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Facile isomerization of glucose into fructose using anion-exchange resins in organic solvents and application to direct conversion of glucose into furan compounds

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Abstract The facile isomerization of glucose into fructose has been developed using commercially available anion-exchange resins (AERs) in organic solvents. Following extensive screening for the amount and type of AERs, solvents and reaction time, glucose was transformed into fructose in yields of up to 50% using Amberlite A-26 with macroreticular morphology and tertiary amine functionality in a protic solvent (ethanol). AERs could be used five times without a significant loss of activity. This isomerization method could be applied to the direct conversion of glucose into furan compounds by integrating the dehydration of fructose with cation-exchange resins.

Keywords Isomerization · Glucose · Fructose · Anion-exchange resins · Organic solvents · Direct conversion

Introduction

Bio-based chemicals from renewable and sustainable resources are attracting attention as substitutes for fossil-based chemicals [1]. Biomass-derived carbohydrates such as cellulose and starch represent 75% of the annually regenerated biomass [2]. Glucose, as a repeating unit of cellulose and starch, is considered the

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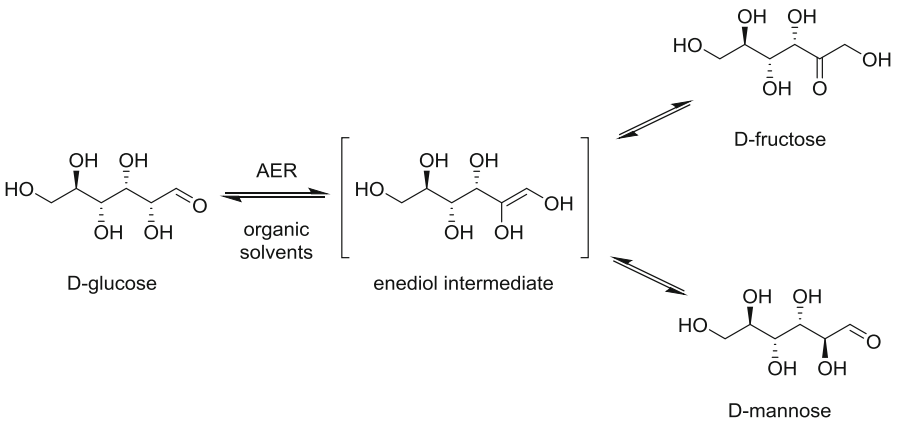
most abundant bio-refinery starter [3]. However, fructose—an isomer of glucose—is attracting research as a more effective starter for creating furan compounds, which possess great potential in industrial applications [4]. For example, 5-hyroxymethyl-2-furfural (HMF) obtained from the dehydration of fructose is a versatile platform chemical that can be converted into fuels and a variety of monomers for bioplastics.

Due to lack of availability, the isomerization of glucose into fructose appears to be a crucial step for the development of a furan platform. The commercialized isomerization of glucose into fructose is conducted using glucose isomerase (also known as xylose isomerase) [5]. This method suffers from various drawbacks due to the sensitive nature of the enzymatic procedure and complications in integrating a chemical process. Other non-biological approaches have been attempted for the isomerization of glucose into fructose. Zhang's group reported that chromium chlorides ($CrCl_2$ or $CrCl_3$) in ionic liquid [(EMIM)Cl] could efficiently assist the isomerization of glucose into fructose [6]. More recently, glucose was isomerized into fructose in *N*,*N*-dimethylformamide (DMF) using hydrotalcite as an inorganic solid base [7]. In addition, Sn-containing zeolite could convert glucose into fructose under aqueous acidic conditions [8]. However, these previously reported procedures still possess drawbacks, including the use of environmentally non-benign chromium salts and relatively expensive ionic liquids, the difficulty in removing and recycling high boiling reaction media, and low yields.

Glucose can be converted into isomers such as fructose and mannose through a proton transfer mechanism called a Lobry–de Bruyn–van Ekenstein transformation under aqueous basic conditions [9]. The isomerization proceeds via an enediol intermediate formed by the base-catalyzed deprotonation of α-carbonyl carbon of glucose [10]. There are several studies on the isomerization of aldose into ketose with an inorganic base or solid base in water [11–13]. However, aqueous conditions reduce the stability of monosaccharides in the presence of basic catalysts. Therefore, we present a facile method for the isomerization of glucose into fructose using anion-exchange resins (AERs) in organic solvents (Scheme 1).



Scheme 1 Isomerization of glucose into fructose using anion-exchange resin

Experimental

Materials and analysis

D-Glucose, D-Fructose, and 5-hydroxymethyl furfural (HMF) (all with >99% purity) were purchased from Sigma-Aldrich and used as reagents or HPLC standards accordingly. Five types of ion-exchange resins including Amberlite IRA-743 (IRA-743), Amberlite IRA-400 (IRA-400), Amberlite IRA-900 (IRA-900), Amberlyst A-26 (A-26), and Amberlyst 15 were purchase from Sigma-Aldrich and used as catalysts. Several solvents such as dimethylsulfoxide (DMSO, ≥99.9%), DMF (anhydrous, 99.8%), ethanol (anhydrous, ≥99.5%), 1,4-dioxane (dioxane, anhydrous, 99.8%), and isopropyl alcohol (IPA, 99.5%) were also acquired from Aldrich. The loading amount of nitrogen on the anion-exchange resins were determined by a CHN elemental analysis (Automatic Elemental analyzer, FLASH 2000 Series; Thermo Scientific, USA) and the specific surface area of the resins was determined on a BET surface analyzer (Brunanuer–Emmett–Teller, ASAP2010; Micromeritics, USA) using N_2 as the adsorbent at liquid nitrogen temperature (77 K) in a relative pressure (P/P_0) range of 0–0.25. The resin samples (in powder forms) were degassed in air for over 12 h at 100 °C prior to analysis. The yields of fructose and HMF were determined using high-performance liquid chromatography (HPLC; Agilent 1200 series) equipped with a refractive index detector and an Aminex HPX-87H column (Bio-Rad). The analysis conditions were as follows: eluent, 0.01 N H_2SO_4; flow rate, 0.6 ml min^{-1}; and column temperature, 45 °C. Prior to HPLC analysis, all samples were subjected to dilution with water (HPLC grade) to prevent signal overload and damage to the system.

Isomerization of glucose into fructose

The isomerization of glucose into fructose was carried out in a tubular-type Carousel 12 Plus Reaction Station reactor (Radley, UK) equipped with a cross-shaped magnetic stirrer. Prior to the reaction, the AER catalysts were treated by shaking in a saturated aqueous $NaHCO_3$ solution at room temperature for 5 h and then dried under vacuum. Glucose samples (100 mg) were placed in the reactor, and the designated amounts of AER and solvent (3 mL) were added. After the reactors were installed into the Carousel 12 Plus Reaction Station, the reaction mixtures were heated and stirred at 700 rpm for a designated time. After the reaction, the AER catalysts were filtered, and the reaction mixtures were cooled to room temperature and diluted with water (HPLC grade) for HPLC analysis.

Direct conversion of glucose into HMF

The direct conversion of glucose to HMF was performed by using both AERs and cation-exchange resins (CERs) simultaneously or sequentially. In a simultaneous system, both AERs and CERS were added from the onset (with the AERs being treated prior to use) and treated for a designated time. On the other hand, in a

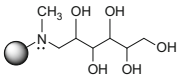
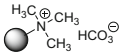
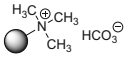
sequential system, the reactions were performed in cycles. In each cycle, the resins were employed by turns: the AER was used first for the isomerization of glucose and then altered by the CER for the conversion into HMF. The resin was filtered out after each turn and new resin was added for the next turn. In our research, the sequential system was repeated up to 6 cycles with varied reaction times for each resin-employed turn. Reaction scales and equipment are similar to the procedure for the isomerization of glucose into fructose. Glucose (100 mg) and a designated amount of ion-exchange resins in solvent (3 mL) were added to the tubular type reactor (Radley), heated and stirred at 700 rpm for a designated time or cycles (in cases of the sequential system studied). After completion, the resins were filtered, the reaction mixtures were cooled to room temperature, diluted with water (HPLC grade) and analyzed by HPLC.

Results and discussion

Characterization of AERs

Four commercially available AERs (IRA-743, IRA-400, A-26 and IRA-900) with differences in resin morphology and terminal-group functionality were evaluated for the isomerization of glucose into fructose (Table 1). IRA-743 is a rigid macroporous resin with a high cross-linking degree, and its terminal is functionalized with *N*-methyl-glucamine. IRA-400 is a gel-type resin with a low cross-linking degree, allowing a substrate that can access the resin surface when sufficiently swollen. IRA-400 has a tetraalkyl ammonium terminal group. A-26 and IRA-900 are macroreticular-type resins composed of small spherical microgel particles agglomerated to form clusters. Their terminal groups are tertiary amine and tetraalkyl ammonium forms, respectively. As for strength of basicity, IRA-400 and IRA-900 are stronger than IRA-743 and A-26 because the basicity of IRA-400 and IRA-900 is provided by counter anions of a quaternary ammonium terminal group, whereas

Table 1 Morphology of anion-exchange resins and functionality of their terminal groups

Name	Morphology of resin	Functionality of terminal group
Amberlite IRA-743 (IRA-743)	Macroporous	
Amberlite IRA-400 (IRA-400)	Gel	
Amberlyst A-26 (A-26)	Macroreticular	
Amberlite IRA-900 (IRA-900)	Macroreticular	

that of IRA-743 and A-26 is provided by unshared electrons of a tertiary amine terminal group.

The amount of basic functional groups on each AER was determined by the loading level of the nitrogen contents per weight of the resin (mmol of 'N' g^{-1} of resin) using a CHN elemental analysis of dried AERs. The loading level of IRA-743 was less than 2.0 mmol g^{-1}, and those of the other AERs were over 3.0 mmol g^{-1}. These results originate from the molecular weights of the attached moieties. IRA-743 has a higher molecular weight moiety (*N*-methyl-glucamine compared to trimethyl or dimethyl moieties of other AERs) and increment in total weight of resin. The surface area of each AER was investigated using a BET analysis. As expected, the gel-type IRA-400 showed very low surface area and the macroporous-type IRA-743 showed the highest surface area at over 18 m^2 g^{-1}. The surface areas of the macroreticular-type A-26 and IRA-900 were 6.62 and 2.00 m^2 g^{-1}, respectively (Table 2).

The swelling property of the AERs in organic solvents was also examined. Taking the solubility of glucose into account, water miscible solvents with high polarity such as DMSO, DMF, dioxane, IPA, and ethanol were selected for screening (Fig. 1). Swelling property is often an important factor in polymer-based heterogeneous catalysis because it can enhance the accessibility of the substrate. The gel-type IRA-400 offered no swelling ability in any of the solvents except ethanol. It was considered that hydrophilic solvents would be limited in accessing hydrophobic polystyrene-based resins with low surface areas. Meanwhile, macroreticular-type AERs (IRA-900 and A-26) showed relatively high swelling abilities. All AERs were best swollen in ethanol with IRA-900 swollen up to nearly 200% of the ratio.

Isomerization of glucose into fructose

All four types of AERs were treated with aqueous $NaHCO_3$ at room temperature for 5 h and dried with a vacuum prior to use. Because of this treatment, the counter anions of IRA-400 and IRA-900 were exchanged into hydrogen carbonate (HCO_3^-) and the tertiary amine groups of IRA-743 and A-26 were changed to free amine. Isomerization was carried out in a tubular-type reactor; a designated amount of AER and 3 mL of solvent were added to 100 mg of D-glucose. The reaction tubes were heated at 80 °C and stirred at 700 rpm for 3 h. After the reaction, the mixture was

Table 2 Loading level and surface area of anion-exchange resins

Name	Loading level (mmol of 'N'/g)	Surface area (m^2/g)
Amberlite IRA-743	1.9	18.76 ± 0.08
Amberlite IRA-400	3.3	0.03 ± 0.02
Amberlyst IRA-26	3.2	6.62 ± 0.03
Amberlite IRA-900	3.8	2.00 ± 0.01

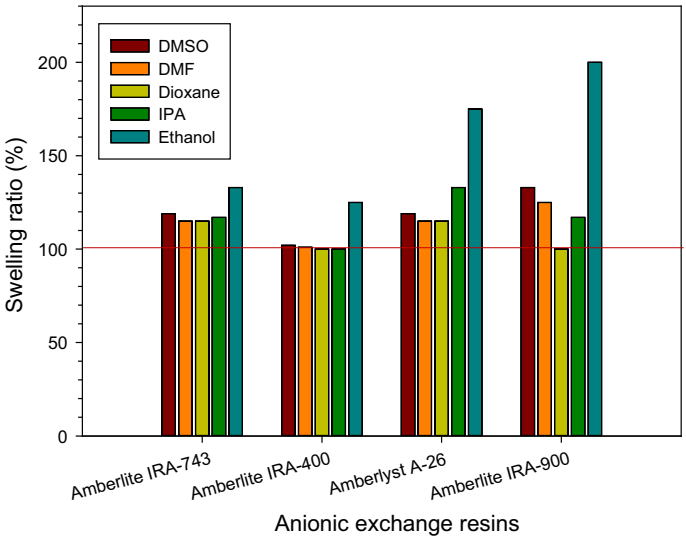


Fig. 1 Swelling properties of AERs in various water-miscible organic solvents

cooled to room temperature, diluted with water (HPLC grade) and analyzed with HPLC. Isomerization of the glucose into fructose was performed in the presence of two different amounts of AERs (20 and 50 mol% of basic moiety based on glucose) using five different solvents, namely DMSO, DMF, dioxane, IPA, and ethanol.

All the results are listed in Table 3. When DMSO (Table 3, entries 1–8) or DMF (Table 3, entries 9–16) was used as a high polar aprotic solvent, low conversions of glucose were shown on all AERs. In particular, the gel-type IRA-400 showed the lowest conversion, with more than 90% of the glucose still remaining even in the presence of large amounts of resin (50 mol%) (Table 3, entries 6 and 14). It appears that the glucose was unable to gain access to the gel-type resin. However, IRA-743 and A-26, having tertiary amine terminal groups, provided a higher conversion of glucose than the IRA-400 and IRA-900 with quaternary ammonium terminal groups. Dioxane increased glucose conversions, but provided a low selectivity of fructose—below 70% regardless of the AERs, their amounts and reaction time (Table 3, entries 17–24). Conversions of glucose were conspicuously improved using a protic solvent such as IPA or ethanol. In particular, higher polar ethanol produced a remarkable difference in the selectivity of fructose compared to IPA. A high conversion (53%) and superior selectivity (94%) of fructose was observed using ethanol in the presence of A-26 (Table 3, entry 35). A larger amount of A-26 (50 mol%) in ethanol enhanced the conversion to 64%, but the selectivity then fell to 70% (Table 3, entry 39). Moreover, the undesired decomposition of glucose could be suppressed in organic solvent at increased temperatures.

The fructose yields obtained from screening the AERs and solvents are depicted in Fig. 2a. Based on this figure, the following facts were clearly confirmed: (1) protic solvents were superior to aprotic solvents; (2) macroporous and macroreticular resins provided higher yields of fructose than gel-type resins; and (3) tertiary

Table 3 Conversion of glucose (*CoG*) and selectivity of fructose (*SoF*) by isomerization of glucose using AERs in various organic solvents

Entry	Catalyst	CoG	SoF	Mol%	Solvent	Polar Index
1	IRA-743	11.3	91.5	20	DMSO	7.2
2	IRA-400	1.8	60.0			
3	A-26	15.8	71.2			
4	IRA-900	6.2	61.3			
5	IRA-743	19.7	88.6	50		
6	IRA-400	6.1	53.9			
7	A-26	24.6	87.6			
8	IRA-900	14.0	79.5			
9	IRA-743	18.5	92.5	20	DMF	6.4
10	IRA-400	4.2	40.1			
11	A-26	11.1	96.6			
12	IRA-900	7.4	73.7			
13	IRA-743	28.3	89.2	50		
14	IRA-400	8.4	37.2			
15	A-26	37.8	73.3			
16	IRA-900	18.1	74.0			
17	IRA-743	51.3	67.5	20	Dioxane	4.8
18	IRA-400	8.4	0.0			
19	A-26	31.5	62.8			
20	IRA-900	15.3	38.3			
21	IRA-743	60.1	61.9	50		
22	IRA-400	10.7	5.1			
23	A-26	42.5	65.8			
24	IRA-900	25.1	65.3			
25	IRA-743	45.0	75.3	20	IPA	3.9
26	IRA-400	22.2	94.0			
27	A-26	44.4	79.0			
28	IRA-900	36.6	84.0			
29	IRA-743	54.8	73.6	50		
30	IRA-400	27.0	94.6			
31	A-26	61.9	72.6			
32	IRA-900	38.7	76.5			
33	IRA-743	57.1	72.3	20	Ethanol	5.2
34	IRA-400	28.7	86.5			
35	A-26	53.1	93.6			
36	IRA-900	34.3	95.1			
37	IRA-743	67.6	66.8	50		
38	IRA-400	29.0	96.3			
39	A-26	64.1	70.0			
40	IRA-900	61.1	69.5			

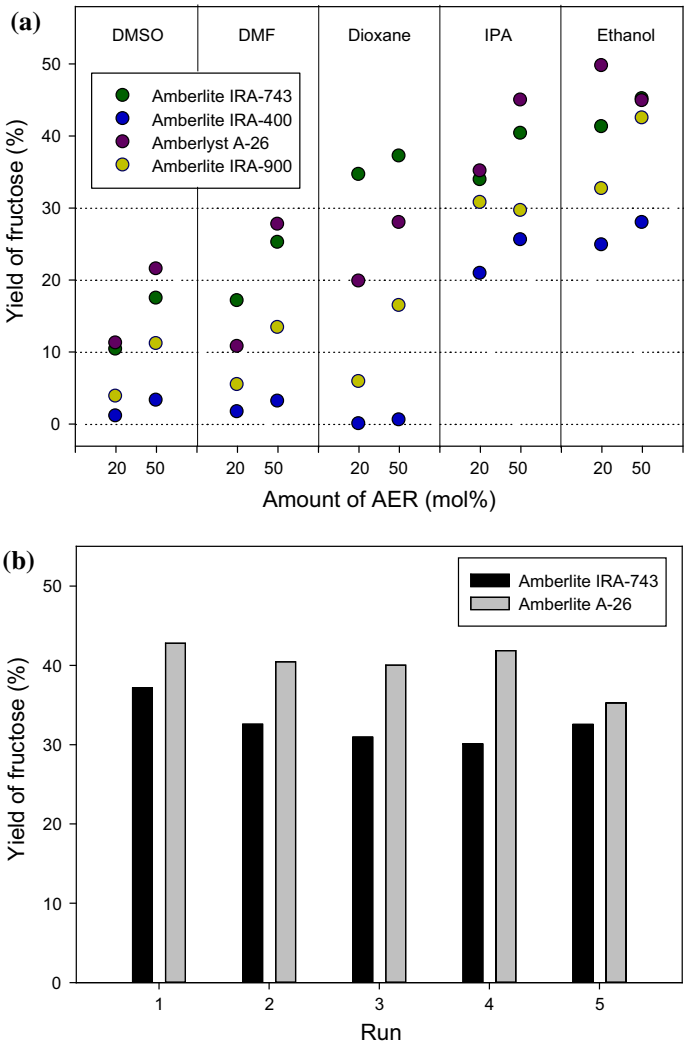


Fig. 2 **a** Fructose yields after isomerization of glucose using AER in organic solvents, and **b** reuse of AERs for isomerization of glucose into fructose

amine functionalities were beneficial compared to tetraalkyl ammonium functionalities. Furthermore, reuse tests of IRA-743 and A-26 were carried out for the isomerization of glucose into fructose, demonstrating that both AERs can be used five times in ethanol without a significant loss of activity (Fig. 2b).

From a mechanistic point of view, it is well known that aldose has been isomerized into ketose via a proton transfer mechanism called the Lobry–de Bruyn–van Ekenstein transformation (see yellow area in Fig. 3) under aqueous basic condition [9, 14]. The isomerization proceeds with base-catalyzed deprotonation of the α-carbonyl carbon of aldose to form enolates [10]. There have been several

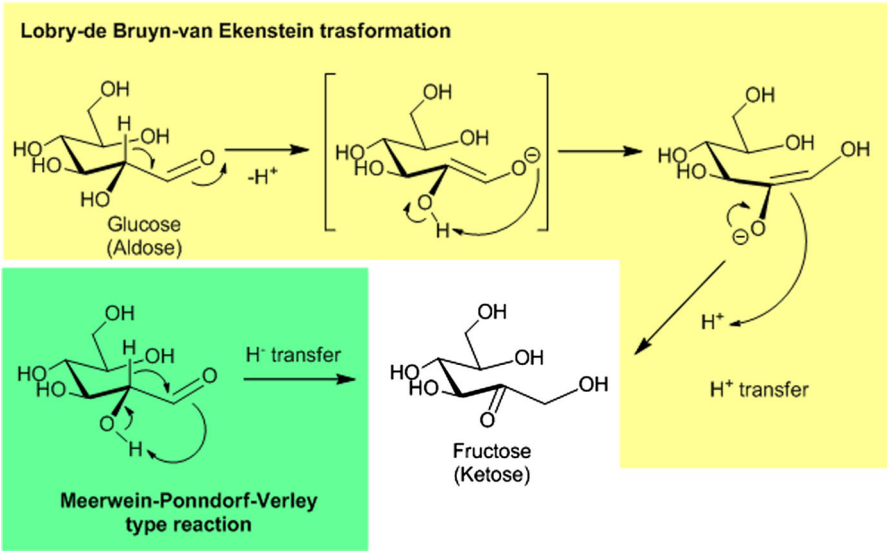
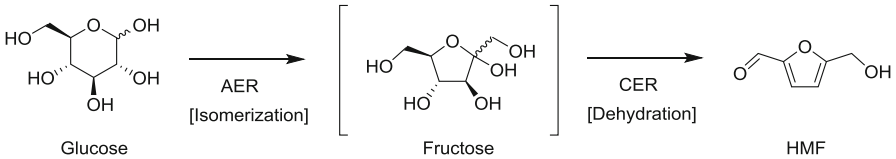


Fig. 3 Proposed mechanism of isomerization of glucose into fructose in organic solvents via the Lobry–de Bruyn–van Ekenstein transformation (proton transfer) and the Meerwein–Ponndorf–Verley reaction (hydride transfer). (Color figure online)

studies on the isomerization of aldose into ketose with general base [11] or solid base [12, 13] in water. However, the situation is more complicated when organic solvents are used. The isomerization of aldose into ketose in organic solvents can also occur via intramolecular transfer of hydride by the similar pathway such as the Meerwein–Ponndorf–Verley reaction (see green area in Fig. 3), [15] which can lead to an enhancement of isomerization. Indeed, the isomerization was markedly accelerated by the addition of organic solvents such as ethanol and acetone [16, 17]. Additionally, the enhanced effect can be explained by the increasing amount of the α-pyranose form of glucose in organic solvents [18].

Direct conversion of glucose into HMF

As previously mentioned, HMF is a versatile platform that can be converted into a variety of valuable fuels and chemicals [19]. It can be readily transformed from fructose by dehydration using a CER as a solid acid catalyst in DMSO [20], DMF [21], dioxane [22], and ethanol [23]. Therefore, the direct conversion of glucose into



Scheme 2 Direct conversion of glucose into furan compounds using AERs and CERs

HMF was explored by integrating an isomerization step with AERs and a dehydration step with CERs (Scheme 2).

The direct conversion of glucose into HMF was initially performed in DMSO and DMF (Table 4). Both solvents are well known as preferred media for the dehydration of fructose in the presence of CERs. A negligible amount of HMF was created with a CER (Amberlyst 15) in DMSO at 100 °C after 5 h because the isomerization of glucose into fructose scarcely occurred (Table 4, entry 1). When AER (IRA-743) was simultaneously used with a CER (wt/wt = 1:1) under the same conditions (DMSO, 100 °C, 5 h), HMF was formed at a yield below 10% (Table 4, entry 2). DMF was more effective than DMSO, in creating HMF at a yield greater than 10% (Table 4, entry 3). Increasing the ratio of AER to CER (wt/wt = 2:1) produced a greater yield of HMF (23%) (Table 4, entry 4) but a prolonged reaction time was unnecessary (Table 4, entry 5). Next, just an AER was initially treated in DMSO at 100 °C for 3 h. CER was then added, and the reaction was continued for another 2 h to produce an HMF yield of 16%, slightly higher than the simultaneous treatment of AER and CER from the onset (Table 4, entry 2 vs. 6). In an attempt to improve the HMF yield, turn-by-turn treatments of AER and CER were repetitively performed in multiple cycles. In each cycle, the AER was treated and then filtered out, and the CER was subsequently added to the filtrate (reaction mixture). After the turn-by-turn treatment of the AER and CER for 1 h each in three cycles and for 0.5 h each in six cycles (in both cases, the total reaction time was 6 h) in DMSO at 100 °C, 29 and 26% yields of HMF were obtained, respectively (Table 4, entries 7 and 8). Using DMF as a solvent can improve HMF yield to 34% (Table 4, entry 9).

A direct conversion of glucose into HMF was then conducted in ethanol. The use of ethanol in glucose isomerization has several advantages. First, ethanol is a renewable solvent and is now produced on an industrial scale from biomass.

Table 4 Direct conversion of glucose into HMF using AER and CER in DMSO and DMF

Entry	Solvent	AER (mg)[a]	CER (mg)[a]	Reaction time (h)[b]	HMF yield (%)
1	DMSO	–	100	5	<1
2	DMSO	100	100	5[c]	7
3	DMF	100	100	5[c]	13
4	DMF	200	100	5[c]	23
5	DMF	200	100	9[c]	23
6	DMSO	100	100	3 + 2	16
7	DMSO	200	100	(1 + 1) × 3	29
8	DMSO	200	100	(0.5 + 0.5) × 6	26
9	DMF	200	100	(1 + 1) × 3	34

[a] IRA-743 and Amberlyst 15 were used as an anion-exchange resin (AER) and a cation-exchange resin (*CER*), respectively

[b] Notation of treatment time: $(b + a) \times t$, where b and a are the times for basic AER and acidic CER treatments, respectively; t is the number of turns

[c] AER and CER were used together from the onset (simultaneous system)

Second, ethanol has a low boiling point (78 °C) and can be easily removed after the reaction compared to other high-boiling solvents such as DMSO (189 °C) and DMF (153 °C). Third, the dehydration of fructose in ethanol can produce 5-ethoxymethyl-2-furfural (EMF), a promising candidate for bio-fuels and a more stable platform chemical than HMF for use as a precursor for valuable chemicals. This reaction employed a turn-by-turn treatment of AER and CER at 80 °C for 1 h each in three repeated cycles. HMF and EMF were obtained in 23 and 11% yields, respectively. A total of 20% glucose and 34% fructose remained after the reaction, and it was believed that the dehydration of fructose into furan compounds was incomplete at this low temperature. An investigation of the reaction profile clearly showed that fructose was produced during the treatment of the AER, whereas furan compounds (HMF and EMF) formed as fructose was consumed during the treatment of the CER (Fig. 4).

Conclusion

A facile isomerization of glucose into fructose was developed using AERs in an organic solvent. Fructose yields of 40–50% of were achieved with Amberlyst A-26 and Amberlite IRA-743 bearing tertiary amine functionalities in a protic solvent, namely ethanol. The AERs could be used five times without a significant loss of

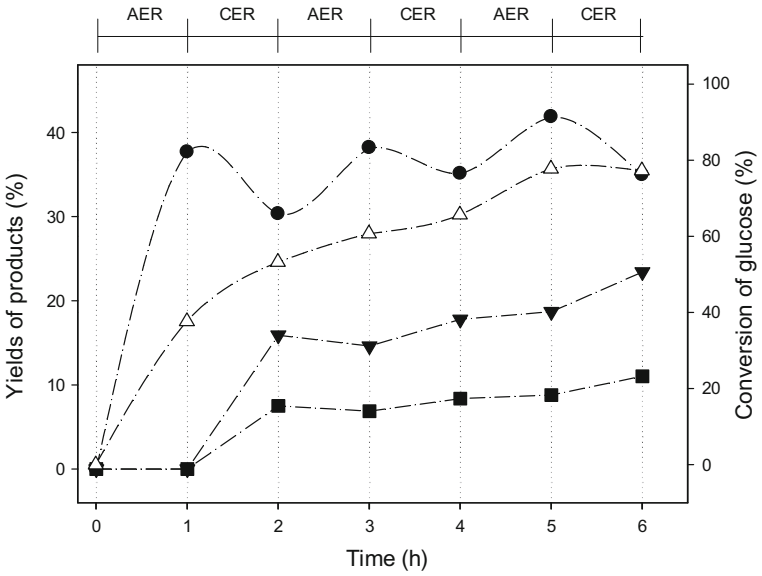


Fig. 4 Reaction profiles according to ion-exchange resin treatment: Glucose (300 mg) and ethanol (9 mL) were used as substrate and solvent, respectively. IRA-743 (600 mg) was used for anion-exchange resin treatment and Amberlyst 15 (300 mg) was used for cation-exchange treatment at 80 °C. Each *symbol* represents the conversion of glucose (*open triangle*) and the yields of fructose (*filled circle*), HMF (*filled inverted triangle*), and EMF (*filled square*). *Solid* and *dotted arrows* indicate sections for anion-exchange resin and cation-exchange resin treatments, respectively

activity. This procedure has the advantage of using common industrial solvents and commercially available AERs. Applying an organic solvent reaction system and a heterogeneous catalyst allows for easy separation of the product as well as recovery and reuse of the solvent and catalyst. In addition, the sequential dehydration of fructose into furan compounds could be integrated without replacing the solvent system.

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