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Highlights

- The intramolecular dehydration of biomass-derived hexitols was performed.
- The rate constants for the dehydration steps in the reaction networks were determined.
- The yield of each product was estimated as a function of reaction time and temperature.
- Products can be selected by choosing the appropriate reaction time and temperature.

Kinetic analyses of intramolecular dehydration of hexitols in high-temperature water

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Abstract

Intramolecular dehydration of the biomass-derived hexitols D-sorbitol, D-mannitol, and galactitol was investigated. These reactions were performed in high-temperature water at 523–573 K without added acid catalyst. The rate constants for the dehydration steps in the reaction networks were determined at various reaction temperatures, and the activation energies and pre-exponential factors were calculated from Arrhenius plots. The yield of each product was estimated as a function of reaction time and temperature using the calculated rate constants and activation energies. The maximum yield of each product from the dehydration reactions was predicted over a range of reaction time and temperature, allowing the selective production of these important platform chemicals.

Keywords

Dehydration; Sugar alcohol; High-temperature water; Isosorbide; Isomannide

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1. Introduction

The production of chemicals from renewable lignocellulosic biomass has attracted much attention because of possible improvements in environmental sustainability relative to other sources for production [1–3]. Cellulose and hemicellulose are major polysaccharide components of lignocellulosic biomass; they can be hydrolyzed into sugars such as glucose and xylose and then hydrogenated into sugar alcohols [4–6]. The sugar alcohols sorbitol and xylitol are on the DOE list of the top 12 platform chemicals [5] (that is, chemicals that can be used as building blocks and converted to a wide range of materials), and also on the new list produced by Bozell and Petersen of the top 10 chemicals derived from biomass [2]. Fukuoka et al. reported the use of supported metal catalysts and hydrogen to convert cellulose directly into sorbitol [7–10]. The conversion of cellulose into sorbitol has been further developed by other research groups [10–15]. Hemicellulose has also been directly converted into sugar alcohols through hydrolysis and hydrogenation reactions over supported metal catalysts under hydrogen [16]. In previous studies we have reported that cellulose and hemicellulose in lignocellulosic biomass could be directly converted to sugar alcohols such as sorbitol, mannitol, and xylitol without delignification of the biomass [17–19].

The dehydration of hexitols has attracted attention as a means to provide valuable chemicals from biomass-derived sugar alcohols [20–23]. Isosorbide and isomannide, which can be obtained from the dehydration of sorbitol and mannitol, have a rigid structure with two hydroxyl groups; thus, they are promising monomers for the preparation of polyesters and polycarbonates, and provide enhanced heat resistance when compared with monomer ethylene glycol [24]. Anhydrohexitol is also a key material for the production of fatty acid esters, which are naturally derived surfactants and nontoxic food additives [25, 26].

Some researchers have reported the dehydration of sorbitol with inorganic acid catalysts such as sulfuric acid and hydrochloric acid at 377–408 K [27, 28] or with zeolite catalysts [23, 29]. High-temperature water has also attracted much attention as a promising reaction medium for acid-catalyzed reactions [30–32]. In our previous work, we have reported the dehydration of hexitols such as sorbitol, mannitol, and galactitol, in high-temperature water without the addition of any acid catalysts [20, 21, 33]. We have also reported the rate constants and activation energies of each step in the reaction networks of these hexitol dehydrations.

The prediction of products from dehydration reactions by using functions of reaction time and temperature is important, as it allows valuable products to be obtained efficiently from biomass. In this manuscript, we compare the intramolecular dehydration of biomass-derived hexitols D-sorbitol, D-mannitol, and galactitol in high-temperature water without the addition of any hazardous acid catalyst; furthermore, we calculate the products as functions of reaction time and temperature with the rate constants and activation energies of these hexitol dehydrations. The reaction time and temperature required for the maximum yield of each product from the dehydration reactions can be determined, allowing selective production.

2. Experimental

D-sorbitol, D-mannitol, and galactitol were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

The dehydration of hexitols was performed in a batch reactor (inner volume: 6 cm^3) made of a stainless steel 316 tube [20, 21, 33]. An aqueous solution of sorbitol or mannitol (3 cm^3, 0.5 mol dm^{-3}) was loaded into the reactor and then purged with argon gas to remove the air. For the dehydration of galactitol, 3 cm^3 of 0.1 mol dm^{-3} was used because of its low solubility in water. The reactor was submerged into a molten-salt bath at the desired reaction temperature for a given reaction time and then submerged into a water bath to cool quickly to ambient temperature after the reaction.

A mixture of the reactant and products was rinsed out of the reactor with distilled water, and the solids were separated by filtration.

The quantitative analysis of the unreacted reactant and the liquid products was conducted using high-performance liquid chromatography (HPLC, Shimadzu) equipped with a SUGAR SC1211 column (Shodex) with a refractive index detector (Shimadzu, RID-10A) and a UV–Vis detector (Shimadzu, SPD-20AV). The products were identified by comparing the retention times with those of standard materials: 1,4-anhydro-D-sorbitol and 2,5-anhydro-D-sorbitol (Toronto Research Chemicals, Inc.); isosorbide (Alfa Aesar); 1,5-anhydro-D-sorbitol, 1,4-anhydro-D-mannitol, 1,5-anhydro-D-mannitol, and 2,5-anhydro-D-mannitol (Carbosynth, Ltd.); and isomannide (Tokyo Chemical Industries Co., Ltd.). The HPLC peaks that could not be identified by comparison with the standard materials were identified by collecting the appropriate fractions with a fraction collector, removing the solvent with a rotary evaporator, and performing ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Bruker AVANCE III HD 400 MHz). The products and rate constant for each step are shown in Scheme 1.

3. Results and discussion

3.1. Dehydration of hexitols

We have previously reported reaction mechanism of the intramolecular dehydration of polyalcohols from the results of (2*R*,5*R*)-(–)-2,5-hexanediol dehydration into 2,5-dimethyltetrahydrofuran (2,5-DMTHF) [32]. The high *cis* selectivity of 2,5-DMTHF in the products indicated that the polyalcohol dehydration proceeded mainly via an S_N2 substitution process as follows. At first, hydroxyl groups connected with C-2 or C-5 position was protonated, and then oxygen atom in unprotonated hydroxyl group attacked carbon atom connected with protonated hydroxyl group and simultaneous elimination of water occurred (S_N2 mechanism). The dehydration reactions of hexitols such as D-sorbitol, D-mannitol, and galactitol in high-temperature water have been described in previous papers [20, 21, 33]. The reaction schemes are shown in Scheme 1, and yields of products from D-sorbitol, D-mannitol, and galactitol dehydration at 523 K and 573 K are shown in Fig. 1. In the case of hexitol dehydration, the hydroxyl group at the C-*x* position is protonated, and then the oxygen atom at the C-*y* position attacks the C-*x* carbon and a water molecule is eliminated simultaneously, resulting in the production of a cyclic ether, which is represented as *x*-*y*-AH*zz* in this paper where *zz* represents the following two letter codes SO = sorbitol, MA = mannitol, GL = galactitol (the abbreviations of anhydrohexitols are shown in Scheme 1). Briefly, 1-4-AHSO and 1-4-AHGL were the main products from the monomolecular dehydration of D-sorbitol and galactitol, respectively, in high-temperature water at 523 K and 573 K; both 1-4-AHMA and 2-5-AHMA were comparably produced from the monomolecular dehydration of D-mannitol. Isosorbide and isomannide were produced by the further dehydration of 1-4-AHSO and 1-4-AHMA, respectively (Scheme 1). The yield of isosorbide was higher than that of isomannide because D-sorbitol was dehydrated to 1-4-AHSO with a high yield. Dehydration of 1-4-AHGL did not proceed in high-temperature water even at 573 K. The dehydration rates of D-sorbitol, D-mannitol, and galactitol increased with increasing reaction temperature (Fig. 1).

The hydroxyl groups at the C-3 and C-6 positions are located on the same side of the tetrahydrofuran ring in the molecular structure of 1-4-AHSO and 1-4-AHMA (Scheme 1), allowing the further dehydration of these anhydrohexitols between the hydroxyl groups at the C-3 and C-6 positions via an S_N2 substitution process. Conversely, the hydroxyl groups at the C-3 and C-6 positions are located on different sides across the tetrahydrofuran ring in the molecular structure of 1-4-AHGL (Scheme 1(c)) [33–35] because the oxygen atom at the C-3 (C-6) position cannot attack the C-6 (C-3) carbon.

Previously, we showed that the dehydration reactions of hexitols have a first-order dependence on their concentrations [20]. To understand the kinetics of the hexitol dehydration, the rate constants (Scheme 1) were estimated from linear regression analyses by minimizing the residuals of the data (Table 1) with the following equations in the cases of D-sorbitol and D-mannitol (equations for galactitol have been presented in the Supporting Information of our previous paper [33]).

$$\frac{d[\mathrm{A}]}{dt} = -k_{1\mathrm{A}}[\mathrm{A}] - k_{2\mathrm{A}}[\mathrm{A}] - k_{3\mathrm{A}}[\mathrm{A}] - k_{6\mathrm{A}}[\mathrm{A}] \qquad (1)$$

$$\frac{d[\text{1-4-AH-A}]}{dt} = k_{1\mathrm{A}}[\mathrm{A}] - k_{4\mathrm{A}}[\text{1-4-AH-A}] \qquad (2)$$

$$\frac{d[\text{2-5-AH-A}]}{dt} = k_{2\mathrm{A}}[\mathrm{A}] \qquad (3)$$

$$\frac{d[\text{dianhydro-A}]}{dt} = k_{4\mathrm{A}}[\text{1-4-AH-A}] - k_{5\mathrm{A}}[\text{dianhydro-A}] \qquad (4)$$

$$[\mathrm{A}] = [\mathrm{A}]_i \exp\{(-k_{1\mathrm{A}} - k_{2\mathrm{A}} - k_{3\mathrm{A}} - k_{6\mathrm{A}})t\} \qquad (5)$$

$$[\text{1-4-AH-A}] = \frac{k_{1\mathrm{A}}}{k_{4\mathrm{A}} - k_{1\mathrm{A}} - k_{2\mathrm{A}} - k_{3\mathrm{A}} - k_{6\mathrm{A}}}[\mathrm{A}]_i[\exp\{(-k_{1\mathrm{A}} - k_{2\mathrm{A}} - k_{3\mathrm{A}} - k_{6\mathrm{A}})t\} - \exp(-k_{4\mathrm{A}}t)] \qquad (6)$$

$$[\text{2-5-AH-A}] = \frac{k_{2\mathrm{A}}}{k_{1\mathrm{A}} + k_{2\mathrm{A}} + k_{3\mathrm{A}} + k_{6\mathrm{A}}}[\mathrm{A}]_i[1 - \exp\{(-k_{1\mathrm{A}} - k_{2\mathrm{A}} - k_{3\mathrm{A}} - k_{6\mathrm{A}})t\}] \qquad (7)$$

$$[\text{dianhydro-A}] = \frac{k_{1A}k_{4A}}{k_{4A}-k_{1A}-k_{2A}-k_{3A}-k_{6A}}[\text{A}]_i\left[\frac{\exp\{(-k_{1A}-k_{2A}-k_{3A}-k_{6A})t\}-\exp(-k_{5A}t)}{k_{5A}-k_{1A}-k_{2A}-k_{3A}-k_{6A}} - \frac{\exp(-k_{4A}t)-\exp(-k_{5A}t)}{k_{5A}-k_{4A}}\right] \tag{8}$$

In the equations, A represents D-sorbitol or D-mannitol, and $[\text{A}]_i$ represents the initial concentration of A. The rate constants for the dehydration reactions at 523 K and 573 K are summarized in Table 1, and the activation energy and pre-exponential factor were evaluated from Arrhenius plots using the kinetic data at 523 K, 548 K, 560 K, and 573 K (Table 1). The fitting results (calculated yields from the equations and the parameters in Table 1) are shown in Figure 1. In all cases, the correlation coefficients (R^2) are more than 0.97, indicating that the fitting results are reasonable.

3.2. Product yields from hexitol dehydration as functions of reaction temperature and time

The rate constant as a function of reaction temperature can be estimated from the activation energy and pre-exponential factor for the corresponding step in the dehydration network (Table 1). The yield of each product from the hexitol dehydration as a function of reaction time can be calculated from the rate constants and rate equations (eqs. (5)–(8)). Therefore, the yield of each product can be estimated as a function of reaction time and temperature (Fig. 2).

In the case of sorbitol dehydration, the 1-4-AHSO yield is predicted to increase with decreasing reaction temperature. The maximum yield of 1-4-AHSO within the reaction time of 10 h is estimated to be 64.6% at 525 K for 10 h; the maximum yield of isosorbide from the dehydration of sorbitol is estimated to be 57.6% at 590 K for 1 h (Fig. 2 (a)).

We predict that the individual products from sorbitol dehydration can be produced selectively by controlling the reaction time and temperature. In the case of mannitol dehydration, the yield of 2-5-AHMA is calculated to be always higher than that of 1-4-AHMA in the temperature range of 500–600 K (Fig. 2 (b)). The maximum yields of 1-4-AHMA and 2-5-AHMA are predicted to be 23.5% (at 540 K for 10 h) and 40.5% (at 550 K for 10 h), respectively. Isomannide can be obtained after the peak of 1-4-AHMA and the maximum yield of isomannide is estimated to be 25.3% at 585 K for 10 h, indicating that selective production of isomannide is difficult from mannitol dehydration in water. However, isomannide can be produced from mannitol dehydration by using the solid acid catalyst Hβ zeolite (yield 63%) [36]. For the galactitol dehydration, 1-4-AHGL is the main product and the predicted maximum yield of 1-4-AHGL is 62.4% at 550 K for 10 h (Fig. 2 (c)).

4. Conclusions

The intramolecular dehydration of biomass-derived sugar alcohols D-sorbitol, D-mannitol, and galactitol was carried out in high-temperature water at 523 K – 573 K without any added acid catalyst. The kinetic parameters of the dehydration reactions were estimated. The yield of each product from the dehydration reaction was calculated as a function of reaction time and temperature. The maximum yield of 1-4-AHSO within the reaction time of 10 h is predicted to be 64.6% (at 525 K for 10 h), and of isosorbide to be 57.6% (at 590 K for 1 h) from the sorbitol dehydration. By controlling the reaction time and temperature, it is predicted that individual products can be produced selectively.

Acknowledgements

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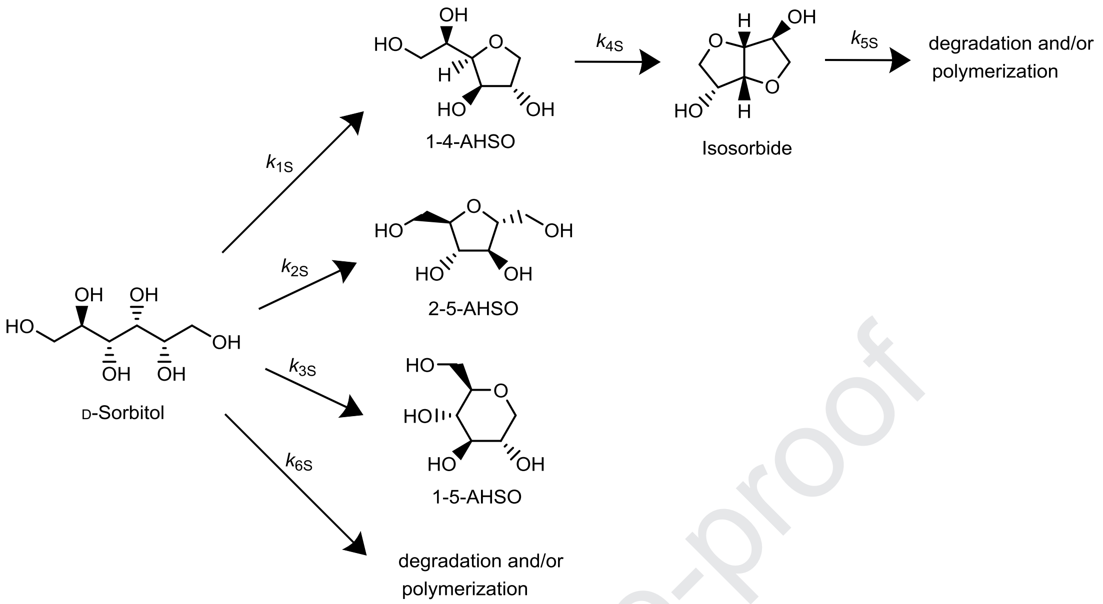
(a)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1-4-AHSO
k_{4S}
Isosorbide
k_{5S}
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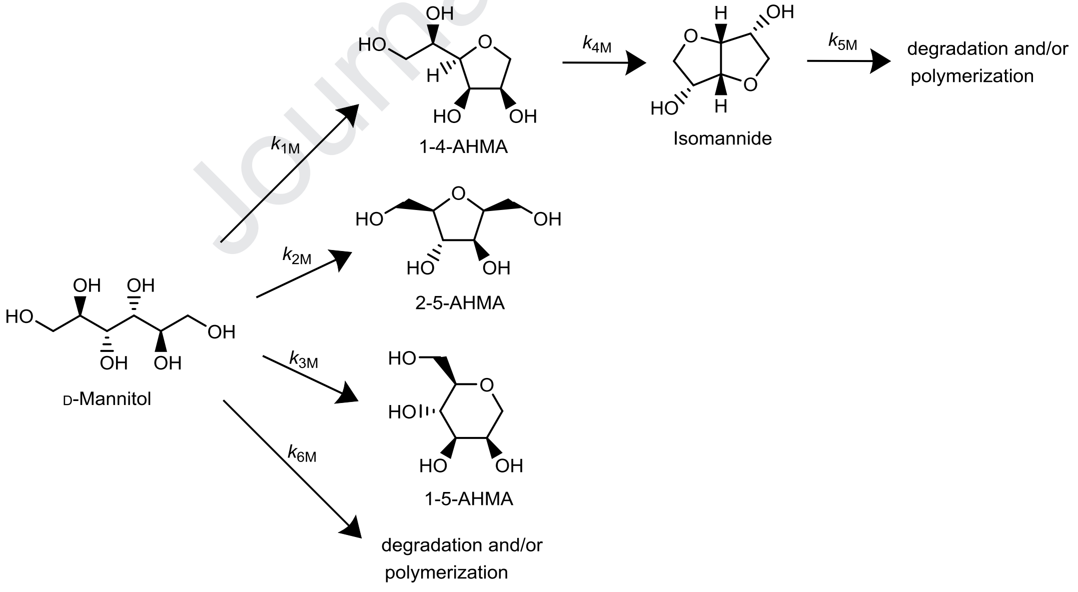
degradation and/or polymerization

(b)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Isomannide
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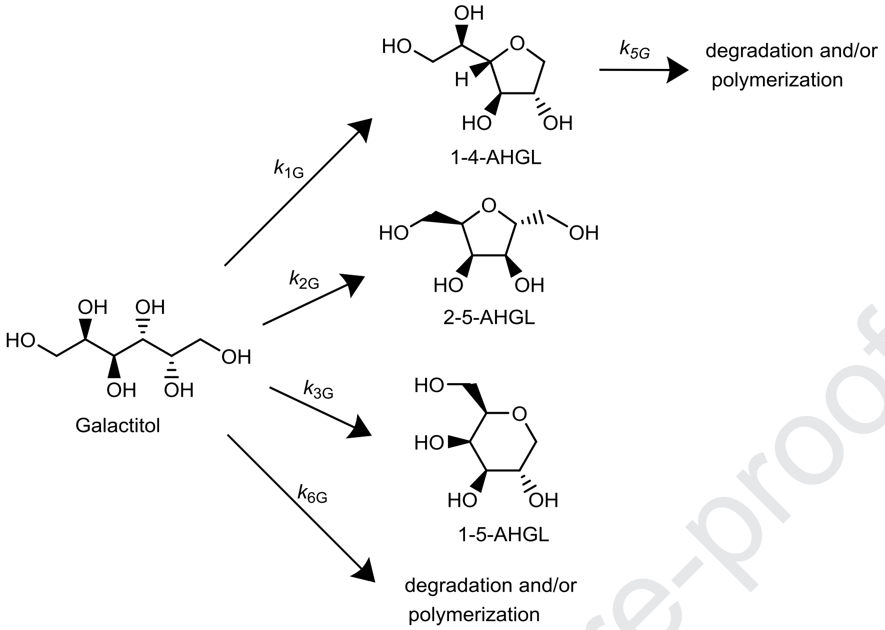
(c)



Scheme 1 The reaction pathways for the dehydration of (a) D-sorbitol, (b) D-mannitol, and (c) galactitol.

Table 1 Kinetic parameters for the dehydration reactions of D-sorbitol, D-mannitol, and galactitol

Rate constant (h^{-1})	Reaction temperature (K)		Activation energy (kJ mol^{-1})	Pre-exponential factor (h^{-1})
	523	573		
k_{1S}	0.13	0.84	127	8.4×10^{11}
k_{2S}	0.013	0.32	166	3.1×10^{14}
k_{4S}	0.016	0.78	195	5.8×10^{17}
k_{5S}	0.0083	0.11	136	5.9×10^{11}
k_{1M}	0.023	0.44	148	1.6×10^{13}
k_{2M}	0.028	0.60	153	5.3×10^{13}
k_{3M}	0.0044	0.065	135	1.5×10^{11}
k_{4M}	0.0093	0.17	151	1.1×10^{13}
k_{6M}	0.0097	0.51	196	3.7×10^{17}
k_{1G}	0.049	0.84	144	1.2×10^{13}
k_{2G}	0.0056	0.14	133	1.1×10^{14}
k_{5G}	–	0.062	–	–
k_{6G}	0.017	0.24	163	3.0×10^{11}

$k_{3S} = k_{6S} = k_{5M} = k_{3G} = 0$

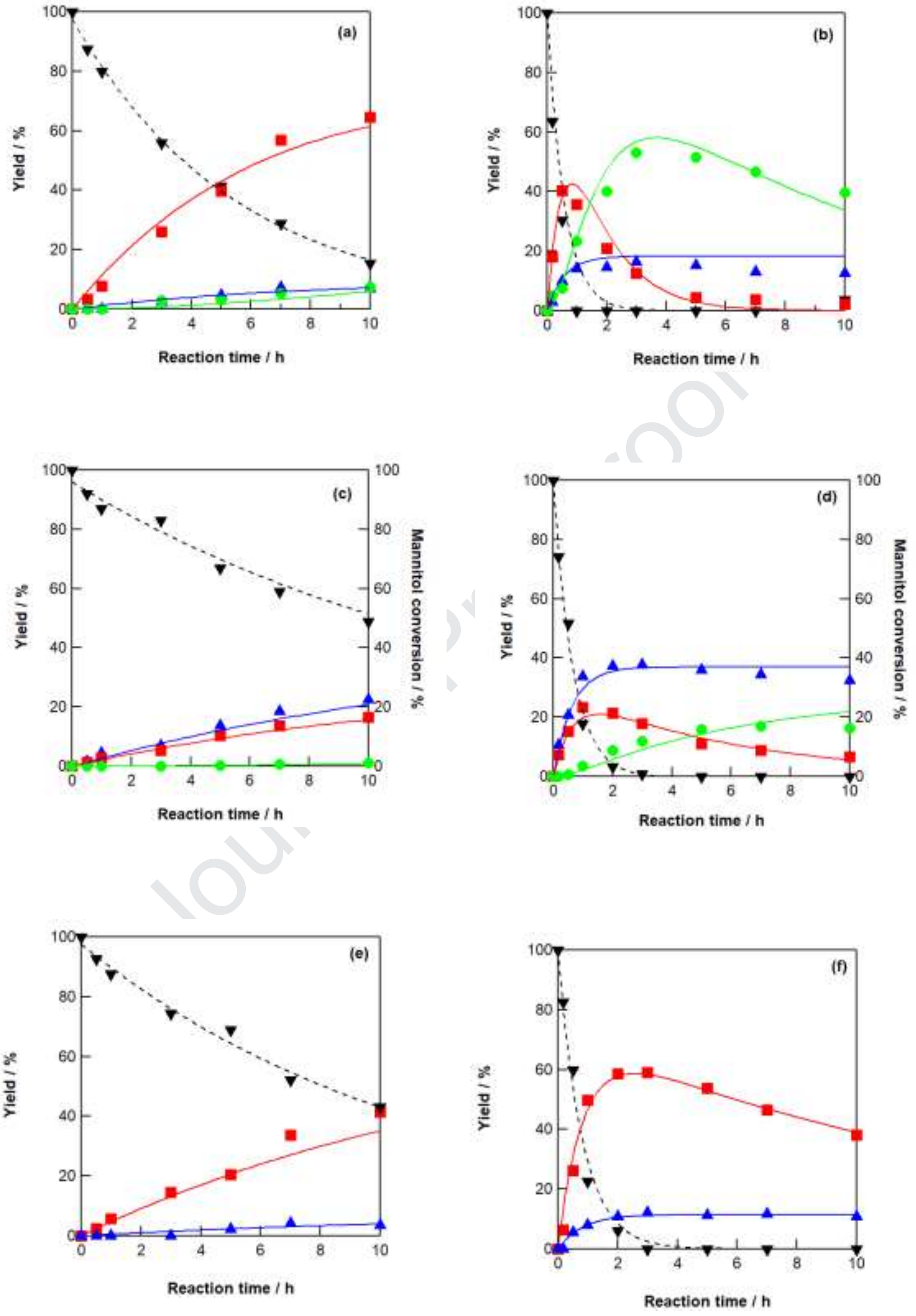
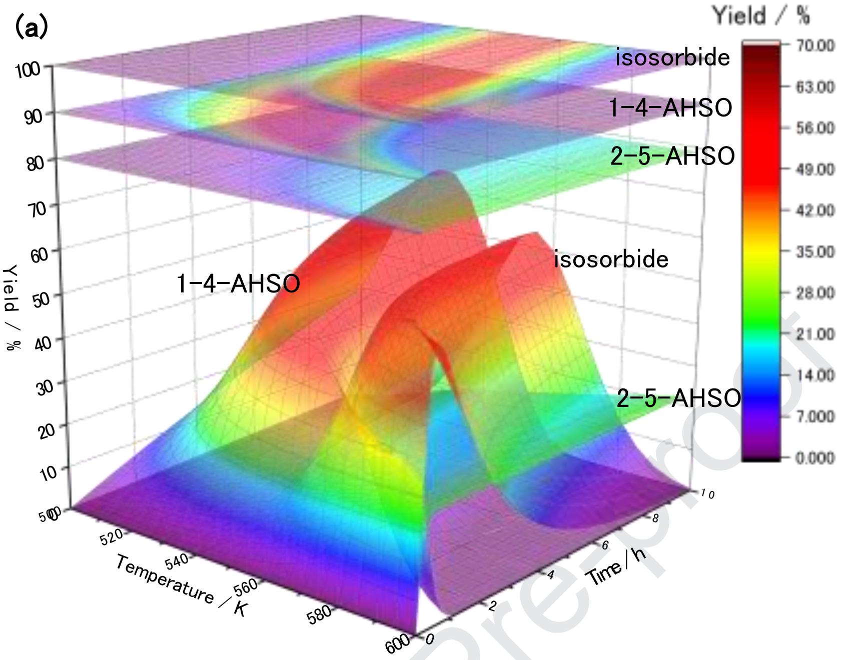
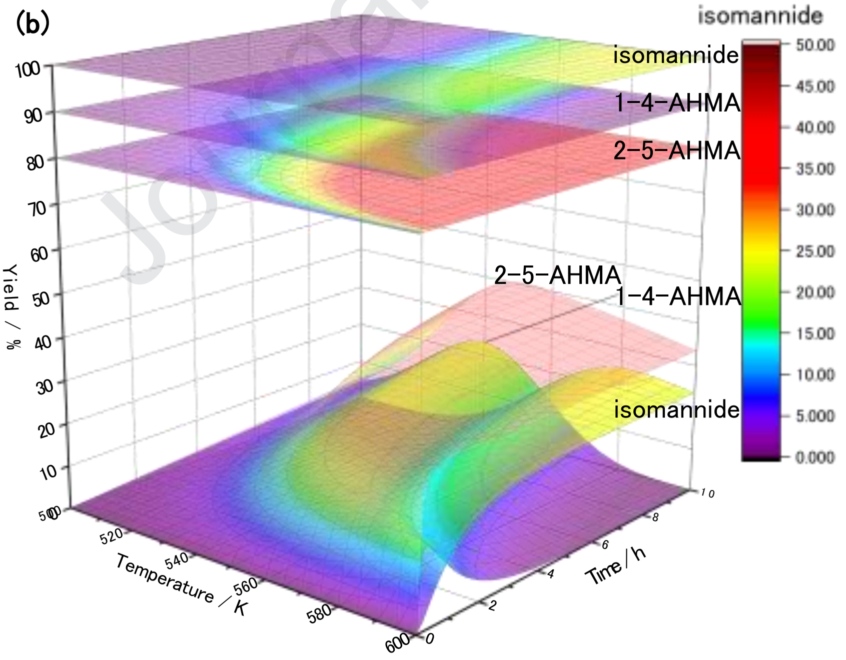

(a)
(b)
(c)
(d)
(e)
(f)
Yield / %
Mannitol conversion / %
Reaction time / h
0
2
4
6
8
10
20
40
60
80
100

Fig. 1 Dehydration yields in high-temperature water as a function of elapsed time. Sorbitol dehydration at (a) 523 K and (b) 573 K: 1-4-AHSO (■), 2-5-AHSO (▲), isosorbide (●), and unreacted sorbitol (▼). Mannitol dehydration at (c) 523 K and (d) 573 K: 1-4-AHMA (■), 2-5-AHMA (▲), isomannide (●), and unreacted mannitol (▼). Galactitol dehydration at (e) 523 K and (f) 573 K: 1-4-AHGL (■), 2-5-AHGL (▲), and unreacted galactitol (▼). The lines show the fitting results of the obtained data to the equations (5) – (8) with the kinetic parameters in Table 1.


(a)
Yield / %
70.00
63.00
56.00
49.00
42.00
35.00
28.00
21.00
14.00
7.000
0.000
isosorbide
1-4-AHSO
2-5-AHSO
1-4-AHSO
isosorbide
2-5-AHSO
Yield / %
100
90
80
70
60
50
40
30
20
10
0
500
520
540
560
580
600
Temperature / K
0
2
4
6
8
10
Time / h


(b)
isomannide
50.00
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.000
0.000
isomannide
1-4-AHMA
2-5-AHMA
2-5-AHMA
1-4-AHMA
isomannide
Yield / %
100
90
80
70
60
50
40
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4
6
8
10
Time / h

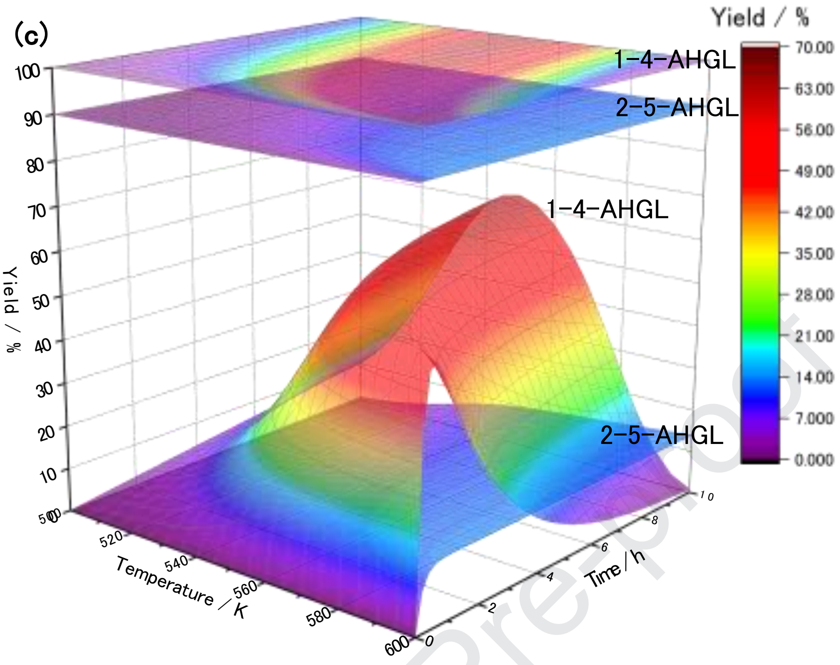
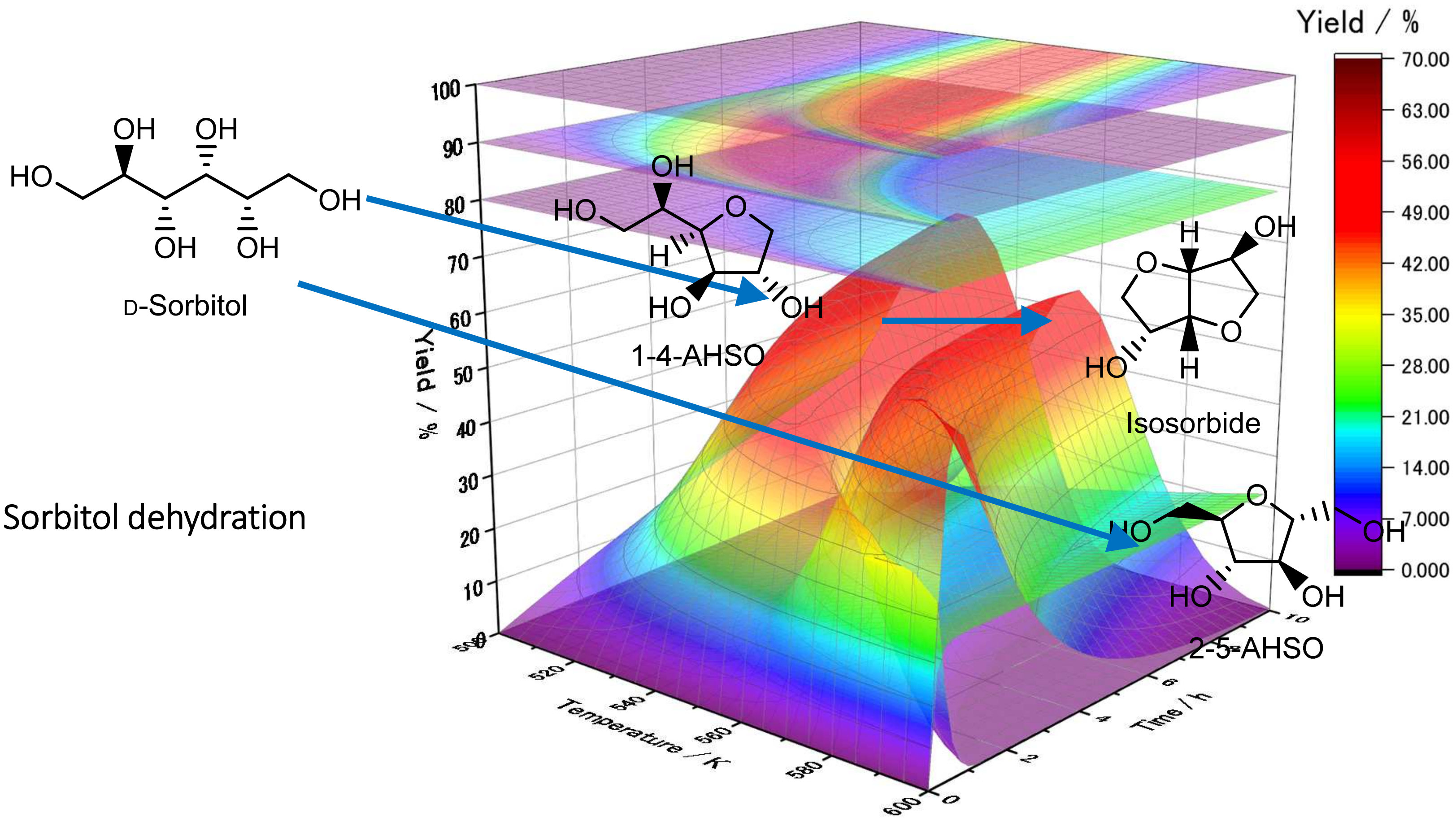


Fig. 2 Predicted dehydration yields in high-temperature water as functions of reaction time and temperature. (a) Yields of 1-4-AHSO, 2-5-AHSO, and isosorbide from sorbitol dehydration; (b) yields of 1-4-AHMA, 2-5-AHMA, and isomannide from mannitol dehydration; and (c) yields of 1-4-AHGL and 2-5-AHGL from galactitol dehydration.


Sorbitol dehydration
D-Sorbitol
1-4-AHSO
Isosorbide
2-5-AHSO
Yield / %
70.00
63.00
56.00
49.00
42.00
35.00
28.00
21.00
14.00
7.000
0.000
Yield / %
100
90
80
70
60
50
40
30
20
10
0
500
520
540
560
580
600
Temperature / K
0
2
4
6
10
Time / h

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Dear Prof. Kan Ding,

All the authors declare no conflicts of interest associated with this manuscript.

Very sincerely yours,

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