathway for maleic acid production from lignocellulosic biomass can be predicted (Scheme 1). Xylose is initially produced from hemicellulose by pretreatment, then dehydrated to furfural using an acid catalyst. 2-(5H) furanone is produced by the Baeyer–Villiger oxidation of furfural, and maleic acid is produced by the oxidation of 2-(5H) furanone [15]. Hydrolysates contain monosaccharides (such as xylose and glucose) and various organic acids, and formic and acetic acids promote maleic acid production. Thus, hydrolysates might contain an abundance of precursors for maleic acid production. Here, yellow poplar (*Liriodendron tulipifera*) was pretreated using oxalic acid, which selectively degrades hemicellulose, to obtain xylose-rich hydrolysates. Then, the sequential production of furfural and maleic acid was evaluated by dehydrating xylose and oxidizing furfural. Additionally, the effects of various chemicals in the hydrolysate on maleic acid production were investigated.

Scheme 1. Conversion of lignocellulosic biomass to maleic acid.

2. Materials and Methods

2.1. Hydrolysate Production from Yellow Poplar Pretreatment with Oxalic Acid

Furfural and maleic acid were produced from the first hydrolysate, as described [20]. Yellow poplar (*Liriodendron tulipifera*) powder (20–80 mesh) was reacted with various concentrations of oxalic acid at 160 °C (Table 1). Table 2 shows the chemical composition of the first hydrolysate [20]. The schematic diagram of the entire experiment in this study is shown in Figure 1. The experiments were performed in triplicate.

Table 1. Pretreatment of yellow poplar using oxalic acid [20].

Sample No.	Time (min)	Acid Concentration (mM)	CSF *
1	30	82	1.89
2		139	2.08
3	50	41	1.92
4		122	2.29

* Combined severity factors (CSFs) = $\log\{t \times \exp[(T_H - T_R)/14.75]\} - \text{pH}$ (t : pretreatment reaction time (min), T_H : reaction temperature ($^{\circ}\text{C}$), T_R : reference temperature, most often 100°C , and pH: acidity of aqueous solution).

Table 2. Sugars, xylo-oligomer, and inhibitors in first hydrolysate, depending on oxalic acid pretreatment conditions [20].

CSF	Glu	Xyl	XO	FA	AA	HMF	Fur	pH
g/L								
1.89	3.02 (0.22)	15.17 (0.62)	2.50 (0.25)	2.12 (0.11)	8.02 (0.14)	0.21 (0.01)	1.95 (0.05)	2.10 (0.02)
1.92	2.46 (0.16)	14.95 (0.89)	2.65 (0.18)	1.33 (0.30)	8.33 (0.33)	0.22 (0.03)	1.73 (0.12)	2.19 (0.05)
2.08	3.69 (0.19)	14.37 (0.37)	2.06 (0.19)	2.67 (0.36)	7.95 (0.12)	0.27 (0.08)	2.45 (0.45)	1.84 (0.03)
2.29	4.26 (0.02)	12.80 (0.63)	1.99 (0.34)	2.59 (0.37)	8.19 (0.14)	0.38 (0.05)	3.37 (0.32)	2.00 (0.07)

The first hydrolysate was obtained from oxalic acid pretreatment of yellow poplar. Glu: Glucose, Xyl: Xylose, XO: Xylo-oligomer, FA: Formic acid, AA: Acetic acid, HMF: 5-Hydroxymethylfurfural, Fur: Furfural. The numbers in parentheses indicate the standard deviation.

Figure 1. Maleic acid production from yellow poplar.

2.2. Furfural Production Using the First Hydrolysate

The first hydrolysate (3 mL) was added to 72% H_2SO_4 (0.07, 0.13, and 0.2 mL) in test tubes with screw caps. The final H_2SO_4 concentrations in the mixtures were 1.64%, 3.0%, and 4.5%, respectively. Reactions proceeded in the test tubes placed in an oil bath under constant magnetic stirring. The reaction temperature was increased to 180°C and held for 10 min; then, the mixture was cooled and separated into solid (humin) and liquid (second hydrolysate) fractions. The chemical composition of the second hydrolysate

was analyzed by high-performance liquid chromatography (HPLC). Furfural yield, xylose conversion, xylo-oligomer conversion, and furfural selectivity were calculated using Equations (1)–(4) [6,21]. The experiments were performed in triplicate.

$$\text{Yield of furfural (\%)} = \text{furfural produced (mol)} / \text{starting xylose + starting xylo-oligomer (mol)} \times 100 \quad (1)$$

$$\text{Conversion of xylose (\%)} = \text{xylose reacted (mol)} / \text{starting xylose (mol)} \times 100 \quad (2)$$

$$\text{Conversion of xylo-oligomer (\%)} = \text{furfural produced (mol)} / \text{starting xylo-oligomer (mol)} \times 100 \quad (3)$$

$$\text{Selectivity of furfural (\%)} = \text{furfural produced (mol)} / \text{xylose reacted + xylo-oligomer reacted (mol)} \times 100 \quad (4)$$

2.3. Maleic Acid Production Using the Second Hydrolysate

Maleic acid was produced using the second hydrolysate with the modified method of Li et al. [22]. The second hydrolysate (4 mL) was mixed with formic acid (1, 2.5, and 4 mL) and H₂O₂ (30%, w/w, 4, 2.5, and 1 mL). The total volume of the reaction mixture was 9 mL. The reaction was carried out at 100 °C for 40 min in the oil bath. The reaction mixture was cooled; then, the chemical composition of the liquid fraction (3rd hydrolysate) was analyzed by HPLC. The experiments were performed in triplicate. The yields of maleic acid and the intermediate product were calculated using Equation (5) [23]:

$$\text{Yield of maleic acid (\%)} = \text{maleic acid produced (mol)} / \text{starting furfural (mol)} \times 100 \quad (5)$$

2.4. Analysis of Factors Affecting Maleic Acid Production

Synthetic chemical mixtures of furfural, acetic acid, and formic acid were prepared to analyze their effects on maleic acid production. The chemical concentrations were controlled based on those in the second hydrolysate. The reaction conditions were as described in Section 2.3. The experiments were performed in triplicate.

2.5. Analysis of the Hydrolysate

Sugars and degradation products in the hydrolysate were analyzed with HPLC using a Waters 2695 system (Waters Corp., Milford, MA, USA) equipped with a 300 × 7.8 mm Aminex 87H column (Bio-Rad Laboratories Inc., Hercules, CA, USA) and a refractive index detector (Waters Corp., 2414). The flow rate of the eluent, 5 mM H₂SO₄, was 0.6 mL/min. The intermediates generated from maleic acid production, such as fumaric acid and 2-(5H)-furanone, were analyzed by HPLC Waters 2695, using a C18 column (4.6 × 250 mm) and a UV/Vis detector (Waters 2489, Milford, MA, USA). The mobile phase was a 2:8 ratio of methanol and 1% phosphoric acid, and the flow rate was 0.6 mL/min [12]. The xylo-oligomer was determined using the National Renewable Energy Laboratory procedure [24]. All experiments were performed in triplicate.

2.6. Statistical Analysis

The factors affecting maleic acid production were assessed by one-way analysis of variance (ANOVA), using SPSS version 23 (IBM Corp., Armonk, NY, USA). Correlations between variables were determined using Duncan's tests. Results with a *p*-value of <0.05 were considered significantly different.

3. Results and Discussion

3.1. Furfural Production from the First Hydrolysate

Furfural is produced by the sequential hydrolysis and dehydration of pentosans in lignocellulose under aqueous mineral acid conditions [25]. In this study, furfural was produced from the first hydrolysate of oxalic acid-pretreated yellow poplar, using the acid catalyst H₂SO₄, which promotes the dehydration of pentose sugars, such as xylose and arabinose; thus, the amount of furfural produced differs depending on the acid concentration [26]. Because furfural is a maleic acid precursor, high concentrations of furfural in hydrolysates are favorable for maleic acid production. Figure 2 shows the

amount of furfural produced from the first hydrolysate using various H_2SO_4 concentrations. Xylose and xylo-oligomer were converted into furfural, and more furfural was converted with all CSF as the H_2SO_4 concentration increased. However, the furfural yield and furfural selectivity decreased with increasing H_2SO_4 concentrations. This is because some xylose is not converted to furfural because of the production of humin and furan during the dehydration reaction at high acid concentrations [21,26,27]. The factors involved in furfural production are reaction temperature, pH, reaction time, and the catalyst [25]. Among these, temperatures $> 170\text{ }^\circ\text{C}$ and a low pH decrease the yield of thermally unstable furfural [28]. Therefore, furfural yield and selectivity were low in 4.5% H_2SO_4 at all CSFs in this study. However, the furfural yield was relatively high in 1.64% H_2SO_4 at all CSFs. The furfural yield was compared by preparing a synthetic medium with the same concentration as xylose obtained from the first hydrolysate (Figure 3). The furfural yield was higher in the first hydrolysate than in the synthetic medium. The first hydrolysate contained xylo-oligomer, a precursor of furfural, and formic acid and acetic acid, which can act as catalysts in the furfural production; thus, the furfural yield from hydrolysate was higher than that of the synthetic medium [21].

Figure 2. Xylose conversion, xylo-oligomer (XO) conversion, furfural yield, and furfural selectivity depending on CSF and H_2SO_4 concentration (a) CSF 1.89, (b) CSF 1.92, (c) CSF 2.08, (d) CSF: 2.29.

Figure 3. Furfural production from xylose in the first hydrolysate and synthetic medium, depending on CSF.

Table 3 shows the amount of humin produced at different H_2SO_4 concentrations. In general, furfural is unstable and polymerizes to form humins, owing to the condensation of furan and sugars. Therefore, the yield and selectivity of furfural from xylose and xylo-oligomer were reduced, owing to humin formation [29]. Here, humin production increased with increasing acid concentrations at each CSF. A high concentration of H_2SO_4 promoted humin formation and xylose dehydration, thereby reducing the furfural yield [30]. The yield of furfural was 46.71% with 1.64% H_2SO_4 at CSF 1.92. Under the same conditions, the rates of xylose and xylo-oligomer conversion to furfural were 70.95% and 75.47%, respectively. The rate of xylose conversion was >81% in 4.50% H_2SO_4 , whereas the furfural yield and selectivity were relatively low at 17.60–33.47% and 19.08–37.44%, respectively, compared with those under other conditions.

Table 3. Humin production during dehydration of xylose into furfural at various H_2SO_4 concentrations (Unit: g).

H_2SO_4 (%)	Combined Severity Factors (CSF)			
	1.89	1.92	2.08	2.29
1.64	0.37 (0.05)	0.50 (0.05)	0.68 (0.10)	0.57 (0.08)
3.00	0.49 (0.09)	0.79 (0.06)	0.70 (0.07)	0.90 (0.09)
4.50	0.97 (0.07)	1.10 (0.05)	1.31 (0.07)	1.09 (0.07)

The numbers in parentheses indicate the standard deviation.

Figure 4 shows the chemical composition of the second hydrolysate obtained by xylose dehydration of the first hydrolysate. The yield of furfural was 46.70% with 1.64% H_2SO_4 at CSF 1.92 (Figure 2), whereas the production was high at 7.10 g/L with 1.64% H_2SO_4 at CSF 1.89. Furfural production decreased with increasing CSF. Under most reaction conditions, some xylose and xylo-oligomers were not converted to furfural and remained in the second hydrolysate after xylose dehydration, indicating that these reaction conditions were not appropriate for converting xylose to furfural.

At high H_2SO_4 concentrations, formaldehyde, acetaldehyde, and formic acid are byproducts of furfural decomposition; thus, formic acid concentrations increased slightly compared with those in the first hydrolysate [21,26]. Glucose undergoes multiple acid-catalyzed reactions and generates HMF as an intermediate, which can be hydrated to produce levulinic acid. Therefore, concentrations of glucose and HMF decreased compared with those in the first hydrolysate, and that of levulinic acid increased with increasing H_2SO_4 concentrations [31]. However, some acetic acid remained in the second hydrolysate at low pH; these factors likely affected the yield of maleic acid.

Figure 4. Sugars, xylo-oligomer, and degradation products in second hydrolysates, depending on H_2SO_4 concentrations (Glu: Glucose, Xyl: Xylose, XO: Xylo-oligomer, FA: Formic acid, AA: Acetic acid, HMF: 5-Hydroxymethylfurfural, Fur: Furfural, LA: levulinic acid, (a) CSF 1.89, (b) CSF 1.92, (c) CSF 2.08, (d) CSF: 2.29).

3.2. Maleic Acid Production from the Second Hydrolysate

Figure 5 shows maleic acid produced from the second hydrolysate using formic acid and H_2O_2 . The process of maleic acid production from lignocellulosic biomass involves the hydrolysis of hexosans/pentosans to hexoses/pentoses, dehydration of hexose/pentose to HMF/furfural, and oxidation of HMF/furfural to maleic acid [11]. The catalytic conversion of pentoses to furfural consumes less energy and results in a higher conversion yield than that of hexoses to HMF. Therefore, furfural has been considered a cost-effective starting material for maleic acid production [32]. Here, the yield of maleic acid converted from furfural was calculated. Furfural was completely converted to maleic acid and other degradation products under all reaction conditions, but the maleic acid yield depended on the second hydrolysate. The high maleic acid yield was 92.90% at CSF 2.29 with 1.64% H_2SO_4 . However, the optimal conditions for maximal maleic acid yield (91.44%) were CSF 1.89 with 1.64% H_2SO_4 . Li et al. produced 95% maleic acid through a synthetic medium using H_2O_2 and formic acid [22]. The yield of maleic acid production obtained from the hydrolysate of the yellow poplar was slightly lower than that, but the results of this study confirmed that maleic acid can be produced from the hydrolysate of biomass. The oxidation reaction using H_2O_2 and an acid catalyst has low selectivity; thus, various degradation products, such as succinic acid, fumaric acid, and 2-(5H)-furanone, are produced in the maleic acid production process. Fumaric acid and 2-(5H)-furanone were intermediates of maleic acid production, at ratios <2%.

The maleic acid yield was not proportional to the furfural content in the second hydrolysate. Furfural concentration reached 7.05 g/L with 1.64% H_2SO_4 at CSF 2.08, whereas maleic acid yield was 78.47%. This implies that maleic acid production was affected by various degradation products as well as furfural in the second hydrolysate.

Figure 5. Maleic acid produced from furfural in the second hydrolysate using formic acid (4 mL) and H_2O_2 (1 mL), depending on combined severity factors (CSFs) and H_2SO_4 concentration (a) CSF 1.89, (b) CSF 1.92, (c) CSF 2.08, (d) CSF: 2.29.

3.3. Effects of Catalyst and Degradation Products on Maleic Acid Production from the Second Hydrolysate

The yield of maleic acid produced at CSF 1.89 with 1.64% H_2SO_4 , depending on the ratios of formic acid to H_2O_2 , was investigated (Figure 6). A synthetic medium was prepared with the same concentration of furfural as that in the second hydrolysate to determine the effects of degradation products in the second hydrolysate on maleic acid production. At a 4:1 ratio of formic acid (4 mL) and H_2O_2 (1 mL), the maleic acid yield from the second hydrolysate was 91.44%, whereas that from the synthetic medium with the same furfural concentration was 78.72%. The second hydrolysate contained various degradation products, such as organic acids and furans. Therefore, other degradation products in the second hydrolysate positively affected maleic acid production. The highest yield of maleic acid in the synthetic medium was 87.32% at a 1:1 ratio of formic acid (2.5 mL) and H_2O_2 (2.5 mL). The yield was lower than that of the second hydrolysate.

Figure 6. Maleic acid production from furfural in the second hydrolysate and synthetic medium, depending on the ratio of formic acid (FA) to H₂O₂.

Maleic acid production is affected by various factors such as the H₂O₂ concentration, catalyst type, and reaction temperature [33]. Li et al. reported that formic and acetic acids promote maleic acid production [22]. The effects of acetic and formic acids in the second hydrolysate on maleic acid production were investigated. A synthetic medium was prepared with similar furfural and organic acid contents to the second hydrolysate; then, the yield of maleic acid produced under formic acid:H₂O₂ (4:1) was evaluated. Maleic acid yield slightly increased when acetic and formic acids were added to the synthetic medium, compared with that when only furfural was added (Table 4). Acetic and formic acids supposedly act as influencing factors to promote maleic acid production. However, the yield was lower than that in the second hydrolysate (91.44%). This implies that other degradation products are involved in maleic acid production in addition to acetic and maleic acids.

Table 4. Maleic acid production from the synthetic medium using formic acid (4 mL) and H₂O₂ (1 mL).

Condition	Maleic Acid Yield (%)
Furfural	78.82 (0.99) ^a
Furfural + acetic acid	79.11 (0.08) ^b
Furfural + formic acid	79.66 (0.25) ^b
Furfural + acetic acid + formic acid	79.94 (0.78) ^c

Furfural, acetic acid, and formic acid concentration are similar to those in second hydrolysate. The same letters on the column are not significantly different from each other at $p < 0.05$. The numbers in parentheses indicate the standard deviation.

Figure 7 shows the mass balance for maleic acid production from the hydrolysate of yellow poplar. The hydrolysate was obtained at CSF 1.89, and furfural was produced in 1.64% H₂SO₄. In total, 9.54 g of xylose was produced from 100 g of yellow poplar. After that, 1.08 g of furfural and 0.08 g of humin were produced from xylose, and 0.63 g of maleic acid was produced. These findings confirm that maleic acid can be produced from a hydrolysate derived from lignocellulosic biomass.

Figure 7. Mass balance for maleic acid production from lignocellulosic biomass.

4. Conclusions

Maleic acid was produced from xylose contained in a hydrolysate generated by the oxalic acid pretreatment of yellow poplar. Maleic acid was obtained by xylose dehydration, furfural oxidation, and 2(5H)-furanone oxidation in the hydrolysate. In the furfural production, the xylose conversion rate increased with increasing H_2SO_4 concentrations, but furfural selectivity decreased. This implies that xylose was not completely converted to furfural and various intermediates, and that interfering byproducts were generated. Maleic acid was produced using hydrolysates obtained from furfural production. The yield was improved by degradation products, such as formic and acetic acids. Overall, hydrolysates derived from yellow poplar contained an abundance of xylose, which is a suitable raw material for the production of furfural and maleic acid. The result of this study will contribute to the development of eco-friendly and efficient alternatives to fossil fuel-based processes.

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