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Reaction kinetics and mechanism for hydrothermal degradation and electrolysis of glucose for producing carboxylic acids

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Abstract Electrolysis in subcritical water can convert biomass-derived saccharides into value-added chemicals and fuels without any additives. In this work, we aim to understand reaction behaviours of glucose under subcritical water degradation or electrochemical conditions for the purpose of developing a new method for producing useful carboxylic acids. Degradation of glucose was carried out using a continuous flow-type reactor in subcritical water at various operating conditions, and electrochemical reactions of their product solutions were conducted at identical conditions with a 500-mL batch autoclave. Gaseous products obtained were analyzed by gas chromatography-thermal conductivity detection (GC-TCD), and liquid products were analyzed by high-performance liquid chromatography (HPLC) and gas chromatography-flame ionization detection (GC-FID). The total organic carbon (TOC) in the aqueous product solution was determined by using a TOC analyzer. Based on the experimental results, a reaction pathway for glucose is proposed for subcritical water degradation and electrolysis.

Keywords Hydrothermal degradation · Electrolysis · Glucose · Carboxylic acids

Introduction

Nowadays, production and use of biochemicals and biofuels have garnered much attention because they possess various advantages as alternatives to petroleum-

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based chemicals and fuels, e.g., they are renewable, possess favorable energy balance, have lower harmful emissions and are non-toxic. Presently, in many biodiesel plants with low capacity, crude glycerol is discharged in wastewater as a main byproduct, together with some methanol, alkali and low concentration of fatty acids. As a result of this, both environmental pollution and economical losses are generated. Glycerol is used in medical, pharmaceutical and other applications, mainly as a means of improving smoothness, providing lubrication and as a humectant. It is found in cough syrups, elixirs and expectorants, toothpastes, mouthwashes, skin care products, shaving creams, hair care products and soaps. Additionally, in foods and beverages, glycerol serves as a humectant, solvent and sweetener, and may help preserve foods. It is also used as a filler in commercially prepared low-fat foods (e.g., cookies), and as a thickening agent in liquors. Glycerol and water also serve as preservatives for certain types of leaves. So far, conversion of glycerol to various compounds has been investigated. Catalytic dehydration of glycerol in sub- and supercritical water and its reaction mechanism have been studied. According to this research, it was found that the OH group on various catalysts can catalyze dehydration of glycerol to 3-hydroxypropionaldehyde, 1,3-propanediol, acrolein and other degradation products through subsequent hydrogenation [1–3]. In another study, it was reported that both ionic reaction and pyrolysis of glycerol took place in near- and supercritical water, and it was shown that the products of glycerol degradation were methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide and hydrogen [4, 5]. Moreover, pyrolysis of glycerol has been studied in steam, with the major products being acrolein, formaldehyde and acetaldehyde [6, 7]. At higher temperatures, other products such as carbon dioxide, molecular hydrogen, ethylene and methane are observed, indicative of more complex chemistry.

One method of particular interest is conversion of glycerol to lactic acid. Kishida et al. [8] showed that glycerol can be converted to lactic acid by hydrothermal decomposition experiments of glycerol in subcritical water under alkaline conditions. Studies on the conversion pathway have suggested that glycerol is first decomposed to pyruvaldehyde with elimination of hydrogen by H-shift to the adjacent hydrogen. The pyruvaldehyde is then converted to lactic acid ion by benzilic acid rearrangement. In this study, the main product was lactic acid. In addition, small amounts of pyruvaldehyde, acetic acid and formic acid were detected. In another study, the conversion mechanism of cellulosic biomass to lactic acid in subcritical water without addition of any alkaline catalyst was discussed. The results showed that this conversion mechanism appeared to follow the same pathways elucidated in the conversion of sugar to lactic acid in alkaline solution [9].

Recently, the authors have carried out analysis to elucidate the reaction pathway of glycerol and 1-butanol with hydrothermal electrolysis treatment [10, 11]. We have studied electrolysis of glycerol in subcritical water with a continuous flow reactor to explore high-yield lactic acid production [12]. This work clearly indicates that this method can be expected to form one of the novel techniques with low environmental impact. However, we also have to evaluate the possibility of the development of production of furan derivatives from biomass resources with hydrothermal electrolysis techniques.

The first purpose of this work is to determine an optimum condition where cellulose can be hydrolyzed and glucose obtained in subcritical water. Next, for selective production of 5-(hydroxymethyl)-2-furfural (5-HMF) and related furan derivatives from cellulose and glucose, we carried out experiments of glucose degradation in subcritical water. Also, we aimed to clarify the gaseous and liquid products, and the effects of electrolysis current and alkali concentration on the decomposition of glycerol. In this study, subcritical water was selected as a reaction medium because it is cheap, non-toxic, non-flammable, non-explosive and offers essential advantages compared with other substances, particularly in the field of “green chemistry” [13]. Recent studies have demonstrated that heating water above its boiling point under enough pressure to maintain its liquid state causes some physicochemical changes that are useful in reducing the rate problems as well as increasing the solubility of organics in water; for example, the dielectric constant is much lower, and the number of hydrogen bonds is diminished. Additionally, the ion product or dissociation constant (K_w) for water as it approaches the critical point is about three orders of magnitude higher than it is for ambient liquid water. As a result, water becomes an excellent solvent for organic compounds. It can also boast a higher H^+ and OH^- ion concentration than liquid water under certain conditions [14, 15]. In terms of economic feasibility, subcritical water minimizes the amount of energy consumed for electrolysis, because the efficiency in terms of current as a function of reaction progress increases with increasing water temperature toward its critical point [16]. In addition, reactions of glucose have been carried out in two types of reactors to understand the reaction behavior and mechanism in subcritical water and to evaluate the possibility of realizing a novel process of recovery of chemicals from waste biomass resources using the hydrothermal electrolysis technique.

Experimental

Materials

Cotton was used as starting material for hydrolysis in subcritical water. Glucose (99% purity) was purchased from Wako Pure Chemical Co. (Osaka, Japan).

Experimental procedures and analysis

For hydrolysis of cotton biomass, a semi-batch reaction system was used. Figure 1 shows a schematic representation of the semi-batch-type reaction system used in this study. Prior to each experiment, a given amount of cotton sample was packed into the extraction cell (10-30 mL inner volume) and sealed. Then, distilled water was fed into the system at flow rate of 8.0 mL/min by using a HPLC pump (PU-2080, JASCO) with heating to the desired temperature (220 or 250 °C), and the reactive extraction was initiated. Typical experimental conditions are listed in Table 1. During the experiment, reaction solutions were recovered every 10 min. Each reaction solution was then quantified by HPLC-Ultraviolet and refractive

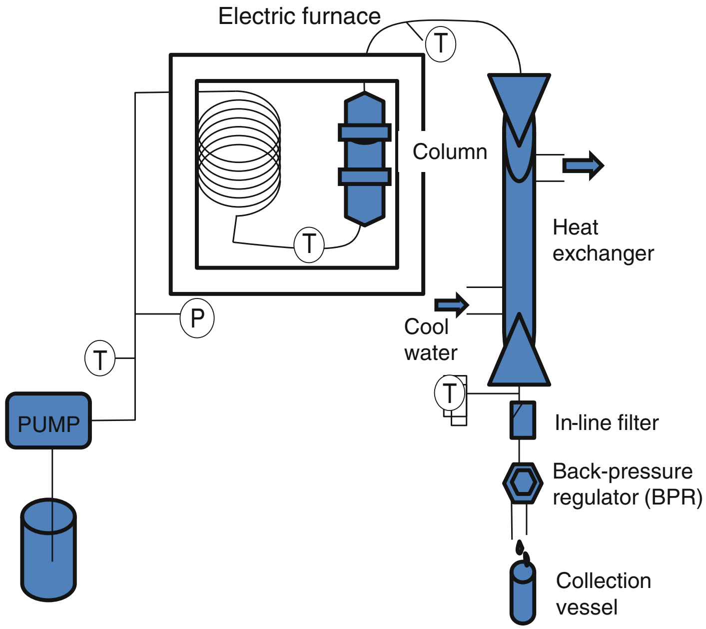


Fig. 1 Schematic representation of the semi-batch-type reactor used in this study

Table 1 Experimental conditions for cotton hydrolysis in subcritical water

Entry	Material	*T* (°C)	*L*/*D* (–)	Flow rate (mL/min)	*P* (MPa)
1	Cotton	220	2	8	5
2	Cotton	250	2	8	5

index (UV/RI) detections [column: SUGAR SH-1011 (Shodex); mobile phase: 3 mmol/L $HClO_4$ aq. 0.5 mL/min; colouring medium: Bromothymol blue (BTB) soln. 1.0 mL/min; detector: UV–Vis (430 nm) and RI; column temperature: 60 °C], the solid residue was recovered after quenching the system and dried in an oven at 50 °C for 48 h, and the dried solid residue was weighed to determine the cellulose conversion, X. The yield of each product i, Y_i, was calculated by Eq. 1.

$$Y_i\ (\mathrm{w/w\%}) = \frac{C_i}{C_0} \times 100. \tag{1}$$

For the electrolysis experiment in subcritical water, a stirred tank reaction system was employed in this study. Figure 2 shows the apparatus. A cylindrical iridium plate electrode (23 mm diameter, 30 mm length), coaxial to the titanium beaker (74 mm internal diameter, 100 mm length), was used as an anode, and the titanium beaker was used as a cathode to promote cathodic protection of the autoclave from corrosion. Glucose aqueous solution (0.1 mol/L) was used as starting material. Phosphoric acid and sulphuric acid were employed as electrolytes, and the pH of each solution was adjusted to 2.0–2.8. Before starting each experiment with the

Fig. 2 A stirred tank reaction system for hydrothermal electrolysis

stirred tank reactor, the system was purged with inert gas (argon) and then initially charged with 2 MPa argon gas. The reactor was heated from room temperature to the desired temperature (150–280 °C). The temperature was measured using a thermocouple inserted in the reactors during the experiment. When the system reached the desired temperature after 30–40 min, a constant electric current was passed between the electrodes in water at high-temperature high-pressure conditions. No current was passed for hydrothermal degradation runs.

At the end of reaction, both gas and liquid samples were collected for GC-FID, HPLC-UV/RI, gas chromatography-mass spectrometry (GC-MS), and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF)/MS. Solid samples were not specifically analyzed, because no measurable solid products were observed. Total organic carbon in the liquid product solution was monitored by using a TOC analyzer (TOC-5000A; Shimadzu Co., Ltd.).

Results and discussion

Non-catalytic hydrolysis of cellulose for glucose production

It is well known that cellulose can be selectively hydrolyzed to glucose in sulphuric acid solution or phosphoric acid solution. Cellulose can be also hydrolyzed to form saccharides in subcritical water without any catalyst, but it is quite difficult to generate glucose with high yield and selectivity [17–23]. However, most research regarding non-catalytic hydrolysis of celluloses in sub- and supercritical water does not discuss the relationship between glucose yield and the physical properties of

Table 2 Experimental results of cellulose degradation in subcritical water

Entry	Cotton conv. (%)	Residual rate (%)	DP6 ~2, glucose yield (%)	DP6 ~2, yield (%)	Glucose yield (%)	5-HMF
1	44.61	55.39	46.61	27.53	19.08	1.05
2	84.69	15.31	64.42	16.01	48.41	4.93

water. Therefore, in this study, the authors aimed to explore the optimum conditions where glucose could be obtained from cellulosic materials in high yield in subcritical water with no catalyst. As a result, it was found that the maximum yield of glucose reached 57.2% with non-catalytic treatment of cotton in subcritical water at 250 °C, as shown in Table 2. At 220 °C, the yield of water-soluble saccharides reached almost 100%, although the glucose yield was 43.8%.

Degradation of glucose in subcritical water

To clarify the effect of electrochemistry and thermal degradation separately, glucose degradation experiments in subcritical water at 180–260 °C were carried out with the application of direct current (DC). At all the temperatures, straight lines were obtained, as shown in Fig. 3, indicating that the hydrolysis of glucose followed a pseudo-first-order reaction rate law at these conditions. The obtained degradation rate of glucose, k [min^{-1}], was plotted against reciprocal temperature. As a result, as shown in Fig. 4, the degradation rate for glucose was found to follow an Arrhenius-type reaction rate law.

Electrolysis of glucose in subcritical water

When glucose was used as starting material, liquid products obtained by this experiment at constant voltage of 30 V were 5-HMF, 2-furfural, lactic acid, glyceraldehyde, glycolaldehyde, glycolic acid, acetic acid and formic acid. As gaseous products, from the hydrothermal electrolysis of glucose, hydrogen, carbon monoxide and carbon dioxide were generated. The product distributions resulting from the glucose treatment at each temperature were examined by HPLC-UV/RI. Figure 5 shows typical HPLC chromatograms of the aqueous product solution obtained by the hydrothermal electrolysis at 230 °C. At short electrolysis times at 210–230 °C, the main products were 5-HMF, formic acid and levulinic acid, indicating that thermal reactions such as glucose dehydration and 5-HMF degradation were dominant at these conditions. This is probably because of the long heating period in the experiments. As a pre-experiment, we determined the glucose conversion and product distribution immediately after the heating step of the experiment at 230 °C. As a result, about 30% of the glucose had already been converted into other products. This result clearly indicates that glucose was not stable in subcritical water and was therefore easily decomposed to 5-HMF or other chemical species even during the heating period used in this kind of experiment.

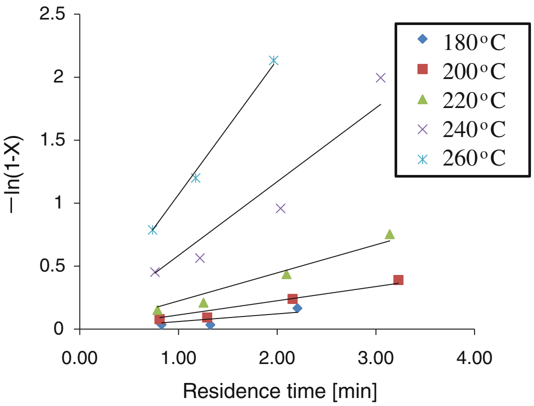


Fig. 3 Relationship between −ln(1−*X*) versus residence time for glucose degradation in subcritical water

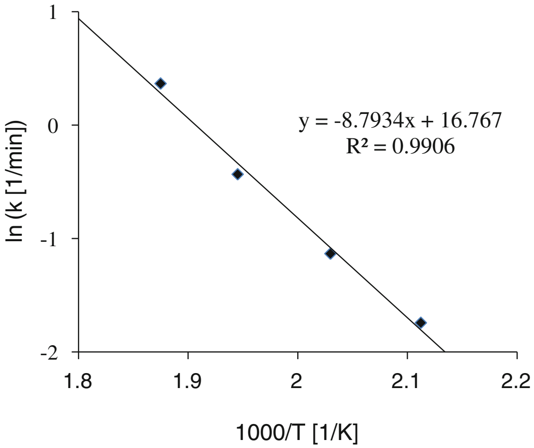


Fig. 4 Arrhenius plot for glucose degradation in subcritical water

This study focusses on high yield of mono- and dicarboxylic acids such as levulinic acid, gluconic acid and 2,5-furandicarboxylic acid (FDCA) from glucose via partial oxidation of aldehyde or hydroxymethyl groups in the glucose molecule using electrolysis in subcritical water. Figure 6 shows the time course of glucose conversion at 160 and 230 °C in subcritical water. In general, in the absence of any oxidants, degradation rates of monosaccharides are quite small, and therefore it takes quite a long reaction time to convert them into products at low temperatures such as 160 °C. In this work, however, glucose conversion reached about 40% and 60% at 120 and 180 min, respectively. This result clearly indicates that electrolysis in subcritical water can promote degradation of glucose. At 230 °C, the conversion reached 100% within 30 min. According to the kinetic analysis for glucose degradation, as shown in Figs. 3 and 4, it can be considered that the contribution of thermal degradation to the overall glucose degradation is dominant at higher temperatures such as 230 °C.

Figure 7 shows the time courses of yields of glucose electrolysis products at 160 and 230 °C. The yield of 5-HMF increased with time and reached 17% at 10 min.

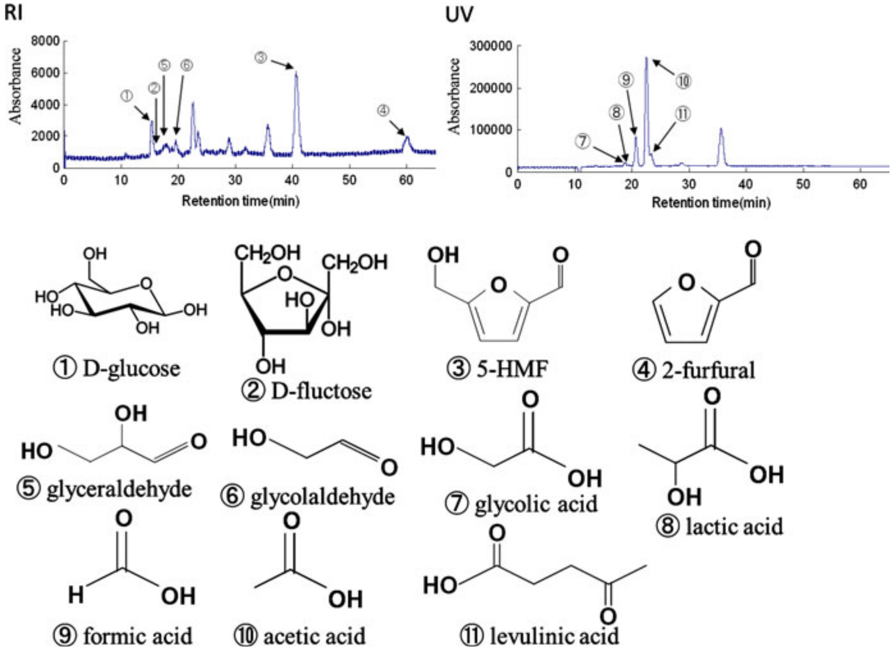
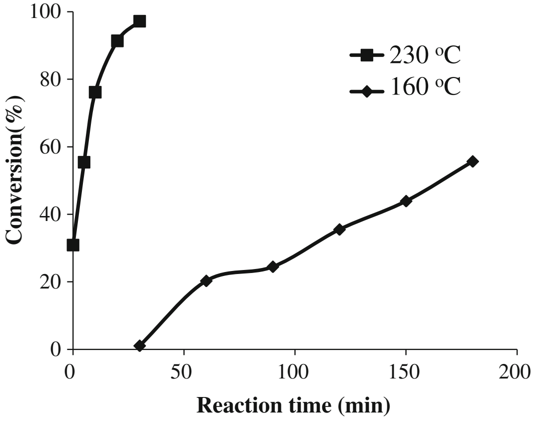


Fig. 5 HPLC chromatograms and detected products from electrolysis treatment of glucose in subcritical water at 230 °C. Conditions: 0.1 mol/L glucose aqueous solution, 230 °C, 30 V, 30 min, and glucose conversion $X = 97.1\%$

Fig. 6 Time course of glucose conversion with electrolysis in subcritical water at 160 and 230 °C



After that, it decreased and the yields of levulinic acid and formic acid became larger. This result indicates that glucose was easily dehydrated to 5-HMF, followed by conversion to levulinic acid plus formic acid, probably due to the influence of the thermal instability of glucose and 5-HMF at 230 °C. In this case, products formed via retro-aldol condensation of glucose (glycolaldehyde, glyceraldehydes etc.) were also generated. No formation of FDCA was observed at this condition. In contrast, at the lower temperature of 160 °C, main products were formic acid and gluconic

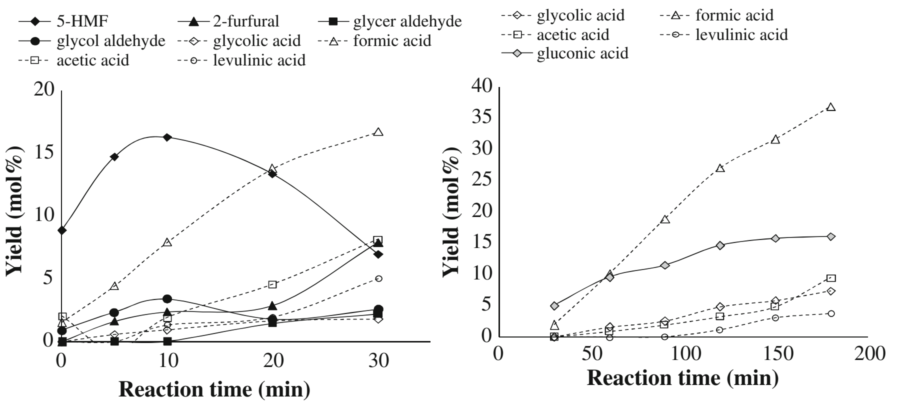


Fig. 7 Main aqueous products after hydrothermal electrolysis of glucose at (**a**) 230 °C and 30 V, and (**b**) 160 °C and 3 A

acid. In generating gluconic acid, the aldehyde group at the C1 position of a glucose molecule should be oxidized during the treatment. This indicates that glucose was oxidized electrochemically even if there was no oxidant under subcritical water condition. The reason why formic acid was generated is probably due to the

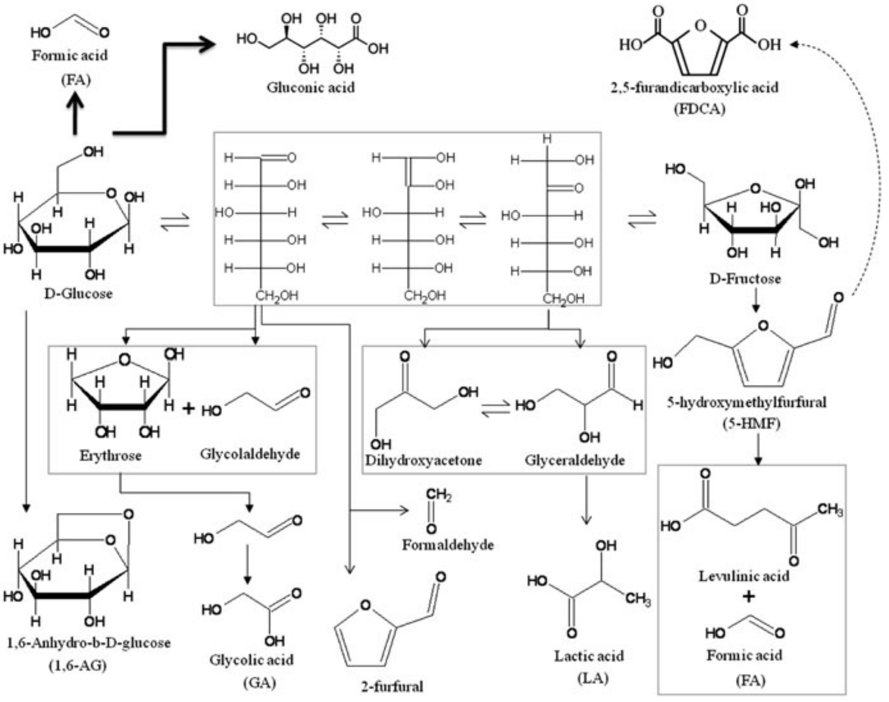


Fig. 8 Possible reaction pathway for glucose in subcritical water. Gluconic acid and 2,5-furandicarboxylic acid (FDCA) can be generated by electrochemical treatment

promotion of cleavage of carbon–carbon bond linkages in the glucose molecule under acidic conditions or thermal degradation of glucose at temperatures such as 230 °C.

Considering the results obtained in this study and reports from the literature [24, 25], reaction pathways of glucose are summarized in Fig. 8. In the absence of catalysts, possible reactions of glucose are tautomerism to form fructose, dehydration to 5-HMF and retro-aldol condensation to form erythrose or glycolaldehyde. Especially, dehydration is dominant compared with the other reactions in subcritical water. With addition electrical power to the hydrothermal atmosphere, glucose or some intermediates (e.g. aldehydes) can be converted to mono- or dicarboxylic acids via partial oxidation to form gluconic acid with high selectivity. If this reaction process can be optimized correctly, a novel technique to obtain mono- and dicarboxylic acids from glucose or cellulosic biomass through subcritical hydrolysis and subsequent electrolysis could be developed.

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