

Dehydration of D-glucose in high temperature water at pressures up to 80 MPa

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Abstract

Reaction of D-glucose in water to yield 5-hydroxymethylfurfural (5-HMF), 1,2,4-benzenetriol (BTO) and furfural was studied at high temperatures (up to 400 °C) and high pressures (up to 80 MPa) using a continuous flow reactor. Maximum temperature and pressure conditions gave maximum furfural yield. Increasing pressure from 40 to 70 and 80 MPa enhanced dehydration reactions to 5-HMF, but also enhanced hydrolysis of 5-HMF leading to the production of BTO and thus lead to lower yields of 5-HMF (below 10%). Remarkably, the dehydration reaction to 5-HMF and the hydrolysis of 5-HMF were both enhanced by the increase in water density at 400 °C.

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1. Introduction

Biomass is an abundant carbon-neutral and renewable resource which has the potential to produce energy [1,2] and chemicals [3,4] for the future sustainable industries. Biomass resources from agricultural residues, wood and herbaceous energy crops consist of biopolymers such as cellulose (35–50%), hemicellulose (25–30%) and lignin (25–30%) [3]. The chemistry of sugars such as D-glucose, which is the unit compound of cellulose, to valuable compounds is very important considering the downstream chemical processing from biomass resources [5,6].

Water is the most environmentally friendly solvent for chemical reactions and therefore would be the solvent of choice for a biomass process. High temperature and high pressure water (HHW) has high potential as a reaction solvent due to its tunable solvent properties [7,8].

Reactions of D-glucose, D-fructose and 5-HMF in HHW have been investigated using a flow reactor [9–12]. The main reactions of D-glucose in HHW were found to be dehy-

dration, retro-aldol, hydration and tautomerization reactions. Various linear compounds (lactic acid, levulinic acid, glycerinaldehydes and glycolaldehyde), and ring compounds (5-hydroxymethylfurfural (5-HMF), furfural, 1,2,4-benzenetriol (BTO)), with multi-functionalities could be obtained in one-pot reactions in HHW [9–12].

Among these chemicals 5-HMF, lactic acid and furfural are of great value [6,13], with 5-HMF having the potential to replace terephthalic acid [14] and furfural being the starting material for polymers such as nylon 6,6 and nylon 6 [4]. Though all these compounds can be produced in low yields (below 35%) at hydrothermal conditions (90–300 °C, saturation) [10,15,16], supercritical conditions can possibly allow control of competitive reactions.

One way of controlling reactions and improving the yield of product compounds of monosaccharide conversion in HHW is to use additives such as organic solvents [17,18], heterogeneous catalysts [19,20] and homogeneous catalyst [10,16]. However, in general, it would be preferable to minimize the use of additives, since these would complicate downstream processing.

Another way of controlling the reaction of saccharides is to use pressure that can influence the properties of near-critical region of water (350–400 °C). Organic chemical reactions can be controlled by variation of ion product (K_w) and physical

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properties such as density [7,8]. In addition, water in itself, can promote chemical reactions by participating in the transition state and lowering reaction energies by forming a so-called “water bridge” [8,21,22]. These effects should be a function of the thermal energy (temperature) and water density (pressure). In our previous studies, we observed that the dehydration of D-fructose, an isomer of D-glucose, to 5-HMF increased with increasing water density at 400 °C [11]. Although the reaction of D-fructose and D-glucose in HHW produces low 5-HMF yields below 35% [10,11,18,23], these studies indicate that selective formation 5-HMF is possible by tuning the pressure and temperature of HHW.

The above reports have studied reactions that have been limited to pressures less than 40 MPa. However, the above experimental evidence shows that further improvement in selectivity of the products can possibly be achieved by increasing the water density via pressure. Therefore, we developed a continuous reactor system that could achieve pressures up to 80 MPa at temperatures up to 400 °C. Exploring higher pressure reactions in water, up to 80 MPa in HHW, is not only interesting to understand the nature or chemical reactions in HHW, but will also allow us to examine the effect of pressure on additives of previous studies. The objective of this paper is to study the reaction of D-glucose in high temperature high pressure water at pressures up to 80 MPa and to determine the reaction parameters. In particular, we consider the formation of 5-HMF from D-glucose.

2. Experimental

D-Glucose was obtained from Wako Chemical and used as received. Water was distilled with a water distillation apparatus (Yamato Co., model WG-220) and the resulting water had a conductivity of 18 MΩ/cm.

Experiments were performed with the flow reactor as shown in Fig. 1. Air driven intensifier pumps (FLO-TEC Ltd., Yokohama, Japan) were used. For the areas that required high

temperatures, Inconel 625 tubes (3.2 mm o.d. and 0.9 mm i.d.) connected with BuTech fittings (Butech Pressure Systems Inc., Pittsburgh) were welded together to withstand the high temperature and high pressure conditions. For the portions that were not in the high temperature regions, SUS316 tubes were used. The reactor was made of an Inconel 625 tube (3.2 mm o.d. and 0.9 mm i.d.). The reactor tube was wrapped with a ribbon heater and then glass wool was wrapped over the reactor for insulation. The tubing from the mixing point to the end of this wrapping was defined as the reactor. The residence time of the reactions were varied from 0.2 to 1.7 s without changing the total flow rate at the given temperature and pressure by shortening and extending the reactor length and thus changing the reactor volume. The distance of the cooling jacket and the end of the reactor was kept 0.5 cm apart. The temperature profile along the reactor was kept to within 3 °C of the reaction temperature. Two-backpressure regulators (Koatsu-System Co. Ltd., Saitama) were connected in series and the pressure was reduced equally in two steps to atmospheric pressure. The two-step pressure reduction was essential to reliable operation and helped to reduce the degree of mechanical attrition of the packing in the backpressure regulator caused by the expanding fluid stream.

Water was fed into the apparatus at a flow rate of 10–20 ml/min by a pump and the pressure was controlled using a backpressure regulator. The stream was then preheated to supercritical temperatures by an electric furnace before it was introduced into the reactor. A D-glucose solution (0.15 M) kept at room temperature was also introduced into the reactor from a different line. Bubbling of the D-glucose solution with N₂ gas was done for more than 12 h to remove dissolved oxygen gas prior to each experiment. The weight ratio between the flow rates of the solution and the preheated water was 2:1. The concentration of the D-glucose solution after mixing at the reactor was 0.05 M. The reaction temperature was achieved by mixing the pressurized solution and preheated water at the mixing point. The solution reacted as flowing through the reactor and

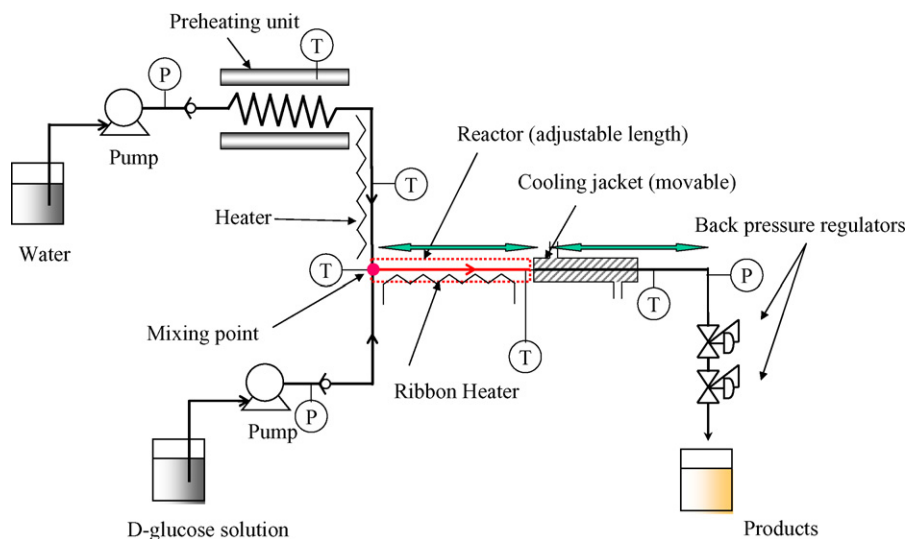


Fig. 1. Flow reactor for studying reactions of D-glucose in water at high temperature and high pressures.

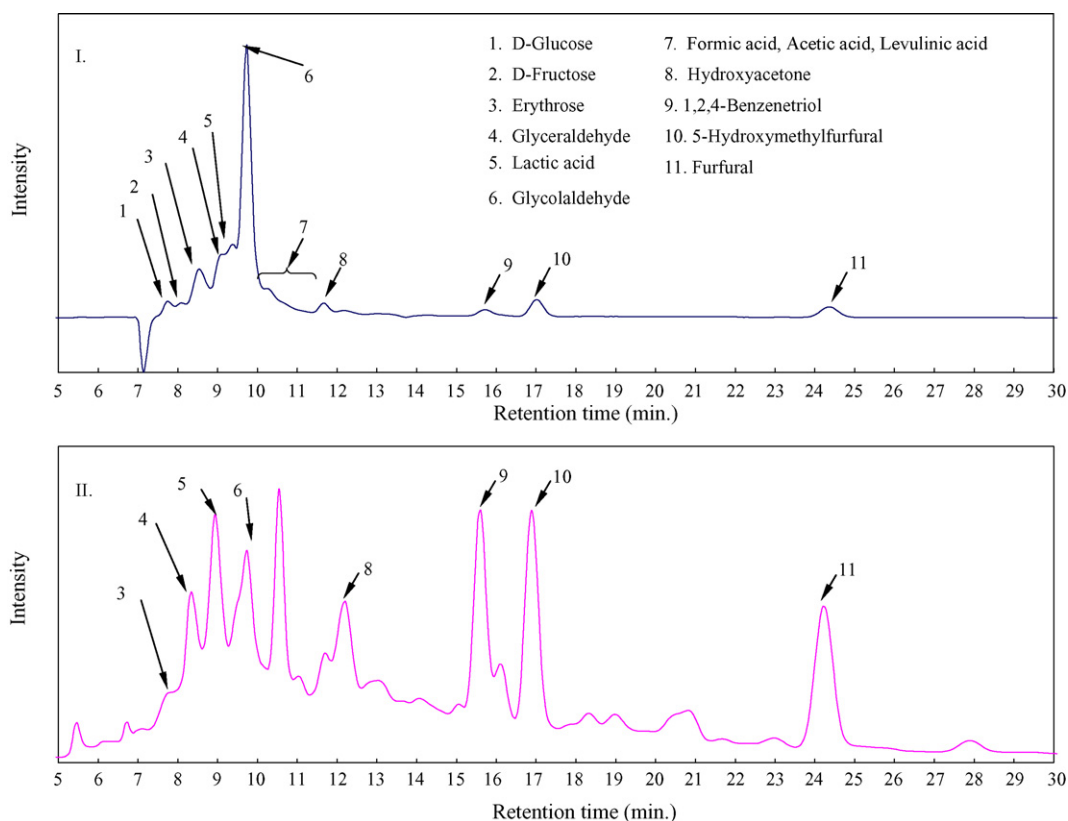


Fig. 2. Chromatograms: (I) HPLC-RI and (II) HPLC-UV (210 nm), for D-glucose reaction in water at 400 °C, 80 MPa, 0.8 s residence time.

was rapidly cooled by the cooling jacket area. Experiments were performed at temperatures of 350 and 400 °C and pressures of 40, 70 and 80 MPa. The residence time (τ) of the solvent was calculated by the following equation:

$$\tau(\text{s}) = V \times \frac{\rho_{T,P}}{F_{\text{total}}} \quad (1)$$

where V (cm^3) is the reactor volume, $\rho_{T,P}$ (g/cm^3) the water density at temperature T and pressure P and F_{total} (g/s) is the sum of the two flow rates, solution and water, at each experiment condition. The deviation of the flow rates of water and D-glucose solution at the reactor was kept within 5% of the total flow rate, which corresponds to about 5% error in the residence time. Further, the product will have a 5% error based on its yield.

The Reynolds numbers were calculated for the experiments using experimental conditions and physical properties [24] to have values greater than 2000. Thus, we judged that the mixing of the preheated water and sample solution was sufficient and the deviation of reaction time was not large.

Analysis of the liquid products were performed by HPLC-RI/UV (Shodex 8.0 mm \times 300 mm KC-811 column, mobile phase; 5 mM H_3PO_4 aqueous solution at 1 ml/min). The amount of carbon in the recovered solution was evaluated by a total organic carbon detector (Shimadzu, model TOC-5000A) to give carbon balances. D-Glucose conversion (X) and product yields (Y) were evaluated on a percentage carbon basis.

3. Results

Fig. 2 shows typical HPLC-RI and HPLC-UV chromatograms for products obtained from the reaction of D-glucose in water at 400 °C, 80 MPa and 0.8 s residence time. The wavelength of the UV detector was 210 nm. The compounds that were detected by HPLC were D-glucose (1), D-fructose (2), erythrose (3), glycolaldehyde (4), glyceraldehyde (5), hydroxyacetone (6), lactic acid (8), BTO (9), 5-HMF (10) and furfural (11). We were not able to detect compounds such as formic acid, acetic acid or levulinic acid separately. For use in later discussion, we summarized and constructed a reaction scheme of D-glucose in HHW without catalysts (Scheme 1) [9–12]. The compounds that

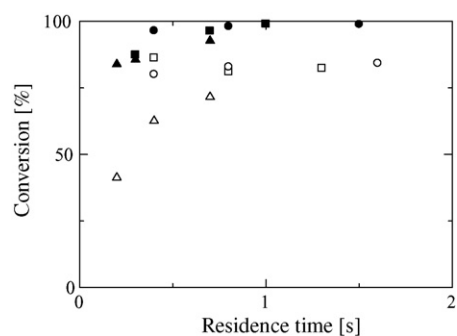


Fig. 3. D-Glucose conversion as a function of residence time: (Δ) 350 °C, 40 MPa; (\square) 350 °C, 70 MPa; (\circ) 350 °C, 80 MPa; (\blacktriangle) 400 °C, 40 MPa; (\blacksquare) 400 °C, 70 MPa; (\bullet) 400 °C, 80 MPa.

were quantified in this study were D-glucose (**1**), D-fructose (**2**), BTO (**9**), 5-HMF (**10**) and furfural (**11**). The products that were produced through the retro-aldol reaction of D-glucose, were not quantified because the focus of this paper was on dehydration reactions. Table 1 summarizes the experimental conditions, carbon balances, and product yields. From the carbon balance values, it can be seen that the reaction of D-glucose gave water-soluble products above 83% for all the reaction conditions.

Fig. 3 shows conversion of D-glucose as a function of residence time at 350 and 400 °C at 40, 70 and 80 MPa. D-Glucose conversion increased with increasing residence time and attained a value of 80 and 100% at 350 and 400 °C, respectively. At 350 °C, increasing pressure promoted D-glucose conversion. At 400 °C, pressure did not seem to affect D-glucose conversion.

Fig. 4 shows the yields of D-fructose (Fig. 4a), 5-HMF (Fig. 4b), BTO (Fig. 4c) and furfural (Fig. 4d) versus residence time. The yield of D-fructose at 350 °C increased with increasing residence time. At a given temperature, the D-fructose yield increased with decreasing pressure. At a given pressure, higher D-fructose yield was obtained for 400 °C than 350 °C.

The yield of 5-HMF increased with increasing residence time at 350 °C conditions. At pressures of 70 and 80 MPa, higher 5-HMF yields were obtained at 350 °C compared with those at 400 °C and longer residence times. The maximum yield of 5-HMF (8%) was obtained at 350 °C, 80 MPa and 1.6 s residence time. For a given temperature, the yield of 5-HMF increased with increasing pressure.

The yields of BTO and furfural also showed dependence on temperature, pressure and residence time. The yield of BTO became significant at 70 and 80 MPa compared to 40 MPa at given temperatures. At 70 and 80 MPa conditions, increasing temperatures increased the yields of BTO. The yield of furfural increased with increasing residence time at given temperatures. Also, increasing pressures at given temperatures, increased the yield of furfural giving a maximum yield of 12.2% at 400 °C and 80 MPa.

4. Discussion

Experimental results and consideration of the effect of the pressure and temperature on the reaction pathways will be discussed using Scheme 1. The effect of pressure on the various pathways can be explained by consideration of the water density.

The product 5-HMF (**10**) is obtained through the dehydration reaction of D-fructose (**2**). BTO (**9**) is a product of 5-HMF (**10**). The reaction starts from the hydrolysis of the furan ring of 5-HMF (**10**) followed by aldol-like reaction and finally dehydration reaction.

Fig. 5 shows the yields of BTO (**9**), 5-HMF (**10**) and furfural (**11**) as a function of water density and temperature at residence time of 0.7 and 0.8 s. The yields of BTO (**9**), 5-HMF (**10**) and furfural (**11**) all increased with increasing water density at constant temperature. The maximum yields of 5-HMF (**10**) at 350 and 400 °C were similar, though the sum of 5-HMF (**10**) and BTO (**9**) yields were higher for 400 °C than 350 °C conditions. This indicates that the increase of temperature and water density

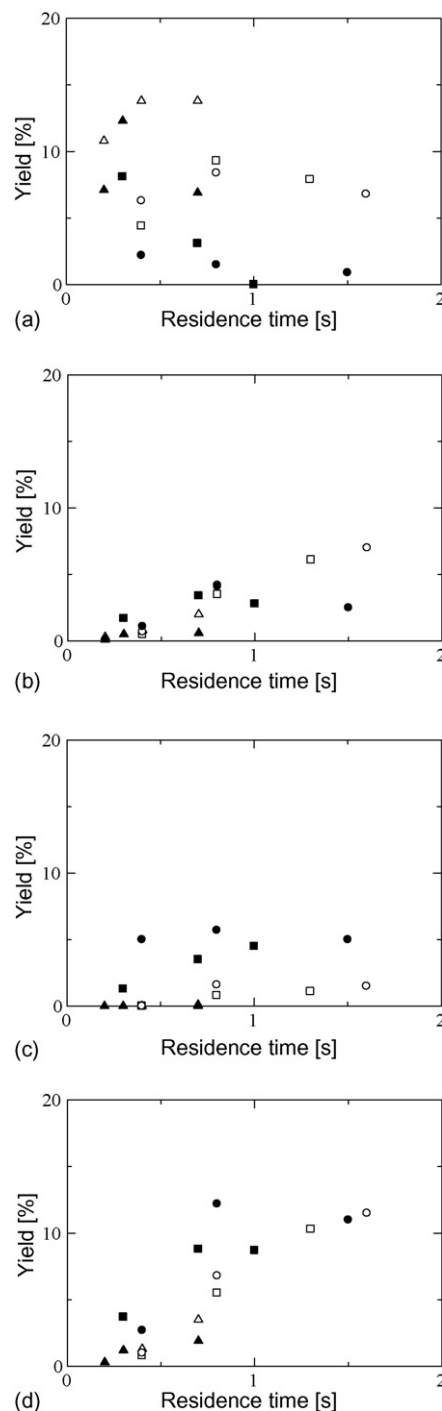


Fig. 4. (a) D-Fructose yield as a function of residence time: (Δ) 350 °C, 40 MPa; (□) 350 °C, 70 MPa; (○) 350 °C, 80 MPa; (▲) 400 °C, 40 MPa; (■) 400 °C, 70 MPa; (●) 400 °C, 80 MPa. (b) 5-Hydroxymethylfurfural (5-HMF) yield as a function of residence time: (Δ) 350 °C, 40 MPa; (□) 350 °C, 70 MPa; (○) 350 °C, 80 MPa; (▲) 400 °C, 40 MPa; (■) 400 °C, 70 MPa; (●) 400 °C, 80 MPa. (c) 1,2,4-Benzenetriol (BTO) yield as a function of residence time: (Δ) 350 °C, 40 MPa; (□) 350 °C, 70 MPa; (○) 350 °C, 80 MPa; (▲) 400 °C, 40 MPa; (■) 400 °C, 70 MPa; (●) 400 °C, 80 MPa. (d) Furfural yield as a function of residence time: (Δ) 350 °C, 40 MPa; (□) 350 °C, 70 MPa; (○) 350 °C, 80 MPa; (▲) 400 °C, 40 MPa; (■) 400 °C, 70 MPa; (●) 400 °C, 80 MPa.

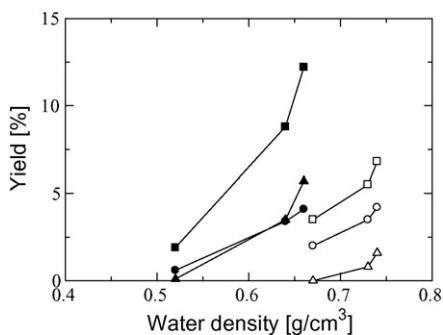


Fig. 5. Yields of 5-hydroxymethylfurfural (5-HMF), 1,2,4-benzenetriol (BTO) and furfural as a function water density and temperature at residence time 0.7 and 0.8 s; white and black symbols represent reactions conducted at 350 and 400 °C, respectively: (○, ●) 5-HMF; (△, ▲) BTO; (□, ■) furfural.

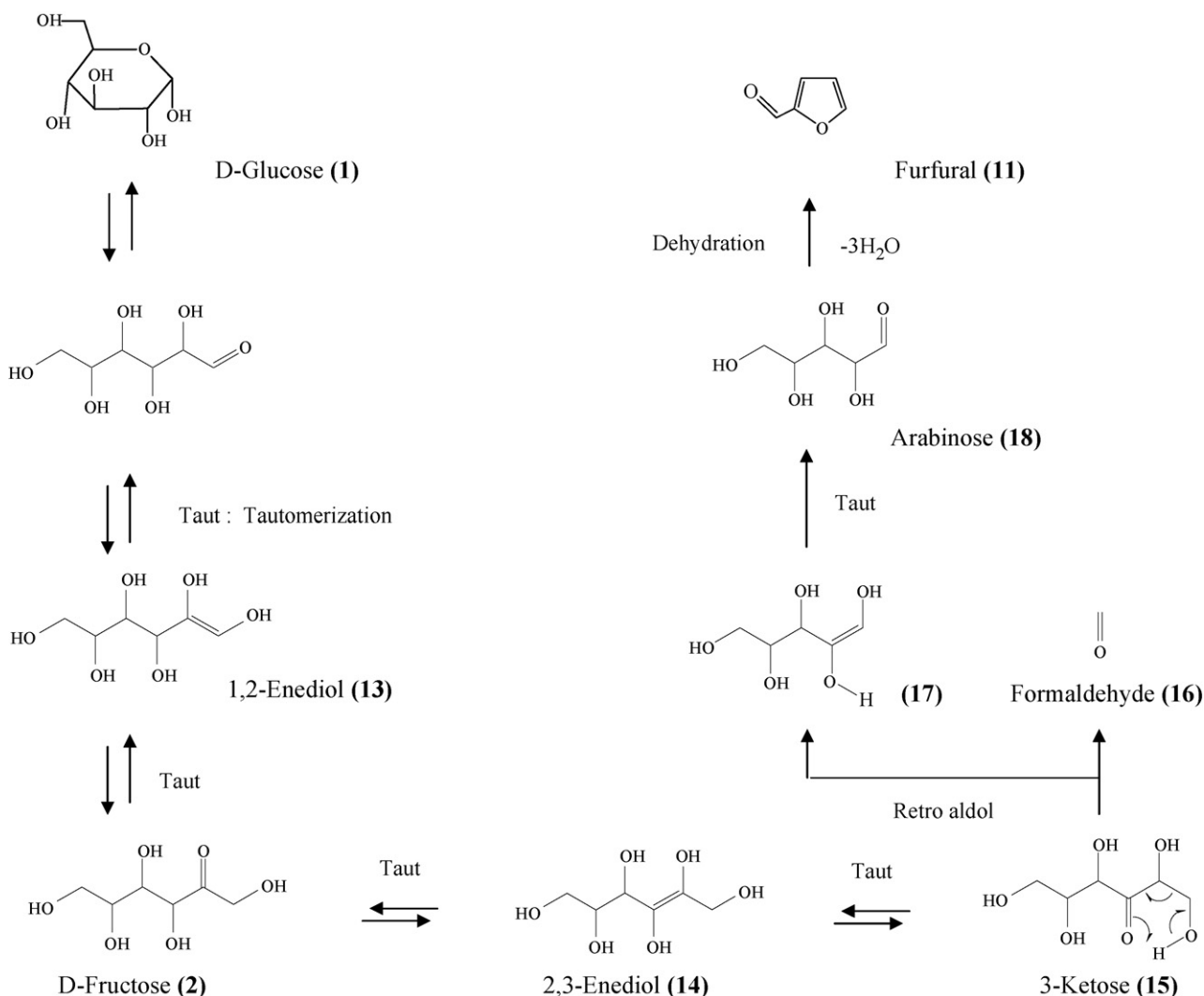
enhanced both dehydration reactions to 5-HMF (10) and hydrolysis reactions of 5-HMF (10), lead to the production of BTO (9). The formation of levulinic acid from 5-HMF (10) in high temperature high pressure water has been reported by Luijckx et al. [9]. It may be possible that the formation of levulinic acid (12)

from 5-HMF (10) [9,25] is enhanced by the increase of water density, though in this study, this cannot be discussed, since we were unable to analyze levulinic acid (12) by our HPLC method.

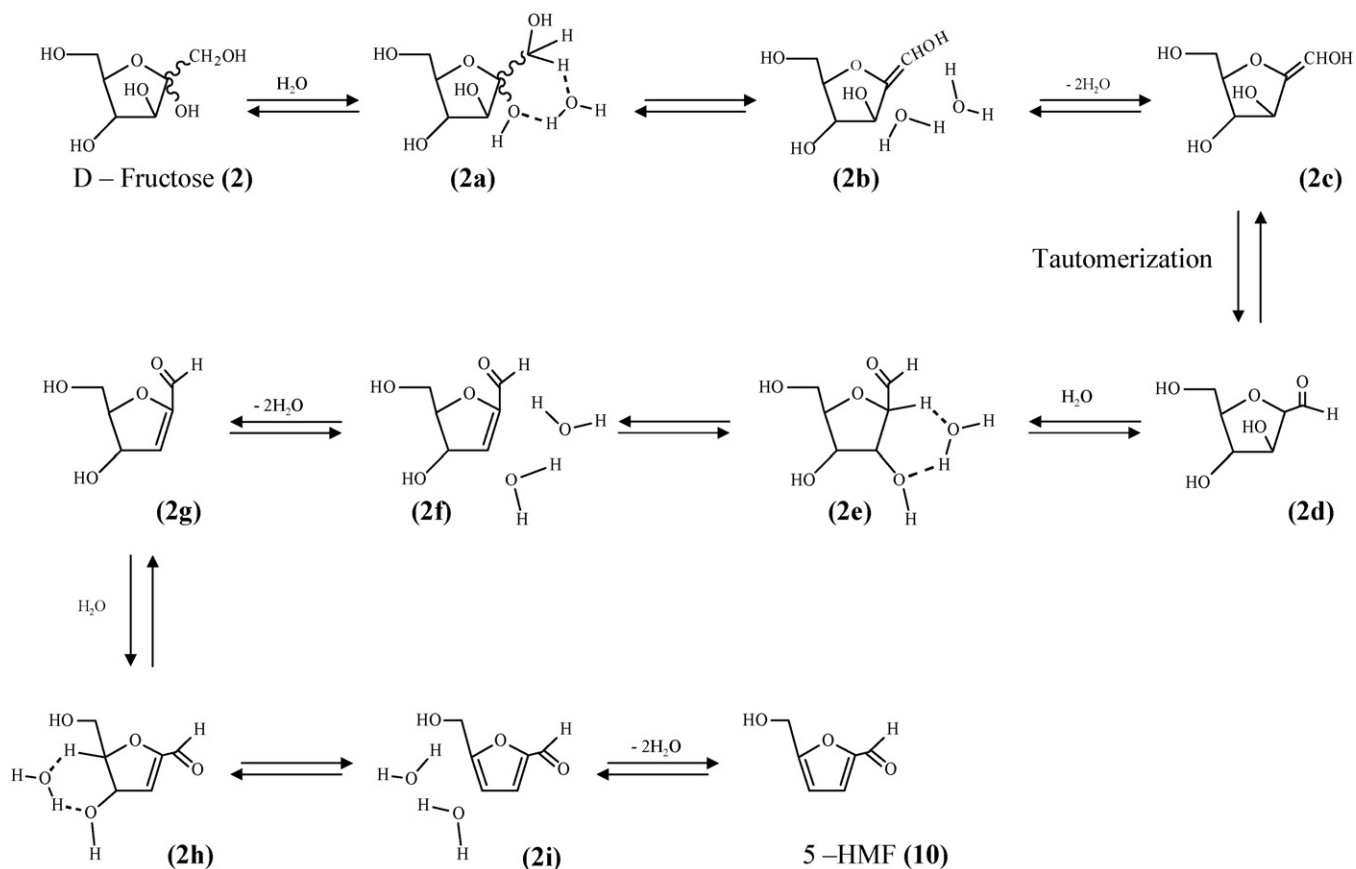
High temperatures, high water densities and short residence times seem to be advantageous for increasing 5-HMF (10) selectivity by kinetically preventing the formation of BTO (9). On the other hand, high temperatures, high water densities and long residence times might increase BTO (9) yields. As for furfural (11), high temperatures and high water densities and long residence times seem to increase furfural yields.

The 5-HMF (10) yields were low (below 10%) and this may be attributed to the tautomeric forms of D-fructose (2). Vogel and co-workers [18] have reported that D-pyranoid forms are in majority, compared to furanoid forms for D-fructose (2) in pure water at 25 °C. They suggested if this is so during the reaction, only the minor population of furanoid form of D-fructose (2) can react to form 5-HMF (10), leaving the majority to react through retro-aldol reactions to decomposition compounds.

The production of furfural (11) from 5-HMF (10) has been reported by Luijckx et al. [9]. We consider that another reaction path to furfural, that is, not via 5-HMF (10), may exist,



Scheme 2. Estimated reaction mechanism to furfural (11) from D-glucose (1) in water at high temperature and high pressures [23,26].



Scheme 3. Estimated reaction mechanism of dehydration of D-fructose (**2**) to 5-HMF (**10**) in water at high temperature and high pressures adopted from Antal et al. [10] for the acid hydrolysis.

which can be deduced from the yields of 5-HMF (**10**) and furfural (**11**) at 350 °C. If furfural (**11**) is formed via 5-HMF (**10**), the 5-HMF (**10**) yield should decrease as furfural (**11**) increases with residence time since furfural (**11**) was obtained in higher yields than 5-HMF (**10**). However, our results showed that both furfural (**11**) and 5-HMF (**10**) increased as a function of residence time at 350 °C. One possible reaction mechanism has been reported by Krishna et al. [25], who proposed a reaction mechanism that consisted of: (1) isomerization of D-fructose and D-glucose to 1,2-enediol (**13**), (2) dehydration of 1,2-enediol to 3-deoxy-hexosulose followed by dehydration and decomposition reaction forming formaldehyde, and another dehydration reaction to form furfural. We suggest another possible reaction mechanism from D-glucose (**1**) to furfural (**11**) as shown in Scheme 2. First, D-glucose (**1**) will react to D-fructose (**2**), 1,2-enediol (**13**), 2,3-enediol (**14**) and form a 3-ketose (**15**) through tautomerization reactions. The formation of 3-ketose (**15**) from D-glucose (**1**) has been reported based on a series of ^{14}C labeled hexose experiments done in potassium hydrogen phosphate buffer (pH 6.7) to form acetol [26]. This 3-ketose (**15**) may go through a retro-aldol reaction forming formaldehyde (**16**) and arabinose (**18**). The formation of furfural from pentoses such as D-xylose and D-arabinose (**18**), have been reported by Antal et al. [27] and Srokol et al. [23], respectively. Although we were not able to detect arabinose (**18**) or formaldehyde (**16**) in the experiments, our data show that the yield of furfural (**11**)

increased with increasing water density at 400 °C and consider that this was due to the enhancement of dehydration reactions with increasing water density.

One explanation for the pressure effect (density effect) on the dehydration and hydrolysis reactions may be obtained by considering the estimated transition states. Water molecules can enhance chemical reactions by participating in the transition state by forming the so-called “water bridge” and lowering the transition energy [8,21,22]. We constructed a reaction mechanism (Scheme 3) based on that proposed by Antal et al. [10]. If we assume that water participates in the transition state of the dehydration reactions and forms a 6-member ring transition state (**2a**, **2e**, **2h**), thus lowers the transition energy, and so the increase of water density will increase the population of these transition states and enhance dehydration reactions. As for the hydrolysis reactions, increasing water density would cause an increase in the collisions of water molecules and 5-HMF (**10**) and thus providing some enhancement. Spectroscopic analyses at these conditions would be useful to clarify the detailed mechanisms.

Another explanation for the pressure effect (density effect) on the dehydration and hydrolysis reactions may be due to the change in of ion product (K_w) of HHW. Higher K_w values have been reported to enhance dehydration and hydration reactions by increasing the activity of the acid catalyst [7]. The K_w value of HHW increases from -11.3 to -10.7 (mol/kg) 2 at 350 °C and

from -12.5 to -11.1 (mol/kg)² at 400 °C when the pressure is increased from 40 to 80 MPa [28]. This increase in K_w may promote the acid catalyst effect on the dehydration and hydration reactions.

5. Conclusions

Reaction of D-glucose in water at high temperatures (350 and 400 °C) and high pressures (up to 80 MPa) was studied using a flow reactor. At given temperatures, an increase in pressure from 40 to 80 MPa lead to an increase in yields of 1,2,4-benzenetriol, 5-HMF and furfural. An increase in pressure (40 MPa to 70 and 80 MPa) and temperature (350 – 400 °C) enhanced dehydration reactions to provide 5-HMF, but also enhanced hydrolysis of 5-HMF leading to the production of BTO.

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