



Treball Final de Grau

Production of isosorbide from sorbitol: A critical review

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L'energia renovable no és més cara que el combustible fòssil quan es té en compte els costos del cicle de vida.

Piyush Goyal

Vull agrair primerament al Roger Bringué i a l'Eliana Ramírez pel seu temps, tutela i consells, sense la seva ajuda segur que seguiria encallat en algun punt del treball. Als meus amics del grau per animar-me i recordar-me que al final sempre ens en sortim.

Gràcies a la meva família que els estimo moltíssim, als meus pares per estar sempre fent-me costat, a la meva germana per treure'm sempre el millor dels meus somriures i al meu germà informàtic, que sempre acudeix al meu rescat quan tinc desavinences amb la tecnologia, sense ell no hagués pogut recuperar aquest treball.

Per últim, vull agrair al meu Pare Celestial i a Jesucrist, com més aprenc, més meravellat estic de la seva Creació.

CONTENTS

SUMMARY	i
RESUM	iii
1. INTRODUCTION	1
2. OBJECTIVES	3
3. SORBITOL DEHYDRATION TO SORBITOL	5
3.1. SORBITOL	5
3.2. ISOSORBIDE	6
3.3. REACTION DESCRIPTION	6
4. REACTION CATALYSIS	9
4.1. HOMOGENEOUS CATALYSIS	9
4.1.1. Brønsted acids	9
4.1.2. Lewis acids	11
4.2. HETEROGENEOUS CATALYSIS	14
4.2.1. Zeolites	14
4.2.2. Acidic resins	16
4.2.3. Metal phosphates	18
5. REACTION CONDITIONS	21
5.1. INFLUENCE OF REACTION TEMPERATURE	21
5.2. INFLUENCE OF CATALYST AMOUNT	23
5.3. INFLUENCE OF REACTION PRESSURE	24
6. PRODUCTION PROCESS	27
6.1. PROPOSED PRODUCTION PROCESS	28

7. CONCLUSIONS	31
REFERENCES AND NOTES	33
ACRONYMS	37

SUMMARY

The problems arising from the use of plastics are one of the biggest challenges facing society. One way to combat them is through the use of isosorbide as a monomer for the production of plastics. Isosorbide can be produced from biomass without the use of petroleum, is non-toxic and give plastics very favourable properties.

The production of isosorbide is set by a series of sequential reactions that start with cellulose and culminating in the conversion of sorbitol to isosorbide by dehydration. This requires an acid catalyst for good results; industrially it is homogeneously catalysed in the presence of strong mineral acids. There are two major drawbacks associated with this process: the corrosion problems suffered by the equipment and the cost of separating the catalyst.

This work consists of a bibliographic review of the available studies and patents on the dehydration of sorbitol, giving importance to the use of different catalysts to suggest a more beneficial process.

Keywords: Isosorbide, sorbitol, dehydration, reaction conditions, heterogeneous catalysis, homogeneous catalyst.

RESUM

Els problemes derivats de l'ús dels plàstics suposen un dels reptes més grans que afronta la societat. Una manera de combatre'ls és amb l'ús de la isosorbida com a monòmer per la producció de plàstics. Aquesta es pot produir a partir de la biomassa sense la utilització de petroli, no presenta toxicitat i concedeix unes propietats molt favorables als plàstics.

La producció d'isosorbida ve fixada per una sèrie de reaccions seqüencials que s'inicien amb la cel·lulosa i culminen amb la conversió del sorbitol a isosorbida mitjançant una deshidratació. Aquesta requereix un catalitzador àcid per obtenir bons resultats, industrialment es catalitza homogèniament en presència d'àcids minerals forts. Aquests porten associats dos grans inconvenients, els problemes de corrosió que pateixen els equips i els costos de separació del catalitzador.

Aquest treball consisteix en una revisió bibliogràfica dels estudis i patents disponibles sobre la deshidratació del sorbitol donat importància a l'ús de diferents catalitzadors amb l'objectiu de poder suggerir un procés més beneficiós.

Paraules clau: Isosorbida, sorbitol, deshidratació, condicions de reacció, catàlisis heterogènia, catàlisis homogènia.

1. INTRODUCTION

The growth of the plastics industry in the 20th century allowed us to discover and develop new plastics [1]. Thanks to their versatility and properties that have contributed to the development of humanity. For example, the vast majority of our daily devices could not have been developed without plastics. Therefore, plastics have become a fundamental and indispensable material for society, but also, one of the biggest problems.

Most plastics are made by petroleum derivatives, and consequently, CO₂ is emitted into the atmosphere during the manufacturing process. Petroleum is a raw material obtained by the fossilization of buried biomass. Due to their slowness, several hundred thousand years are required for its degradation while its consumption speed is immense. Each day around 100 Mb (million barrels of petroleum) of petroleum is consumed [2]. That is why the products derived from petroleum are considered to be of non-renewable origin. This is one of the most important reasons to replace the origin of plastics by one of renewable.

However, the main problem with conventional plastics is their difficulty in degrading [3], accumulating in the environment, expelling volatile organic and toxic compounds. Among these compounds, there is bisphenol A (BPA), a monomer widely used in the manufacture of plastics. Due to their stability and rigid structure (Figure 1), it forms polymers that show excellent thermal and mechanical properties [4]; this makes understandable its large production volume above 3 million tons [5]. It should be noted that it is an endocrine disruptor that can have serious health effects for humans and inhibits plant growth and development [6].

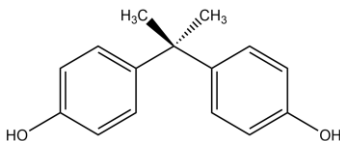


Figure 1. Structure of the molecule of BPA.

To minimize the problems derived from plastics, the development of bio-based polymers is studied, in order to obtain these plastics from renewable resources. The investigation focuses on searching for substitutes for harmful compounds, e.g. D-isosorbide. It can be obtained from cellulose [7], the biomolecule that forms most of the terrestrial biomass. If cellulose is hydrolytically depolymerized, glucose can be obtained, which can be reduced to produce sorbitol and by catalytic methods produce isosorbide. The sequence of reactions is outlined in Figure 2.

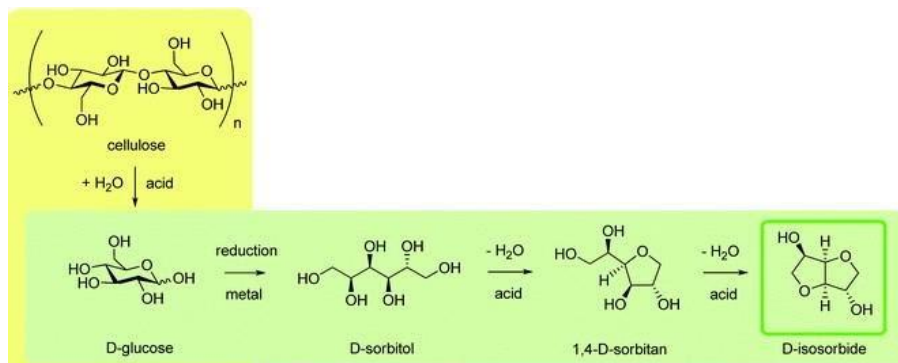


Figure 2. Simplified reaction pathway for the catalytic conversion chain of cellulose to isosorbide [4].

Isosorbide is one of the best options in the development of polymers and it is interesting when it comes to replacing BPA. It allows the increase of glass-transition temperature, hardness and performance for mouldable plastics [8]. However, the catalytic reaction to produce it presents selectivity issues that cause low yields.

Currently, the synthesis of isosorbide by dehydration of sorbitol is carried out industrially by homogeneous catalysis using mineral acids. These have several disadvantages such as corrosion problems suffered by the equipment and the cost of separating the catalyst, which cannot be reused. This review aims to study this reaction, as well as the effect of different catalyst and reaction conditions. For this purpose, open information in the literature and patents will be used.

2. OBJECTIVES

This literature review focus on the current studies and patents available on the dehydration of sorbitol using different catalysts to:

- Understand the reaction mechanism for sorbitol dehydration and know the side-products that can be formed.
- Study the effect of the different catalysts on the reaction.
- Observe how is the effect of the different parameters that define the operating conditions.
- Propose a process for the production of isosorbide that is more environmentally sustainable, while is economically profitable.

3. SORBITOL DEHYDRATION TO ISOSORBIDE

3.1. SORBITOL

Sorbitol ($C_6H_{14}O_6$) is a polyhydric alcohol obtained by hydrogenation of glucose; hence it is also called glucitol. This hexahydric alcohol (Figure 3) is a sugar with the appearance of a white crystalline powder and her sweetness is about 60 % of sucrose [9].

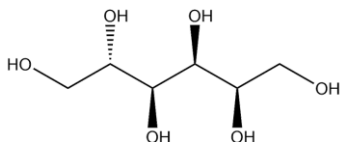


Figure 3. Sorbitol structure.

Sorbitol is a starting point for a large number of products, which means that it is one of the most important platform molecules. Its applications extend to the food, the cosmetics and the pharmaceutical sectors. This is because of their properties as an anti-drying agent and preservative. For example, it can be used as a raw material in vitamin C, in medicine tablets and alkyd resins. It is also widely used in anti-caries products because it cannot be exploited by any bacteria [10, 11].

The industrial production of sorbitol is carried out from the hydrogenation of refined glucose, obtained by starch saccharification, under heating and high pressure with the existence of nickel catalyst, to refine the product, it is necessary to pass the resulting solution of sorbitol through an ion exchange resin [11].

3.2. ISOSORBIDE

Isosorbide ($C_6H_{10}O_4$) is bi-heterocyclic diol with two secondary hydroxyl groups in the 2- and 5- positions (Figure 4) derived from glucose. Isosorbide is not toxic, biodegradable and thermally stable. Isosorbide is a white solid soluble in water, alcohols and ketones.

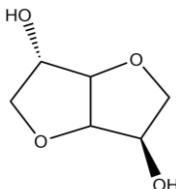


Figure 4. Isosorbide structure.

Isosorbide is a polymer component that can improve the characteristics behaviour of plastics, it can raise the glass-transition temperature and performance for mouldable plastics. The major applications are as a copolymer with PET for use in bottle production [8].

Because of its high stability and two functional hydroxyl groups, isosorbide is a versatile platform chemical that can be derivatized using methods of organic chemistry, such as esterification, etherification, nitration, etc., and converted into compounds with interesting properties [12].

3.3. REACTION DESCRIPTION

The dehydration of sorbitol to isosorbide is formed by two successive dehydrations. Firstly, the acidic hydrogen attacks the hydroxyl group attached to carbon 1 of the sorbitol, the molecule of water formed leaves the compound leaving it unstable, with a positive charge that promotes the folding of the molecule with the oxygen located at carbon 4 producing the 1,4-sorbitan and regenerating the acid catalyst. In the second dehydration the procedure is repeated but on carbon 6 and folding occurs and binds to carbon 3. The mechanism can be seen in Figure 5 [13].

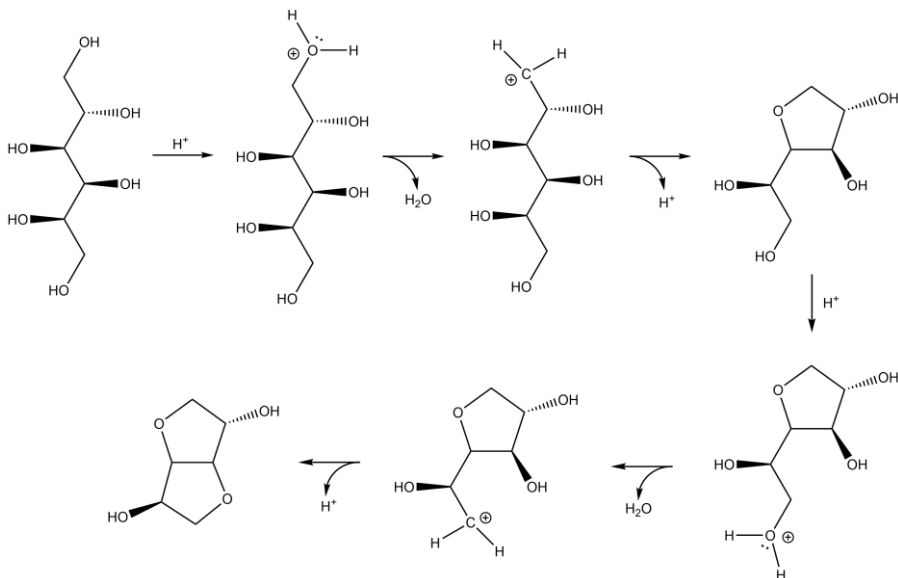


Figure 5. Mechanism of sorbitol dehydration to isosorbide via formation 1,4-sorbitan.

The reaction of dehydration leads to the formation of several side-products preventing good yields in the reaction [14]. These side-products are obtained in the first dehydration, as observed in Figure 6. 3,6-sorbitan is another intermediate product that reacts to isosorbide, but is generated in low quantities.

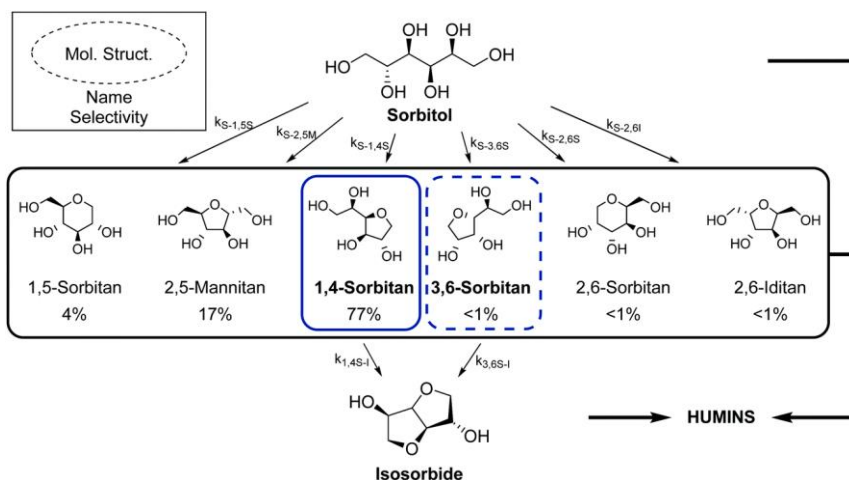


Figure 6. Isosorbide production from sorbitol, synthesis and limitations [14].

1,5-sorbitan and 2,5-mannitan are the side products with more presence. On the other hand, we have 2,6-sorbitan and 2,6-iditan that are formed in low quantities. Most of them, are converted in humins, polymeric undefined structures with a dark brownish colour that has little industrial use. It should be emphasized that both sorbitol and isosorbide and their intermediate products can be affected by oligomerization processes and form other by-products [14].

4. REACTION CATALYSIS

The sorbitol molecule requires an acidic catalyst to protonate the hydroxyl groups. Nowadays, homogeneous catalysis is applied to produce isosorbide at an industrial level, due to its high conversions at low operating temperatures. On the contrary, it presents a series of disadvantages, since it is acidic liquids, the equipment will be affected by corrosion and as we talk about a single phase, a subsequent separation operation with higher costs will be required to separate the catalyst.

Additionally, the use of heterogeneous catalysis would avoid the problems of corrosion and separation, but these are being studied to improve selectivity and yield, achieving a more economically viable proposal.

4.1. HOMOGENEOUS CATALYSIS

The activity of acid catalysts will depend on their acid strength and the nature of the acid sites. We can distinguish between two types, Brønsted acids, proton donors, and Lewis acids, electron pair acceptor [15].

4.1.1. Brønsted acids

Among the Brønsted acids, we can find mineral and organic acids. The mineral acids are characterized by being derived from inorganic compounds and can be very weak, such as boric acid, or very strong such as sulfuric acid and hydrochloric acid [16]. The organic acids are organic compounds with acidic properties, in general, they are weak acids although some can be very strong as p-toluenesulfonic acid (PTSA) or trifluoroacetic acid (TFA), the organic acids are typically less corrosive and easy in handling [17].

The mineral acids have been used to synthesize isosorbide for years, the synthesis with sulfuric acid has been patented as early as 1930 [18]. Over time other mineral acids have been used, but these have proven to be less efficient, Fleche and Huchette studied the use of HCl

($pK_a = -6.3$) and H_3PO_4 ($pK_a = 2.1$) under moderate temperature (135 °C) and reaction time of 20 h and compared them to H_2SO_4 ($pK_a = -3$). The results show that the HCl and H_2SO_4 , which are strong acids ($pK_a < pK_{a, H_3O^+} = -1.74$), presented a complete sorbitol conversion and high yields of isosorbide (70-75 %). Generally, HCl is less suitable as it readily distills with water under low-pressure reaction conditions. By contrast, H_3PO_4 is not a strong acid, and therefore is not completely dissociated in a solution, showed 87 % sorbitol conversion and lowest isosorbide yield, 12 % [19].

Dabbawala et al. studied the effect of Brønsted acid catalyst by choosing acids of different acid strength and compared with H_2SO_4 . Among them were TFA, PTSA, methanesulfonic acid (MSA), sulfamic acid (SFA), sodium hydrogen sulphate, $NaHSO_4$ (SHS), citric acid (CTA), and boric acid (BA). Results of dehydration of sorbitol are summarized in Table 1 [15].

Table 1. Dehydration of sorbitol using Brønsted acid catalyst (reaction condition: sorbitol = 54.9 mmol, stirring speed = 800 rpm) [15].

Catalyst (H ⁺ mmol)	pKa (pH) ^a	Temp. (°C)	Time (min)	Conv. (%)	Yields (%)		
					IS	ST	UN
H_2SO_4 (SA) (0.52)	-3 (3.29)	160	30	100	48	39	13
			60	100	68	16	16
TFA (0.52)	-12 (3.21)	160	30	100	39	46	15
			60	100	63	18	19
PTSA (0.52)	-2.8 (3.27)	160	30	100	45	43	12
			60	100	66	19	15
MSA (0.52)	-1.9 (3.25)	160	30	100	46	43	11
			60	100	66	20	14
SFA (1.04)	1.0 (2.8)	180	30	95	13	67	14
			60	100	41	43	16
SHS (1.04)	1.99 (2.9)	180	30	92	9	75	6
			60	98	14	77	7
CTA (1.56)	3.13 (3.5)	180	60	48	2	43	3
			120	64	4	55	5
BA (1.56)	9.24 (6.7)	180	60	41	1	37	3
			120	55	2	49	4

IS: isosorbide, ST: sorbitan (1,4-sorbitan + 1,5-sorbitan), UN: unknown, non-detected product ("Humins"), calculated as the conversion minus the sum of the yields (IS + ST)

^a pH of reaction mixture after reaction (2% aqueous solution).

In Table 1 we can see two zones, the zone of strong catalyst ($pK_a < -1.74$) where the sorbitol conversion is complete and the isosorbide yields are high (63-68 %) at short times (1 h). Then, the zone of weak acids ($pK_a > -1.74$), where sorbitol conversion is not completed and the yields are low. It can be seen that conversion and the yields tend to be reduced while the pK_a increases.

For very weak acids ($pK_a > 2.99$) the activity is drastically reduced, resulting in low sorbitol conversions and isosorbide yields, despite the doubling of study times.

The study shows that Brønsted acid needs to be highly strong to obtain better results. These strong acids are beneficial because they are completely dissociated in the solution. In conclusion, a high isosorbide yield could be possible with activity in moderate temperatures as 160 °C. However, among the strong acids, the behaviour is similar, presenting almost a comparable isosorbide yield, highlighting that the H_2SO_4 is situated somewhat above the three strong organic acids.

All the acids that are not strong enough to be completely dissociated, decrease the isosorbide yield and catalytic activity gradually due to the increase of its pK_a value and its acid strength decrease.

In, conclusion, organic and mineral Brønsted acids have the same behaviour and are defined by acidity. Organic acids have the advantage of being less corrosive and easy to handle, this could be a benefit when it comes to operating in a reactor. Nevertheless, sulfuric acid is a commodity product, the vast majority of acid production worldwide is acid sulfuric. That means a lower cost compared to organic acids with high strength.

4.1.2. Lewis acids

A Lewis acid is capable of taking an electron pair from a Lewis base to form an acid-base adduct. Transition metals are considered Lewis acids and they form metal salts by joining an anion. Dabbawala et al. studied the effect of different metals with specific anions, as shown in Table 2 [15].

Table 2. Dehydration of sorbitol using Lewis acid catalyst (reaction condition: sorbitol = 54.9 mmol, catalyst = 0.52 mmol, stirring speed = 800 rpm) [15].

Catalyst (H ⁺ mmol)	pH ^a	X _i ^b	Temp. (°C)	Time (min)	Conv. (%)	Yields (%)		
						IS	ST	UN
CuCl ₂	5.79	–	180	120	100	12	82	6
CuSO ₄	5.51	9.5	170	120	35	0	34	1
				60	99	44	47	9
				120	100	61	23	16
Fe ₂ (SO ₄) ₃	3.04	12.6	170	60	56	2	49	4
				120	77	7	62	8
Al ₂ (SO ₄) ₃	3.97	10.5	170	60	99	31	56	12
				120	100	56	29	15
Zr(SO ₄) ₂	2.94	12.6	160	30	100	48	38	14
				60	100	65	18	17
Ti(SO ₄) ₂	3.01	13.5	160	30	100	50	38	12
				60	100	68	16	16
Yb(OTf) ₃	5.6	–	160	60	21	0	20	0
				60	96	20	67	9
				120	100	55	33	12
Sc(OTf) ₃	3.8	–	160	30	100	49	38	13
				60	100	67	18	15

^a pH of reaction mixture after reaction (2 % aqueous solution).

^b X_i = (1 + 2Z) X_o; where X_o, electronegativity of the neutral atom; Z, charge of the ion [19].

The isosorbide yields comparison obtained for the metallic copper salt (180 °C and 120 min) shows that Lewis acids with chlorides as anions present lower reactivities than sulfuric acid. The activities from sulphated metal oxides manifest changes when varying the metal used, the metals with the highest activities are Ti and Zr. Dabbawala et al. justify that this situation might be due to their higher electronegativity. The Fe, despite its high electronegativity, its low solubility in molten sorbitol, resulted in lower isosorbide yields [15].

During the reaction, water is generated, as can see in Figure 5. The molecules of water coordinated with metal, thereby polarizing the OH bond and induce Brønsted acidity [21]. Therefore, electronegativity favours polarisation and Brønsted acidity, leading to better yields.

On the other side, it can be assumed that the metal sulphates react with the hydroxyl groups of the sugar (sorbitol) to form metal alkoxides, $M(OR)_n H_2SO_4$, generating acidic Brønsted sites. As is the case with the metal chlorides [22].

Metal triflates have proven to be an interesting candidate to promote the synthesis of isosorbide from sorbitol; as shown by the acid $Sc(OTf)_3$, whose activity is slightly below $Ti(SO_4)_2$. To better understand the behaviour of triflate metals, a patent has been studied [23].

Table 3. Dehydration of sorbitol using metal triflates (reaction conditions: 100 g sorbitol, 0.05 mol% triflate salt, 160 °C, 5 mbar, 1 h) [23].

Acid	X_i	Conv. (%)	Yields (%)			
			IS	1,4-ST	2,5-ST	UN
$Bi(OTf)_3$	14.14	99.43	25.25	60.18	9.13	4.87
$In(OTf)_3$	12.46	100.00	31.12	55.71	9.83	3.34
$Sc(OTf)_3$	9.52	96.69	15.38	68.14	8.43	4.74
$Ga(OTf)_3$	14.07	100.00	71.31	7.64	8.30	12.75
$Sn(OTf)_3$	13.72	85.51	10.65	69.05	7.14	-1.33
$Al(OTf)_3$	11.27	100.00	26.08	58.80	8.85	6.27
H_2SO_4		69.22	4.05	53.67	5.52	5.98

Table 3 shows that, unlike the sulphated metal oxides, the isosorbide yields of triflate metals have not shown a direct dependence on electronegativity. Low isosorbide yields are watched at the given conditions (low catalyst concentration, 0.05 mol%), except for the high yield of $Ga(OTf)_3$, that a 1h already obtains an isosorbide yield of 71 %.

A possible reason for this result could be that it can dissolve more easily in molten sorbitol, facilitating its action. It would be interesting to experiment with the solubilities of the different triflate metals and compare them with isosorbide yields.

Comparing the results obtained for the H_2SO_4 with those obtained for triflate acids in Table 3. It is concluded that the triflate acids are much more efficient. However, being critical of the results watched for H_2SO_4 , they are lower than they should be. The conversion and isosorbide yields are too low when working at a temperature of 160 °C for 1 hour.

Nevertheless, if we compare the results obtained for H_2SO_4 in Table 1 with the results of $\text{Sc}(\text{OTf})_3$ in Table 2, at the same conditions of temperature, agitation and reactant concentration, they show similar conversion and yields to isosorbide.

A negative unknown yield is obtained for $\text{Sn}(\text{OTf})_3$, which is impossible, as the sum of the yields cannot exceed the conversion. This is most likely an error in the results taking.

In general terms, the activity of most triflates acids is similar to that of sulphuric acid. However, $\text{Ga}(\text{OTf})_3$ stands out, making it an interesting candidate as a catalyst. Because the high isosorbide yields at a short time would allow working with shorter residence times. However, it also has a drawback, the high unknown yield (13 %). Most of it will be composed of humins, which are of no industrial interest.

4.2. HETEROGENEOUS CATALYSIS

For heterogeneous catalysis, solid catalysts are used. They avoid corrosion problems, facilitate subsequent separation, and can be reused and regenerated if deactivated, being more sustainable than a homogeneous catalyst. There is a great variety of solid catalysts and in this work, we will talk about the most outstanding ones.

4.2.1. Zeolites

Zeolites are aluminosilicate minerals formed by AlO_4 and SiO_4 tetrahedra linked by oxygen atoms that form a porous structure that can accommodate a wide variety of cations. Their acidic forms are used as catalysts in many varieties of reactions, highlighting their use in oil cracking.

Research shows that H-Beta type zeolites displayed higher sorbitol conversion and isosorbide yield [24, 25] as can be seen in Figure 7, where they outperform other types of zeolites.

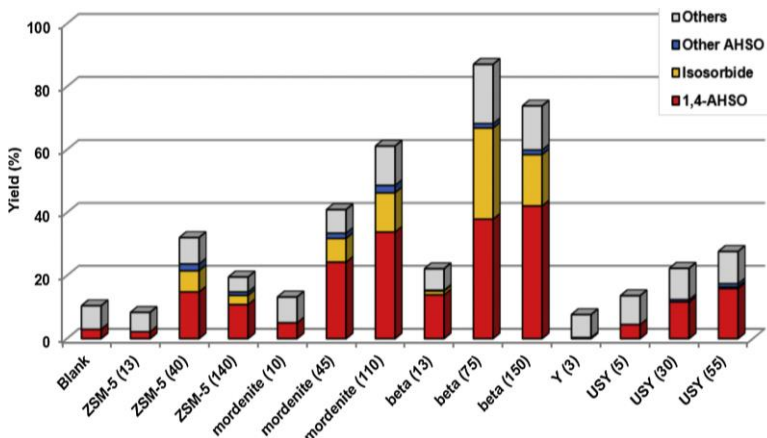


Figure 7. Dehydration of sorbitol in different types of zeolites [25].

Figure 7 shows different isosorbide yields for different zeolites. Being higher for modernites and H-beta zeolites. Studies have shown that the Si/Al ratio influences the reaction rates. When the sorbitol conversion and the isosorbide yield are represented in different Si/Al ratios we obtain Figure 8.

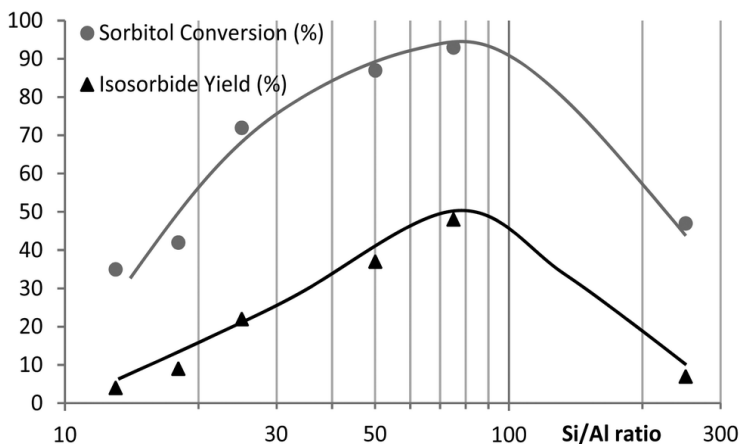


Figure 8. Influence of the Si/Al ratio in dehydration of sorbitol to isosorbide in presence of H-beta zeolites. [14]

It can be seen that the reaction ratios increase together with the Si/Al ratio, reaching a maximum of 75 Si/Al ratio. Otomo et al. reported the maximum isosorbide yield for this ratio is at 81 % at a temperature of 180 °C, with a high reaction time (60 h) [25].

As the catalyst is used, it is deactivated due to the deposition of carbonaceous matter on the catalyst. After the third use, the activity is affected and by the fourth use, it is significantly reduced (Figure 9). Regeneration of the catalyst can be achieved by simple calcination at 550 °C [25].

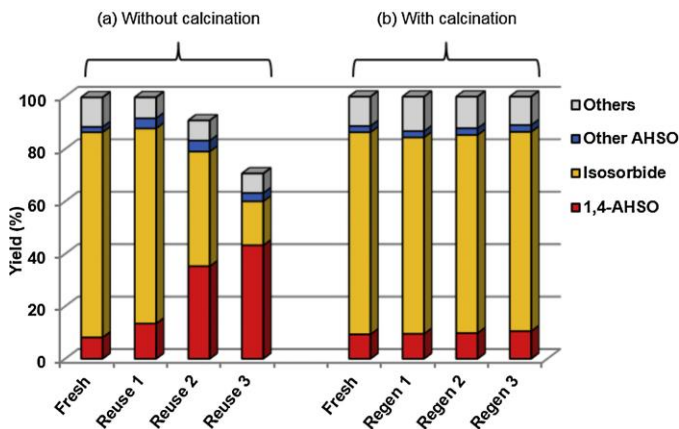


Figure 9. Recycling use of beta (75) catalyst (a) without calcination and (b) with calcination at 550 °C after each run. Reaction conditions: Sorbitol/Al ratio equal to 50; sorbitol 7.5 mmol; water 15 mL; Temperature, 200 °C; Time, 18 h [25].

4.2.2. Acid resins

Acid resins are a type of ion exchange resins that are characterized by having an acid functional group. There is a wide variety of resins on the market, however, there are few that present greater interest, of which Table 4 has been constructed. The data comes from different studies.

Purolite, Amberlyst and Dowex are commercial sulfonic acid resins. The difference between these acid resins is their acidic properties, as well as in their thermal and mechanical stabilities [26, 27].

If we compare the results obtained for the different commercial sulphonc resins in entries 2, 3 and 4 of Table 4, we can see that under the same conditions the two Amberlyst resins (35 and 70) behave without any significant difference. In comparison to Purolite CT269, they are less efficient, as the isosorbide yield of the latter is somewhat higher.

If we compare entries 6 and 9, we can see that Dowex-50W x 2 show isosorbide yields better than Amberlyst-15.

Table 4. Dehydration of sorbitol using acid resins.

Entry	Catalyst	Reaction conditions			Time (h)	Conv (%)	IS Yield (%)	Ref.
		Solvent (mol %)	T (°C)	P				
1	Purolite CT269	Free	140	High Vacuum	12	100	75	[26]
2			140	High Vacuum	1.5	93	35	[26]
3	Amberlyst-35	Free	140	High Vacuum	1.5	91	31	[26]
4	Amberlyst-70	Free	140	High Vacuum	1.5	92	31	[26]
5	Amberlyst-15	Free	120	1000 Pa	10	93	71	[28]
6		Free	130	High Vacuum	24	100	67	[29]
7		SO ₃ H (5)	130	High Vacuum	2	-	41	[29]
8		SO ₃ H (20)	130	High Vacuum	2	-	87	[29]
9	Dowex-50W x 2	Free	130	High Vacuum	24	100	78	[29]
10	SiO ₂ -SO ₃ H	Free	120	-	10	100	84	[28]
11	Glu-Fe ₃ O ₄ -SO ₃ H (10 wt.%)	Free	120	-	5	-	30	[30]
12	Glu-Fe ₃ O ₄ -SO ₃ H (20 wt.%)	Free	120	-	5	100	89	[30]
13		Free	140	-	1	100	94	[30]

SiO₂-SO₃H is a micro-bead silica catalyst. It needs a long time to achieve full conversion and very high isosorbide yields of 84 %. It was observed that it can be reused a few times. In the experiment, it was reused ten times, without losing activity [28].

Glu-Fe₃O₄-SO₃H is a glucose derived magnetic solid acid. According to the authors, the isolated isosorbide yield reached 94 % after 1 h at 140 °C, its high rate is due to the large amount of catalyst used, 20 wt.%. This method apparently avoids the formation of side-products. However, the purity of the products was attested by ¹³C NMR. However, this analytical technique does not take into account the formation of oligomeric/polymeric by-products that can be elsewhere obtained [14, 30].

Glu-Fe₃O₄-SO₃H can be separated using magnetic force and reused up to five times without any significant loss in yields after each recycling step [14, 30].

4.2.3. Metal phosphates

Metal phosphates are used in catalysed processes due to their high thermal stability and acid-base properties. Research has focused on both quadrivalent phosphates and trivalent phosphates.

Quadrivalent phosphates are metal (IV) phosphates that can be prepared by adding phosphoric acid to an aqueous solution of metal ion and subjected the resulting solution to hydrothermal treatment at 453 K for a long time. Among these, we can find zirconium, tin and titanium phosphates (respectively ZrPO, SnPO, TiPO). Mingyan Gu et al. [20] disclose that for dehydration of sorbitol to isosorbide in gas-phase, among the aforementioned phosphates, tin phosphate showed the highest selectivity to isosorbide (65.4 %) and 1,4-sorbitan (33.6 %) but with moderate sorbitol conversion (72.1 %).

Table 5. Catalytic performance of sorbitol dehydration over metal (IV) phosphates (reactions conditions: sorbitol feedstock: 10 wt.%, sorbitol flow rate: 1.2 mL h⁻¹, N₂ flow rate: 30 mL min⁻¹, catalysts: 0.5 g, TOS: 120 min, temperature: 300 °C) [31].

Catalyst	S _{BET} (m ² g ⁻¹)	Acid amount (mmol g ⁻¹)	Ac. density (mmol m ⁻²)	Conv. (%)	Yields (%)		
					IS	1,4-ST	UN
SnPO	37.0	4.60	0.124	72.1	47.2	24.2	0.7
ZrPO	32.9	3.04	0.092	55.9	29.2	14.4	12.3
TiPO	75.1	2.00	0.027	97.1	45.1	3.0	49.0

Table 5 shows that the acidity density presented by SnPO is the highest one. This may explain why it presents the best isosorbide and 1,4-sorbitan yields. Titanium phosphate, whose selectivity is the lowest together with its acidity density, proved to be the most active, this can be attributed to its high specific area.

SnPO shows little humins formation (< 1 %), however, the yields of metal (IV) phosphates are low, despite working at high temperatures (300 °C). This means that high temperature and therefore higher energy cost would be required for their use.

They also have the disadvantage of being high energy cost for their preparation and, in some cases, they can be toxic such as tin phosphates. For these reasons, research has focused on trivalent phosphates, these are the cheapest because their preparation is simple, it is only necessary to mix a soluble source of the trivalent metal cation and a source of the phosphate anion, without the need for high temperatures [32].

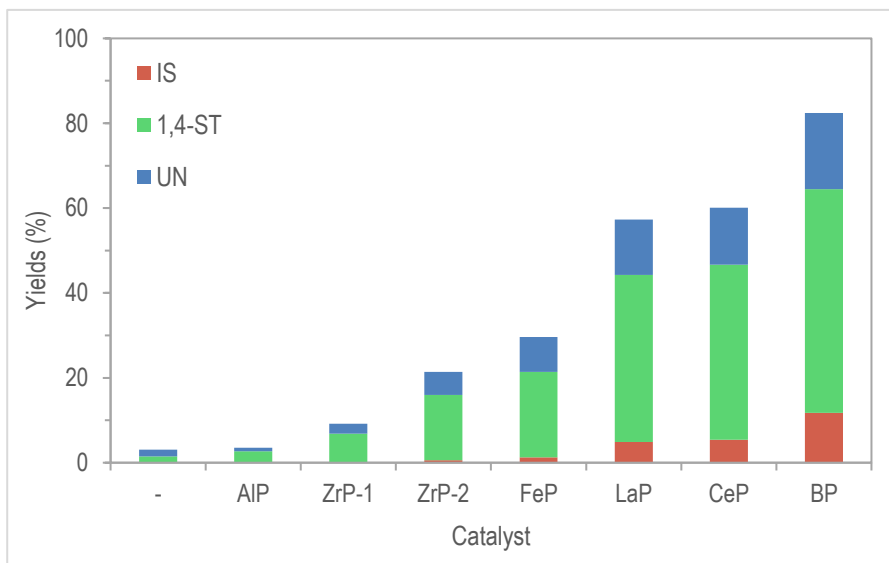


Figure 10. Yields of trivalent phosphates in dehydration of sorbitol to isosorbide. Reaction conditions: 0.23 g of catalyst; temperature: 200 °C, time on reaction: 2 h, autogenous pressure: 1–14 bars, $V_{\text{reaction}} = 25 \text{ mL}$ aqueous 70 wt.% sorbitol solution; 1100 rpm (Data extracted from ref [32]).

Figure 10 shows that trivalent phosphates exhibit widely varied yields and conversions. The reaction rates of the different trivalent phosphates do not respond to a single factor, rather a combination of several parameters (solid acidity, surface area, average pore radius, pH, reaction conditions, etc.). This makes it difficult to conclude, although it can be said that under the observed conditions the activity varies as follows: AIP < ZrP < FeP < LaP < CeP < BP. With boron (III) phosphate being the most active, with a sorbitol conversion of 82 % and isosorbide yield of 12 %.

If we compare the quadrivalent phosphates and trivalent phosphates, the latter despite being observed at much lower temperatures, the conversions are shown are higher. In terms of

yields, the low temperature means that the 1,4-sorbitan prevails, yet certainly, at 300 °C the trivalent phosphates would certainly better.

5. REACTION CONDITIONS

The physicochemical parameters of temperature, pressure and catalyst concentration, determine the activity and yields of the reaction.

The operating conditions to carry out the reaction will depend on the catalyst that is selected. In this work, we will study how the variation of conditions affects different catalysts and the best working conditions for industrial production.

5.1. INFLUENCE OF REACTION TEMPERATURE

Temperature is an important parameter to consider when it comes to the reaction. Due to their influence on the reaction rate.

To know its effect, it is observed how the temperature affects different heterogeneous catalysts, starting with the results shown by the zeolites.

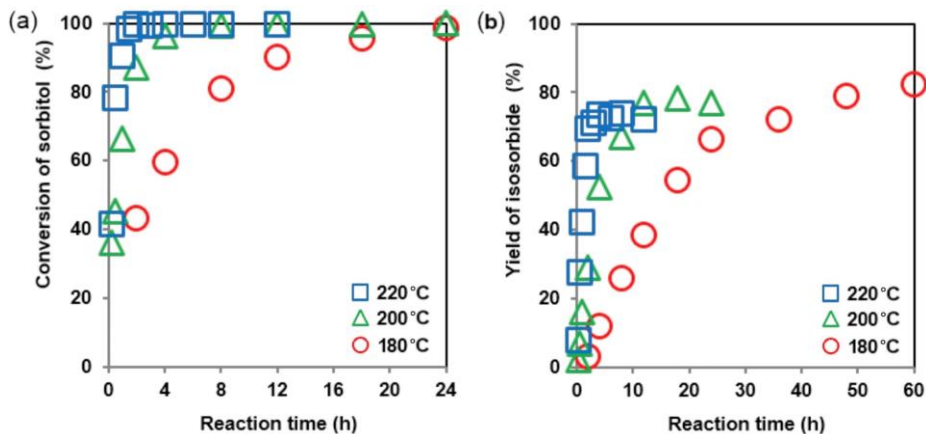


Figure 11. Temperature dependence of (a) conversion of sorbitol, and (b) yield of isosorbide. Reaction conditions: catalyst, beta (75); Sorbitol/Al ratio equal to 50; sorbitol, 7.5 mmol; water, 15 mL [25].

Figure 11 shows that the sorbitol conversion after 2 h was 43 % at 180 °C and 86 % at 200 °C, while more than 99 % conversion of sorbitol was achieved at 220 °C. The yield of isosorbide after 2 h was less than 10 % at 180 °C, 29 % at 200 °C and 41 % at 220 °C. These yields are affected by reaction rate, therefore, the yield of isosorbide at prolonged reaction time is observed. This was 81, 77, and 74 % at 180, 200 and 220 °C, respectively. The decrease in the maximum isosorbide yield with increasing temperature is due to the side reactions of sorbitol are more favoured to form side-products.

Observations that can be drawn are that operation at moderate temperature is favourable for the selectivity of 1,4-sorbitan and non-favourable for side-products. Then, we can achieve a high isosorbide yield, although it needs a long reaction time.

To check the accuracy of these statements, Figure 12 is taken from the literature to see how temperature affects the selectivity of the reaction. The catalyst used is MC-PhSO₃H [33].

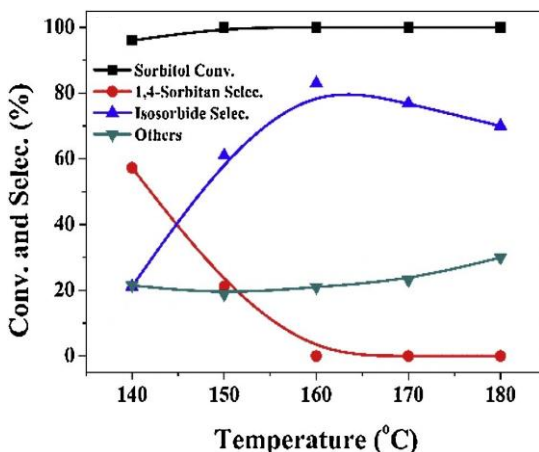


Figure 12. Conversion and selectivity over MC-PhSO₃H affected by reaction temperature (90 min, 0.3 g catalyst) [33].

Figure 12 shows that as the temperature increases, the selectivity of unwanted products increases. This and the rapid formation of isosorbide causes the selectivity of 1,4-sorbitan to be drastically reduced. It can also be seen that at full conversions the selectivity of the isosorbide decreases with temperature, reaffirming that high temperatures decrease the maximum isosorbide yield that can be reached by the reaction.

Using the Amberlyst-15 resin and sulfonic acid, it has been found that the optimum temperature for best yields is 130 °C (Figure 13). If it is at such a low temperature, it is due to the use of SO₃H in high concentration.

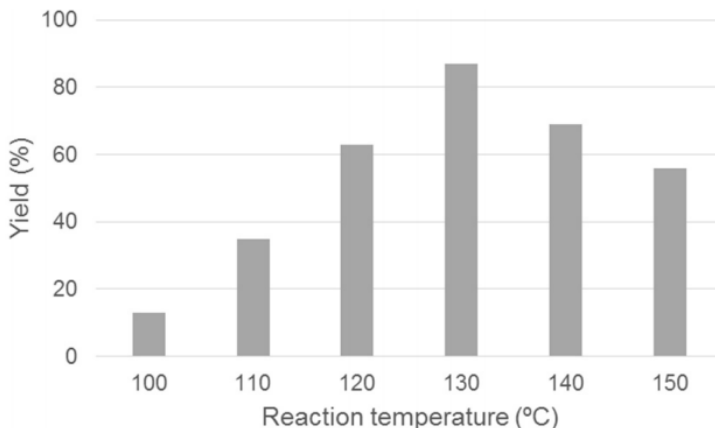


Figure 13. Effect of reaction temperature on sorbitol dehydration with Amberlyst-15 (reaction conditions: 20 mol% SO₃H, 2 h, 3x10⁻² mbar) [29].

Unlike heterogeneous catalyst, homogeneous catalysts exhibit high reaction rates at moderate temperatures, achieving high yields in short times.

5.2. INFLUENCE OF CATALYST AMOUNT

By increasing the amount of catalyst, it is expected that the reaction will be accelerated due to a higher specific surface, and thus also the number of active centres. To check whether this hypothesis is fulfilled, we will examine how the amount of catalyst affects the conversion and isosorbide yield of the reaction.

Figure 14 shows that by increasing the amount of catalyst, higher conversions and yields are achieved in shorter times. As more catalyst is added to the system, the increase in the rate of reaction is reduced.

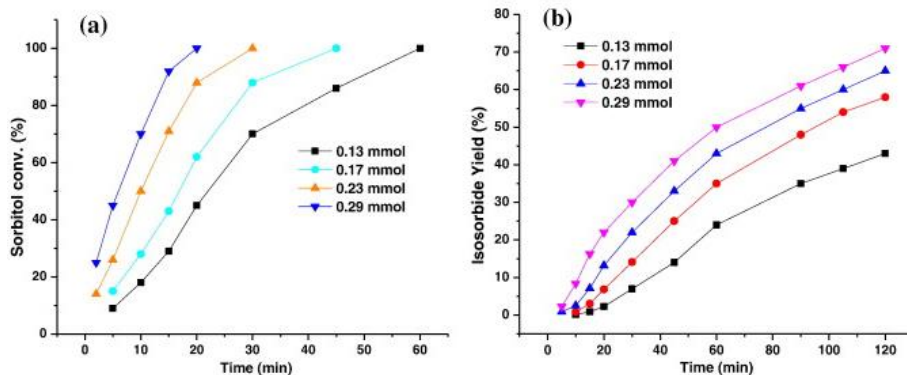


Figure 14. Effect of catalyst amount on sorbitol conversion (a) and isosorbide yield (b) in Ar/SBA-15 catalysed dehydration of sorbitol; sorbitol = 32.9 mmol, temp. = 170 °C [34].

5.3. INFLUENCE OF REACTION PRESSURE

Throughout the work, it has been observed that experimentally, work is carried out under vacuum conditions (below atmospheric pressure). As in the case of triflate metals (5 mbar) in Table 3 and the acids resins in Table 4. This is to favour the extraction of the water formed in the reaction medium and thus shift the equilibrium towards isosorbide production.

Therefore, the lower the reaction pressure, the faster the reaction shifts to product formation. Polaert et al. studied how vacuum pressure affected the initial rate of sorbitol consumption [35].

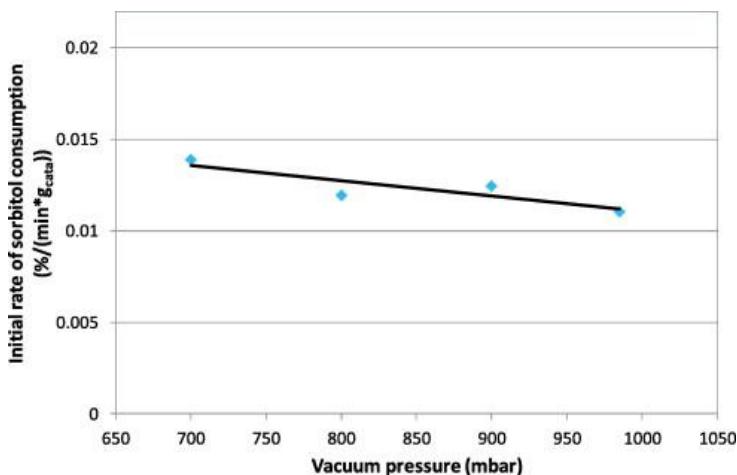


Figure 15. Influence of vacuum pressure on the catalytic dehydration of pure sorbitol (m_0 (sorbitol) = 40 g; m_{cat} = 3.4 to 4 g; T = 150 °C; agitation speed = 400 rpm; nitrogen flowrate = 150 g/h) [35].

Figure 8 shows that by reducing the pressure the reaction does indeed occur faster. However, the effect is moderate, reducing 300 mbar results in a rate increase of less than 0.005 %/(min·g_{cat}). Working at very low pressure causes the vacuum pump to pull a high proportion of isosorbide together with the water.

6. PRODUCTION PROCESS

Current commercial processes for the production of isosorbide are designed to avoid the formation of by-products. Among these processes are the two-stage process and continuous process.

In the two-stage process, first, a dehydration stage is carried out in a continuous reactor, where sulphuric acid (1 wt.%) is added, starting from a 70 % concentrated sorbitol solution. In the first stage, the aim is to produce 1,4-sorbitan, avoiding the formation of unwanted species. This is done under vacuum conditions (1000 Pa) with a relatively low residence time and temperature, approximately 120 min and 122 °C [13, 36].

Afterwards, the reaction product is then loaded into a new reactor, where the temperature is increased to 130 °C and the residence time is 30 minutes so that most of the 1,4-sorbitan is converted to isosorbide, achieving conversions of 97 % and a yield of more than 80 % isosorbide.

DuPont patented a process based on a continuous reactor (Figure 16) fed by a stream of sorbitol diluted to 45 % by weight is introduced with a 10 % aqueous solution of sulphuric acid.

The flow is subjected to a temperature gradient between 125 and 145 °C and a pressure of 2400 Pa. A steam reflux is added to facilitate the separation and subsequent purification of the isosorbide formed, due to its high affinity. This process allows obtaining high conversions and a high purity product, 97 % by weight of isosorbide [13, 37].

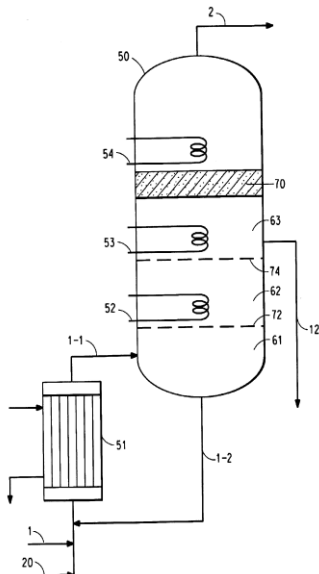


Figure 16. Schematic of the continuous reactor for the synthesis of isosorbide using H_2SO_4 [37].

Sulphuric acid will be the catalyst that allow isosorbide production with lower associated cost, due to its low cost and the high yields that can be achieved in a short time at moderate temperatures. Research is still needed to find a catalyst that can overcome the advantages of sulphuric acid.

6.1. PROPOSED PRODUCTION PROCESS

For the proposed production process, $Glu-Fe_3O_4-SO_3H$ has been chosen among the different heterogeneous catalysts, because it has shown good isosorbide yields avoiding significantly the formation of side-products.

The industrial process will work in two stages in a single batch reactor. In the first stage, the slurry agitation reactor will be loaded with the catalyst (20 wt.%) and pure sorbitol without any solvent (catalyst showed good results for that condition). This will be operating under vacuum conditions, around 700 mbar, at a temperature of 130 °C for a residence time of 2.5 h. The temperature has been reduced and the reaction time has been increased compared to the best conditions seen for the catalyst (in entry 13 of Table 4). To achieve a decrease in the yield of undesired products such as humins.

Once the time passes, the temperature of the reactor will be increased to 140 °C and it will be left operating for 0.5 h to finish converting the 1,4-sorbitan to isosorbide. At the end of the reaction, with the help of an external magnetic force, the product would be separated from the catalyst. This avoids filtration because filters have clogging problems when used with a slurry reactor.

The times chosen are approximate considering the times seen at 120 and 140 °C (entries 12 and 14 in table 4) for the $\text{Glu-Fe}_3\text{O}_4\text{-SO}_3\text{H}$. It would be necessary to experiment at 130 °C to obtain the most suitable times. With this process, an almost complete conversion and an isosorbide yield close to 90 % could be assumed, as well as the experimental results obtained with the catalyst.

The catalyst showed excellent catalytic activity for at least five runs without any significant decrease in product yield. After exhausting the catalyst, it can be dried at 100 °C for 12 h for reuse.

7. CONCLUSIONS

The conclusions drawn from this bibliographical work are the following:

- For Brønsted acids, strong acidity is required to achieve high conversion and yields at moderate temperatures.
- Lewis acids are favoured by electronegativity, as it induces Brønsted acidity, allowing activities comparable to Brønsted acids. For triflate metals, it would be interesting to study the relationship between their solubility in sorbitol and the isosorbide yields.
- Heterogenous catalyst requires high temperatures to achieve high reaction rates. Deep research would be needed for developing a heterogeneous catalyst capable of competing with the activity of homogeneous catalysts at moderate temperatures.
- Among the different heterogeneous catalysts, the most remarkable are SnPO and Glu-Fe₃O₄-SO₃H due to their low humins production.
- To achieve high isosorbide yields, it is necessary to work at moderate temperatures to avoid side reactions.
- Under vacuum conditions, displacement towards product formation in sorbitol dehydration is favoured.

Table 6. Proposed production process to carry out sorbitol dehydration.

Sorbitol dehydration			
Discontinuous reactor	Slurry agitation reactor	P (mbar)	700
Catalyst concentration (wt.%)	20	T₁ (°C)	130
Catalyst	Glu-Fe ₃ O ₄ -SO ₃ H	t₁ (h)	2,5
Side-products	1,5-sorbitan 2,5-mannitan Humins	T₂ (°C)	140
Intermediate products	1,4-sorbitan 3,6-sorbitan	t₂ (h)	0,5
Conversion (%)	> 99	IS Yield (%)	≈ 90
Simplified reaction mechanism			

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ACRONYMS

BPA	Bisphenol A
PTSA	P-toluenesulfonic acid
TFA	Trifluoroacetic acid
PET	Polyethylene terephthalate
MSA	Methanesulfonic acid
SFA	Sulfamic acid
SHS	Sodium hydrogen sulphate
CTA	Citric acid
BA	Boric acid
SA	Sulfuric acid
IS	Isosorbide
ST	Sorbitan
UN	Unkonwn

