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Production of isosorbide from biomass as a substitute for bisphenol A.

Producción de isosorbida a partir de la biomasa como sustituto del bisfenol A.

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REPORT

Contents

1. SUMMARY

In order to meet the sustainability criteria demanded by today's society and industry, it is necessary to work with eco-efficient processes, i.e. "producing more with less", in a way that promotes better management of resources and energy while minimising environmental impacts. Hence the importance of the term "biomass".

Meeting the growing needs of plastic production while improving sustainability has been a major focus of academic and industrial research. Creating a new generation of sustainable biomass-derived materials as competitive alternatives to petroleum-based plastics can be challenging due to the need for these new materials to match both the performance and cost-effectiveness of commonly used petroplastics.

This work aims to cover the most relevant catalytic strategies designed for the conversion of sorbitol, a biomass-derived platform molecule, to isosorbide. Thus, it is shown which is the best pretreatment to separate the lignocellulosic biomass, the subsequent hydrolysis of cellulose to glucose (or other C_6 sugars), how from this sugar sorbitol is obtained and how from this sugar the isosorbide molecule is obtained.

Isosorbide has been shown to be a good substitute for bisphenol A, as it is a molecule with very similar characteristics but is less toxic to human health and the environment

2. BIOMASS, AN ALTERNATIVE RAW MATERIAL

Biomass was the most important energy source for mankind until the Industrial Revolution when it was massively replaced by fossil fuels. Until this stage, the energy use of this source was developed through the direct combustion of biomass. In recent decades, due to the problems presented by the global energy landscape, there has been a resurgence of interest in this renewable raw material and increasingly efficient, reliable and cleaner biomass utilization systems have been developed, which has caused industries to begin to consider this energy source as an alternative to fossil fuels (1,2,3,4).

Biomass is a very interesting option because, unlike products derived from fossil raw materials, biomass has a neutral carbon dioxide balance, since the amount released into the atmosphere at the end of the bioproducts' life cycle is identical to the amount of atmospheric CO_2 that was captured and fixed by photosynthetic organisms during the formation of the biomass.

The carbon used to build biomass is absorbed from the atmosphere in the form of carbon dioxide (CO_2) by plant life, using energy from the sun. Plants can subsequently be eaten by animals and thus converted into animal biomass. However, the primary absorption is carried out by plants. When this biomass decomposes, depending on the process involved, carbon is released into the atmosphere basically in the form of carbon dioxide (CO_2) or methane (CH_4). These processes are what is known as the carbon cycle (Figure 1)(1,2,4,8).

(Image taken from https://mychaume.com/biogeochemical-cycles-worksheet/)
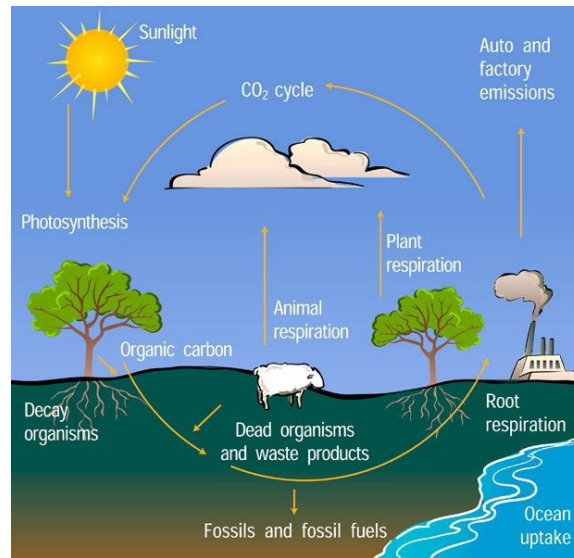
Biomass is organic matter originating from a biological process, excluding matter that has undergone profound changes in composition, such as those that have taken place during mineralization processes occurring in the formation of coal, oil or gas. The term biomass refers to all organic matter from forest residues (trees, branches, bark, chips, prunings, etc.), agricultural residues (residues from food crops, such as olive prunings, cereal straw, corn stover, etc.), energy crops, urban residues (frying oils, food waste, sewage sludge, etc.) and residues from the pulp and paper industries.

As mentioned above, biomass could provide a renewable alternative to fossil resources through the combination of its low environmental impact and new technologies. It could establish a new sustainable supply chain to produce high-value chemicals and fuels.

Biomass has a complex composition, so its utilization requires its initial separation into a series of groups of intermediate products. Further treatment and processing of these intermediates will lead to a range of end products. This constitutes the basic principle of

biorefineries as an extension of the operating principle of oil refineries, the concept of biorefinery will be defined in section 3 (7,8,9,11,18).

Depending on the predominant fraction, or fraction of interest for end-use, biomass can be distinguished into lignocellulosic, starchy, sugary, or oleaginous biomass (Figure2).

Figure 2. Types of biomass

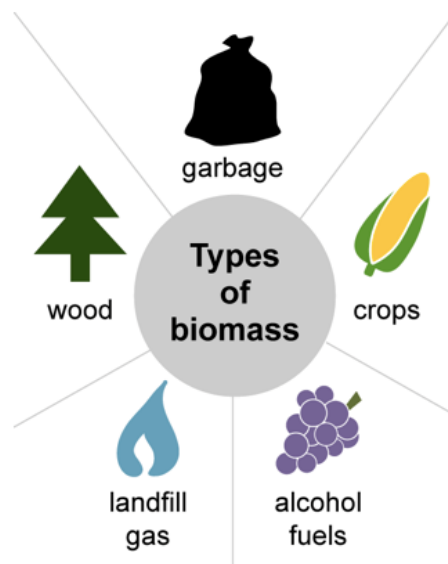Lignocellulosic biomass, which comes from the structural part of plants, can be hydrolyzed to produce chemical components that in turn can be used as renewable sources of carbon to produce biofuels and chemical compounds. Second-generation biofuels are made from lignocellulosic feedstock, which is composed of cellulose (40 to 50%), hemicellulose (25 to 35%) and lignin (15 to 20%) (Figure3) (8,9,11).
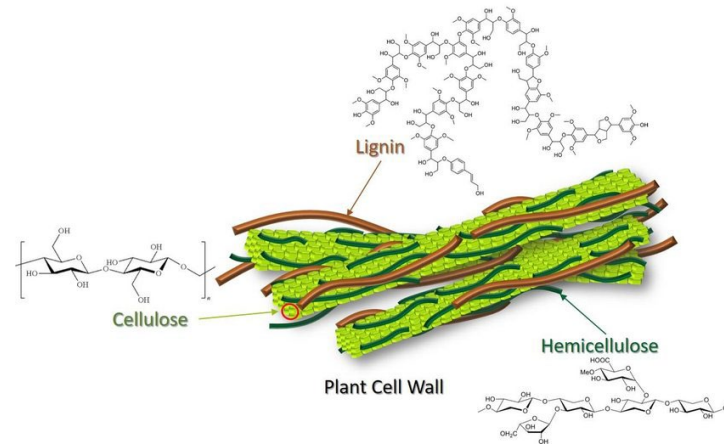
Figure 3. Chemical structure of biomass feedstocks

(Image taken from Green Chen, 2010,12, 1493-1513)

Cellulose is the most abundant organic polymer in the world. It is a linear polysaccharide with a high molecular weight and a high degree of polymerization, besides being the main component of plant cell walls. The higher the degree of polymerization, the more difficult cellulose is to hydrolyze.

Hemicellulose is composed of polymers of different sugars with shorter and more branched chains, which makes it more amorphous and easier to hydrolyze into its constituent sugars than cellulose. The main monosaccharides found in hemicellulose are five, glucose, mannose and galactose which are hexoses and xylose and arabinose which are pentoses. Their role is to provide the link between lignin and cellulose to provide rigidity to the cell wall and they are insoluble in water.

Lignin is the third most abundant biopolymer on Earth behind cellulose and hemicellulose. It is found mainly in the middle lamella of the cell wall and the cell wall layers forming together with hemicellulose a matrix around the cellulose microfibrils.

Lignocellulosic biomass also contains smaller amounts of other minority components such as; proteins (3-10%), lipids (1.5%), soluble sugars and minerals (10.5%), which in chemical analysis are estimated as ash.

. These components interact and entangle to form the lignin-carbohydrate complex. The breakdown of these leads to the formation of chemical compounds that can be used to produce biofuels and chemical compounds. Cellulose is a glucose polymer that can be depolymerized through hydrolysis into monomers, these sugars obtained can be transformed into bioproducts through fermentation or chemical transformation in biorefineries (8,9,11,18).

Due to their complex chemical nature, these materials are resistant to enzymatic and hydrolytic conversion into biofuel. Therefore, pretreatment before hydrolysis is recommended.

3. PLATFORM MOLECULES

In 2004, the U.S. Department of Energy published a list of the "top 10 chemicals" that could be used as platform molecules or building blocks for the synthesis of bio-based chemicals. Among the "top 10", some were the subject of intense research and development over the past few years, while there was comparatively modest interest in organic acids, such as fumaric, malic, aspartic, glutamic and itaconic acids (Figure 4) (1,2,3,4,18).
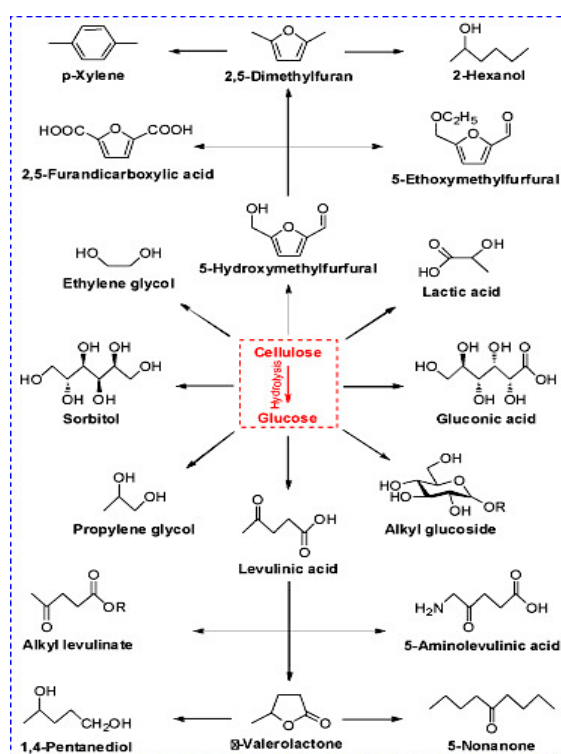

Figure 4. Possible products of the acid-catalysed hydrolysis of a lignocellulosic material

(Image is taken from The Empty Palm Oil Fruit Bunch as the Potential Source of Biomass in Furfural Production in Indonesia: Preliminary Process Design and Environmental Perspective Article (PDF Available) in Journal of Physics Conference Series) 1363:012096 · November 2019)

We will focus on platform molecules that have been extensively studied in recent years, such as 5-hydroxymethylfurfural, furfural, levulinic, lactic and succinic acids, as well as the new industrial derivatives of sorbitol and glycerol (4,18).

Glycerol is a wonderful platform molecule from which many useful intermediates or speciality chemicals can be produced, but its availability may be overrated. Glycerol has hundreds of applications as food and feeds ingredient, and in cosmetics, pharmaceuticals, explosives, etc., and is now being used for the industrial production of intermediates such as epichlorohydrin and propylene glycol.

Research on glycerol conversion was often justified by the need to utilize the growing surplus of glycerol formed as a co-product of biodiesel production from vegetable oils. However, vegetable oils are mainly used to meet growing food needs and the remainder is also destined for the expanding oleochemical industry. As the demand for glycerol is continuously increasing, the market price of high-quality glycerol suitable for chemical applications will remain at a level hardly compatible with an economic production of high tonnage intermediates. Unless new abundant and cheap sources of triglycerides become available, e.g. from algae, glycerol should rather be used as a platform for producing high-value-added chemicals.

5-HMF and its derivatives, levulinic acid, 2,5-bis(hidoxymethyl)-furan (2,5-BHF), 2,5-diformylfuran (2,5-DFF) and 2,5-furandicarboxylic acid (2,5-FDCA) were identified early on as very promising chemical intermediates obtained by catalytic conversion of carbohydrates based on C6 units (Fig. 5). 5-HMF was obtained by dehydration of fructose in the presence of soluble or solid acid catalysts or from glucose or even polysaccharides by more complex catalytic systems and reaction media. The key issue was to prepare 5-HMF with economically acceptable processes that could be scaled up industrially (4,18).
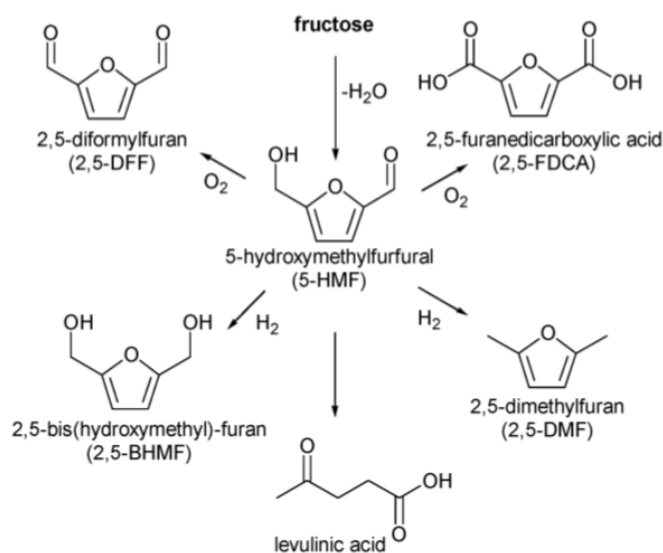
Figure 5. Possible products of the 5-HMF

(Image taken from Green Chen, 2010,12, 1493-1513)

Xylose was hydrogenated to xylitol, a polyol widely used as a food, cosmetic and pharmaceutical additive. The hydrogenation reactions were mainly achieved industrially in the presence of Raney nickel catalysts, with up to 98% yield, but the catalysts suffered from deactivation due to leaching of promoters, surface restructuring and poisoning by strongly adsorbed organic molecules. Ru/C catalysts have higher activity than Raney nickel and are less prone to deactivation. Xylitol yields higher than 98% were reported for Ru/SiO$_2$ and Ru/ZrO$_2$ catalysts.

Furfural is produced industrially (about 250,000 tons per year) by hydrolysis of agricultural or forestry residues with concentrated sulfuric acid. Interestingly, furfural is the only large-volume unsaturated chemical produced from carbohydrates. It is used as a binder for foundry sands, in the refining of lubricating oils and as an intermediate to produce furfuryl alcohol, furan and tetrahydrofuran (Figure 6) (4, 18).
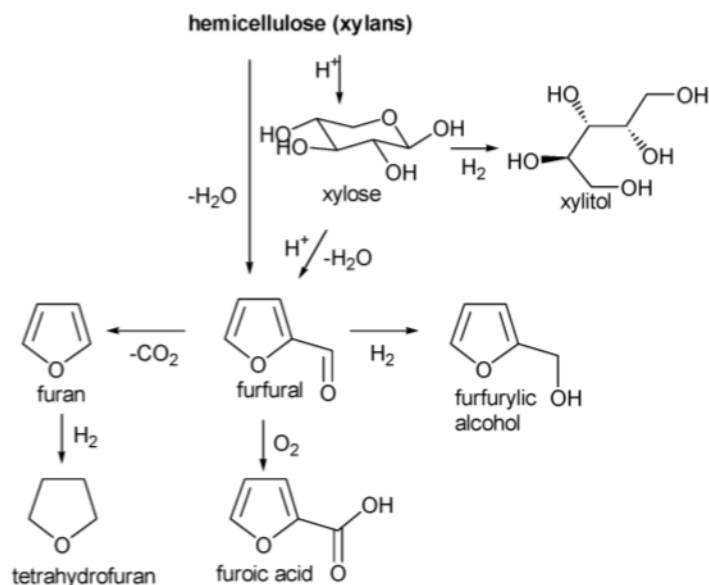
Figure 6. Possible products of the furfural

(Image taken from Green Chen, 2010,12, 1493-1513)

Levulinic acid has been of interest for many years because it can be converted into valuable chemicals. The renewable BIOFIN process was developed on an industrial scale to produce levulinic acid from cellulose and hemicellulose present in agricultural or forestry residues.

In recent years, attention has focused on g-valerolactone (GVL) obtained by hydrogenation of levulinic acid (Figure 7). Horvath and co-workers pointed out the unique physical and chemical properties of GVL that make it an ideal liquid for use as a solvent, intermediate in the chemical industry or for energy storage.

However, the environmental and economic sustainability of a multi-step value chain from cellulose to butene via levulinic acid and GVL must be addressed (4,18).
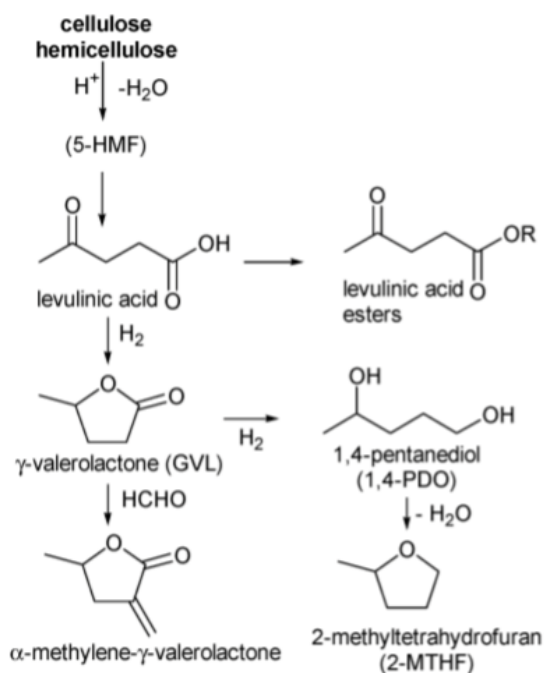
Figure 7. Possible products of the levulinic acid

(Image taken from Green Chen, 2010,12, 1493-1513)

Most succinic acid (SA) production (about 25,000 tons per year) is currently obtained from maleic anhydride produced by the oxidation of n-butane or butadiene. However, recent advances in carbohydrate fermentation and purification technologies have made bio-based succinic acid economically attractive. Economic and environmental analysis of a biorefinery producing succinic acid showed that bio-succinic acid can become a promising intermediate product provided that its production cost can be reduced (Figure 8) (4,18).

Figure 8. Possible products of the succinic acid

(Image taken from Green Chen, 2010,12, 1493-1513)

Lactic acid (2-hydroxypropanoic acid) has been produced by carbohydrate fermentation and used in the food industry for a long time, and fermentation and purification technologies were reviewed. Recent improvements in the biotechnological production of enantiomerically pure lactic acid were described. Alternative synthetic routes from glycerol and derivatives were described. Thus, lactic acid and methyl lactate were obtained by conversion of glyceraldehyde and dihydroxyacetone in H-USY zeolites (Figure 9). However, these investigations starting from expensive pure glycerol could not guarantee an economical alternative to fermentation processes (4,18).
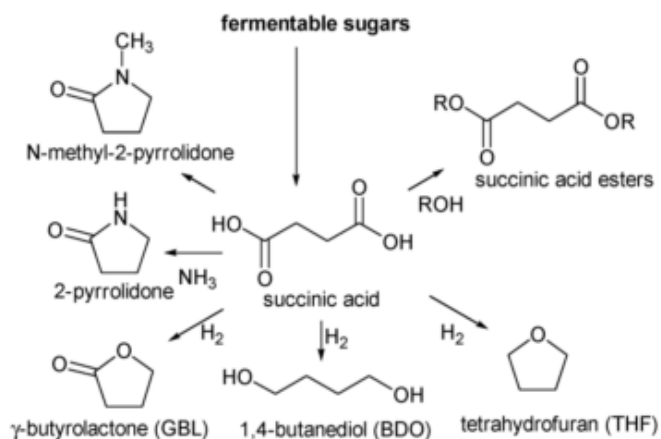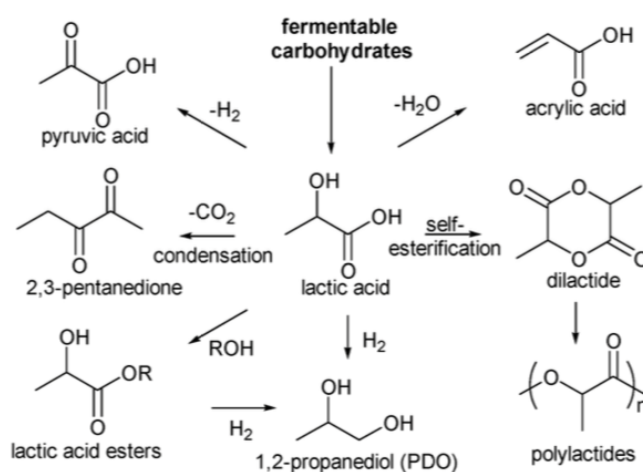

Figure 9. Possible products of the lactic acid

(Image taken from Green Chen, 2010,12, 1493-1513)

Finally, we will talk about Sorbitol and its derivative isosorbide, as they are the main molecules of this work, we will dedicate a section to them (3.1 and 3.2).

3.1.Sorbitol features and Applications

Sorbitol (SL), a carbohydrate-derived polyol, is identified as one of the main renewable chemical compounds with increasing importance in the manufacture of bio-based material to replace petroleum products.

D-sorbitol finds application in many different areas, such as food additives (low-calorie sweetener), cosmetics (humectant), drug formulation (excipient) and a wide range of other industrial applications. This versatility has led to sorbitol being included as one of the updated groups of useful platform molecules to address the chemical industry's transition from crude oil to biomass as a starting feedstock (Figure 10). Global sorbitol production has been estimated at more than 500,000 tons per year (22,23,25,30).
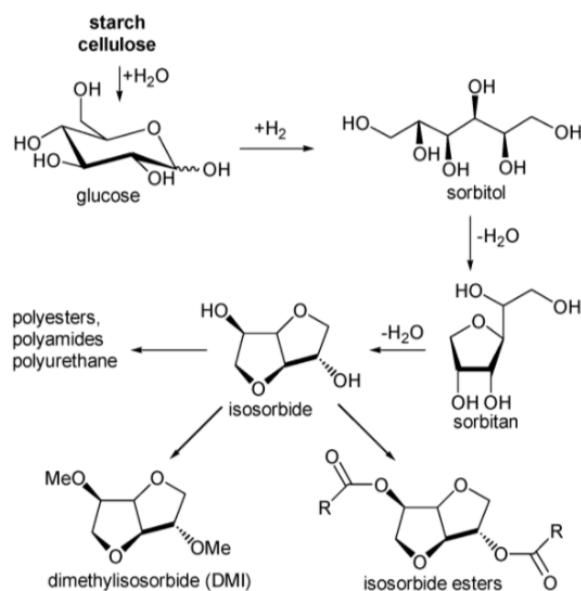
Figure 10. Possible products of the sorbitol

(Image taken from Green Chen, 2010,12, 1493-1513)

Among manufacturers, Roquette Freres is the world's largest sorbitol producer, together with Cargill and SPI Polyols have a market share of over 70%.

Among the SL anhydrides, the isosorbide molecule (ISB) has attracted great interest from researchers and industries in the field of applied polymer chemistry (Figure 11) (32,33,36).
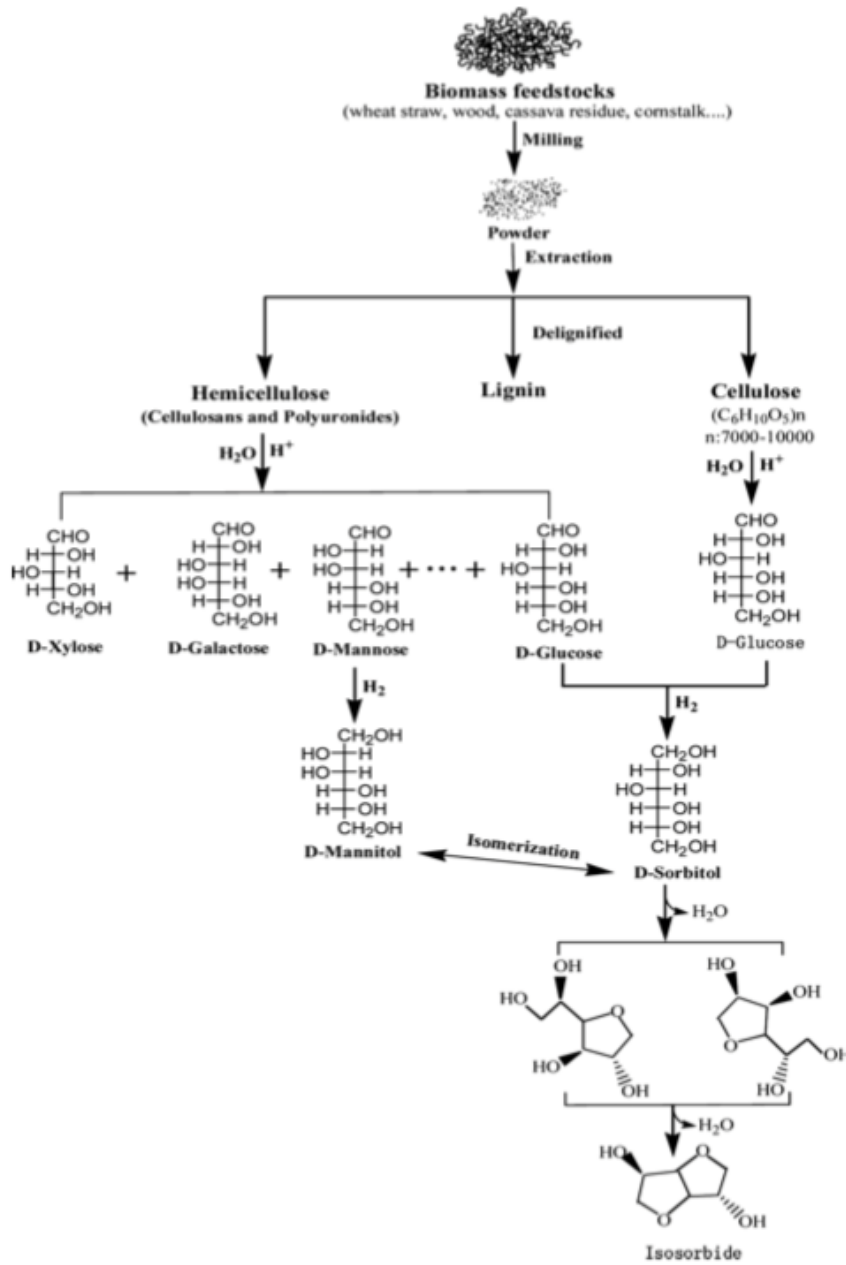
Figure 11. Isosorbide production from lignocellulosic biomass

(Image taken from Green Chen, 2010,12, 1493-1513)

3.2.Isosorbide features and Applications

Isosorbide is a rigid, bi-heterocyclic diol derived from glucose. The two cis-fused tetrahydrofurans (THF) rings exhibit a puckered conformation (120°C) with secondary alcohols at positions 2 and 5. The C_2 hydroxyl group extends outside the ring system (exo) and the C5 hydroxyl group is located within the "V" shape of the rings (endo), the latter participating in hydrogen bonding with the adjacent THF ring. It is believed that this hydrogen bonding is at least partially responsible for the higher reactivity normally observed in the endo hydroxyl group.

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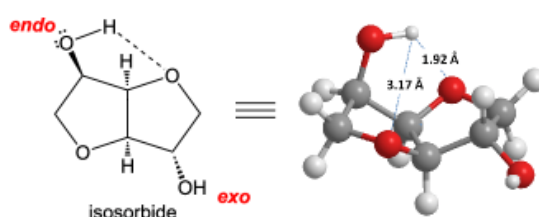
Figure 12. Isosorbide structure

(Image taken from Aricò, Fabio & Tundo, Pietro. (2016). Isosorbide and dimethyl carbonate: A green match. Beilstein Journal of Organic Chemistry. 12. 2256-2266. 10.3762/bjoc.12.218.)

Because of the low overall reactivity of the alcohol groups of isosorbide, isosorbide step-growth polymers are often limited to low molecular weights (Mn10 kg mol-1) and low isosorbide content (< 50 mol%). If larger amounts of isosorbide are to be incorporated into polymers, very high temperatures, long reaction times, and/or complex processes are necessary. The limited thermal stability of isosorbide (Td= 270 °C) can be problematic under the high-temperature conditions commonly employed in polycondensation reactions.

In addition, many methods of direct polymerization of isosorbide require the use of toxic reagents (e.g., phosgene, isocyanates) that decrease its sustainability. Some of these problems can be solved by using isosorbide derivatives that are amenable to controlled polymerization (8,10,26,27,28).

ISB with a V-shaped backbone is composed of two fused furan units and two hydroxyl groups with unequal reactivity, exhibiting a unique rigid scaffold associated with bifunctionality that enables its potent applications in polymer industries. In particular, the use of ISB as a monomer in polyester production has significantly improved the glass transition temperature, transparency and mechanical properties of the polymer.

Until recently, the high cost of isosorbide was a major obstacle to the manufacture of commercial isosorbide-based polymers. In 2015, Roquette became the largest producer of isosorbide by commissioning a new plant with an annual production capacity of 20,000 tons. In 2018, the global isosorbide market was $190 million and is expected to reach $350 million by 2023. Despite the high cost of isosorbide over time, it has been studied extensively in the polymer literature as it is structurally robust and rich in functionality. Isosorbide-based polymers exhibit many excellent properties ranging from optical clarity to strong resistance to UV irradiation, heat, chemical degradation, impact and abrasion. Because of these properties, these materials have shown great promise as sustainable alternatives for commercial applications such as packaging and electronic displays, as well as materials for more specialized areas, particularly in the biomedical field (29,31,32,33). Isosorbide-containing polymers are increasingly being used as biomedical engineering materials due to their biodegradability and biocompatibility.

Other authors reported a method to improve the mechanical properties of polyurethanes by incorporating isosorbide as a chain extender for an isocyanate-terminated poly(lactide) series.

The coatings industry has also increasingly employed isosorbide-based polyesters and polycarbonates. The resulting polymers have properties similar to those of a commercial polyester commonly used in coating applications (Crylcoat 1771-3), including melt viscosity (5500 mPa s vs. 4900 mPa s at 200 °C) and Tg (60 °C vs. 56 °C).

Isosorbide-based co-polycarbonates have also been studied for coating applications. For example, polycarbonates have been performed by melt polycondensation of isosorbide and 1,3-propanediol or 1,4-butanediol with triphosgene or diphenyl carbonate. The resulting materials had modest molecular weights ranging from 1.3 to 7.2 kg mol-1 and exhibited Tg values ranging from 43 to 138 °C.

The pressure-sensitive adhesives industry has also benefited from isosorbide-based polymers. Forming elastomers with higher Tg values than non-isosorbide analogues (-18 °C versus 46 °C) with the ability to modulate other properties such as viscoelasticity and interfacial adhesion.

The cosmetic-textile industry has also benefited from the use of isosorbide-derived polymers for microcapsule walls. Microencapsulation of materials is a useful technique for the controlled delivery of substances. Novel microcapsules containing a polyurethane copolymer wall made by interfacial polycondensation of isosorbide and bis-isocyanates have been reported. Modification of the polyurethane backbone and formulation process (addition of a cationic surfactant) resulted in improved adhesion to fibres and slower release of perfume over 40 wash cycles (35,34,36).

Although isosorbide-based polymers have been used in a variety of applications such as those mentioned above, in this work we highlight their use as a substitute for bisphenol A.

Bisphenol A (BPA) is a chemical used in the manufacture of plastics and resins, widely used in polycarbonates used to make food containers such as bottles, plates and cups. They are also present in epoxy resins used to make protective coatings on food and beverage containers.

BPA can migrate in small amounts into food and beverages stored in these containers. According to several studies, high doses of bisphenol A can cause negative effects on human health.

For this reason, isosorbide, a commercially available biomass derivative, has attracted a great deal of interest as a substitute for bisphenol A. It has very similar qualities but is less toxic (28, 29, 33).

4. BIOREFINERY

With the use of biomass as a renewable resource, the concept of the biorefinery is born, as the refining industry to produce energy, fuels, materials and chemical products from plant biomass.

The aim is to develop technologies that allow obtaining, from the different components of biomass, energy, biofuels and families of basic products that can be useful to different production industries. Integrated biorefineries are facilities where all types of biomass from forestry, agriculture, aquaculture, industrial and household waste, including wood, crops, organic waste (plant and animal-derived), forestry waste and aquatic biomass (algae and seaweed) can be used to produce a wide range of products including energy (electricity, heat), biofuels, chemicals and biomaterials (3,4,5,9).

This will increase the cost-effectiveness of biomass utilization and provide greater flexibility in the face of possible market fluctuations and changing consumer needs. In addition, the integrated biorefinery concept is associated with complex conversion methods, both biochemical and thermochemical, for obtaining a wide range of products. These conversion processes will be more energy-efficient, increasing the sustainability of the overall process.

Biorefineries are so named by analogy with conventional refineries that also process a complex feedstock, and in both cases result in a wide variety of chemical products and fuels with maximum utilization of raw materials. There is a wide variety of definitions of biorefinery, one of the most accepted definitions has been made by the National Renewable Energy Laboratory (NREL) of USA: A biorefinery is a facility that facilitates comprehensive biomass conversion processes and equipment to produce fuels, energy and value-added chemicals from biomass.

Another definition has been proposed by the US Department of Energy (US-DOE): A biorefinery is a general concept of a processing plant where biomass is converted into a spectrum of value-added products. The International Energy Agency (IEA) defines a biorefinery as a facility where a broad spectrum of products of commercial interest is sustainably generated from biomass.

The choice of given biomass as feedstock for obtaining energy and other products (biofuels, biopolymers, and base chemical molecules) will be determined by the characteristics and activities of the region in which it is produced: availability and soil and climatic characteristics of the territory, predominant activities of the agricultural and industrial sectors, population size, etc. The composition of the biomass selected will determine the transformation processes applicable in a biorefinery.

For the above reasons, a biorefinery is not a typical facility, but depending on the type of biomass it must process, it is composed of a series of basic units. Most biorefinery studies have focused on obtaining fuel and energy from biomass.

In a biorefinery a series of processes take place, first, a series of homogenization and uniformization operations are necessary at the entrance of the treatment plants to facilitate the subsequent transformations since, as explained above, the structure of the biomass is very complex. Initial treatment operations include drying, pressing, shredding, chipping, chopping, grinding, etc.

Once the treatment has been carried out, depending on the final product to be obtained and the type of biomass used as raw material, there are different conversion technologies: thermochemical platform, lipid platform, biogas platform, protein platform and sugar and lignocellulose platform.

Thermochemical biorefineries are facilities based on the decomposition of biomass by thermochemical processes for its transformation into chemical products of interest or fuels. This decomposition can be divided into three main blocks: liquefaction, pyrolysis, and gasification.

Lipid platforms are based on the use and transformation of oils and fats from biomass (plants and animals). The first product and possibly the best-known example is the production of 1st generation biodiesel by transesterification of vegetable oils.

The biogas platform is based on obtaining and using biogas, which is a mixture of gases containing methane and carbon dioxide as the main components. The biomass is subjected to the action of anaerobic microorganisms to obtain biogas. Biogas can be used to obtain energy and other products.

The protein platform is based on the utilization and use of proteins present in biomass. The most common plant sources of protein are soybean, corn, rapeseed, and wheat gluten. Practically all protein production is destined for the food industry, but new applications are being investigated, such as the synthesis of fibers and polymers from vegetable proteins or poly-amino acids. It is also possible to genetically modify the properties of these proteins to adapt them to subsequent applications. They are also of interest in the fields of pharmaceuticals, cosmetics, and agrochemicals (11,12,14,18,20).

The lignocellulosic biorefineries or sugar and lignocellulose platform, such as the one used to produce isosorbide, will be explained in more detail in section 5.

5. LIGNOCELLULOSIC BIOREFINERIES

In recent years, the interest in not using raw materials in conflict with food supply coupled with the need for forest preservation has made the use of alternative lignocellulosic materials for the manufacture of fuels and chemicals a strategic objective.

Biorefining of lignocellulosic materials can process a wide variety of low-cost feedstocks (straw, reeds, wood, waste paper, etc.) and their conversion products have a good position in both the traditional petrochemicals market and future bioproducts markets (8,10,13,14).

As specified in section 3, lignocellulosic biomass consists of three primary chemical components or precursors that can be the source of a wide range of chemicals: hemicellulose, cellulose and lignin. Therefore, the objective of the biorefinery of lignocellulosic materials is the fractionation of lignocellulosic biomass into these three components and the subsequent processing of these components to obtain various end products.

The objective of this work is to study the obtention of Isorbide as a Bisphenol substitute. Next, the possible procedures that such a biorefinery would have to have been considered.

Therefore, we will discuss the pretreatment necessary to separate the lignocellulosic biomass, the hydrolysis of cellulose to glucose (or C_6 sugars), the production of D-Sorbitol from glucose, the production of isosorbide by hydrogenation of sorbitol, and the production of D-Sorbitol from glucose.

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5.1.Pretreatment of lignocellulosic biomass

Fractionation is the key stage since it conditions to a great extent the performance and efficiency of the subsequent treatments of each of the separated fractions. The separation of lignin and hemicellulose, the reduction of cellulose crystallinity as well as the increase of the porosity of the materials will be the objectives to be achieved with the pretreatment to favour cellulose hydrolysis. The success of pretreatment depends to a large extent on the conditions applied, but also significantly on the composition of the raw material and its resistance to treatment. Thus, woody biomass (e.g. forest crops, fruit tree prunings, etc.) in addition to different physical properties has a higher lignin content than non-woody biomass (straw, grass, etc.) which makes it more resistant to enzymatic and microbial digestion.

For effective pretreatment, several characteristics must be followed: reduction of biomass particle size, limited formation of degradation products that inhibit the growth of fermentative microorganisms, minimization of energy, low catalyst cost and a balance between biomass cost, downstream processing cost, operating cost and capital cost (13,14,16,17,19,21).

A wide variety of processes have been proposed for the pretreatment of lignocellulosic materials, including physical, physicochemical, chemical or biological processes.

Physical pretreatment includes shredding and hydrothermolysis. Shredding is the reduction of biomass particle size by mechanical means that can be of different types, such as dry, wet, vibratory and compression milling.

Physical chemical can be a steam explosion, CO_2 explosion or ammonia fibre explosion.

Chemical includes acids and bases. The most used acids and bases are H2SO4 and NaOH respectively. The chemical additive category mainly involves cellulose solvents that can greatly enhance the alteration of biomass structure before hydrolysis. Alkaline

H_2O_2, ozone, glycerol, dioxane, phenol and ethylene glycol are a few of the cellulose solvents(13,14,16,17,19,21).

Finally, biological pretreatment is based on the use of fungi.

5.2. Hydrolysi of cellulose

Once the cellulose has been separated from the lignin and hemicellulose, cellulose hydrolysis can proceed. Cellulose is found forming a structure of microfibril chains, which in turn are linked by numerous hydrogen bonds between them, making it very difficult to hydrolyze.

The simplest way to chemically hydrolyze cellulose into glucose is by using an acid catalyst. The cellulose polymer is composed of glycopyranosyl monomers linked by β-(1,4)-glycosidic bonds, and these bonds can be broken in the presence of an acid catalyst.

Chemically catalyzed cellulose hydrolysis has seen several periods of renaissance and has occasionally been combined with biocatalytic fermentation steps to convert sugars into secondary chemical compounds. Industrially speaking, the most important process is hydrolysis with concentrated or dilute mineral acids, predominantly sulfuric acid. An advantage of this process over enzymatic hydrolysis is its high rate of hydrolysis. However, depending on the reaction conditions, glucose can be transformed into other smaller molecules, thus decreasing the yield (13,14,16,17,19,21).

The dissolution of cellulose or lignocellulosic biomass in ionic liquids facilitates greatly the hydrolysis of biopolymers (cellulose and hemicellulose) due to the elimination of the structural protection barriers, Van der Wals bonds and hydrogen bonds, of the hydrolysis centres. Thus, once dissolved in ionic liquid, acid hydrolysis

occurs even at temperatures below 100 °C. In the first stage, cellulose is hydrolyzed to oligomers (1,4-β-glucans) and glucose.

From the reduction of these monosaccharides, some sugar alcohols can be obtained by hydrogenation, namely D-sorbitol and D-mannitol (Figure 13), which can be doubly dehydrated to obtain their respective isohexides (13,14,16,17,19,21,30).
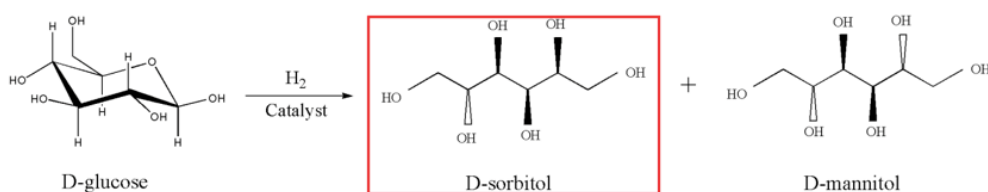

Figure 13. Hydrolysis of cellulose to sorbitol

(Image take from Green Chen, 2010,12, 1493-1513)

5.3. Sorbitol production

As the most abundant source, cellulose, a linear polymer of glucose with β-1,4-glycosidic bonds, can be hydrolyzed into glucose and subsequently hydrogenated into sorbitol, while starch formed from glucose via α-1,4-glycosidic bonds can also be used as an ideal source with excellent hydrolysis. However, starch should be considered mainly as a food source, so great effort has been directed to cellulose conversion.

Obtaining sorbitol was introduced early by hydrogenation of glucose in the presence of a suspension catalyst in 1942 for the first time, and then developed in a mixed bed reactor in combination with a Raney nickel catalyst.

These classical hydrogenation catalysts exhibit good catalytic activity and low cost, but also rather low stability and suffer from metal leaching. In addition, some sorbitol applications (food, medicine, cosmetics, etc.) require that trace nickel be completely

removed from the final product, thus requiring costly separation and purification operations (7,8,22,23).

Regarding the right catalyst for this reaction, there are many studies, then a few will be detailed in table 1.

Author	Raw materials	Catalyst	Operating temperature	Yield [%]
Claus	glucose	LaNi5	313K	97
Hoffer	glucose	Ru/C	393K	100
Other researchers	glucose	C6H9O6Ru	373K	72,9
Other researchers	glucose	Ru/MCM-41	393K	94,4
Zhu et al.	glucose	IL	-	94

Table 1: summary of the different studies

(10,22,23,25,30,33,35,34,36)

Studies revealed that the activity of Raney-nickel could be significantly improved by the addition of some promoters.

Hoffer et al. reported that the activity of Mo-modified Raney-nickel showed excellent stability without leaching in the reaction solution. With in-depth studies, the specific surface area increased by 30% to 35% on the Cr-modified Raney-nickel catalyst.

Overall, the Mo- and Cr- modified catalysts have great potential for possible application in industrial-scale production after thorough comparison. Considering the production environment of sorbitol on modified Raney-nickel catalysts, special attention should be paid to the following aspects. First, adequate H_2 pressure is needed to achieve high glucose conversion, and a higher reaction temperature leads to glucose

carbonization and generates some by-products. Second, the desired pH value of the reaction solution was 8.0-9.0 when the Raney-nickel catalyst was used.

However, glucose can easily isomerize to mannose under alkaline conditions and then hydrogenate to mannitol. Therefore, an appropriate pH value should be chosen to prolong the catalyst life and avoid glucose isomerization. In industrial production, a pH of around 7.5 is proposed.

Claus made a great effort for the development of supported Ni catalysts. They reported that the activity followed the sequence Al_2O_3> TiO_2> SiO_2 > C, while all these tested catalysts were leached. In most cases, catalysts prepared by impregnation showed higher activity compared to those prepared by incipient wetting. With an in-depth study, it was found that Ni precursors played an important role in the performance of the obtained catalysts.

The amorphous hydrogen storage alloy developed in recent years has gained increasing interest as an alternative target for its hydrogenation/dehydrogenation properties. It was reported that high yield and selectivity of sorbitol could be achieved under mild reaction conditions when the amorphous hydrogen storage alloy was used in the hydrogenation of glucose. For example, the conversion of glucose reached 97% at 313 K and 834 kPa for $LaNi_5$ as catalyst and HAc as additive.

To completely overcome the nickel leaching problem and further increase the selectivity of sorbitol, the increasing need for new catalysts is essential. Ruthenium catalysts have attracted superior activity. Hoffer et al. first reported that the carbon-supported Ru catalyst was a promising alternative to Raney-type Ni.

It was found that Ru/C showed almost 100% selectivity to sorbitol under 4 MPa H_2, and above all, Ru exhibited excellent stability that effectively addressed the leaching problem in nickel catalysts.

With different ruthenium complexes as precursors, the essential properties of the catalyst can be of considerable difference. Some researchers reported that glucose

conversion increased by about 5% when ruthenium acetate was used as a precursor. A glucose conversion of 72.9% was achieved at 373 K under 3 MPa H_2.

5.4. Isosorbide production

The dehydration of sorbitol to isosorbide occurs through two consecutive steps: the first cyclization with the loss of a water molecule, which can give rise to different chemical intermediates such as 2,5- and 1,5-sorbitan, considered by-products since they do not evolve to isosorbide, and 1,4- and 3,6-sorbitan, whose subsequent dehydration and cyclization give rise to isosorbide (Figure 14).

The key step in the synthesis of isosorbide is the double dehydration of sorbitol. The dehydration of sorbitol leads after the first dehydration step to several different monoanhydrohexitols called sorbitans. Among them, only 3,6-sorbitan and 1,4-sorbitan are isosorbide precursors after a second dehydration step. The other sorbitans finally lead, after further intramolecular or intermolecular dehydration steps, to coloured oligomeric species called "humins". The formation of humins contributes drastically to reducing the mass balance of the reaction.
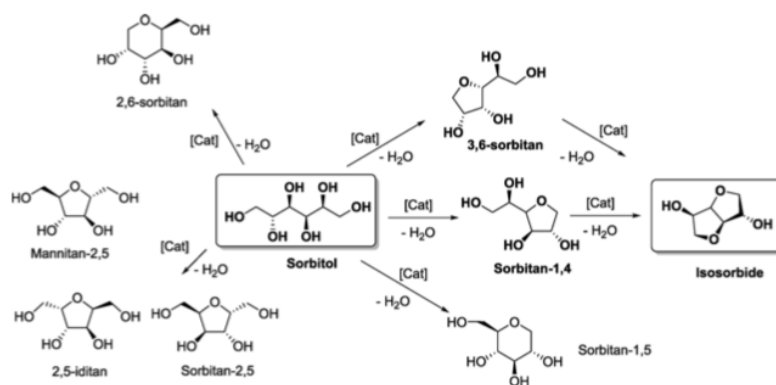

Figure 14. Dehydration of sorbitol to isosorbide

(Image is taken from C. Dussenne, H. Wyart, V. Wiatz, I. Suisse and M. Sauthier, Catalytic dehydration of sorbitol to isosorbide in the presence of metal tosylate salts and metallized sulfonic resins Mol. Catal., 2019, 463, 61–66)

This process is carried out industrially under homogeneous catalysis in the presence of strong mineral acids. Although these systems provide high sorbitol conversion at low temperatures, the drawbacks associated with high separation costs and equipment corrosion problems have prompted the search for alternative processes. In this context, the development of solid acid catalysts represents a more economically and environmentally sustainable alternative and would allow modulating selectivity in some cases.

Regarding the right catalyst for this reaction, there are many studies, then a few will be detailed in table 2.

Author	Raw materials	Catalyst	Operating temperature	Yield [%]
Huchette and Fleche	glucose	H_2SO_4	408K	77
Xiao et al.	glucose	SO_3H	423K	88
Fukuoka et al.	glucose	Zeolite Beta	-	76
Makkee et al.	glucose	Ru/MCM-41	-	95
Other researchers	glucose	Amberlyst-35	423K	94

Table 2: summary of the different studies

(10,26,27,28,29,31,32,33,34,35,36))

The acid catalyst is commonly used to increase the reactivity of the SL molecule during the dehydration reaction. Commercially, ISB is produced by homogeneously catalyzed SL dehydration using strong Brönsted acid, such as sulfuric acid. It was reported that the formation and yield of ISB are highly dependent on the nature of the acid sites and their acidic strength. Compared with Lewis acid, a strong Brönsted acid catalyst exhibited higher activity and selectivity to ISB. The superior performance of the strong Brönsted acid catalyst was attributed to its higher affinity to protonate the hydroxyl

group of SL, one of the crucial steps in the mechanism of ISB formation through SL dehydration. In addition, the synthesis of ISB via SL dehydration that employed the weak acid catalyst such as Lewis acid was also more susceptible to the formation of side products, especially coke.

Homogeneous Brönsted strong acid catalysts such as HCl, H_2SO_4, H_3PO_4 and p-toluene sulfonic acid have demonstrated outstanding performance in catalyzing SL dehydration for ISB production at normal atmospheric pressure, elevated pressure and microwave-assisted conditions.

However, the preeminence of the homogeneous Brönsted acid catalyst is offset by its severe drawbacks in corrosion of the resulting equipment and additional downstream separation processes requiring additional capital and operating costs. From an economic and environmental point of view, the catalysis of SL dehydration to produce ISB has been oriented toward a green and sustainable heterogeneous catalytic System.

Huchette and Flèche reported that sorbitol was dehydrated to isosorbide in 77% yield using sulfuric acid as catalyst under vacuum at 135 °C. Although this process achieved a high yield, it requires neutralization and decolourization of the dark-coloured mixture.

As we have discussed for industrial application, a heterogeneous reaction system has advantages at many points and various types of heterogeneous catalysts have been explored; for example, modified metal oxides, zeolites, metal phosphates, supported heteropolyacids, supported metals and ion exchange resins.

Xiao et al. reported that a polymer-based mesoporous catalyst containing SO_3H groups efficiently promoted the dehydration of sorbitol under vacuum, achieving a ca. 88% isosorbide yield at 423K.

Very recently, Fukuoka et al. achieved 76 % isosorbide yield using a beta zeolite with high silica content under clean conditions.

Numerous examples of sorbitol dehydration without any solvent or in organic solvents such as xylene have also been reported.

Makkee et al. reported the production of isosorbide from cellulose in molten salt hydrate medium, achieving a yield of 95%. Since sorbitol can be produced through hydrolytic hydrogenation of cellulose, performing the dehydration reaction in water could simplify the isosorbide production process. Although high yields of isosorbide have been achieved under pure conditions, successful production of isosorbide by dehydration in water with heterogeneous catalysts has not been reported.

Recently, metal-loaded zeolites have been found to be excellent catalysts for the hydrolytic hydrogenation of cellulose to sorbitol in water, presenting the possibility that isosorbide production from cellulose can be achieved in a single vessel if sorbitol dehydration can be performed in high yield in water with a zeolite catalyst.

Sulfonic acid resins have also been evaluated as solid acid catalysts for the conversion of sorbitol to isosorbide, and the best catalytic results have been obtained with Amberlyst-35. The conventional resin showed high conversion (94 %) and selectivity to isosorbide (72 %) at 423K.

Combining green chemistry with process intensification is one of the challenges required for the future. In this context, microwave processes offer many advantages.

Khan et al, have studied the catalytic dehydration of sorbitol in a Teflon autoclave seal placed in a multimode microwave oven and compared it with classical heating. The results were very promising, the microwaves accelerated the reaction by about 20 to 34 times, with no noticeable effects on the selectivity of isosorbide or sorbitan.

In contrast to classical heating processes, for which energy is transferred due to thermal gradients by conduction, convection or radiation across a heated surface, microwave energy is directly delivered to the materials through molecular interaction with the electric tromagnetic field.

In contrast to research on the development of solid acid catalysts for the dehydration of SL to ISB, research on the product distribution and kinetics of this reaction is rather scarce despite its importance for process and equipment design.

Polaert et al. evaluated the kinetics of microwave-assisted ISB synthesis via SL dehydration using a heterogeneous catalyst (AM 35) under vacuum conditions. The yield obtained was up to 70% at 413 K for 5 h. The kinetic data were fitted with the PH and Langmuir Hinshelwood (LH) models. It was found that the LH model best describes the reaction kinetics of SL to ISB dehydration. Unlike the reaction without using a catalyst, the energy barrier of ST to ISB dehydration was lower than that of SL to ST dehydration with the introduction of AM 35 as a catalyst.

A unique example of direct synthesis of isosorbide from lignocellulosic biomass utilizes carbon-supported Ru and ion exchange resins for a one-step conversion. This process offers a direct advantage over similar methods, as no "pretreatment" step is required to remove lignin and hemicellulose from the biomass. Using Ru/C and Amberlyst 70, the authors report a yield of 25.4% isosorbide from Japanese cedar chips in the one-step process. The authors propose that the choice of starting lignocellulosic biomass is important, as lower yields were obtained when using eucalyptus chips or sugarcane bagasse chips due to the higher content of other unusual components (i.e., lignin and hemicellulose) that decrease catalyst activity.

6. PROCESS PROPOSAL

According to the bibliographical information, the following process is proposed (figure 14).
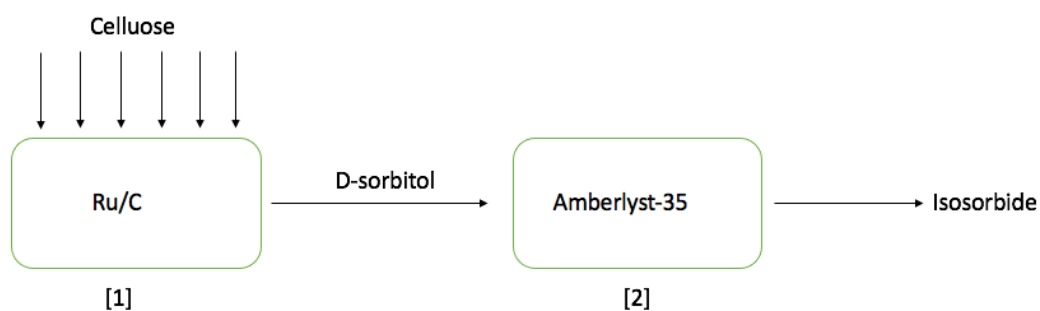

Figure 14. Process proposal

Cellulose is first introduced gradually, as this has been shown to promote humin reduction. Cellulose is hydrolysed to glucose. Subsequently, the glucose is hydrolysed to D-sorbitol with Ru/C as a catalyst at 393K, as this is the catalyst that has given the best results according to the different studies mentioned above (100% yield).

Once D-sorbitol is formed it is dehydrated to 1,4-sorbitan, which is subsequently dehydrated to isosorbide. For these dehydrations, according to different studies, the best performance is obtained with Amberlyst-35 as a catalyst at 423K (94% yield).

7. CONCLUSIONS

The production and utilization of sorbitol have great potential due to the rapid development of the food and chemical industry, especially in the fields of energy and fuels.

In brief, glucose and biomass feedstocks can be converted into sorbitol by using nickel-based catalysts, hydrogen storage alloy and ruthenium catalysts. Isosorbide is obtained by double dehydration of sorbitol or one-step conversion of lignocellulose materials with engineered reaction systems.

Although great progress has been achieved in the field of sorbitol preparation and transformation, improvements in productivity and selectivity are still needed in many cases to reach the goal of industrial production of these processes. On the one hand, metal catalysts, especially Ni, Ru and Pt, show excellent catalytic performance in the production of sorbitol and derived chemicals. Much of the work should focus on the realization of the regulatory mechanism of the target products. However, efficient and inexpensive catalysts or rational reaction systems are also badly needed for further commercialization.

With the introduction of green chemistry, efforts in biomass conversion should be devoted to the economical, fast and environmentally friendly production of sorbitol and isosorbide-based chemicals. High-temperature liquid water and microwave heating are of great interest in catalytic reactions.

A viable pathway for the industrial conversion of biomass into these chemicals still needs to be explored further. This suggests that steps involving pretreatment of the material and subsequent sectional processing can be clearly considered. Another point worth noting is that catalyst activation and reuse and efficacious separation of target products are always hot topics in catalytic processing research.

In conclusion, in this work we have seen that Ru/C and Amberlyst-35 catalysts are a good choice for these reactions, both for their low environmental impact and their high yield.

8. NOTATION

- BPA: Bisphenol A
- 5-HMF: 5-hydroxymethylfurfura
- GVL: G-valerolactone
- SA: Succinic acid
- NREL: National Renewable Energy Laboratory
- US-DOE: US Department of Energy GHG: Greenhouse gases
- IEA: International Energy Agency
- SL: Sorbitol
- IL: Ionic liquids
- ISB: Isosorbide

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