SELECTIVE CATALYTIC CONVERSION OF CELLULOSE AND GLUCOSE INTO SORBITOL IN SUBCRITICAL WATER

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ABSTRACT

SELECTIVE CATALYTIC CONVERSION OF CELLULOSE AND GLUCOSE INTO SORBITOL IN SUBCRITICAL WATER

The goal of this study was to add high value to cellulose as the most abundant source of biomass and glucose by producing a building-block chemical-Sorbitol-, which is not produced in our country and has very large market share. In this manner, the effect of reaction time (1-2 h), catalyst amount (1-2 g) and catalyst type on conversion of cellulose and glucose and yield of sorbitol with presence of various catalysts in subcritical water environment were investigated. The hydrogenation of both glucose and cellulose over Ruthenium based catalysts (Ru/AC, Ru/SiO_2, Ru-SBA15 and Ru-SBA15/SO_3), using a high pressure-high temperature reactor (Parr 5500 High Pressure Compact Reactor) at a reaction pressure of 5 bar and reaction temperature of 150°C were studied. Ruthenium based catalysts were prepared by wet impregnation method. The synthesized Ru based catalysts with various metal based were characterized by various characterization tools such as Scanning Electron Microscope (SEM), Fouirer Transform Infrared Spektrofotometre (FT-IR) and Brunauer-Emmett-Teller (BET). The catalytic performances were evaluated in hydrogenation of cellulose and also glucose to produce sorbitol under subcritical water conditions. As a result of these analyzes, the highest sorbitol yield and cellulose conversion were found to be 234.98 ppm and 28.64%, respectively for 2 gram of Ru-SiO_2 catalyst for 2 hours. For glucose conversion, the catalyst of Ru-SBA15/SO_3 showed better catalytic performance than other catalysts.

ÖZET

KRİTİK ALTI SUDA SELÜLOZ VE GLİKOZUN SORBİTOLE SEÇİCİ KATALİTİK DÖNÜŞÜMÜ

Bu çalışmanın amacı, ülkemizde üretilmeyen ve çok büyük pazar payına sahip bir kimyasal yapı taşı olan sorbitol üreterek, en çok bulunan biyokütle kaynağı olan selüloza ve glikoza yüksek değer katmaktır. Bu şekilde, reaksiyon süresi (1-2 saat), katalizör miktarı (1-2 gram) ve katalizör tipinin selülozun ve glikozun dönüşümü ve sorbitol veriminin kritik altı su ortamında çeşitli katalizörlerin varlığı üzerindeki etkisi araştırıldı. Hem glikoz hem de selülozun hidrojenasyonu Rutenyum bazlı katalizörler üzerinde (Ru/AC, Ru/SiO$_2$, Ru-SBA15 and Ru-SBA15/SO$_3$), yüksek basınç-yüksek sıcaklık reaktörü kullanarak (Parr 5500 Yüksek Basınçlı Kompakt Reaktör) 5 bar reaksiyon basıncında ve 150°C reaksiyon sıcaklığında çalışıldı. Rutenyum bazlı katalizörler ıslak emprenye yöntemi ile hazırlandı. Çeşitli metaller ile sentezlenmiş Ru bazlı katalizörler, Taramalı Elektron Mikroskobu (SEM), Fourier Dönüşümlü Kızılötesi Spektroskopisi (FT-IR) ve Brunauer-Emmett-Teller (BET) gibi çeşitli karakterizasyon araçları ile karakterize edildi. Katalitik performanslar, kritik altı su koşulları altında sorbitol üretmek için selüloz ve ayrıca glikozun hidrojenasyonunda değerlendirildi. Bu analizler sonucunda, en yüksek sorbitol verimi ve selüloz dönüşümü 2 saat boyunca 2 gram Ru-Si0$_2$ katalizörü için sırasıyla 234.98 ppm ve 28.64% olduğu bulunmuştur. Glikoz dönüşümü için Ru-SBA15/SO$_3$ katalizörü, diğer katalizörlerden daha iyi katalitik performans gösterdi.

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CHAPTER 1

INTRODUCTION

The increasing energy needs, fast consumption of fossil fuels and environmental problems cause many concerns; brings up the use of biomass as a renewable raw material as a source of both energy and valuable platform chemicals. Therefore, there have been many researchers focused on converting the most abundant lignocellulosic biomass source of cellulose, as well as the conversion of glucose into high-value chemicals via various processes. In this study, it is aimed to add high value to cellulose as the most abundant source of biomass by obtaining sorbitol, which is not produced in our country and has very large market share. Furthermore, another goal is to contribute to the economy of the country by obtaining a product with a high value added from a low value raw material and to limit the foreign dependency of our country in this regard by reducing the import of valuable chemicals such as sorbitol.

Cellulose is a promising raw material that is more easily identifiable than hemicellulose and lignin and can be used in the conversion processes to various platform chemicals in the presence of various catalysts. Cellulose has an intact polymer structure and it is not dissolved in water and has high chemical stability, so it is efficiently converted into various platform chemicals (Yabushita, Kobayashi, and Fukuoka 2014). Besides cellulose, glucose is the basic sugar unit, the content of which is more than 50% biomass. Glucose can be obtained from the hydrolysis of cellulose, starch of cassava or algae, cane sugar and so on.

Hydrothermal liquefaction method using subcritical water has become a prominent method for the conversion of cellulose into various platform chemicals in an efficient way, due to its low cost and performing reactions under moderate reaction conditions (Kruse, Funke, and Titirici 2013). Biomass products are primarily depolymerized by hydrolysis and disintegrate with reactions carried out in sub-critical water environment, and then they are reduced to smaller components by dehydration, hydrogenation, deoxygenation and hydrodeoxygenation reactions (Hashaikeh et al. 2007). In addition, the subcritical water environment is a very effective for the conversion of various biomass that supports ionic, polar non-ionic and free radical reactions (Pavlovič, Knez, and Škerget 2013).

Biomass conversions with catalysts in subcritical water environment can be obtained with more selective products, higher conversion can be achieved and the reaction can be performed in more moderate conditions. Besides, the use of catalysts can be reduced carbonization and tarting (Toor, Rosendahl, and Rudolf 2011). The reaction mechanism of biomass conversions with presence of catalysts in subcritical water environment is affected by many parameters such as temperature, pressure, reaction time, raw material and catalyst type. Acids and bases can be used as catalysts for liquefaction of biomass. Acids are used to transform biomass into water-soluble products such as sugar, carboxylic acid and furfural whereas bases and alkaline salts can be used to increase bio-oil yield and reduce residue/deposit formation (Toor, Rosendahl, and Rudolf 2011).

Sorbitol is one of the most popular sugar alcohols that is mainly used in food, pharmacy, cosmetic products and as an intermediate product of vitamin C synthesis. Sorbitol is listed as an original platform chemical like organic acids (succinic acid, itaconic acid, fumaric acid etc.), polyols (glycerol, sorbitol, and xylitol) and others (exm, ethanol, bio-hydrocarbons, furans, etc.). Sorbitol is one of the twelve most important building blocks derived from biomass resources (Moreno et al. 2017). If the increasing demand to sorbitol is taken into account, it is very important to develop a new process for the selective production of it.

There are several methods to produce sorbitol; biotechnological, electrochemical and chemical production of sorbitol. Chemical production of sorbitol is basically the most efficient, most widely used and cheaper than the other methods. The production of sorbitol is commonly carried out by the use of nickel-based catalysts (Raney Nickel) through the hydrogenation reaction of glucose. Raney nickel catalysts have desirable properties such as good catalytic activity, low cost and excellent precipitation, however, making the process less economical due to its low selectivity for sorbitol and leaching. Therefore, many researchers have focused their attention on developing other active metal-containing catalysts such as cobalt, platinum, palladium, rhodium and ruthenium to overcome these disadvantages. Among these supported metal catalysts, only ruthenium (Ru) based catalysts have been found to be usable instead of nickel based catalysts because they show high activity against sorbitol, require less loading and show less deactivation. Although ruthenium is more expensive than nickel, it is much more active than nickel and less likely to leach (Dhepe and Fukuoka 2007). Ruthenium nano-particles and nano-powders are especially effective catalytic materials for hydrogenation reactions.

This study describes the use of Ru-based catalyzed (Ru/SiO_2, Ru-SBA15, Ru-SBA15/SO_3 and Ru/AC) for the selective hydrogenation of glucose and cellulose to sorbitol in liquid phase using water as green solvent. The effects of many parameters such as reaction time, catalyst type and catalyst amount were discussed on biomass conversions with presence of catalysts in subcritical water environment.

CHAPTER 2

LITERATURE SURVEY

2.1. The Aim and the Importance of the Study

The aim of this study is to add high value to cellulose as the most abundant source of biomass and glucose by producing a building-block chemical such as sorbitol and to develop an environmentally friendly and applicable process in the presence of catalyst. The other objective is to understand the effects of reaction time (60-120 min), catalyst amount (1-2 g), and catalyst type (Ru/AC, Ru/SiO_2, Ru-SBA15 and Ru-SBA15/SO_3) on the conversion of cellulose and glucose to sorbitol. Sorbitol is selected as the target product, since it has large market share and it is not produced in Turkey. If the increasing demand to sorbitol is considered, it is very important to develop a new process for the selective production of it.

2.2. Description of Biomass

Biomass is generally called as renewable and sustainable organic material. Biomass is one of the most important energy resources of the future. It is the fourth major resource of energy with providing 14% of the world’s primary energy requirements, it is commonly refers as a carbon neutral source in contrast to fossil fuels such as coal, petroleum and natural gas. It can be used to meet a various of energy needs such as electricity generation, heating, refueling vehicles and as raw materials to produce the chemicals. It provides a clean and renewable energy source that can improve environment energy securities and economy (Tekin, Karagöz, and Bektaş 2014). Among whole the renewable resources of energy, biomass is unique as it stores solar energy effectively. The only renewable carbon source is biomass that can be converted into appropriate solid, liquid and gaseous fuels with different conversion processes. Furthermore, biomass can be obtained from various sources such as wastes, standing forests and energy crops (Saxena et al. 2012).

2.3. Components of Biomass

The basic structure of biomass consists of heterogeneous mixtures of organic substances: cellulose, hemicelluloses, lignin, and little amount of inorganic substances which includes in the ash. The composition of biomass component changes with respect to biomass type, tissue type growing conditions and growth stage. The dry weight of biomass consists of 30-40% oxygen, 30-60% carbon and 5-6% hydrogen depending on the ash contents and also nitrogen sulphur and chlorine less than 1%. Biomass generally contain about 38-50% cellulose, 23-32% hemicellulose and 15-25% lignin. However cellulose and hemicellulose form the carbohydrate portion of the biomass, lignin is non-carbohydrate part of biomass. Cellulose and hemicellulose ensure mechanical and structural strength to the plant, whereas lignin maintains the stability of the structures (Tekin, Karagöz, and Bektaş 2014).

Cellulose is the most common natural polymer on Earth that founds about 35-50% of most plant material. It has a long chain polymer wither higher degree of polymerization (approximately 10,000) and a large molecular weight (approximately 500,000) and its generic formula is $(C_6H_{10}O_5)_n$. Cellulose is primarily formed by D-glucose, which consist of six carbons or hexose sugars that are given in Figure 1. Furthermore, cellulose is insoluble in water at room temperature while it is partially soluble at subcritical water conditions (330°C). Additionally, cellulose is insoluble in most solvents due to hydrogen bonding that gives a strong fiber structure.

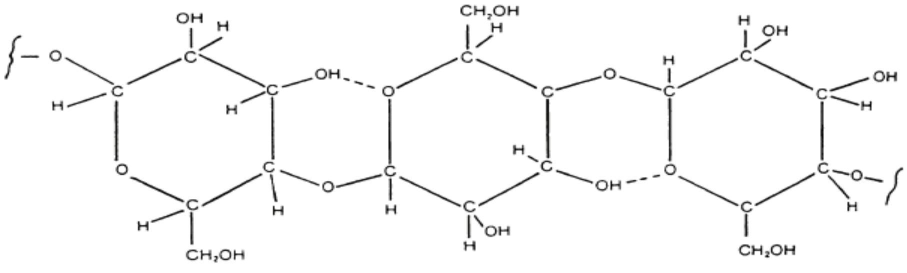

Figure 1. Structure of cellulose (Source: Basu & Mettanant, 2009)

Hemicellulose is an amorphous heteropolymer and has a random and a lower degree of polymerization than cellulose (about 100 sugars per hemicelluloses molecule). Its generic formula is $(C_5H_8O_4)_n$. Most hemicelluloses include D-xylose, D-mannose, D-glucose, l-ababinose, D-glucurnoic acid, and D-galactose. Hemicellulose tends to produce more gas and also less tar than cellulose. Hemicellulose that forms hydrogen bonds by cellulose, forms covalent bonds by lignin, and ester bonds by acetyl units and also hydroxycinnamic acids (Tekin, Karagöz, and Bektaş 2014). Hemicellulose degrades more easily than cellulose with heat treatment because of its lower degree of crystallinity and less stable structure. Furthermore it is soluble in weak alkaline solutions and is hydrolyzed by dilute acid or base (Toor, Rosendahl, and Rudolf 2011). Figure 2 shows the molecular arrangement of some hemicellulose monomers.

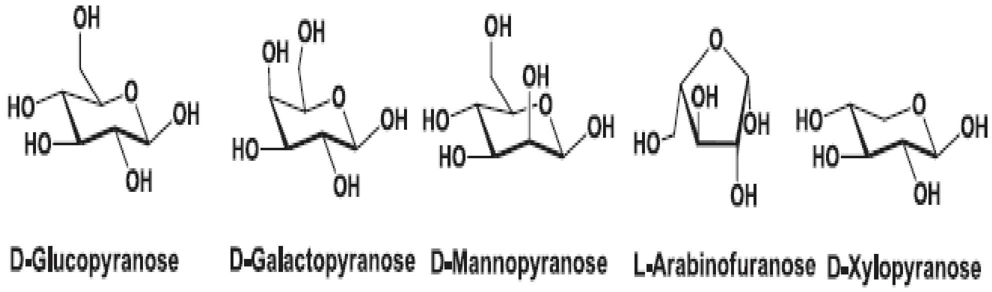

Figure 2. Basic structures of hemicellulose monomers (Source: Tekin et al. 2014)

Lignin is a complex aromatic polymer of phenylpropane with hydroxyl and methoxy groups through ether bonds. It is the most abundant organic polymers on the earth except cellulose. Lignin is amorphous polymer, hydrophobic and highly insoluble, even in sulphuric acid. Furthermore, its molecular weight is high and it has a complex structure which is given in Figure 3. It has higher energy content compared with cellulose and hemicellulose, so lignin content increases with heating value of biomass.

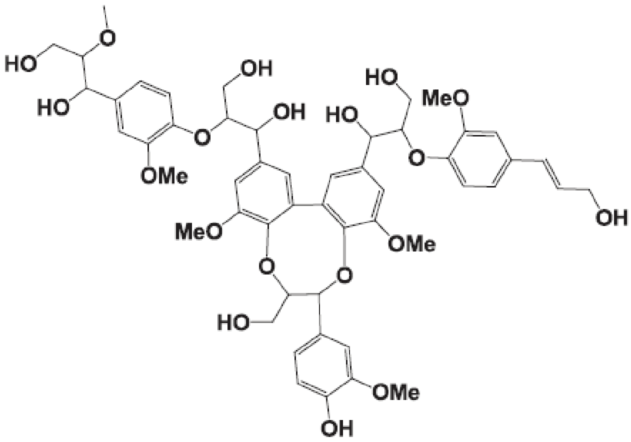

Figure 3. Structure of a sample lignin (Source: Tekin et al. 2014)

Extractives are heterogeneous substances that can be extracting from biomass. They are soluble in water or organic solvents. They consist of a wide range of organic and inorganic compounds such as proteins, fats, fatty acids, phenols, sugars, terpenes, resin and resin acids (Tekin, Karagöz, and Bektaş 2014). They are significant contributors to plant, such as colour, smell, taste and durability (Sengupta and Pike 2012).

2.4. Subcritical Water and Supercritical Water

Subcritical water, also called as hot compressed water and pressurized hot water, is defined as water above the boiling point (100°C) and below critical temperature (374°C) under enough pressure to keep its liquid state. The phase diagram of water along with temperature and pressure is given in Figure 4. Basically at below the critical point and above the triple point all the water below is liquid or gas so, it is not a physically defined condition (Tekin et al. 2014).

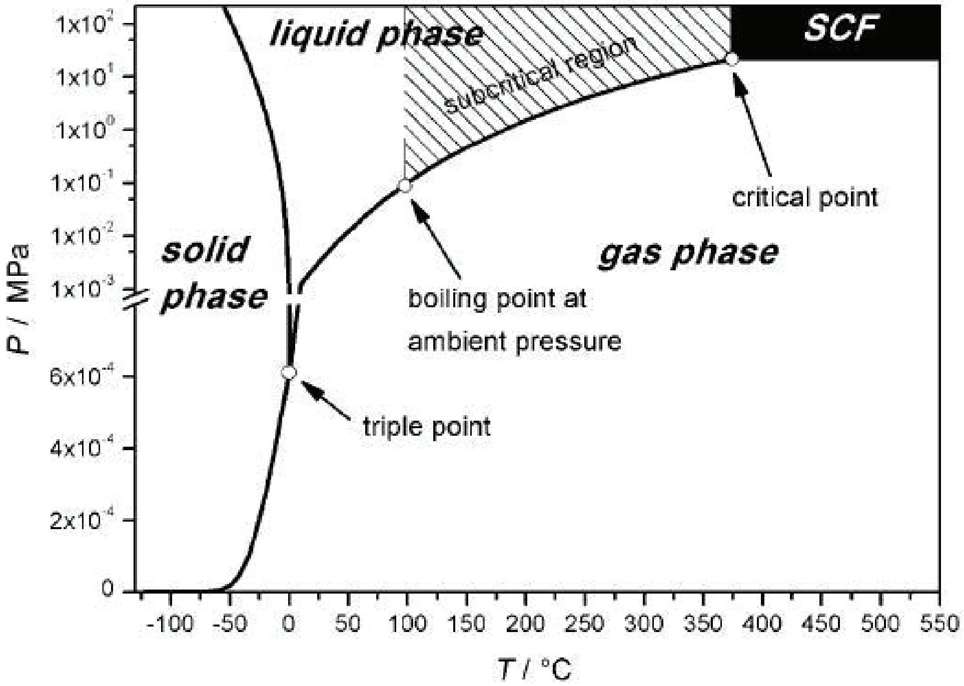

Figure 4. Phase diagram of water in different temperature and pressure (Source: Möller et al. 2011)

There are several advantages of subcritical water due to their various properties. Near critical point, the properties of water including dielectric constant, ion product, viscosity, density, and diffusivity change with temperature and pressure (Tekin et al. 2014). The ionic product of water close to the critical temperature is greater than that at room temperature; water can be also an efficient medium for acid–base-catalysed reactions under critical conditions. Temperature increases with decreasing the viscosity of water and it reaches the viscosity of water vapor close to the critical point. Furthermore, low viscosity provides high diffusion coefficient and accelerates the reaction rates (Möller et al. 2011). The polarity of water changes with increasing temperature and becomes non-polar, which allows organic compounds to dissolve. The ion product (K_w) of water increases with temperature and reaches 10^{-11}, which is almost three orders of magnitude higher than the ambient water (Akiya and Savage 2002).

Supercritical water (SCW) occurs at pressures higher than 22.1 MPa and temperatures above 374°C. Water is a nonpolar solvent that can mix completely with organics at supercritical conditions while it has very poor solubility at subcritical conditions. This solvent feature helps to easily dissolve organic compounds containing lignocellulosic materials in supercritical water, thereby break the boundary between phases during gasification. SCW behaves as a nonpolar dense gas and the dissolving properties are similar to those of low-polar organic solvents. SCW provides full miscibility with permanent gases such as oxygen, nitrogen and carbon dioxide whereas inorganic salts (KCl, NaCl, $CaSO_4$ etc.) are not almost soluble in SCW. Furthermore, SCW has high diffusivities, low dielectric constant and low viscosities like gas that provides better mass transfer (Qiao et al. 2012). SCW is characterized by the incoming high ion product that means high concentration of $[H^+]$ and $[OH^-]$ in supercritical water. Therefore, it enables SCW to act as a base or acid catalyst in reactions (Basu and Mettanant 2009).

Subcritical water behaves very differently both of from room temperature water and from supercritical water. In recent years, the use of subcritical water as a reaction medium and a solvent for the biomass conversion has attracted great attention. Some properties of normal water, sub- and supercritical water are given in Table 1.

Table 1. Properties of water at various conditions (Source: Toor et al. 2011)

	Normal water	Subcritical water		Supercritical water	
Temperature (°C)	25	250	350	400	400
Pressure (MPa)	0.1	5	25	25	50
Dielectric constant, ε (F/m)	78.5	27.1	14.07	5.9	10.5
Ionic product, pKw	14.0	11.2	12	19.4	11.9
Heat capacity Cp (kJ/kg K)	4.22	4.86	10.1	13.0	6.8
Dynamic viscosity, h (mPa s)	0.89	0.11	0.064	0.03	0.07

2.5. Sorbitol

Sorbitol, also called as D-glucitol, D-sorbitol, and D-glucohexane-1,2,3,4,5,6-hexol that was discovered by the French chemist Boussingault in the berries of the mountain ash (*Sorbus aucuparia L.*) in 1872. Sorbitol is a type of carbohydrate called as a natural sugar alcohol or a polyol-$C_6H_{14}O_6$ which is given in Figure 5.

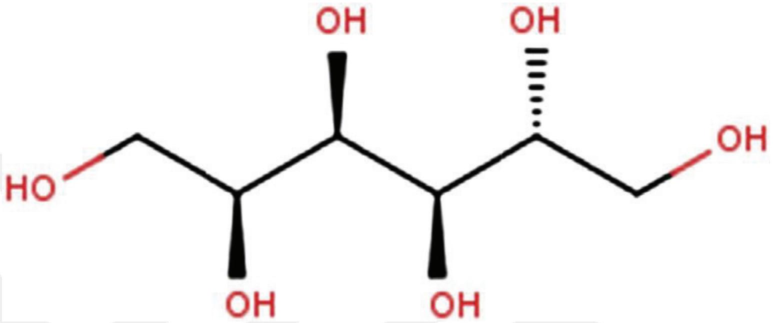

Figure 5. Sorbitol structure (Source: Moreno et al. 2017)

Sorbitol contains approximately a third less calories than sugar and is 60% sweet compared to sucrose. It is all low-caloric, sugar-free, and alternative sweeteners. It is an odourless, noncariogenic, white crystalline powder. Its solubility is 2350 g/L and a pH around 7.0. Table 2 shows that the physical properties of sorbitol in detail. Sorbitol is found naturally in a variety of fruits such as apples, pears, peaches, cherries and blackberries. Table 3 shows that content of sorbitol in these fruits.

Table 2. Physical Properties of Sorbitol (Source: Zhang et al. 2013)

Molecular Weight (g/mol)	Refractive index[a]	Density (kg/m3)[b]	Melting point (K)	Boiling point (K)
182.17	1.3477	1489	361−375	569

a Value for 10% by weight aqueous solution. b Value given for 268 K.

Table 3. Sorbitol Content in Some Fruits (Source: Jonas and Silveira 2004)

Apples	0.20–1.01 g/100 g
Pears	1.20–2.80 g/100 g
Plums	0.60–2.01 g/100 g
Peaches	0.50–1.25 g/100 g
Sweet cherries	1.40 g/100 g
Black grapes	0.20 g/100 g
White grapes	No sorbitol
Berries (strawberries, blackberries, raspberries)	Traces

The artificial version is the same as nature. Sorbitol has a sweet, cool and pleasant taste. At room temperature, liquid sorbitol has a tendency to crystallize. The liquid sorbitol can either be spray dried for production the powder or the liquid sorbitol can be also converted to a solid by melt crystallisation. Due to the fact that sorbitol powders can be easily compressed, sorbitol storage is very important to ensure that the products remain free flowing. Their storage temperatures is 20-25°C for non-bulk deliveries because of their low molecular weight whereas the temperature of bulk storage 50-60°C to prevent crystallisation of syrups with higher sorbitol content (Molinary and Quinlan 2012).

2.6. Major Applications of Sorbitol

Sorbitol is mainly used in food & beverage, pharmacy, cosmetic products and as an intermediate product of vitamin C synthesis. It is a sugar substitute with low-calorie, so it can be used in dietetic foods for diabetics. Sorbitol is listed as an original platform chemical like organic acids (succinic acid, itaconic acid, fumaric acid etc.), polyols (glycerol, sorbitol, and xylitol) and others (exm, ethanol, bio-hydrocarbons, furans, etc.). In addition, it is used in many products such as gum, candy, ice cream, mints, baked goods, toothpaste, and cough syrups. The percentage of sorbitol by application areas in 2007 is given in Figure 6. The important applications of sorbitol are summarized below.

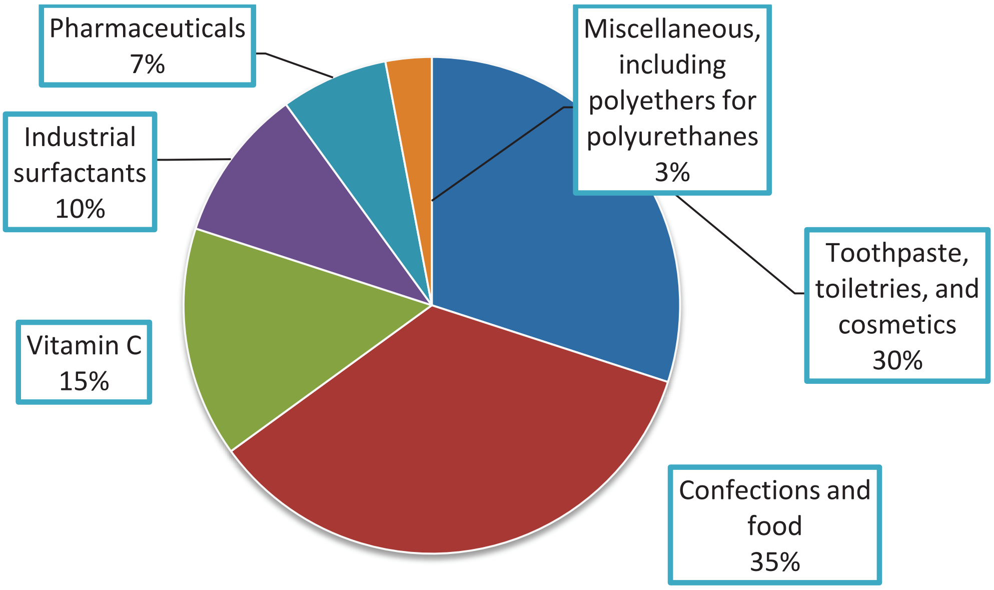

Figure 6. Using percentages for Sorbitol in 2007 (Source: Marques et al. 2016)

Food Applications: Sorbitol is used in dietary foods and also beverages as it acts as an effective substitute for sugar because of its low calorie content. Sorbitol is a nutritive sweetener with 2.4 - 2.6 calories per gram whereas table sugar has about 4 calories per gram (Marques et al. 2016). Sorbitol is used as a replacement of sucrose and other sugars because of increasing demand of products with fewer calories. The use of sorbitol helps to increase the shelf life of such products.. Some examples are chewing gum, hard candy dried roasted nuts, cured meat products, pet foods, icings and toppings, coconut, beverages, and special dietary foods (Molinary and Quinlan 2012).

Pharmaceutical Applications: Sorbitol is mostly used in pharmaceutical carrier for filler-binder in tablet or the formulation of soft gelatin capsules because of its solubility properties, sweet taste, and cooling sensation. For instance, Tylenol, that is a common North American antiinflammatory drug, sodium cyclamate and also sorbitol are used in as sweetness (Marques et al. 2016). Furthermore, sorbitol can be used as a natural laxatives because eating some types of fruits (pears and prunes and etc.) is produced a laxative effects. Therefore, sorbitol is used as especially on this purpose. It can produce an osmotic diarrhea. For syrups, it prevents the crystallization around caps of bottles. Sorbitol is also used in various cough syrups and is generally an inactive ingredient. Too much sorbitol (10 to 50 g or more for adults) can lead to gastrointestinal problems (Ines, Albrecht, and Leopold 2013). Even during surgery, sorbitol can be used for irrigation. Additionally, it is important for in sugar-free formulations. There are some advantages of using sorbitol compared to other marker used to estimate in liver blood flow due to higher extraction ratio. It is good at protected in liver disease and it makes the effect of metabolic changes less significant (Burggraaf et al. 2000).

In Toothpaste: It is the largest application area for sorbitol. Since sorbitol provides as a sweetener, act as a humectant and as an emulsifier. Generally, toothpastes contain sorbitol or glycerin or both of them due to its low glycemic index. It is also safe for teeth because oral bacteria does not metabolize by sorbitol. Its sweetness is not as intense as some consumers want; therefore many manufacturers add saccharin for increasing the sweet taste. The moistening potential of D-sorbitol prevents the crystallization of abrasives. The moisturizing potential of sorbitol prevents the crystallization of abrasives (Molinary and Quinlan 2012).

Cosmetic Applications: Sorbitol is also used in some cosmetic applications because of thermal treatment. It has important effect on its stability in oil in water emulsions (Chanasattru, Decker, and McClements 2009). According to some experiments, 50 mM of sorbitol is protected epidermal keratinocytes made by sodium chloride from osmotic toxicity. Other clinical experiments showed that skin subjected to chronically hot and dry environments got better with sorbitol in its barrier repair and moisturization, especially exposed to dry environmental conditions (Muizzuddin et al. 2013).

Vitamin C: Sorbitol is a substrate in the process of biological transformation by acetic acid bacteria, resulting in l-sorbose, a pioneer in industrially used vitamin C synthesis (Šefčovičová et al. 2011).

Surfactants: Other areas of application include the use of foaming, wetting agents, detergents, dispersants and emulsifiers as surfactants. They are also nonionic surfactants. There are no charge groups. Their head groups provide great emulsifying and stabilizing effects (Marques et al. 2016).

Specialized Applications: Sorbitol is also used in rollers, leather, writing inks, stabilizer for vinyl resins, varnishes, and in antifreeze mixtures with glycerol or glycols. For example, the biocomposites containing sorbitol polyglycidyl ether can be used in wooden floors because they have higher tensile strength than the classic cured neat resin (Shibata et al. 2013).

As a platform chemical: Sorbitol is used as a platform of isosorbide, ethylene glycol, propylene glycol, and glycerol production. Glycerol, ethylene glycol, and propylene glycol are significant chemicals generally used in the production of polyester resins, surfactants, pharmacy, and functional fluids (Marques et al. 2016). Isosorbide is an important well-known industrial chemical that is generally manufactured by dehydration of sorbitol on a strong acid catalyst. The usage area of sorbitol is shown in Figure 7.

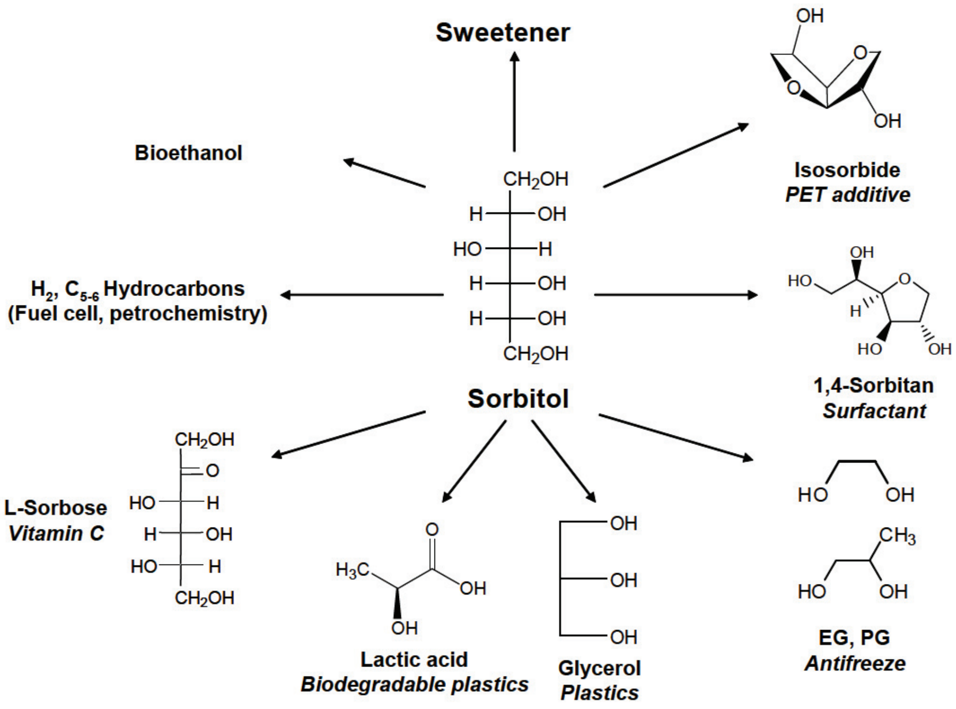

Figure 7. Usage area of sorbitol as a precursor (Source: Dhepe and Fukuoka 2007)

2.7. Sorbitol Market

Sorbitol was discovered by the French chemist Boussingault in the fruits of the mountain ash (*Sorbus aucuparia L.*) in 1872. It was just obtained from natural resources during several decades. In 1935 and 1936, sorbitol and mannitol was started to produce 1400 $t.year^{-1}$ by electroreduction of D-glucose from corn starch a result of the rapidly growing demand. A few years after, the more economical high pressure catalytic hydrogenation was started to use that is currently the only worldwide operated chemical process for sorbitol production instead of the electrochemical process. The industrial importance of sorbitol has been increased since that time. This importance will increase in the coming period as it requires the use of building materials to produce intermediates and materials necessary to maintain the standard of biomass-derived chemicals, due to the worldwide trend for transition from petro-economy to bioeconomy. Actually, sorbitol is the top 12 chemicals derived from carbohydrates that could be used as a platform chemical by US Department of Energy (Marques et al. 2016).

The global sorbitol market was approximately 1830 kt in 2013, and is estimated to grow at 3.6% CAGR from 2014 to 2020 until 2337 kt in total, providing a global market of 3.9 billion $ by 2020. The base year considered is 2013 while the forecast period is from 2014 to 2020. Sorbitol is available in both crystal/powder and liquid/syrup forms. Liquid/syrup was the leading product segment with a market value of over $ 850 million in 2013 and it is estimated to increase owing to sweet syrups. But crystal/powder sorbitol has limited applications in the food and also pharmaceutical industries. The global sorbitol market both of crystal/powder and liquid/syrup forms by 2012-2020 is given in Figure 8.

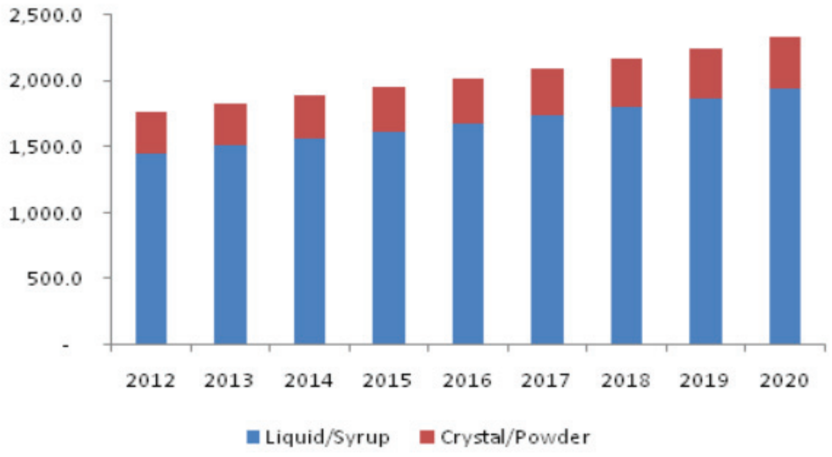

Figure 8. Global sorbitol market, between 2012-2020 (Kilo tons) (Source: Radiant Insights Inc. 2015)

The global sorbitol market is affected by several factors. Demand of low calorie food and beverages is one of the notable factors for the growth of sorbitol market. In addition, the number of patients with diabetes is increasing worldwide. The demand for sorbitol is increasing due to consumer preference for prepared food products. Diabetic and dietary foods and beverages is biggest use and had a value over $ 400 million in 2013 (24% market share). For instance, food & beverage manufacturers such as Kellogg, Danone, and KFC have started using sorbitol. Toothpaste is the second largest application areas (24% market share in 2013) and it was estimated to grow significantly since the high refractive sorbitol index allows to be used as crystal in transparent gels. Toothpaste made up more than 20% of total volume in 2013 and is estimated CAGR of over 4% up to 2020. Gel toothpastes comprise 50% liquid sorbitol. Vitamin C made up about 15% of the total market of sorbitol in 2013 with market value over $ 250 million. Other applications include its surfactants such as wetting and foaming agents, dispersants, detergents, and emulsifiers (Radiant Insights Inc. 2015).

Production of sorbitol has historically been concentrated in Europe (Germany, United Kingdom, France, and Russia) and North America (United States, Canada, and Mexico). China started producing sorbitol to produce vitamin C in the late 1950s. In 2013, Asia Pacific (China, Japan, India, and Indonesia) was the leading sorbitol market with a value of $ 650 million. The Chinese and Indian governments have made numerous attempts to increase the domestic production of the pharmaceutical and personal care industries by allowing foreign direct investment. Europe is the second largest regional market for sorbitol and is expected to grow by over 2.5% by 2020. The European Commission reported the Horizon 2020 Strategy that goals to promote the industrial growth of naturally obtained products (Radiant Insights Inc. 2015). Consequently, new investments are expected for sorbitol in the near future. North America explained for more than 20% of market demand in 2013, and is expected to demand $ 450 million by 2020. China is exporting to many countries such as Pakistan, Ethiopia, The Philippines, Korea, Taiwan, Vietnam, Thailand, and West Africa (Marques et al. 2016).

As a result, the increasing industrial importance of sorbitol attracts undoubtedly great interest in improving the methods in its production and looking at new processes.

2.8. Method for the Production of Sorbitol

2.8.1. Electrochemical Production of Sorbitol

The method of electrochemical production of sorbitol was one of the first industrial processes that produce an organic chemical by using electrosynthesis. Water oxidation resulting in oxygen and protons occurs at the anode whereas the reduction of D-glucose to sorbitol as the main product and mannitol as a by-product is the cathodic reaction (Moreno et al. 2017). The electrosynthesis of sorbitol from D-glucose is shown in Figure 9.

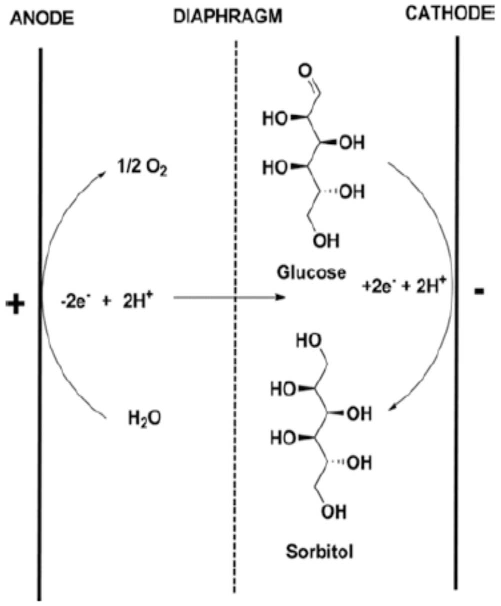

Figure 9. Cathodic and anodic reactions in the electrosynthesis of sorbitol from D-glucose by using divided cells (Source: Moreno et al. 2017)

In 1937, Atlas Powder Company started to produce 1400 tons of per year sorbitol and mannitol through electro-reduction of D-glucose from corn starch. Later on, more cost-effective high-pressure catalytic hydrogenation was started to be used instead of electrochemical process. Unlike chemical synthesis and microbiological synthesis, electrochemical synthesis bibliography is extremely low and the emphasis was placed on reducing manufacturing costs. Decreasing power consumption and increasing cell efficiency by obtaining at the same time a precious chemical at the anode are needed to decrease cost (Moreno et al. 2017).

2.8.2. Biotechnological Production of Sorbitol

Biotechnological production is another alternative to produce sorbitol and involves converting biomass derivative raw materials into sorbitol using enzymes and microorganisms as (bio) catalysts. There are some advantages of biotechnological methods compare to chemical methods and these are ambient temperature and pressure operation that decreases energy costs, and provides a high selectivity and also specificity, which reduces by-product generation. *Zymomonas mobilis*, which found in sugar-rich plant materials and fermented plant waters, is a gram-negative bacteria.

The mechanism of sucrose is converted to sorbitol and gluconic acid using the *Zymomonas mobilis* shown in the Figure 10. As shown in the figure, the enzyme appears to be responsible for both steps; these are oxidation of D-glucose to glucono-δ-lactone and reduction of fructose to sorbitol. The enzyme is D-glucose fructose oxidoreductase (GFOR; EC1.1.199) containing a firmly bound NADP as a cofactor. The enzyme can be like the classic ping-pong mechanism. First, D-glucose turns into glucolaclatone that leaves the enzyme (GFOR), and then fructose is reduced to sorbitol.

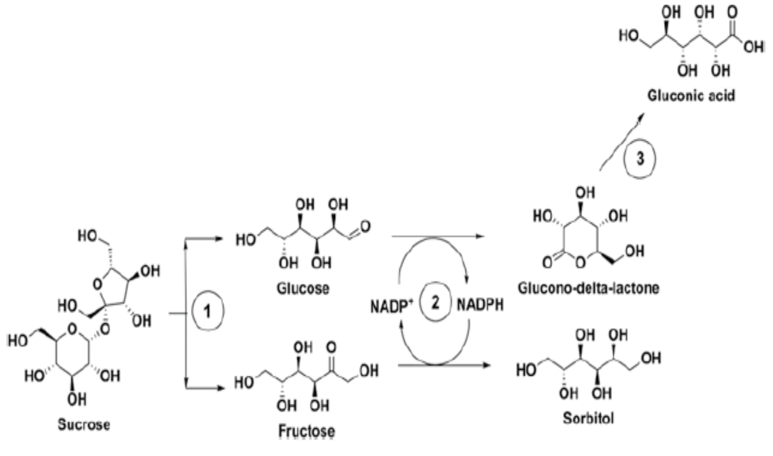

Figure 10. Conversion mechanism of sucrose with *Z. mobilis* to sorbitol and gluconic acid *1*: Invertase; *2*: GFOR; *3*: gluconolactonase (Source: Moreno et al. 2017)

The advantage of this method is that it is a self-renewable redox enzyme system and it is not necessary to add exogenously adenine nucleotide cofactors, which are expensive and unstable owing to the tight binding of NADP to the enzyme. Sorbitol collects in culture medium by fermentation of D-glucose and fructose by Z-mobilis whereas gluconic acid is metabolized via the Entner-Doudoroff and results in ethanol and CO_2 production. It can be possible to obtain only primary products, namely sorbitol and gluconic acid with cell-free system or with the purified GFOR. According to Silveira et al. (1999) the use of an equimolar mixture of 650g/L D-glucose and fructose caused almost complete biotransformation to sorbitol and gluconic acid without ethanol formation, and yielded more than 91% for both of the products (Silveira et al. 1999).

For biotechnological production of sorbitol using Z. mobilis, it has been used in low-cost substrates as an alternative to fructose such as sucrose, Jerusalem artichoke, Sugar cane molasses, inulin and cassava starch.

Sorbitol synthesis with *Z. mobilis* is not fermentation but a biocatalytic process. Briefly, GFOR enzyme is a biocatalyst that is attached to bacterial, therefore it can be called as a full cell biocatalyst. The process consists of two separate steps that are biocatalyst generation and biocatalytic reaction. In the first step biocatalyst generation, it is made by microorganism culture to produce as much biomass as possible in biocatalysis. That’s why, the first step is definitely a true fermentation (Marques et al. 2016).

The electrodialysis system, which is also connected to the bioreactor to remove gluconic acid from the medium, is used to recover and purify sorbitol. The electrodialysis cannot economically possible to remove gluconic acid. As an alternative method, sorbitol and sodium gluconate are by selectively precipitating sodium gluconate with organic solvents such as methanol and ethanol (Silveira et al. 1999). A complete sorbitol recovery procedure from the complex biotechnical reaction medium has not fully developed yet, and research should be continued to achieve this goal. Therefore, chemical process is still preferred rather than the biotechnological method to produce sorbitol.

2.8.3. Chemical Production of Sorbitol

Sorbitol can be produced from different sugars such as glucose and cellulose by catalytic hydrogenation using metallic catalysts. Compared with cellulose, glucose has many remarkable advantages in terms of chemical engineering process. Above all, glucose is highly water soluble, which makes its transportation very suitable for chemical engineering operation. Secondly, glucose is more active than cellulose and also does not need to enter the stage of determining the rate of hydrolysis during catalytic conversion. Consequently, glucose conversion is more efficiently than the cellulose conversion. Besides the advantages of glucose conversion, there are some important problems. For example, glucose undergoes side reactions under high reaction temperatures and high reagent concentrations due to its high chemical activity. Eventually, side reactions significantly reduce targeted sorbitol production (Zhao et al. 2013).

The reaction is carried out elevated temperature (typically, 373–443 K) and pressure (typically, 3–15 MPa) conditions. The reaction time (1–3 h) depends on reaction conditions for batch production. Water is used as reaction solvent.

Although most production methods defined in the literature are called batch processes, it should be noted that most run at constant hydrogen pressure, thereby feeding the hydrogen continually as it is consumed, thereby causing semi-batch processes. Batch (semi-batch) processes are widely used in industrial for production of sorbitol due to the good use of the catalyst and good temperature control (Doluda et al. 2016). Unfortunately, the main disadvantage is recycling to remove the catalyst which leads to progressive catalyst deactivation and increased costs. The more efficient processes are needed due to increasing demand for sorbitol. As a result of, the continuous methods must be developed owing to higher space-time efficiencies and lack of an expensive catalyst separation step (Marques et al. 2016).

2.8.3.1. D-Glucose Hydrogenation

Sorbitol is mostly produced by catalytic hydrogenation of glucose which is an abundant and cheap raw material from renewable resources and the synthesis causes the highest purity of the product. However, a lot of side products are formed such as D-mannitol, gluconic acid. The formation of side products leads to reduced process selectivity. In the literature, sorbitol is obtained from glucose with various catalysts, but the sequence of activity is Ru > Ni > Rh > Pd (Singh et al. 2018). The supported ruthenium catalysts show the best activities. The detailed description of catalyst activity is given below. Additionally, the reaction mechanism of D-glucose hydrogenation to D-sorbitol is depicted in Figure 11.

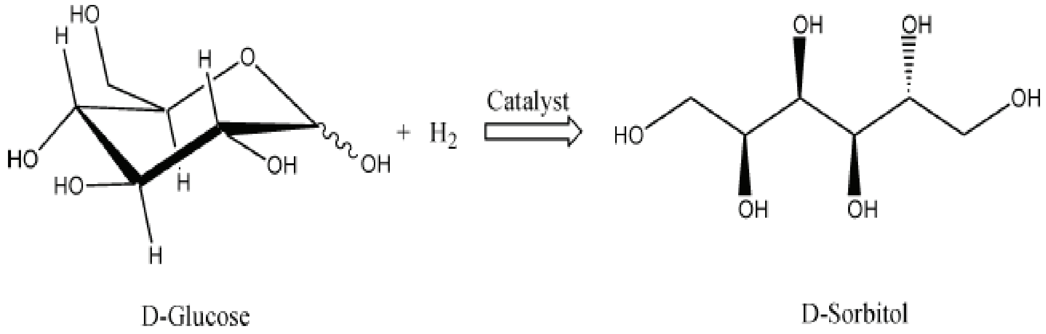

Figure 11. Reaction scheme of D-sorbitol production from D-glucose (Source: Maris et al. 2006)

Nickel-based catalysts: Sorbitol was first obtained by glucose hydrogenation with the suspension catalyst in 1942, and thereafter a fixed bed reactor was used with Raney-nickel catalyst (Zhang et al. 2013). Nickel-based catalysts are traditionally used for the hydrogenation of glucose to sorbitol due to their low cost compared to other metal-based catalysts and their high selectivity for sorbitol. However, there are some disadvantages of nickel based catalysts in usage of industrial: deactivation by sintering, infiltration of the reaction mixture, increased purification prices and poisoning. Furthermore, many issues need to be considered for the production of sorbitol in modified Raney-nickel catalyst. First, the appropriate H_2 pressure is selected to achieve high glucose conversion, and the higher reaction temperature causes glucose carbonization and also produces some by products. Second, the suitable pH of the reaction solution is 8.0−9.0. However, glucose can be isomerized into the mannose in the alkaline state easily and after hydrogenated into the mannitol. That’s why, an appropriate pH value should be decided to prolong the catalyst life and also prevent glucose isomerization. pH of about 7.5 is recommended in industrial production (Zhang et al. 2013). Nickel should be completely removed from sorbitol for the usage of medical, food and cosmetic applications and this means high extra prices. Therefore the industry needed more stable and active one as an alternative to nickel-based catalysts, cobalt, platinum, palladium, rhodium and ruthenium-based catalysts can be used. Other alternative is to add promoters to Raney nickel catalysts or use supports (Marques et al. 2016).

The addition of adding magnesium (Mg), titanium (Ti), iron (Fe), copper (Cu) and molybdenum (Mo) to Raney nickel significantly increases the stability and activity of the catalysts. According to Court et al. (1988), the catalyst of $Ni_{2-x}M_xAl_3$ (where M is Cr, Fe, Co, Cu, Mo and $x \leq 0.4$) promotes the aluminium retention and the promoters except cobalt improve the nickel activity. Iron has a very apparent promoting impact. This metal oxidate throughout the catalytic reaction and thus, it protects a clean metallic nickel surface by preventing potential oxidation of active nickel sites (Court et al. 1988).

Mo, Cr, Sn and Fe were used as promoters for Raney nickel catalysts by Gallezot et al. (1994), The aim of the study is to measure the initial conversion rates and investigate the activity of catalysts, so there is no information about the conversion and selectivity. The activity of Mo and Cr supported catalysts decreases little by recycling because of poisoning of cracking products created in side reactions. Fe- and Sn-supported catalysts are deactivated very quickly due to leakage from the surface, but they remain in the catalyst micropores by leaking iron into the liquid phase (Gallezot et al. 1994).

The other study was used Ni–B/SiO_2 amorphous catalyst with and without metal promoters. It contained 1 wt% of catalyst and D-glucose in stainless steel autoclave at 373 K, 4.0 MPa during 6 hours. With the addition of promoters W, Mo and Cr, the conversion increased from 30% to 35%, 42% and 49%, respectively, the optimum content of W, Mo and Cr were 10, 5 and 10% by weight, respectively. Furthermore, their selectivity was closed to about 100% (Li, Li, and Deng 2002).

Raney Nickel Catalysts with the promoter of Mo and Cr/Fe was studied by Hoffer et al. (2003). They used the three-phase slurry reactor at 4.0 MPa and 393 K. Their selectivity was also closed to about 100%. The concentration of promoters (wt%) were dissimilar at bulk (1.4% Mo, 2.4%/3.6% Cr/Fe) and surface (8.7% Mo, 3.8%/5.9% Cr/Fe) catalyst, being substantially as oxides. Additionally, promoters have shown an improvement and stabilization in the BET surface area, causing a rise in catalyst activity. The BET surface areas were increased from 56 m^2 $gcat^{-1}$ in Raney nickel catalyst to 77 and 112 m^2 $gcat^{-1}$ in the Mo and Cr/Fe promoters with catalysts, respectively. As a result of this research, increasing the reaction rate by the promoters was defined as promoters being more electropositive than Ni and functioning as adsorption sites for glucose, which produces an ionic species sensitive to hydrogen attack. Catalyst stability was increased by these promoters, with less activity loss (30% and 16% for Mo- and Cr/Fe-supported catalysts, respectively) than in unpromoted catalyst (48%) after three recycles (Hoffer et al. 2003).

The use of supports (SiO_2, TiO_2, Al_2O_3 and so on) to improve Ni activity and stability has proven to be a good strategy to rise the metal distribution and have a large surface area.

Kusserow, Schimpf, and Claus (2003) studied the carriers (C, SiO_2, TiO_2, Al_2O_3, ZrO_2) to produce sorbitol from40–50 wt% aqueous D-glucose solution at 393 K, 12 MPa H_2 for 5 hours by using 1 wt% catalyst load and also the catalyst preparation method such as precipitation, impregnation, template and sol-gel. Catalyst prepared by impregnation method showed mostly a higher activity compared to other methods. The order of selectivity SiO_2 (2.1–4.1 wt%) > C (3.4–6.3 wt%) > Al_2O_3 (5.5–7.5 wt%) > TiO_2 (~8 wt%). Furthermore, the importance of particle size was investigated to prevent Ni leaching. The catalyst activity was highly dependent on the pre-treatment conditions. Pre-reduction calcination causes higher conversion (19-45%) and sorbitol selectivity (81-92%) than direct conversion (conversion: 10-16% and selectivity: 21-59%) without calcination pre-treatment after reaction time (5 hours), respectively (Kusserow, Schimpf, and Claus 2003).

Another study mentioned the performance of Raney-type nickel catalysts supported on ZrO_2, TiO_2, ZrO_2/SiO_2, ZrO_2/TiO_2, and $MgO/Al_2O_3/SiO_2$, in comparison with a Ni/SiO_2 catalyst, prepared by precipitation method. 50 wt% D-glucose aqueous solution and 1.5 wt%. Ni contents in catalysts were used at 393 K and 12 MPa H_2 for 4 h. Conversion datas were not specified. The yield of sorbitol: $Ni/ZrO_2/SiO_2$ (97.8%)>Ni/TiO_2 (97.5%)>$Ni/ZrO_2/TiO_2$ (96.7%)>Ni/ZrO_2 (93.2%)>Ni/SiO_2 (92.4%)>$Ni/MgO/Al_2O_3/SiO_2$ (83.9%). Considering that it was equivalent to 96.7% to 97.8% sorbitol yields because of analytical uncertainty, TiO_2 content catalysts were observed to have better catalytic performance than Ni/SiO_2 catalyst (Geyer et al. 2012).

Ruthenium based catalysts: The specific activity and stability of ruthenium based catalysts is about 50 times higher than nickel based catalysts for glucose hydrogenation.

It is relatively inexpensive compared to other noble metals such as Pt or Au whereas its cost is higher than Ni. In order to reduce high cost, different solid supports are used such as silica, multi-wall carbon nanotubes, alumina oxides, activated carbons and some synthetic materials (synthetic zeolites). Furthermore, these catalysts are prepared by conventional methods which are impregnation after H_2 reduction (Guo et al. 2014).

According to Hoffer et al. (2003), carbon-supported Ru catalysts offer better alternatives than Raney type Ni catalysts. The authors tried to evaluate the applicability of Ru/C catalysts in the production of D-sorbitol from D-glucose and compare Ru/C catalysts and Raney type Ni of the activity, selectivity and stability. The authors claimed that the Ru/C catalysts had higher activities, Ru did not leak and the activity was directly proportional to the surface area of Ru and was not also dependent of the preparation method. The selectivity was higher than 98% but the conversion data was not available. The reaction of glucose hydrogenation was carried out at a three-phase slurry reactor at 120°C and 4.0 MPa with 10 wt% D-glucose solution. They showed that Ru catalysts were approximately twice as active per Ni catalysts per kg catalyst (Hoffer et al. 2003).

Mishra et al. (2014) examined the status of HY zeolite-supported ruthenium catalysts using a HY zeolite (called HYZ) with a Si/Al ratio equal to 80. These catalysts were prepared using $NaBH_4$ in ethanol as reducing agent by using conventional impregnation–reduction method. The reactions were performed with a 20 wt% aqueous solution of glucose for 20 minutes at 5.5 MPa H_2 and 120°C using a Ru(1 wt%)/HYZ catalyst in a concentration of 2.5 wt% relative to glucose (Mishra et al. 2014). Additionally, the same research group studied with Ru(1 wt%)/NiO-TiO_2 and Ru(1 wt%)/TiO_2 catalysts and a Ru(5 wt%)/C commercial catalyst (Mishra et al. 2012). Based on the results of these two studies, metal dispersions were found as 23.6, 4.4, 8.6 and 6.7 for Ru(1 wt%)/HYZ, Ru(1 wt%)/TiO_2, Ru(1 wt%)/NiO-TiO_2, and Ru(5 wt%)/C, respectively. The catalyst of Ru(1 wt%)/HYZ showed higher conversion (19.4%), selectivity (97.6%) and TOF (1275 h^{-1}) than other used catalysts. After optimization, the reaction time was increased up to 2 hours with the same experimental conditions, resulting in 100% conversion and 98.7% selectivity. As a result of these studies, the acidity (mild acidity) of zeolite support showed an increase in both selectivity and activity of sorbitol.

Aho et al. (2015) investigated the effect of Ru nanoparticle size on the catalytic activity for glucose hydrogenation. Hydrogenation of the glucose was carried out on a few Ru/C catalysts in semi-batch mode at 120°C and 19 bar H_2 pressure with various metal dispersions. Catalysts with a ruthenium particle size ranging from 1.2 to 10 nm were used. Whole catalysts were found to be active in sorbitol for glucose hydrogenation. Sorbitol selectivity was observed to have a quite high range of 87-96%, excluding 10 nm particle catalysts (28.8%). The highest sorbitol selectivity was observed in the 2.5 Ru particle size (96.1%) (Aho et al. 2015).

Lazaridis et al. (2015) studied the hydrogenation/hydrogenolysis of glucose at low hydrogen pressure (16 bar) and high reaction temperature (453 K) with low glucose concentration (2.7%) using platinum and ruthenium catalysts supported on activated micro/mesoporous carbon (AC). They also investigated the impact of metal content (1–5 wt. %), method of metal pre-treatment and reduction ($NaBH_4$ or H_2 at 350°C) and reaction time (1-12 h). They prepared Ru and Pt based catalysts by wet impregnation method by using a micro and mesoporous activated carbon. All conversion of Ru and Pt/AC catalyst were found higher than 97% because these catalysts were very active. Moreover, the selectivity of sorbitol were found high (sel.≥90%) for Pt/AC catalysts regardless of the content of metal and reduction method and also reaction time. Even though the maximum sorbitol selectivity was found 95% that was low value compared to industrially desired value owing to high temperature. Therefor it was caused hydrogenolysis resulting in a lot of lower sugar alcohols, such as 1,2,5,6-hexanetetrol, threitol, arabinitol, 1,2-propanediol and glycerol. On the other side, Ru/AC catalysts were less selective for sorbitol (sel. 55-93%). The 93% sorbitol selectivity was achieved results with using a metal content of 3% by weight and reaction time only 1 hour using only $NaBH_4$ as a metal reducing agent. Additionally, sorbitol selectivity increased when the reaction time decreased from 12 h to 1 h and also when ruthenium loading increased from 1% to 3-5% by weight in the same experimental conditions. For reduction method, sorbitol selectivity was observed to be lower for $NaBH_4$ reduced catalysts than for hydrogen reduced. The Pt/AC catalysts high sorbitol selectivity might be related to its well-formed and abundant of single crystal Pt particles (2–6 nm) comparing the low crystal structure of Ru/AC catalyst (Lazaridis et al. 2015).

Li, Liu, and Wu (2018) studied with a carbonized cassava dregs- supported Ru nanoparaticles catalysts (Ru/CCD), Ru/AC and Pt/CCD which were prepared by simple impregnation-chemical reduction method. The reaction was carried out in a 50 mL high pressure reactor with 10 wt.% D-glucose solution, 1.0 wt.% prepared catalyst at 120°C and 3 MPa H_2 gas for 1.5 h. According to results, when no catalyst or just CCD was used, sorbitol was not seen, but the conversions of D-glucose were 9.8% and 20.6%, respectively. The catalyst of Ru/CCD showed D-glucose conversion 99.7% whereas Ru/AC showed D-glucose conversion 100%. The sorbitol yield for Ru/CCD and Ru/AC was found 98.6% and 96.5%, respectively. For Pt/CCD, the conversion of D-glucose and sorbitol yield were 100% and 93.3%, respectively. These results showed us that Ru has higher catalytic performance than Pt for production of sorbitol from D-glucose. Furthermore, they investigated the influence of reaction temperature. Higher reaction temperature resulted in little increases of D-glucose conversion, but the yield of D-sorbitol decreased and the yield of mannitol increased. They chose the optimum temperature as 120°C (Li, Liu, and Wu 2018).

Zhang et al. (2011) studied with Ru/MCM-41 catalyst for production sorbitol from glucose. These catalysts prepared by using an impregnation formaldehyde reduction method. The reaction was performed in high pressure reactor (PARR 5500) with 10 wt % glucose at several temperatures under 3 MPa H_2. Various reaction time (1-6 h), reaction temperature (100-140°C), recycling times of catalyst (1-4), dosage of catalyst (0-30 wt.%) and different types of catalyst were tried to find optimum. As the reaction time extended, glucose conversion increased rapidly. Glucose was fully converted at 3 h. The highest sorbitol yield was at 1.5 h. So, the optimum reaction time was found 1.5 hours. The maximum sorbitol yield was 92.13% at 125°C although the main reaction was performed at 120°C. As expected, the sorbitol yield increased with an increase in the dosage of catalyst. It was observed that the yield did not change significantly and glucose was already fully converted. Thus, the dosage of catalyst was 20 % by weight when sorbitol yield was stable. Moreover, the sorbitol yield decreased from 83.13% to 68.21% after reused. After three of four times reusing, the sorbitol yield did not change significantly since ruthenium might be well loaded in MCM-41. Besides Ru/C showed relatively high catalytic performance compared to others, the sorbitol selectivity was found 59.7% (Zhang et al. 2011). Table 4 shows some examples of glucose hydrogenation to sorbitol by using different catalysts.

Table 4. Examples of glucose hydrogenation to sorbitol in literature

Catalyst	Reactor	Reaction Conditions	Glucose Conversion (%)	Sorbitol Yield (%)	Reference
Ru/SiO_2	100 mL of batch reactor	2 g glucose, 48 g water and 0.1 g catalyst at 100°C and 5.5 MPa for 10 hours for 1 h	Not given	38	Dabbawala et al. 2015
AC	stainless steel high-pressure autoclave reactor (Parr)	0.14 g glucose, 0.06 g catalyst and 5 mL water at 1.6 MPa, 180◦C for 3 h	12	0	Lazaridis et al. 2015
Ru/AC	50 mL high pressure reactor (PARR 5500)	25 ml of 10 wt.% D-glucose solution, 1.0 wt.% catalyst at 120°C and 3 MPa H_2 for 1.5 h.	100	52	Li et al. 2018
Ru/AC			100.0	96.5	

2.8.3.2. Starch Hydrogenation

Starch is a polymeric carbohydrate consisting of many glucose with a molecular formula $(C_6H_{10}O_5)_n$ which is shown in Figure 12. It is the main ingredient of rice, potatoes and corn.

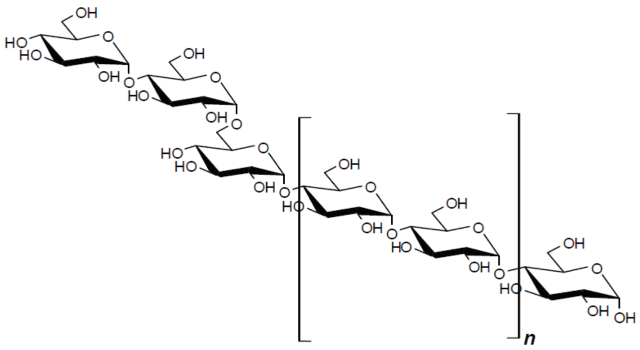

Figure 12. Structure of starch (Source: Dhepe and Fukuoka 2007)

Thus, Heilig (1994) studied with a 37.5 wt% starch aqueous solution in 75 minutes by hydrogenating at 433–473 K under of 5–20 MPa hydrogen pressure. They achieved 60% sorbitol yield with 0.01 to 1 % by weight based on the amount of starch of Lewis acid such as magnesium chloride ($MgCl_2$), nickel sulphate ($NiSO_4$) or stannous chloride ($SnCl_2$). The highest sorbitol purify achieved 97% (Heilig 1994).

The other study was found sorbitol selectivity higher than 95%. They used 10-30 wt% aqueous corn starch at 403-453 K under 5.5 MPa hydrogen pressure with Ru (3 wt%) based on H-USY zeolite as a catalyst for 1 hour (Jacobs and Hinnekens 1990).

2.8.3.3. Cellulose Hydrogenation

Cellulose is one of the most attractive raw materials thanks to large abundance and unlike starch it does not interfere with the food chain. Starch is soluble in hot water whereas cellulose is insoluble in water or organic solvents except in ammoniacal copper hydroxide, concentrated aqueous solution of zinc chloride, etc. Cellulose is difficult to disintegrate because of its strong crystal structure with hydrogen bonds. Additionally, the annual net photosynthesis yield is 1.8 trillion tons and approximately 40% is cellulose (Fukuoka and Dhepe 2006). Furthermore, the researchers have focused on converting sorbitol from cellulose instead of glucose because cellulose is the low price of raw material and has the simplified procedure without any separation of intermediates (Gao et al. 1810). Figure 13 is shown that two steps of conversion of cellulose to sorbitol.

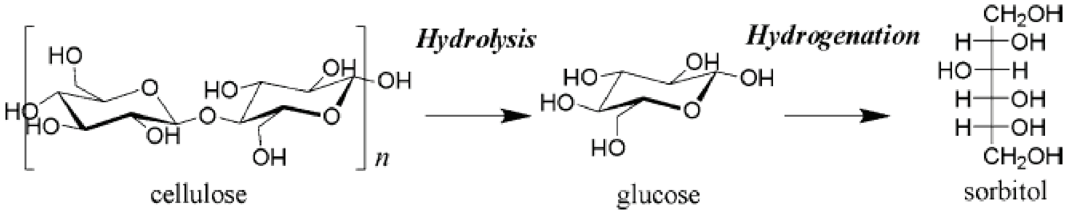

Figure 13. Reaction scheme for the conversion of cellulose into sorbitol (Source: Zhang and Wang 2009)

The first step includes the hydrolysis of the β-1,4-glucosidic bond whereas the second step includes hydrogenation of the glucose. It is easily understood that the catalyst is required since the first stage requires acidity whereas the second stage requires active hydrogen species (Zhang and Wang 2009).

Zhang and Wang (2009) studied with Ru based catalyst supported of carbon nanotubes (CNTs) under 5 MPa H_2 at 185°C for 24 hours in a 100 ml Teflon lined stainless-steel autoclave for cellulose conversion to sorbitol. They investigated the performance of Ru catalysts loaded on various supports (SiO_2, CeO_2, Al_2O_3, MgO, and CNT). According to results of this study, the neutral and basic oxides (SiO_2, CeO_2 and MgO) supports were not efficient whereas the acidic Ru/Al_2O_3 had the better catalytic performance. Contrary to these catalysts, Ru/CNT showed the highest sorbitol yield (69%). They also investigated the effect of catalyst amount on sorbitol yield with 0.14 g of cellulose. As expected that the sorbitol yield increased with increasing the catalyst amount up to 0.14 g (Zhang and Wang 2009).

In another study, 50 mg of ball-milled cellulose, 20 mg of catalyst, and 12 ml of water were used in the stainless steel reactor at 165°C and 50 bar of hydrogen gas for 24 hours. They investigated the effect of reaction time, reaction temperature, and the amount of Ru for the sorbitol production. Ruthenium nanoparticles on activated carbon supports treated with sulphuric acid was used as a catalyst. The sulfonate groups were found to be effective for forming glucose in the hydrolysis of cellulose. In the cases, both of no catalyst and activated carbon were used, sugar alcohols were not observed, even though conversions were about 40%. When Ru/AC was used without acidic sites, sugar alcohols were not seen, however a high conversion of 79.2% was achieved. The sorbitol yield and cellulose conversion for 10 wt. % Ru/AC-SO_3H (dual-functionalized catalysts containing 10 wt.% Ruthenium and sulfonate groups) were found 58.7% and 81%, respectively. They also investigated the effect of different metals such as Pt/AC-

SO_3H, Pd/AC-SO_3H and Ni/AC-SO_3H, but the sorbitol yield was found lower than Ru. According to other results, the conversion of cellulose increased as the temperature, however the maximum sorbitol yield showed at 165°C. Since, the products were observed to degrade at higher temperatures. Moreover, the sorbitol yield was found directly proportional to reaction time; the maximum yield was 71.1% for 36 hours. The sorbitol yield decreased for longer reaction times, even though the conversion of cellulose closed to 100% (Han and Lee 2012).

Ribeiro, Órfão, and Pereira (2015) used Ru/AC to develop for production of sorbitol from cellulose. Incipient wetness impregnation of activated carbon (sieved between 0.1 mm and 0.3 mm) was used to prepare the catalyst. 750 mg of cellulose, 300 mL of water and 300 mg of catalyst (0.4%Ru/AC) were used in 1000 mL stainless steel reactor (Parr) at 205°C and 50 bar. After 5 hours, the cellulose conversion and selectivity o sorbitol were reached 36% and 40%, respectively. When using ball-milled cellulose, conversion was approximately 90%, with 50% sorbitol selectivity. Ball-milling is mechanical techniques for breaking the cellulose crystal structure because the hydrogen bonds of cellulose are separated (Ribeiro, Órfão, and Pereira 2015).

Zhu et al. (2014) studied with ruthenium catalyst supported with a sulfonic acid-functionalized silica (Ru/SiO_2–SO_3H) and Ru/SiO_2 for hydrogenolysis of cellulose into sorbitol. They selected the silica gel as a catalyst support owing to its good hydrothermal stability, which was subsequently inoculated with sulfonic acid, following the accumulation of Ru nanoparticles. The function of sulfonic acid groups in bifunctional catalysts acts as active sites for acid hydrolysis and hydrogenation of Ru nanoparticles. The reaction was carried out at 150°C and under 4.0 MPa H_2 for 10 hours by using different catalysts (0.2 g) and 0.25 g cellulose with 7.5 mL water. When using only sulfonic acid functionalized silica, a glucose yield of 56.6% was achieved, but sorbitol was not seen due to the lack of hydrogenation sites. While using Ru/SiO_2 without acidic sites, cellulose conversion was 36.2%, however almost sorbitol was not obtained. The bifunctional Ru/SiO_2–SO_3H catalyst showed higher catalytic performance. According to results, the cellulose conversion and sorbitol yield were found 90.5% and 61.2%, respectively. In particular, they said that there was a powerful synergistic effect between approximate Ru region and acid region in converting cellulose to sorbitol. They also investigated the effect of reaction temperature which resulted in the cellulose conversion increased from 31.8% to 90.3% and the sorbitol yield increased from 10.3% to 61.2% when temperature increased from 120°C to

150°C. The maximum sorbitol yield was found at 150°C (Zhu et al. 2014). Table 5 is shown cellulose hydrogenation of some examples by using different catalyst.

Table 5. Examples of cellulose hydrogenation to sorbitol in literature

Catalyst	**Reactor**	**Reaction Conditions**	**Cellulose Conversion (%)**	**Sorbitol Yield (%)**	**Reference**
Ru/SiO_2	50 mL stainless steel autoclave reactor	0.25 g cellulose, 0.2 g catalyst and 7.5 mL water, 150°C and under 4 MPa for 10 hours	36.2	1.4	Zhu et al. 2014
Ru/SiO_2	100 mL teflon-lined stainless-steel autoclave	0.16 g cellulose,0.05 g catalyst and 20 ml water at 5 MPa, 185 °C for 24 h	not given	7	Zhang and Wang. 2009
Ru/AC	stainless steel autoclave reactor	50 mg cellulose, 20 mg catalyst, 12 ml water, 165 °C, 5 MPa for 24 h	79.2	0	Han and Lee. 2012
Ru/AC	1000 mL stainless steel reactor (Parr)	750 mg cellulose, 300 mL water and 300 mg catalyst, at 205°C and 5 MPa for 1 h	61.1	26.2	Ribeiro et al. 2015
Ru/SBA 15	100 mL stainless steel high-pressure reactor	1 g of cellulose, 0,6 g catalyst, 50 ml water, at 210°C , 3.5 MPa for 1 h	25	7.7	Reyes-Luyanda et al. 2012

CHAPTER 3

EXPERIMENTAL

3.1. Chemicals

All chemicals used in this study were given in Table 6. Furthermore, de-ionized water was used to prepare solutions and cleaning.

Table 6. List of used chemicals during experiment

Name	Manufacturer
Microcrystalline cellulose	Alfa Aesar
D-Glucose	Merck
Polyethylene glycol (P123)	Aldrich
Ruthenium (III) chloride ($RuCl_3$ 99.9%, Ru 38% min)	Merck
Tetraethyl orthosilicate (TEOS)	Alfa Aesar
Nonionic triblock copolymer surfactant EO20PO70EO20 (P123)	Aldrich
Hydrochloric acid	Merck, 37%

3.2. Catalyst Preparation

3.2.1. Synthesis of Silica Supported Ruthenium Catalyst (Ru/SiO_2)

1 gram of $RuCl_3$ was dissolved in 10 mL of deionized water. Silica nanoparticles (5%, w/w) were added to the solution. After, the prepared solution was dried at 110°C for 4 hours. The resulting sample was to form Ru/SiO_2 (Saxena et al. 2012).

3.2.2. Synthesis of Ru-SBA15 Catalyst

2 gram of P123 was dissolved in 70 mL of HCl solution which is called solution A. TEOS (3.2 mL) and $RuCl_3$ were mixed with 5 mL deionized water and stirred for approximately 10 minutes at room temperature which was called solution B. Then solution B was added to solution A. The mixture of solution A and B was stirred strongly at 40°C for 20 h. It was transferred into autoclave at 100°C for 24 h. After that, it was filtered, washed, and also dried at 60°C for 15 hours. It was calcined at 500°C for 10 hours, and Ru-SBA15 samples were finally obtained (Li et al. 2005).

3.2.3. Synthesis of Ru-SBA15/SO_3 Catalyst

Firstly, 4 gram of P123 was added into 125 gram of HCl at room temperature. This mixture was stirred and after heated to 40°C. After the TEOS was hydrolyzed 45 minutes, the MPTMS and aqueous H_2O_2 solution were simultaneously added to the solution, and the final mixture was stirred for a further 20 hours at 40°C and aged for a further 24 hours under static conditions. The solid product was rescued by filtration and then air dried overnight at room temperature. The P123 template was removed from the synthesized substance by washing ethanol under reflux for 24 hours. Finally, the material was washed with ethanol several times and vacuum dried overnight at 60°C (Won et al. 2012).

3.2.4. Synthesis of Ru/AC Catalyst

Activated carbon (AC) was impregnated in aqueous solution of $RuCl_3 \cdot 3H_20$ (5% by weight). This solution and activated carbon were mixed slowly at room temperature. The resulting was dried at 110°C (in air) for 6 hours and stored in a hermetic bottle. Finally, Ru/AC catalyst was ready (Prasad and Singh 2005).

3.3. Catalyst Characterization

For the catalyst characterization, Scanning Electron Microscope (SEM), BET (Brunauer-Emmett-Teller) surface area analysis device and Fourier Transform Infrared Spectrometry (FT-IR) techniques were used. SEM (Philips XL 30S FEG) was used to closely examine changes in morphological structures. The samples were fixed with double-sided adhesive tapes conducting onto the aluminum plate before the analysis and coated with gold by spraying method. The coating was carried out at 24 mA under partial vacuum for 12 minutes (in the presence of argon) to prepare the products for analysis. The BET surface area device was used to examine the surface area, pore size and pore volume of the catalysts during the reaction. The BET-specific surface area was evaluated using adsorption data in a pressure range of 0.1 to 0.25. FT-IR (FTIR-Shimadzu IRPrestige-21 FTIR 8400S) was used to analyze the bond breakage and new bond formation. The samples were diluted with KBr and pressed onto the discs before analysis. The pellets were prepared with 2 mg sample amount and KBr to reach a total amount of 150 mg. The analysis was performed with 4 scans in the range of 400-4000cm^{-1} with a resolution of 4.00 cm^{-1}.

3.4. Experimental Apparatus

The reactions were carried out in a batch-type reactor (Parr 5500 High Pressure Compact Reactor). Construction material of this reactor is Type 316 Stainless Steel and the reactor volume is 300 ml. The reactor that was given in Figure 14 has gas inlet and outlet valves, a pressure gage, an internal thermocouple and an internal stirrer. It has a cooling system that water and ethylene glycol were used as coolant.

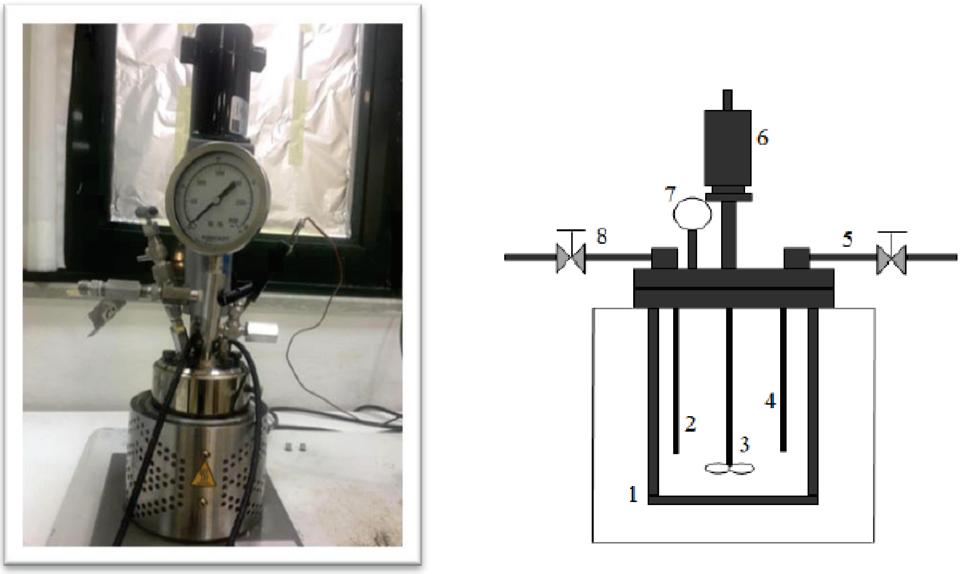

Figure 14. Parr 5500 High Pressure Compact Reactor and Hydrothermal conversion reactor: 1) stainless steel beaker, 2) thermocouple, 3) stirring impeller, 4) gas inlet, 5) input nitrogen gas, 6) magnetically driven stirrer, 7) pressure gauge, 8) gas sample collecting valve (Source: Gökalp Gözaydin 2016)

3.5. Experimental Procedure

The cellulose hydrogenation reactions were carried out in a 300 mL stainless steel Parr reactor (Parr 5500 series). 4 g of cellulose, 1 or 2 g of the prepared catalyst, and 100 ml of de-ionized water were introduced into the reactor under stirring at about 200-1250 rpm. Then the reactor was flushed ten times with N_2 to remove air. The reactor was heated to the set temperature at 150°C. The reaction time was initiated when the temperature reached 150°C. Temperature and pressure (5 bar) values were noted every 10 minutes during the experiment. The temperature-pressure profile formed during the heating of the reactor to 150°C is shown in Figure 15. At the end of the specified reaction time (1-2 h), the heater was turned off and the system was allowed to cool with chiller (ethylene glycol and water). At about 50°C, the reactor was opened and the solid and liquid fractions were separated by filter paper. The resulting liquid sample was stored in the refrigerator for HPLC. The solid product was dried under vacuum at 50°C for about 24 hours. The following equation 3.1 was used for the calculating conversion of cellulose. m_0 and m_1 represent mass of starting cellulose and mass of remaining cellulose after the reaction, respectively. The equations 3.2 and 3.3

were used to calculate the yield of sorbitol and glucose. C_S, C_C and C_G represent concentration of sorbitol after the reaction, concentration of starting cellulose and concentration of starting glucose, respectively.

$$\text{conversion of cellulose (\%)} = \frac{m_0 - m_1}{m_0} \times 100 \tag{3.1}$$

$$\text{yield of sorbitol (\%)} = \frac{C_S}{C_C} \times 100 \tag{3.2}$$

$$\text{yield of glucose (\%)} = \frac{C_S}{C_G} \times 100 \tag{3.3}$$

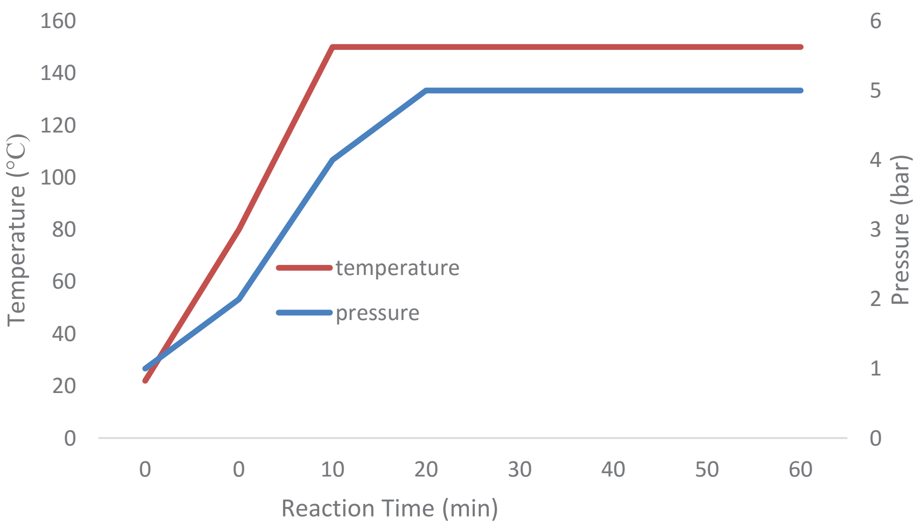

Figure 15. Temperature-pressure profile during the heating of the reactor to 150°C

The glucose hydrogenation reactions were carried out the same reactor. 2.8 g of cellulose, 1.2 g of the prepared catalyst, and 100 ml of water were introduced into the reactor under stirring at about 200-1250 rpm. The same steps were applied in glucose conversion as mentioned above. A summary of the experimental steps is given in the Figure 16.

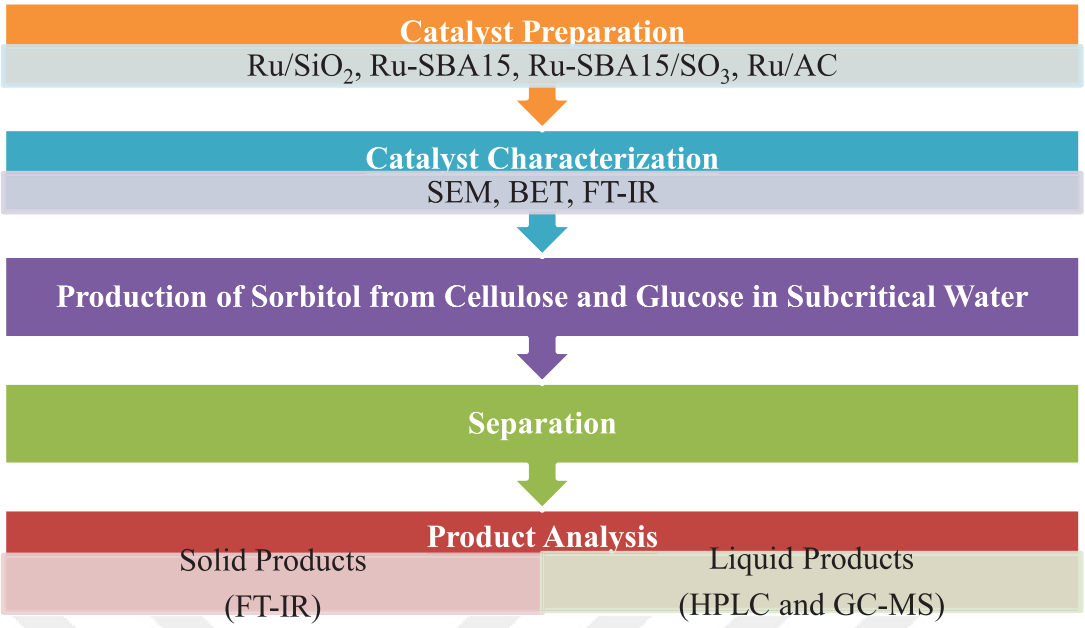

Figure 16. The general diagram of experimental procedure

Multiple experiments were done by changing the several variables and the results were compared to determine the effect of the relationship with a variable on the results. The experiments are tabulated in Table 7 .

Table 7. The experiments to produce sorbitol from cellulose and glucose

Reactant	Catalyst amount	Reaction Time (hour)
cellulose	-----	1
cellulose	1 g Ru-SBA15	1
cellulose	2 g Ru-SBA15	1
cellulose	1 g Ru-SBA15/SO_3	1
cellulose	2 g Ru-SBA15/SO_3	1
cellulose	1 g Ru-SBA15/SO_3	2
cellulose	1 g Ru/SiO_2	1
cellulose	1 g Ru/SiO_2	2
cellulose	2 g Ru/SiO_2	1

(cont. on the next page)

Table 7 (cont.)

Reactant	Catalyst amount	Reaction Time (hour)
cellulose	2 g Ru/SiO_2	2
cellulose	1 g silica gel	1
cellulose	1 g AC	2
cellulose	1 g Ru/AC	2
glucose	------	1
glucose	1,2 g Ru/SBA15	2
glucose	1.2 g Ru-SBA15/SO_3	1
glucose	1.2 g Ru-SBA15/SO_3	2
glucose	1.2 Ru/SiO_2	1
glucose	1.2 Ru/SiO_2	2
glucose	1.2 g silica gel	1
glucose	1.2 g silica gel	2
glucose	1.2 g AC	2
glucose	1.2 g Ru/AC	2

3.6. Product Analysis

HPLC was used for the analysis of liquid products containing the target product sorbitol. HPLC analysis was done both of in Environmental Development Application & Research Center of IZTECH and Food Engineering Department at IZTECH. Liquid products collected for HPLC (Agilent 1100) were passed through a 0.45 µm pore diameter membrane filter prior to analysis. The products were then diluted with the aqueous phase (5 mM H_2SO_4) and ultra-pure water to be used during the analysis. Analyzes were performed on a hydrogen ionic form column (Shodex Sugar SC1011-8x300 mm) at 50°C column temperature and at 80°C column temperature (Rozex RPM-Monosaccharide 300x7.80 mm) in Food Engineering Department. The mobile phase, 5 mM H_2SO_4, and ultra-pure water was passed through the column at a flow rate of 0.5 ml/min and 0.6 ml/min. Refractive index (RI) detector was used as detector. Table 8 shows the properties of HPLC analysis used in this study. Furthermore, the calibration curve of sorbitol is given in the Figure 17.

Table 8. The properties of HPLC analysis.

Analysis Place	Column	Column temperature	Mobile Phase	Flow rate	Detector
Environmental Development Application Center at IZTECH	Shodex Sugar SC1011-8x300 mm	50°C	5 mM H_2SO_4	0.5 ml/min	Refractive index (RI)
Food Engineering Department at IZTECH	P column (Rozex RPM-Monosaccharide 300 x 7.80 mm)	80°C	ultra-pure water	0.6 ml/min	Refractive index (RI)

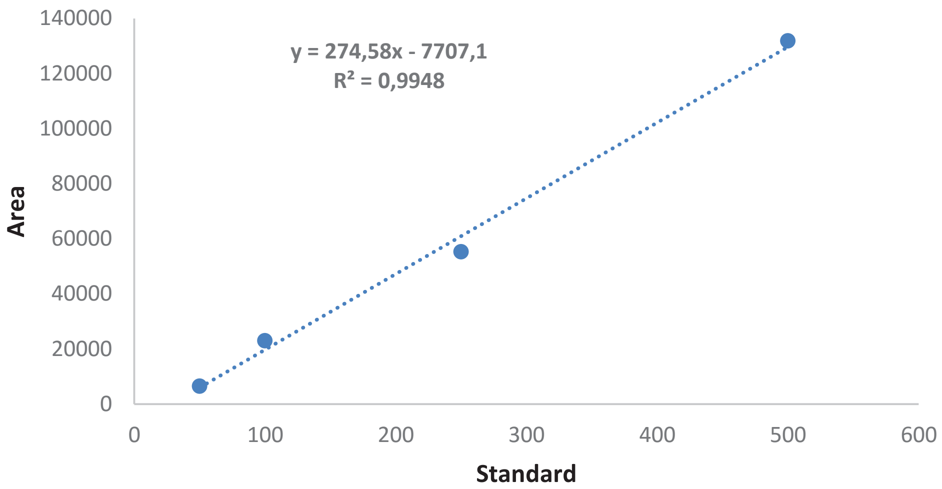

Figure 17. The calibration curve of sorbitol

FT-IR (FTIR-Shimadzu IRPrestige-21 FTIR 8400S) was used for the analysis of solid products after reaction. The samples were diluted with KBr and pressed onto the discs before analysis at room temperature. The analysis was performed with 4 scans in the range of 400- 4000 cm^{-1} with a resolution of 4.00 cm^{-1}.

Gas chromatography-mass spectrometry (GC-MS) (Agilent 6890 N/5973 N Network) with Restek Stabilwax-43 DA column and Agilent 5973 Mass Selective Detector (S/SL inlet) were used to verify formed products except sorbitol. This analysis was carried out in Environmental Development Application and Research Center of IZTECH.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Characterization of Catalysts

In the characterization part, the properties of the catalysts were determined by SEM, BET and FT-IR.

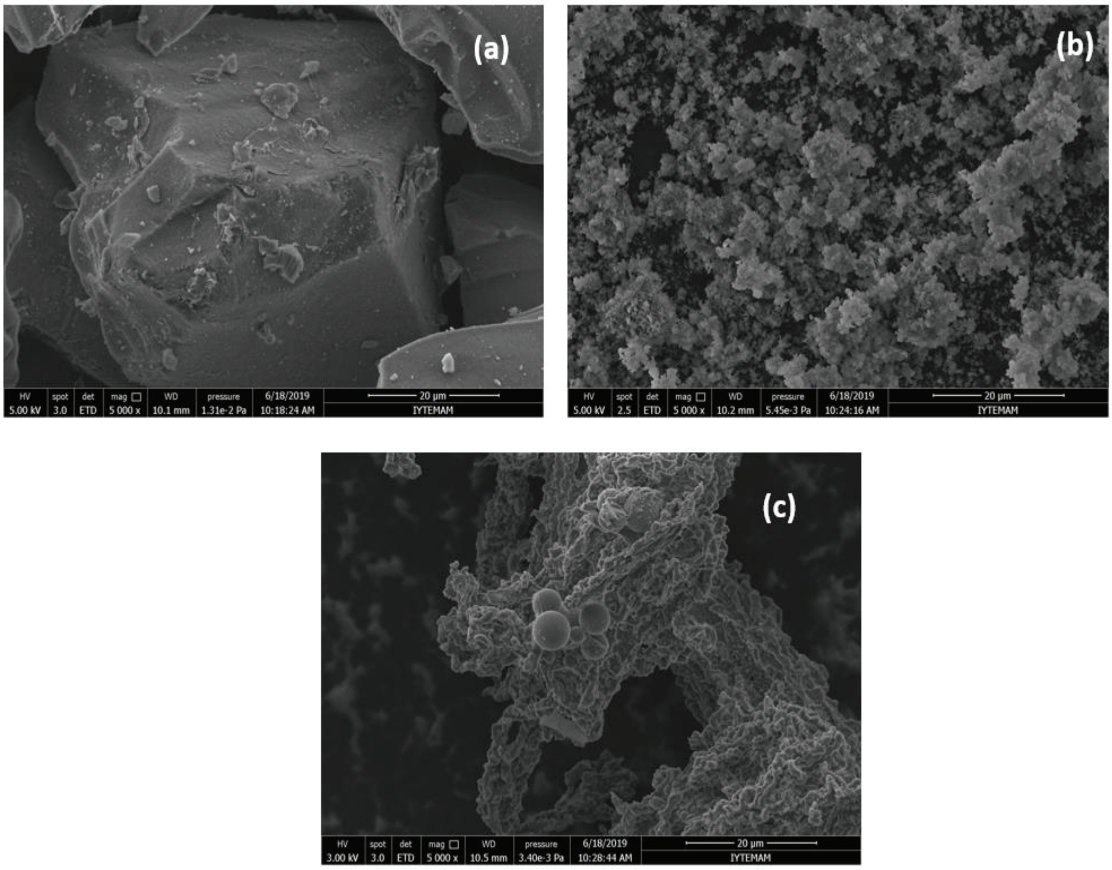

Figure 18. SEM images of synthesized catalysts at a magnification of 5000x (a) Ru/SiO_2, (b) Ru-SBA15, (c) Ru-SBA15/SO_3

SEM analysis was performed at different magnification rates for synthesized catalysts. The results of SEM analysis obtained by using 5000x magnification for Ru/SiO_2, Ru-SBA15 and Ru-SBA15/SO_3 catalysts are given in Figure 18, respectively.

It is clear that these catalysts have a very porous structure. Ru-SBA15 catalyst has uniform dimensions of between 5-6 μm length and 1.3-1.9 μm width on average (Reyes-Luyanda et al. 2012). Functionalizing SBA-15 with sulfonic acid was made because it is thought to increase catalyst activity for hydrolysis compared to SBA-15. The pore structure of the sulfonated Ru-SBA15 appears to have changed.

The characterization of these catalysts was conducted in a BET (Brunauer-Emmett-Teller) apparatus. The results of BET analysis for Ru/SiO_2, Ru-SBA15, Ru-SBA15/SO_3 and Ru/AC catalysts are given in Table 9.

Table 9. BET results of synthesized catalysts

Catalysts	**BET surface area [m^2/g]**	**Pore volume [cm³/g]**	**Pore size [Å]**
Ru/SiO_2	391.74	0.620	55.244
Ru-SBA15	527.42	0.561	49.347
Ru-SBA15/SO_3	168.04	0.248	47.308
Ru/AC	198.97	0.157	44.132

The BET surface area of Ru/SiO_2 was 391.74 m^2/g whereas it was found 355.3 m^2/g in literature (Reyes-Luyanda et al. 2012). According to another study, the surface area and pore volume of SBA15 was 725.4 m^2/g and 4.28 cm³/g, respectively (Song et al. 2018). Another study in the literature reported that the BET surface area of the Ru-SBA15 catalyst was 616 m^2/g (Y. Li et al. 2005). However, the surface area of the synthesized Ru-SBA15 catalyst was determined to be 527.42 m^2/g. The pore size was between 44 Å and 55 Å for four different types of catalyst. The pore volume was between 0.1 and 0.6. When sulfone was connected to Ru-SBA15, BET surface area was decreased significantly. Likewise, the pore volume and size also decreased. But after grafting with sulfonic acid, the pore size of SBA15 did not change significantly. As the pore size and pore volume decreased, the surface area increased. But it was not observed for Ru/SiO_2 catalyst. At the same time, it was not expected that the pore size of Ru/SiO_2 was seen bigger than the other catalysts according to SEM images due to experimental error. For Ru/AC, the BET surface area was 198.97 m^2/g while it was 847 m^2/g in literature (Ribeiro et al. 2017).

FT-IR spectra of the synthesized catalysts are given in Figure 19. In the FT-IR data of $RuSiO_2$, the band observed at 1078 cm^{-1} shows the presence of Si-O-Si asymmetric tensile vibrations in the catalyst structure. The broad band around 3431 cm^{-1} shows the O-H group. The bands at 785 cm^{-1} and 459 cm^{-1} indicate the presence of Si-O-Si asymmetrical tensile vibrations.

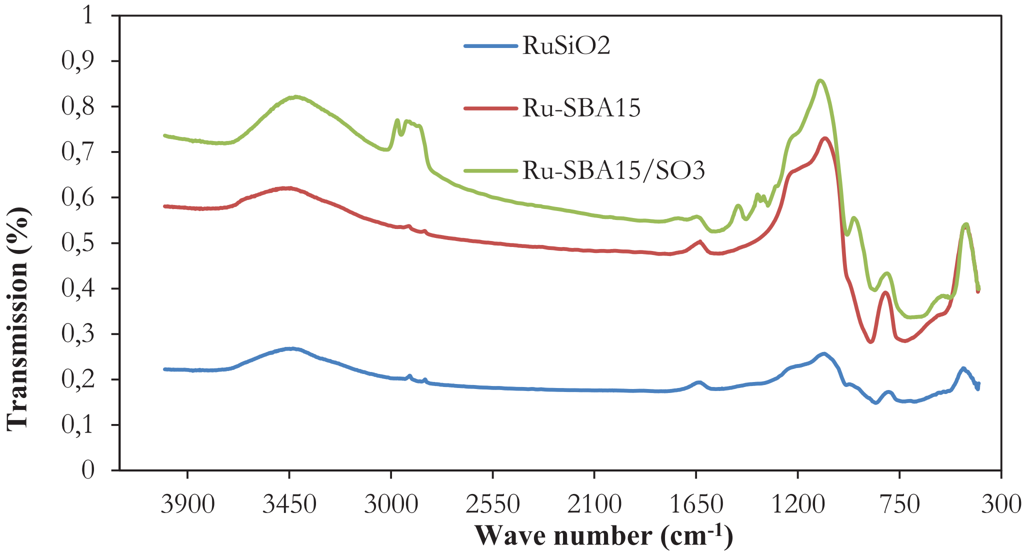

Figure 19. FT-IR result for Ru/SiO_2, Ru-SBA15 and $Ru/SBA15-SO_3$ catalysts

The SBA-15 structure has three types of silanol groups (Si-OH). These are germinal, isolated and hydrogen bonded, which can act as Brønsted acids, hydrogen bond acceptors or hydrogen bond donors depending on their range and density (Reyes-Luyanda et al. 2012). The strong absorbent band seen at 1105 cm^{-1} in the FTIR spectrum plotted for Ru-SBA15 shows the presence of Si-O-Si asymmetric tensile vibrations in the structure of the catalyst. The presence of these peaks indicates that the catalysts have been synthesized successfully. The wide band around 3400 cm^{-1} shows the adsorbed O–H group. The two peaks at 800 and 447 cm^{-1} indicate the presence of Si–O–Si asymmetric tensile vibrations. At low wavelengths, it can be associated with metal-oxygen stretching vibrations. The bands at around 3478 cm^{-1}, 1631 cm^{-1} and 962 cm^{-1} were shown to original groups of SBA-15 (Si-OH and Si-O-Si) (Song et al. 2018).

For $RuSBA15-SO_3$ catalyst, the peak observed at 1000-1200 cm^{-1} represents S=O. The peaks at 939 and 792 cm^{-1} indicate the presence of Si-O-Si stretching vibrations. The weak peak at 1357cm^{-1} is due to the asymmetric stress of the sulfonic acid groups. FT-IR shows that SBA-15 has been successfully functionalized with sulfonic acid groups.

It was observed that only Ru-SBA15/SO_3 had a significant peak around 3000 cm^{-1} which was showed O-H groups. Peaks between 1041 cm^{-1}-1074 cm^{-1} were caused by the presence of Si-O-Si asymmetric tensile vibrations. The wide band between 3346 cm^{-1} and 3458 cm^{-1} indicated the presence of O–H group.

4.2. Product Analysis

4.2.1. Effect of Catalyst Amount and Reaction Time on the Conversion of Cellulose to Sorbitol

The effects of the amount of catalyst and reaction time in cellulose hydrogenation to sorbitol were examined using Ru/SiO_2 as shown in the Figure 20. The minimum conversion (8.2%) was observed with the addition of 1 g Ru/SiO_2 for 1 hour reaction time. The maximum conversion achieved was 28.64 with 2 g of Ru/SiO_2 as catalyst and reaction time 2 hours.

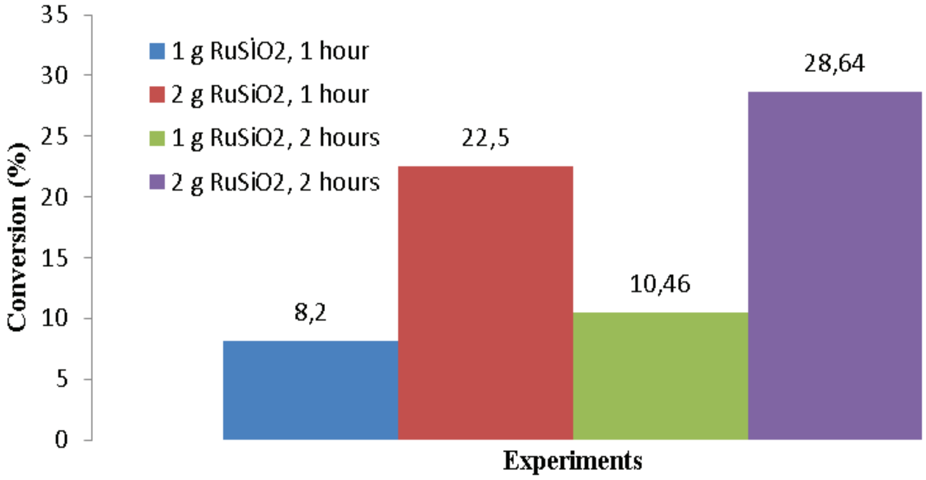

Figure 20. Effect of catalyst amount and reaction time on the conversion of cellulose to sorbitol (4 g cellulose, 1 g or 2 g Ru/SiO_2, 100 ml water, 5 bar H_2, 150°C, 1 h or 2 h)

Figure 21 shows the sorbitol concentrations in the liquid product resulting from experiments under four different conditions (1 g catalyst 1 hour, 1 g catalyst 2 hours, 2 g catalyst 1 hour and 2 g catalyst 2 hours) using the $RuSiO_2$ catalyst. The highest concentration was observed in 2 grams of catalyst and 2 hour experiment. As expected, the lowest concentration was observed in the catalyst amount at least and in 1 hour experiment.

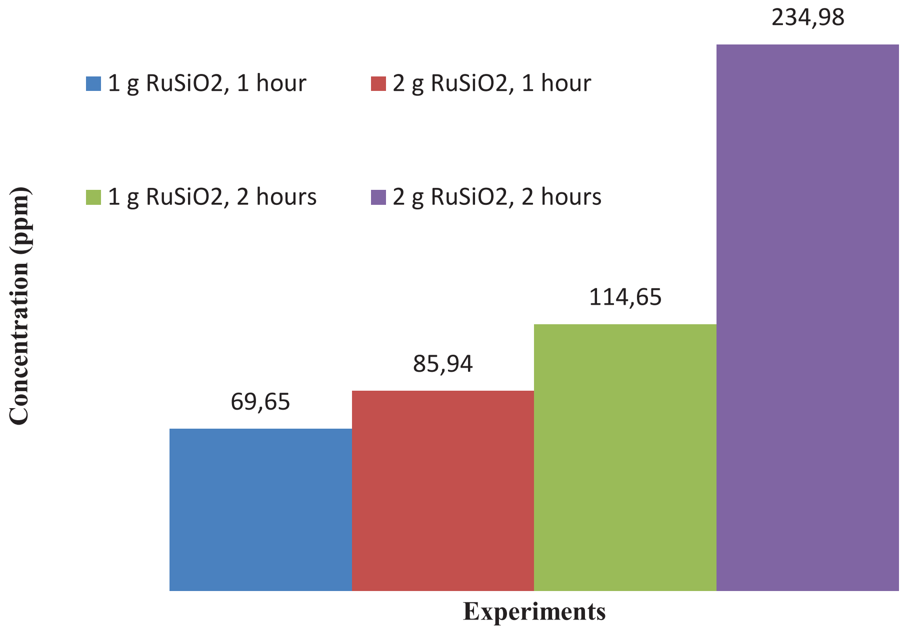

Figure 21. Sorbitol concentration of experiments with Ru/SiO_2 catalyst (4 g cellulose, 1 g or 2 g Ru/SiO_2, 100 ml water, 5 bar H_2, 150°C, 1 h or 2 h)

According to the figures, it can be said that a suitable amount of catalyst can improve the production of sorbitol. The conversion of cellulose increased with an increase in reaction time. Longer reaction times were tried in many articles, but sorbitol was observed to degrade with longer reaction times. Zhu et al. tried to find the maximum cellulose conversion and sorbitol yield by using $RuSiO_2$ catalyst at 150°C for reaction times of 2-14 h. When the reaction time increased; cellulose conversion increased and approached 100%. However the sorbitol yield initially increased and then decreased with longer reaction times. Furthermore, the maximum yield of sorbitol was 43% for 10 h. As a result of, sorbitol was turned into its isomers and also the degradation alcohol products (Zhu et al. 2014).

4.2.2. Effect of Various Catalysts on the Conversion of Cellulose and Yield of Sorbitol

The catalytic performance of several Ru-loaded supports was investigated and the results are given in Table 10. In the cases in which no catalyst was used, no sugar alcohols were observed, even though conversions were approximately 4.45% whereas the conversion was found approximately 40% in literature (Han and Lee 2012). The cellulose conversion was 4.88% for silica gel and 15.85% for activated carbon. While Ru/AC was used, cellulose conversion of 13.81% was observed, under same conditions, yield of sorbitol was 5.73%. In the literature, after 1 hour and 5 hours cellulose conversions with catalyst of 0.4%Ru/AC at 205°C and 50 bar were found as 17% and 36%, whereas sorbitol yields were 10% and 14.5%, respectively (Ribeiro, Órfão, and Pereira 2015). When comparing Ru/AC results, it can be concluded that increasing the temperature was not very effective in increasing the conversion percentage of cellulose to sorbitol for the Ru/AC catalyst. When Ru/SiO_2 was used as catalyst, cellulose conversion and sorbitol yield were achieved as 8.2% and 0.17% at the end of one hour, respectively. Comparing with the literature, the conversion was found 36.2% with 0.2 g Ru/SiO_2 and 0.25 g cellulose at 150°C, 4 MPa H_2 after 10 h (Zhu et al. 2014). Moreover, when Ru-SBA15 was used as catalyst, cellulose conversion achieved as 10.31%. When sulfonated SBA-15 was used, a conversion of 29.1% was obtained, but no sorbitol was observed due to the reaction temperature. Sorbitol could be obtained with the same catalysts at high temperature. For example, with the Ru-SBA15 at 210°C and 35 bar H_2, 25% cellulose conversion was achieved in 1 h experiment (Reyes-Luyanda et al. 2012). In our reactor, when we exceed 150°C, we had some problems such as gas releasing. Therefore, it was not possible to exceed 150°C for the experiments. Functionalizing of SBA-15 with sulfonic acid further enhanced catalytic activity compared to SBA-15 for cellulose hydrolysis.

Table 10. Conversion of cellulose and yield of sorbitol with various solid catalysts. (4 g cellulose, 1 g of different catalysts, 100 ml water, 5 bar H_2, 150°C, 1 h or 2 h)

Reactant	**Catalyst type**	**Reaction Time (h)**	**Cellulose Conversion (%)**	**Sorbitol Yield (%)**
cellulose	---	1	4.45	---
	silica gel	1	4.88	---
	AC	2	15.85	0.34
	Ru/AC	2	13.81	5.73
	Ru/SiO_2	1	8.2	0.17
	Ru-SBA15	1	10.31	---
	Ru-SBA15/SO_3	2	29.1	---

4.2.3. FT-IR Results for Cellulose to Sorbitol

FT-IR results of solid products made under different parameters and dried under vacuum for 24 hours were performed. In Figure 22, FT-IR spectra of pure cellulose before the reaction and the remaining cellulose after the reaction carried out in sub-critical water environment without catalyst are given comparatively.

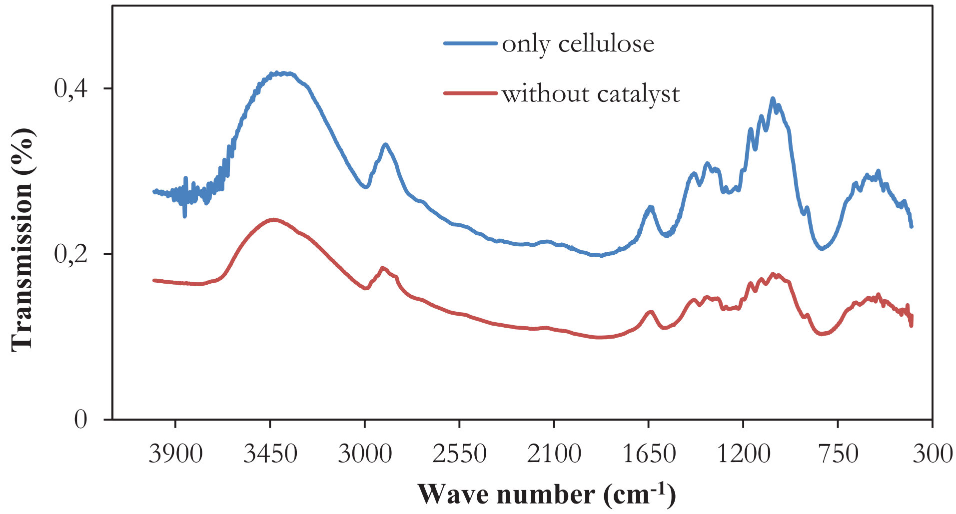

Figure 22. FT-IR spectra of cellulose before reaction and experiment with cellulose at 150°C without using catalyst

A comparison of experiments with Ru-SBA15 is given in Figure 23. In the experiment with Ru-SBA15, the reaction time was fixed and the amount of catalyst was changed. When we increased the amount of catalyst, there was no change in the location of the peaks.

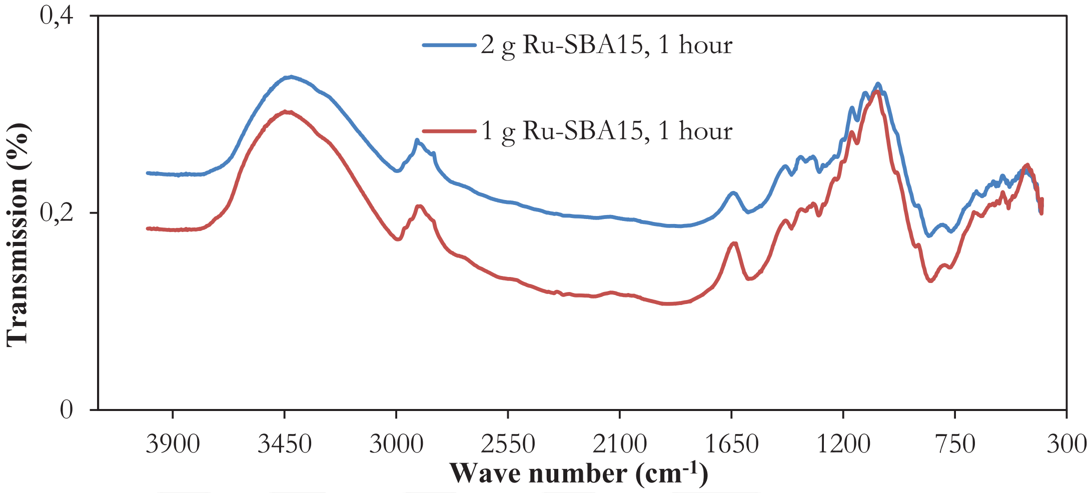

Figure 23. FT-IR spectra of solid products obtained in experiments with Ru-SBA15

Figure 24 was showed the comparison of experiments with Ru-SBA15/SO_3. Peaks resulting from sulfone bonds between 1342 cm^{-1} and 1450 cm^{-1} are clearly visible.

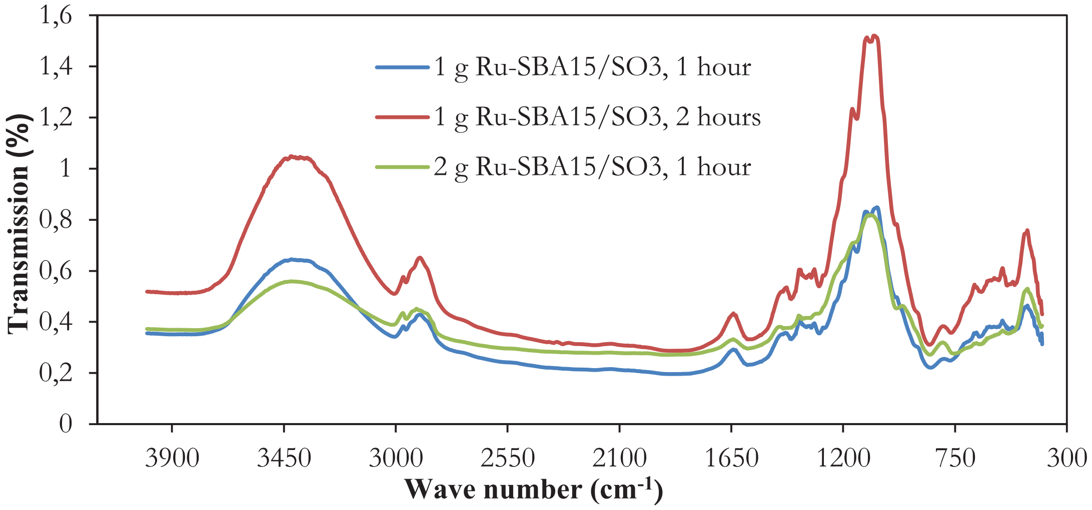

Figure 24. FT-IR spectra of solid products obtained from experiments with Ru-SBA15/SO_3

In the experiments with Ru-SBA15 and Ru-SBA15/SO_3, the structure of cellulose was not deteriorated. It was not sufficient to degrade the cellulose structure in increasing the test time or catalyst amount.

Four different experiments with Ru-SiO_2 (1 hour 1gram, 1 hour 2 grams, 2 hours 1 gram and 2 hours 2 gram) were showed a slight change in the bond structure of cellulose in Figure 25. For the other two catalysts (Ru-SBA15 and Ru-SBA15/SO_3), no change in the structure of cellulose was observed. In the RuSiO_2 sorbitol formation was observed, although the desired maximum efficiency was not reached. In two experiments using 1 gram Ru-SiO_2, less deterioration was observed as expected than 2 grams.

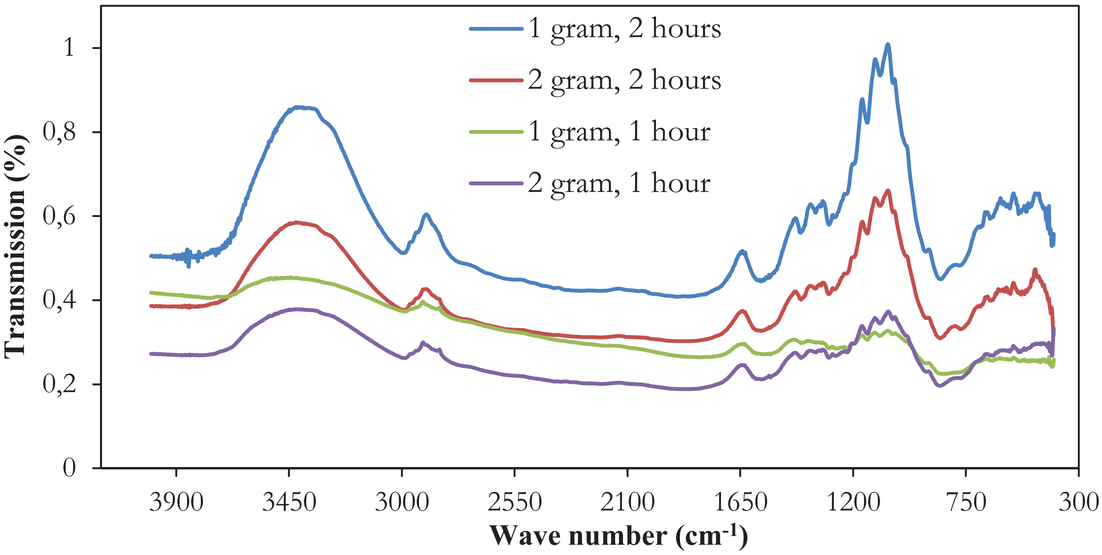

Figure 25. FT-IR spectra of solid products obtained from experiments with Ru-SiO_2

FT-IR spectra of experiments with AC and Ru/AC were shown in Figure 26. The FT-IR spectra of AC support showed the characteristic absorbance peaks.

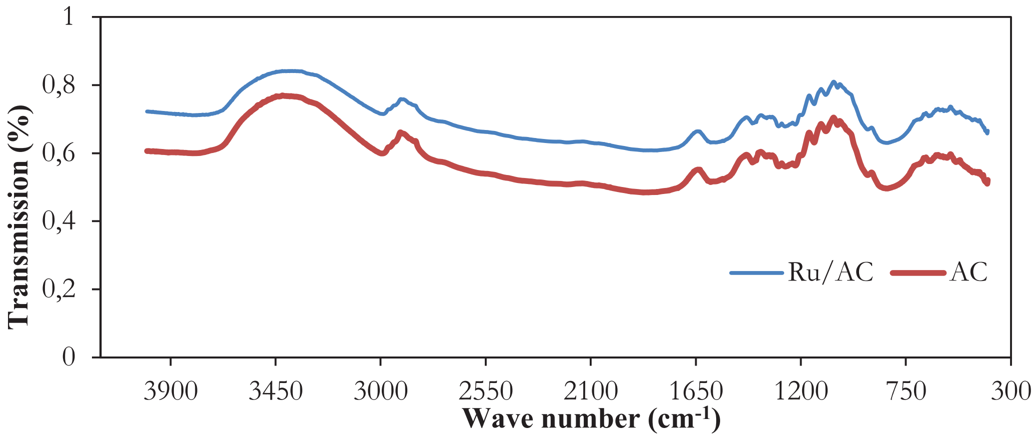

Figure 26. FT-IR spectra of solid products obtained from experiments with AC and Ru/AC

4.2.4. Effect of Various Catalysts on the Conversion of Glucose to Sorbitol

The various catalysts prepared in this study were tested in the production of sorbitol from glucose and the conversion results are given in Table 11. As expected, the conversion of glucose was as high as 99.94%. The Ru nanoparticles played an important role in the hydrogenation of glucose into sorbitol Among the catalysts studied Ru/SiO_2 displayed better catalytic performance than other catalysts for the production of sorbitol.

Table 11. Conversion of the glucose and yield of sorbitol with various solid catalysts. (2.8 g glucose, 1.2 g different catalysts, 100 ml water, 6 bar H_2, 150°C, 2 h)

Reactant	**Catalyst type**	**Time (h)**	**Glucose Conversion (%)**	**Sorbitol Yield (%)**
glucose	silica gel	2	99,93	2.75
	AC	2	99,92	4.30
	Ru/AC	2	99,91	0.40
	Ru/SiO_2	2	99,92	3.81
	Ru-SBA15	2	99,93	---
	Ru-SBA15/SO_3	2	99,94	0.36

4.2.5. Effect of Reaction Time on the Conversion of Glucose and Yield of Sorbitol

The effect of the reaction time in production of sorbitol from glucose was also examined using Ru-SBA15/SO_3 as shown in the Table 12. As expected, concentration and the conversion were increased when the reaction was increased from 1 hour to 2 hours. As can be seen from the table, conversion of glucose reached almost 100% conversions even after 1 hour of the reaction.

Table 12. Conversion of glucose and yield of sorbitol with Ru-SBA15/SO_3 catalysts. (2.8 g glucose, 1.2 g of Ru-SBA15/SO_3, 100 ml water, 6 bar H_2, 150°C, 1-2 h)

Reactant	**Catalyst Type**	**Reaction Time (h)**	**Concentration (ppm)**	**Glucose Conversion (%)**	**Sorbitol Yield (%)**
glucose	Ru-SBA15/SO_3	1	105.3	99.91	3.76
		2	141.8	99.94	0.36

The liquid product was also analysed by GC-MS to verify the liquid products formed. Figure 27 is an example of GC–MS chromatograms of the liquid products with Ru/SBA15 at the end of 2 hours and Table 13 shows the list of these liquid products.

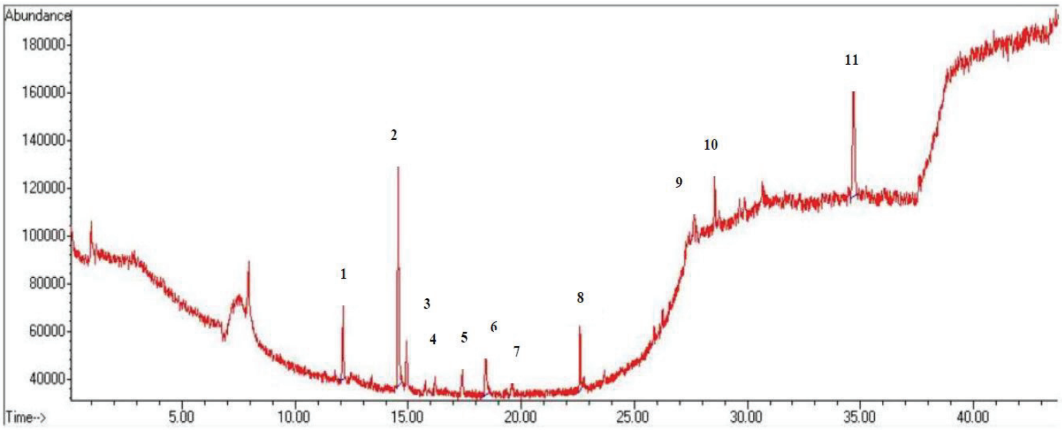

Figure 27. GC–MS chromatograms of liquid products after reaction (2.8 g glucose, 1.2 g of Ru /SBA15, 100 ml water, 6 bar H_2, 150°C, 2 h)

Table 13. The results of GC–MS analysis (2.8 g glucose, 1.2 g of Ru /SBA15, 100 ml water, 6 bar H_2, 150°C, 2 h)

Number	**Retention Time**	**Side Product**
1	12.11	2-Propanone,1-hydroxy-
2	14.56	Acetic acid
3	14.94	Furfural
4	16.05	Formic acid
5	17.40	2-Furancarboxaldehyde
6	18.43	1,2-Ethanediol
7	19.58	Furanmetahnol
8	22.59	1,3-Cyclopentanedione
9	27.40	2-Propanone
10	28.55	15-Crown-5
11	34.68	2-Furancarboxaldehyde, 5-(hydroxymethyl)-

4.2.6. FT-IR Results for Glucose to Sorbitol

Figure 28 was showed the comparison of experiments with silica gel, Ru/SiO_2, Ru-SBA15 and Ru-SBA15/SO_3 to produce sorbitol from glucose. As you can see, the peaks from the sulfone bonds between 1342 cm^{-1} and 1450 cm^{-1} are clearly visible. Furthermore, the peak formed in 809 cm^{-1} belonging to the sorbitol was seen clearly for catalyst of Ru-SBA15 and Ru-SBA15/SO_3.

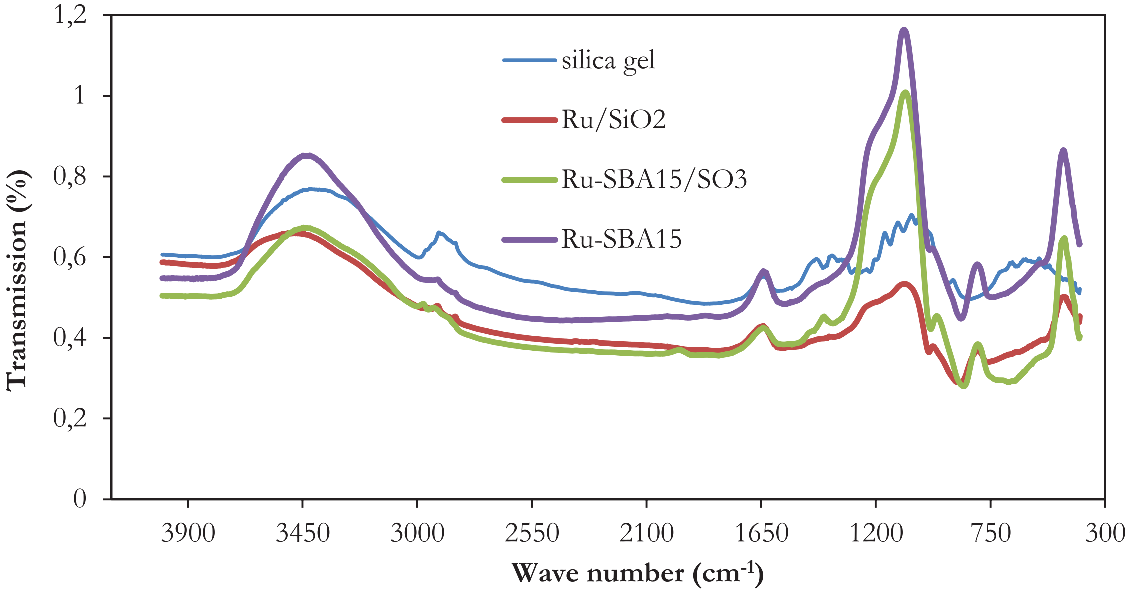

Figure 28. FT-IR spectra of solid products obtained from experiments with silica gel, Ru/SiO$_2$, Ru-SBA15 and Ru-SBA15/SO$_3$ for 2 hours

FT-IR spectra of catalyst of Ru/AC and solid products obtained from experiments with AC and Ru/AC for 2 hours were shown in the Figure 29 to produce of sorbitol from glucose. The peak of glucose formed around 3400 and 2900 cm^{-1} was not seen, since glucose was decomposed.

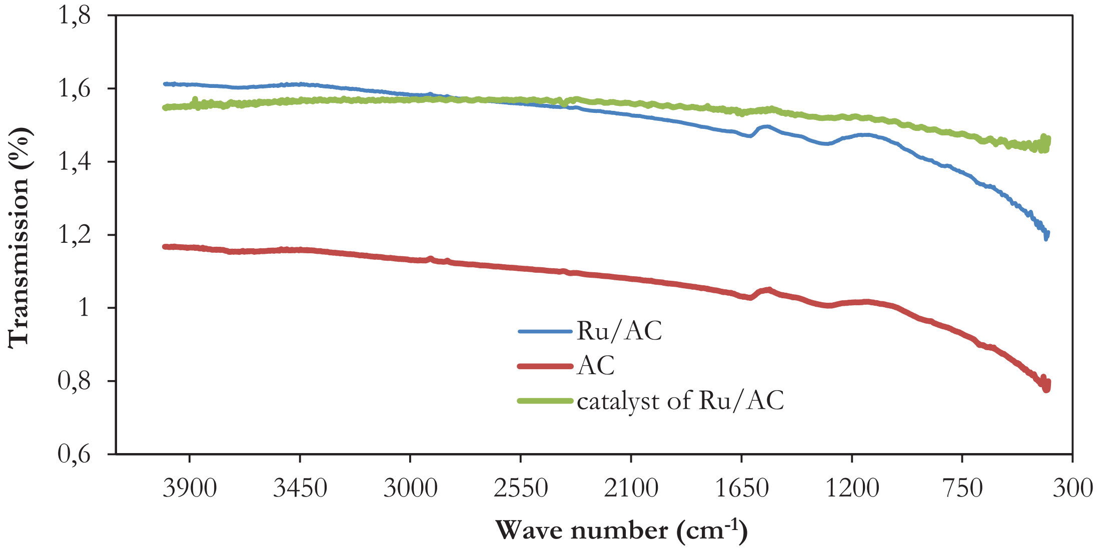

Figure 29. FT-IR spectra of catalyst of Ru/AC and solid products obtained from experiments with AC, Ru/AC for 2 hours

CHAPTER 5

CONCLUSION

The sorbitol production has great potential owing to the rapid development of the food, pharmaceutical and chemical industries. If the increasing demand to sorbitol is considered, it is very important to develop a new process for the selective production of it. The feasibility of production of sorbitol from both of glucose and cellulose by using Ruthenium supported catalysts based on AC, SiO_2, SBA15 and SBA15/SO_3 were investigated under selected conditions. The catalysts were prepared by wet impregnation method and then, the characterization study (SEM, FT-IR and BET) were carried out. After that, the reaction parameters such as catalyst amount (1-2 g), reaction time (1-2 h) and different support materials affecting the sorbitol production and the highest sorbitol production conditions were determined. The use of different catalyst amount allowed increasing the conversion and the increasing reaction time caused the increasing conversion. Among the catalysts studied, Ru-SBA15/SO_3 showed better catalytic performance than other catalysts for the production of sorbitol from glucose. The concentration of sorbitol and conversion of glucose with Ru-SBA5/SO_3 were found as 141.8 ppm and 99.94%, respectively at 150°C, 6 bar H_2, 2 hours. In the case of cellulose conversion, RuSiO_2 catalyst gave the best results as 28.64% at 150°C, 6 bar H_2 after 2 hours. Under same conditions, sorbitol concentration was calculated as 234.98 ppm at the end of 2 hours.

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