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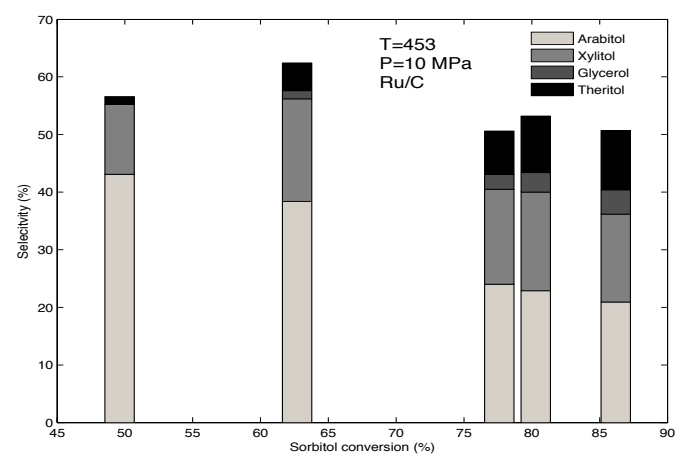
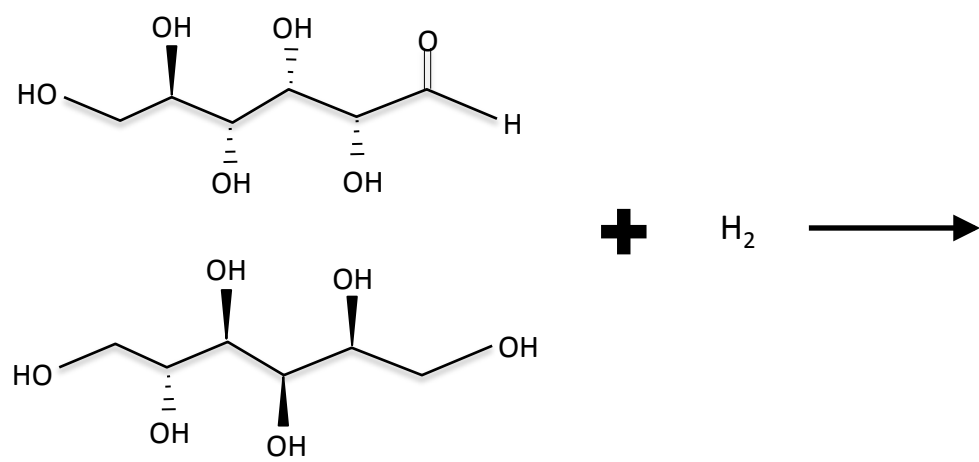


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Temperature range: 453 – 503 K  
Hydrogen pressure range: 3 – 10 Mpa  
Catalysts: Ru/C, Pt/C  
Poisoning: Sulfur  
Initial pH range: 7-14

**Goal: clarify sugar reaction pathway and gain information on product selectivity**

## Conversion of glucose and sorbitol in presence of Ru/C and Pt/C catalysts

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+ The authors would like to thanks Dr Carlo Maria Paciolla for giving them the opportunity to gather together and cooperate. This article is dedicated to his memory.

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**Abstract.** The conversion of glucose and sorbitol in presence of Ru and Pt catalysts supported on carbon was carried out at different pressure and temperature conditions, using a batch and a semi-batch reactor. Attempts were made to improve selectivity of glycols and alcohols (ethanol), introducing promoter and inhibitor of the hydrogenolysis in the reactant mixture. On the basis of these results, which confirm the higher activity of Ru with respect to Pt, and the important role of inhibitor like sulphur, it is clearer the mechanism driving these reactions and the promising thermocatalytic conditions.

### 1. Introduction

The conversion of raw materials of vegetable origin into biofuels and bio-based chemicals is a promising alternative to exploitation of fossil oil, leading to economical and environmental impacts<sup>1</sup>. As recently highlighted by Ruppert et al<sup>2</sup>, hydrogenolysis of sugars derived by hydrolysis of lignocellulosic materials can offer an encouraging opportunity for future biomass-based refinery<sup>2</sup>. In this context, starting from lignocellulosic biomass as well as from C6- sugars, bioethanol and other biofuels target products are increasing in importance from a research point of view<sup>3</sup>. For instance, in the recent years the interest concerning hydrogenolysis of sorbitol (also obtained from glucose) to chemicals like propanediol, ethylene glycol and glycerol has increased<sup>4</sup>. Even if currently glycerol can be obtained in terms of by-product from biodiesel production, the catalytic hydrogenolysis of carbohydrate offers the chance to use “renewable and less costly resources” to obtain valuable chemicals<sup>2</sup>.

Many efforts were made to understand and improve the transformation of sorbitol into di- and polyhydric alcohols, mainly in presence of supported metal catalysts, as summarized in the comprehensive review by Ruppert et al.<sup>2</sup>. Within this regard, ruthenium has attracted a great deal of attention<sup>5-16</sup>, because of its high activity for hydrogenolysis reaction when compared to other noble metals like rhodium, platinum and palladium. The effects of the catalyst on product distribution have been also investigated for different support materials, such as activated carbon, SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, NaY<sup>8,10,17</sup>. Among them activated carbon exhibits excellent stability (it is inert and stable at high temperature and pressure) and shows large dispersion of active components<sup>7</sup>.

The products obtained from sugars and polyols hydrogenolysis depend on process conditions (type of catalyst, temperature, pressure, pH) and may include propylene

glycols and glycerol, as well as ethylene glycol, ethanol, methanol and also xylitol and erythritol (selectivities up to 60-90%). The literature documents that transformation mechanism can generate many different compounds with different selectivity.

Also to clarify some aspects as sugar reaction pathway through the corresponding alcohol or how similar reaction parameters apparently give different process improving, we report our contribution to the sugars and sugar alcohols hydrogenolysis process development via batch and semi-batch operating conditions. The study examined the role of process parameters such as pressure, temperature, type and amount of catalyst, presence of an inhibitor, glucose and sorbitol concentration on product selectivity and reactant conversion. In order to promote reactions towards diols and alcohols<sup>18</sup>, the reacting system behaviour was investigated at high temperature ranges, spanning from 453 to 513 K, and at high hydrogen pressure, from 3 to 10 MPa. Two heterogeneous commercial catalytic systems were used: Ru/C and Pt/C with metal catalyst loading equal to respectively 5% and 3%. Ruthenium is indeed considered as the most active catalysts for hydrogenolysis reactions and for its promising properties has been recently used by several authors<sup>19-21</sup>. Platinum was considered because it shows less selectivity towards alkane with respect to ruthenium<sup>19,22</sup>, therefore it seemed a good candidate to drive the reaction towards the desired oxygenated products. Furthermore, the carbon has been selected as metal support because it is inert and stable at the conditions used for the experimental campaign. A thorough analysis of the results in terms of selectivity was provided and attempts were made to individuate the conditions promoting the required combination of C-C and C-O bond cleavage leading to high selectivity for glycols and alcohols.

## 2. Experimental

### 2.1 Materials

Activated carbon (C) supported noble metal catalysts 5% Ru/C (Engelhard) and 3% Pt/C (Chimet) were used for the experiments. The reactants were glucose (Sigma – Aldrich, purity 98%) and sorbitol (Sigma – Aldrich, purity 97%). Reactions in presence of a base were conducted with sodium hydroxide (Carlo Erba, purity 98%), whereas the catalysts poisoning were obtained using sodium hydrosulfide hydrate,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , (Sigma – Aldrich, purity 98%).

### 2.2 Hydrogenolysis reaction

Glucose and sorbitol hydrogenolysis was conducted in a 500 ml autoclave stainless steel (AISI 316 – Pressure and Products Industries Inc.) using 300 or 400 ml of an aqueous solution of 100 g/l of reactant. Then the catalyst powder was added. The sealed autoclave was first purged at least 3 times with helium gas to get rid of the air present in the reaction vessel, then it was purged with hydrogen to eliminate helium. The reactor pressure was set at the desired value by feeding hydrogen, in such a way that the set-point pressure was reached when the temperature was at the desired value. The mixture was stirred at 1000 rpm. After the reaction was finished, the autoclave was cooled with cold water.

The reactor was equipped with a dip tube, connected to a micrometric valve for liquid sampling. The sample (10 ml) first flowed in a tube made in a serpentine fashion, which was immersed in a cold bath to decrease temperature to circa 25°C. During the experimental runs, samples were collected from the autoclave every hour, and the first sample had been taken as soon as the system reached the operating conditions in terms of pressure and temperature. Considering the dead volume of the sampling tube, the first collected sample volume equal to 5 ml was not considered for the analysis of the product mixture.

The experiments were carried out in batch and semibatch reactor mode. In the first case, the reactor pressure was kept constant by adding hydrogen. Using the semi-continuous mode, the gas phase flowed continuously through the batch of reactant solution. In this configuration, it was possible to keep constant the hydrogen partial pressure and collect gaseous products during the reaction by 5 litres sample-bag (Chrompack).

### 2.3 Product analysis

Hydrogenolysis products contained the following compounds: sugars (C5-C6), polyols (C3-C6), glycols (C6-C2), alcohols (C6-C1), alkanes (C1-C3) and carbon dioxide. Quantitative and qualitative analyses for the products of hydrogenolysis were performed by the means of chromatography.

Gas chromatography analysis of hydrocarbon gases and carbon dioxide was done using a TermoQuest GC 8000 with a Thermal Conductivity Detector (TCD) using a Poraplot-Q (Chrompack) column (10 m x 0.32 mm x 10 µm). The specific instrument parameters follow:

Column:	CP – PoraPLOT Q, 10 m X 0.32 mm i.d., thickness 10 µm
Cas carrier:	helium
Oven:	50°C
Pressure:	20 kPa
Injection:	1 ml split 19 : 1, temperature 50°C
Detector:	TCD, temperature 200°C, filament 180°C

Liquid products were analysed using both gas chromatography (TermoQuest GC 8000) and high-performance liquid chromatography (HPLC Perkin Elmer –200LC). The specific GC parameters are the following:

Column:	DB – WAX, 30 m X 0.32 mm i. d., thickness 0.5 µm
Gas carrier:	helium
Pressure :	80 kPa
Temperature program:	35°C X 5 min; from 35 to 245°C 10°C/min, 245°C x 2 min
Detector:	FID, 310°C
Injection volume:	0.9 µl
Split:	20 : 1

The specific HPLC parameters follow:

Column :	Carbohydrate Pb; 300 mm X 7.8 mm i. d.
Mobile phase:	water

Flow: 0.4 ml/min  
 Temperature : 74°C  
 Detector: RI  
 Injection volume: 20 µl

The experimental results were analyzed in terms of reactant conversion and selectivity, according to the following definition:

$$\text{Conversion(\%)} = 100 - \frac{\text{g of reactant after reaction}}{\text{g of reactant in the feedstock}} \cdot 100$$

$$\text{Selectivity(\%)} = \frac{\text{g of product}}{\text{g of converted reactant}} \cdot 100$$

It is worth noticing that we did not identify all the obtained products, but we could only identify C6-C1 sugars or polyols (including also diols and alcohols) classes. According to the definition, the sum of selectivity could be less than 100.

### 3. Results and discussion

#### 3.1 Glucose and sorbitol conversion operating in batch mode

The first experimental campaign has been carried out with a batch reactor, using an aqueous solution of glucose and Pt/C or Ru/C catalyst, at different operating conditions. Results obtained in presence of Pt/C catalysts are reported in Table 1, where the selectivity of the wide variety of products in the liquid phase formed during reaction is shown.

**Table 1** Glucose conversion (%) and products selectivity (%) obtained in presence of Pt/C. S = sorbitol, A = arabitol, X = xylitol, G = glycerol, H = 1,2-hexanediol, B = 2,3- and 1,2-butanediol, P = 1,2- propanediol, Et = 1,2-ethanediol, R.T. = Reaction time.

	T	P	R.T.	Pt/Glucose	Conversion	Selectivity (%)							
	(K)	(MPa)	(h)	(g/g)	(%)	S	A	X	G	H	B	P	Et
GPt1	453.0	10.0	2.0	0.0015	45.5	7.0	11.6	0.0	0.0	7.8	1.1	0.4	1.1
GPt2	453.0	5.0	3.0	0.0015	76.5	7.8	11.0	3.0	3.1	6.9	1.6	0.7	0.7
GPt3	453.0	10.0	2.0	0.003	73.5	16.1	9.1	2.9	5.7	5.2	2.3	1.1	0.7
GPt4	473.0	10.0	2.0	0.003	98.7	9.4	3.5	4.2	12.2	8.0	1.5	5.2	2.2
GPt5	493.0	10.0	2.0	0.003	100.0	8.4	3.9	4.6	7.1	12.4	5.6	9.0	2.8
GPt6	493	10.0	4	0.003	100.0	8.0	4.2	4.6	7.6	10.2	4.4	6.3	1.7

As shown in Table 1, glucose conversion increases as temperature varies from 453 to 473 K, reaching almost the total conversion. In the same temperature range, sorbitol selectivity decreases, while the two identified C5 polyols have opposite behaviour (arabitol decreases and xylitol increases), but the total C5 selectivity decreases of about 33%. As shown by other authors<sup>19</sup> C-O bond cleavage activity increases with

temperature, and this is verified by the greater production of 1,2-hexanediol. The C3-C4 bond cleavage leading to glycerol and propanediol is favored when passing from 453 to 473 K, because the selectivity of both compounds increases. C4 and C2 diols are formed through a C2-C3 bond cleavage and decarbonylation reactions, but at the intermediate temperature used for this campaign the butanediols selectivity is lower than at 453 K, while ethanediol increases. It could be hypothesized a C2-C3 bond cleavage of arabitol leading to glycerol and ethanediol, because the C5 polyols selectivity decreases in this temperature range.

A further increase of temperature up to 493 K does not significantly change sorbitol selectivity, which slightly decreases, but it leads to an increase of arabitol and xylitol. At the highest temperature the highest selectivity of C6 diol is obtained, being the C – O bond cleavage favoured, and glycerol is probably transformed to propanediol with the same mechanism<sup>12</sup>, because the C3 diol selectivity decreased of about 41%. In the range 473-493 K, butanediols selectivity increases indicating higher selectivity for C – O scission and more probably C2 – C3 bond cleavage of C6 sugar or polyols.

It is worth noticing that 1,2-hexanediol selectivity is higher with respect to other diols, implying that the C – O scission can compete with C – C bond cleavage. The precursor of the reaction leading to the elimination of a hydroxyl group (OH) is quite unstable, because it has two double bonds (C = O, C = C). Being the reactor a reducing environment, one of the double bond is easily hydrogenated but, if the catalyst activity is not enough strong, it is possible the persistence of the other double bond which leads to the further break of another C – O bond. According to this, the glucose maintains the – C – C - chain, but loses the hydroxyl groups implying hexanediol formation.

A schematic representation of possible products is reported in Figure 1. The reaction route is based on the identified products in the liquid phase, without considering the exact mechanism.

Increasing the reaction time at the highest temperature value (493 K) does not significantly change the selectivity of polyols, indicating that platinum is not able to catalyse dehydrogenation, the precursors of polyols hydrogenolysis<sup>18</sup>. This result has been also assessed feeding the reactor with an aqueous solution of 100 g/l of sorbitol. Experimental runs have been conducted at 493 K and 10 MPa for two hours and a very low conversion of sorbitol (11.3%) to arabitol and carbon dioxide has been observed, but no other compounds were detected.

The bond cleavage of C – C in terminal position of glucose molecule, which is attested by the presence of arabitol and xylitol, does not lead to the production of methanol, but carbon dioxide was found in the gaseous phase, as according to other studies<sup>9,22</sup>.

The hydrogenolysis of glucose was then carried out in presence of ruthenium in batch mode and the operating conditions and results are reported in Table 2. In this experimental campaign, only the reaction time was varied from 2 to 4 h, while temperature and pressure were kept constant at 473 K and 10 MPa. The conditions were selected considering the experiments with platinum that led to highest selectivity towards glycols. After 2 hours of reaction, the most favourite compounds were sorbitol and arabitol. Less selectivity was detected for xylitol, threitol and glycerol.

The amount of polyols with four carbons was very low, indicating two most probably cleavage sites, terminal position (pentols) and central position (glycerol), even if the latter occurred with less frequency. Increasing the reaction time, the total amount of compounds in the liquid phase decreased, and the selectivity of threitol and glycerol increased, while sorbitol was almost completely converted into lower molecular weight molecules. In presence of ruthenium, the gaseous phase contained high concentration of gaseous hydrocarbon, mostly methane and less quantity of ethane and propane.

**Table 2.** Glucose conversion (%) and product selectivity (%) in presence of Ru/C. S = sorbitol, A = arabitol, X = xylitol, T = threitol, G = glycerol.

	T	P	R.T.	Ru/Glucose	Glucose conversion	Selectivity (%)				
	(K)	(MPa)	(h)	(g/g)	(%)	S	A	X	T	G
GRu1	473.0	10.0	2.0	0.0015	100.0	23.0	25.0	11.2	2.0	6.2
GRu2	473.0	10.0	4.0	0.0015	100.0	7.4	11.9	8.6	6.6	7.4

The results in Table 2 suggested that ruthenium had a strong activity for hydrogenation and glucose was first transformed to sorbitol, which then reacted to form the other polyols, according to Zhang et al.<sup>22</sup>, and C1 – C3 straight chain alkanes.

The new experimental campaign was carried on using a reactant mixture containing sorbitol instead of its sugar, such as the first reaction step (hydrogenation) was skipped. The reactions were conducted at three levels of temperature (453, 473, 493 K) and two levels of pressure (5 – 10 MPa), maintaining constant the reaction time (4 h) and ratio Ru/Sorbitol (g/g). The dependence of sorbitol conversion on pressure and temperature is summarized in Figure 2, considering the samples taken at different reaction time. The obtained results indicate that pressure favoured conversion of sorbitol at higher temperature (473 and 493 K), whereas a lower effect was evident with respect to temperature at 5 MPa. Conversion was almost constant when temperature was increased from 473 to 493 K. The increase of hydrogen pressure implied that more hydrogen molecules could access to Ru active sites, which determined a higher sorbitol conversion especially at higher temperature. At 453 K the effect was less evident, probably because the reversible reactions of the mechanism of sorbitol hydrogenolysis (dehydrogenation and retro-aldol condensation) were not so slow<sup>7</sup>.

The main products obtained in the different experimental runs were pentols, in particular arabitol and xylitol, threitol and glycerol, as in case of hydrogenolysis of glucose in presence of ruthenium. The selectivity of the different products is reported in Figure 3.

The first observation is that products obtained through C – C bond cleavage of sorbitol in terminal position (pentols) had a higher selectivity at lower temperature, while as temperature increased they were converted to lower polyols. Indeed, as sorbitol conversion increased, arabitol selectivity decreased being likely converted to

threitol and glycerol. Pressure had a lower effect on pentols selectivity, giving a slight higher value when it was set at 5 MPa. Arabitol selectivity was always greater than that of xylitol, but arabitol had also a higher conversion rate, which increased with temperature. It is worth noticing, that unlike the results shown by Deutsch et al.<sup>9</sup>, who carried out reaction in presence of a base, the hydrogenolysis of sorbitol at the investigated conditions did not produce ribitol, and xylitol was not formed in nearly equal quantities to arabitol. This last observation is therefore in agreement with the work of Sun and Liu<sup>8</sup>, who found that xylitol, in neutral solution, is predominantly converted to arabitol.

The production of glycerol was favoured by pressure, except at 453 K, and it increased with temperature. Being the selectivity of glycerol always higher than that of threitol, it was probably obtained through a C3 – C4 bond cleavage, while the absence of ethylene glycol could imply that threitol was derived by a bond cleavage in terminal position of a five carbon polyol.

The presence of propylene glycol had been detected only at 473 and 493 K, with the greatest selectivity at 10 MPa. The maximum value of selectivity was around 3%, obtained at the end of the batch, setting temperature at 493 K and pressure at 10 MPa. It is worth noticing that the presence of ruthenium as catalyst led to the formation of threitol, whereas this compound was not detected in presence of platinum.

The gas analysed at the end of the reactions evidenced the presence of methane, small quantity of ethane and carbon monoxide.

Figure 4 shows a scheme of the products obtained by the hydrogenolysis of sorbitol, without considering the exact mechanism of reaction.

### 3.2. Sorbitol conversion in semi-continuous reactor

The hydrogenolysis of sorbitol was also conducted operating in semi-continuous mode, where the gas phase continuously flowed through the vessel. The initial solution consisted of 100 g of sorbitol in 100 g of water. All the experiments were carried out with 300 ml of the aqueous sorbitol solution, excepted for the experiments SSRu1 and SSRu2, where the reactor was filled with 400 ml. The hydrogen flow rate was maintained constant in all the runs and set equal to 1000 Nml/min. In this case four temperature levels (453-473-493-513 K) and three pressure levels (3-5-10 MPa) were investigated. The results are reported in Table 3 in terms of selectivity for the products in the liquid phase.

The first two experiments led to the total conversion of sorbitol, but no polyols, diols or alcohols were detected in the aqueous solution. The analysed outlet gas stream contained straight chain alkanes, mainly methane and ethane, and presence of alcohols like butanol and pentanol. Reducing the reaction time up to 1 h (SSRu3), sorbitol is completely consumed but the selectivity for polyols increases as they have not been converted to lower molecular weight products. Increasing the reaction time of half an hour implies again the complete conversion of the whole polyols, diols and alcohols mainly into gaseous straight alkanes.

In order to increase the selectivity for polyols and decrease the production of methane and ethane, the catalyst concentration was lowered. The reduction of catalyst has the same effect of reducing reaction time (cf. SSRu3 and SSRu5). A further decrease to 0.0005 (g/g) of the ratio Ru/sorbitol implied a reduction of the conversion (SSRu6) of sorbitol and increased selectivity of arabitol and xylitol. The percentage of carbon converted into gaseous hydrocarbon was strongly reduced. When increasing the reaction time (SSRu7), the sorbitol conversion increased while pentols selectivity decreased, being they converted to lower molecular weight compounds through C–C bond cleavage in terminal position.

**Table 3** Sorbitol (S) conversion and products selectivity. A = arabitol, X = xylitol, T = threitol, G = glycerol, D = diols (butandiol, propandiol and ethanediol), Al = alcohols. (n.d. = not detected)

	T (K)	P (MPa)	R.T. (h)	Ru/S (g/g)	Sorbitol conversion (%)	Selectivity (%)					
						A	X	T	G	D	Al
SSRu1	473	5.0	4.0	$3 \cdot 10^{-3}$	100.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SSRu2	473	5.0	3.0	$3 \cdot 10^{-3}$	100.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SSRu3	473	5.0	1.0	$3 \cdot 10^{-3}$	98.2	4.5	3.1	4.4	12.1	2.7	1.1
SSRu4	473	5.0	1.5	$3 \cdot 10^{-3}$	100.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SSRu5	473	5.0	2.0	$1 \cdot 10^{-3}$	98.0	4.5	0.9	4.6	11.5	3.7	2.0
SSRu6	473	5.0	2.0	$5 \cdot 10^{-4}$	86.4	25.6	15.7	11.4	9.7	1.4	n.d.
SSRu7	473	5.0	4.0	$5 \cdot 10^{-4}$	91.5	13.7	9.2	6.9	14.0	1.1	<0.1
SSRu8	473	10.0	2.0	$5 \cdot 10^{-4}$	86.4	30.2*	14.2	(see A)	14.2	n.d.	0.5
SSRu9	473	10.0	4.0	$5 \cdot 10^{-4}$	87.9	23.9*	11.9	(see A)	16.7	1.8	1.0
SSRu10	453	10.0	4.0	$5 \cdot 10^{-4}$	71.6	24.0	12.6	n.d.	8.4	n.d.	n.d.
SSRu11	493	10.0	4.0	$5 \cdot 10^{-4}$	91.0	11.3	11.0	6.2	16.5	0.7	2.2
SSRu12	493	5.0	4.0	$5 \cdot 10^{-4}$	96.6	10.4	5.0	5.8	16.9	3.9	0.7
SSRu13	453	5.0	4.0	$5 \cdot 10^{-4}$	73.0	36.0	13.1	n.d.	10.1	n.d.	n.d.
SSRu14	453	3.0	4.0	$5 \cdot 10^{-4}$	65.5	37.2	14.0	n.d.	n.d.	n.d.	n.d.
SSRu15**	493	3.0	4.0	$5 \cdot 10^{-4}$	70.2	23.1	7.5	n.d.	17.8	5.3	3.8
SSRu16	513	10.0	4.0	$5 \cdot 10^{-4}$	98.1	8.3	3.0	n.d.	15.9	5.4	2.8

\* This selectivity is calculated considering both A and T (the peaks are unresolved)

\*\* During this test there was also the formation of xylose, with selectivity equal to 11.4%

Keeping the lower quantity of catalysts in order to favour production of lower polyols, the effects of temperature and pressure on the product distribution were

analysed, according to the conditions of the experiments referred as SSRu7, SSRu9-SSRu16. The obtained results are also summarized in Figure 5. Figure 6 shows a scheme of the possible reactions, which is based on the identified products in the liquid phase.

At Ru/Sorbitol equal to  $5 \cdot 10^{-4}$ , sorbitol conversion was generally favoured at high temperature and pressure. The effect of temperature was less significant at 3 MPa (Figure 5a).

The results on arabitol selectivity are reported in Figure 5b, but the data at 473 K and 10 MPa are missing because we were not able to resolve the peaks of the pentol and threitol. Arabitol derives from C1 – C2 bond cleavage of sorbitol and its selectivity is higher at lower temperature, because at such condition its conversion is less likely to occur. The reduction of arabitol selectivity as temperature increased was due to its conversion to glycols, alcohols and C1, C2 alkanes (c.f. Figures 5d-e-f).

The selectivity of xylitol was lower than arabitol at every investigated condition (Figure 5c). This result is in agreement with the observation of Sun and Liu<sup>8</sup>, who find that xylitol preferentially is converted to arabitol, in presence of Ru/C.

Glycerol selectivity increased as temperature varied from 453 to 473 K (Figure 5d). In the range 473 – 513 K it seemed less affected by temperature and at 10 MPa selectivity was almost constant. Glycerol could be formed from sorbitol by a C3–C4 bond cleavage, but it seemed not easily converted to lower polyols as temperature increased.

Alcohols and diols were always present in very small amount and their selectivity increased as temperature was raised to 493 and 513 K. Figure 5e shows the selectivity of the sum of diols (butandiols, propandiols and ethandiols) and C5 – C1 alcohols.

Higher temperature led to higher selectivity for methane and ethane, whereas at 453 K, no gaseous straight chain alkanes have been detected at the three pressure values considered (Figure 5f). In fact, at lower temperature (453 and 473 K), C – O bond cleavage rate is disadvantaged with respect to C – C bond cleavage. Alcohols like propanol, butanol, pentanol, ethanol and methanol were also detected in the outlet gas stream.

It is worth noticing that at 493 K and 3 MPa (SSRu15), xylose was produced by hydrogenolysis of sorbitol, with selectivity equal to 11.4%. The C5 sugar may derive by dehydrogenation of C5 xylitol, but the subsequent transformation to lower polyols did not occur probably because of the low hydrogen pressure<sup>19</sup>.

### 3.3. Sorbitol conversion in presence of an inhibitor of the reaction

According to previous studies<sup>6,13</sup>, the effects of inhibitor of reaction was considered, and ruthenium was poisoned adding sulphur at the reactant solutions. The main purpose was to reduce the selectivity of straight chain alkanes, favouring the formation of glycols and alcohols. First, a preliminary study was conducted to analyse the behaviour of the system when starting from a basic solution<sup>4,7,19</sup>. The experiments

were conducted at 523 K, 10 MPa, with catalyst concentration equal to 0.001 g Ru/g S.

**Table 4** Experimental results of hydrogenolysis of sorbitol aqueous solution in semi-continuous mode at different pH, with hydrogen flow rate equal to 1000 Nml/min, Ru/S = 0.001 (g/g), P = 10 MPa, T = 513 K, and reaction time equal to 4 h. B = butanediol, P = propanediol, Et = ethanediol, Eth = ethanol.

	pH	Sorbitol conversion (%)	Selectivity			
			B	P	Et	Eth
NaSSRu1	14	100.0	-	5.3	6.0	0.7
NaSSRu2	12	88.7	4.2	23.0	12.4	0.2
NaSSRu3	10	96/0	4.2	9.9	6.8	1.7

The results in terms of selectivity considering the liquid products contained in the reactor at the end of the run have been reported in Table 4. It is evident that the solution pH had a great effect on the reaction and, differently from the previous results here presented, the production of alcohols increases. Considering the diols production, the best choice is to select an initial pH equal to 12. Most of the products obtained in presence of the base, NaOH, has not been recognised with the analytical techniques at our disposal. It is also worth noticing that alcohols may be dragged by the gas flow leaving the reactor.

Starting from this result and considering the patent of Dubeck and Knapp<sup>6</sup>, sulphur has been also added to the reactant solution in order to increase the selectivity of alcohols (ethanol) and glycols. The experimental runs have been conducted in semi-continuous mode, according to the condition reported in Table 5. The first experimental run was conducted following the patent of Dubeck and Knapp<sup>6</sup>, considering that condition leading to the maximum selectivity of ethanol.

At the condition of PSSRu1, most of the products were likelihood entrained in the gas stream. The analysis of the aqueous solution in the trap for volatile compounds downstream the reactor evidenced a high concentration of ethanol (circa 30 g/l) and methanol (7 g/l). Other alcohols like propanol, butanol, pentanol were present in lower quantities. The reaction leading to the highest yield in terms of diols and alcohols is PSSRu3, where the maximum amount of catalyst and poisoning were used, leading to high catalysts dispersion with low activity. The presence of sulphur reduced ruthenium activity and minimized the formation of straight chain hydrocarbon, favouring C2 – C3 oxygenates. Decreasing the amount of catalyst, keeping constant the ratio sulphur on ruthenium, the selectivity of glycols became quite high, but sorbitol conversion was highly reduced (PSSRu5).

**Table 5** Experimental results of hydrogenolysis of sorbitol aqueous solution in semi-continuous mode, with hydrogen flow rate equal to 1000 Nml/min, reaction time equal to 4 h, at 513 K and 10 MPa. S = Sorbitol, A = arabitol, X = xylitol, T = threitol, G = glycerol, B = butanediol, P = propanediol, Et = ethanediol, Al = alcohols.

	Ru/S (g/g)	Sulfur/Ru (mol/mol)	pH	Sorbitol conversion (%)	Selectivity (%)							
					A	X	T	G	B	P	Et	Al
PSSRu1	0.00625	4.0	14	100.0	-	-	-	-	7.0	4.4	3.2	-
PSSRu2	0.003	0.3	10	16.0	26.9	9.4	-	15.0	-	35.6	16.9	-
PSSRu3	0.009	5.0	10	44.3	-	-	-	-	4.7	24.9	20.2	8.3
PSSRu4	0.009	0.3	10	40.0	15.0	9.0	5.0	8.8	2.0	14.4	9.3	-
PSSRu5	0.003	5.0	10	14.0	-	-	-	-	-	40.7	25.7	4.3

#### 4. Conclusion

In this work, we investigated the effect of different parameters on the catalysed conversion of glucose and sorbitol in presence of hydrogen, in order to clarify the mechanisms driving these reactions. A wide variety of compounds had been obtained due to the occurrence of different class of reactions: C – C bond scissions, C – O bond scission and hydrogenation. Based on the conversion of polyols, platinum showed to be less active, while it has favoured the conversion of glucose. Starting from the simple sugar in presence of Pt/C, pentols (arabitol and xylitol) showed the higher selectivity along with carbon dioxide as gaseous products. It is demonstrated that Pt/C has a highest selectivity to C6 (hesanendiol) indicating a weaker activity to C – C bond cleavage<sup>19</sup>.

In presence of ruthenium, results showed higher activity with respect to polyols conversion, with the prevalence of hydrodeoxygenation reaction and the formation of straight chain alkanes, particularly methane and ethane. The selectivity of oxygenated compounds, especially glycols and alcohols, had been increased by using an inhibitor of the reaction starting with an initial basic environment.

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### Figure captions

Figure 1. Schematic representation of products obtained by hydrogenolysis of glucose in presence of Pt/C.

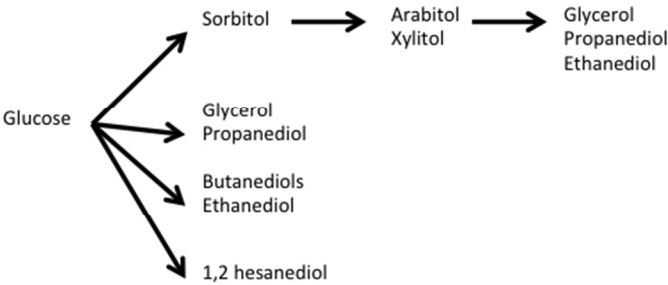
Figure 2. Conversion of sorbitol at different sampling time, with Ru/S equal to 0.0015 (g/g), at 10 MPa (a) and 5 MPa (b) at the following temperature: 453 K (circle), 473 K (square), and 493 K (star).

Figure 3. Selectivity behaviour with respect to sorbitol conversion, with Ru/sorbitol equal to 0.0015 g/g, for arabitol (plus), xylitol (square), glycerol (circle), and threitol (star), at the following conditions: P =10 MPa, 453 K (a), 473 K (b), 493 K (c); P = 5 MPa 453 K (d), 473 K (e), 493 K (f).

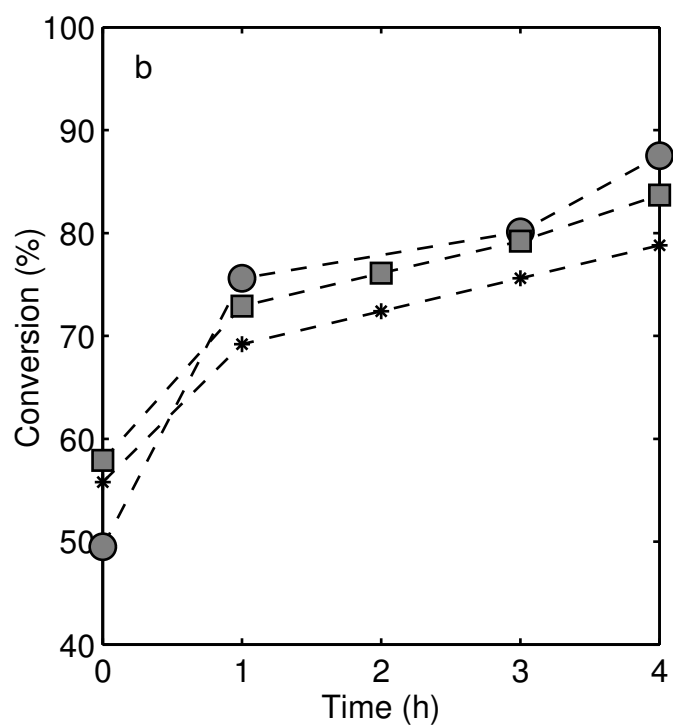
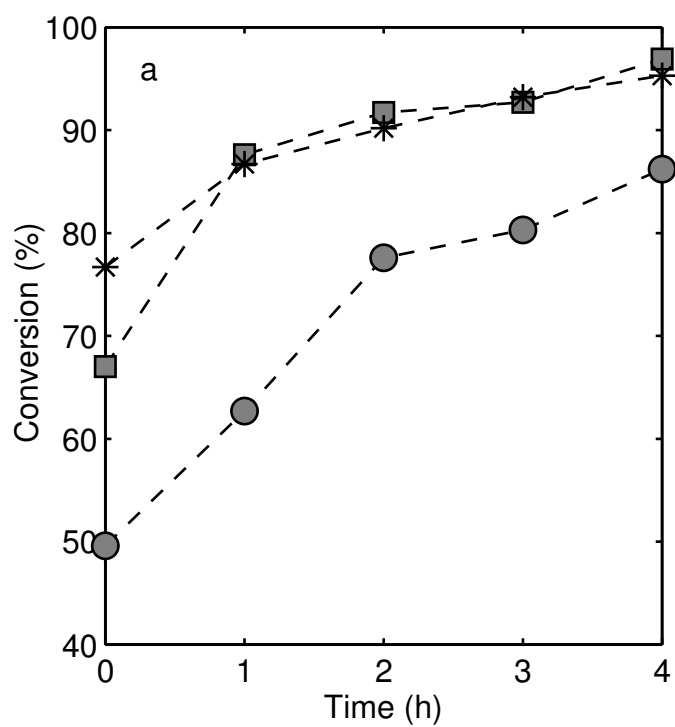
Figure 4. Schematic representation of products obtained by hydrogenolysis of sorbitol in presence of Ru/C.

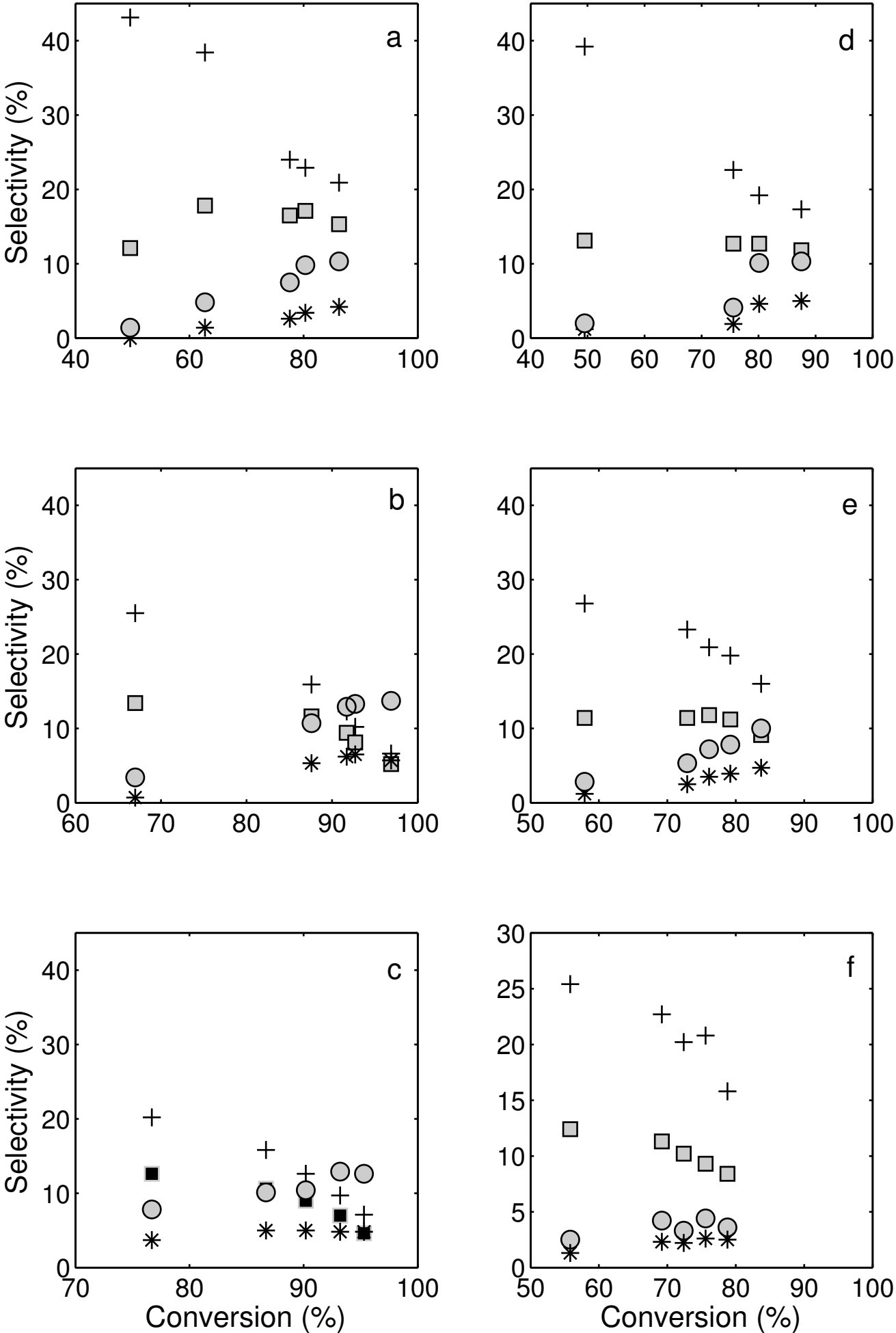
Figure 5. Conversion of sorbitol (a), and product selectivity for the experimental campaign carried out in semi-batch mode, with Ru/Sorbitol =  $5 \cdot 10^{-4}$  g/g, reaction time = 4h, hydrogen flow rate equal to 1000 Nml/min. Arabitol (b), xylitol (c), glycerol (d), diols+alcohols (e), methane and propane (f).

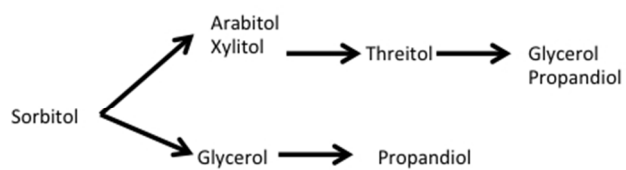
Figure 6. Schematic representation of products obtained by hydrogenolysis of sorbitol in presence of Ru/C carried out in semi-continuous reaction mode.



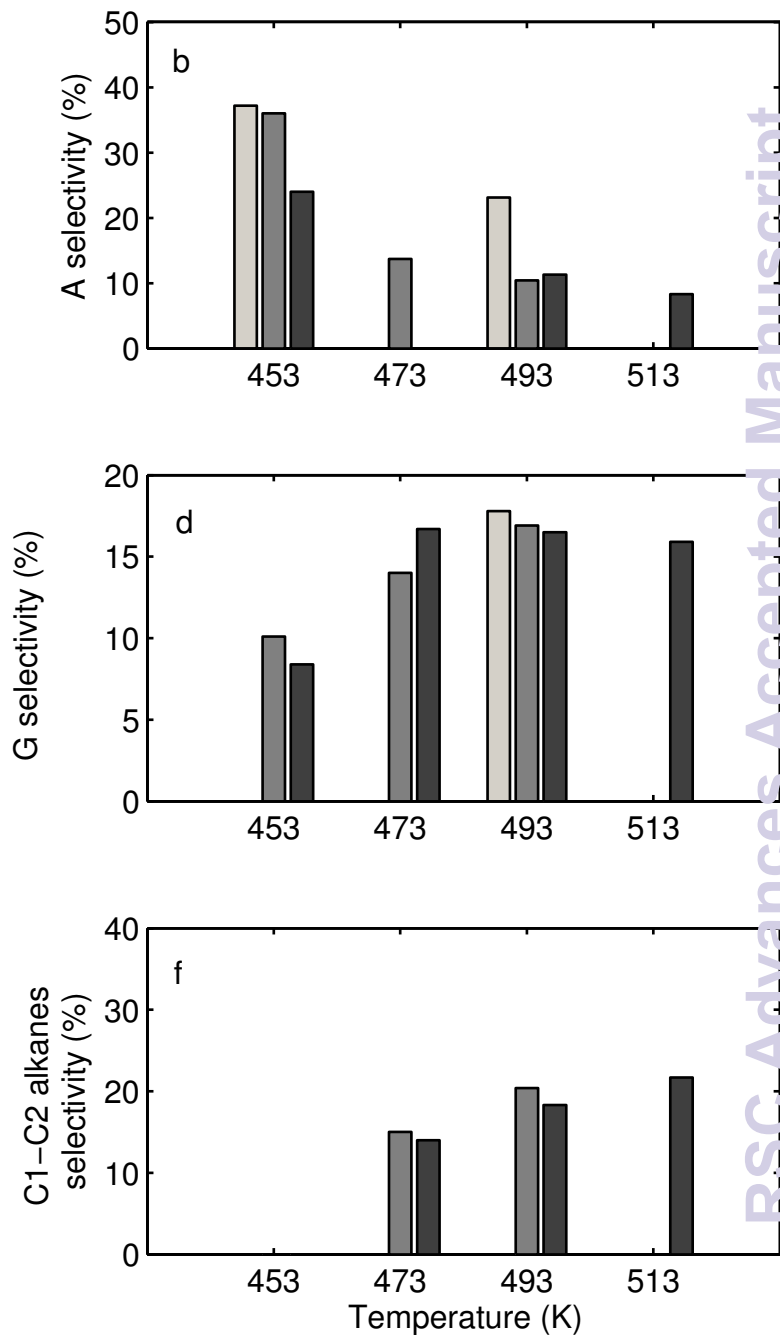
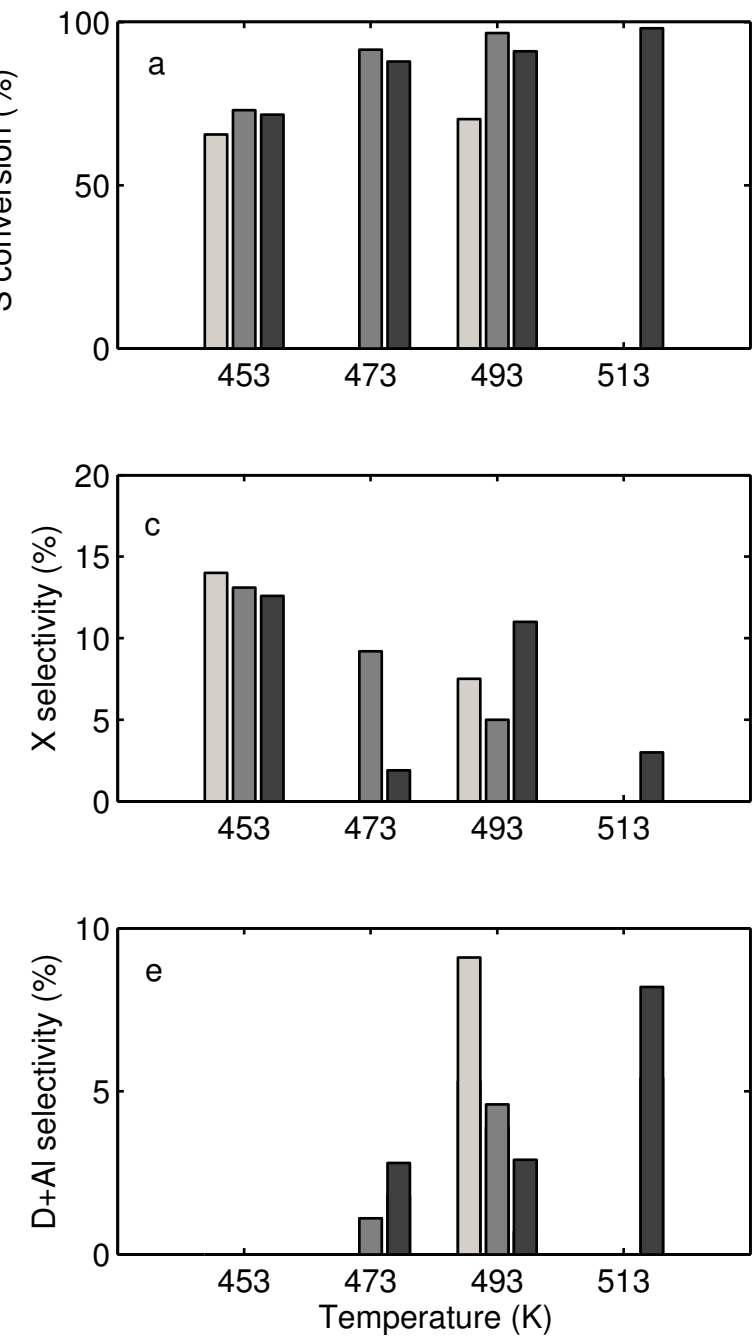
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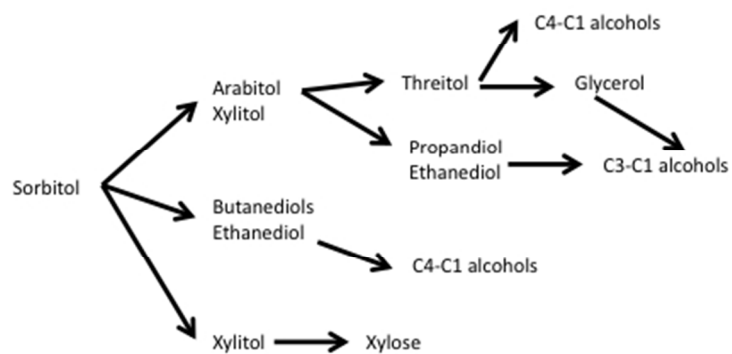




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