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A contribution to the study of the fructose to isosorbide conversion reaction.

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The process of scientific discovery is, in effect, a continual flight from wonder

Albert Einstein

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SUMMARY

The search for an alternative to the rejection of petroleum derivatives as raw materials is one of the most important challenges facing the chemical industry. The increasing stringency of environmental legislation and the need to eliminate harmful products from industry present biomass as a viable and promising resource.

Isosorbide is a molecule of particular interest which can be obtained from agricultural and forestry waste. It can be used in a wide range of applications, such as the bioplastic production, and allows the substitution of bisphenol A, a monomer used, until recently, in some packaging in the food industry and which is harmful to consumers.

For the production of isosorbide, a reaction mechanism is taking part. The final stage, a double dehydration of sorbitol that requires an acid catalyst, is the one under study. Currently, to obtain acceptable selectivity and yield values, sulphuric acid or a similar strong mineral acid is used. These homogeneous catalysts have present disadvantages due to energy consumption, the need for subsequent separation and neutralisation treatments, and the costs derived from the equipment corrosion.

For this reason, the main interest is the search for heterogeneous catalysts that allow obtaining a good yield and selectivity with moderate conditions that promote energy costs savings.

The experiments carried out in this study have proved the viability of using acidic ion exchange resins as catalysts evaluating their catalytic behaviour. Resins with a lower cross-linking degree and a higher specific volume of swolling polymer have given the best results.

CT-482 resin has shown the best activity, obtaining a maximum isosorbide yield of 70% for a temperature of 180°C.

In addition, sorbitol solubility has been studied to determine possible substitutes for water. Regarding this, protic solvents with a higher polarity are the ones that have provided the best solubility values. Keywords: Sorbitol, Isosorbide, ion-exchange resins, dehydration, solubility, Bisphenol A

Resum

La cerca d'una alternativa al rebuig de derivats del petroli com a primeres matèries és un dels reptes més importants als quals s'enfronta la indústria química. La creixent duresa de la legislació mediambiental i la necessitat d'eliminar els productes nocius de la indústria, presenta la biomassa com una opció viable i prometedora.

La isosorbida és una molècula de gran interés que pot obtenir-se partint de restes vegetals. Pot utilizar-se en un gran ventall d'aplicacions com la producción de bioplàstics i permet la substitució del Bisfenol A, un monòmer que fins fa pocs anys s'emprava en alguns envasos a la industria alimentaria i que és perjudicial per a la salut dels consumidors.

Per a la producció de la isosorbida, té lloc un mecanisme de reacció en la que la darrera etapa, una doble deshidratació del sorbitol en la que es precisa d'un catalitzador àcid, és la que està sent subjecte de diferents estudis. Actualment, per a obtenir una selectivitat i rendiments considerables, s'empra àcid sulfúric o algun àcid mineral fort similar. Aquests són catalitzadors homogenis i presenten molts inconvenients tant pel consum energètic, per la necessitat de tractaments posteriors de separació i neutralització, com per les despeses derivades per la corrosió dels equips.

És per aquest motiu que el principal interès és la cerca de catalitzadors heterogenis que permetin l'obtenció d'un bon rendiment i selectivitat amb unes condicions moderades per a afavorir l'estalvi energètic.

Els experiments realitzats en aquest treball han comprovat la viabilitat d'emprar resines àcides de bescanvi iònic com a catalitzadors, avaluant-ne el seu comportament catalític. Aquelles resines amb un menor grau de reticulació i un major volum específic de polímer inflat han ofert els millors resultats. La resina CT-482 ha presentat la millor activitat, obtenint un rendiment màxim d'isosorbida d'un 70% per a una temperatura de 180°C. Paral·lelament, s'ha estudiat la solubilitat del sorbitol en diferents dissolvents orgànics per a determinar-ne possibles substituts de l'aigua. Els dissolvents pròtics amb una major polaritat són els que han ofert els millors valors de solubilitat.

Paraules clau: Sorbitol, isosorbida, resines de bescanvi iònic, deshidratació, solubilitat, Bisfenol A

1. INTRODUCTION

1.1. BIOMASS AS A RENEWABLE RESOURCE

The current model of chemical industry bases its production on the use of petroleum derivatives as raw materials. A finite resource which will be depleted in a not-too-distant future and whose consumption presents a high environmental impact. The emission of greenhouse gases (GHG) is one of the main focuses of global warming and chemical industry is responsible for 7% of this emission [1].

Efforts to improve this model are primarily aimed at finding another sustainable, renewable and economically viable resource that will enable to obtain products capable of replacing those of the current chemical routes. One of the most promising alternatives is biomass.

Biomass is defined as organic matter originating in animals, plants or microorganisms. Considering its use as feedstock in the chemical sector, using plant biomass has some interesting advantages. It would allow the GHG emission problem to be controlled. Carbon dioxide released into the atmosphere by its consumption at the end of the cycle would be limited since, during their growth, plants fix it through photosynthetic reactions [2]. Moreover, among the different types of plant biomass available, forestry and agricultural waste become particularly attractive. Valorising unavoidable waste and integrating it into industrial processes is a key aspect for achieving a greener chemical industry. Also, the use of this non-edible biomass avoids problems arising from the economic competition with food crops.

This type of biomass is composed of 80% lignocellulose [3], an organic substance present on the wall of plant cells. This, in turn, is mainly composed of three components: cellulose, a polymer formed by large linear chains of glucose molecules; hemicellulose, present in shorter chains composed of different sugar types (pentose and hexose); and lignin, a three-dimensional phenyl-propene aromatic compound. These components are present to a greater or lesser extent depending on the type of plant, but generally present the following percentages: 35-50% cellulose, 15-35% hemicellulose and 10-35% lignin [4].

Cellulose and hemicellulose can be subjected to a hydrolysis process in an acidic medium to depolymerise the chains and obtain C_5 and C_6 sugars. These, in turn, can be reduced by a hydrogenation process and produce building blocks capable of being transformed into other products with a high added value. Sometimes, this second process is carried out in combination with the previous hydrolysis.

Lignin, on the other hand, is used as a fuel [5].

1.2. SYNTHESIS OF ISOSORBIDE FROM SORBITOL

1.2.1. Sorbitol

In 2004, the US Department of Energy published a report that collected the 12 building blocks obtained from biomass with great potential for the chemical industry [6].

Among them, there is sorbitol ($C_6H_{14}O_6$), also known as glucitol, a polyalcohol formed by 6 carbon atoms and containing 6 hydroxyl groups as shown in *Figure 1*. It is naturally present in some fruits and, industrially, is traditionally obtained by catalytic hydrogenation of glucose [7]. However, it can be obtained from a biotechnological pathway in which the bacterium *Zymomonas mobilis* reduces glucose and fructose [8].



Figure 1. Chemical structure of sorbitol

Physically, it is usually commercialised as a crystalline solid in the form of a white powder. It is odourless and has a sweetness of about 60% of sucrose. For this reason, one of its main

applications is as an additive and sweetener in the food industry. It is also used in the pharmaceutical and cosmetics industries [9].

Concerning the chemical industry, sorbitol is of special interest as it is the starting point of a broad-spectrum of chemical routes to obtain high-value products.

1.2.2. Isosorbide

Isosorbide (C₆H₁₀O₄) is a V-shaped chiral molecule obtained from sorbitol. Its structure consists of two fused tetrahydrofuran rings and two hydroxyl groups as shown in *Figure 2*.



Figure 2. Chemical structure of isosorbide

The configuration of the two functional groups differs and, consequently, so is their reactivity. The hydroxyl group of position 2 has an *endo* configuration and is inside the V structure, while the second one, at position 5, has an *exo* configuration and is outside.

Isosorbide has two isomers that can be obtained by similar reaction mechanisms: isomannide and isoiodide. The difference between them lies in the configuration of the hydroxyl groups. In the former, both OH confer an *endo* configuration and, in the case of the latter, and *exo*. For this reason, all three molecules have different physicochemical properties and reactivities[10].

Hydroxyl groups in endo configuration are more acidic than those in the opposite as can form a hydrogen bond with the oxygen of the facing tetrahydrofuran ring [11].

Among the isomers, isomannide is a low reactive molecule and isoiodide, although it has higher reactivity, is difficult to produce because its precursor cannot be obtained from biomass. Therefore, isosorbide is the most attractive one [11].

In addition, due to its rigid structure and properties, isosorbide is gaining interest in the polymeric industry for the production of bioplastics. It is presented as a viable possibility by substituting other petroleum derivatives such as bisphenol A, a toxic molecule used in food-industry packaging [3].

However, the main problem lies in the difficulty of producing isosorbide on an industrial scale. The reaction mechanism for obtaining it presents low yields and selectivity, below industry standards. For this reason, research is geared toward the design of a more efficient process.

1.2.3. Reaction mechanism

The process to obtain isosorbide consists of a two-stage reaction mechanism in which double dehydration of sorbitol occurs.

The main difficulty lies in the formation of side-products that contribute to the reduction in the yield of isosorbide. As shown in *Figure 3*, in the first dehydration, different anhydrosorbitols are obtained but, among them, only 1,4-sorbitan and 3,6-sorbitan can form isosorbide.

The difference between these two molecules lies in which of the two rings is the first to form. In the case of the former the carbons C1 and C4 are first cycled, then C6 and C3. As for 3,6sorbitan, the order is reversed.

Of all intermediates, 1,4-sorbitan is the one that is formed in the highest proportion[12]. For their formation, two possible pathways can be thought of depending on which hydroxyl group is attacking and which carbon is attacked. First, it could occur that the OH group on the C1 was responsible for attacking the C4 and forming the tetrahydrofuran ring. Also, it could be assumed that it was the hydroxyl group in C4 that attacked C1. Studies have shown that, between these two pathways, the second one is the most energy-favoured [13] [14].

Therefore, dehydration takes place by an SN2 reaction mechanism in which the hydroxyl group in carbon C1 is protonated. Then, this is attacked by the OH group in C4 and a water molecule is released.



2,5-sorbitan

Figure 3. Double dehydration of sorbitol to isosorbide mechanism

The remaining molecules formed during the first step such as 1,5-sorbitan and 2,5-sorbitan are considered side-products and contribute to decreasing the yield reaction since they do not form isosorbide. Likewise, humins are formed, insoluble compounds of polymeric nature which are generated through the reaction by condensation or degradation of the molecules [15]. Yamaguchi A. et al. reported the formation of humins. Operating at a temperature of 573 K, they observed a reduction of the isosorbide yield during the reaction time due to a polymerisation of isosorbide with other compounds such as 2,5-sorbitan [16].

This process requires an acid catalyst and the election of it is one of the key factors in achieving good performance. Dabbawala A. et al. published a comparative study of various acids of different nature to determine which are the most effective [17]. They concluded that Brönsted acids, or catalysts with Brönsted active sites, performed better than Lewis acids.

Traditionally, isosorbide has been obtained using strong mineral acids, mainly sulfuric acid. The first patent in which it was used was published in 1930 [18] and, to this day, remains of significant industrial importance. However, the use of these mineral acids as homogeneous catalysts has several drawbacks. Firstly, they involve an increase in the overall cost of the process due to the requirement to implement treatments, often distillation equipment, to separate them from the product solution. Likewise, their corrosive nature makes production more difficult due to damages to the equipment.

Research is focused on finding alternatives to these catalysts. Yamaguchi et al. carried out the reaction in an aqueous medium at high temperature and pressure without any catalyst, taking advantage that, under these conditions, water autoionization is produced [16]. A 57% of isosorbide yield was obtained after an hour of reaction at 590 K. However, undertaking such extreme conditions still has a high economic impact.

The use of heterogeneous solids catalysts seems to be a good alternative to reduce that cost. Different studies using metal phosphates[19] [20], zeolites [21] and acid resins [22] have been described in the literature. *Table 1* contains a description of some of these experiments.

| Def | 6 0-1-1 | Catalyst | Cohront | т | t | X _{SOH} a | : | Selectivity | r [%] |
|------|----------------|-----------|-------------------|------|-----|--------------------|-----|-------------|--------|
| Rei. | Catalyst | load | Solvent | [°C] | [h] | [%] | IB⁵ | 1,4ST⁰ | Others |
| [19] | SnPO | 0.5 g | Water (SOH 10wt%) | 300 | 2 | 72 | 65 | 34 | 1 |
| [19] | ZrPO | 0.5 g | Water (SOH 10wt%) | 300 | 2 | 56 | 52 | 26 | 22 |
| [19] | TiPO | 0.5 g | Water (SOH 10wt%) | 300 | 2 | 97 | 46 | 3 | 51 |
| [20] | BP | 1 wt% | Water (SOH 70wt%) | 250 | 2 | 100 | 70 | 6 | - |
| [21] | Beta(75) | SOH/AI=50 | Water (SOH 9wt%) | 200 | 2 | 87 | 33 | 43 | 24 |
| [21] | Beta(150) | SOH/AI=50 | Water (SOH 9wt%) | 200 | 2 | 73 | 22 | 56 | 22 |
| [21] | Modernite(110) | SOH/AI=50 | Water (SOH 9wt%) | 200 | 2 | 60 | 20 | 55 | 25 |
| [22] | P-CT275 | 5 wt% | Free | 140 | 1,5 | 96 | 40 | - | - |
| [22] | P-CT269 | 5 wt% | Free | 140 | 1,5 | 93 | 33 | - | - |
| [22] | Amberlyst 70 | 5 wt% | Free | 140 | 1,5 | 92 | 31 | - | - |
| [22] | Amberlyst 35 | 5 wt% | Free | 140 | 1,5 | 91 | 31 | - | - |

TABLE 1. Summary of experiments using heterogeneous catalysts

(a) sorbitol conversion

(b) Isosorbide

(c) 1,4-sorbitan

Among all these catalysts, ion exchange resins are the ones which allow to operate at lower temperatures, achiving high sorbitol conversions, although selectivities are still low. For this reason it is interesting to further study the reaction using these catalysts.

1.2.4. Solubility

Sorbitol melts at 95°C, consequently, at higher temperatures the reaction can be carried out without the use of any solvent. Nevertheless, its high viscosity and possible crystallisation at lower temperatures can hinder the process. For this reason, the selection and incorporation of a solvent in the reaction mixture may be of interest.

The election of the solvent is a key factor, thence solubility studies are necessary. The solvent must allow the complete dissolution of sorbitol under the established operating conditions and thus, avoid the formation of two phases inside the reactor. Also, following environmental criteria, it must be safe, non-toxic and non-contaminating.

For a mixture, solubility depends on temperature, pressure and solvent composition but, in binary systems and operating at atmospheric pressure, solubility depends exclusively on temperature.

1.3. ION EXCHANGE RESINS AS HETEROGENEOUS CATALYST

As mentioned above, the use of homogeneous catalysts has drawbacks that hinder chemical processes, in consequence, heterogeneous catalysis is most commonly used. At the industrial level, approximately 80% of catalytic processes use it [23].

In heterogeneous catalysis the reagent and the catalyst are in different phases, being the most common one in which the catalyst is a solid and the reactant is a fluid (gaseous or liquid).

Solid catalysis can be explained as a chemical process in which different elementary stages take place. The first one is the adsorption of the reactant onto the solid. As it is a surface phenomenon, the adsorption occurs at the active sites on the surface of the catalyst. For this reason, porous particles are often used to maximise the surface area per unit volume. Once the reactant is attached, a chemical reaction takes place and the reagent is transformed into a product. Finally, the desorption of this product from the particle occurs.

Thus, the catalytic solid does not interfere with the reaction permanently. At the end of the cycle, it is recoverable and can be reused, although not indefinitely. During the chemical reaction, the catalyst could undergo alterations in its structure and composition which will directly affect its activity. Therefore, it is important, when choosing a catalyst, to consider not only its selectivity and activity but also its lifespan i.e., the number of cycles it can withstand before suffering a reduction in its capacity.

Structurally, solid catalysts consist of a support, an active phase, and may also contain promoters. The active phase or active component is responsible for the objective of the catalyst i.e., to increase the reaction rate. The support contains these components and usually present a large surface area. Finally, promoters are substances that enhance the catalyst activity.

Among the different types of heterogeneous catalysts, ion exchange resins are materials capable of exchanging ions of their structure with those of another polar solution with which they come into contact. They consist of a matrix of hydrocarbon chains in the shape of a three-dimensional network with functional groups attached to it. They are usually commercialized as small spherical particles with a typical size distribution of 0,3 to 1,2 mm in diameter [24].

The most commonly used resins contain a styrene-divinylbenzene (PS-DVB) support. They are obtained through a polymerisation process of styrene and a consequent addition of divinylbenzene, a component that provides the crosslinking degree to the resin and is responsible for its stability and insolubility [25]. This last property is particularly interesting as it allows the easy recovery of the catalyst with low economic impact operations such as filtration or decantation.

Once the structure is obtained, the resin is functionalised and the corresponding functional groups are added. The different types of groups provide different properties. For the purposes of this work, the resins used are acidic and require a sulphonation process with sulphuric acid. The final structure is shown in *Figure 4*. According to their sulphonation degree, resins could be distinguished between over sulfonated, conventionally sulphonated and partially sulphonated.

Depending on the structure of the matrix, resins can be classified into two main groups: Geltype resins and macroporous resins.

Gel-type resins have a low percentage of DVB (1-5%) [26] and, consequently, a low crosslinking degree. They do not present a permanent porosity and require the presence of a

solvent to swell. They are also known as microporous resins because, once swollen, the space between hydrocarbon chains is small.



Figure 4. Matrix of a sulphonated PS-DVB resin

On the other hand, macroporous resins present a higher percentage of DVB (5-60%) [26] and, consequently, a higher crosslinking degree. They consist of spherical agglomerates alternating with macropores. The structural difference to the gel type lies in the polymerisation process. In macroporous resins, porogens are added and, after subsequent extraction and drying, they form permanent holes. If macroporous resins come into contact with solvents, they swell and the size of these pores can change.

Resins are usually characterised dry by means of analytical processes such as nitrogen adsorption-desorption to obtain their surface area. However, as mention above, in contact with certain solvents, the resin increase in size and, therefore, their structure differs. By means of ISEC (inverse size exclusion chromatography), resins can be characterised in their swollen form in aqueous solution.

The swelling degree of the resin depends on both on the thermodynamic affinity of the polymeric support for the solvent and on the type of structure of the matrix. The properties of gel-type resins depend on the crosslinking degree. The lower the amount of DVB, the greater the increase in volume they will undergo. In the case of macroporous resins, on the other hand, the behaviour is more complex as they contain the polymeric fraction and the holes between

pores. The polymeric phase follows the same behaviour as the gel-type. The space between pores, on the other hand, depend on the solvent. In *Figure 5* the swelling behaviour of a gel-type and a macroporous resins is compared.



Figure 5. Swelling behaviour of gel-type and macroreticular resins [27]

The application of ion exchange resins is limited by their stability, which can be altered by mechanical, chemical or thermal factors.

Mechanical stability is given by the breaking and compressive resistance of the particles. Macroporous resins, for example, are more fragile than gel-types resins and if they are used in highly agitated reactors, may break into small particles more easily. Chemical stability is defined as the resistance of the resin to the presence of strong oxidising agents that cause a degradation of its structure. As for thermal stability, each resin has a maximum operating temperature. Above this temperature, irreversible changes in the structure occur, leading to a loss of catalytic activity. These are caused by the breaking of the bonds between the functional groups and the support or between the atoms of the matrix itself.

Finally, although not considered as causes of catalyst instability, it is important to note that resin lifespan and activity can be affected by other phenomena such as a functional group poisoning or fouling.

2. OBJECTIVES

This work is part of a study for the synthesis of products derived from biomass. It focuses on the use of acidic ion exchange resins as catalysts for the double dehydration reaction of sorbitol in aqueous media. The main objectives are described below:

- 1. To determine the solubility of sorbitol in different organic solvents.
- To perform a screening of different ion exchange resins and select the most suitable one according to conversion, selectivity and yield criteria.
- 3. To study the effect of temperature on the best resin.

3. EXPERIMENTAL SECTION

3.1. SORBITOL SOLUBILITY

3.1.1. Experimental materials

To perform the experimental process, sorbitol (CAS:50-70-4, 98% purity) have been used as solute and methanol (CAS:67-56-1, 99% purity), ethanol (CAS: 64-17-5, 99% purity), n-butanol (CAS: 71-36-3, 99% purity) and acetone (CAS: 67-64-1, 99% purity) have been used as solvents. *Table 2* shows some physicochemical properties of the organic solvents.

| Salvant | MW | MW T _m | | ρ | μ | δ | E-N c |
|-----------|---------|-------------------|-------|-----------------------------------|-------------------|------------------------------------|----------------|
| Solvent | [g/mol] | [K] | [K] | [g/cm ³] ^a | [cP] ^a | [MPa ^{1/2}] ^b | L L., C |
| Methanol | 32.04 | 175.6 | 337.8 | 0.793 | 0.538 | 36.2 | 0.762 |
| Ethanol | 46.07 | 159.0 | 351.4 | 0.800 | 1.077 | 26.2 | 0.654 |
| n-Butanol | 74.12 | 183.3 | 390.8 | 0.806 | 2.554 | 28.7 | 0.586 |
| Acetone | 58.08 | 178.3 | 329.4 | 0.788 | 0.306 | 19.7 | 0.355 |

TABLE 2. Summary of some properties of the studied solvents

^a Values obtained at 1 atm and 298 K from Aspen Plus v 12.1

^b Hildebrand solubility parameters [28]

° Normalised solvatochromic solvent polarity parameters [29]

3.1.2. Experimental SET UP

In *Figure 6* a scheme with the experimental system is represented. It consists of a jacketed flask of (50 mL) connected to a thermostatic water bath (LAUDA Alpha A) with a maximum operating temperature of 70°C.

During the experiments, the flask is stirred using a magnetic stirrer with a hotplate (Stuart SB 162). A digital thermometer with an accuracy of $\pm 0,1$ °C was used to determine the mixture temperature during sampling.



Figure 6. Scheme of the experimental set up

3.1.3. Experimental procedure

3.1.3.1. Solubility measurement

Solubility determination of sorbitol in different organic solvents has been carried out using a gravimetric analysis method. For this purpose, the jacketed flask is filled with the desired solvent and an excess amount of sorbitol to ensure the solution saturation. The flask is connected to a thermostatic water bath to regulate its temperature and it is stirred with a magnetic stirrer for about 24 hours to reach solid-liquid equilibrium. To avoid large heat loss, the flask is also covered with a heating mantle.

Before sampling, the stirring is stopped for about two hours. The temperature of the solution is measured using a temperature sensor. Then, three 5mL aliquots of the supernatant are transferred, using filters, to three evaporation vials previously weighted. These vials are capped and reweighted. Finally, they are uncapped and left open at room temperature to allow the solvent to evaporate. In cases in which the solvent under study is not highly volatile, they are left for a few days in an oven at 60°C.

The bath temperature is then raised by 5 °C, the flask is refilled with the solvent and the stirring is connected again for the next samples.

Once the solvent is evaporated from the vials, they are weighed again and the corresponding calculations for the solubility determination are made.

3.1.3.2. Clean up

Once all the samples of a solvent have been taken, the stirring is switched off and the thermostatic bath is disconnected to cool down the flask to room temperature. The contents are filtered through a vacuum pump and a sample of the suspended solid is collected for further analysis.

The flask is cleaned with distilled water and dried using synthetic air. Finally, once dried, the device is prepared for the study of another solvent. It is important, for the correct determination of solubility, that the flask is completely dry.

3.1.4. Experimental conditions

A total of four experiments were carried out at atmospheric pressure with different durations depending on the temperature range studied (*Table 3*). The initial temperature was 25°C, which was increased by increments of 5°C up to the maximum temperature. This temperature differs between solvents and has been set considering the boiling temperature of the solvent and the maximum temperature reached by the thermostatic bath.

| Solvent | T min [°C] | T max [°C] |
|-----------|------------|------------|
| Methanol | 25 | 65 |
| Ethanol | 25 | 65 |
| n-butanol | 25 | 60 |
| Acetone | 25 | 50 |

| | TABLE 3. tem | perature | range | studied | for | each | solven | t |
|--|--------------|----------|-------|---------|-----|------|--------|---|
|--|--------------|----------|-------|---------|-----|------|--------|---|

Samples were taken every 24 h, considering that, after this time, the liquid-solid system has reached equilibrium.

A first experiment to determine the solubility of sorbitol in water was attempted, but it was not possible to carry out. The system presents a high solubility and it was not possible to saturate the solution. As the concentration of sorbitol increased, the viscosity of the system also increased, being impossible to stir or to carry out sampling. Hence, another method of analysis would be required to determine the solubility.

This would justify the choice of water as the best solvent to carry out the reaction. Also, considering that after the hydrolysis stage, the resulting mixture is aqueous, it would be the most logical choice. But, in reality, it has a fundamental drawback. Water is one of the products of the sorbitol dehydration, so its use significantly reduces the reaction rate. As will be seen in later sections, long reaction times are required to achive a high reactant conversion. For this reason, it is important to find a solvent which can be used as a substitute for water.

3.1.5. Calculations

The solubility of a substance can be expressed in a variety of units. In this work, sorbitol solubility has been calculated in two different ways. *Equation 1* shows a ratio between the mass of solute (m_1) and solvent (m_2) .

$$c^* = \frac{m_1}{m_2} = \frac{m_{vial+cap+solid} - m_{vial+cap}}{m_{vial+cap+solution} - m_{vial+cap+solid}} \left[\frac{g_{solute}}{g_{solvent}}\right]$$
(1)

From this mass ratio, solubility has been expressed in terms of mole fraction by *Equation 2*, where M₁ and M₂ correspond to the molar mass of the solute and solvent respectively.

$$x_{eq} = \frac{c^* \cdot M_2}{(c^* \cdot M_2 + M_1)}$$
(2)

Finally, the Van't Hoff enthalpy change has been obtained from the graphical representation of the relationship expressed in *Equation 3* [30].

$$\left(\frac{\partial \ln x_{eq}}{\partial \ln(1/T)}\right) = -\frac{\Delta_{sin}^{\nu H} H^o}{R}$$
(3)

3.2. SORBITOL DEHYDRATION REACTION

3.2.1. Experimental materials

Sorbitol (Alfa Aesar, CAS: 50-70-4), with a purity of 98%, and water (Mili-Q, Millipore) were used to carry out the dehydration of sorbitol to isosorbide reaction.

In addition, Isosorbide (Alfa Aesar, CAS:652-67-5) and 1,4-Sorbitan (Sigma-Aldrich, CAS: 27299-12-3) with a purity of 98% and >99% respectively, were also used for the calibration of the chromatograph. *Table 4* shows some properties of these substances:

| Properties | Sorbitol | 1,4-Sorbitan | Isosorbide |
|--------------------------------|----------------|----------------|----------------|
| Formula | $C_6H_{14}O_6$ | $C_6H_{12}O_5$ | $C_6H_{10}O_4$ |
| MW [g/mol] | 182.17 | 164.16 | 146.14 |
| Density [g/cm ³] a | 1.29 | 1.57 | 1.30 |
| T _m [°C] | 98-100 | 112-113 | 63 |
| T₅ [°C] | 295 | 443 | 175 |

| TABLE 4. Properties of | reagents | used |
|------------------------|----------|------|
|------------------------|----------|------|

a for T=25°C

The stirred batch reactor was pressurised with nitrogen gas supplied by Abelló Linde and with a purity of 99,9995%.

Concerning the catalysts, five sulfonated ion exchange resins were used: Amberlyst 45 (A-45), Amberlyst 70 (A-70), Purolite CT-482 (CT-482), Amberlyst DL-H/03 (A DL-H/03) and Amberlyst DL-I/03 (A DL-I/03). The first three catalysts are commercial resins while the other ones are prototypes. All of them present a macroporous structure with different percentages of DVB and are thermostable in the operating temperature range since the catalyst screening is carried out at a temperature of 170°C. *Table 5* contains some of their main properties.

| | | Δ 45 | Δ 70 | | | CT-482 |
|----------------------------|---|-----------|-------|-------|--------|--------|
| | | ~ ** | A 10 | | | 01-402 |
| Туре | | macro | macro | macro | macro | macro |
| Acid capacity [meq H*/g] | | 3.67 | 2.62 | 3.1 | 5.4 | 4.25 |
| DVB [%] | | medium | low | low | medium | low |
| T _{max,operation} | [°C] | 170 | 190 | 170 | 170 | 190 |
| Water reter | ntion [%] | 51-55 | 53-55 | 50-52 | 51-55 | 48-58 |
| | dp [mm] | 0.58-0.75 | 0,57 | 0.711 | 0.644 | 0.81 |
| Drav | d pore ^a [nm] | 19.0 | | | 27.2 | 26.7 |
| Swollen In water | S g ª [m²/g] | 49.0 | 0.018 | 0.087 | 19.77 | 8.7 |
| | V _{pore} ^a [cm ³ /g] | 0.23 | | | 0.17 | 0.06 |
| | θ ª [%] | 25.4 | | | 21.6 | 8.2 |
| | d _{pore} b [nm] | 9.5 | 13.3 | 8.2 | 12.0 | 19.6 |
| | S g ^p [m²/g] | 220.2 | 66 | 283.1 | 153.3 | 214.0 |
| | V _{pore} b[cm ³ /g] | 0.52 | 0.22 | 0.577 | 0.459 | 1.05 |
| | V _{sp} ^b [cm ³ /g] | 0.97 | 1.149 | 0.87 | 0.744 | 1.081 |
| | θ Þ [%] | 54.4 | 51.9 | 52.8 | 48.7 | 65.7 |

TABLE 5. Properties of ion exchange resin used in this study

^a measured by BET technique

^b measured by ISEC technique

3.2.2. Experimental SET UP

Figure 7 a scheme of the device used for the dehydration reaction of sorbitol is represented. It consists of a stainless steel stirred (316 SS) batch reactor with a capacity of 100 mL (Autoclave Engineers) operating at a pressure of 30 bar. This is measured by a manometer situated between V8 valve (relief valve) and the reactor. It is also equipped with a rupture disc that allows an instantaneous pressure release when the operating pressure exceeds the maximum one (between 50.1 and 54.8 bar).



Figure 7. Scheme of the experimental Set up

The agitation system contains a turbine with four mixed-up paddles connected to a rotor (Magnedrive II Series 0.7501). The stirring speed is controlled by a frequency converter model T-VERTER N2 SERIES. A baffle is placed next to the stirrer to promote the homogenisation of the mixture. Likewise, the reactor contains a thermocouple to measure the temperature inside the reactor and which is part of a PID temperature control system.

To add the catalyst, the reactor has a cylindrical injector (316 SS), through which a nitrogen stream can circulate by means of valves V1-V4.

The heating system consists of an electric furnace connected to the temperature control system via another thermocouple which measures the temperature of the outer wall of the reactor. Once the setpoint is reached, and the temperature is established, its value remains constant with an error of ± 0.1 °C.

Finally, samples are extracted through a filter that avoids the loss of catalyst particles. This extraction is carried out manually through valves V3, V6 and V7. Although the system is connected to a gas chromatograph, samples are analysed by a high-performance liquid chromatograph (HPLC).

A Hi-Plex Ca column with a size of 250 x 4,6 mm operating at a temperature of 80°C and using Millipore water as mobile phase with a flow rate of 0.3 ml/min has been used for the analysis.

3.2.3. Experimental procedure

3.2.3.1. Reactor loading and launching

First, the reaction mixture is prepared. The reactant (sorbitol) and the solvent (water) are weighted separately and added to the reactor. Then, it is closed by three safety screws.

To ensure that the reactor is completely closed and that no leakage will occur, a tightness test is done. Valve V1 is opened and valve V3 is set to position 1 to allow the entry of nitrogen into the reactor. Once it is pressurised, V3 is closed. The pressure indicated by the manometer must remain constant. Then, valve V8 is opened to reduce the pressure to 10 bar.

The heating furnace is fastened around the reactor and it is switched on. The stirring is also connected.

The catalyst is taken out of the oven, where it has been for at least 24 hours at 110°C to remove moisture, weighted and introduced into the injector by unscrewing over valve V4 and using a paper funnel (It is important to check valve V5 is closed to prevent resin from being added to the reactor in advance). Due to its high hygroscopic behaviour, this step must be carried out quickly to avoid the capture of moisture from the environment.

Once the reactor temperature reaches the setpoint, the catalyst is injected. For this purpose, valves V2 and V4 must be open to pressurise the injector. The manometer must indicate a pressure around 10 bar. If it is higher, it is reduced by opening valve V8. Inside the reactor, the pressure must not be much higher since a pressure difference of at least 20 bar is required for the catalyst to be injected correctly. Likewise, it must not be lower, because it is necessary to keep the solvent (water) liquefied to avoid its loss when valve V8 is opened.

Valve V5 is opened and then closed quickly, as soon as the pressure inside the reactor reaches the nitrogen line pressure. Using valve V8, the pressure is reduced to 10 bar and the process is repeated at least 5 times to ensure the full injection of catalyst.

3.2.3.2. Sampling

For sampling, valve V7 is placed in position 1. Valve V6 is opened slowly and the sample is collected in a 1,5 ml vial. Once it is obtained, V6 is closed and V7 is placed in position 2.

To recover the sample retained in the pipe with valve V3 in position 2, the relief valve V8 is opened to reduce the pressure inside the reactor to 10 bar and, at the same moment that this valve is closed, V6 is opened to let nitrogen pass through and push the solution remains inside. Once the manometer indicates the line pressure value, the valve is closed.

This procedure is followed for all samples. The first one is obtained when the reactor has reached the setpoint temperature, just before the catalyst is added. The time of catalyst injection is considered as the initial time of reaction (t=0). From then on, samples are taken every half hour for the first 2.5 hours of reaction and then every hour thereafter, until an experimental time of 8.5 hours is reached.

In a high-performance liquid chromatograph (HPLC), a sample of 50 μ L is analysed. For this purpose, a flow rate of 0.3 ml/min of Millipore water is used as eluent and the column temperature is set to 80°C. Due to the high concentration of reactant, the analysed sample is diluted. Therefore, each extraction is diluted 1:2 with Millipore water.

3.2.3.3. Clean up

After the last sample is obtained, the stirring and heating are stopped, valve V1 is closed and the reactor is cooled down at room temperature before cleaning.

After cooling, the three safety screws are unscrewed and the reaction mixture is filtered. A vial with a sample of the final reactor contents and the filtered catalyst are separately collected.

It is important to check that the catalyst has been fully injected to ensure a correct discussion of the experimental results. For this purpose, the reactor, previously cleaned with deionised water and dried, is placed at the end of the injector. Valves V1, V2 and V4 are opened and V5 is quickly opened and closed several times.

For cleaning the internal accessories, several steps are followed. First, valves V3 and V7 are set to position 2 to remove any remaining solution from the piping. Then, valve V6 is opened to allow nitrogen to push it through the filter.

The reactor is then filled with deionised water and closed. The heating furnace is placed, fastened correctly around it and switched on to heat the water to about 70°C. Valve V3 is placed

in position 1 to pressurise the reactor and, with valve V7 in position 1 and opening V6, the water is extracted and collected in a breaker.

Finally, the reactor is cooled down. The heating furnace is removed, the reactor is unscrewed and cleaned again with an ethanol-acetone mixture and dried with synthetic air.

3.2.4. Experimental conditions

The experiments had a reaction time of 8.5 h and were carried out at a pressure of 30 bar to ensure that the mixture remained in the liquid phase.

Initial composition was one of the parameters that were kept constant between the experiments. 4,5 g of sorbitol were added to a volume of 90 mL of water (4,7 wt%), Also, to compare the behaviour of different ion exchange resins, the mass of dry catalyst was fixed at 1g.

These resins were not subjected to any sieving process. Thus, they present the size distribution of the commercial sample. Also, before being used in the experiments, they were left for a minimum of 24 hours in an oven at 110°C and atmospheric pressure to remove the water molecules they contain.

Concerning the operation temperature, for one of the catalysts, five experiments have been carried out at a different temperature in the range of 150-190°C and, for each experiment, it has remained constant.

Finally, as for the stirring, the influence of external mass transfer has not been studied, so it has been set at 750 rpm, based on previous experience with similar systems, and the resistance has been assumed to be negligible.

3.2.5. Calculations

To analyse the temperature effects on reaction and to be able to compare the best performing catalysts, the reactant conversion and the intermediate and products selectivity and yield have been calculated.

The conversion for a batch system indicates the fraction of reactant consumed in a specific time regarding its initial amount. In *equation 4*, it is defined for the system under study.

$$X_{SOH}(t) = \frac{n_{SOH}^0 - n_{SOH}(t)}{n_{SOH}^0}$$
(4)

On the other hand, selectivity, also for a discontinuous system, is a parameter that indicates the amount formed of a given substance regarding the total moles of reactant consumed for a certain time. For the system studied, it is defined in *equation* 5, where j corresponds to a specific species (1,4-sorbitan, isosorbide or 2,5-sorbitan).

$$S_{j}(t) = \frac{n_{j}(t)}{n_{SOH}^{0} - n_{SOH}(t)}$$
(5)

Finally, using the selectivity and conversion values, a specific substance yield can be obtained from *equation 6*.

$$Y_j(t) = S_j(t) \cdot X_{SOH}(t)$$
(6)
4. RESULTS AND DISCUSSION

4.1. SORBITOL SOLUBILITY

The solubility curves of sorbitol obtained for four organic solvents are represented in *Figures* 8 and 9. In the temperature range studied, it can be observed that solubility increases with temperature and shows an exponential dependence for those solvents with higher solubility. This trend is notably visible for methanol. Furthermore, as solubility decreases, this dependence is in turn weaker, presenting practically linear behaviour in the case of acetone.



Figure 8. Mass ratio solubility of sorbitol in different solvents

To justify this variation, the structures of the solvents must be compared. All of them present a polar nature, but a distinction can be made between protic (alcohols) and aprotic (acetone) solvents. The difference between them resides in the presence or absence of hydrogen atoms bonded directly to a highly electronegative atom. Alcohols contain a hydroxyl group (OH) with this characteristic, which is not present in the case of acetone.



Figure 9. Molar fraction solubility of sorbitol in different solvents

To be considered a good solvent, a substance must be able to replace bonds between solute molecules with solute-solvent ones. For attractions of a similar nature, the energy required for such substitution will be lower and, consequently, the solubility of the system will be higher.

Sorbitol molecules are linked together by the formation of hydrogen bonds between their hydroxyl groups. Protic solvents are the only ones capable of forming such bonds, which is why acetone, as an aprotic solvent, has such low solubility. In this case, dipole-dipole interactions are generated which are weaker than hydrogen bonds.

In *Table 6*, the mole fraction solubilities for the four solvents are given. They have also been compared with the values found in the literature. It can be seen that, for all cases, the values obtained are similar.

| Solvent | x _{eq} (this work) ^a | x _{eq} (literature) ^b [31] |
|--------------------------|---|---|
| Methanol | 0,00616 | 0,00739 |
| Ethanol | 0,00198 | 0,00181 |
| n-Butanol | 0,00086 | 0,00106 |
| Acetone | 0,00032 | 0,00044 |
| ^a for T= 301K | | |

TABLE 6. Sorbitol solubility reported in literature

^a for T= 301I

[▶] for T=303K

However, it should be noted that, among alcohols, the range of values is quite wide, with solubility decreasing as the number of carbon atoms in the molecule increases (MeOH > EtOH > BuOH). Therefore, the length of the chain is another factor to consider.

Hydrocarbon chains are practically non-polar structures. They contain two different types of bonds: between two carbon atoms and between a carbon and a hydrogen atom. The former has no polarity and, in the case of the latter, it is weak. Therefore, in molecules with a high number of carbons, the effect of the non-polarity of the hydrocarbon chain concerning the overall molecule will be much greater than the influence of the polar functional group. Consequently, the solute-solvent bonds will be weaker and the solubility will be lower.

Finally, *Figure 10* shows the ln (X_{eq}) regarding the inverse of temperature for each solvent. It can be seen that, for all of them, it shows a linear behaviour.



Figure 10. Representation of Van't Hoff plot of sorbitol solubility

The enthalpy change (Δ_{sin}^{vH} H^o) can be obtained from the slope of the regression equation (solid lines) according to the Van't Hoff equation. Their values, standard errors and regression coefficients are shown in *Table* 7.

| TABLE 7. Van't Hoff enthalpy change for each studied solvent | | | | | | | | | | | | |
|--|----------|---|-------------|------|-----------|-----|------|---------|-----|------|---|-----|
| | Methanol | | Ethanol | | N-Butanol | | | Acetone | | | | |
| Δ sln ^{vH} H⁰ [kJ/mol] | 42.2 | ± | 1.8 | 37.5 | ± | 1.5 | 31.5 | ± | 1.6 | 17.6 | ± | 2.3 |
| R ² | 0.984 | | 0.992 0.981 | | | 0. | 936 | | | | | |

This magnitude indicates the dependence of solubility on temperature. All values obtained are positive because, as mentioned above, for the four solvents solubility increases with temperature. Furthermore, a relationship between the capacity of a solvent to dissolve sorbitol and the enthalpy value of the solution can be observed. The higher the solubility in a solvent, the higher the Van't Hoff enthalpy.

In *Table 8* this values are compared with those reported in the literature. As can be observed, the results are quite similar, being slightly higher for alcohols and slightly lower for acetone. In both cases these differences are attributable to experimental error.

| Solvent | Δ _{sin} ^{vH} H ^o [kJ/mol] | | | | |
|-----------|---|-------------------|--|--|--|
| Solvent | (this work) | (literature) [31] | | | |
| Methanol | 42.2 | 38.3 | | | |
| Ethanol | 37.5 | 34.0 | | | |
| n-Butanol | 31.5 | 27.7 | | | |
| Acetone | 17.6 | 21.0 | | | |

TABLE 8. Van't Hoff enthaply change reported in literature

4.2. SORBITOL DEHYDRATION REACTION

4.2.1. MONITORING OF AN EXPERIMENT

After obtaining and analysing the samples, a graphical representation like *Figure 11* is obtained, showing the evolution of the moles regarding the reaction time.

As mentioned in the introduction section, the reaction mechanism for obtaining isosorbide from sorbitol consists of two dehydration reactions in series. In the first one, the intermediate 1,4-sorbitan is formed and, in the latter, it is consumed and isosorbide is formed. Furthermore, in the first stage, several parallel reactions take place in which other sorbitans are formed.



Figure 11. Moles of SOH, IB, 1,4-ST and 1,5-ST vs. reaction time (catalyst: A-70, T=170°C)

From the analysis sample, through calibration (Appendix 1), SOH, IB and 1,4-ST have been identified and quantified. However, in all the experiments, another signal of a substance has been reported.

The trend of this signal is increasing during the reaction time until it reaches a value where it stabilises. Due to this behaviour, the possibility that it was 3,6-sorbitan has been discarded since, in the same way as 1,4-sorbitan, it would lead to the formation of isosorbide and its consumption should have been observed.

Different authors have reported the presence of 2,5-sorbitan in greater quantities than the rest of secondary sorbitans [12][13][31]. In some cases, it is the only one detected. Therefore, it has been considered that the signal corresponds to this substance.

This compound has been impossible to obtain so, knowing that it is an isomer of 1,4sorbitan, the same calibration has been used for quantification.

Finally, since the eluent used in the HPLC is water, neither the solvent nor the water produced during the reaction was detected in the analysis. This was the main reason why, when

carrying out the calibration, it was decided to relate known concentrations of the species to the area obtained instead of using the percentage of area.

4.2.1.1. Experimental error

Before analysing the different results and drawing conclusions, it is important to know the error associated with the experiments. For this purpose, a mass balance has been verified for each experiment by carrying out a carbon mass balance and quantifying a possible deviation.

In all the experiments it was found a deviation from mass balance which corresponds to an error of approximately 20%. In all of them, this variation is positive, i.e. the analyses of the samples always present a higher concentration of species than expected.

It has been concluded that, of the whole experimental process, the greatest source of error is found in sampling. For the analysis, samples must be taken manually, as the HPLC is not directly connected to the reactor. It is worth remembering that the reaction mixture contains a large amount of water and the reactor is operating at a high temperature, above 100°C. So it is necessary to pressurise the reactor to keep the solvent in the liquid phase. This pressure decreases drastically when the sample is extracted. Therefore, a fraction of the solvent is released as vapor, which results in a more concentrated sample.

Likewise, in order to check the reproducibility of the experiments, three replicates were carried out using A-70 resin as catalyst and with an operating temperature of 170 °C. *Table* 9 presents the reactant conversion and the selectivity and yield of the intermediate and products at the final reaction time (t=510 min) together with their associated deviation.

| TABLE 9. | Conversion, | selectivities | and yields o | of reagents | for repli | cates a | nd its a | associated | deviation |
|----------|-------------|---------------|--------------|-------------|-----------|---------|----------|------------|-----------|
| | | (α=0 |),1). T=170° | C, t=510mi | in , C=A- | -70 | | | |

| Хзон [%] | S⊪ [%] | S 1,4-ST [%] | S2,5-ST [%] | Y _{IB} [%] | Y1,4-ST [%] | Y 2,5-ST [%] |
|----------|--------|----------------------------|-------------|---------------------|-------------|--------------|
| 97.6 | 52.2 | 39.9 | 7.9 | 48.0 | 35.4 | 16.6 |
| ± 0.6 | ± 14.1 | ± 14.2 | ± 0.2 | ± 25.2 | ± 8.7 | ± 25.6 |

The error between the replicates is quite significant, but it is similar to that quantified in the mass balances, so it can be assumed that it corresponds to the loss of solvent in sampling.

4.2.2. SCREENING OVER ION-EXCHANGE RESINS

The reaction was carried out using five different resins, fixing the rest of the experimental conditions. In order to observe the complete consumption of the reactant, the operating temperature has been set at 170°C. For this reason, catalysts have been chosen based on their thermostability and not prioritising the structural differences. Therefore, all resins are macroporous.

Figure 12 shows the evolution of sorbitol conversion during the reaction time for each resin. It can be seen how, with four of them, almost complete conversion is achieved, although this is reached at different times.

On the other hand, the experiment using resin A-45 shows a lower final conversion, not reaching 90% after 8.5 hours of reaction.



Figure 12. Sorbitol convertion vs. reaction time T=170°C

However, in order to justify the selection of one catalyst or another, the analysis will focus on the comparison of selectivities and yields between the different compounds. The main product is isosorbide, so the resin that maximises its production will be the one with the best catalytic behaviour and will be chosen to subsequently study the temperature effect. Table 9 contains the results obtained for each catalyst. CT-482 resin is the one that shows the best results both in the final reactant conversion and in the selectivity and yield of isosorbide.

| | X [%] | | S [%] | | | Y [%] | | D _{pore} | ∑V _{sp} | Acid cap. | DVB |
|----------|-------|------|--------|--------|------|--------|--------|-------------------|----------------------|-----------|--------|
| | SOH | IB | 1,4-ST | 2,5-ST | IB | 1,4-ST | 2,5-ST | [nm] | [cm ³ /g] | [H+/eq] | [%] |
| A-45 | 87.6 | 24.7 | 67.7 | 7.6 | 21,6 | 59.3 | 6.7 | 9.5 | 0.52 | 3.7 | Medium |
| A-70 | 97.6 | 53.0 | 39.1 | 7.9 | 51,8 | 38.2 | 7.7 | 13.3 | 0.22 | 2.6 | Low |
| ADL-H/03 | 96.1 | 39.3 | 53.5 | 7.2 | 37.8 | 51.4 | 6.9 | 8.2 | 0.58 | 3.1 | Low |
| ADL-1/03 | 96.9 | 40.5 | 52.4 | 7.2 | 39.2 | 50.7 | 7.0 | 12 | 0.46 | 5.4 | Medium |
| CT-482 | 97.0 | 56.1 | 36.1 | 7.8 | 54.4 | 35.0 | 7.6 | 19.6 | 1.05 | 4.3 | Low |

TABLE 10. Summary of results and parameters for each catalyst

As for the rest of the substances, it should be noted that 2,5-ST has very similar selectivities and yields for all catalyst. Therefore, none of these resins seems to notably improve the selectivity in favour of the formation of 1,4-ST in the first stage of the reaction mechanism.

To understand these differences, it is important to relate the results to the properties of each catalyst.

Figure 13 correlates selectivities with the resin acid capacity, i.e. the number of sulphonic groups available to carry out the exchange. It might be expected that this would be one of the most decisive parameters, but the results reveal the opposite.



Figure 13. Selectivity vs. Acid capacity T=170°C t=510 min

Resins A DL-H/03 and A DL-I/03 present similar isosorbide selectivities (39.3% and 40.5% respectively) and yields (37.8% and 39.2%) but their acid capacities are quite different. From all resins, the latter has the maximum value of 5.4 H⁺/eq. while the former is 3.1 H⁺/eq. Likewise, resin A-70, which has the second higher isosorbide yield value, is also the one with the lowest acid capacity.

Therefore, it seems to indicate that other factors related to the accessibility of reactants to these sulphonic groups have a greater influence that the amount a resin contains. For example, in general, a correlation between pore diameter of the swollen state and selectivity does appear to be found (*Figure 14*). For larger diameters, the greater the selectivity of isosorbide, while for smaller diametres, the greater the selectivity of the intermediate.

This might be due to the reactant molecules volume. 1,4-ST contain a tetrahydrofuran ring which gives the molecule a larger volume compared to sorbitol. The small pore diameters hinder the access of larger molecules to the active sites and hence, in the present study, the yield of the second reaction decreases.



Figure 14. Selectivity vs pore diameter T=170°C t=510 min

However, there are other factors to consider. Resin A-45, for example, does not respond to the expected trend, since its pore diameter (9.5 nm) is larger than that of resin A DL-H/03 (8.5 nm). Moreover, their acid capacities are similar, the former being slightly higher (3.7 H⁺/eq and 3.1 H⁺/eq respectively). But isosorbide yield for A-45 is much lower, 21.6% compared to 37.8% for A DL-H/03.

The main difference between this resins lies in the percentage of DVB contained in their structure. Although no specific values have been found, the amount of DVB of A DL-H/03 is low and that of A-45, medium. DVB provides the crosslinking degree of the polymeric matrix, and gives it rigidity. Therefore, a possible explanation for these results is that a high crosslinking degree hinder reagent molecules to access the inner active sites and, consecuently, they can only react with the outermost ones.

Likewise, the two resins with the best catalytic activity are CT-482 and A-70, whose matrices also contain a low %DVB.

Finally, the possible correlation between the selectivities and the volume of swollen polymer (Vsp) has been analysed (*Figure 15*). In general, resins with higher isosorbide selectivities and yields are those which also present a higher Vsp. Again, this results are related to the accessibility of the active sites. This parameter indicates the swelling capacity of a resin in polar

medium, so that the higher the Vsp, the more the resin will swell and, consequently, the more accessible the active sites will be to the reactant.



Figure 15. Selectivity vs. Vsp T=170°C, t=510 min

It should be noted that the comparison between catalysts is complex, since the catalytic activity is not given by the value of a single property but by a combination of all of them. As it has been observed, the morphological properties of the resin seem to be determinant in obtaining a good selectivity and yield of isosorbide. Therefore, possible variations in the behaviour of the resins could be explained due to differences in the morphology of their gel phase, for which data could not be found for the discussion.

Even so, it can be concluded that, of all the resins estudied, CT-482 is the one with the best results for the production of isosorbide due to its good accessibility of the active sites (low %DVB, large pores and high Vsp) and its good acid capacity.

4.2.3. TEMPERATURE EFFECT

In order to evaluate the effects of the operation temperature on the reaction, five experiments were carried out in a temperature range of 150°C-190°C using CT-482 as catalyst, since it was the one that presented the best catalytic behaviour in the screening.

Firstly, the differences in the evolution of the sorbitol conversion over the reaction time have been analysed (*Figure 16*). It can be observed that the conversion achived at the three highest temperatures is almost complete at 8.5 reaction hours, with values around 98%.



Figure 16. Sorbitol convertion vs. reaction time Catalyst=CT-482

However, it should be noted that progession differs. The higher the temperature, the less time is required to reach this conversion. This is an expected behaviour, since kinetic constants of reactions, following the Arrhenius model, increase their value with temperature and, hence, their reaction rate.

For this reason, the conversion obtained at the end of the experiments at lower temperatures is consequently smaller. Reactant consumtion is slower and, thus, a longer experimental time would be required in order to obtain similar conversion values.

Figure 17 shows the progression, in terms of moles, over time of the species present for each temperature.



Figure 17. mole evolution vs. reaction for different temperatures Catalyst= CT-482

The evolution of isosorbide and 2,5-sorbitan is similar. Both show an increasing trend until they reach a certain value at which they stabilise. 2,5-ST is a product of the first reaction stage and, hence, the value stabilises when sorbitol moles are almost consumed. In constrast, in the case of isosorbide, this behavior is not observed for all temperatures. For 150°C, 160°C and 170°C isosorbide moles increase practically linearly during the whole reaction time, but at the two higher temperatures, the final stabilisation can be intuited.

1,4-sorbitan, the intermediate compound, also shows an expected profile. Its formation until it reaches a maximum value and its subsequent consumption. This peak appears in shorter times with increasing temperature. Again, due to the increase in reaction rate produced by working at higher temperatures.

As occurred with isosorbide, in the experiment carried out at 190°C, it is observed how it stabilises for the last reaction times. It should be noted that sorbitol dehydration to isosorbide is a reaction mechanism consisting of two reversible reactions in series, so that, for an infinite reaction time, the species would reach kinetic equilibrium.

Finally, *Figure 18* compares selectivity at the final time reaction (t=510 min) for the intermediate and both products.



Figure 18. Selectivity of IB, 1,4-ST and 2,5-ST vs tempeture t=510 min Catalyst= CT-482

It can be observed that increasing the operating temperature favours the formation of the desired product, isosorbide. Consequently, since these are two reactions in series, as the yield of isosorbide increases, the selectivity and yield of the intermediate decrease. Therefore, lower temperatures promote the formation of 1,4-ST.

It is worth mentioning that, in the experiments carried out at 180°C and 190°C, both selectivites stabilise. Therefore, from a temperature of 180°C and above, an increase in temperature does not leat to an improvement in isosorbide selectivity and, consequently, in its yield.

Likewise, 2,5-ST shows a constant selectivity for any temperature in the range studied. Therefore, temperature does not seem to be a factor that could improve the 1,4-ST selectivity in the first stage of reaction.

5. CONCLUSIONS

Regarding the study of sorbitol solubility, it can be concluded that, in protic solvents, the solubility value is higher than in aprotic solvents due to their capacity to form hydrogen bonds with the solute molecules. Likewise, comparing the results between the different alcohols, it can be concluded that solubility decreases as the number of carbons in the hydrocarbon chain increases due to a decrease in polarity. Therefore, among all the solvents studied, methanol is the one with the best solubility values.

Regarding the reaction, this study confirms that the double dehydration reaction of sorbitol to isosorbide can be carried out in aqueous media using acidic ion exchange resins. Among the characteristics of these catalysts, the main ones responsible for the catalytic behaviour are their morphological properties. Those resins with a lower percentage of DVB, a larger pore diameter and a higher volume of swelling polymer offer better results, with CT-482 being the best. As for acid capacity, it has not turned out to be a determining property in the final catalytic behaviour of the resin.

Finally, high reaction temperatures increase the reaction rate and improve both selectivity and yield of isosorbide. As for the formation of side-products, 2,5-ST selectivity has remain practically constant for the whole temperature range studied.

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ACRONYMS

| 1,4-ST | 1,4-sorbitan |
|------------------------------|---------------------------------------|
| 2,5-ST | 1,5-sorbitan |
| dp | particle diameter |
| dpore | pore diameter |
| DVB | divynilbenzene |
| nj | Moles of a reagent j |
| IB | Isosorbide |
| ISEC | Inverse size exclusion chromatography |
| Sg | Pore surface |
| Sj | Selectivity of a reagent j |
| SOH | Sorbitol |
| t | time |
| Tb | Boiling temperature |
| Tmax, operation | Maximum operation temperature |
| V _{sp} | Specific volume if swollen polymer |
| V _{pore} | pore volum |
| Xsoh | Sorbitol conversion |
| Yj | Yield of a reagent j |
| $\Delta_{sin}{}^{vH} \; H^o$ | Van't Hoff enthalpy change |
| Θ | porosity |

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APPENDICES

APPENDIX 1: HPLC CALIBRATION

| Compound | Retention time [min] |
|--------------|----------------------|
| 2,5-sorbitan | 7.76 |
| 1,4-sorbitan | 8.64 |
| Isosorbide | 10.54 |
| Sorbitol | 14.20 |

Retention time of each compound

Calibration. Sorbitol



Calibration. Isosorbide

| | С | | | | 1 |
|----|--------|------|-------|------------------|---|
| IB | [g/mL] | Are | a, 10 | ⁶ [-] | |
| 1 | 0,0011 | 0,47 | ± | 0,01 | |
| 2 | 0,0023 | 1,00 | ± | 0,06 | |
| 3 | 0,0033 | 1,4 | ± | 0,1 | |
| 4 | 0,0043 | 1,8 | ± | 0,2 | |
| 5 | 0,0055 | 2,65 | ± | 0,01 | |
| 6 | 0,0069 | 3,2 | ± | 0,4 | |
| 7 | 0,0080 | 3,5 | ± | 0,4 | |
| 8 | 0,0106 | 4,7 | ± | 0,4 | |
| 9 | 0,0128 | 6,3 | ± | 0,7 | |
| 10 | 0,0140 | 6,9 | ± | 0,9 | |
| 11 | 0,0155 | 7,0 | ± | 1,0 | |
| 12 | 0,0170 | 8,5 | ± | 0,8 | |
| 13 | 0,0184 | 9,4 | ± | 1,2 | |
| 14 | 0,0059 | 2,6 | ± | 0,3 | |
| 15 | 0,0070 | 2,78 | ± | 0,09 | |
| 16 | 0,0081 | 3,5 | ± | 0,5 | |
| 17 | 0,0095 | 4,6 | ± | 0,5 | _ |



Calibration 1,4-Sorbitan / 2,5-Sorbitan

| | С | | | | | |
|----|--------|---------------------------|---|------|--|--|
| ST | [g/mL] | Area, 10 ⁶ [-] | | | | |
| 1 | 0,0004 | 0,21 | ± | 0,01 | | |
| 2 | 0,0017 | 0,77 | ± | 0,01 | | |
| 3 | 0,0032 | 1,5 | ± | 0,1 | | |
| 4 | 0,0048 | 1,9 | ± | 0,4 | | |
| 5 | 0,0063 | 2,5 | ± | 0,1 | | |
| 6 | 0,0096 | 4,9 | ± | 0,2 | | |
| 7 | 0,0130 | 6,7 | ± | 0,4 | | |
| 8 | 0,0164 | 8,86 | ± | 0,1 | | |
| 9 | 0,0200 | 10,4 | ± | 0,4 | | |
| 10 | 0,0236 | 12,9 | ± | 0,2 | | |



Calibration equations

| Compound | equation | R ² |
|--------------|--|----------------|
| Sorbitol | y= (1.87E-09 ± 1.3E-10)·x + (3.19E-04 ± 1.3E-03) | 0.994 |
| Isosorbide | y=(1.95E-09 ± 1.1E-10) x + (7.6E-04 ± 5.2E-04) | 0.990 |
| 1,4-sorbitan | | 0.005 |
| 2,5-sorbitan | $Y = (1.01E - 0.9 \pm 1.0E - 10) \cdot X + (7.48E - 0.4 \pm 0.7E - 0.4)$ | 0.995 |

APPENDIX 2: SOLUBILITY EXPERIMENTAL DATA

Experiment 1. n-Butanol

| Vial | T [ºC] | vial+cap [g] | vial+cap+solution [g] | vial+cap+solid [g] |
|------|--------|--------------|-----------------------|--------------------|
| 1 | 23,8 | 11,0378 | 14,8861 | 11,0447 |
| 2 | 23,8 | 11,0704 | 16,0178 | 11,0800 |
| 3 | 23,8 | 11,0304 | 14,4663 | 11,0364 |
| 4 | 28,4 | 11,0611 | 13,4000 | 11,0664 |
| 5 | 28,4 | 11,1066 | 14,8733 | 11,1132 |
| 6 | 28,4 | 11,1095 | 14,0409 | 11,1162 |
| 7 | 32,6 | 11,0159 | 15,2852 | 11,0254 |
| 8 | 32,6 | 11,0458 | 15,9994 | 11,0573 |
| 9 | 32,6 | 10,9999 | 15,6405 | 11,0104 |
| 10 | 38,6 | 10,4407 | 14,0831 | 10,4514 |
| 11 | 38,6 | 10,4166 | 14,6009 | 10,4272 |
| 12 | 38,6 | 10,4154 | 15,2462 | 10,4212 |
| 13 | 43,7 | 10,3296 | 14,5587 | 10,3436 |
| 14 | 43,7 | 10,3226 | 15,0701 | 10,3384 |
| 15 | 43,7 | 10,4501 | 15,3249 | 10,4671 |
| 16 | 48,5 | 10,3793 | 14,5962 | 10,3984 |
| 17 | 48,5 | 10,3414 | 15,1708 | 10,3633 |
| 18 | 48,5 | 10,4406 | 15,116 | 10,4619 |
| 19 | 52,7 | 10,4209 | 14,6645 | 10,4426 |
| 20 | 52,7 | 10,3482 | 15,2812 | 10,3730 |
| 21 | 52,7 | 10,3845 | 15,3684 | 10,4092 |
| 22 | 58,1 | 10,4162 | 14,6879 | 10,4453 |
| 23 | 58,1 | 10,4471 | 15,3503 | 10,4780 |
| 24 | 58,1 | 10,4177 | 15,0484 | 10,4453 |
| 25 | 62,5 | 10,3916 | 14,6764 | 10,4242 |

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|----|------|---------|---------|-------------------------|
| 26 | 62,5 | 10,3519 | 14,9949 | 10,3878 |
| 27 | 62,5 | 10,4125 | 15,2793 | 10,4504 |

Expermient 2. Methanol

| Vial | T [°C] | vial+cap [g] | vial+cap+solution [g] | vial+cap+solid [g] |
|------|--------|--------------|-----------------------|--------------------|
| 28 | 21,1 | 10,4082 | 14,4875 | 10,5291 |
| 29 | 21,1 | 10,3982 | 14,2416 | 10,5101 |
| 30 | 21,1 | 10,3598 | 12,976 | 10,4344 |
| 31 | 25,7 | 10,3513 | 13,0709 | 10,4430 |
| 32 | 25,7 | 10,3886 | 14,1835 | 10,5175 |
| 33 | 25,7 | 10,3622 | 16,9216 | 10,5886 |
| 34 | 28,8 | 10,3522 | 13,6243 | 10,4919 |
| 35 | 28,8 | 10,3403 | 14,3288 | 10,5122 |
| 36 | 28,8 | 10,3829 | 14,7979 | 10,5592 |
| 37 | 39,2 | 10,4348 | 14,5572 | 10,6854 |
| 38 | 39,2 | 10,4143 | 15,3870 | 10,7128 |
| 39 | 39,2 | 10,3799 | 15,6747 | 10,6901 |
| 40 | 44,1 | 10,4118 | 13,9471 | 10,7150 |
| 41 | 44,1 | 10,4225 | 14,4793 | 10,7664 |
| 42 | 44,1 | 10,4585 | 15,1196 | 10,8491 |
| 43 | 49,4 | 10,4256 | 14,8629 | 10,9099 |
| 44 | 49,4 | 10,368 | 14,6647 | 10,8337 |
| 45 | 49,4 | 10,4102 | 15,1894 | 10,9437 |
| 46 | 54,5 | 10,3506 | 14,2722 | 11,0157 |
| 47 | 54,5 | 10,3974 | 12,2534 | 10,6699 |
| 48 | 54,5 | 10,4321 | 12,1149 | 10,6463 |
| 49 | 59,4 | 10,4273 | 13,259 | 10,8212 |
| 50 | 59,4 | 10,3272 | 12,6767 | 10,7136 |
| 51 | 59,4 | 10,3622 | 12,1769 | 10,6997 |
| 79 | 34,7 | 10,4278 | 12,8733 | 10,5473 |
| 80 | 34,7 | 10,4443 | 14,0189 | 10,6217 |
| 81 | 34,7 | 10,365 | 13,1126 | 10,4951 |

| Vial | T [ºC] | vial+cap [g] | vial+cap+solution [g] | vial+cap+solid [g] |
|------|--------|--------------|-----------------------|--------------------|
| 52 | 23.9 | 10.4566 | 13,9902 | 10,4879 |
| 53 | 23.9 | 10.5232 | 14,4156 | 10,5583 |
| 54 | 23.9 | 10.4161 | 13,8393 | 10,4479 |
| 55 | 28.3 | 10.4344 | 13,6369 | 10,4593 |
| 56 | 28.3 | 10.4698 | 13,6286 | 10,4944 |
| 57 | 28.3 | 10.3779 | 14,3472 | 0,4089 |
| 58 | 34.3 | 10.3900 | 12,7462 | 10,4124 |
| 59 | 34.3 | 10.3737 | 13,8945 | 10,4075 |
| 60 | 34.3 | 10.3981 | 13,6166 | 10,4291 |
| 61 | 39.3 | 10.3893 | 13,2377 | 10,4217 |
| 62 | 39.3 | 10.4603 | 13,4087 | 10,4940 |
| 63 | 39.3 | 10.4688 | 13,8800 | 10,5078 |
| 64 | 44.0 | 10.4595 | 12,9622 | 10,4961 |
| 65 | 44.0 | 10.4731 | 13,8705 | 10,5222 |
| 66 | 44.0 | 10.4257 | 13,6073 | 10,4713 |
| 67 | 48.8 | 10.4442 | 12,9273 | 10,4922 |
| 68 | 48.8 | 10.4681 | 13,7600 | 10,5319 |
| 69 | 48.8 | 10.3722 | 14,3542 | 10,4485 |
| 70 | 53.8 | 10.4388 | 12,8929 | 10,4969 |
| 71 | 53.8 | 10.4495 | 13,3728 | 10,5200 |
| 72 | 53.8 | 10.4469 | 13,9694 | 10,5279 |
| 73 | 58.9 | 10.4026 | 12,8197 | 10,4767 |
| 74 | 58.9 | 10.3548 | 13,445 | 10,4502 |
| 75 | 58.9 | 10.4277 | 13,7797 | 10,5285 |
| 76 | 63.4 | 10.3956 | 12,9717 | 10,4876 |
| 77 | 63.4 | 10.4019 | 13,4842 | 10,5128 |
| 78 | 63.4 | 10,4619 | 14.801 | 10,6225 |

Experiment 3. Ethanol

Experiment 4. Acetone

| Vial | T [°C] | vial+cap [g] | vial+cap+solution [g] | vial+cap+solid [g] |
|------|--------|--------------|-----------------------|--------------------|
| 82 | 23.8 | 10,3881 | 13,1795 | 10,3910 |
| 83 | 23.8 | 10,3809 | 13,8445 | 10,3838 |
| 84 | 23.8 | 10,4114 | 13,4473 | 10,4145 |

| 85 | 29.6 | 10,3566 | 13,2369 | 10,3595 |
|----|------|---------|---------|---------|
| 86 | 29.6 | 10,4561 | 13,265 | 10,4590 |
| 87 | 29.6 | 10,3673 | 14,6615 | 10,3716 |
| 88 | 34.7 | 10,4403 | 13,4392 | 10,4438 |
| 89 | 34.7 | 10,3505 | 13,9028 | 10,3551 |
| 90 | 34.7 | 10,3737 | 13,6265 | 10,3775 |
| 91 | 39.6 | 10,2514 | 13,7135 | 10,2557 |
| 92 | 39.6 | 10,4317 | 13,8199 | 10,4358 |
| 93 | 39.6 | 10,4231 | 13,7415 | 10,4269 |
| 94 | 44.4 | 10,3872 | 13,777 | 10,3914 |
| 95 | 44.4 | 10,4184 | 13,8816 | 10,4242 |
| 96 | 44.4 | 10,3819 | 13,4489 | 10,3864 |
| 97 | 49.6 | 10,4009 | 13,6232 | 10,4063 |
| 98 | 49.6 | 10,3964 | 14,2196 | 10,4043 |
| 99 | 49.6 | 10,392 | 13,6651 | 10,3977 |
| | | | | |

APPENDIX 3. REACTION EXPERIMENTAL DATA

The data of the experiments used for the study are attached below:

Experiment 1. Screening

| Catalyst | A-45 | m catalyst [g] | 1,0053 |
|----------------|------|--------------------------------------|--------|
| T [°C] | 170 | m sorbitol [g] | 4,5068 |
| Stirring [rpm] | 750 | m H ₂ O [g] | 89,70 |

| | | Area _j [-] | | | | nj [r | mol] | |
|---------|----------|-----------------------|---------|--------|--------|--------|--------|--------|
| t [min] | SOH | IB | 1,4-ST | 2,5-ST | SOH | IB | 1,4-ST | 2,5-ST |
| 0 | 14094241 | 0 | 336758 | 0 | 0,0261 | 0 | 0 | 0 |
| 30 | 14161761 | 0 | 562278 | 0 | 0,0262 | 0 | 0,0019 | 0 |
| 60 | 12858875 | 15367 | 1022071 | 62896 | 0,0239 | 0,0010 | 0,0028 | 0,0009 |
| 90 | 12209374 | 72208 | 1749328 | 94545 | 0,0227 | 0,0011 | 0,0042 | 0,0010 |
| 120 | 11266034 | 123541 | 2442176 | 127498 | 0,0209 | 0,0012 | 0,0056 | 0,0011 |
| 150 | 9788662 | 222718 | 3283172 | 171179 | 0,0182 | 0,0015 | 0,0072 | 0,0011 |
| 210 | 7613199 | 455267 | 4817514 | 257328 | 0,0143 | 0,0020 | 0,0103 | 0,0013 |
| 270 | 5694809 | 770200 | 6087404 | 336858 | 0,0107 | 0,0028 | 0,0127 | 0,0015 |
| 330 | 4580526 | 1142024 | 7279308 | 415833 | 0,0087 | 0,0036 | 0,0151 | 0,0016 |
| 390 | 3192931 | 1397958 | 7388624 | 440574 | 0,0062 | 0,0042 | 0,0153 | 0,0017 |
| 450 | 2239126 | 1691600 | 7496114 | 461317 | 0,0044 | 0,0049 | 0,0155 | 0,0017 |
| 510 | 1602123 | 1985924 | 7571546 | 483209 | 0,0032 | 0,0056 | 0,0157 | 0,0018 |

Experiment 2. Screening

| Catalyst | A DL-H/03 |
|----------------|-----------|
| T [°C] | 170 |
| Stirring [rpm] | 750 |

| m catalyst [g] | 1,0065 |
|-----------------------|--------|
| m sorbitol [g] | 4,5013 |
| m H₂O [g] | 89,45 |

| | | Area _j [-] | | | | n j [I | mol] | |
|---------|----------|-----------------------|---------|--------|--------|---------------|--------|-----------------|
| t [min] | SOH | IB | 1,4-ST | 2,5-ST | SOH | IB | 1,4-ST | 2,5 - ST |
| 0 | 13239713 | 0 | 0 | 0 | 0,0247 | 0 | 0 | 0 |
| 30 | 13056575 | 0 | 844808 | 57938 | 0,0243 | 0 | 0,0025 | 0,00093 |
| 60 | 11882866 | 71391 | 1622808 | 93153 | 0,0222 | 0,0011 | 0,0040 | 0,00100 |
| 90 | 10139450 | 147010 | 2501192 | 139939 | 0,0190 | 0,0013 | 0,0057 | 0,00109 |
| 120 | 10095360 | 223309 | 3524668 | 182162 | 0,0189 | 0,0015 | 0,0078 | 0,00117 |
| 150 | 8294104 | 371900 | 4524916 | 233936 | 0,0156 | 0,0018 | 0,0097 | 0,00128 |
| 210 | 4983443 | 984665 | 6230376 | 343988 | 0,0095 | 0,0033 | 0,0131 | 0,00149 |
| 270 | 2946423 | 1535377 | 7231389 | 424819 | 0,0057 | 0,0046 | 0,0151 | 0,00165 |
| 330 | 1508363 | 2025607 | 7398488 | 470514 | 0,0031 | 0,0058 | 0,0154 | 0,00174 |
| 390 | 1003532 | 2901692 | 7922246 | 549689 | 0,0022 | 0,0079 | 0,0164 | 0,00190 |
| 450 | 510877 | 3312841 | 7080312 | 540792 | 0,0013 | 0,0088 | 0,0148 | 0,00188 |
| 510 | 351302 | 4068946 | 7012441 | 589063 | 0,0010 | 0,0107 | 0,0146 | 0,00197 |

Experiment 3. Screening

| Catalyst | A DL-I/03 |
|----------------|-----------|
| T [°C] | 170 |
| Stirring [rpm] | 750 |

| | | Area _j [-] | | | | nj [r | nol] | |
|---------|----------|-----------------------|---------|--------|--------|--------|--------|--------|
| t [min] | SOH | IB | 1,4-ST | 2,5-ST | SOH | IB | 1,4-ST | 2,5-ST |
| 0 | 13623066 | 0 | 0 | 0 | 0,0253 | 0 | 0 | 0 |
| 30 | 13165724 | 0 | 1293915 | 67320 | 0,0245 | 0 | 0,0034 | 0,0009 |
| 60 | 11299635 | 95308 | 2462109 | 116023 | 0,0211 | 0,0012 | 0,0057 | 0,0010 |
| 90 | 9378510 | 182431 | 3481618 | 160860 | 0,0175 | 0,0014 | 0,0077 | 0,0011 |
| 120 | 7668139 | 385189 | 4970016 | 231435 | 0,0144 | 0,0018 | 0,0106 | 0,0013 |
| 150 | 5849422 | 777526 | 6037276 | 289382 | 0,0111 | 0,0028 | 0,0127 | 0,0014 |
| 210 | 2971342 | 1525154 | 7841846 | 409438 | 0,0058 | 0,0046 | 0,0162 | 0,0016 |
| 270 | 1242226 | 2248915 | 7935894 | 446504 | 0,0026 | 0,0063 | 0,0164 | 0,0017 |
| 330 | 614720 | 2886848 | 7664037 | 463574 | 0,0014 | 0,0078 | 0,0159 | 0,0017 |
| 390 | 377727 | 3517513 | 7372488 | 529493 | 0,0010 | 0,0093 | 0,0153 | 0,0019 |
| 450 | 289803 | 4128625 | 7105217 | 570362 | 0,0008 | 0,0108 | 0,0148 | 0,0019 |
| 510 | 260795 | 4040821 | 6613317 | 549521 | 0,0008 | 0,0106 | 0,0138 | 0,0019 |

| Experiment 4. Screening | Experiment | 4. | Screening |
|-------------------------|------------|----|-----------|
|-------------------------|------------|----|-----------|

| Catalyst | CT-482 | m catalyst [g] | 1,0015 |
|----------------|--------|--------------------------------------|--------|
| T [⁰C] | 170 | m sorbitol [g] | 4,5037 |
| Stirring [rpm] | 750 | m H ₂ O [g] | 89,40 |

| | | Area _j [-] | | | | nj [r | mol] | |
|---------|----------|-----------------------|---------|--------|--------|--------|--------|--------|
| t [min] | SOH | IB | 1,4-ST | 2,5-ST | SOH | IB | 1,4-ST | 2,5-ST |
| 0 | 11940119 | 0 | 0 | 0 | 0,0223 | 0 | 0 | 0 |
| 30 | 9608838 | 378842 | 3670335 | 218410 | 0,0180 | 0,0018 | 0,0080 | 0,0012 |
| 60 | 7091594 | 837405 | 5616424 | 350129 | 0,0133 | 0,0029 | 0,0119 | 0,0015 |
| 90 | 4604723 | 1332959 | 7175745 | 465608 | 0,0088 | 0,0041 | 0,0149 | 0,0017 |
| 120 | 2787131 | 1985869 | 7841864 | 541641 | 0,0054 | 0,0057 | 0,0163 | 0,0019 |
| 150 | 1544424 | 2538076 | 8254656 | 605193 | 0,0032 | 0,0070 | 0,0171 | 0,0020 |
| 210 | 619159 | 3569766 | 7857934 | 654099 | 0,0015 | 0,0095 | 0,0163 | 0,0021 |
| 270 | 327517 | 4002378 | 6921871 | 646529 | 0,0009 | 0,0105 | 0,0144 | 0,0021 |
| 330 | 236151 | 4647127 | 6501001 | 682081 | 0,0007 | 0,0120 | 0,0136 | 0,0022 |
| 390 | 213853 | 5193722 | 5901490 | 692500 | 0,0007 | 0,0133 | 0,0124 | 0,0022 |
| 450 | 212484 | 5380963 | 5197285 | 665387 | 0,0007 | 0,0138 | 0,0110 | 0,0021 |
| 510 | 191198 | 6059103 | 4671794 | 691524 | 0,0007 | 0,0154 | 0,0100 | 0,0022 |

Experiment 5. Replicates

| Catalyst | 4-70 | m catalyst [g] | 1,0007 |
|----------------|------|-----------------------|--------|
| T [°C] | 170 | m sorbitol [g] | 4,5061 |
| Stirring [rpm] | 750 | m H₂O [g] | 89,70 |

| | Area _i [-] | | | | | n j [mol] | | | | |
|---------|-----------------------|--------|---------|--------|--------|------------------|--------|--------|--|--|
| t [min] | SOH | IB | 1,4-ST | 2,5-ST | SOH | IB | 1,4-ST | 2,5-ST | | |
| 0 | 15616549 | 0 | 0 | 0 | 0,0291 | 0 | 0 | 0 | | |
| 30 | 12997969 | 47466 | 1001350 | 60189 | 0,0243 | 0,0010 | 0,0028 | 0,0009 | | |
| 60 | 10690064 | 148107 | 3102320 | 150275 | 0,0200 | 0,0013 | 0,0069 | 0,0011 | | |
| 90 | 8589739 | 305945 | 4465657 | 219396 | 0,0162 | 0,0017 | 0,0096 | 0,0013 | | |
| 120 | 6432161 | 539805 | 5645762 | 283267 | 0,0122 | 0,0022 | 0,0120 | 0,0014 | | |

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|-----|---------|---------|---------|--------|--------|--------|------------|----------------|
| 150 | 4425744 | 1045824 | 6707261 | 348671 | 0,0085 | 0,0034 | 0,0141 | 0,0015 |
| 210 | 2204542 | 1770179 | 7759356 | 451571 | 0,0044 | 0,0052 | 0,0161 | 0,0017 |
| 270 | 1055807 | 2464792 | 7883020 | 509542 | 0,0023 | 0,0068 | 0,0164 | 0,0018 |
| 330 | 643791 | 3238118 | 8244567 | 588700 | 0,0015 | 0,0087 | 0,0171 | 0,0020 |
| 390 | 352302 | 3472866 | 6937521 | 551314 | 0,0010 | 0,0093 | 0,0145 | 0,0019 |
| 450 | 234773 | 3664345 | 5949511 | 525493 | 0,0007 | 0,0097 | 0,0126 | 0,0019 |
| 510 | 188994 | 3891841 | 5231116 | 518681 | 0,0007 | 0,0103 | 0,0111 | 0,0018 |

Experiment 6. Replicates

| Catalyst | A-70 | m catalyst [g] | 1,0015 |
|----------------|------|--------------------------------------|--------|
| T [°C] | 170 | m sorbitol [g] | 4,5037 |
| Stirring [rpm] | 750 | m H ₂ O [g] | 89,40 |

| | | Area _j [-] | | | | n j [I | nol] | |
|-------|----------|-----------------------|---------|--------|--------|---------------|--------|--------|
| t | 0011 | 10 | 4 4 97 | 0 C 0T | 0011 | in | 4.4.07 | 0 C 0T |
| [min] | SOH | IB | 1,4-51 | 2,5-51 | SOH | IB | 1,4-51 | 2,5-51 |
| 0 | 6685944 | 0 | 0 | 0 | 0,0247 | 0 | 0 | 0 |
| 30 | 10692263 | 197234 | 3087989 | 172608 | 0,0200 | 0,0014 | 0,0069 | 0,0012 |
| 60 | 7890620 | 435088 | 4774634 | 282586 | 0,0148 | 0,0020 | 0,0102 | 0,0014 |
| 90 | 5313035 | 1021817 | 6627321 | 410622 | 0,0101 | 0,0034 | 0,0139 | 0,0016 |
| 120 | 3368788 | 1606148 | 7998549 | 519430 | 0,0065 | 0,0048 | 0,0166 | 0,0018 |
| 150 | 2003199 | 1899250 | 7792525 | 525254 | 0,0040 | 0,0055 | 0,0162 | 0,0019 |
| 210 | 891700 | 2820921 | 8005104 | 606912 | 0,0020 | 0,0077 | 0,0166 | 0,0020 |
| 270 | 530339 | 3537033 | 7719273 | 635075 | 0,0013 | 0,0094 | 0,0160 | 0,0021 |
| 330 | 35401 | 4093483 | 7054940 | 643451 | 0,0004 | 0,0107 | 0,0147 | 0,0021 |
| 390 | 251982 | 4717932 | 6660830 | 667943 | 0,0008 | 0,0122 | 0,0140 | 0,0021 |
| 450 | 214501 | 4699260 | 5484018 | 620010 | 0,0007 | 0,0122 | 0,0116 | 0,0020 |
| 510 | 188064 | 5476798 | 5346743 | 678208 | 0,0007 | 0,0140 | 0,0114 | 0,0022 |

Experiment 7. Replicates

| Catalyst | A-70 |
|----------------|------|
| T [°C] | 170 |
| Stirring [rpm] | 750 |

| m catalyst [g] | 1,0044 |
|------------------|--------|
| m sorbitol [g] | 4,5034 |
| m H₂O [g] | 89,47 |

| | | Areaj [-] | | | | nj [I | nol] | |
|-------|----------|-----------|---------|--------|--------|--------|--------|----------------|
| t | 2011 | ID | 4 4 CT | 2 5 GT | 60U | ю | 4 4 67 | 2 5 6 T |
| լուոլ | 30n | ID | 1,4-51 | 2,5-51 | 30n | ID | 1,4-51 | 2,3-31 |
| 0 | 13303153 | 0 | 0 | 0 | 0,0248 | 0 | 0 | 0 |
| 30 | 9334176 | 368717 | 4010502 | 242711 | 0,0175 | 0,0018 | 0,0087 | 0,0013 |
| 60 | 5979027 | 926076 | 6178780 | 388324 | 0,0113 | 0,0031 | 0,0130 | 0,0016 |
| 90 | 3405664 | 1425811 | 7090266 | 432746 | 0,0066 | 0,0043 | 0,0148 | 0,0017 |
| 120 | 1844574 | 2129920 | 7615336 | 549918 | 0,0037 | 0,0060 | 0,0158 | 0,0019 |
| 150 | 1059441 | 2644068 | 7830375 | 599968 | 0,0023 | 0,0072 | 0,0162 | 0,0020 |
| 210 | 387555 | 3625744 | 7046022 | 641035 | 0,0010 | 0,0096 | 0,0147 | 0,0021 |
| 270 | 270673 | 4386267 | 6297358 | 654710 | 0,0008 | 0,0114 | 0,0132 | 0,0021 |
| 330 | 194004 | 5496533 | 5932880 | 717744 | 0,0007 | 0,0141 | 0,0125 | 0,0022 |
| 390 | 178577 | 6228851 | 5364696 | 744277 | 0,0006 | 0,0158 | 0,0114 | 0,0023 |
| 450 | 150721 | 6363369 | 4516621 | 718663 | 0,0006 | 0,0161 | 0,0097 | 0,0022 |
| 510 | 137172 | 6693526 | 3994525 | 717369 | 0,0006 | 0,0169 | 0,0087 | 0,0022 |

Experiment 8. Temperature effect

| Catalyst | CT-482 | m catalyst [g] | 1,0015 |
|----------------|--------|--------------------------------------|--------|
| T [°C] | 150 | m sorbitol [g] | 4,5037 |
| Stirring [rpm] | 750 | m H ₂ O [g] | 89,86 |

| | Area _i [-] | | | | n j [mol] | | | |
|-------|-----------------------|---------|---------|---------------|------------------|--------|--------|--------|
| t | 0011 | 10 | 4 4 07 | 0 5 0T | 0011 | 10 | 4 4 97 | 0 5 OT |
| [min] | 50H | IB | 1,4-51 | 2,3-51 | 50H | IB | 1,4-51 | 2,5-51 |
| 0 | 17206962 | 0 | 0 | 0 | 0,0321 | 0 | 0 | 0 |
| 30 | 13880455 | 0 | 424635 | 0 | 0,0260 | 0 | 0,0017 | 0 |
| 60 | 11780031 | 92741 | 2179069 | 10059 | 0,0221 | 0,0012 | 0,0051 | 0,0008 |
| 90 | 10291400 | 156407 | 2924949 | 131947 | 0,0193 | 0,0013 | 0,0066 | 0,0011 |
| 120 | 9450007 | 240802 | 3927290 | 177843 | 0,0178 | 0,0015 | 0,0086 | 0,0012 |
| 150 | 8207161 | 368972 | 4810704 | 221627 | 0,0155 | 0,0018 | 0,0103 | 0,0013 |
| 210 | 5942243 | 768972 | 5993108 | 290334 | 0,0113 | 0,0028 | 0,0127 | 0,0014 |
| 270 | 3856858 | 1030148 | 6352012 | 327050 | 0,0074 | 0,0034 | 0,0134 | 0,0015 |
| 330 | 2901766 | 1333582 | 6936800 | 360561 | 0,0057 | 0,0041 | 0,0145 | 0,0015 |
| 390 | 2232325 | 1927725 | 7814673 | 478735 | 0,0044 | 0,0056 | 0,0163 | 0,0018 |
| 450 | 1370074 | 1882334 | 7620575 | 450796 | 0,0028 | 0,0054 | 0,0159 | 0,0017 |
| 510 | 924258 | 1890831 | 6394889 | 375643 | 0,0020 | 0,0055 | 0,0135 | 0,0016 |

Experiment 9. Temperature effect

| Catalyst | CT-482 | m catalyst [g] |
|-------------------|--------|--------------------------------------|
|] | 160 | m sorbitol [g] |
| i ng [rpm] | 750 | m H ₂ O [g] |

| | Area _j [-] | | | | n j [mol] | | | |
|------------|-----------------------|---------|---------|--------|------------------|--------|--------|--------|
| t [min] | SOH | IB | 1,4-ST | 2,5-ST | SOH | IB | 1,4-ST | 2,5-ST |
| 0 | 14270471 | 0 | 0 | 0 | 0,0266 | 0 | 0 | 0 |
| 30 | 14124323 | 50151 | 864413 | 52227 | 0,0263 | 0,0010 | 0,0025 | 0,0009 |
| 60 | 10827730 | 203584 | 3312180 | 176866 | 0,0203 | 0,0014 | 0,0073 | 0,0012 |
| 90 | 8937118 | 384002 | 4535270 | 242511 | 0,0168 | 0,0018 | 0,0098 | 0,0013 |
| 120 | 6922527 | 592014 | 5493618 | 297535 | 0,0131 | 0,0023 | 0,0117 | 0,0014 |
| 150 | 4732210 | 1243696 | 7149150 | 422369 | 0,0090 | 0,0039 | 0,0149 | 0,0016 |
| 210 | 3454244 | 1661473 | 7831904 | 487051 | 0,0067 | 0,0049 | 0,0163 | 0,0018 |
| 270 | 2040436 | 2188708 | 8239800 | 539779 | 0,0041 | 0,0062 | 0,0171 | 0,0019 |
| 330 | 1218416 | 2651064 | 8225895 | 570404 | 0,0026 | 0,0073 | 0,0170 | 0,0019 |
| 390 | 784858 | 3071956 | 8054063 | 590513 | 0,0018 | 0,0083 | 0,0167 | 0,0020 |
| 450 | 555097 | 3268949 | 7719584 | 588364 | 0,0013 | 0,0087 | 0,0160 | 0,0020 |
| 510 | 402515 | 3623786 | 7361592 | 617144 | 0,0011 | 0,0096 | 0,0153 | 0,0020 |

Experiment 10. Temperature effect

| Catalyst | CT-482 | m catalyst [g] |
|----------------|--------|-----------------------------|
| C] | 180 | m sorbitol [g] |
| Stirring [rpm] | 750 | m H₂O [g] |

| | Area _j [-] | | | | n _j [mol] | | | |
|------------|-----------------------|---------|---------|--------|----------------------|--------|--------|--------|
| t [min] | SOH | IB | 1,4-ST | 2,5-ST | SOH | IB | 1,4-ST | 2,5-ST |
| 0 | 14302114 | 0 | 0 | 0 | 0,0268 | 0 | 0 | 0 |
| 30 | 12929629 | 222005 | 2315401 | 127093 | 0,0242 | 0,0015 | 0,0054 | 0,0011 |
| 60 | 3679294 | 1228796 | 5933105 | 417893 | 0,0071 | 0,0039 | 0,0126 | 0,0016 |
| 90 | 2057785 | 2190184 | 7608920 | 594361 | 0,0041 | 0,0062 | 0,0159 | 0,0020 |
A contribution to the study of the process of fructose to isosorbide conversion.

| 120 | 1015050 | 3002738 | 7626928 | 657322 | 0,0022 | 0,0081 | 0,0159 | 0,0021 |
|-----|---------|---------|---------|--------|--------|--------|--------|--------|
| 150 | 536623 | 3476506 | 7047303 | 670923 | 0,0013 | 0,0093 | 0,0148 | 0,0021 |
| 210 | 265226 | 4910708 | 6393263 | 743816 | 0,0008 | 0,0127 | 0,0135 | 0,0023 |
| 270 | 204136 | 5940453 | 5484777 | 774225 | 0,0007 | 0,0152 | 0,0117 | 0,0024 |
| 330 | 176457 | 6591616 | 4691270 | 786869 | 0,0006 | 0,0168 | 0,0101 | 0,0024 |
| 390 | 82820 | 6808552 | 3984626 | 775148 | 0,0005 | 0,0173 | 0,0087 | 0,0024 |
| 450 | 77994 | 7313063 | 3787217 | 796045 | 0,0005 | 0,0185 | 0,0083 | 0,0024 |
| 510 | 119265 | 7374899 | 3532971 | 788280 | 0,0005 | 0,0187 | 0,0078 | 0,0024 |

Experiment 11. Temperature effect

| Catalyst | CT-482 | m catalyst [g] | 1,0017 |
|----------------|--------|--------------------------------------|--------|
| T [°C] | 190 | m sorbitol [g] | 4,5013 |
| Stirring [rpm] | 750 | m H ₂ O [g] | 89,49 |

| | Area _j [-] | | | | n j [mol] | | | |
|------------|-----------------------|---------|---------|--------|------------------|--------|--------|--------|
| t [min] | SOH | IB | 1 4-ST | 2 5-ST | SOH | IB | 1 4-ST | 2 5-ST |
| 0 | 15567211 | 0 | 0 | 0 | 0.0290 | 0 | 0 | 0 |
| 30 | 5160312 | 1198730 | 6442727 | 449099 | 0.0098 | 0.0038 | 0.0135 | 0.0017 |
| 60 | 1704093 | 2566666 | 8186567 | 700681 | 0,0034 | 0,0071 | 0,0169 | 0,0022 |
| 90 | 526982 | 4155986 | 7471858 | 723504 | 0,0013 | 0,0109 | 0,0155 | 0,0022 |
| 120 | 384438 | 5701189 | 7187911 | 840820 | 0,0010 | 0,0146 | 0,0150 | 0,0025 |
| 150 | 257972 | 5987872 | 6375360 | 868280 | 0,0008 | 0,0152 | 0,0134 | 0,0025 |
| 210 | 198542 | 6886328 | 5317237 | 889906 | 0,0007 | 0,0174 | 0,0113 | 0,0026 |
| 270 | 319243 | 7220731 | 4500156 | 869331 | 0,0009 | 0,0182 | 0,0097 | 0,0025 |
| 330 | 227935 | 7336721 | 4363146 | 879791 | 0,0007 | 0,0185 | 0,0094 | 0,0025 |
| 390 | 167501 | 7535069 | 4398006 | 896540 | 0,0006 | 0,0189 | 0,0095 | 0,0026 |
| 450 | 386639 | 7708309 | 4414869 | 919871 | 0,0010 | 0,0194 | 0,0095 | 0,0026 |
| 510 | 262912 | 7742376 | 4161945 | 870809 | 0,0008 | 0,0194 | 0,0090 | 0,0025 |