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Levulinic acid production through two-step acidic and thermal treatment of food waste using dilute hydrochloric acid

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Abstract−This research investigated the concept of a two-step acidic and thermal treatment for glucose extraction and levulinic acid (LA) production from food waste using dilute hydrochloric acid (DHA) as a catalyst, and subsequently analyzed the properties of the resulting humins. Glucose extraction was performed under various reaction conditions (reaction temperature range: 120-190 °C, DHA concentration range: 0.2-0.5% v/v); the glucose extraction yield of the acidic treatment step reached 83.17% under the optimal conditions (150 °C in 0.5% DHA). LA production was achieved during the thermal treatment step, which was investigated using two independent experiments to determine the influence of the reaction conditions (reaction time: 5-140 min, concentration factor: 1.5-3.0, reaction temperature: 160-190 °C). The LA production process was affected by the concentration factor and the reaction temperature due to the low pH of solution and the rapid reaction rate, respectively. The thermal stability of the humins was highest at a concentration factor of 3.0 because of the 13.07 C/H ratio of the humins.

Keywords: Food Waste, Glucose, Levulinic Acid, Humins, Dilute Hydrochloric Acid

INTRODUCTION

The demand for food and energy is expanding exponentially each year due to the increase in global population [2,6]. The combination of ineffective waste management strategy and sudden urbanization can lead to the accumulation of food waste, which causes serious environmental issues. Only a few methods currently exist to treat these massive quantities of food waste. While precautionary measures to reduce the generation of food waste are a good solution, the treatment of accumulated food waste still must be solved [28].

Food waste is an abundant resource that does not affect the food supply, thus avoiding the ethical issues associated with some other food-based technologies. It has significant potential as an alternative material for the production of fuel and other industrially available chemicals [8,35]. Food waste can be converted into a diverse range of functionalized molecules through various routes: value-added compounds can be produced via extraction, fly ash through incineration, bioethanol or butanol through pre-treatment and subsequent fermentation, and methane gas through anaerobic digestion [4,5].

Levulinic acid (LA), or 4-oxopentanoic acid, has been classified as one of the twelve most noteworthy value-added chemicals by the United States Department of Energy (DOE) [44,46]. LA is synthesized by several consecutive steps: a conversion step in which glucose is isomerized to fructose, a dehydration step to form the cyclic intermediate 5-hydroxymethylfurfural (HMF), and a hydrolyzation step to yield the acyclic compounds LA and formic acid (FA) [1,35]. LA is a short fatty acid chain comprising a ketone group and a carboxyl group; these two functional groups make LA a versatile platform molecule that can be used to produce a variety of value-added chemicals with potential industrial applications [26,42]. In particular, compounds derived from LA can be utilized as feedstocks for the production of transportation fuels, such as gasoline and diesel. For instance, levulinic esters can be used as diesel additives, and 2-methyl-tetrahydrofuran (MTHF) can serve directly as a gasoline blend-stock [3,7] Additionally, γ-valerolactone (GVL) can be used as an alternative to ethanol in gasoline-ethanol blend liquid transportation fuels [14].

The presence of water-insoluble humins can lead to the undesirable formation of black lumps in the LA production process [21]. In continuous-mode biorefining processes, humins are removed to avoid pipeline or reactor blockage, and to eliminate their inhibitory effect on the LA recovery [25]. However, the humins originate from glucose, fructose, or HMF, and have a higher thermal stability than the raw materials owing to their high carbon content. In fact, potential industrial applications of humins have been considered due to the finding that the thermal stability of humins increases as the amount of unreacted cellulose in the residual solids of the LA production process decreases [43].

The conversion of lignocellulosic biomass into a feedstock for LA production using homogeneous catalysts (HCl, HNO_3, H_2SO_4, etc.) has been investigated due to the high hexose sugar content of biomass [15,16,19,41]. However, to obtain pure hexose sugars from biomass requires a two-step fractionation process. The first step involves the extraction of hemicellulose using acidic catalysts, and in the second, lignin is extracted using an alkaline. Unreacted cellulose and

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lignin are undesirable in the LA production process, as they can give rise to unfavorable results, such as the disruption of the conversion of hexose sugars and LA production [15,24]. Additionally, the residual solids associated with lignin and humins have high adhesive strength and tend to clog reactors and pipelines [21,43]. In contrast, LA production from food waste requires only a simple acidic fractionation process to extract the hexose sugars, which are dissolved in the liquid. Unlike the solid-based feedstock used in the production of LA from biomass, food waste feedstocks are liquid-based. This difference can improve the LA production yield and selectivity; additionally, the residual solids after LA production do not contain undesirable substances, like unreacted cellulose and lignin. Thus, the humins in residual solids of food waste-based LA production may be particularly suitable for industrial applications. Finally, LA production is a two-step acidic and thermal treatment to increase the effect of LA production by inhibiting the inducing of humins based on liquid feedstock.

The objectives of our research were to investigate the concept of a two-step acidic and thermal treatment for glucose extraction and LA production from food waste using dilute hydrochloric acid (DHA) as a catalyst, and to analyze the properties of the resulting humins.

MATERIALS AND METHODS

1. Raw Materials

The raw food waste used in this study was provided by multi-treatment process from Ultra Feed Company in Anseong, Korea. The Korean food waste was dewatered by a screw press and dried by a steam boiler at 150 °C. The dried waste was ground by a grinder and separated by a trammel separator. The sample particles had a moisture content of 5.5% based on the total wet food waste weight. However, the food waste was not dried, as its chemical composition could be affected by high temperature. Because of this, we adjusted the dilution of the DHA solution to take the existing moisture content of the waste into account. Hydrochloric acid (HCl, 36% w/w), sulfuric acid (H_2SO_4, 96% w/w), and sodium hydroxide (NaOH, 98% w/w) were purchased from DAEJUNG, ACROS, and SAMCHUN, respectively.

2. Glucose Extraction via Acidic Treatment

As the first step, we subjected the food waste to acidic treatment under various conditions to obtain the best extraction yield of glucose. The treatments were conducted in 30 ml tubular reactors constructed from stainless steel tubing (SS316) (KHT Engineering Co. Ltd., Gunpo, Gyeonggi, Korea) with a long bomb of 86 mm and an inner diameter of 25.4 mm. The reactors were capped and placed in an oil bath (LKLAB Co Ltd., Namyangju, Korea). Each reactor was loaded with 1.0 g of food waste (wet basis) and corrected DHA solution (0.2-0.5% w/w) at a solid:liquid ratio of 1 : 10 (g/ml). The reactions were performed at a temperature of 120-190 °C for 70 min (preheating and cooking time were 10 and 60 min, respectively). When the reaction time had elapsed, the reactors were promptly transferred to a water bath for 10 min to quench the reactions. The slurry was transferred into a 50 ml conical tube and centrifuged at 5,000 rpm for 10 min to separate it into two phases, the fractionated solid and the liquor. Subsequently, 2 ml of the liquor was transferred to a 15 ml conical tube and hydrolyzed using 0.1 ml of sulfuric acid (72% w/w) in an autoclave (HEMOSS, Korea) at 121 °C for 60 min. The hydrolysates were analyzed to determine the extraction yield of glucose using a high performance liquid chromatograph (HPLC).

3. Scale-up to a 7 L Reactor under the Optimal Conditions

We scaled the process up using the optimal conditions to obtain a large amount of hydrolysates for LA production. A capped 7 L reactor constructed from stainless steel tubing (SS316) (KHT Engineering, Korea) used. The reactor was loaded with 400 g of food waste (wet basis) and 0.5% DHA solution at a solid:liquid ratio of 1 : 10. The reactions were performed using the optimal conditions (150 °C for 60 min) determined for the 30 ml reactors. The fractionated solid and liquor were separated using a pressure-reducing filtration system. The liquor was hydrolyzed at pH 1±0.05 using sulfuric acid (96% w/w) in an autoclave at 121 °C for 60 min to convert the oligomeric sugars into monomeric sugars [17]. The fractionated solid was recovered after washing with deionized water and was analyzed to calculate the extraction mass balance (EMB).

4. Production of Levulinic Acid via Thermal Treatment

Prior to LA production, we carried out a concentration process to adjust the glucose content and pH of the hydrolysate and to extract salt compounds without additional catalyst inflow. The hydrolysate was concentrated by various factors (1.5-3.0) at 105 °C. The salt compounds were recovered using a pressure-reducing filtration system. Subsequently, the thermal treatment step was carried out using various conditions to obtain the best carbon yield of LA using a 30 ml tubular reactor. The reactors were loaded with 5.0 ml of the concentrated hydrolysate. The reactions were performed at 160-190 °C for 5-140 min. When the reaction time had elapsed, the reactors were promptly transferred to a water bath for 10 min. The mixtures were separated into humins and LA-based liquor by filtration with a previously weighed filter paper (ADVANTEC Qualitative Filter Paper Grade 2, 5-10 μm, 110 mm). The LA-based liquor was analyzed to calculation the conversion ratio of glucose and the carbon yield of the products (HMF and LA) using the HPLC.

The conversion ratio of glucose (CR_{glu}) was calculated using Eq. (1):

$$CR_{glu} = \frac{n_{initial} - n_{final}}{n_{initial}} \quad (1)$$

where $n_{initial}$ and n_{final} are defined as the number of moles of glucose before the concentration process and the number of moles of glucose in the concentrated hydrolysate, respectively. The carbon yield of the products ($CY_{products}$) was calculated using Eq. (2):

$$CY_{products} = \frac{C_{products} \times n_{products}}{C_{glucose} \times (n_{initial} - n_{final})} \quad (2)$$

where $C_{glucose}$ and $C_{products}$ are defined as the number of carbon atoms of glucose and the products, respectively, and $n_{products}$ is the number of moles of the products obtained from HPLC analysis.

5. Analysis of the Properties of the Solid Fractions

The solid fractions included the raw material, the fractionated solid, and the humins. The chemical composition of the raw material and fractionated solid were analyzed using the National Renewable Energy Laboratory (NREL) standard analytical procedures NREL/TP-510-42619 (determination of extractives in biomass), NREL/

TP-510-42618 (determination of structural carbohydrates and lignin in biomass), NREL/TP-510-42623 (determination of sugars, byproducts, and degradation products in liquid fraction process samples), and NREL/TP-510-42622 (determination of ash in biomass) [30-33].

The raw material and humins were analyzed to assess their thermal stability and to measure their content of CHNS-O elements using thermogravimetric analysis (TGA, PerkinElmer, Co., Ltd., Pyris 1, USA) and an automatic elemental analyzer (AEA, Thermo Scientific, FlashSmart, Germany), respectively.

6. Analysis of the Content of Glucose, LA, and other Chemicals in the Liquid Fractions

The liquid fractions included the hydrolysate, concentrated hydrolysate, and LA-based liquor. The concentration of sugars (glucose, xmg, and arabinose), organic acids (formic acid, acetic acid, and levulinic acid), and decomposition products (5-hydroxymethylfurfural and furfural) in these liquid fractions was quantitatively analyzed using HPLC (Shimadzu Co., Nakagyo, Kyoto, Japan), which was equipped with refractive index (RI) and ultraviolet (UV) detection. The samples were filtered using a syringe filter before analysis (HLB-M, 0.45 μm pore size, Advanced Microdevices Pvt, Ltd). The column (Aminex HPX-87H, 300 mm×7.8 mm, Bio-Rad Laboratories Inc., Hercules, CA) was maintained at 60 °C, with 0.005 N H_2SO_4 as the mobile phase and a flow rate of 0.6 mL/min for 50 min. The sugars, organic acids, and decomposition products were identified from their RI and UV peak values and subsequently quantified by comparison to the retention times of authentic standards.

The elemental composition of the salt compounds in the concentrated hydrolysates was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer, Co., Ltd., Optima 8300, USA).

In this paper, XMG (capitalized) is defined as the sum of the oligomeric sugars (xylan, mannan, and galactan), while xmg (small letters) is the sum of the monomeric sugars (xylose, mannose, and galactose). The quantification and calibration of xmg was calculated on a xylose basis, because the Aminex HPX-87H column does not distinguish peaks of monomeric sugars [38,39]. Also, the xmg is composed of the xylose more than 90% [38].

RESULTS AND DISCUSSION

1. Chemical Composition of the Food Waste

The carbohydrate composition of the food waste was determined to be 22.93±0.92% glucan, 7.66±0.23% XMG (xylan+mannan+galactan), and 3.73±0.06% arabinan. These included non-structural carbohydrates soluble in water or ethanol, which constituted 11.25±0.94% glucan, 0.39±0.19% XMG, and 1.58±0.07% arabinan. The non-carbohydrate components of the waste were composed of 31.72±0.14% water extractives, 1.98±0.35% ethanol extractives, 13.55±0.67% ash, 6.43±0.18% lactate, and 11.26±0.55% acid insoluble residues. The mass closure on the components of food waste reached 99.26%, as shown in Table S1. The chemical composition analysis was conducted using three independently performed experiments; the error values given represent their standard deviations.

2. Assessment of the Effects of Acid Loading and Reaction Temperature During Glucose Extraction via Acidic Treatment

Table 1 lists the extraction yields of glucose and the concentrations of HMF, FA, and LA that were produced during the acidic treatment of food waste under various acid loadings and reaction temperatures. The extraction yield of glucose increased proportionally with the acid loading and temperature until 150 °C, at which it

Table 1. The extraction yield of glucose and the concentrations of HMF, FA, and LA obtained via acidic treatment of food waste as the function of reaction the reaction temperature and acid loading

Temp (°C)	DHA (% v/v)	Extraction yield (%)	Concentration (g/L)			Temp (°C)	DHA (% v/v)	Extraction yield (%)	Concentration (g/L)		
		Glucose	HMF	FA	LA			Glucose	HMF	FA	LA
120	0.2	45.53±1.31	0.03	0.75	0.19	160	0.2	64.76±1.63	0.15	0.85	0.29
	0.3	48.69±1.05	0.04	0.76	0.21		0.3	66.12±1.24	0.18	0.86	0.34
	0.4	54.52±0.72	0.03	0.77	0.21		0.4	76.20±0.70	0.27	0.88	0.30
	0.5	56.15±1.02	0.04	0.77	0.22		0.5	70.57±1.28	0.32	0.93	0.40
130	0.2	52.15±0.86	0.04	0.82	0.21	170	0.2	70.47±0.58	0.16	0.92	0.30
	0.3	51.31±1.95	0.06	0.84	0.23		0.3	69.74±1.13	0.27	1.11	0.39
	0.4	59.42±0.65	0.06	0.76	0.21		0.4	69.15±1.31	0.46	1.11	0.44
	0.5	57.47±1.46	0.08	0.84	0.25		0.5	62.6±1.62	0.73	1.14	0.50
140	0.2	55.45±0.86	0.05	0.76	0.33	180	0.2	79.35±0.73	0.81	1.46	0.71
	0.3	58.96±1.09	0.08	0.77	0.23		0.3	60.99±0.76	1.46	1.57	1.06
	0.4	58.30±0.99	0.08	0.76	0.23		0.4	57.89±0.89	2.28	1.67	1.57
	0.5	65.96±1.82	0.13	0.89	0.27		0.5	54.63±0.77	3.86	1.78	1.71
150	0.2	60.74±1.57	0.08	0.80	0.23	190	0.2	55.02±1.01	0.96	1.60	0.68
	0.3	61.98±1.99	0.11	0.81	0.24		0.3	40.36±1.90	1.25	1.68	0.85
	0.4	77.21±0.68	0.13	0.85	0.28		0.4	35.42±1.17	2.56	1.78	1.43
	0.5	83.17±0.78	0.21	0.87	0.31		0.5	41.25±0.51	2.78	1.86	2.06

The reaction time was 70 min (10 min preheating, 60 min cooking time).
HMF: hydroxymethylfurfural; FA: formic acid; LA: levulinic acid.

Table 2. Variation of pH and elemental composition after the concentration of hydrolysate as the function of concentration factor

Concentration factor[a]	pH	Content of each element in the concentrated hydrolysate (mg/L)							Salt compounds (g)
		Na	K	Ca	Mg	Al	P	S	
1.5	0.808	845.91	882.19	939.53	147.70	5.21	828.57	2985.16	6.98
2.0	0.656	1536.26	1571.48	963.92	245.44	8.44	1424.42	4666.89	10.31
2.5	0.466	2051.17	2099.08	926.96	338.16	12.57	1933.70	5955.75	12.47
3.0	0.313	2975.11	3020.53	833.48	502.03	16.15	2974.84	7731.80	14.06

The initial concentration of glucose in the hydrolysate was 17.03 g/L (15.79% glucan content).
[a]Concentration factor=(content of glucose in the concentrated hydrolysate/initial content of glucose derived from the food waste treated in the in 7 L reactor).

reached its highest value of 83.17% (19.08% extraction content of glucan) at 0.5% DHA. These results illustrate the difference between the processing of food waste and lignocellulosic biomass. In this study, the cellulose in the food waste could be decomposed to glucose and subsequently extracted into the liquor by acidic treatment. However, under the same conditions, the cellulose in biomass could not be extracted because the hemicellulose decomposes to xmg and is extracted into the liquor, due to its coupled structure, which protects the cellulose [15,24,47].

The extraction yield of glucose decreased with an increase in acid loading and reaction temperature at 160 °C or higher, except for the specific conditions of 160 °C and 0.2 and 0.3% DHA. The extraction concentrations of HMF, FA, and LA increased rapidly above 170 °C, due to the increased decomposition of glucose into HMF, FA, and LA with increasingly harsh reaction conditions. The extracted concentration of HMF increased as with temperature up to 180 °C, at which its highest value of 3.86 g/L was measured in 0.5% DHA. The sharp increase in the extraction concentration of HMF indicated that high temperature conditions were required for this reaction. This result suggests that the activation energy barrier for the dehydration of glucose to HMF is higher than that of the rehydration of HMF to LA [42,43]. However, the HMF conversion decreased at 190 °C in 0.5% DHA, due to the conversion of HMF into LA and FA was increased to a greater degree than the conversion of glucose into HMF. As a result, the optimal conditions for glucose extraction were an acid loading of 0.5% DHA and a reaction temperature of 150 °C.

Glucose can be converted to fructose by isomerization or to cellobiose and levoglucosan by polymerization (also known as the reversion reaction). Fructose was not detected in the reaction mixtures, because most of the fructose was converted into HMF due to the lower activation energy barrier; this tendency was consistent with previous studies [9,26].

3. High-capacity Production of the Glucose-containing Hydrolysate via Scale-up to a 7 L Reactor under the Optimized Conditions

Scale-up to a 7 L reactor was carried out to obtain a large amount of the hydrolysate. The EMBs of the scaled-up reaction are described in Table S2, which lists estimates of the amounts of various compounds recovered and lost from the raw material. While EMBs of more than 85.00% were achieved for arabinan and AIR, the EMBs of glucan and XMG were very low at 74.18 and 58.22%, respectively. This was probably due to glucan and XMG being extracted into the acidic liquor and further decomposed into HMF, furfural, LA, and FA due to the harsh reaction conditions [15,29,42,43,45].

A difference of 3.28% was observed between the glucan content extracted in the 7 L and 30 ml reactions under the same conditions. The content of glucan in the 7 L reaction exhibited a similar value to that obtained between 160 and 170 °C with 0.5% DHA in the 30 ml reaction. This result suggests that the glucose was hydrolyzed into HMF and LA due to the increased pre-heating time (typically 40-50 minutes) in the larger reactor [18,43]. The concentrations of the decomposition products and organic acids also increased in the scaled-up reaction, with values of 0.985±0.149 g/L HMF, 0.329± 0.084 g/L furfural, 1.316±0.136 g/L FA, and 1.087±0.118 g/L LA. In particular, furfural was detected only in the products of the 7 L reaction. This result was consistent with previous results, in which the EMB of XMG was very low due to its decomposition into furfural [15,45].

4. Variation of the pH, Glucose Content, and Elemental Composition of the Concentrated Hydrolysates after Concentration

Three parameters showed major variations depending on the concentration factor; these variations are summarized in Table 2. Increased concentration factor led to decreased pH, increased glucose content, and increased extraction of salt compounds. While the Na, K, Mg, Al, and P content in the concentrated hydrolysates increased proportionally with the concentration factor, the Ca content remained constant. This result suggests that Ca was extracted as a salt compound; the solubility of Ca in water is limited, and the Ca concentration may have reached saturation. However, additional experiments are needed to identify the main constituents of the salt compound, as the proportion of Ca in the salt compounds was very low. The S content increased with an increase in concentration factor because the sulfuric acid that was introduced during the hydrolysis process became concentrated. As a result, the pH of solution also decreased; this pH drop was a very important factor in the thermal treatment to produce LA production.

5. Assessment of the Effects of the Concentration Factor and Reaction Time on the Thermal Treatment Step for LA Production

Fig. S2 depicts the overall reaction scheme of the production of LA from cellulose. First, the cellulose was decomposed to form oligosaccharides including cellotriose and cellobiose [10]. These water-soluble oligosaccharides were further hydrolyzed to monosaccharides, such as glucose. The glucose could then react through three parallel pathways: (1) isomerization to form fructose, (2) dehydration to form HMF, and (3) decomposition to form humins [19,27].

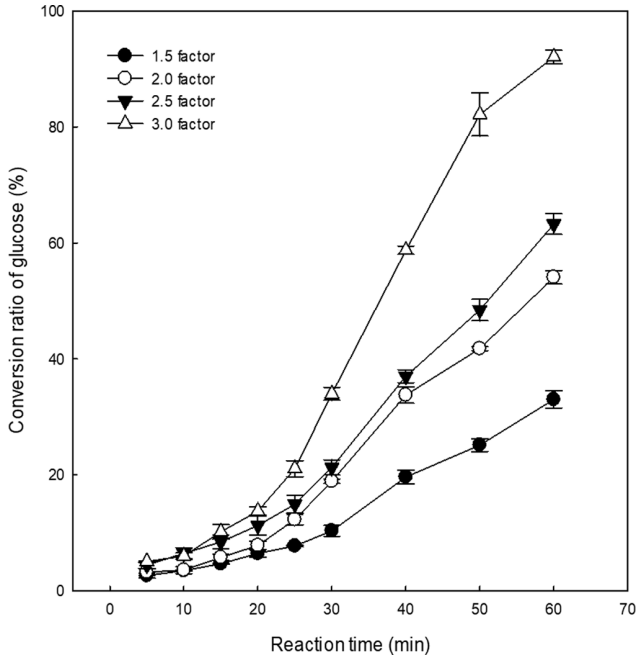

Fig. 1. Glucose conversion ratio after the thermal treatment of the concentrated hydrolysate without additional catalyst as the function of reaction time and concentration factor (Reaction temperature was fixed at 170 °C).

Fructose could also be dehydrated to form HMF. Subsequently, the HMF could be rehydrated to produce LA and FA, or could decompose to form furfural, accompanied by the loss of formaldehyde [11,19,27,40]. Formic acid was produced by the hydration reaction of furfural. During the LA production, dark-colored solids known as humins were also produced from compounds derived from cellulose, including cellobiose, glucose, fructose, HMF, and furfural [20,37].

LA production involved using thermal treatment under various conditions, including different concentration factors, reaction times, and temperatures. Figs. 1 and 2 depict the conversion ratio of glucose and the carbon yield of the products as a function of the concentration factor and reaction time. The conversion ratio increased with an increase in reaction time and increased sharply at longer reaction times. The carbon yields of HMF at concentration factors of 1.5-2.5 increased continuously with an increase in reaction time, but the yield at a concentration factor of 3.0 decreased sharply after reaching a maximum value. The conversion and yield decreased proportionally to the concentration factor. These results suggest that high pH could hinder the decomposition of glucose and also cause incomplete conversion into HMF. The decrease in the carbon yield of HMF at a concentration factor of 3.0 was probably due to the conversion of HMF into LA. However, this decrease did not immediately lead to an increase in LA. The carbon yield of LA also increased with an increase in reaction time and reached a maximum of 41.53% at a concentration factor of 3.0. As a result, a high conversion ratio of glucose and the yield of LA were obtained using a high concentration factor due to the change that occurred as a result of the hydrolysate concentration process, such as the removal of water and the decrease in pH, which led to the effective conversion of glucose into LA.

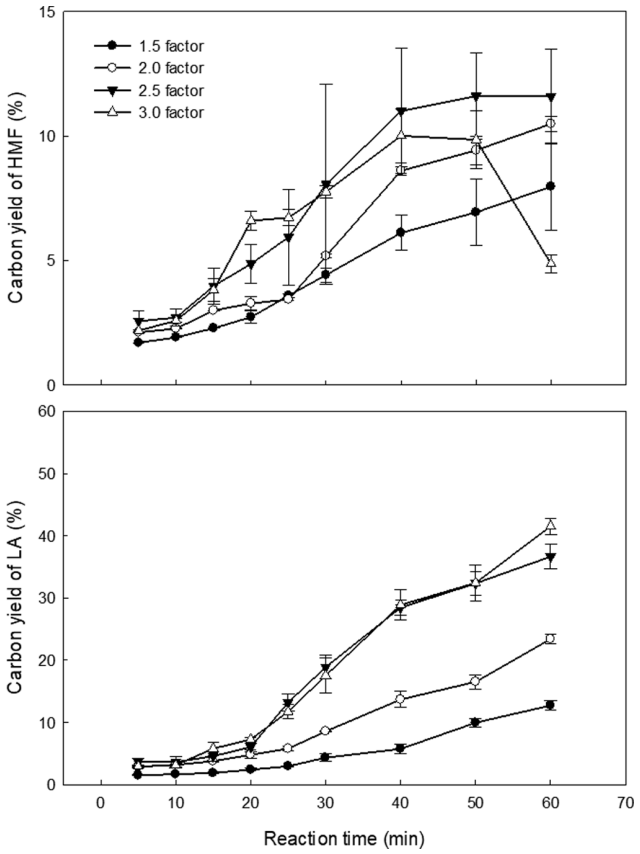

Fig. 2. Carbon yields of HMF and LA after the thermal treatment of the concentrated hydrolysate without additional catalyst as the function of reaction time and concentration factor (Reaction temperature was fixed at 170 °C).

We additionally performed experiments using concentration factors of 2.5 and 3.0 for 70-140 min to the increase the conversion and yield and to confirm the maximum yield of LA, as shown in Table S3. Although the increase was small, the conversion ratio of glucose reached approximately 90% after 80 and 70 min at concentration factors of 2.5 and 3.0, respectively, after which it remained constant. However, the conversion ratio never reached 100%. We can speculate as to the reason for this; in previous studies, glucose was converted into anhydro sugars and disaccharides, such as levoglucosan, 1,6-anhydro-B-D-glucofuranose, isomaltose, and gentiobiose, by intra- and intermolecular condensation reactions [9]. These compounds were difficult to separate, because their retention times were similar to that of glucose, and their concentrations were difficult to measure due to their low relative content. The carbon yield of HMF decreased constantly with an increase in reaction time, reaching maximum values of 11.61% at 50 min at a concentration factor of 2.5 and 10.01% at 40 min at a concentration factor of 3.0, because the HMF was quickly converted into LA, FA, and humins. As the reaction progressed, the yield of HMF approached zero. The carbon yield of LA reached a maximum value of 48.64% at a concentration factor of 2.5 after 90 min and 50.85% at a concentration factor of 3.0 after 100 min, and then decreased with further reaction time. Interestingly, the generated data presented a good value compared with previous results of 50% [20,23].

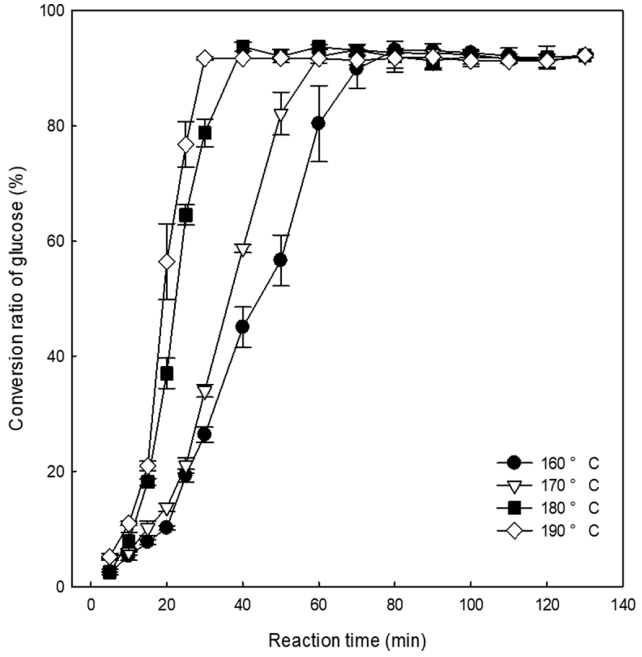

Fig. 3. Conversion ratio of glucose after the thermal treatment of the concentrated hydrolysate without additional catalyst as the function of reaction time and temperature (Concentration factor was fixed at 3.0).

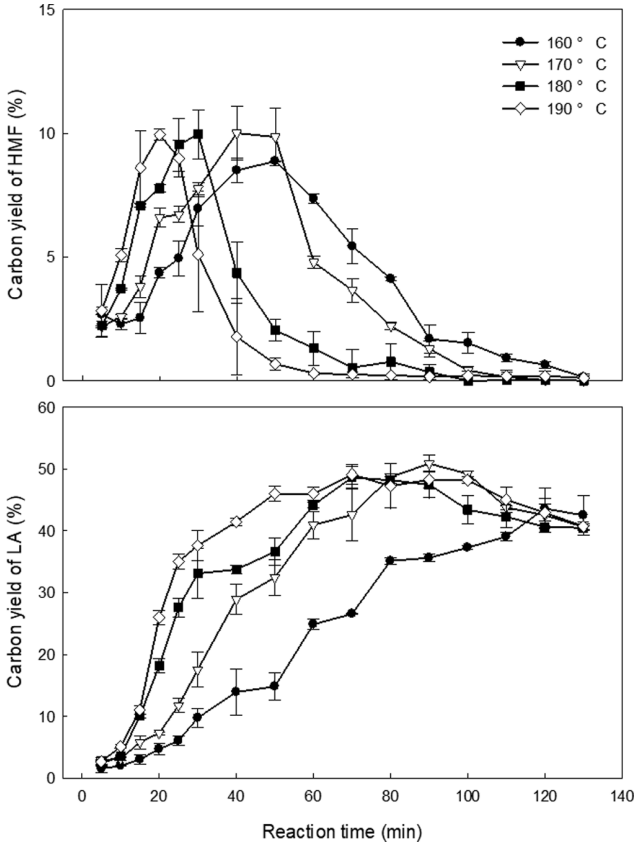

Fig. 4. Carbon yield of HMF and LA after the thermal treatment of the concentrated hydrolysate without additional catalyst as the function of reaction time and temperature (Concentration factor was fixed at 3.0).

These results can be explained using two facts: (1) HMF is a feedstock used in LA production, and its exhaustion causes a decrease in LA production [23,36]. (2) There is a delay between the decrease in the HMF decomposition and the increase in the LA production because the conversion into LA does not occur via a single step process rather than a multistep one, such as the conversion pathway suggested by Horvat [13,21].

6. Assessment of the Effects of the Reaction Temperature and Time on the LA Production via Thermal Treatment

Figs. 3 and 4 depict the conversion ratio of glucose and carbon yield of the products as a function of the reaction temperature and time. The conversion ratio of glucose remained constant after reaching maximum values of 91.76% at 190 °C after 30 min, 93.76% at 180 °C after 40 min, 93.07% at 170 °C after 60 min, and 93.16% at 160 °C after 80 min. The maximum values of conversion did not differ significantly with temperature, but the reaction time required to reach the maximum value generally decreased in proportion to the temperature. In particular, the reaction times became much longer below 180 °C. The carbon yield of HMF decreased rapidly after reaching its maximum value of 9.95% at 190 °C for 20 min, 9.96% at 180 °C for 30 min, 10.01% at 170 °C for 40 min, and 8.87% at 160 °C for 50 min, respectively. The carbon yield of LA reached maximum value of 49.09, 48.59, 50.85, and 43.57% at 190 °C for 70 min, 180 °C for 70 min, 170 °C for 90 min, and 160 °C for 120 min, respectively.

The maximum values of HMF and LA did not differ significantly with the temperature, except for at 160 °C. However, the reaction rate was strongly affected. The initial reaction rate was dominated by the reaction temperature but did not show significant differences after 80 minutes. Thus, the results indicated that the LA production process was affected by the reaction temperature, and that a reaction temperature of over 170 °C was required to obtain a high carbon yield and rapid reaction rate.

7. Determination of the Elemental Composition and Thermal Stability Analysis of the Humins using AEA and TGA

Humins are a by-product that is inevitably generated during the conversion of sugar feedstocks into LA. The HMF-derived compound 2,5-dioxo-6-hydroxy-hexanal leads to the formation of humins through aldol addition and condensation reactions; this is an important process in acid-catalyzed conversion [12,21,22,37]. Table 3 lists the elemental composition (CHNS-O) of the food waste and humins for different concentration factors. No great differences in the elemental compositions of the humins were observed for the different concentration factors, except for the 61.27% carbon content observed at a concentration factor of 1.5. The results were similar to elemental compositions of humins that have been previously reported in the literature (C, H, O: 57-63, 4-5, 33-38%, respectively [1,9,32]. However, the oxygen content of the humins was very low at less than 25%. This was attributed to the low oxygen content of 26.81% in the food waste feedstock. The C/H and C/O ratios increased with the conversion of the food waste into humins. The increased C/H ratios suggested that the carbon-hydrogen bond became stronger through the conversion of single bonds into double or triple bonds via condensation reactions. The increased C/O

Table 3. Elemental analysis results of samples produced by thermal treatment at various concentration factors

Samples	Content of each element the sample (%)					Ratio	
	N	C	H	S	O	C/H	C/O
Food waste	2.21	44.68	5.28	0.79	26.81	8.47	1.67
Humins_1.5	3.20	61.27	4.72	1.59	22.85	12.98	2.69
Humins_2.0	3.35	57.14	4.63	1.25	22.17	12.33	2.58
Humins_2.5	3.29	56.53	4.41	1.79	23.82	12.83	2.37
Humins_3.0	3.35	58.32	4.46	1.37	23.81	13.07	2.45

Humins_*X*: produced from a hydrolysate with a concentration factor of *X*.

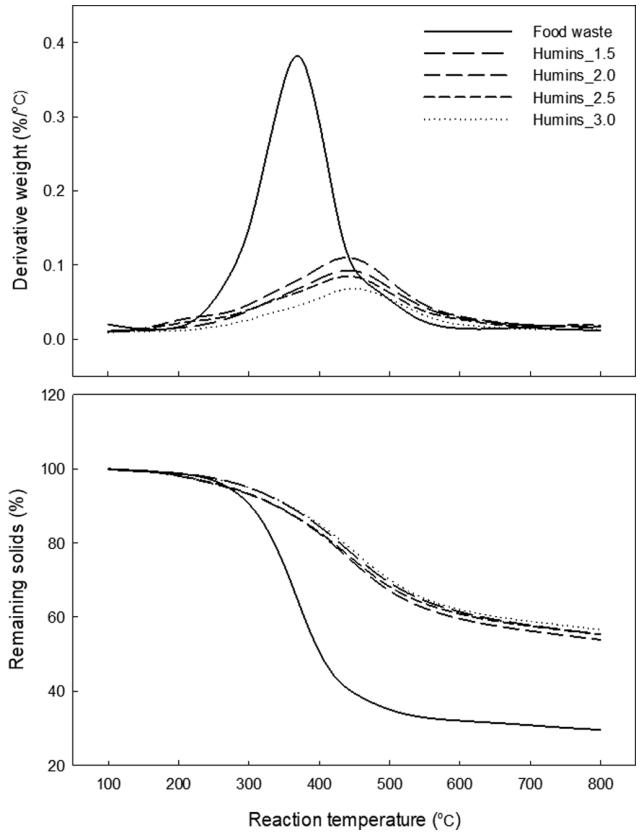

Fig. 5. TGA results of the samples recovered from the thermal treatment for different concentration factors (Reaction time was 60 minutes for each sample).

ratios suggested that oxygen was removed due to the dehydration effect of the condensation reaction. The N and S content increased slightly with the conversion into humins. These results may indirectly indicate that the inorganic substances in the food waste were removed by the two-step acidic and thermal treatment.

Fig. 5 depicts the remaining solids and the derivative weight of the food waste and humins as a function of the reaction temperature in the range of 100-800 °C. The thermal stability was estimated from the final amount of solid residue and the change in the derivative weight. While the food waste showed a distinct derivative peak, the humins showed a broader and shifted peak due to a decrease in the cellulose content of the samples. The remaining solids of the food waste and humins were quite different. This was due to the strengthening of the intra- and intermolecular bonds of the humins through condensation reaction and the removal of oxygen via the dehydration effect. The thermal stability of the humins was highest for a concentration factor of 3.0. This was consistent with the finding that the C/H ratio was highest at a concentration factor of 3.0, as described above.

CONCLUSIONS

The cellulose in food waste could be extracted into the liquor to form water-soluble oligosaccharides through an acidic treatment with DHA as the catalyst, because, unlike lignocellulosic biomass, the process is not impeded by hemicellulose or lignin. The maximum glucose extraction yield was 83.17% under the optimal conditions of 150 °C and 0.5% DHA. The glucose content decreased when the reaction was scaled-up from a 30 ml to a 7 L reactor due the increased pre-heating time and conversion into HMF and LA. The salt compounds, which were over-saturated relative to their solubility in water, could be extracted from the hydrolysate by the concentration process. The carbon yield and reaction rate of the LA production were strongly affected by the concentration factor and reaction temperature, respectively. The maximum carbon yield of LA was 50.85% at a concentration factor of 3.0 due to the low pH of solution. The reaction rate of LA production was proportional to the reaction temperature, except at 160 °C. The humins had a higher carbon content and lower oxygen content than the food waste due to the condensation reaction and resulting dehydration effect. The thermal stability of the humins increased in proportion to the concentration factor, as identified through the broadening and shifting of the derivative peak and unvaried remaining solids.

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NOMENCLATURE

AEA : automatic elemental analysis
DHA : dilute hydrochloric acid
DOE : department of energy in U.S.
EMB : extraction mass balance

FA : formic acid
GVL : γ-valerolactone
HMF : 5-hydroxymethylfurfural
ICP : inductively coupled plasma spectrometry
LA : levulinic acid
MTHF : 2-methyl-tetrahydrofuran
TGA : thermogravimetric analysis
CR_{Glu} : conversion ratio of glucose
CY_{HMF} : carbon yield of HMF
CY_{LA} : carbon yield of levulinic acid
Decomposition product : 5-hydroxymethylfurfural and furfural
Organic acid : formic acid, acetic acid, and levulinic acid
Products : 5-hydroxymethylfurfural and levulinic acid
Sugar : glucose, xmg, and arabinose
xmg : xylose, mannose, and galactose
XMG : xylan, mannan, and galactan

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

REFERENCES

1. K. D. Baugh and P. L. McCarty, *Biotechnol. Bioeng.*, **31**, 50 (1988).
2. K. R. Bräutigam, J. Jörissen and C. Priefer, *Waste Manage. Res.*, **32**, 683 (2014).
3. A. Caretto and A. Perosa, *ACS Sustainable Chem. Eng.*, **1**, 989 (2013).
4. F. Cherubini, *Energy Convers. Manag.*, **51**, 1412 (2010).
5. S. P. Das, R. Ravindran, S. Ahmed, D. Das, D. Goyal, C. M. Fontes and A. Goyal, *Appl. Biochem. Biotechnol.*, **167**, 1475 (2012).
6. J. Esteban and M. Ladero, *Int. J. Food Sci. Technol.*, **53**, 1095 (2018).
7. S. W. Fitzpatrick, *ACS Symp. Ser.*, **921**, 271 (2006).
8. S. S. Chen, T. Maneerung, D. C. Tsang, Y. S. Ok and C. H. Wang, *Chem. Eng. J.*, **328**, 246 (2017).
9. B. Girisuta, L. P. B. H. Janssen and H. J. Heeres, *Chem. Eng. Res. Des.*, **84**, 339 (2006).
10. M. Goto, R. Obuchi, T. Hirose, T. Sakaki and M. Shibata, *Bioresour. Technol.*, **93**, 279 (2004).
11. D. J. Hayes, S. Fitzpatrick, M. H. Hayes and J. R. Ross, *Biorefineries: Ind. Processes Prod.*, **1**, 139 (2006).
12. J. Heltzel, S. K. Patil and C. R. Lund, Humin formation pathways, in *Reaction pathways and mechanisms in thermocatalytic biomass conversion II*, Springer, Singapore, 105 (2016).
13. J. Horvat, B. Klaić, B. Metelko and V. Šunjić, *Croat. Chemica. Acta*, **59**, 429 (1986).
14. I. T. Horváth, H. Mehdi, V. Fábos, L. Boda and L. T. Mika, *Green Chem.*, **10**, 238 (2008).
15. H. Jeong, S. K. Jang, C. Y. Hong, S. H. Kim, S. Y. Lee, S. M. Lee and I. G. Choi, *Bioresour. Technol.*, **225**, 183 (2017).
16. H. Ji, C. Dong, G. Yang and Z. Pang, *BioResources*, **14**, 725 (2019).
17. S. J. Kim, H. S. Kwon, G. H. Kim and B. H. Um, *Ind. Crops Prod.*, **67**, 395 (2015).
18. Y. S. Kim, J. Y. Jang, S. J. Park and B. H. Um, *Waste Manage.*, **74**, 231 (2018).
19. X. Li, R. Xu, J. Yang, S. Nie, D. Liu, Y. Liu and C. Si, *Ind. Crops Prod.*, **130**, 184 (2019).
20. M. R. Park, H. S. Kim, S. K. Kim and G. T. Jeong, *Fuel Process. Technol.*, **172**, 115 (2018).
21. S. K. Patil and C. R. Lund, *Energy Fuels*, **25**, 4745 (2011).
22. S. K. Patil, J. Heltzel and C. R. Lund, *Energy Fuels*, **26**, 5281 (2012).
23. F. D. Pileidis and M. M. Titirici, *ChemSusChem*, **9**, 562 (2016).
24. D. W. Rackemann and W. O. Doherty, *Biofuels, Bioprod. Biorefin.*, **5**, 198 (2011).
25. D. W. Rackemann, J. P. Bartley and W. O. Doherty, *Ind. Crops Prod.*, **52**, 46 (2014).
26. C. Gong, J. Wei, X. Tang, X. Zeng, Y. Sun and L. Lin, *Korean J. Chem. Eng.*, **36**, 740 (2019).
27. H. Rasmussen, H. R. Sørensen and A. S. Meyer, *Carbohydr. Res.*, **385**, 45 (2014).
28. R. Ravindran and A. K. Jaiswal, *Trends Biotechnol.*, **34**, 58 (2016).
29. T. H. Kim, Y. J. Jeong, K. K. Oh and T. H. Kim, *Korean J. Chem. Eng.*, **30**, 1339 (2013).
30. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, NREL/TP-510-42623, National Renewable Energy Lab, Golden, CO, USA (2006).
31. A. Sluiter, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, NREL/TP-510-42619, National Renewable Energy Lab, Golden, CO, USA (2008).
32. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, NREL/TP-510-42622, National Renewable Energy Lab, Golden, CO, USA (2008).
33. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, NREL/TP-510-42618, National Renewable Energy Lab, Golden, CO, USA (2010).
34. I. V. Sumerskii, S. M. Krutov and M. Y. Zarubin, *Russ. J. Appl. Chem.*, **83**, 320 (2010).
35. J. Trivedi, A. K. Bhonsle and N. Atray, *Academic Press.*, **19**, 427 (2020).
36. S. Tulaphol, M. A. Hossain, M. S. Rahaman, L. Y. Liu, T. K. Phung, S. Renneckar and N. Sathitsuksanoh, *Energy Fuels*, **34**, 1764 (2019).
37. G. Tsilomelekis, M. J. Orella, Z. Lin, Z. Cheng, W. Zheng, V. Nikolakis and D. G. Vlachos, *Green Chem.*, **18**, 1983 (2016).
38. B. H. Um, M. N. Karim and L. L. Henk, *Appl. Biochem. Biotechnol.*, **105**, 115 (2003).
39. B. H. Um and G. P. van Walsum, *Appl. Biochem. Biotechnol.*, **168**, 406 (2012).
40. R. J. Van Putten, J. C. Van Der Waal, E. D. De Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, **113**, 1499 (2013).
41. R. Weingarten, J. Cho, W. C. Conner Jr. and G. W. Huber, *Green Chem.*, **12**, 1423 (2010).
42. R. Weingarten, J. Cho, R. Xing, W. C. Conner and G. W. Huber, *ChemSusChem.*, **5**, 1280 (2012).
43. R. Weingarten, W. C. Conner and G. W. Huber, *Energy Environ. Sci.*, **5**, 7559 (2012).
44. T. Werpy and G. Petersen, NREL/TP-510-35523, National Renewable Energy Lab, Golden, CO, USA (2004).
45. R. Xing, W. Qi and G. W. Huber, *Energy Environ. Sci.*, **4**, 2193 (2011).
46. K. Yan, C. Jarvis, J. Gu and Y. Yan, *Renew. Sust. Energy Rev.*, **51**, 986 (2015).
47. Z. Yang, H. Kang, Y. Guo, G. Zhuang, Z. Bai, H. Zhang and Y. Dong, *Ind. Crops Prod.*, **46**, 205 (2013).