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Glucose isomerization reaction to fructose over basic catalysts

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You have got to get up every morning with determination if you are going to go to bed with satisfaction.

George Lorimer

Vull donar les gràcies als meus tutors, Dr. Bringué i Dra. Ramírez per tota l'ajuda prestada durant la realització del treball. En especial, durant el període de quarantena que sempre han estat disposats a resoldre tots els dubtes que sorgien i donar ànims.

També vull agrair als meus pares el suport que m'han donat durant els estudis, confiant en mi en tot moment.

Finalment, agrair als meus amics els bons moments viscuts durant aquests anys, fent el camí molt més fàcil.

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SUMMARY

The growing concern for the climate change and the reduction of petroleum and natural gas reserves has led to the research of new renewable sources of energy. Biomass is the largest source of renewable energy and it is also used for the production of commodity chemicals and bio-based materials.

Lignocellulose is a form of biomass used in the production of biofuels and other chemical products such as biogas, biodiesel, syngas or bioalcohols.

5-hydroxymethylfurfural (5-HMF) is an intermediate product in the production of biofuels from lignocellulose and it has more applications in other areas such as the production of bioplastics, adhesives, solvents, etc. 5-HMF can be obtained from the glucose that comes from the treatment of lignocellulose. Nevertheless, fructose reactivity is higher than glucose reactivity.

In this work, the most effective heterogeneous catalyst for the glucose to fructose isomerization is determined in terms of glucose conversion, fructose yield and fructose selectivity.

The catalysts tested are the following basic ion exchange resins: Amberlyst 21, Amberlyst 26(OH^-) and Purolite CTA196. Amberlyst 26(OH^-) is the resin that obtained the highest values of glucose conversion (51.32 ± 1.33 %), fructose yield (37.37 ± 0.08 %) and fructose selectivity (72.84 ± 2.06 %), operating at 80 ºC for 6 hours. The final fructose concentration has been of (0.19 ± 0.01) mol/L, from an initial glucose concentration of 0.5 mol/L.

Also, Amberlyst 21 has been tested for different operating temperatures. The increase of the temperature from 80 ºC to 90 ºC has led to the increases of glucose conversion (+11.38 %), fructose yield (+64.43 %) and fructose selectivity (+46.97 %).

Results obtained experimentally have been compared with those ones obtained in another study, using glucose isomerase as catalyst (Solà Mas, S. Glucose Isomerization by Enzymes. TFG. Publicacions i Edicions de la Universitat de Barcelona, Barcelona, 2020). Results obtained

for the production of fructose (glucose conversion and final fructose concentration) using Amberlyst 26(OH^-) were slightly higher than the ones obtained operating with glucose isomerase. However, results obtained using glucose isomerase, were operating with 1 g of enzyme while the results obtained with Amberlyst 26(OH^-) have been achieved using 5 g of resin. It could be deduced that, if the catalyst masses were the same, better results would be obtained using glucose isomerase as catalyst. Nevertheless, the main disadvantage of glucose isomerase is its high price in comparison with Amberlyst 26(OH^-).

Finally, the results obtained with the ion exchange resins used in this study have been compared with the results obtained in other studies from the available scientific literature. Although the experimental conditions of these studies are different, the heterogeneous catalysts that showed high effectiveness towards the production of fructose from glucose are: Amberlite IRA400(OH^-), MgO, Sn-Beta zeolite, Amberlyst 26(OH^-) and meglumine. To determine which catalyst is the most effective, there should be done experiments at the same conditions for each one of these catalysts.

Keywords: biomass, lignocellulose, biofuels, 5-hydroxymethylfurfural, glucose to fructose isomerization, heterogeneous catalysts, ion exchange resins, glucose isomerase.

RESUM

La creixent preocupació pel canvi climàtic i la reducció de les reserves de petroli i gas natural ha portat a la investigació de noves fonts renovables d'energia. La biomassa és la major font d'energia renovable i també és utilitzada en la producció de productes químics bàsics i biomaterials.

La lignocel·lulosa és una forma de biomassa que s'utilitza en la producció de biocombustibles i altres productes químics com el biogàs, biodièsel, gas de síntesi o bioalcohols.

El 5-hidroximetilfurfural (5-HMF) és un producte intermedi en la producció de biofuels a partir de lignocel·lulosa i té més aplicacions en altres àrees com la producció de bioplàstics, adhesius, dissolvents, etc. El 5-HMF pot ser obtingut a partir de la glucosa provinent del tractament de la lignocel·lulosa. Tot i així, la reactivitat de la fructosa és major a la de la glucosa.

En aquest treball, es determina el catalitzador heterogeni més efectiu en la isomerització de glucosa a fructosa en termes de conversió de la glucosa, rendiment de la fructosa i selectivitat de la fructosa.

Els catalitzadors que s'han provat són les següents resines d'intercanvi iònic bàsiques: Amberlyst 21, Amberlyst 26(OH^-) i Purolite CTA196. La resina Amberlyst 26(OH^-) és amb la que s'han obtingut majors valors de conversió de la glucosa (51.32 ± 1.33 %), rendiment de la fructosa (37.37 ± 0.08 %) i selectivitat de la fructosa (72.84 ± 2.06 %), treballant a 80 ºC durant 6 hores. La concentració final de fructosa ha sigut de (0.19 ± 0.01) mol/L, partint d'una concentració de glucosa inicial de 0.5 mol/L.

A més, l'Amberlyst 21 ha sigut provada per diferents temperatures d'operació. L'increment de la temperatura de 80 ºC a 90 ºC ha portat als increments de la conversió de la glucosa (+11.38 %), rendiment de la fructosa (+64.43 %) i la selectivitat de la fructosa (+46.97 %).

Els resultats obtinguts experimentalment han sigut comparats amb els obtinguts en un altre estudi, utilitzant glucosa isomerasa com a catalitzador (Solà Mas, S. Glucose Isomerization by Enzymes. TFG. Publicacions i Edicions de la Universitat de Barcelona, Barcelona, 2020). Els resultats obtinguts en la producció de fructosa (conversió de glucosa i concentració final de fructosa) van ser lleugerament més alts que els obtinguts treballant amb glucosa isomerasa. Tot i així, els resultats obtinguts emprant glucosa isomerasa van ser operant amb 1 g d'enzim mentre que els obtinguts amb Amberlyst 26(OH^-) han sigut aconseguits utilitzant 5 g de resina. Es pot deduir que, si les masses de catalitzador fossin iguals, s'haguessin obtingut millors resultats utilitzant glucosa isomerasa com a catalitzador. Tot i així, el principal desavantatge de la glucosa isomerasa és el seu alt preu en comparació amb l'Amberlyst 26(OH^-).

Finalment, els resultats obtinguts amb les resines d'intercanvi iònic en aquest estudi han sigut comparats amb els resultats obtinguts en altres estudis de la literatura científica disponible. Encara que les condicions experimentals d'aquests estudis són diferents, els catalitzadors heterogenis que han mostrat una alta efectivitat en la producció de fructosa a partir de glucosa són: Amberlite IRA400(OH^-), MgOs, Sn-Beta zeolita, Amberlyst 26(OH^-) i meglumina. Per determinar quin catalitzador és el més efectiu, s'haurien de realitzar experiments en les mateixes condicions per cada un d'aquests catalitzadors.

Paraules clau: biomassa, lignocel·lulosa, biocombustibles, 5-hidroximetilfurfural, isomerització de glucosa a fructosa, catalitzadors heterogenis, resines d'intercanvi iònic, glucosa isomerasa.

1. INTRODUCTION

During the past years, the concern for the climate change and the reduction of petroleum and natural gas reserves has increased and one of the most studied topics to deal with is the substitution of non-renewable fossil resources by renewable ones to produce energy.

As shown in Figure 1, the energy produced in the EU from renewable resources is projected to increase in the following years as opposed to other energy sources.

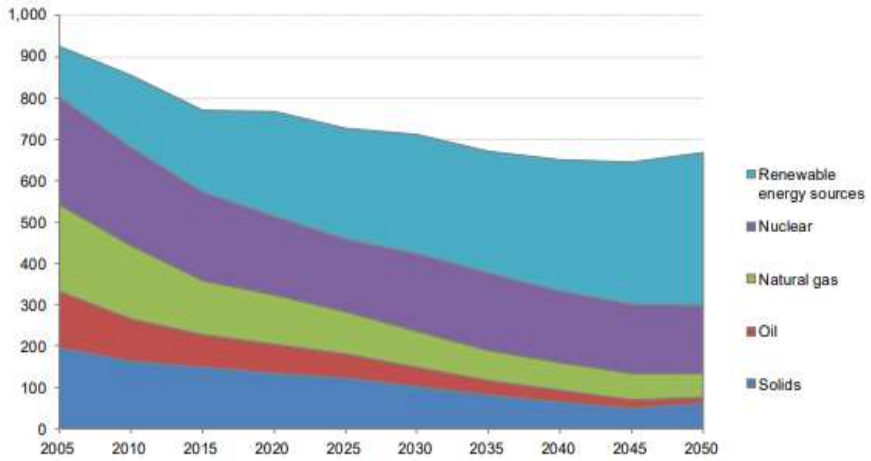

Figure 1. EU projected energy production (Mtoe)[1].

Bioenergy is the largest renewable energy source globally. In 2016, total primary energy supply of biomass resources constituted the 70% of all renewable energy sources[2].

Apart from producing biofuels, biomass is also used in the production of commodity chemicals and bio-based materials such as bioplastics[3].

Depending on the source of biomass, biofuels are classified into different categories[4]:

- First-generation biofuels are derived from sugar, animal fats, starch or vegetable oil.
- Second-generation biofuels are derived from lignocellulosic biomass.
- Third-generation biofuels are produced from algae oil.

Lignocellulose refers to plant dry matter and it is composed of cellulose, hemicellulose and lignin. Lignocellulose is the most abundant biomass available on Earth[5] and it is used in the production of biofuels and chemical products such as biogas, biodiesel, syngas or bioalcohols.

The sugars contained in lignocellulose are treated to produce the different products as showed in Figure 2:

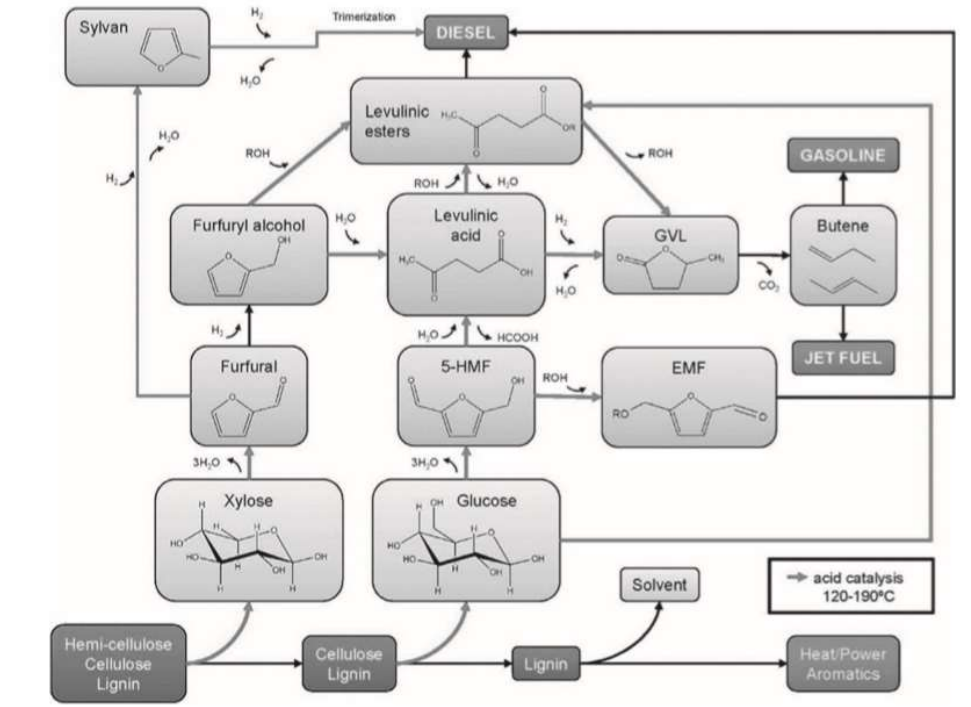

Figure 2. Scheme of the main molecular transformations from lignocellulosic biomass to biofuels[3].

One of the main reactions of this process is the production of 5-hydroxymethylfurfural (5-HMF) from glucose dehydration using catalysts. The mechanism of the formation of 5-HMF is not clear, and two different pathways have been proposed[6] (Figure 3):

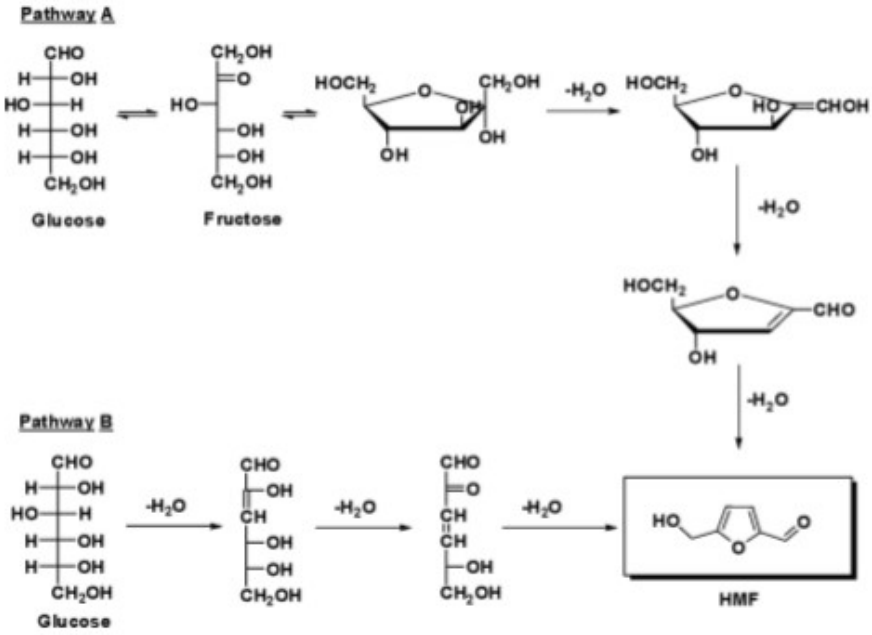

Figure 3. Pathways of 5-HMF formation from glucose[6].

The main areas of 5-HMF application are the production of biofuels, materials such as bioplastics or adhesives, solvents, drugs or metal–organic frameworks (MOFs)[7].

While glucose is a cheaper and more available source than fructose, fructose reactivity is higher than glucose reactivity. It is explained by the higher abundance of acyclic fructose compared to acyclic glucose. Glucose can form a very stable ring structure, so the enolisation rate is lower than fructose, which forms less stable ring structures. This step determines the rate of 5-HMF formation so it is important to optimize the glucose isomerization to fructose to achieve the biggest 5-HMF production[6].

1.1. GLUCOSE TO FRUCTOSE ISOMERIZATION

The glucose to fructose isomerization is one of the largest biocatalytic processes in the world for the production of high fructose corn syrups (HFCS) in the food industry because of the high sweetening power of the fructose and its low glycemic index[8]. Nowadays, the isomerization also takes place as an intermediate reaction in the production of biofuels from biomass.

The catalysed isomerization mechanism, consists in the transfer of a hydrogen from C2 to C1 and from the hydrogen of the hydroxyl group of C2 to the O in C1 forming a ketone from an aldehyde. The mechanism can be done by a proton transfer or a hydride shift as shown in Figure 4[9].

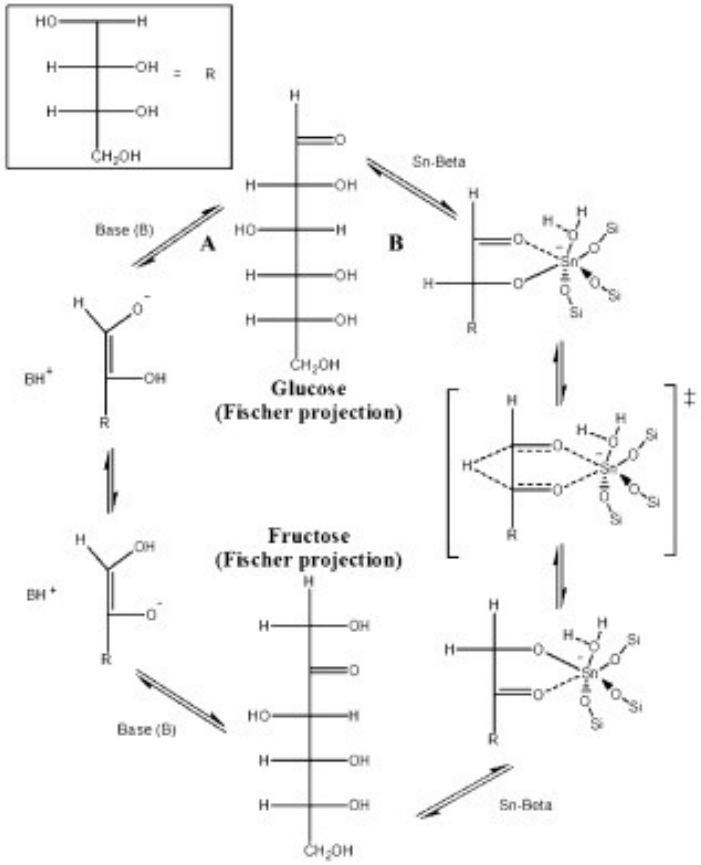

Figure 4. Glucose to fructose isomerization mechanism. Way A is done by a proton transfer and B by a hydride shift[9].

1.2. CATALYSTS

Catalysts are substances that speed up a chemical reaction without being consumed. That increase in the rate of the reaction is caused by the reduction of the activation energy of the reaction (Figure 5).

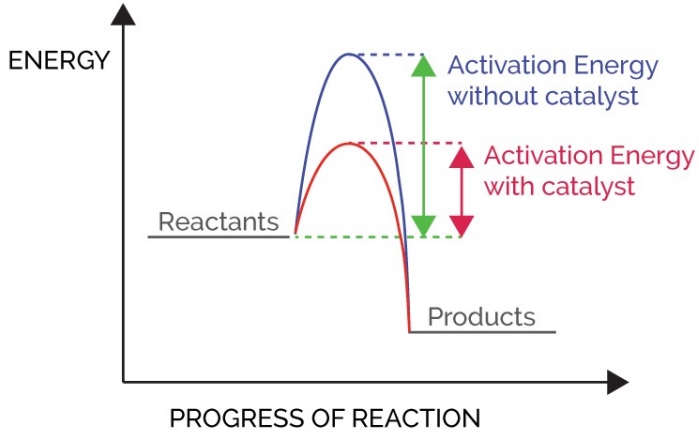

Figure 5. Representation of the different activation energies of a catalysed and non-catalysed chemical reaction.

Nowadays, more than 80% of the industrial chemical processes involve catalysts[10].

Depending of the phase the catalyst is in comparison with the phase of the reactants, catalysts are classified as heterogeneous and homogeneous catalysts. Heterogeneous catalysts are in a different phase than the reactants and homogeneous ones are dispersed in the same phase as the reactants. The most common heterogeneous catalysts are solids that interact with reactants in liquid or gas phase[10].

Homogeneous catalysts tend to be more active and selective than heterogeneous ones but the main advantage of heterogeneous catalysis is the easier separation of the catalysts from the reactants as they are in different phases[11]. For this reason, the glucose to fructose isomerization will be studied using heterogeneous catalysts.

The main steps in the heterogeneous catalysis are:

1. Adsorption of the reactants on the surface of the catalyst.
2. Diffusion of the reactants through the surface of the catalyst.
3. Reaction of the adsorbed reactants.

4. Desorption of the products from the catalyst

The most common heterogeneous catalysts are inorganic solids such as metals, metal salts, oxides and sulphites, but they can also be organic materials such as ion exchange resins, hydroperoxides and supported enzymes[10].

The main physical properties of heterogeneous catalysts are[10]:

- Surface area.
- Porosity. Pores are classified as micropores (pore width < 2nm), mesopores (pore width 2 - 50 nm) and macropores (pore width > 50 nm).
- Dispersion of active particles in the catalyst and particle size.
- Structure.
- Density.

The main chemical properties of heterogeneous catalysts are[10]:

- Chemical composition.
- Valence and bonding states.
- Acidity and basicity.

1.2.1. Ion exchange resins

An organic ion exchange resin is composed of high molecular weight polyelectrolytes that can exchange their mobile ions for other ones with similar charge from the surrounding medium. Each resin has a different number of mobile ion sites that set the maximum quantity of exchanges per unit of resin[12, 13].

While reactions catalysed by classical inorganic catalysts proceed on the interface between solid and fluid phase, the reactions catalysed by ion exchange resins proceed inside the polymer matrix[14].

The most important features of an ideal ion exchange resin are[13]:

- Hydrophilic structure of regular and reproducible form.
- Controlled and effective ion exchange capacity.
- Reversible and rapid rate of ion exchange.
- Chemical stability towards electrolyte solutions.
- Mechanical stability.
- Consistent particle size and effective surface area.

- Thermal stability.

Ion exchange resins are classified depending on the ion they exchange with the solution that surrounds them. If the ions exchanged are positively charged, resins are called cation exchange resins while if the ions are negatively charged, they are called anion exchange resins. Even so, both of them are produced from the same basic organic polymers[12, 13].

Ion exchange resins can behave like strong or weak acids or bases[12, 13, 15]:

- Strong acid cation resins: the chemical behaviour of these resins is similar to strong acids. The functional group of these resins are sulfonic groups ($-SO_3^-$), being highly ionized in the acid ($R-SO_3H$) or the salt ($R-SO_3Na$) form. In Figure 6, it is represented the structure of a strong acid cation resin. The cations exchange capacity of strong acid resins does not depend on the solution pH.

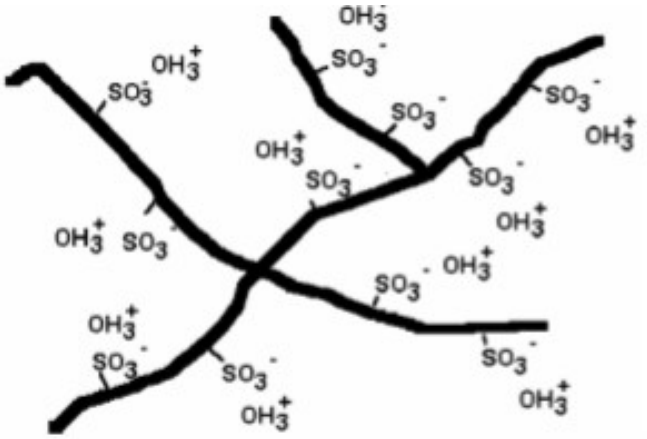

Figure 6. Representation of a strong acid cation exchange resin in aqueous medium[14].

- Strong base anion resins: the chemical behaviour of these resins is similar to strong bases. These resins contain quaternary amines. They can also be used at any pH like strong acid resins.
- Weak acid cation resins: the chemical behaviour of these resins is similar to weak organic acids. The ionisable group is the carboxylate ($-COO^-$). Weak acid resins have a much higher affinity for hydrogen ions than strong acid resins. Unlike the strong

acid reins, the degree of dissociation of these resins highly depends on the pH, making the capacity of the resin very limited below pH of 6.0.

In this category, also exist the heavy metal selective chelating resins. Chemical behaviour of these resins is similar to weak acid cation resins but have a high selectivity for heavy meal cations.

- Weak base anion resins: they behave like weak bases. These resins contain ternary amines. The cation exchange capacity of weak base resins also depends on the pH, limiting it above pH of 7.0.

In this work, the glucose to fructose isomerization is carried out using basic ion exchange resins because the fructose production is higher using basic ion exchange resins than acidic ones[16].

Depending on the differences in the structure of the resins, they can be classified in macroreticular or gel type resins[10, 14, 15].

In the gel type resins, the cross-link bonds are homogenously distributed through the polymer and the size of the voids between the chains of polymers (pores) is very small and constant as represented in Figure 7. The matrix has a pseudo-crystalline structure[10, 14, 15].

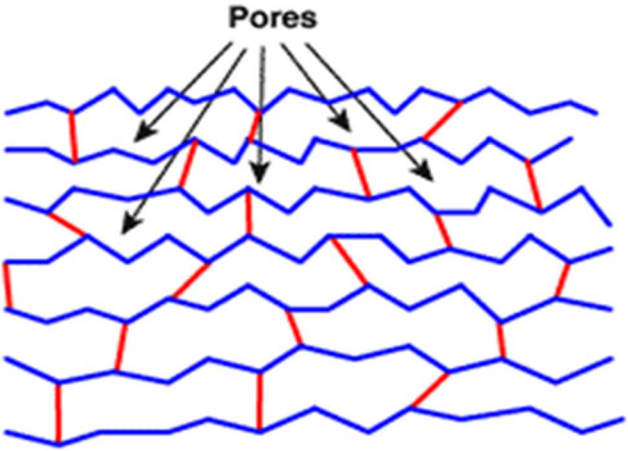

Figure 7. Gel type resins structure[15].

Due to the small size of pores, this type of resins are difficult to activate[10, 14, 15].

Macroreticular resins have been created to overcome this problem. In the making of these resins, a third component (called porogen or phase extender) is incorporated in the reaction

mixture to create larger pores without reacting with the monomers. Once the polymerisation reaction is over, the porogen is washed out leaving voids in the polymer structure called macropores[10, 14, 15] as represented in Figure 8.

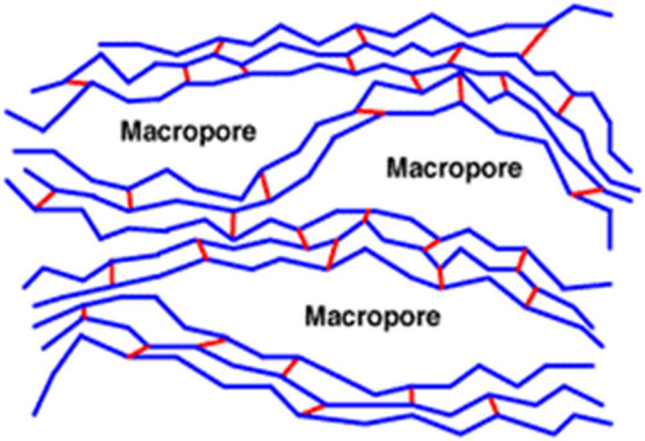

Figure 8. Macroreticular resins structure[15].

Macroreticular resins end up having two types of pores: the small ones of the initial matrix and the macropores. Due to the high amount of cross-link bonds, this type of resins are very stable and due to the large pores, they can exchange larger ions than gel type resins[10, 14, 15].

1.2.2. Enzymes

Enzymes are proteins that act as biological catalysts. The sequence of the amino acids specifies the structure of the enzyme and determines the catalytic activity of it.

The mechanism of action of the enzyme is based on a chemical reaction, in which the enzyme binds to the substrate forming an enzyme-substrate complex. The reaction takes place in the active site of the enzyme. The active site consists of the binding site (amino acid residues that form temporary bonds with the substrate) and the catalytic site (amino acid residues that catalyse the reaction of the substrate to products). During the reaction, the enzyme forms a transition-state complex. Once the products are formed, they disassociate from the enzyme and it returns to its original state[17].

Enzymes have not rigid structures. Instead, the binding of the substrate to the enzyme induces a change in the shape of the enzyme to achieve the proper alignment of the catalytic groups on its surface[17].

Figure 9 shows the process of the enzyme catalytic action mechanism:

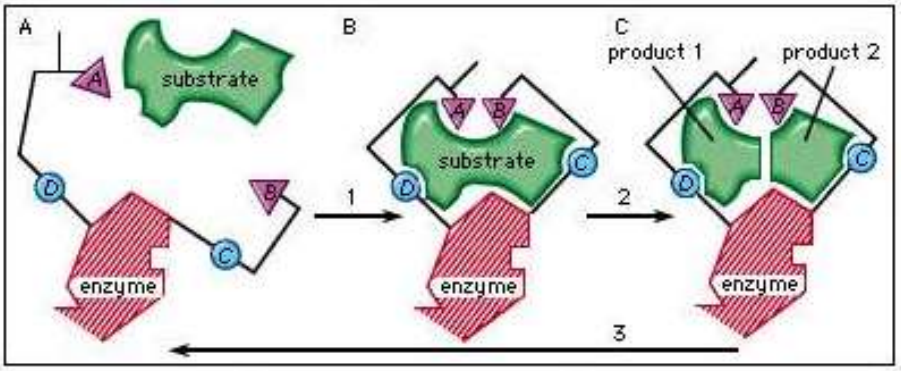

Figure 9. Enzyme catalytic action mechanism. The substrate approaches the surface of the enzyme and binds to it by the binding groups of the enzyme (circles C and D) (step 1). This causes a change in the enzyme shape that results in the proper alignment of the catalytic groups of the enzyme (triangles A and B). The catalytic groups react with the substrate forming the products (step 2). Finally, the products separate from the enzyme and the sequence is repeated (step 3)[18].

The activity of the enzyme is highly decreased by extreme conditions of pH or temperature, so they operate most efficiently under mild conditions[17].

1.2.2.1. Glucose isomerase

Glucose isomerase (GI) is an enzyme that has the ability to isomerize a wide variety of substrates such as pentoses, hexoses, sugar alcohols and sugar phosphates. The most common applications of GI are the catalysis of the isomerization of D-glucose and D-xylose to D-fructose and D-xylulose, respectively, being the most used catalyst for the isomerization of glucose into fructose in the industry. It also can catalyse reactions where the substrates are D-ribose, L-arabinose, L-rhamnose, D-allose or 2-deoxyglucose[19].

GI requires a divalent cation such as Mg^{2+}, Co^{2+}, Mn^{2+} or a combination of these cations for maximum activity. Although Mg^{2+} and Co^{2+} are essential for activity, their roles are different. Co^{2+}

is responsible of the stability of the enzyme by holding the ordered conformation and Mg^{2+} is better than Co^{2+} as an activator[19].

The optimum work temperature of GI is generally between 60 to 80 ºC and the optimum pH ranges between 7.0 and 9.0[19].

2. OBJECTIVES

The main goal of this work is to determine the heterogeneous catalyst that provides the highest production of fructose from glucose to fructose isomerization.

This will be done following the next steps:

- To determine the best basic ion exchange resin for the reaction experimentally, operating under the same conditions.
- To compare the results obtained experimentally with the basic ion exchange resins with the results obtained operating with an enzyme (glucose isomerase) under the same conditions in another study.
- To compare the results obtained experimentally with the basic ion exchange resins with the results obtained with other catalysts used in other studies from the available scientific literature.

3. EXPERIMENTAL

3.1. CHEMICALS AND CATALYSTS

The glucose isomerization experiments were done using α-D-glucose (anhydrous 96%) diluted in Millipore water. Glucose was supplied by Sigma-Aldrich Corporation.

The basic resin catalysts used were Amberlyst 21 (A-21), Amberlyst 26(OH^-) (A-26) and Purolite CTA196 (Purolite). Amberlyst resins were supplied by Dow Chemical Company while Purolite resin was supplied by Purolite Company.

Table 1 shows the main properties of the employed catalysts:

Table 1. Properties of the catalysts used in the experiments.

Catalyst	**A-21**	**A-26**	**Purolite**
Type	Macroreticular	Macroreticular	Macroreticular
Ionic form	Free base	Hydroxide (OH^-)	Free Base
Shipping weight (g/L)	660	675	655-685
Base capacity (eq/L)	1.30	0.80	1.80
Particle size (μm)	490-690	560-700	425-1200
Moisture (%)	56-62	66-75	45-52
T_{max} (ºC)	100	60	60
Pore diameter (Å)	110	290	
Surface area (m2/g)	35	30	
Pore volume (mL/g)	0.10	0.20	

For the HPLC analysis (calibration curves included), the employed substances were α-D-glucose (anhydrous 96%) and D-Fructose (99%) diluted in Millipore Water, H_2SO_4 0.05 M and

ethanol. Glucose and fructose were supplied by Sigma-Aldrich while sulphuric acid and ethanol were supplied by Fischer Chemicals.

3.2. EXPERIMENTAL SETUP

The installation used for the experiments consisted of a batch reactor to carry out the glucose to fructose isomerization and a High Performance Liquid Chromatograph (HPLC) to analyse the samples.

The batch reactor installation (Figure 10) was composed of:

- 100 mL stainless steel cylindrical tank.
- 4 helix agitation system.
- Sampling filter.
- Electrical heat exchanger jacket.
- Thermocouple.
- Pressure gauge.
- PID controller for the temperature inside the reactor and the agitation system.
- Relief valve.
- Rupture disc (breaks at a pressure of 300 bar).
- Catalyst injector.
- Nitrogen injector.
- Sampling valve.

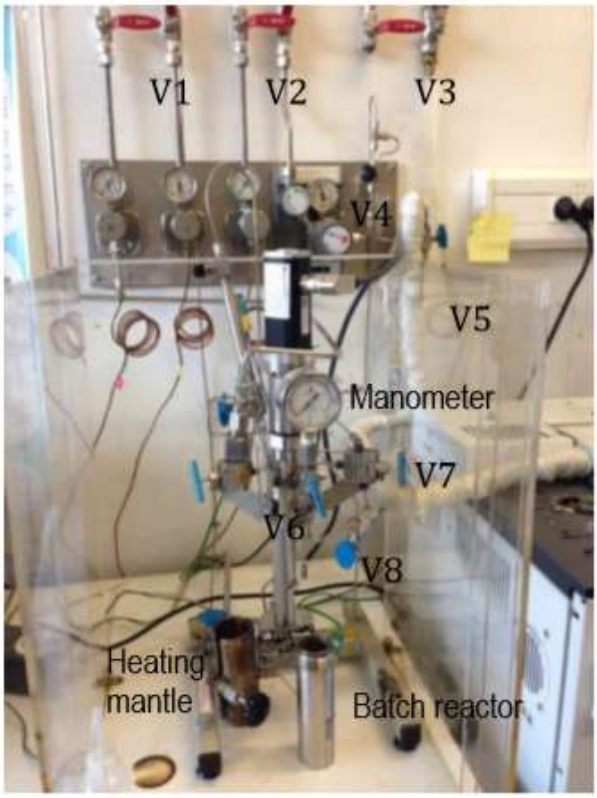

Figure 10. Batch reactor setup[16].

The HPLC installation carried out the analysis using a column (Agilent Hi-Plex H) with a Refractive Index Detector (RID).

3.3. EXPERIMENTAL PROCEDURE

3.3.1. Preparation of the glucose solution and catalysts

24 hours before the experiment was carried out, the catalyst was introduced in the oven at 100 ºC to remove the water. Due to the loss of weigh in the oven, the mass of catalyst introduced in it was approximately 3 times of the mass needed for the experiment (5 g).

For safety reasons, the volume of the solution introduced into the reactor should not exceed 70% of reactor capacity.

For the preparation of 70 mL of glucose solution 0.5 M, the mass of glucose needed is calculated as:

$$70\ mL \cdot \frac{1L}{1000\ mL} \cdot \frac{0.5\ mol}{1\ L} \cdot \frac{180.156\ g}{1\ mol} = 6.0355\ g\ glucose$$

For the glucose solution preparation, 6.3055 g of glucose were weighed using an analytical balance (0.1 mg precision) and introduced in a 100 mL graduated cylinder. Then, Millipore water was added into the graduated cylinder until the 70 mL mark. Finally, the mixture was shaken until all the glucose was dissolved.

Once the solution was prepared, the catalyst was removed from the oven.

3.3.2. Experiment launching and sampling

First of all, the glucose solution and the dried catalyst were introduced in the reactor and it was coupled to the installation. Then, the agitation (500 rpm) and temperature were set using the PID controller. For reaching the desired temperature, the heat exchanger jacket temperature was set at 10ºC above the desired temperature of the reactor.

Once the temperature of the reactor reached the desired one, experimental time started. The samples were taken at initial time, 30 min, 1 h and every hour from that point up to 6 hours and they were kept in the fridge at 4 ºC.

Sampling procedure steps:

1. Open the valve V7.
2. Put the valve V8 downwards and take the sample in a vial.
3. Put the valve V8 upwards.
4. Put the valve V5 downwards.
5. Reduce the reactor pressure about 5 bar opening the valve V6.
6. Close the valve V7.
7. Depressurize the valve V8.
8. Put the valve V5 upwards.
9. Pressurize the reactor opening the valve V4.

10. Close the valve V4.

Once the experiment was finished, the agitation and the temperature were switched off.

3.3.3. Reactor cleanup

After finishing the experiment, the heat exchanger jacket was removed from the reactor and it was left to cool to 50 ºC approximately to be able to disassemble it.

The remaining mixture inside the reactor was filtered with filter paper to separate the catalyst from the solution.

The filter was washed with deionized water and dried with pressurized air.

The reactor was washed with water and soap and then it was coupled, full of deionized water, to the reactor installation and the sampling procedure was done to clean the sampling pipes.

Finally the reactor was uncoupled and dried with pressurized air.

3.3.4. Sample analysis

The samples were analysed with a High Performance Liquid Chromatography.

For the analysis, the flow rate of the installation was set at 0.6 mL/min. The flow rate was increased from 0.1 mL/min to 0.6 mL/min, increasing it 0.1 mL/min every 3 minutes. Once it reached 0.6 mL/min, it was stabilized for 30 min before starting the analysis to stabilize the refractive index baseline.

Also, the temperature of the column was set at 60 ºC and the refractive index detector (RID) at 50 ºC.

For the correct analysis of the samples, they had to be in a 1:50 dilution. It was done introducing 1 mL of the sample in a 50 mL volumetric flask and adding Millipore water up to the 50 mL mark. Also, they had to be filtered with a filter (0.2 µm diameter of pore) to prevent obstructions in the HPLC column.

The samples volume introduced into the HPLC was 20 µL and the analysis lasted 15 min.

Once the analysis was finished, the results were shown in the computer as in Figure 11:

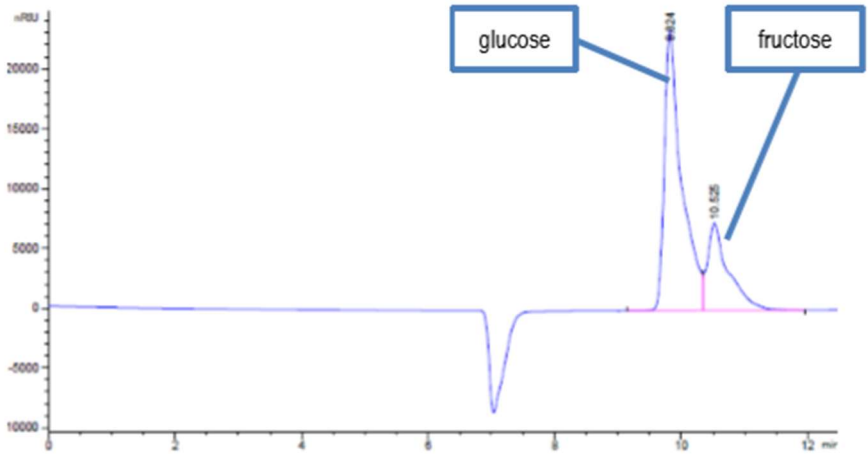

Figure 11. Example of the results of a sample analysis[16].

Each substance spends a certain time in the HPLC column depending on its chemical composition. This time is called retention time. According with the results obtained, glucose retention time is (9.966 ± 0.006) min and fructose retention time is (10.641 ± 0.006). So, the first curve in Figure 11 shows the glucose concentration in the sample while the second one shows the fructose concentration.

Once all the samples were analysed for that day, the HPLC flow rate had to be set at 0.1 mL/min decreasing it 0.1 mL/min every 3 min.

3.4. EXPERIMENTAL CONDITIONS

The original idea of this work was to make an extensive study of the reaction of glucose to fructose isomerization catalysed by multiple heterogeneous catalysts at different experimental conditions such as different operating temperatures and different catalyst/glucose ratios. Finally, the results obtained were going to be compared with the results from another TFG (Solà Mas, S. Glucose Isomerization by Enzymes. TFG. Publicacions i Edicions de la Universitat de Barcelona, Barcelona, 2020, ref. 20) operating with glucose isomerase as catalyst.

Due to the exceptional situation caused by the virus SARS-CoV-2, only a few of these experiments were carried out.

Experiments were carried out at 30 bar (to avoid water evaporation) and at 500 rpm of stirring rate. The initial glucose concentration was 0.5 M and the catalyst mass was 5 g (0.83 catalyst/glucose mass ratio).

The different experimental conditions are shown in Table 2:

Table 2. Experimental conditions.

Experiment	Catalyst	Temperature (ºC)
1	Amberlyst 21	80
2	Amberlyst 26(OH^-)	80
3	Purolite CTA196	80
4	Amberlyst 21	90

All the experiments were replicated twice but, due to the situation caused by the virus, only the repetition of the experiment 2 could be analysed.

3.5. CALCULATIONS

Glucose and fructose concentrations were determined with the area below the curves obtained in the HPLC analysis using the following equations (for details, look at Appendix 1):

$$glucose\ concentration\ \left(\frac{mg}{mL}\right) = 4 \cdot 10^{-6} \cdot glucose\ area - 0.0114 \quad (1)$$

$$fructose\ concentration\ \left(\frac{mg}{mL}\right) = 3.456 \cdot 10^{-6} \cdot fructose\ area - 0.004 \quad (2)$$

Then, those concentration values were multiplied by 50 because the samples analysed were in a 1:50 dilution and divided by the molar mass of glucose or fructose (180.156 g/mol) to obtain the concentrations expressed in mol/L.

Glucose conversion, fructose yield and fructose selectivity were obtained with the following expressions:

$$glucose\ conversion\ (\%) = \frac{mol\ of\ glucose\ reacted}{initial\ mol\ of\ glucose} \cdot 100 \quad (3)$$

$$fructose\ yield\ (\%) = \frac{mol\ of\ fructose\ produced}{initial\ mol\ of\ glucose} \cdot 100 \quad (4)$$

$$fructose\ selectivity\ (\%) = \frac{mol\ of\ fructose\ produced}{mol\ of\ glucose\ reacted} \cdot 100 \quad (5)$$

4. RESULTS

4.1. EXPERIMENTAL ERROR EVALUATION

As all the samples were analysed twice and experiment 2 was replicated (as previously commented in "Experimental conditions"), experimental error has been determined.

Errors related to the repetition of the sample analysis are separated from the ones related to the replication of experiments.

Figure 12 and Figure 13 show the different results obtained for the repetition of the analysis of the same samples for the experiments carried out at 80 ºC with Amberlyst 21 and Amberlyst 26(OH^-) as catalysts.

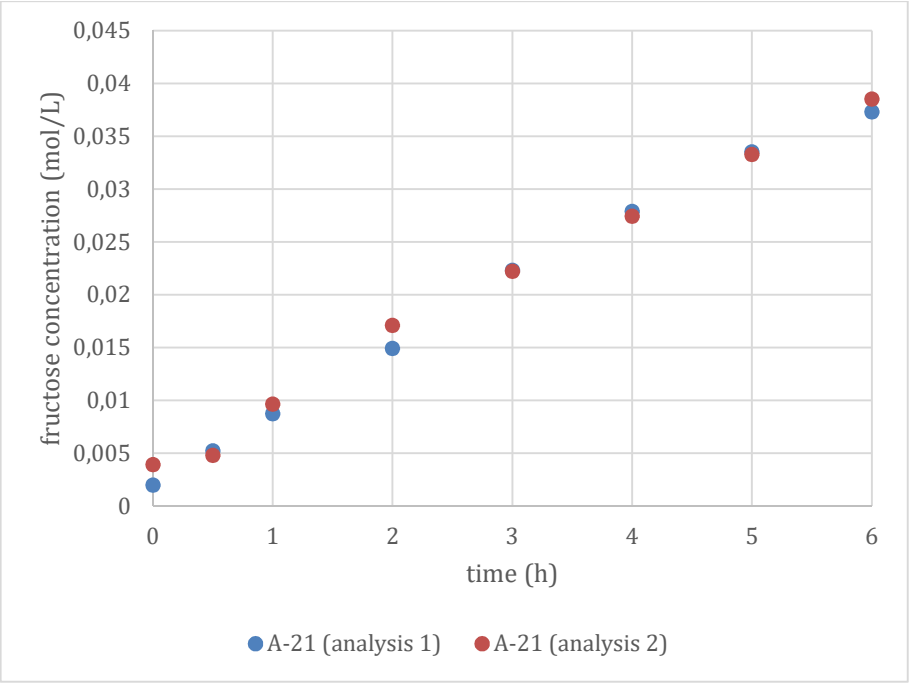

Figure 12. Evolution of fructose concentration using Amberlyst 21 (experimental conditions: 80 ºC, 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

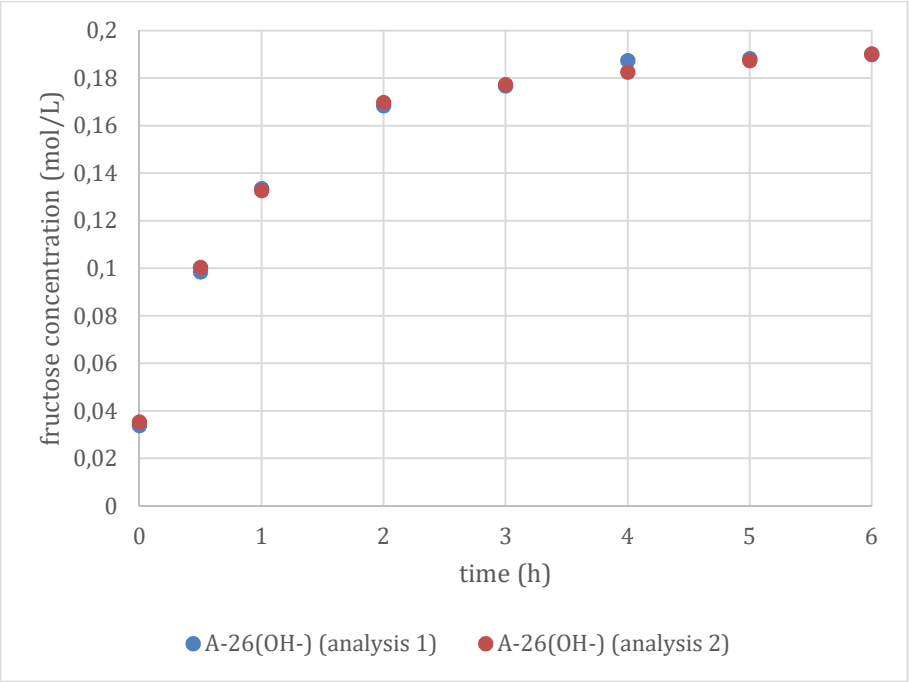

Figure 13. Evolution of fructose concentration using Amberlyst 26(OH^-) (experimental conditions: 80 ºC, 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

As seen, the analytical method is reproducible since the difference between injections is very low.

Figure 14 and Figure 15 show the results obtained for the two experiments carried out at the same conditions with Amberlyst 26(OH^-).

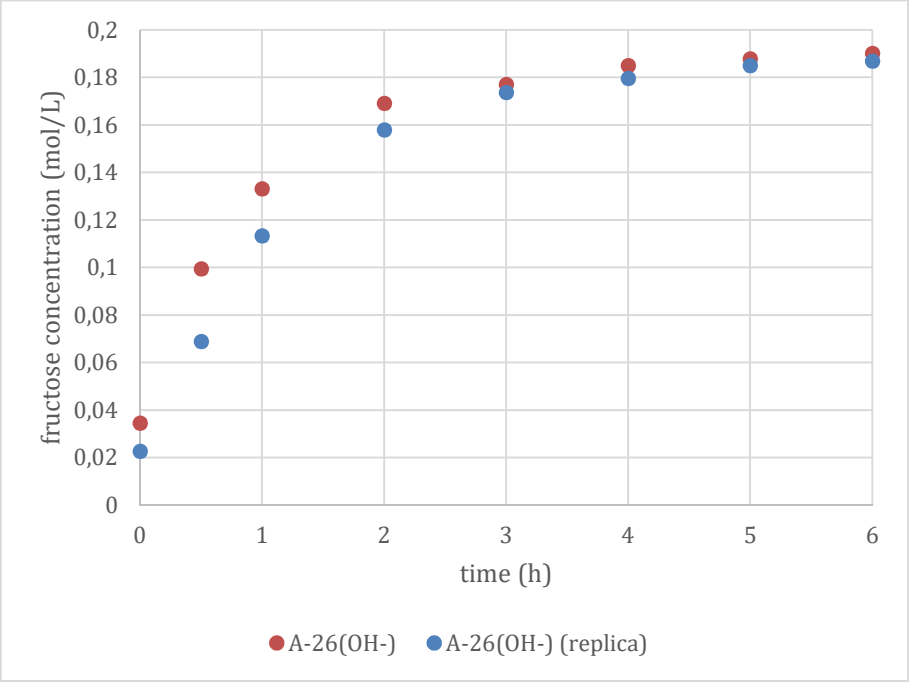

Figure 14. Evolution of fructose concentrations using Amberlyst 26(OH^-) (experimental conditions: 80 ºC, 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

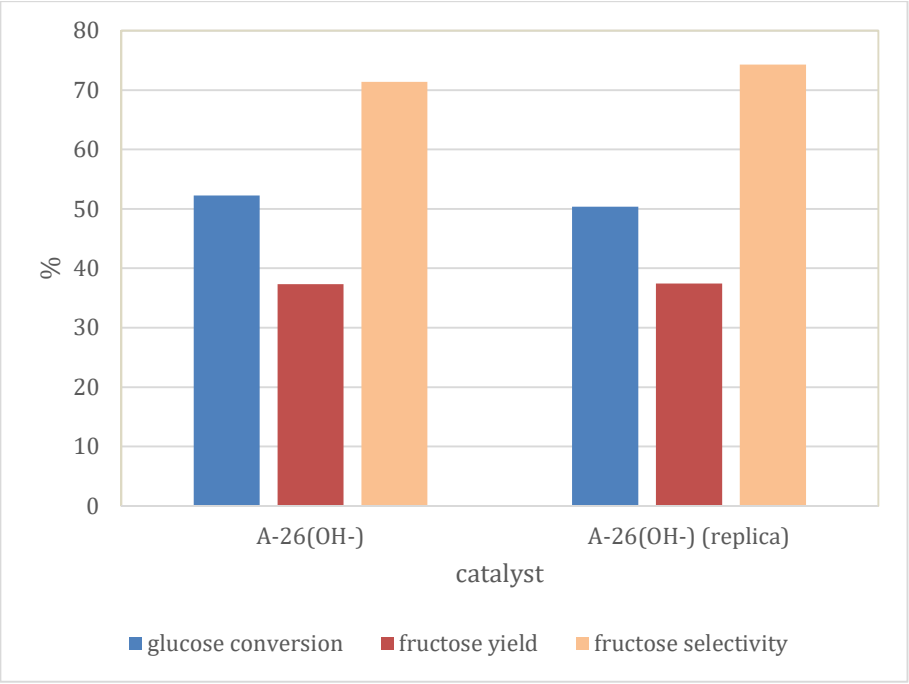

Figure 15. Glucose conversion, fructose yield and fructose selectivity obtained at 6 h using Amberlyst 26(OH^-) (experimental conditions: 80 ºC, 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

The average glucose conversion, fructose yield and fructose selectivity, with its associated errors, obtained from the replication of the experiments with A-26 are: (51.32 ± 1.33) %, (37.37 ± 0.08) % and (72.84 ± 2.06) %, respectively. These errors will be assumed for the other experiments as this is the only experiment which its replica could be analysed.

In the figures shown in the following sections, only the errors related with the repetition of the sample analysis will be represented and the errors associated with the replication of the experiments will be commented below the graphics.

4.2. COMPARISON OF VARIOUS BASIC ION EXCHANGE RESINS

The evolution of fructose concentration obtained for every experiment at 80 ºC are shown in Figure 16. Fructose obtained using the resin Amberlyst 26(OH^-) is clearly higher than that obtained with the other catalysts.

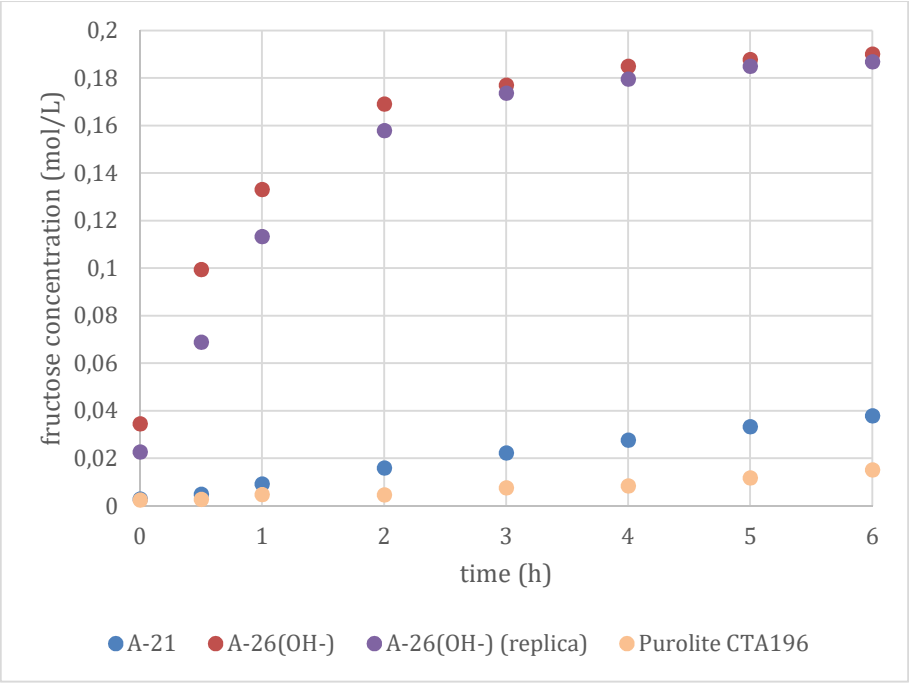

Figure 16. Evolution of fructose concentrations using different basic ion exchange resins (experimental conditions: 80 ºC, 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

The equilibrium of the reaction depends on the operating temperature. It is achieved at 60 ºC when, approximately, the final fructose concentration is 45 % of the initial glucose concentration. At 90 ºC, the final fructose concentration is 55 % of the initial glucose concentration[21]. The isomerization seems to be close to the equilibrium when A-26 is used as the last variations of fructose concentrations are quite small and final fructose concentration is (0.19 ± 0.01) mol/L, 38 % of the initial glucose concentration. Instead, equilibrium is not reached using A-21 or Purolite as fructose concentrations follow a linear tendency and final fructose concentrations in those experiments are far from final glucose concentrations.

Figure 17 shows glucose conversion, fructose yield and fructose selectivity at 6h for the experiments carried out at 80 ºC.

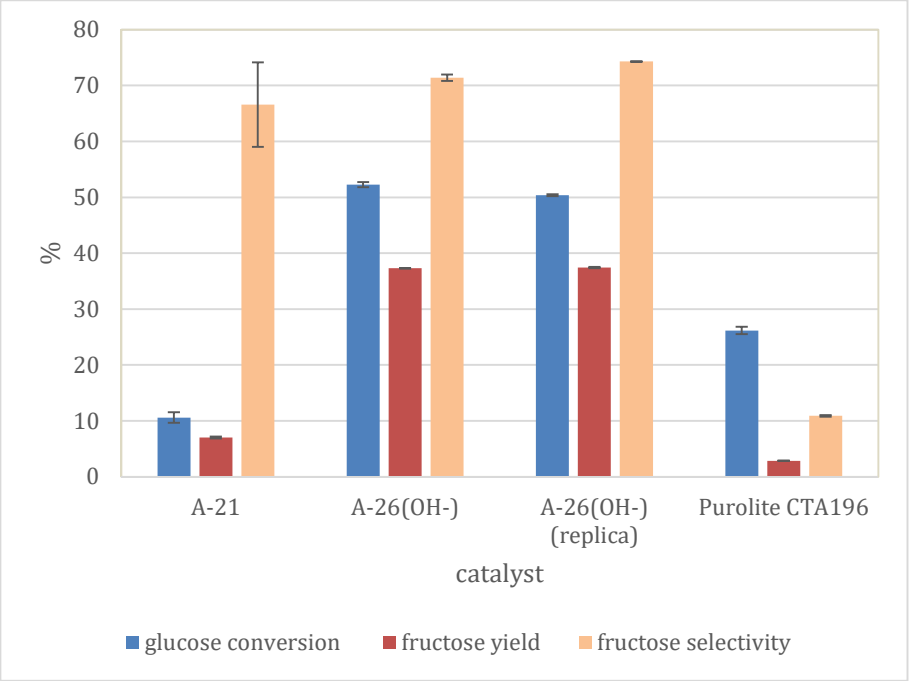

Figure 17. Glucose conversion, fructose yield and fructose selectivity obtained at 6 h for every catalyst used (experimental conditions: 80 ºC, 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

The three parameters are higher using Amberlyst 26(OH^-): (51.32 ± 1.33) % glucose conversion, (37.37 ± 0.08) % fructose yield and (72.84 ± 2.06) % fructose selectivity. This could be explained because A-26 has larger pore diameter and pore volume despite having lower base capacity than the other two catalysts. It could imply that glucose molecules have a better access into the resin.

For the other two catalysts, glucose conversion is higher working with Purolite CTA196 (26.17 ± 1.33 %), while fructose yield and fructose selectivity are higher using A-21 (7.01 ± 0.08 % and 66.57 ± 2.06 %, respectively).

Although fructose selectivity is below 100 %, no other products were detected in the analysis. One hypothesis to explain that is the formation of polymers from glucose and fructose that kept retained in the resins instead of the solution.

4.2.1. Effect of the operating temperature

Figure 18 shows the evolution of fructose concentrations at different temperatures using A-21 as catalyst. More fructose is produced operating at 90 ºC than 80ºC as it was expected.

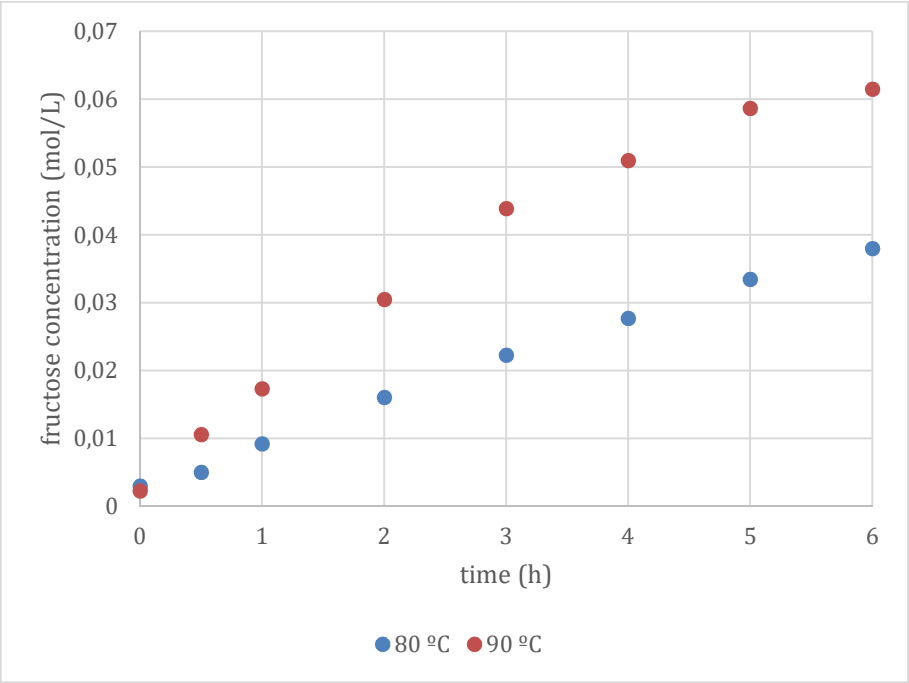

Figure 18. Evolution of fructose concentrations using A-21 at 80 ºC and 90 ºC (experimental conditions: 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

In Figure 19, there are shown glucose conversion, fructose yield and fructose selectivity at 6 h for the experiments carried out at 80 ºC and 90 ºC using A-21. The three parameters are higher operating at 90 ºC.

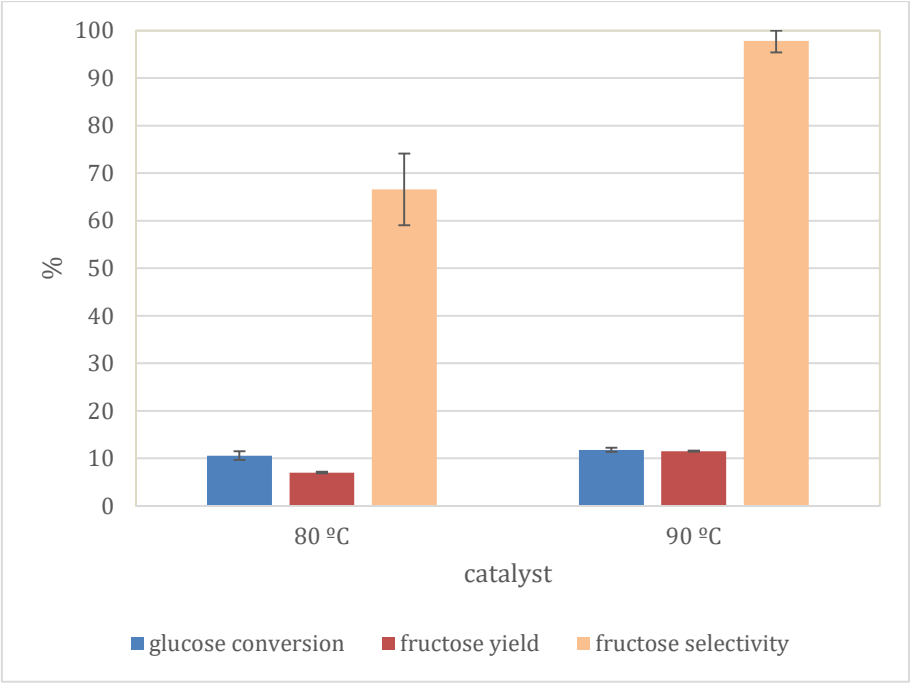

Figure 19. Glucose conversion, fructose yield and fructose selectivity obtained at 6 h using A-21 as catalyst and operating at 80 ºC and 90 ºC (experimental conditions: 30 bar, 500 rpm, initial glucose concentration of 0.5 M, catalyst mass of 5g).

Glucose conversion, fructose yield and fructose selectivity increases from operating at 90 ºC instead of 80 ºC are 11.38 %, 64.43 % and 46.97 %, respectively. However, these increases cannot be assumed the same for the isomerizations using A-26 and Purolite because its maximum operating temperature is 60 ºC and increasing the temperature from 80 ºC to 90 ºC would reduce the stability of the resins.

4.3. COMPARISON OF THE STUDIED BASIC ION EXCHANGE RESINS WITH GLUCOSE ISOMERASE

In this part, the results obtained experimentally with basic ion exchange resins are compared with the ones obtained in the TFG: Solà Mas, S. Glucose Isomerization by Enzymes. TFG. Publicacions i Edicions de la Universitat de Barcelona, Barcelona, 2020, ref. 20.

The glucose isomerase particles used in that study had cylindrical shape, 0.2 - 0.4 mm of diameter, 1 - 1.5 mm of length and the particle density was 3300 kg/m^3. The microorganism to immobilize the glucose isomerase used in the study is a selected strain of *Streptomyces Murinus*.

The experiments done in that study were carried out at atmospheric pressure, temperature between 60 ºC and 90 ºC and pH between 6.6 and 9.6, using Na_2CO_3. $MgSO_4 \cdot 7H_2O$ was used for the activation and stabilization of the glucose isomerase. For all the experiments, the concentration of glucose in the initial solution was 0.5 M.

The highest final fructose concentration and glucose conversion were obtained operating at 90 ºC and a pH of 9.6, with approximately 0.21 mol/L of fructose concentration and 42 % of glucose conversion after 225 minutes. Also, good results were obtained operating in the following conditions:

- 80 ºC and pH of 8.6, obtaining 0.15 mol/L of fructose concentration and 30 % of glucose conversion after 225 minutes.
- 70 ºC and pH of 8.6, obtaining 0.15 mol/L of fructose concentration and 30 % of glucose conversion after 225 minutes.
- 80 ºC and pH of 7.6, obtaining 0.14 mol/L of fructose concentration and 27 % of glucose conversion after 225 minutes.
- 60 ºC and pH of 9.6, obtaining 0.12 mol/L of fructose concentration and 29 % of glucose conversion after 225 minutes.

Even if the best fructose production was obtained at a high temperature and a high pH, the stability under these conditions was not good. So, glucose isomerase could not be reused[20].

Looking at Figure 16, the maximum fructose concentration obtained in our study at 225 min was operating with A-26 at 80 ºC and it was about 0.18 mol/L. Glucose conversion obtained in these conditions reached a value around 45 % at 225 min.

Although glucose conversion is higher using A-26 instead of glucose isomerase and the final fructose concentration is also slightly higher (except in the experiment carried out at 90 ºC and 9.6 of pH with GI), the catalyst mass was much higher using A-26 (5 g) than GI (1 g). This seems to indicate that, with the same catalyst mass, the usage of glucose isomerase as catalyst implies a higher glucose conversion and a higher final fructose concentration, working at the same conditions, than A-26. The main disadvantage of GI is that it is much more expensive than A-26.

4.4. COMPARISON OF THE STUDIED BASIC ION EXCHANGE RESINS WITH OTHER HETEROGENEOUS CATALYSTS

The scientific papers related to glucose isomerization used in this section are:

1. Pérez-Maqueda, J.; Arenas-Ligioiz, I.; López, O.; Fernández-Bolaños, J. Eco-friendly preparation of 5-hydroxymethylfurfural from sucrose using ion-exchange resins. Chemical Engineering Science, 2014, 109, 244-250, ref. 22.
2. Souzanchi, S.; Nazari, L.; Rao, K.; Yuan, Z.; Tan, Z.; Xu, C. Catalytic isomerization of glucose to fructose using heterogeneous solid Base catalysts in a continuous-flow tubular reactor: Catalyst screening study. Catalysis Today, 2019, 319, 76-83, ref. 23.
3. Marianou, A.; Michailof, C.; Ipsakis, D.; Karakoulia, S.; Kalogiannis, K.; Yiannoulakis, H.; Triantafyllidis, K.; Lappas, A. Isomerization of Glucose into Fructose over Natural and Synthetic MgO Catalysts. ACS Sustainable Chem. Eng., 2018, 6, 16459−16470, ref. 24.
4. Moliner, M.; Román-Leshkov, Y.; Davis, M. Tin-containing zeolites are highly active catalysts for the isomerization of glucose in water. PNAS, 2010, 107, 14, 6164-6168, ref. 25.
5. Chen, S.; Tsang, D.; Tessonnier, J. Comparative investigation of homogeneous and heterogeneous Brønsted base catalysts for the isomerization of glucose to fructose in aqueous media. Applied Catalysis B: Environmental, 2020, 261, 118-126, ref. 26.

The maximum glucose conversion achieved in study 1 was 52 % using DIPEA as catalyst, working in an aqueous solution in a proportion of 1.45 equiv. catalyst/equiv. glucose at 70 ºC for 72 h. Fructose selectivity achieved in this experiment was 85 %. However, DIPEA is a homogeneous catalyst. The maximum fructose selectivity was achieved operating in an aqueous solution using Amberlite IRA400(OH^-) in a proportion of 0.19 equiv. catalyst/equiv. glucose at 70 ºC for 20 h. Glucose conversion achieved in this experiment was only 4 %. Nevertheless, high glucose conversions and fructose selectivity values were achieved using Amberlite IRA400(OH^-) at higher catalyst/glucose proportions.

In study 2, experiments were performed in a continuous-flow tubular reactor at 100 ºC with an initial glucose concentration of 100 mg/mL (aqueous solution), 4 g catalyst loading and a

feeding flow rate of 0.5 mL/min. The samples were taken 2 hours after reaching the steady state condition. The highest glucose conversion and fructose yield (36.3 % and 22.8 %, respectively) were obtained using MgO as catalyst, while highest fructose selectivity (78.1 %) was achieved using HT-C-R (calcined-rehydrated hydrotalcite).

Among all MgO catalysts tested in study 3, the natural industrial sample of high purity (∼1 wt % SiO2 and CaO), small crystal size (19.5 nm), moderate surface area (63 m^2/g) and relatively low ratio of strong to weak/medium basic sites, was the most efficient and selective catalyst toward fructose, achieving a fructose selectivity of 75.81 %, a high glucose conversion (44.02 %) and a fructose yield of 33.37 %. The MgO catalyst that achieved the highest value of glucose conversion (62.38 %) was the one with a purity of approximately 5 wt % SiO2 and 2.5 wt % CaO, high crystal size (42.9 nm), small surface area (20 m^2/g) and a low ratio of strong to weak/medium basic sites. This catalyst was also the least selective towards fructose (41.76 % fructose selectivity). This results were achieved working with an aqueous solution of 4 wt % glucose and a catalyst/glucose mass ratio of 1/8 for 45 min at 90 ºC.

In study 4, the catalyst which achieved the highest glucose conversion (over 80 %) was Sn-Beta zeolite with a fructose selectivity around 30 %. The highest fructose selectivity was reached operating with Ti-Beta zeolite with a value of 45 % approximately and a glucose conversion near 50 %. This results were obtained working with an aqueous solution of 10 wt % glucose and a metal/glucose ratio of 1/50 for 90 min at 140 ºC.

To determine the catalyst which reaches the maximum fructose yield, reactions performed with the same conditions of reactants were performed. The highest fructose yields were achieved operating with Sn-Beta as seen in Table 3.

Table 3. Experimental conditions and highest fructose yields obtained in study 4.

Catalyst	Temperature (ºC)	Time (min)	Fructose yield (wt/wt %)
Sn-Beta	110	30	32
Sn-Beta	140	12	30
Sn-Beta/HCl (pH = 2)	110	30	33

Experiments at study 5 were carried out with 10 wt/wt % glucose/deuterium oxide and 12 mol% N relative to glucose of catalyst at 100 ºC for 30 min. Among the various catalysts used in this study, the highest glucose conversion (69 %) was achieved using Amberlyst-26, obtaining

values of 23 % of fructose selectivity and 16 % of fructose yield. The maximum fructose selectivity was obtained working with $Mg(OH)_2$, reaching a value of 99 %. Glucose conversion and fructose yield values obtained were low (15 % both). Meglumine achieved the highest fructose yield (35 %) and it also obtained high values of glucose conversion (40 %) and fructose selectivity (87 %) in comparison with the other catalyst tested.

As seen in these studies, even if the experimental conditions are different in all the experiments, the catalysts that show high effectiveness towards the production of fructose from glucose are DIPEA (homogeneous catalyst), Amberlite IRA400(OH^-), MgOs, Sn-Beta zeolite, A-26 (as in our study) and meglumine. To determine which one is the most effective catalyst under specific conditions, there should be done experiments at the same experimental conditions with each one of these catalysts.

5. CONCLUSIONS

Among the three basic ion exchange resins used as catalysts in this study, Amberlyst 26(OH^-) is the one that provided higher glucose conversion, fructose yield and fructose selectivity, obtaining values of (51.32 ± 1.33) %, (37.37 ± 0.08) % and (72.84 ± 2.06) %, respectively and a final fructose concentration of (0.19 ± 0.01) mol/L, from an initial glucose concentration of 0.5 mol/L. This higher values could be explained by the fact that A-26 has larger pore diameter and pore volume, giving better access to the glucose molecules into the resin, despite having lower base capacity than the other two catalysts.

Between Amberlyst 21 and Purolite CTA196, higher glucose conversion was obtained using Purolite (26.17 ± 1.33 %), while higher fructose yield (7.01 ± 0.08 %) and fructose selectivity (66.57 ± 2.06 %) were obtained using A-21.

The increase of the operating temperature from 80 ºC to 90 ºC led to the increases of glucose conversion, fructose yield and fructose selectivity of 11.38 %, 64.43 % and 46.97 %, respectively.

Results consulted for the glucose to fructose isomerization using glucose isomerase as catalyst (Solà Mas, S. Glucose Isomerization by Enzymes. TFG. Publicacions i Edicions de la Universitat de Barcelona, Barcelona, 2020, ref. 20) showed a maximum glucose conversion of 42 % and a final fructose concentration of 21 mol/L operating with 1 g of GI at 90 ºC and pH of 9.6 for 225 min. Other experimental conditions for the reaction using GI, without the problem of the low stability of the enzyme as in the conditions previously cited, resulted in slightly lower values of glucose conversion and fructose concentration in comparison with the ones obtained with A-26 in our study for the same reaction time (225 min). However, the results obtained with the usage of GI, were operating with 1 g of enzyme while the results obtained with A-26 were achieved using 5 g of resin. If the catalyst masses were the same, better results would be obtained using glucose isomerase as catalyst. The main disadvantage of glucose isomerase is its high price in comparison with Amberlyst 26(OH^-).

For the studies consulted from the available scientific literature, the heterogeneous catalysts that showed high effectiveness towards the production of fructose from glucose are: Amberlite IRA400(OH^-), MgO, Sn-Beta zeolite, A-26 (as in our study) and meglumine. All these experiments

were carried out at different conditions such as different catalyst/glucose ratio, temperature, experimental time, etc. There should be done experiments at the same conditions for each one of these catalysts to determine which one is the most effective for the production of fructose from glucose under specific conditions.

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ACRONYMS

5-HMF 5-Hydroxymethilfurfural

MOF Metal-organic framework

HFCS High fructose corn syrups

-SO_3^- Sulfonic group

-COO^- Carboxylate group

GI Glucose isomerase

A-21 Amberlyst 21

A-26 Amberlyst 26(OH^-)

Purolite Purolite CTA196

T_{max} Maximum operating temperature

HPLC High Performance Liquid Chromatograph

RID Refractive Index Detector

HT-C-R Calcinated-rehydrated hydrotalcite

APPENDICES

APPENDIX 1: CALIBRATION

To link the areas below the curves obtained in the HPLC analysis with the concentrations of glucose and fructose of the samples, solutions of glucose and fructose of known concentrations have to be prepared and analysed using the HPLC.

Due to the situation caused by the virus SARS-CoV-2, these solutions could not be prepared so the calibration is taken from another TFG (Dupuy Pol, C. Glucose isomerization reaction to fructose by means of ion-exchange resins. TFG. Publicacions i Edicions de la Universitat de Barcelona, Barcelona, 2017, ref. 16).

The calibration curves are showed in Figure 20 and Figure 21:

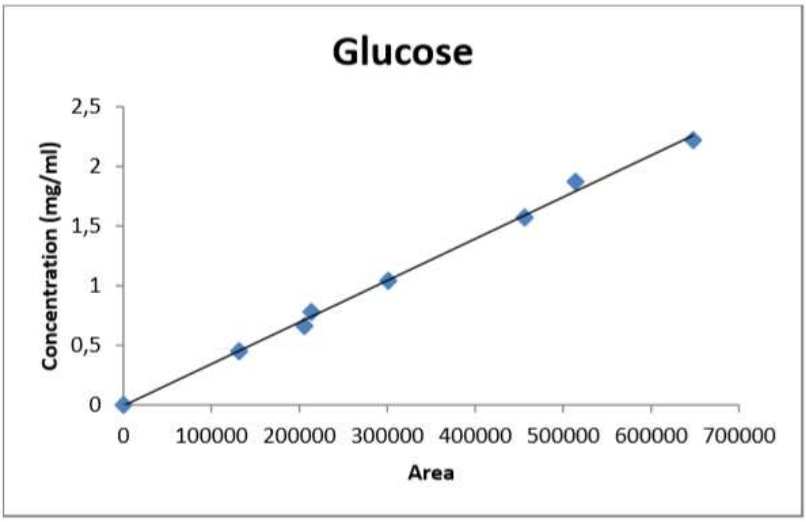

Figure 20. Glucose calibration curve[16].

The equation obtained is:

$$glucose\ concentration\ \left(\frac{mg}{mL}\right) = 4 \cdot 10^{-6} \cdot glucose\ area - 0.0114 \quad (1)$$

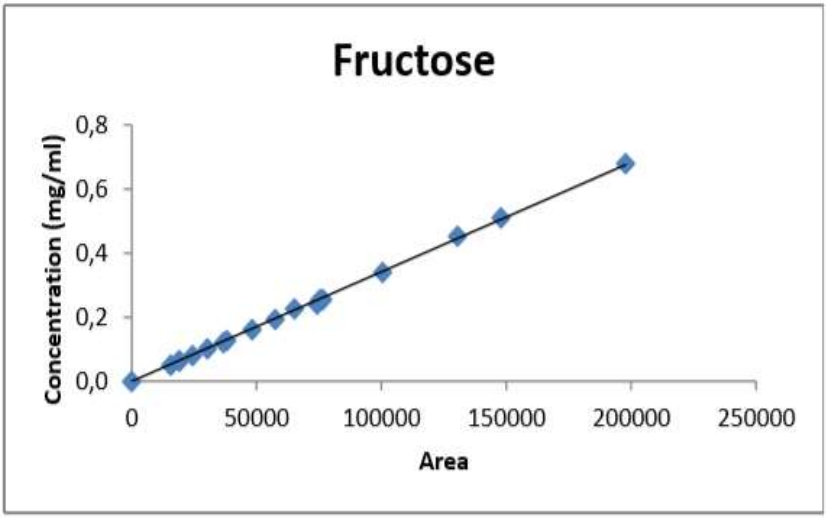

Figure 21. Fructose calibration curve[16].

The equation obtained is:

$$fructose\ concentration\ \left(\frac{mg}{mL}\right) = 3.456 \cdot 10^{-6} \cdot fructose\ area - 0.004 \quad (2)$$