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Production of levulinic acid from glucosamine by dilute-acid catalyzed hydrothermal process

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ABSTRACT

Glucosamine is a basic unit of the chitin/chitosan structure, which is derived from crustacean (e.g. crab, shrimp) and insect shells. In this study, the production of levulinic acid (LA) from glucosamine via dilute-acid-catalyzed hydrothermal hydrolysis was investigated. Among the reaction conditions, reaction temperature, reaction time, and substrate concentration were more effective than catalyst concentration. The optimal conditions for LA production, as determined by the response-surface methodology (RSM), were as follows: 188 °C reaction temperature, 4 wt% catalyst concentration, 49 min reaction time, 120 g/L substrate concentration. Under these conditions, the LA yield was 30.3 g/L (25.3 wt%), while the 5-HMF concentration was zero. These results might provide basic knowledge essential to the production of valuable chemicals derivable from renewable marine resources and utilizable as fuel additives and polymer building blocks.

1. Introduction

Amid concerns about fossil-fuel depletion and supply limitations, renewable energy has received significant attention. Several forms of renewable energy, especially bioenergy such as liquid fuel and chemicals, can be produced from sugar-, starch- or wood-based feedstocks by thermo-chemical and biochemical processes (Hoekman, 2009; Jeong and Park, 2010; Schenk et al., 2008). Recently too, marine feedstocks (micro-algae and macro-algae) and crustaceans' waste shells have been introduced to the bioenergy production process (Jang et al., 2012; Jeong and Park, 2010, 2011; Meinita et al., 2013; Omari et al., 2012; Wang et al., 2013).

The carbohydrates of biomass are composed mainly of hexose and pentose as the basic compositional units. These sugars are converted to various fuels and chemicals such as ethanol, butanol, lactic acid, 5-hydroxymethylfurfural, levulinic acid and furfural by hydrothermal, thermo-chemical or biochemical processes (Hayes et al., 2006; Jang et al., 2012; Jeong and Park, 2010, 2011; Meinita et al., 2013; Wang et al., 2013).

Chitin, a natural polysaccharide, is a polymer of partially deacetylated β-(1-4) *N*-acetyl-D-glucosamine residue (Rinaudo, 2006) (Fig. 1). It is produced from crustacean (e.g. crab, shrimp) and insect shells, the skeletal components of molluscs (e.g. squid), and the cell-wall components of fungi, yeasts, and mushrooms. The annual generated amount is estimated to be about one hundred billion tons, which is comparable to the amount of cellulose on land (Coh et al., 2003; Inokuma et al., 2013). Indeed, chitin's chemical structure is similar to that of starch or cellulose (Coh et al., 2003). Most recently, utilization of glucosamine has focused on health-food, feed, pharmaceutical and medical applications. Additionally, some work on the production of biofuels and chemicals, for example of 5-HMF, LA and ethanol from chitosan, chitin and glucosamine, has been reported (Coh et al., 2003; Inokuma et al., 2013; Omari et al., 2012; Wang et al., 2013).

Chemical intermediates, versatile chemical platform compounds such as 5-hydroxymethylfurfural (5-HMF) and levulinic acid, are converted from biomass-derived sugars by a thermo-chemical process (Hayes et al., 2006; Inokuma et al., 2013; Jeong and Park, 2010, 2011; Omari et al., 2012). 5-HMF can be converted into many chemicals such as 2,5-dihydroxymethylfuran, 2,5-bis(hydroxymethyl) tetrahydrofuran, and 2,5-dimethylfuran, which are promising liquid fuels, or 5-furandicarboxylic acid, which can be used instead of terephthalic acid in polyester production (Chheda et al., 2007; Hu et al., 2009; Ilgen et al., 2009; Mascal and Nikitin, 2010; Omari et al., 2012). Moreover, it can be converted to liquid fuel as a potential alternative to bioethanol (Hoekman, 2009; Jeong and Park, 2010; Lecomte et al., 1999; Su et al., 2009).

Levulinic acid (4-oxopentanoic acid, LA), one of the 12 compounds selected by the U.S. Department of Energy (DOE) as "Top Value Added Chemicals from Biomass" (PNNL and NREL, 2004), is along with its derivatives, a substitute for chemical intermediates in the synthesis of fine chemicals and plastics. LA is the

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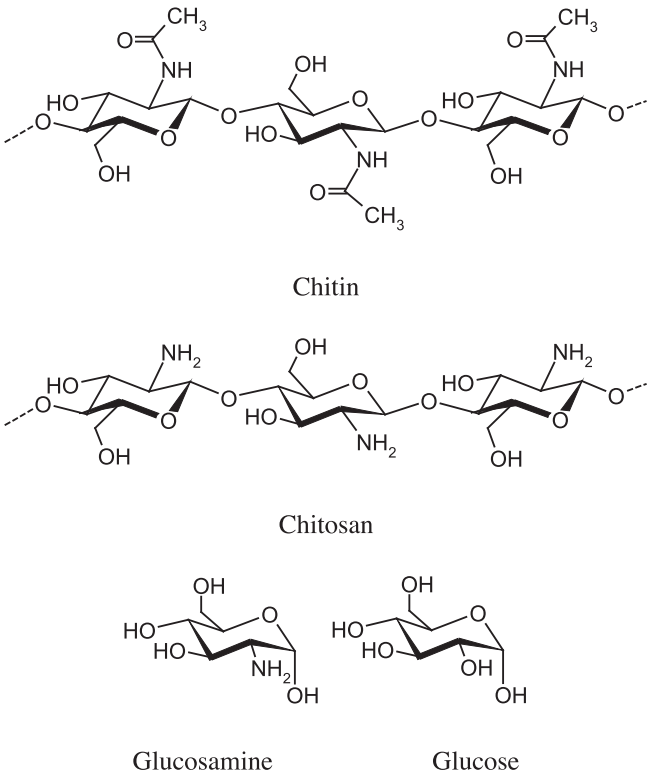

Fig. 1. The structure of chitin, chitosan and glucosamine.

starting material to synthesize many chemicals such as ethyl levulinate and 2-methyltetrahydrofuran (used as diesel fuel additives), 1,4-pentanediol, diphenolic acid and β-acetylacrylic acid (used as polymer building blocks), and δ-aminolevulinic acid (used as a herbicide) (Mascal and Nikitin, 2010; Omari et al., 2012). For all of that, the high production costs of 5-HMF and LA remain an obstacle to their commercialization (Hayes et al., 2006; Jeong and Park, 2011; Schenk et al., 2008).

The response-surface methodology (RSM), which, by means of multiple regression analysis, can assess effects among independent factors and their reciprocal interactions, has been applied to the optimization of chemical and biochemical processes (Jeong et al., 2007; Jeong and Park, 2010, 2011). In the present study, we optimized LA conversion from glucosamine via a dilute-acid catalyst and the RSM. In order to evaluate the effects of four experimental parameters (reaction temperature, reaction time, catalyst concentration, substrate concentration) and their reciprocal interactions on LA yield, we applied the RSM's five-level-four-factor central composite rotatable design (CCRD).

2. Experimental

2.1. Chemicals

Glucosamine HCl as the substrate, 5-hydroxylmethylfurfural, sulfuric acid and calcium carbonate, as obtained (Sigma–Aldrich Co. Ltd., USA), were of reagent grade. The LA (Acros Chemicals, Japan) was of analytical grade. All of the other chemicals used also were of analytical grade.

2.2. Batch experimental procedure

Preparatory to a batch reaction, the designed concentrations of substrate and catalytic sulfuric acid were filled into a glass bottle of 2 mL size. The bottle was sealed by firing and then inserted into a stainless steel reactor. The temperature of the reactor was controlled by means of an oil bath equipped with a PID temperature controller. Upon completion of the reaction, the reactor was quickly cooled to room temperature using cool water. The hydrolysate was neutralized to pH 6.5 with calcium carbonate, and then the supernatant was separated by 20 min of 15,000 rpm centrifugation. The supernatant finally was recovered and filtered through a 0.2 μm syringe filter for use as an HPLC sample.

Table 1
Factors and their levels in CCRD.

Factors	Symbol	Coded factor levels				
		−1.68	−1	0	1	1.68
Reaction temperature (°C)	X_1	145	160	175	190	205
Catalyst amount (wt%)	X_2	1	2	3	4	5
Reaction time (min)	X_3	5	20	35	50	65
Substrate conc. (g/L)	X_4	30	60	90	120	150

2.3. Experimental design and statistical analysis

As the experimental design, a five-level-four-factor CCRD requiring 30 experiments was introduced (Jeong et al., 2007). The experimental parameters (and their levels) were as follows: reaction temperature (145–205 °C), catalyst concentration (1–5 wt%), reaction time (5–65 min), substrate concentration (30–150 g/L). Table 1 lists the coded and uncoded parameters (X_i) and their levels. The data's statistical significance was evaluated via multiple regression using the Design-Expert 7 program (Stat-Ease, Inc., USA). The quality of the second-order polynomial equation model was evaluated based on the coefficient of determination (R^2) and analysis of variance (ANOVA) (Jeong et al., 2007; Jeong and Park, 2010, 2011). The model was adjusted to the following Eq. (1),

$$Y = \beta_0 + \sum_{i=1}^{4}\beta_i x_i + \sum_{i=1}^{3}\sum_{j=i+1}^{4}\beta_{ij} x_i x_j + \sum_{i=1}^{4}\beta_{ii} {x_i}^2 \quad (1)$$

where Y is the response, x_i the ith independent parameter, β_0 the intercept, β_i the linear coefficient, β_{ii} the quadratic coefficient, and β_{ij} the interaction coefficient between i and j.

2.4. Analytical method

The concentrations of 5-HMF and LA were analyzed using an Agilent 1100 HPLC system (Agilent, San Jose, CA, USA) with a refractive index detector. The sample was separated using a Bio-Rad Aminex-87H column at a 60 °C oven temperature. The mobile phase was 5 mM sulfuric acid, and the flow rate was 0.6 mL/min.

3. Results and discussion

3.1. Formation of LA and 5-HMF

The possibility of LA and 5-HMF formation from glucosamine was determined by dilute-acid-catalyzed hydrothermal reaction. Fig. 2 shows the time-course of those formations under the 175 °C reaction temperature, 3 wt% catalyst concentration, and 90 g/L substrate concentration conditions during 35 min of reaction time. With the passage of reaction time, the formation of LA was sharply increased: at 65 min, 21.3 g/L of LA had been produced. Significantly, the 5-HMF concentration was as high as 1.59 g/L at 5 min, whereas, past 5 min, it decreased. At 65 min, 5-HMF was not detectable. Generally, it is known that LA is converted from 5-HMF by hydration: initially, glucosamine is converted to 5-HMF, and subsequently, 5-HMF is degraded, by hydration, to LA and formic acid (Hayes et al., 2006; Jeong and Park, 2010; Su et al., 2009).