

Valorization of chitosan into levulinic acid by hydrothermal catalytic conversion with methanesulfonic acid

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Abstract—As a potential renewable aquatic resource, chitosan is the second most abundant biopolymer. Methanesulfonic acid is a catalyst that is strongly acidic and biodegradable. We used chitosan and methanesulfonic acid to produce platform chemicals via an acid-catalyzed hydrothermal reaction. In the methanesulfonic acid-catalyzed hydrothermal conversion of chitosan, an optimal levulinic acid yield of $28.21 \pm 1.20\%$ was achieved under the following conditions: 2% chitosan and 0.2 M methanesulfonic acid at 200 °C for 30 min. These results indicated that a combination of chitosan and methanesulfonic acid would be suitable for platform chemical production.

Keywords: Chitosan, Methanesulfonic Acid, Platform Chemicals, 5-Hydroxymethylfurfural, Levulinic Acid

INTRODUCTION

Bioresources are promising alternatives to carbon-based fossil resources [1,2]. Bio-based products, produced from bioresources, such as biofuels and other chemicals, can replace fossil resources [3-7]. Among different platform chemicals, 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA) have high potential owing to reactive groups that can participate in the versatile synthesis of fuels and materials [1-4,6,7]. 5-HMF and LA can be synthesized from several carbohydrates such as sugar, starch, lignocellulose, macro-algae, and chitin/chitosan [1-3,6-11]. 5-HMF can be converted by hydrogenation and various chemical reactions to several useful products such as fuels, pharmaceuticals, solvents, resins, textiles, fungicides, and polymer materials [3,6,12]. LA (3-acetylpropionic acid, 4-oxovaleric acid, 4-oxopentanoic acid, or γ -keto-valeric acid) has one carbonyl, one carboxyl, and α -H in its inner structure, which contribute to its versatile chemical properties (Fig. 1) [13]. LA is one of several sustainable platform chemicals that can be converted to valuable chemicals and materials [14]. It can be converted to several derivatives such as levulinate esters, Δ -amino-levulinic acid, succinic acid, diphenolic acid, angelica lactone, hydroxypentanoic acid, γ -valerolactone, etc. [14]. In addition, LA and its derivatives can be used in pharmaceuticals, fuel additives,

food additives, agricultural products, dyes, resins, solvents, polymers, etc. [3,6,7,12].

LA production can be carried out by three routes. The first is a five-step chemical route from maleic anhydride, which is not economical on a large scale [13]. The second is a direct conversion from furfuryl alcohol, which is the product of furfural hydrogenation [15]. The third involves the acid treatment of six-carbon sugars and complex carbohydrates such as starch, lignocellulose, macro/micro-algae, and chitin/chitosan [15]. The production of LA from mono-sugars such as fructose and glucose is well established using homogeneous mineral acids and salts [3,13]. Moreover, several heterogeneous catalysts (ion-exchange resins, heteropoly acids, solid Lewis acids, zeolites, etc.) can be used [13,16-18]. In recent studies, various carbohydrates derived from biomasses such as cellulose, giant reed, water hyacinth, corn stalk, rice straw, wheat straw, sugarcane bagasse, poplar sawdust, inulin, empty fruit bunch, kenaf, red algae, chitin, and chitosan have been used for LA production with various thermochemical processes [13,14]. The use of these raw and waste biomasses is an attractive and sustainable approach in the field of LA production [13,14].

In the present study, we used chitosan as biomass for the production of chemical intermediates such as 5-HMF and LA. Chitosan is a linear polysaccharide with $\beta(1 \rightarrow 4)$ glycosidic bonds that form linkages with glucosamine (2-amino-2-deoxy-D-glucopyranose) and *N*-acetylglucosamine [19,20]. Chitosan is obtained by the partial *N*-deacetylation of chitin, the second most abundant polysaccharide on earth [19,21]. Approximately 100 billion tons of chitin are generated every year [22,23]. Chitin is the main structural component of the cellular walls of fungi and the exoskeletons of crustaceans [19,24]. Commercially, large quantities of chitin are obtained from the food waste of aquatic organisms such as crabs and shrimp shells [19]. Annually, around 6-8 million tons of seafood waste such as shrimp, crab, and lobster shells are generated globally [22,25]. Most waste shells are disposed of in landfills or the sea because of ignorance of the potential of waste shells for the chemical industry [22]. They have only been used recently for the

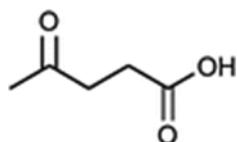


Fig. 1. Chemical structure of levulinic acid.

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production of fertilizers, chitin/chitosan, and animal feed supplements [22]. Shell biorefinery refers to the fractionation of crustacean shells into their major components (chitin, calcium carbonate, protein, lipid, and astaxanthin) and conversion to valuable chemicals and materials [26]. It has been in the spotlight recently [22]. Chitosan is a biocompatible, biodegradable, and non-toxic biopolymer that has been widely used in biomedicine, cosmetics, chemical industries, fibers, food, sewage treatment, and environmental protection [24]. Although further studies are required, the conversion of chitin/chitosan to valuable chemicals and materials has been reported for furan derivatives without nitrogen (5-HMF, 5-chloromethylfurfural), N-containing furan derivatives (3-acetamido-5-acetylfuran (3A5AF), 2-acetamido-2,3-dideoxy-D-erythro-hex-2-enofuranose (Chromogen I), 3-acetoamido-5-(1',2'-dihydroxyethyl) furan (Chromogen III)), organic acids (LA, acetic acid, α -amino acids), amino sugars (GlcNAc, GlcNH₂, chito-oligomers), amino sugar ethers, amines, amide polyols (2-acetoamido-2-deoxy-D-sorbitol), and heterocyclic pyrazines (pyrrole, deoxyfructosazine, fructosazine) [26-35].

The use of chitin/chitosan to produce 5-HMF and LA has been investigated with several processes [8-11]. The conversion of chitin/chitosan to 5-HMF and LA is a key step for producing liquid fuels and valuable chemicals [1]. Recently, the use of methanesulfonic acid as catalyst in 5-HMF and LA production from sugars and bagasse was reported [36-38]. However, thus far, there are no studies on using methanesulfonic acid as catalyst in the conversion of chitosan to platform chemicals such as 5-HMF and LA.

Methanesulfonic acid is strong (pK_a=-1.9), non-oxidizing, non-foaming, and biodegradable, indicating that its use causes fewer environmental problems compared with inorganic acids [17-19]. In addition, it is compatible with oxidizing agents and biocides. It is a strong acid that is widely used as a catalyst in esterification, alkylation, etc. Moreover, it could be an attractive alternative to organic and inorganic strong acids in various applications [37-39].

In this study, the methanesulfonic acid-catalyzed conversion of chitosan to chemical intermediates, such as 5-HMF and LA, was investigated. To optimize the production of 5-HMF and LA from chitosan, the effects of reaction factors were investigated. Furthermore, the efficiency of catalytic conversion was evaluated using the combined severity factor (CSF).

MATERIALS AND METHODS

1. Materials

Chitosan (96.27% glucosamine, 89.69% deacetylated form, 355-500 μ m particle size), which was used as the substrate, was obtained from Amicogen Co. Ltd. (Korea). The employed methanesulfonic acid (Samchun Pure Chemical Co., Ltd., Korea) was of reagent grade, and LA, 5-HMF, and all other chemicals were of analytical grade.

2. Experimental Procedure

In the batch experiment, a fixed amount of chitosan and 30 mL of methanesulfonic acid were transferred to a 50 mL stainless steel reactor. Before the reaction, the reactant was sufficiently mixed by magnetic stirring for 10 min. The reaction was initiated when the set temperature of the reactor in the oil bath was achieved using a

PID temperature controller. The preheating time was around 5 min. During the reaction, the reactant was mixed with a magnetic stirrer at 200 rpm. Upon completion of the reaction, the reactor was quickly cooled to room temperature by dipping in tap water. The product solution was recovered by centrifugation at 17,000 rpm for 10 min and filtered using a 0.2 μ m syringe filter for HPLC analysis [8,9].

3. Conversion of Chitosan with Methanesulfonic Acid

The methanesulfonic acid-catalyzed conversion of chitosan was performed to evaluate four reaction factors: reaction temperature, catalyst concentration, biomass concentration, and reaction time. The effect of various reaction temperatures (160-210 °C) was investigated with 2% (w/w) chitosan and 0.2 M methanesulfonic acid for 30-90 min. The effect of various catalyst concentrations (0-1.0 M methanesulfonic acid) was investigated with 2% chitosan at 200 °C for 15-30 min. The effect of different chitosan concentrations (0.5-5% (w/w)) was investigated with 0.2 M methanesulfonic acid at 200 °C for 30 min. Finally, the effect of different reaction times (0-120 min) was investigated with 2% (w/w) chitosan and 0.2 M methanesulfonic acid at 200 °C. All of the experiments were repeated two or more times, and the data are presented as the mean \pm SD.

4. Effect of the Combined Severity Factor

The effect of the methanesulfonic acid-catalyzed hydrothermal reaction was investigated by using the CSF to evaluate 5-HMF and LA production from chitosan. The CSF is defined as the severity of the reaction, which is a function of the reaction conditions (temperature, time, and acidity of the solution) [20,21]. $CSF = \log\{t \exp[(T - T_{ref})/14.75] - pH\}$, where $T(t)$ is the reaction temperature (°C), T_{ref} is the reference temperature (i.e., 100 °C), t is the reaction time (min), and 14.75 is the fitted value of the arbitrary constant. Prior to the reaction, the pH of the solution was measured at room temperature [39,40].

5. Analysis

The concentrations of 5-HMF and LA were analyzed using an Agilent 1100 HPLC system (Agilent, San Jose, CA, USA) with Bio-Rad Aminex-87H column and refractive index detector. The HPLC operation conditions were as follows: 65 °C oven temperature, 5 mM sulfuric acid as the mobile phase, and 0.6 mL/min flow rate [8].

6. Determination of Conversion Yield

The conversion yield of chitosan to 5-HMF and LA was calculated by the following equation: conversion yield (%) = concentration of product (g/L)/concentration of initial chitosan (g/L) \times 100. The results are presented as the mean \pm SD.

7. Statistical Analysis

All of the experiments were repeated two or more times, and the data are presented as the mean \pm SD. The statistical significance of differences in the experiments was evaluated with one-way analysis of variance (ANOVA) and Duncan's multiple range test ($P < 0.05$) using SPSS version 23 (SPSS, Cary, NC, USA).

RESULTS AND DISCUSSION

1. Methanesulfonic Acid-catalyzed Hydrothermal Conversion of Chitosan

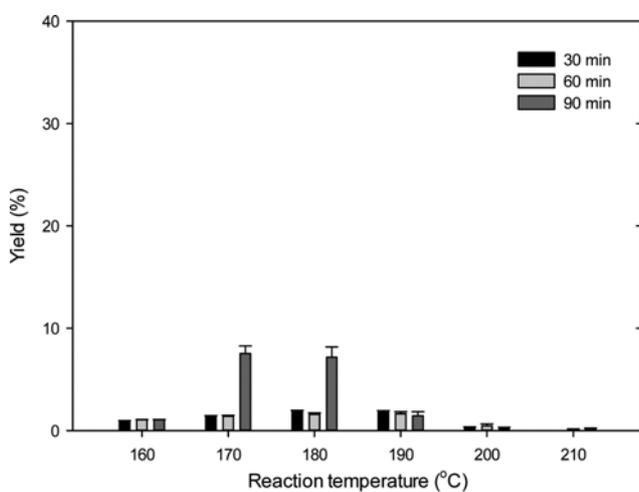
In this study, the methanesulfonic acid-catalyzed hydrothermal

reaction was conducted to produce 5-HMF and LA from chitosan. For optimization of 5-HMF and LA production, the effects of reaction factors (reaction temperature, methanesulfonic acid concentration, chitosan concentration, and reaction time) on the conversion of chitosan were investigated.

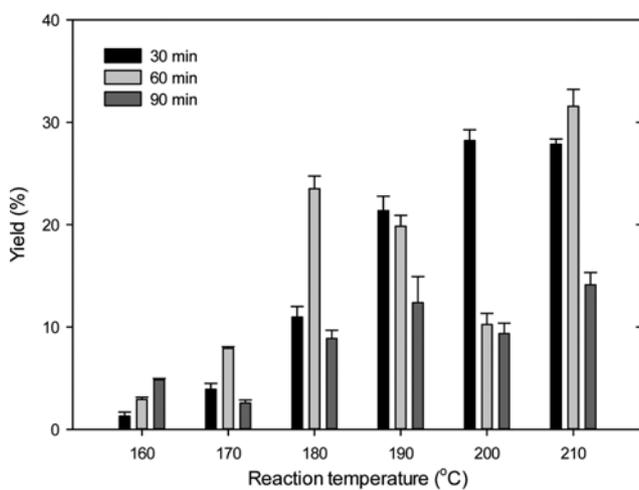
Fig. 2 shows the effect of reaction temperature on the conversion of chitosan to 5-HMF and LA in the range of 160–210 °C using 2% (w/w) chitosan and 0.2 M methanesulfonic acid for 30–90 min. Fig. 2(a) reveals that at all reaction temperatures, 5-HMF yield was low (below 4%). The highest 5-HMF yield (7.53%) was obtained at 170 °C and 90 min. At 170 °C, 5-HMF yield was increased over time. A temperature higher than 200 °C reduced the formation of 5-HMF. Overall, average temperatures (170–180 °C) over an extended time enhanced 5-HMF yield. In comparison, Lee and Jeong [9] reported a peak in 5-HMF yield at 180 °C in the sulfuric acid-catalyzed hydrothermal hydrolysis of chitosan. Higher temperatures caused the over-degradation of the produced 5-HMF to LA and FA [9]. In addition, Omari et al. [10] reported that 5-HMF

production from chitosan peaked at 200 °C under microwave irradiation with a SnCl_4 catalyst. Moreover, 5-HMF was not detected below 170 °C. Yu et al. [41] obtained the highest 5-HMF yield from chitin at 190 °C in a DMSO-water mixture with FeCl_3 as catalyst. These results of 5-HMF yields with peak patterns over a range of reaction temperatures suggest that the activation energy of 5-HMF formation from chitosan or its monomer could be higher than that of 5-HMF decomposition to LA [1,42].

Fig. 2(b) shows that increasing the reaction temperature to 200 °C for 30 min increased LA yield. The highest LA yield (31.41%) was achieved at 210 °C and 60 min. After 60 min, the yield was decreased over time. Increasing the reaction time at a high temperature caused a reduction in LA yield. This decrease in LA yield indicated that constant heat energy and acidic catalysis accelerated the degradation and condensation of 5-HMF and LA to humin products [3,9,43]. In comparison, a linear increase in LA yield was obtained with increasing temperature in the range of 80–180 °C in

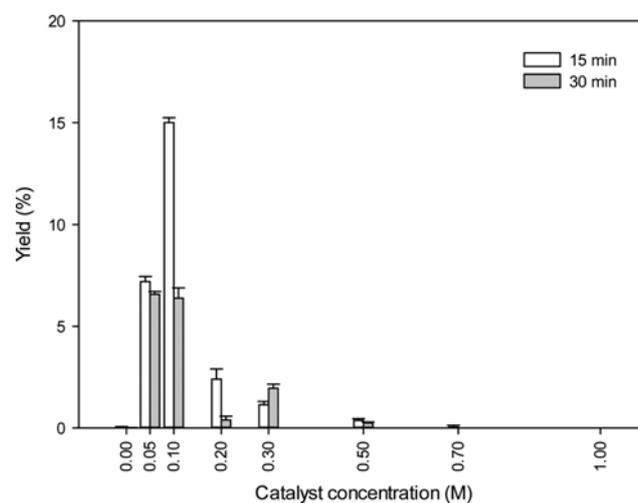


(a) 5-HMF

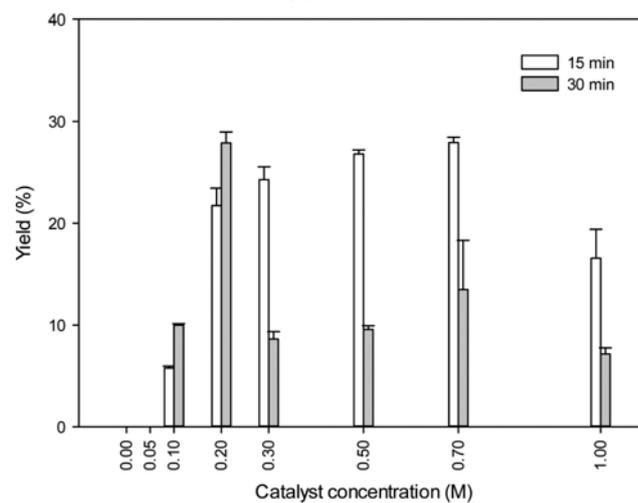


(b) Levulinic acid

Fig. 2. Effect of the reaction temperature on 5-HMF and levulinic acid production from chitosan by methanesulfonic acid-catalyzed hydrothermal conversion under the 2% (w/w) chitosan, 0.2 M methanesulfonic acid, and 30, 60, 90 min conditions.



(a) 5-HMF



(b) Levulinic acid

Fig. 3. Effect of the catalyst concentration on 5-HMF and levulinic acid production from chitosan by methanesulfonic acid-catalyzed hydrothermal conversion under the 200 °C, 2% chitosan, and 15 and 30 min conditions.

the sulfuric acid-catalyzed hydrothermal hydrolysis of *Gelidium amansii* [43]. Furthermore, LA yield was linearly enhanced with increasing temperature in the hydrothermal conversion of glucosamine catalyzed by sulfuric acid [8]. Rackeman et al. [36] reported that LA yield was increased with increasing temperature in the range of 160–180 °C. On the other hand, further increases in temperature to 200 °C led to a decrease in LA yield over time in glucose conversion using methanesulfonic acid as catalyst [36]. In this study, a high temperature of 200 °C in the methanesulfonic acid-catalyzed hydrothermal conversion of chitosan favored a higher LA yield. Therefore, further conversion experiments were carried out at a reaction temperature of 200 °C.

Fig. 3 shows the effect of catalyst concentration (0–1.0 M methanesulfonic acid) with 2% chitosan at 200 °C for 15–30 min. Fig. 3(a) reveals that a low catalyst concentration (below 0.1 M) increased 5-HMF yield to 15.0% at 15 min and decreased 5-HMF yield to 6.38% at 30 min. Increasing the catalyst concentration above 0.2 M maintained a low 5-HMF yield. Considering that an increase in methanesulfonic acid concentration would be associated with an increase in the availability and number of active sites of the catalyst [1,41], it is suggested that the degradation of 5-HMF to LA and FA in highly acidic conditions led to low 5-HMF yields [3,7,9]. Overall, a high 5-HMF yield was obtained with 0.1 M catalyst concentration for 15 min. In a comparable study, the yield of 5-HMF peaked at 2% catalyst concentration in the sulfuric acid-catalyzed hydrolysis of chitosan [9].

Fig. 3(b) shows that increasing the catalyst concentration to 0.7 M in a short reaction time of 15 min increased LA yield. However, further increases in the catalyst concentration decreased the yield. The highest LA yield (27.93%) was achieved with 0.7 M catalyst concentration for 15 min. At 30 min, the yield peaked at 27.88% with 0.2 M catalyst concentration. A higher catalyst concentration at 30 min led to a lower LA yield. This result indicates that a high catalyst concentration may cause a further decrease in LA concentration because of condensation to humins [3,7,9]. Overall, a high LA yield was achieved with low methanesulfonic acid concentration and longer reaction time. In comparison, Jeong [8] reported that sulfuric acid concentration did not considerably enhance LA yield at 175 °C in the conversion of glucosamine to LA. Rackemann et al. [36] reported that an optimal furfural yield was obtained with 0.25 M methanesulfonic acid concentration in the conversion of 0.3 M xylose. Furthermore, Rackemann et al. [37] produced LA from bagasse using methanesulfonic acid as catalyst in the range of 0.1–0.5 M. The highest LA yield from soda low lignin pulp was 76.8 mol% with 0.3 M methanesulfonic acid at 180 °C for 40 min [37]. Rackemann et al. [36] also reported that a high LA yield was obtained from glucose using 0.5 M methanesulfonic acid as catalyst (in the range of 0.25–0.75 M) under the following conditions: 180 °C for 30 min with 0.1 M glucose as substrate. Despite the higher cost of methanesulfonic acid compared with inorganic acid, methanesulfonic acid is a suitable catalyst for 5-HMF and LA production. Because it has low corrosivity, is easily biodegradable, and ultimately degrades to sulfate and CO₂, moreover, it causes less environmental problems during and after reaction [36,44]. In this study, further experiments were conducted to achieve a high LA yield with a low amount of catalyst by using 0.2 M methanesulfonic acid.

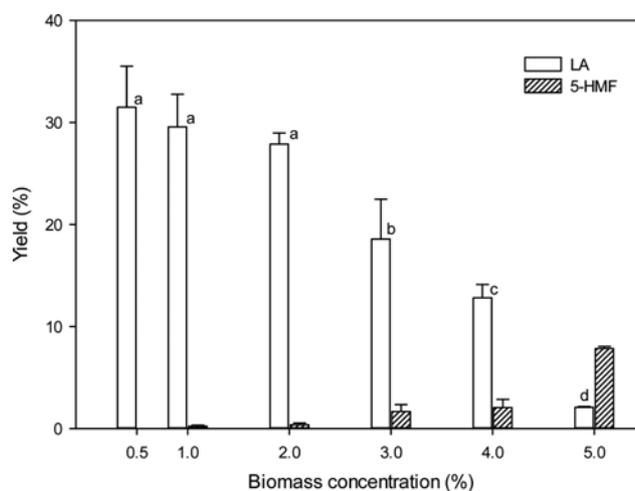


Fig. 4. Effect of the biomass concentration on 5-HMF and levulinic acid production from chitosan by methanesulfonic acid-catalyzed hydrothermal conversion under the 200 °C, 0.2 M methanesulfonic acid, and 30 min conditions. Different letters indicate significant difference with each biomass concentration ($P < 0.05$, Duncan's test).

sulfonic acid.

Fig. 4 shows the effect of 0.5–5% (w/w) chitosan concentration on 5-HMF and LA production at 200 °C using 0.2 M methanesulfonic acid for 30 min. The increase in chitosan concentration slightly increased 5-HMF yield. At 5% chitosan concentration, 5-HMF yield was 7.84%. However, a higher chitosan concentration sharply decreased LA yield. A chitosan concentration of 0.5% produced the highest LA yield (31.49%). Above 3% chitosan concentration, the yield was sharply reduced. At high chitosan concentrations, the limited amount of catalyst would prevent the efficient conversion of chitosan. These results indicated that the high LA yield at a low chitosan concentration may be explained by limitations in contact and activity between the biomass and catalyst at a certain catalyst concentration [8,40]. In comparison, LA yield was slightly decreased by increasing biomass concentration (50–120 g/L) in the sulfuric acid-catalyzed hydrolysis of glucosamine [8]. Rackemann et al. [36] also reported that the highest LA yield was obtained from 0.4 M glucose (in the range of 0.05–0.4 M) under the following conditions: 180 °C for 30 min with 0.25 M methanesulfonic acid as catalyst. Nevertheless, comparing the LA yield obtained in this study with others is difficult due to differences in reaction conditions (reactor design and material, heating rates, and substrate and catalyst) [36]. In particular, substrate types such as polymers (i.e., chitosan) or monomers (glucosamine and glucose) could significantly influence the production of 5-HMF or LA as polymers need to be hydrolyzed to monomers. By taking into consideration the concentration and yield of LA, further experiments on LA yield were carried out by using 2% chitosan.

Fig. 5 shows the effect of reaction time (0–120 min) on 5-HMF and LA production at 200 °C using 2% (w/w) chitosan and 0.2 M methanesulfonic acid. 5-HMF formation was increased until 10 min but subsequently declined over time. The highest 5-HMF yield (4.81%) was achieved at 10 min. After 10 min, the yield was sharply

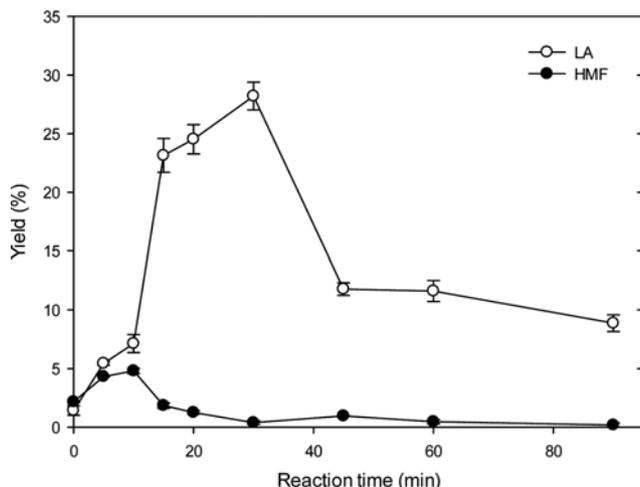


Fig. 5. Effect of the reaction time on 5-HMF and levulinic acid production from chitosan by methanesulfonic acid-catalyzed hydrothermal conversion under the 200 °C, 2% (w/w) chitosan, and 0.2 M methanesulfonic acid conditions.

decreased. However, LA yield showed a linearly increasing pattern until 30 min. At 30 min, the highest LA yield was 28.21%. After 30 min, the yield was sharply decreased and remained at below 8%. This result suggests that the degradation and condensation of 5-HMF and LA to humin products caused the decrease in LA yield, which may be attributed to a constant supply of heat energy and acidic conditions [3,9,43]. Based on the overall results, the reaction conditions for LA production from chitosan were optimized at 200 °C using 2% (w/w) chitosan and 0.2 M methanesulfonic acid for 30 min. Under this optimized condition, 28.21% LA and 0.39% 5-HMF were obtained. These results suggest the potential and availability of chitosan and methanesulfonic acid in the field of platform chemical production from renewable bioresources.

The recovery of LA from the product solution involved using

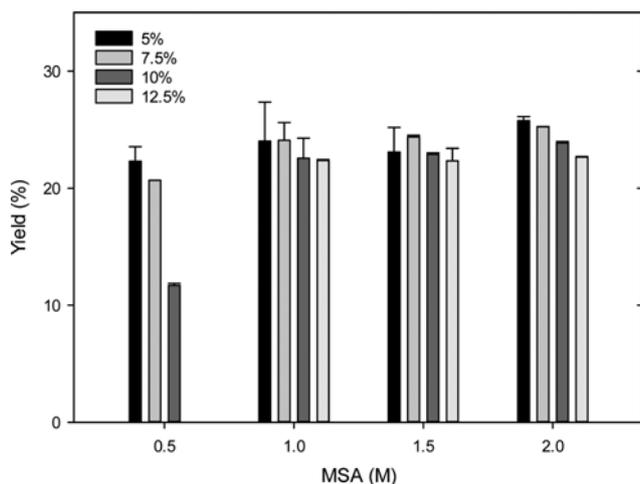


Fig. 6. Effect of the higher biomass and catalyst concentration on 5-HMF and levulinic acid production from chitosan by methanesulfonic acid-catalyzed hydrothermal conversion under the 200 °C and 15 min conditions.

vacuum distillation, solvent extraction, steam stripping, membrane separation, adsorption, and ionic liquids [7,14,45]. In this study, the recovery of LA from the product solution will be conducted by further study.

Fig. 6 shows the effect of high chitosan concentration (5-12.5% (w/w)) and methanesulfonic acid concentration (0.5-2.0 M) on 5-HMF and LA production at 200 °C for 15 min. In this experiment, a higher chitosan concentration increased the viscosity of the reactant, resulting in difficulties in mixing chitosan and methanesulfonic acid homogeneously. Moreover, 5-HMF yields were below 2% under these conditions. With 0.5 M methanesulfonic acid, LA yields were decreased following an increase in chitosan concentration. In particular, with 10% chitosan, only a LA yield of 11.69% was obtained. With 5% chitosan and 0.5 M methanesulfonic acid, 22.3% LA and 0.84% 5-HMF were obtained. With 1.0-2.0 M methanesulfonic acid, high LA yields were achieved at a low chitosan concentration of 5-7.5%. When chitosan concentration was increased to 10-12.5%, LA yields were decreased. The highest LA yield (25.77%) was obtained with 5% chitosan and 2.0 M methanesulfonic acid. Overall, a high LA yield was achieved with low chitosan concentration and high methanesulfonic acid concentration. Nevertheless, higher LA concentration was achieved under the condition of higher chitosan concentration.

Many researchers have proposed the conversion mechanism of 5-HMF, LA, and humins from various carbohydrates [3,8,10,36, 46-48]. The conversion mechanisms of fructose and glucose have been proposed, and these include isomerization, dehydration, rehydration, and condensation or polymerization [36,46,47]. Nevertheless, the conversion mechanism of chitosan to 5-HMF and LA has some differences compared with that of glucose or fructose because of the existence of the amine group (-NH₂) in the monomer [10, 11,48]. First, chitosan is hydrolyzed to glucosamine, which is a pyranose form with an amine group. This glucosamine is then converted to 5-HMF by isomerization, deamination, and dehydration, and LA is formed by the rehydration of 5-HMF [8,10,28].

2. Effect of the Combined Severity Factor

The effect of methanesulfonic acid-catalyzed hydrothermal reaction on the 5-HMF and LA yield from chitosan was investigated using the CSF. Fig. 7 shows the effect of the CSF and 5-HMF or LA yield in the methanesulfonic acid-catalyzed hydrothermal conversion of chitosan. The CSF value, which indicates the strength of the reaction, takes into consideration the temperature, time, and acidity of the solution. Higher CSF values represent severe reaction conditions [39,40]. The relationship between the CSF and 5-HMF yield was evaluated, demonstrating a linear increase in 5-HMF yield within the tested range (2.3-3 CSF). Above 3 CSF, increasing the CSF sharply decreased 5-HMF yields. Above CSF 3.7, the yield was nearly zero. The highest 5-HMF yield (15.0%) was achieved at 2.83 CSF. In addition, the relationship between the CSF and LA yield was evaluated, and an increase in the CSF caused a linear increase in LA yield within the tested range. The highest LA yield (31.4%) was achieved at a CSF of 4.01 (210 °C with 0.2 M methanesulfonic acid and 2% chitosan for 60 min). Above 3.2 CSF, the relationship between CSF values and LA yields could be divided into two groups: high and low LA yield. In the case of low LA yield, the reaction conditions included a high catalyst concentration or

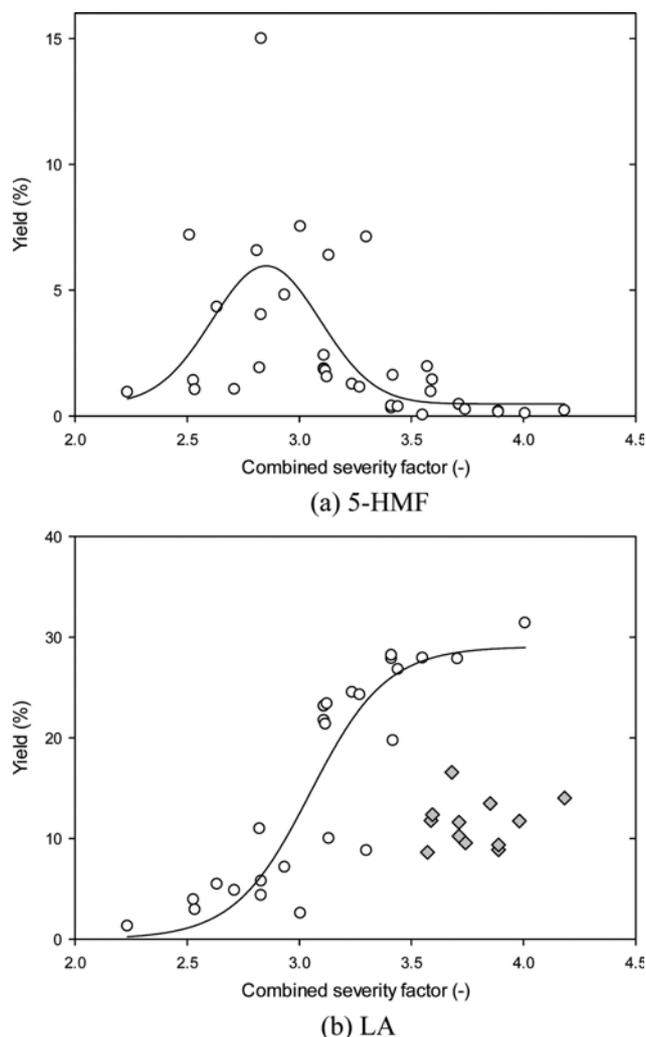


Fig. 7. Effect of the combined severity factor (CSF) on 5-HMF and levulinic acid production from chitosan by methanesulfonic acid-catalyzed hydrothermal conversion.

long reaction time. These harsh reaction conditions are thought to cause the over-degradation and condensation of LA to soluble and non-soluble humins [8,9,43].

3. Comparison of LA Production from Chitosan and Glucose

Due to differences in reactor design, heating method, heating rates, and the type and amount of substrate/catalyst, it is difficult to compare the conversion yield of various biomasses, catalysts, and processes [36]. Table 1 shows the results of comparable studies on

LA production from chitosan, bagasse, and glucose [10,36-48]. Omari et al. [10] achieved a LA yield of 23.9 wt% from chitosan at 200 °C with $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ as catalyst under microwave irradiation. Recently, Rackemann et al. [36] produced LA using methanesulfonic acid as catalyst; 63.13 mol% LA was obtained at 180 °C using 0.1 M glucose and 0.5 M methanesulfonic acid for 15 min. Furthermore, Rackemann et al. [37] reported that in the production of LA from bagasse using methanesulfonic acid, the highest LA yield from soda low lignin pulp was 76.8 mol% using 0.3 M methanesulfonic acid at 180 °C for 40 min. In another study, Mthembu [38] produced LA from glucose solution using methanesulfonic acid; a LA yield of 34.9% was obtained from 42 g/L glucose solution using 0.5 M methanesulfonic acid at 180 °C for 45 min. Similarly, in this study, a LA yield of 28.21% was obtained at 200 °C using 2% (w/w) chitosan and 0.2 M methanesulfonic acid for 30 min in the methanesulfonic acid-catalyzed hydrothermal reaction. Nevertheless, comparing the LA yield obtained in this study with others is difficult because of differences in reaction conditions (reactor design and material, heating rates, and substrate and catalyst) [36]. In particular, substrate types such as polymer (i.e., chitosan) or monomer (i.e., glucosamine and glucose) could significantly influence the production of 5-HMF or LA as polymers need to be hydrolyzed to monomers.

CONCLUSIONS

This study has introduced methanesulfonic acid, which is strongly acidic and biodegradable, as a catalyst in the chitosan conversion to LA. At 200 °C and 30 min with 2% chitosan and 0.2 M methanesulfonic acid, a LA yield of $28.21 \pm 1.20\%$ was obtained. The relationship between CSF and LA yield was evaluated, and an increase in the CSF was found to cause a linear increase in LA yield within the tested range. Above 3.2 CSF, the relationship between CSF values and LA yields could be divided into two groups: high and low LA yield. In the low LA yield group, the reaction conditions included a high catalyst concentration or long reaction time. Our findings suggest that chitosan can be a good bioresource for the production of platform chemicals. Furthermore, methanesulfonic acid would be a suitable catalytic system for bioenergy production.

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Table 1. Comparison of LA production from chitosan and others

Biomass	Reaction conditions	LA	References
Chitosan	MI*, 200 °C, 100 mg chitosan with 4 mL water, 0.24 mmol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 30 min	23.9 wt%	[10]
Glucose	CH**, 180 °C, 0.1 M glucose, 0.5 M methanesulfonic acid, 15 min	63.13 mol%	[36]
Glucose	CH**, 180 °C, 42 g/L glucose, 0.5 M methanesulfonic acid, 45 min	34.9%	[38]
Bagasse	CH**, 180 °C, soda low lignin pulp, 0.3 M methanesulfonic acid, 40 min	76.8 mol%	[37]
Chitosan	CH**, 200 °C, 2% (w/w) chitosan, 0.2 M methanesulfonic acid, 30 min	28.21 wt%	This work

*MI : microwave irradiation; **CH : conventional heating

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