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SOLVENT-FREE DEHYDRATION OF SORBITOL TO ISOSORBIDE CATALYZED BY SULFONIC ACID RESINS

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Abstract

Isosorbide is a biodegradable bicyclic diol widely used for biopolymers, surfactants, plasticizers, solvents and pharmaceuticals production, which is obtained by dehydration of sorbitol. In this investigation the double cyclodehydration of D-sorbitol to isosorbide on Amberlyst 15 and KU-2-8 sulfonic acid resins at 120-140 °C in the batch reactor under vacuum (150-170 mbar) without solvent was studied. It was found that the studied catalysts provide 78-88 % isosorbide yield with a complete conversion of sorbitol at 140 °C for 3 h. More stable Amberlyst 15 produces 10 g of isosorbide per 1 g of catalyst for 3 h at 130 °C. After 5 experiments for 3 h at 125 °C acid site concentration on Amberlyst 15 surface reduced by only 4 %, sorbitol conversion and yield of products remain almost unchanged. KU-2-8 shows high initial catalytic activity, but after only one run this resin loses 40 % of sulfonic groups.

Keywords: biomass; heterogeneous catalysis; isosorbide; polymers; sorbitol dehydration.

ДЕГІДРИТАЦІЯ СОРБИТОЛУ ДО ІЗОСОРБІДУ БЕЗ РОЗЧИННИКА НА СУЛЬФОКАТІОНІТАХ

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Анотація

Досліджено подвійну циклодегідратацію D-сорбіту до ізосорбіду на сульфокатіонітах Amberlyst 15 та КУ-2-8 при 120-140 °C у реакторі періодичної дії під вакуумом (150-170 мбар) без розчинника. Встановлено, що досліджувані каталізатори забезпечують 78-88 % вихід ізосорбіду з повною конверсією сорбіту при 140 °C за 3 год. Більш стабільний Amberlyst 15 продукує 10 г ізосорбіду на 1 г каталізатора за 3 год при 130 °C. Після 5 експериментів протягом 3 год при 125 °C концентрація кислотних центрів на поверхні Amberlyst 15 знижується лише на 4 %, конверсія сорбіту та вихід продуктів залишаються майже незмінними. КУ-2-8 забезпечує високу початкову каталітичну активність, але лише після одного циклу ця смола втрачає 40 % сульфогруп.

Ключові слова: біомаса; гетерогенний каталіз; ізосорбід; полімери; дегідратація сорбіту.

ДЕГИДРИТАЦИЯ СОРБИТОЛА ДО ИЗОСОРБИДА БЕЗ РАСТВОРИТЕЛЯ НА СУЛЬФОКАТИОНИТАХ

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Аннотация

Исследована двойная циклодегидратация D-сорбита до изосорбида на сульфокатионитах Amberlyst 15 и КУ-2-8 при 120-140 °C в реакторе периодического действия под вакуумом (150-170 мбар) без растворителя. Установлено, что исследуемые катализаторы обеспечивают 78-88 % выход изосорбида с полной конверсией сорбита при 140 °C за 3 часа. Более стабильный Amberlyst 15 производит 10 г изосорбида на 1 г катализатора за 3 часа при 130 °C. После 5 экспериментов в течение 3 ч при 125 °C концентрация кислотных центров на поверхности Amberlyst 15 снижается на 4 %, конверсия сорбита и выход продуктов остаются почти неизменными. КУ-2-8 обеспечивает высокую начальную каталитическую активность, но после одного цикла эта смола теряет 40 % сульфогрупп.

Ключевые слова: биомасса; гетерогенный катализ; изосорбид; полимеры; дегидратация сорбита.

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Introduction

The production of commodity chemicals from renewable sources is significant task for sustainable development. In 2004, the U.S. Department of Energy has defined sorbitol as one of the top-ten chemicals and identified the challenge of solid catalysts selection for sorbitol dehydration to isosorbide (1,4:3,6-dianhydro-D-glucitol) [1–2]. According to the 2020 report by IMARC Group [3] the global sorbitol market reached a volume of 2.56 million metric tons in 2019.

Isosorbide is a double cyclodehydration product of D-sorbitol obtained via the hydrogenation of glucose derived from the hydrolysis of starch or to a lesser extent from the cellulosic biomass. Isosorbide derivatives are used as monomer for biopolymers, surfactants, plasticizers, solvents, pharmaceuticals [4–6]. One of its derivatives is isosorbide-based polycarbonate that is a non-toxic alternative to bisphenol A (BPA) [4; 7–10]. According to Expert Market Research [9], the global isosorbide market size attained a value of about 430.6 million USD and a volume of 77 kilo tons in 2020. The main products derived from isosorbide are PEIT (polyethylene co-isosorbide terephthalate), polycarbonate, polyurethane, polyester polyisosorbide succinate and isosorbide diesters. Resins and polymers derived from isosorbide accounted for over 60 % of the total isosorbide market demand in 2019 [10].

In an industry the conversion of sorbitol to isosorbide is usually provided in the presence of sulfuric acid at 130–135 °C in batch reactor during several hours, at that isosorbide yield reaches of 70 % [11–12]. In 1986, Flèche and Huchette [13] reported that molten sorbitol without any solvent was dehydrated 5 times faster at 135 °C using

sulfuric acid as catalyst when water is continuously removed from the reaction zone. In this way, isosorbide yield reached 76 % “without water” in vacuum, in contrast to 11.5 % isosorbide yield “with water” for 3 h. Solid catalysts, such as sulfated oxides [11; 14–17], metal phosphates [18], zeolites [19–22], carbon-based acid catalyst [23–24], phosphotungstic acid catalysts [25] and some sulfonic acid resins [26–31] have already been investigated. Of particular interest are commercially available and inexpensive sulfonic acid resins as relatively stable solid acids. According to previous studies, the best isosorbide yield was about 83 % at 130 °C and 20 mol% of catalyst [29].

The objective of the present work is testing of commercially available sulfonic acid resins as solid catalysts for synthesis of isosorbide by dehydration of sorbitol. In this communication the data on sorbitol dehydration in molten phase under vacuum at moderate temperatures (120–140 °C) are presented.

Results and Discussion

Amberlyst 15 and KU-2-8 are sulfonated resins based on polystyrene crosslinked with divinylbenzene. The textural and acidity properties of these resins are summarized in Table 1. It is noteworthy that KU-2-8 contains about 50 % water and after drying (90 °C, 1 h) it loses half of its mass. Decrease in particle size and increase in bulk density are observed (Table 1). Furthermore, the number of acid sites available to reagents is significantly reduced from 5.2 mmol/g for wet sample to 3.1 mmol/g for dry sample (Table 1). For Amberlyst 15, in turn, the number of acid sites hardly changes after drying.

Table 1

The textural and acidity properties of Amberlyst 15 and KU-2-8					
Catalyst	BET Surface Area, m ² /g	Total Pore Volume, cm ³ /g	Average Pore Diameter, nm	Bulk density, g/cm ³	[HB], mmol/g
Amberlyst 15 (wet)	–	–	–	0.57	4.7
Amberlyst 15 (dry) ^[a]	53	0.40	30	0.56	4.7
KU-2-8 (wet)	–	–	–	0.73	5.2
KU-2-8 (dry) ^[a]	15	2.8	–	0.84	3.1

[a] After drying at 90 °C for 1 h.

The sorbitol dehydration reaction on Amberlyst 15 and KU-2-8 was carried out under solvent-free conditions using a vacuum (150–170 mbar) for 2–4 h at 120–140 °C. The results are summarized in Table 2. According to the ¹³C NMR spectra, isosorbide (1,4:3,6-dianhydro-D-glucitol), 1,4-sorbitan, 2,5-mannitan, 2,5-iditan

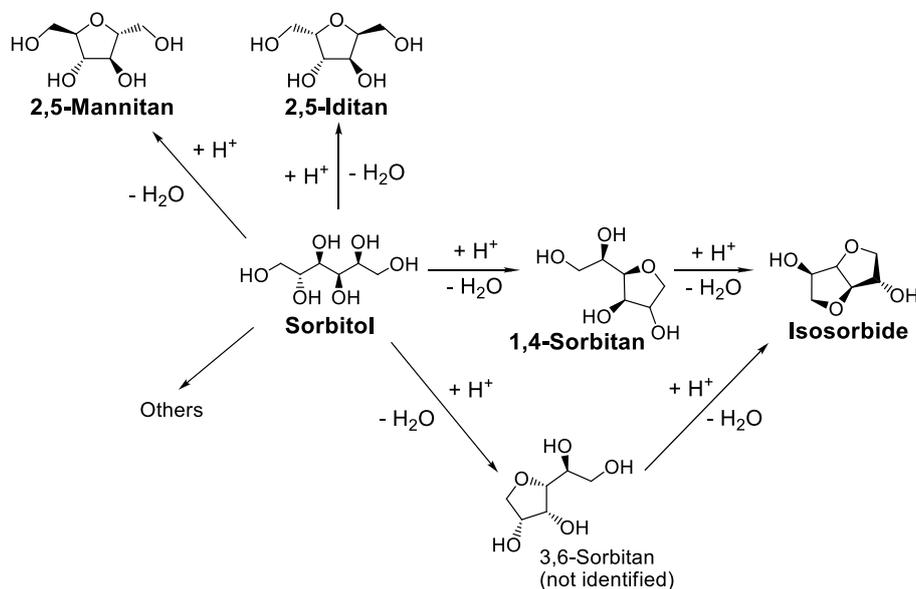
and sorbitol were identified in the reaction products (Table 2, Figure 1). The structures of identified products are shown in Scheme 1.

As known [32–34], the sorbitol dehydration to isosorbide occurs in two steps through the formation of 1,4-sorbitan and 3,6-sorbitan which on the second dehydration step turn into

isorbide (Scheme 1). According to Dussenne and co-authors [33] isorbide yield in the two-stage sorbitol dehydration process could be commonly lower than 75 %.

As mentioned above, wet KU-2-8 has a greater content of acid sites than dry form (Table 1). It

explains the higher sorbitol conversion and yield of products on wet KU-2-8 than on dry KU-2-8. Thus, a higher isorbide yield by 22 % is observed on wet KU-2-8 (Table 2). Therefore, we studied sorbitol dehydration on wet KU-2-8.



Scheme 1. Possible reaction pathways for sorbitol dehydration

Table 2

Product composition of sorbitol dehydration by Amberlyst 15 and KU-2-8^[a]

Catalyst	Reaction time, H	Reaction temperature, °C	Conversion, mol %	Yield of products, mol% ^[b]		Yield of by-products, mol%		
				IS	SN	MN	IN	Others
KU-2-8	3	120	93	36	38	3	7	7
	3	125	96	51	33	3	7	2
	3	130	99	65	18	4	7	5
	3	135	>99	78	6	4	7	5
	3	140	>99	88	<1	4	6	2
	4	125	96	55	25	2	8	6
KU-2-8 ^[c]	5	125	97	58	23	4	8	4
	3	130	96	43	34	5	10	2
Amberlyst 15	3	120	84	31	40	2	8	3
	3	125	94	47	28	3	9	7
	3	130	98	63	18	3	8	6
	3	135	>99	74	8	3	7	8
	3	140	>99	78	4	4	8	6
	4	125	98	55	23	3	8	9
	5	125	>99	65	16	3	8	8

[a] Experimental conditions: 20 g sorbitol, 1.5 g Amberlyst 15 or 2.6 g wet KU-2-8, 170 mbar. [b] IS – isorbide; SN – 1,4-sorbitan; MN – 2,5-mannitan; IN – 2,5-iditan. [c] 1.5 g of dry KU-2-8

Isorbide is formed with 31-51 % yield at 84-96 % sorbitol conversion on the studied sulfonated resins at moderate temperature (120-125 °C) (Table 2). The higher isorbide yield is observed on KU-2-8 in comparison with Amberlyst 15 which is explained by the higher concentration of acid sites on the KU-2-8 surface (Table 1). On both catalysts sorbitol conversion

and total yield of two target products – isorbide and 1,4-sorbitan, increases with temperature rise. KU-2-8 provides isorbide yield of 88 % with >99 % sorbitol conversion and complete conversion of intermediate 1,4-sorbitan at 140 °C for 3 h (Figure 2). Under the same conditions, Amberlyst 15 provides 78 % yield of isorbide with the formation of 4 % 1,4-sorbitan at >99 %

sorbitol conversion ($57 \text{ mmol}_{\text{IS}}/\text{g}_{\text{cat}}$ for 3 h). Thus, the isosorbide yield increases by 47 % (from 31 to 78 %) when temperature rises from 120 to 140 °C (Figure 2).

It is generally accepted that thermal stability of the sulfonated resins is limited by their tendency to lose sulfonic acid groups. For Amberlyst 15 and KU-2-8 maximum operating temperature, declared by the manufacturers, is 120 °C. Siril and co-authors [35] investigated the thermal stability

of Amberlyst 15 and noted that acid site concentrations on its surface following hydrothermal treatment for 6 h at 180 °C in pressure vessel loses only 16 % of acid sites. Also, there are articles [26-27; 29-31] and patent [36] reporting that the Amberlyst 15 and similar polystyrene/divinylbenzene resins remains active in sorbitol dehydration reaction at temperatures above 120 °C.

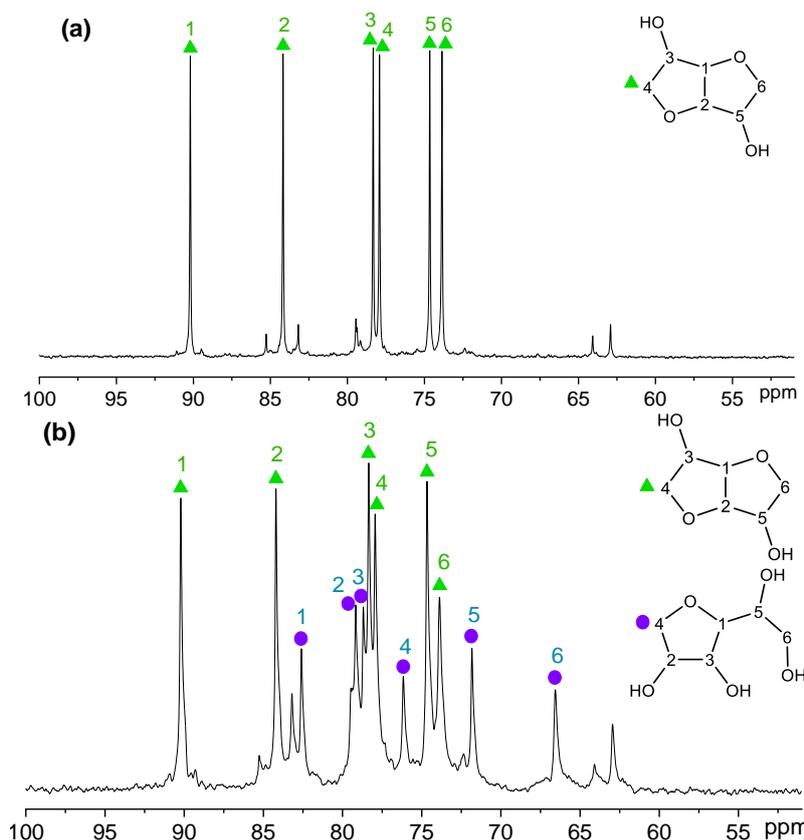


Figure 1. ^{13}C NMR spectra of the sorbitol dehydration products at 140 °C (a) and 120 °C (b) (KU-2-8, 3 h)

Our results confirm that Amberlyst 15 and KU-2-8 keep activity in sorbitol dehydration at 120-140 °C (Table 2, Figure 2). But it should be noted, that distilled off water formed during studied reaction had pH 4-2. It means that

Amberlyst 15 and KU-2-8 lose some the sulfonic acid groups at temperatures above 120 °C. The following experiments to evaluate stability of studied resins carried out a moderate temperature 125 °C.

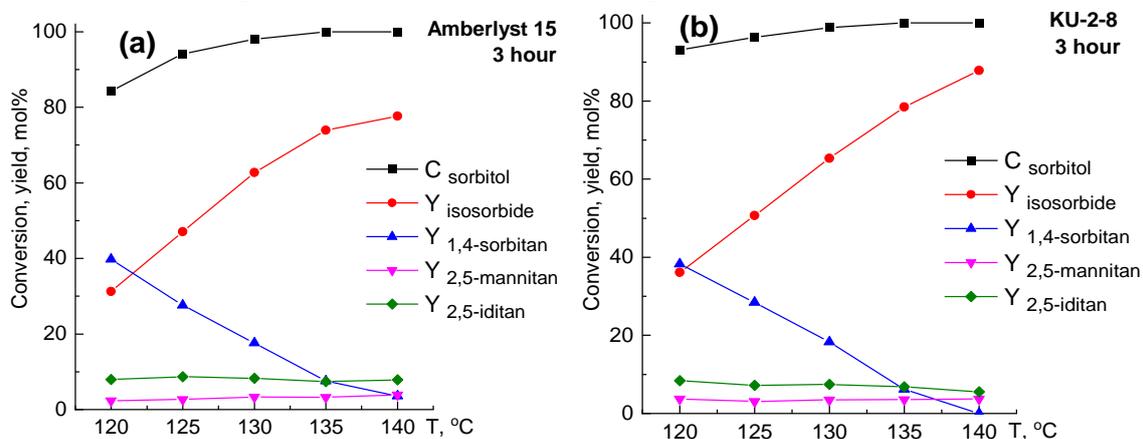


Figure 2. Effect of temperature on sorbitol conversion, yield of products and by-products on Amberlyst 15 (a), and KU-2-8 (b) (20 g sorbitol, 1.5 g Amberlyst 15 or 2.6 g wet KU-2-8, 170 mbar, reaction time 3 h)

With extending the reaction time from 3 to 5 h almost full sorbitol conversion is attained and isosorbide yield increases by 18 % on Amberlyst 15 then as the isosorbide and 1,4-sorbitan yields are 65 % and 16 % respectively (Table 2). For KU-2-8 after 5 h, only a slight isosorbide yield increases by 7 % is observed. According to Amberlyst 15 reuse experiments results (Figure 3), after 5 times for 3 h the acid sites concentration has been reduced by only 4 % from 4.7 mmol/g (Table 1) to 4.5 mmol/g. Conversion of sorbitol and yield of isosorbide remain on the level of 93 % and 46 % respectively that indicates on stability of Amberlyst 15 under these conditions. KU-2-8 loses the sulfonic groups more easily, and their concentration after only one experiment at 125 °C for 3 h decreases significantly from 5.2 mmol/g to 3.2 mmol/g. Therefore, we did not reuse KU-2-8 in sorbitol dehydration reaction.

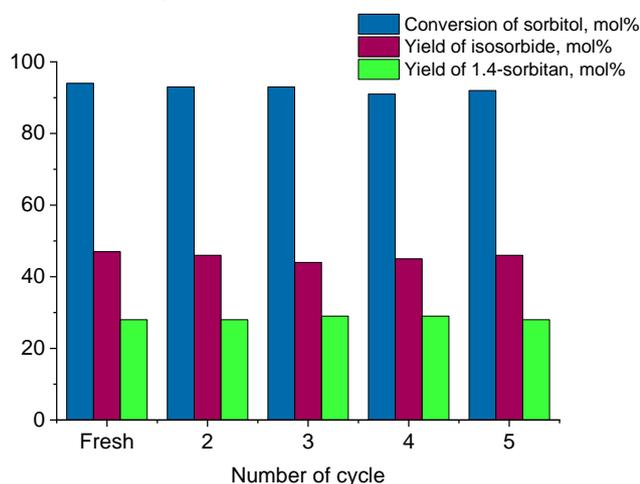


Figure 3. Reuse experiments of Amberlyst 15 in sorbitol dehydration at 125 °C for 3 h

Experimental Section

KU-2-8 (OSTCHEM) and Amberlyst 15 (Dow Chemical Company) sulfonic acid resins were tested as acid catalysts. Total number of acid sites on their surfaces was determined by reverse titration [37] using *n*-butylamine solution in cyclohexane with bromthymol blue as an indicator by the following procedure. 10 mL of 0.05 M solution of *n*-butylamine in purified and dried cyclohexane was added to 100 mg of a sample. After stirring for 30 min the solution was titrated with 0.05 M HCl to determine the amine content in the solution after absorption. The sorbitol dehydration experiments were carried out with no solvent in a 100 mL round-bottom flask. Sorbitol (20 g) was added in a flask, followed by an increase in temperature to 110 °C under stirring (350 r.p.m.) for complete melting of sorbitol. Then, the 1.5 g (in terms of dry weight) of a

catalyst was added and the reactor was heated to the reaction temperature on an oil bath pot and the vacuum (150–170 mbar) was applied. This point was considered as the initial reaction time. The dehydration reaction was carried out in the temperature range of 120 °C to 140 °C. The water that formed during the reaction was distilled off and its pH was measured. Each experiment was repeated at least twice. After the reaction, 8 mL of water was added to the mixture at room temperature. The reaction products in aqueous phase was analyzed by ¹³C NMR spectroscopy (Bruker Avance 400 operating at 100 MHz at ambient temperature) using a database of organic compounds SpectraBase (from John Wiley & Sons, Inc; <https://spectrabase.com/>). A test solution was placed in a 5-mm NMR tube. The ¹³C NMR data were obtained over 256 scans with a 30° flip angle (90° = 12 μs), an acquisition time of 1.3 s, a relaxation delay of 4 s and 32 k data points. Pre-recorded calibration of ¹³C NMR spectra of mixtures of sorbitol : isosorbide with molar ratios in 1 : 1 and 1 : 9 was performed. For quantitative measurements, baselines were corrected and integrals adjusted for bias and slope where appropriate. Chemical shifts are reported relative to CH₃OH and converted to δ(TMS) using δ(CH₃OH) = 50.05 ppm. The structures of identified products (e.g., 1,4-sorbitan, isosorbide, 2,5-mannitan, and 2,5-iditan) are shown in Scheme 1.

¹³C NMR (100 MHz, D₂O, 20 °C, TMS):

Isosorbide – δ = 90.21 (CH, C3), 84.29 (CH, C4), 78.33 (CH, C2), 77.96 (CH₂, C1), 74.64 (CH, C5), 73.96 ppm (CH₂, C6);

1,4-sorbitan – δ = 82.62 (CH, C4), 79.11 (CH, C2), 78.64 (CH, C3), 76.18 (CH₂, C1), 71.77 (CH, C5), 66.5 ppm (CH₂, C6);

2,5-mannitan – δ = 83.3 (CH, C2 and C5), 77.4 (CH₂, C3 and C4), 62.15 ppm (CH₂, C1 and C6);

2,5-iditan – δ = 81.25 (CH, C2 and C5), 77.47 (CH₂, C3 and C4), 60.91 ppm (CH₂, C1 and C6);

sorbitol – δ = 73.98 (CH₂, C2), 72.32 (CH₂, C4), 72.22 (CH₂, C5), 70.75 (CH₂, C3), 63.93 (CH₃, C6), 63.58 ppm (CH₃, C1).

The conversion values of sorbitol (C, mol%) and yield of products (Y, mol%) were calculated from ¹³C NMR spectra by the formulas:

$$C_{\text{sorbitol}} = (\text{moles of sorbitol converted} / \text{moles of initial sorbitol}) * 100 \%$$

$$Y_i = (\text{moles of product defined} / \text{moles of initial sorbitol}) * 100 \%$$

After each reaction cycle, the collected catalysts were sufficiently washed with distilled water and

then isopropyl or ethyl alcohol to remove compounds formed on the catalyst surface. Then the catalysts were dried at 65 °C for 2 h and reused.

Conclusion

In conclusion, both studied sulfonic acid resin catalysts provide 50–88 % yield of isosorbide in the sorbitol dehydration reaction in molten phase “without water” at 125–140 °C under vacuum. According to the ¹³C NMR spectra, isosorbide, 1,4-sorbitan, 2,5-mannitan, 2,5-iditan and sorbitol were identified in the reaction products. More stable Amberlyst 15 provides 35 mmol of isosorbide for 3 h per 1 g of catalyst with full sorbitol conversion and remains active for 5 runs at moderate temperature 125 °C.

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