



Research article

Thermo-chemical conversion for production of levulinic and formic acids from glucosamine

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ARTICLE INFO

Keywords:

Glucosamine
Methanesulfonic acid
Levulinic acid
5-hydroxymethylfurfural
Formic acid
Platform chemicals

ABSTRACT

Glucosamine is a monomer of chitin/chitosan, which is a renewable aquatic resource and the second most abundant biopolymer on the Earth. Moreover, methanesulfonic acid (MSA) is known as an eco-friendly green catalyst. In this study, the MSA-catalyzed conversion of glucosamine to levulinic (LA) and formic (FA) acids was optimized using the Box-Behnken statistical approach. The optimal conditions for LA yield were 50 g/L glucosamine, 0.5 M MSA, 200 °C and 30 min, which yielded 49.9% LA and 50.8% FA. The LA yield increased linearly with increasing combined severity factor (CSF) until 3.5 and then, was maintained as the CSF value was further increased. The FA yield behaved similarly to LA. Both trends fitted well to a sigmoid regression model with a high regression value. These results highlight the potential of glucosamine for biofuel and chemicals production via an MSA-catalyzed conversion system.

1. Introduction

Renewable bioresources, such as lignocellulosics, and macro- and micro-algae, can be considered attractive alternatives of fossil resources [1–3]. Platform chemicals can be produced from several carbohydrates to replace the carbon skeleton derived from fossil resources [1,2,4,5]. Moreover, these platform chemicals can be converted to various valuable chemicals and materials [2,3]. Especially, to replace petrochemical route, it has been widely investigated the conversion of lignocellulosic biomass to platform chemicals such as 5-hydroxymethylfurfural and levulinic acid [2,6,7]. Recently, the hydrothermal conversion of bio-wastes, which is cheap and readily available method, such as various straws, husks, shells and peels, sawdust, paper mill sludge, tobacco chops, spent coffee grounds and cooked tea leaves waste are applied as biomass for the production of LA [8,9].

Among the platform chemicals, levulinic acid (4-oxopentanoic acid; LA), which is considered a valuable bio-based chemical according to the United States Department of Energy (U.S. DOE), is a versatile green chemical due to its two reactive groups (one carbonyl and one carboxylic acid group) with a high potential to be converted into a diverse range of chemicals, fuels and materials [1,2,4,5,10]. The LA is potentially applied to the wide range of fields as fuels (2-methyltetrahydrofuran, 5-nonanone), solvents (γ -valerolactone), functionalized oxygenates (acrylic acid, succinic acid, oxo-esters), plasticizers (1,4-butanediol, 1,4-pentanediol), polymers (Nylon 6,6 (polyamide)), resins (diphenolic acid, acrylic acid), anti-freezing agents (sodium levulinate),

pharmaceutical agents (5-bromolevulinate), herbicides (δ -aminolevulinic acid), flavouring agents (α -angelicalactone, ethyl levulinate) and so on [2,5,7,11–16]. Nowadays, LA is commercially obtained by a petrochemical route, causing environmental issues and consumption of fossil resources [2,5]. Consequently, several works have focused on LA production from renewable bioresources using a range of thermo-chemical processes [2,3,5,7,10,17,18].

Formic acid (FA, methanoic acid) is a simple carboxylic acid that is an important chemical intermediate in organic synthesis and widely applied in industrial fields [2,19–21]. Particularly, the reactions involving FA have been widely considered for the production of hydrogen, chemicals, and alkanes from biomass feedstocks [2,20,22]. More recently, FA has attracted considerable attention as a promising eco-friendly storage and transportation medium for hydrogen, due to the demand for the development of clean renewable energy carriers [19,23]. For considering FA as hydrogen storage medium, the selective dehydrogenation of FA required to produce on-demand hydrogen. The release of H₂ from FA can proceed by decarboxylation of FA into CO₂ and H₂. Also, the possible decarbonylation of FA is the formation of CO and H₂O. These pathways can be controlled by application of suitable homogeneous and heterogeneous catalysts and reaction conditions [24]. The homogeneous catalyst for FA dehydrogenation was firstly reported using several transition-metal complexes (noble metal-based catalyst) with phosphine ligands [25]. Recently, the efficient dehydrogenation (hydrogen liberation) from formic acid using highly active iron catalyst system (Fe(BF₄)₂·6H₂O/P(CH₂CH₂PPh₂)₃) was reported [26].

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During the carbohydrate conversion to platform chemicals, the formation of humins, which is a mixture of dark colored, soluble and insoluble polymers, and heterogeneous amorphous biomacromolecules, takes place as typical side-reaction [27]. The formation mechanism is supposed to be acid-catalyzed condensation between carbohydrate and intermediates during sugar conversion to 5-HMF and LA [28].

In this study, we investigated glucosamine (2-amino-2-deoxy-D-glucopyranose) as a substrate for producing FA and LA. Glucosamine is a major component of chitin/chitosan, the second most abundant biopolymer after cellulose [29,30]. Large amounts of chitin/chitosan, the main structural component of crustacean and insect exoskeletons, are recovered from food waste such as crab and shrimp shells [29,31]. Chitin/chitosan and glucosamine have been widely applied in various industrial fields due to their biocompatible, biodegradable, and non-toxic properties [31]. Consequently, several processes have been investigated for converting chitin/chitosan into 5-hydroxymethylfurfural (5-HMF) and LA as valuable platform chemicals [17,18,32–34]. Moreover, the conversion of *N*-acetyl-*D*-glucosamine to 3-acetamido-5-acetylfuran (*N*-substituted furan) was reported to apply as potential and renewable amines [35].

Efficient conversion of glucosamine using a useful catalyst system is a key step for producing valuable fuels and chemicals [17,18,32,34]. Methanesulfonic acid (MSA) is a strong acid ($pK_a = -1.9$) and is also eco-friendly due to its non-oxidizing, non-foaming, low corrosion, and biodegradable properties, compared to strong inorganic acids, such as sulfuric and hydrochloric [36,38]. Also, it is less toxic (LD_{50} (oral, rat) = 1158 mg/kg), and considered as part of natural sulfur cycle [39]. Therefore, MSA is an attractive alternative to organic and inorganic acids in some processes such as esterification, alkylation, dehydration, condensation, and solvolysis liquefaction of biomass [36,38]. Although the attractive potential of MSA as catalyst is reported in several reaction, there has been limited information reported on 5-HMF and LA production from carbohydrates. Especially, the application of MSA on the production of platform chemicals from chitin, chitosan and glucosamine was not reported.

In this study, we evaluated the possibilities of glucosamine as a renewable feedstock, and MSA as a strong and eco-friendly catalyst for producing valuable platform chemicals such as 5-HMF, FA and LA. In order to optimize the production of LA and FA from glucosamine, the effects and reciprocal interactions of the key reaction variables (reaction temperature, substrate concentration, catalyst amount, and reaction time) were investigated. Also, the efficiencies of MSA-catalyzed conversion were assessed using the combined severity factor (CSF).

2. Materials and methods

2.1. Materials

Glucosamine HCl was obtained from Sigma – Aldrich Co. Ltd. (USA). MSA (Samchun Pure Chemical Co., Ltd., Korea) was of reagent grade. LA, FA and 5-HMF were of analytical grade.

2.2. Batch experimental procedure

In preliminary work, 2-mL glass vials were loaded with pre-defined concentrations of glucosamine (as substrate) and MSA (as a catalyst), sealed, shaken to allow sufficient mixing and then placed into a stainless-steel reactor for hydrothermal reaction. The reaction was monitored and adjusted by a PID temperature controller in an oil bath. The reactor required approximately 5 min to reach temperature. After the selected reaction time, the reactor was rapidly cooled to room temperature by quenching in tap water. For high-performance liquid chromatography (HPLC) analysis, the product was recovered by centrifugation at 17,000 rpm for 10 min and then filtered through a 0.2- μ m syringe filter [40].

2.3. Experimental design and statistical analysis

For experimental design and statistical analysis, a three-level, four-factor Box-Behnken design was applied using Design-Expert 9 software (Stat-Ease, Inc., USA). The four experimental variables were reaction temperature, substrate concentration, catalyst amount, and reaction time. The model equation was estimated by multiple regression, and the model quality was assessed using the coefficients of determination (R^2) and analysis of variance (ANOVA) [40].

The quadratic response surface model was estimated according to Eq. (1).

$$Y = \beta_{k0} + \sum_{i=1}^4 \beta_{ki}x_i + \sum_{i=1}^3 \sum_{j=i+1}^4 \beta_{kij}x_ix_j + \sum_{i=1}^4 \beta_{kii}x_i^2 \quad (1)$$

where Y is the response variable (product yield), x_i is the i th independent factor, β_0 is the intercept, β_i is the first-order model coefficient, β_{ii} is the quadratic coefficient for the factor i , and β_{ij} is the linear model coefficient for the interaction between variables i and j [40].

2.4. Effect of CSF

The effects of the MSA-catalyzed hydrothermal reaction on the production of LA, FA and 5-HMF from glucosamine were assessed using the CSF as follows [3,41]:

$$\text{CSF} = \log(R_0) - \text{pH}, \quad \text{with } R_0 = t \exp.(T - T_{ref})/14.75 \quad (2)$$

where $T(t)$ is the reaction temperature ($^{\circ}\text{C}$), T_{ref} is the reference temperature (100), t is the reaction time (min), and 14.75 is the fitted value of the arbitrary constant. The pH values were measured at room temperature before hydrothermolysis [3,41].

2.5. Analysis

The concentrations of FA, LA, and 5-HMF were analyzed using an Agilent 1100 HPLC system (USA) equipped with a Bio-Rad[®] Aminex-87H column and refractive index detector. The HPLC was operated at 65 $^{\circ}\text{C}$ oven temperature with 5 mM sulfuric acid as the mobile phase at 0.6 mL/min flow rate [40].

2.6. Yield calculation

The product yields were calculated by the following equation: Product yield (mol%) = mole concentration of product (M)/mole concentration of initial substrate (M) \times 100. The results were presented as average \pm standard deviation (SD).

3. Results and discussion

This study investigates the possibility of using glucosamine as a feedstock for producing platform chemicals (FA, LA and 5-HMF) by MSA-catalyzed hydrothermal reaction. The reaction factors were optimized using a Box-Behnken design.

3.1. Production of platform chemicals

Table 1 shows the design and results of the MSA-catalyzed hydrothermal reaction of glucosamine. The conditions for the highest 5-HMF yield, 2.34%, were 100 g/L glucosamine, 0.1 M MSA, 160 $^{\circ}\text{C}$, and 40 min. Conversely, the highest LA yield, 48.9%, was generated from 50 g/L glucosamine and 0.3 M MSA at 200 $^{\circ}\text{C}$ for 40 min. Moreover, the highest FA yield, 48.8%, was achieved from 50 g/L glucosamine and 0.3 M MSA at 180 $^{\circ}\text{C}$ for 60 min. Therefore, the ideal conditions for a high 5-HMF yield were low temperature, low catalyst concentration and short reaction time. However, high LA and FA yields were obtained

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