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Glucose transformations over a mechanical mixture of ZnO and Ru/C catalysts: product distribution, thermodynamics and kinetics

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Abstract

Transformations of glucose to 1,2-propylene glycol were studied over a mechanical mixture of ZnO and Ru/C catalysts in the presence of hydrogen. Different reaction conditions were evaluated by changing the reaction temperature and hydrogen pressure. In addition to the cascade mode of operation, also separate steps in the overall reaction network, such as hydrogenation of pyruvaldehyde and hydroxyacetone to 1,2-propylene glycol were investigated. Fructose as a starting material was also studied resulting in a propylene glycol yield of 37.5%. The optimal temperature for glucose transformation to propylene glycol was found to be 165 °C. The influence of temperature on the catalytic behavior was more prominent than the effect of hydrogen pressure. Thermodynamic analysis of glucose transformation to 1,2-propylene glycol was performed and a plausible kinetic model reflecting a complex reaction network was developed being able to describe the data in a reliable way.

Keywords: glucose, hydrogenolysis, 1,2-propylene glycol; heterogeneous catalysts, ZnO, Ru/C, optimization of reaction conditions, kinetic modelling, thermodynamic analysis.

Introduction

1,2-Propylene glycol (PG) is a versatile compound that can be used in several applications such as an antifreeze agent [1], a building block for polymers, an airplane deicing agent, as well as in food processing and production of pharmaceuticals [2-5]. Currently PG is industrially produced through hydration of propylene oxide, which is synthesized from propylene via hydrochlorination or oxidation routes [2, 6]. The annual market of 1,2-propylene glycol is limited to 2.5 million tons [7]. Nowadays following a quest for alternative production of chemicals from renewable resources, the effort to synthesize of PG from biomass is of high importance. An undesired side-reaction in the overall process is dehydration of fructose yielding 5-hydroxymethylfurfural (5-HMF) [8]. Side reactions of this type inevitably lead to formation of humins and subsequent catalyst deactivation [8].

For transformations of glucose four different main reaction paths can be identified, leading to PG, namely isomerization, retro-aldol splitting, dehydration and hydrogenation.

Aldose-ketose isomerization can be carried out in the presence of heterogeneous catalysts [4, 9-12] and enzymes [13]. Several basic catalysts have been screened in sugar isomerization namely, hydrotalcites [9], magnesium aluminates [9] and ZnO [10]. Not only bases, but also catalysts with Lewis acidity, such as alumina [4], can be active in the isomerization of glucose to fructose. This step in the overall process of glucose transformations to PG has been considered to be the slowest one [4]. It has been reported [11] that retro-aldol reaction of glucose favors the formation of C2-compounds, such as glycolaldehyde and ethylene glycol [12] while fructose is more selective to C3-compounds. In order to control the reaction network towards PG formation, a special care should be taken for isomerization of glucose to fructose which should undergo retro-aldolization to glyceraldehyde and 1,3-dihydroxyacetone. Hydrogenation of carbonyl groups can be easily performed over supported ruthenium catalysts [14]. At the same time hydrogenation of the sugars should be avoided when the desired compound is PG

rather than sorbitol and mannitol which are easily formed during the hydrogenation of glucose and fructose over ruthenium catalysts. To summarize, the catalysts applied in the transformation of glucose to PG should exhibit high activity in both isomerization to fructose and retro-aldolization to C3-compounds, while activity of the hydrogenation catalyst should be moderate to avoid hydrogenation of sugars.

Several studies have been performed on the catalytic transformation of glucose to PG using noble metal catalysts, such as Ru, Rh, Pd and Pt, as well as a large number of different support materials [4, 10, 12, 16] as well as transition metal catalysts [5, 15]. The highest PG yields reported in literature are given in Table 1. The best result was obtained over Pd-WO_x/Al₂O₃ giving 56.1% PG [4]. In addition Ru/C together with ZnO gave promising PG yield under low hydrogen pressure [10]. Interestingly Ru/C catalyst together with 1000 ppm ammonium meta tungstate gave in glucose transformation ethylene glycol as the main product at 240 °C under 40 bar hydrogen [16]. Over transition metal catalysts typically PG yields in the range of 27.9-32 % were obtained under relatively high hydrogen pressures (Table 1).

Table 1. The highest PG yields reported in the literature over different catalysts.

Catalyst	Reactions conditions	PG yield (%)	Reference
Pd-WO _x /Al ₂ O ₃	180 °C, 40 bar H ₂	56.1	[4]
Ru-Sn/C	240 °C, 50 bar H ₂	25	[12]
Ru/C + ZnO	180 °C, 4 bar H ₂	38	[10]
lanthanum oxycarbonate modified Cu/Al ₂ O ₃	200 °C, 34 bar H ₂	32	[15]
Ni/MgO	220 °C, 60 bar H ₂	24.8	[5]
Ni/ZnO	220 °C, 60 bar H ₂	27.9	[5]

In this work a mixture of Ru/C -ZnO catalysts was used in fructose and glucose transformation following the guidelines of the previous work [10]. As a comparison, hydrogenation of pyruvaldehyde and hydroxyacetone over Ru/C catalyst was investigated. In this study, the main emphasis was to explore the role of reaction parameters on the catalytic behavior (e.g. activity and selectivity). In particular, the parameter space was explored by conducting glucose transformation experiments at different temperatures, hydrogen pressures and glucose concentrations. Thermodynamic analysis for synthesis of 1,2-propylene glycol from glucose was performed using the Joback approach [18-20], taking into account the reaction stoichiometry in the liquid phase and starting from the standard enthalpy and the Gibbs free energy. According to our knowledge this is the first thermodynamic analysis of the synthesis of 1,2-propylene glycol from glucose reported in open literature. Based on the proposed reaction scheme a kinetic model was developed and the kinetic parameters were determined with the regression analysis.

Experimental

Chemicals

Commercial Ru/C (4.6 wt% Ru) and ZnO (99.99%, Alfa Aesar) were used as catalysts. Before the experiments the catalysts were dried at 110 °C overnight. Glucose (98%, Fluka), fructose (99%, Sigma), hydroxyacetone (95%, Alfa Aesar) and pyruvaldehyde (40%, Sigma) were used as received.

Catalyst characterization

The basicity of ZnO was quantified through CO₂-TPD (temperature programmed desorption) using a Micromeritics AutoChem 2910 device. Prior to CO₂-TPD zinc oxide was dried at 110 °C overnight and further dried in the U-tube of the AutoChem at 150 °C for 1 h. A higher drying/calcination temperature was also investigated by keeping the temperature at 400 °C for

1 h before adsorption of CO₂. Adsorption of CO₂ was carried out at 100 °C for 1 h, thereafter physisorbed CO₂ was removed from the sample by keeping it at 100 °C for an additional hour. The heating rate used in the desorption was 10 °C/min from 100 °C to 900 °C.

The acidity of ZnO was investigated by Fourier Transformed Infrared Spectroscopy (ATI Mattson FTIR) using pyridine as a probe molecule.

The specific surface area of the Ru/C catalyst was measured with a Micrometrics MicroActive 3Flex 3500. Prior to the surface area measurement, the catalyst sample was outgassed at 110 °C for 4 h. The specific surface area of the microporous carbon was calculated with the Dubinin–Radushkevich method.

Reactor set-up

The experiments were carried out in a reactor autoclave shown in Figure 1. The set-up consisted of a 300 ml stainless steel Parr reactor vessel, a heating mantle, an impeller, a thermocouple and a pressure gauge connected to the reactor. Furthermore, a preheating chamber was coupled to the reactor system for preheating of the reaction mixture. Hydrogen and argon gases with pressure controllers were connected to the set-up. Periodical sampling was carried out through a sampling line. The reactor was operated in semi-batch mode with respect to hydrogen by maintaining a constant pressure.

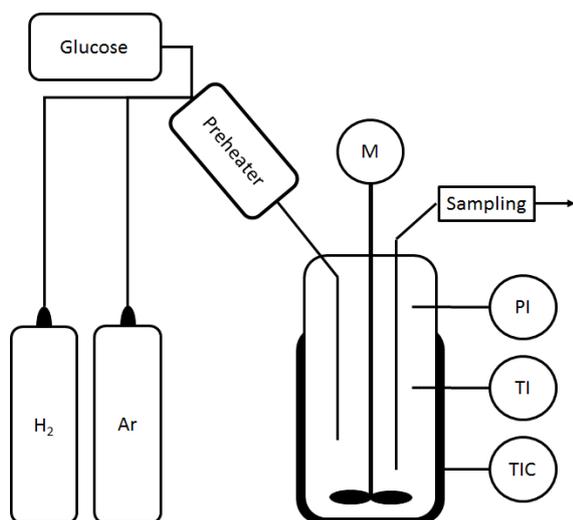


Figure 1. Reactor set-up used for glucose transformations.

Catalytic experiments

The kinetic experiments were carried out in the set-up described above. Both ZnO and Ru/C catalysts were dried overnight in an oven at 110 °C. In a typical experiment, 0.41 g of ZnO and 0.15 g of Ru/C was weighed and placed in the reactor vessel. The reactor was flushed five times with 5 bar of argon and thereafter five times with 5 bar of hydrogen in order to remove air from the reactor. After flushing the reactor, heating of it was started. Typically, 100 ml of 5 wt% solution of glucose was used, which after mixing was poured into the preheating chamber, flushed with argon for ca. 5 min and thereafter with hydrogen, also for ca. 5 min. Prior to pouring the solution to the preheater a zero-sample was taken. Flushing of the preheating chamber with both gases was followed by pressurizing with hydrogen to 5 bar and heating to 80 °C. The sugar solution was heated for 15 min, the pressure in the preheater was increased to the reaction pressure (typically 20 bar hydrogen) with subsequent opening of the inlet valve to the reactor and starting feeding of the glucose solution. When all solution was fed into the reactor the timer and stirrer (720 rpm) were switched on. Samples were withdrawn from the reactor through a 0.5 µm sinter and further filtered through a 0.43 µm syringe filter prior to

HPLC analysis. A small amount of waste was removed from the sampling tube prior to each sample to obtain representative values.

After taking the last sample, heating of the reactor was shut down. When the reactor had cooled to the ambient temperature it was depressurized and opened. The remaining reaction mixture was collected and stored in a separate bottle. The reactor set-up was cleaned with water and tissue paper. Deposits on the set-up which could not be removed by simple washing were removed gently with the aid of 600 mesh wet/dry sandpaper.

Catalytic experiments were conducted with small catalyst particles (below 63 μm) and vigorous stirring eliminating a potential influence of mass transfer limitations on observed data.

The influence of reaction temperature and hydrogen pressure on the conversion and yield was investigated. Furthermore, hydrogenation of pyruvaldehyde and hydroxyacetone was studied along with experiments using fructose as the starting compound.

Calculations

The glucose conversion and product yields were calculated with the equations below. The glucose conversion was calculated with

$$X_{glucose} = 1 - \frac{n_{glucose}(t)}{n_{glucose}(t=0)} \approx 1 - \frac{c_{glucose}(t)}{c_{glucose}(t=0)} \quad (1)$$

where n is the amount of glucose (in mol) in the samples at time t . For simplicity the HPLC was calibrated with known concentrations of the compounds (including glucose) and the conversion was calculated based on the concentration of glucose.

The yield of PG was calculated from

$$Y_{PG} = \frac{N_{C,PG}}{N_{C,glucose}} \cdot \frac{n_{PG}(t)}{n_{glucose}(t=0) - n_{glucose}(t)} \approx \frac{N_{C,PG}}{N_{C,glucose}} \cdot \frac{c_{PG}(t)}{c_{glucose}(t=0) - c_{glucose}(t)} \quad (2)$$

where N_C indicates the number of carbon atoms in either PG or glucose. Similarly, as for calculation of the glucose conversion, the concentrations were used in the calculation of the yields. The yields of other compounds were calculated with analogous equations to (2), but by taking into account that the number of carbons can be different compared to PG.

The carbon balance was calculated as moles of carbon from the concentrations of glucose and all products visible in HPLC analysis after 1200 min divided by moles of initial glucose in the feed. The turnover frequency (*TOF*) of the reactant was calculated from

$$TOF = \frac{n_{reactant}}{t_{full} \cdot D \cdot n_{Ru}} \quad (3)$$

where $n_{reactant}$ indicates the reacted amount of the substrate and t_{full} is the time required for full conversion using a linear approximation of the initial concentration curves. D is the ruthenium dispersion and n_{Ru} is the amount of ruthenium used in the experiment.

Product analysis

The composition of the reaction mixture was analyzed by high performance liquid chromatography (HPLC). The HPLC (Hewlett Packard 1100 series) was equipped with a refractive index detector (RI) and the column used for the separation of the compounds was an Animex HPX-87H applying 5 mM sulfuric acid as the eluent. The temperature of the column was 45 °C and the flow of H₂SO₄ was 0.6 ml/min. The response factors and retention times for several different compounds were determined prior to catalytic experiments and used for calculations of the concentrations. The calibrated compounds were glucose, fructose, sorbitol, glyceraldehyde, erythritol, pyruvaldehyde, lactic acid, glycerol, 1,3-dihydroxyacetone, formic acid, acetic acid, ethylene glycol, 1,2-propylene glycol, hydroxyacetone, 2,3-butanediol, methanol, 1,2-butanediol, 1,4-butanediol, ethanol, 2-propanol, 1-propanol and 5-hydroxymethylfurfural (5-HMF).

The final reaction solution was also analyzed by a Perkin Elmer Inductively Coupled Plasma Optical Emission Spectrometer Optima 5300 DV (ICP) for possible leaching of Zn and Ru. Prior to analysis the reaction solution was filtered with a 0.43 μm syringe filter and diluted with 1.5% nitric acid for Zn analysis and with 1.5% hydrochloric acid for analysis of Ru.

Results and Discussion

Catalyst characterization results

Basicity and acidity was determined for ZnO catalyst. No acidity could be observed by pyridine-FTIR. The CO_2 -TPD profiles of ZnO catalyst are shown in

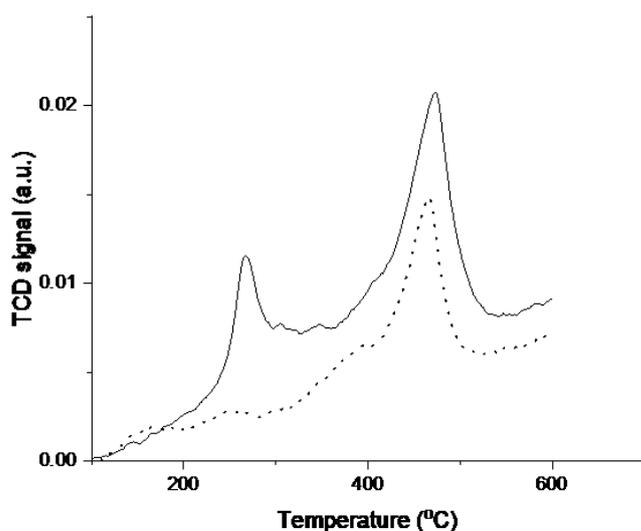


Figure 2. The TCD signal was calibrated for different CO_2 concentrations in helium and integration of the signal (concentration) enabled the quantification of basicity. It was revealed that drying/calcination temperature influenced the basicity. Drying at 150 $^{\circ}\text{C}$ resulted in a TPD profile containing two peaks while the lower temperature peak was absent when ZnO was calcined at 400 $^{\circ}\text{C}$, as seen in Figure 2. The total concentration of basic sites (in terms of CO_2) was 48.0 $\mu\text{mol/g}$ for the dried sample and 19.7 $\mu\text{mol/g}$ for the calcined sample. It has been reported [21] for ZnO supported on activated carbon that the CO_2 desorption can give rise to two peaks, one at 100-300 $^{\circ}\text{C}$ (weak basic sites) and another one at 300-500 $^{\circ}\text{C}$ (moderately

basic sites), similarly to the results in shown in Figure 2. Interestingly, it was previously stated [22] that ZnO does not exhibit basicity due to acidic properties.

The 4.6 wt% Ru/C catalyst has been previously characterized by CO chemisorption [14], showing a mean ruthenium particle size is 2.5 nm, corresponding to a dispersion value of 40%. The specific surface area of Ru/C catalyst was 689 m²/g. The pH of the catalyst suspension was 6.8 indicating low acidity of Ru/C catalyst.

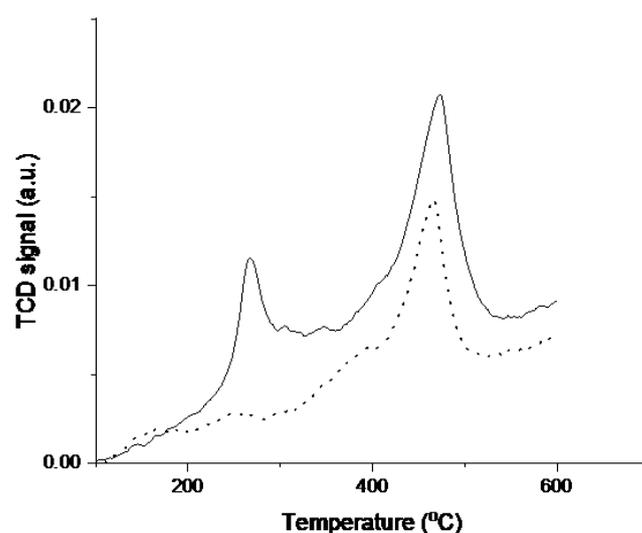


Figure 2. CO₂ TPD signal for ZnO dried at 150 °C (solid line) and calcined (dotted line) at 400°C.

Hydrogenation of pyruvaldehyde and hydroxyacetone over Ru/C catalyst

Prior to starting the experiments with glucose, individual hydrogenation reactions were performed before combining more complex retro-aldolization and isomerization reactions with hydrogenation i.e. starting with sugars. Hydrogenation of pyruvaldehyde and hydroxyacetone was studied over Ru/C catalyst without ZnO at 180 °C and 20 bar total hydrogen pressure (10

bar hydrogen absolute pressure). Hydrogenation of hydroxyacetone was rather rapid as can be seen in Figure 3 which shows the concentration profiles of hydroxyacetone and PG.

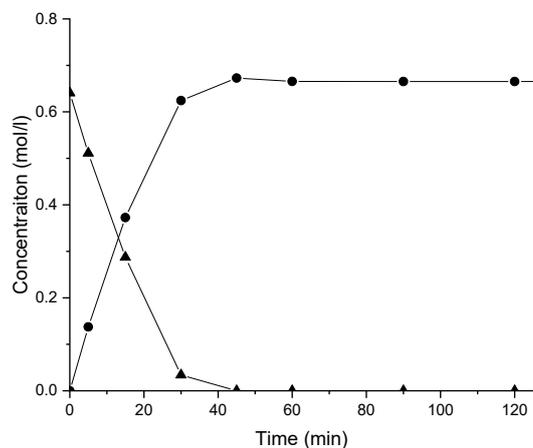


Figure 3. Concentration profiles of hydroxyacetone and PG during hydrogenation of hydroxyacetone at 180 °C and 10 bar hydrogen (absolute pressure) with 0.15 g of Ru/C catalyst. Notation: hydroxyacetone (▲), PG (●), the initial HA concentration was 0.64 mol/l.

Hydrogenation of hydroxyacetone was complete after approximately 32 min with a Ru/C catalyst loading of 1.058 mmol Ru/mol reactant. The turnover frequency TOF was calculated to be 1.24 s⁻¹. The kinetics of low temperature (150 °C) hydrogenation of hydroxyacetone and other bio-oil compounds has been investigated previously by Bindwal et al. over a 5% Ru/C catalyst [23]. The authors did not report directly the TOF providing, however, the value of initial rate of 0.03 mol/(g_cat*min). Recalculation of this value to the mole of ruthenium gives 0.99 s⁻¹. In the current work the initial rate of hydroxyacetone hydrogenation calculated per mole of Ru present in the catalyst is 0.50 s⁻¹. The rates are comparable by taking into account the differences in temperature and hydrogen pressures, namely, 150 and 180 °C, and 20 and 10 bar hydrogen, respectively. The yield of PG at complete hydroxyacetone (45 min) conversion slightly exceeds 100%, which can be explained by inaccuracy in the HPLC analysis.

Hydrogenation of pyruvaldehyde displayed an interesting behavior (Figure 4) showing besides the reactant also three other compounds namely, hydroxyacetone and PG, as well as dihydroxyacetone.

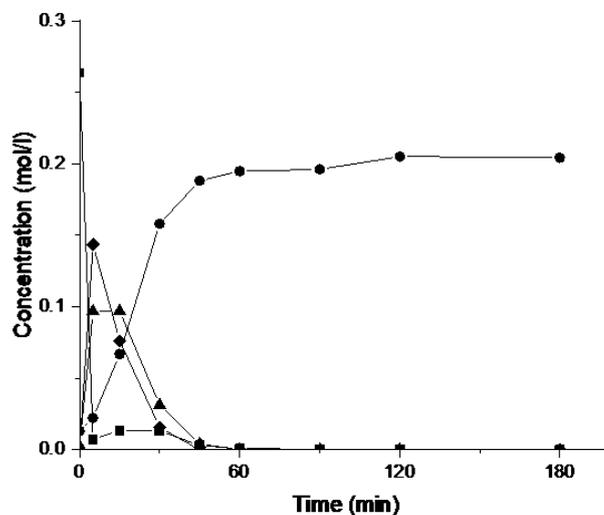


Figure 4. Concentration profiles of pyruvaldehyde, dihydroxyacetone, hydroxyacetone and PG during hydrogenation of pyruvaldehyde at 180 °C and 10 bar hydrogen (absolute pressure) with 0.15 g of Ru/C catalyst. Notation: pyruvaldehyde (■), dihydroxyacetone (◆), hydroxyacetone (▲) and PG (●). The initial pyruvaldehyde concentration is 0.26 mol/l.

As observed from Figure 4 two compounds, dihydroxyacetone and hydroxyacetone, are formed as intermediates during the hydrogenation of pyruvaldehyde to PG. Formation of hydroxyacetone is expected, while the feasibility of hydration was confirmed by thermodynamic calculations as will be discussed below.

Pyruvaldehyde was rapidly converted and after 5 min, and the conversion exceeded 97% while the yield of PG at the same time was only 8.5%. Based on the initial conversion, TOF for the pyruvaldehyde conversion was calculated to be 3.15 s^{-1} . The PG yield reached 77.8% after two hours of the reaction at almost complete pyruvaldehyde conversion (99.8%). To our knowledge hydrogenation kinetics of pyruvaldehyde on Ru/C catalysts has not been reported previously in the open literature. However, hydrodeoxygenation of pyruvaldehyde has been studied earlier

[24] over a molybdenum oxide catalyst. Due to a significantly higher temperature (300 °C) and a different catalyst with the aim of hydrodeoxygenation, pyruvaldehyde was transformed mainly to acetone with a carbon yield of 58.8%.

Transformation of fructose over a mixture of Ru/C and ZnO catalysts

Fructose transformation using a mixture of Ru/C- ZnO catalysts was also performed and the results are displayed in Figure 5. The reaction time selected for the fructose transformation was significantly longer than in the previous experiments, namely 20 hours.

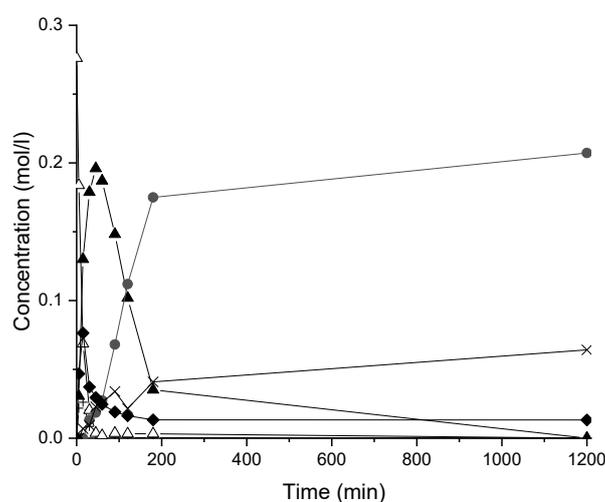


Figure 5. Concentration profiles of the major compounds detected during transformation of fructose to PG at 180 °C and 10 bar hydrogen (absolute pressure) with 0.15 g of Ru/C and 0.41 g of ZnO catalysts. The initial fructose concentration is 0.276 mol/l. Notation: fructose (Δ), glucose (+), hydroxyacetone (\blacktriangle), pyruvaldehyde (\blacksquare), dihydroxyacetone (\blacklozenge), PG (\bullet) and 1-propanol (x).

From Figure 5 it can be observed that fructose is rapidly converted via the retro-aldol condensation and conversions exceeding 99% after 1 hour were obtained while the hydrogenation reactions of the intermediates required longer times to be completed. It is stated in the literature [10] that retro-aldol condensation of fructose occurs on Lewis acidic catalysts via the hydride shift mechanism [25]. Furthermore, glucose isomerisation occurs also on basic sites via a proton transfer mechanism, in which carbonyl group in glucose is deprotonated. Such

mechanism is coined as the Lobry-de-Bruyn-van-Ekenstein mechanism [26]. In addition A small concentration maximum is visible in Figure 5 for glucose, indicating that fructose is isomerized to glucose simultaneously as fructose undergoes retro-aldol reaction resulting in smaller molecules. Transformations of glucose to fructose are known to be limited by thermodynamics, thus some formation of glucose could be anticipated. The maximum concentration of glucose corresponds to a yield of 9.5 %. The presence of glucose in fructose transformation over Ru/C-ZnO was not reported by Hirano et al. [10].

More interestingly in the context of the PG formation is a rapid production of hydroxyacetone which is then hydrogenated to PG (Figure 5). The maximum yield of hydroxyacetone was 35.5% and at the same time the yield of PG was 3.4%. The final yield of PG was 37.5%. Important for achieving higher PG yields is to control the reaction in such a way that the selectivity of the retro-aldol reaction with subsequent dehydration to pyruvaldehyde is maximized. It was confirmed by Hirano et al. [10] that lactic acid was the main product in glucose transformation over ZnO at 140 °C and 4 bar hydrogen indicating that ZnO facilitates C3-C4 cleavage of fructose. ZnO in [10] exhibited a rather low acidity, 6.6 $\mu\text{mol/g}$ determined by ammonia TPD, while its basicity was 14 $\mu\text{mol/g}$ by CO_2 TPD. Furthermore, a non-acidic Cu/La₂O₃CO₃ in the absence of any acidity converted glucose to PG with the yield of 32% at 200 °C and 34 bar hydrogen [15], while an acidic Cu/Al₂O₃ with a low basicity catalyzed formation of sorbitol. Cu/La₂O₃CO₃ exhibited medium and strong basic sites [15]. Thus it can be concluded that in the current work analogously to [15] Ru/C-ZnO facilitated PG formation due to the presence of medium basic sites in ZnO, while Ru/C alone promotes hydrogenation [15], which is suppressed over Ru/C-ZnO. The main observed undesired by-product in the current work was 1-propanol with the yield of 11.6%, being a typical degradation product of PG [15]. It was, however stated in [15] that in the hydrogenation of hydroxyacetone over Cu-La₂O₃/Al₂O₃ exhibiting mainly weak basic sites no propanol was detected. In the current work

the PA/HA ratio was ca. 5 after 3 h when using 10 bar hydrogen, while in Hirano et al. [10] the PA/HA ratio was 1.2 after 4 h under 4 bar of hydrogen, showing a beneficial effect of hydrogen pressure for transforming hydroxyacetone to PG. Furthermore, a high PG yield, 44% has been obtained under harsh reaction conditions in fructose transformation over 5 wt% Ru-3 wt% Sn/AC under 50 bar at 240 °C in 14 min [12].

Glucose transformation over a mixture of Ru/C and ZnO under various reaction conditions

In order to investigate a possibility of increasing the PG yield, different reaction conditions were tested by changing the reaction temperature, hydrogen pressure and glucose concentration and using mechanical mixtures of the same catalysts ZnO and Ru/C, as used above for individual transformations.

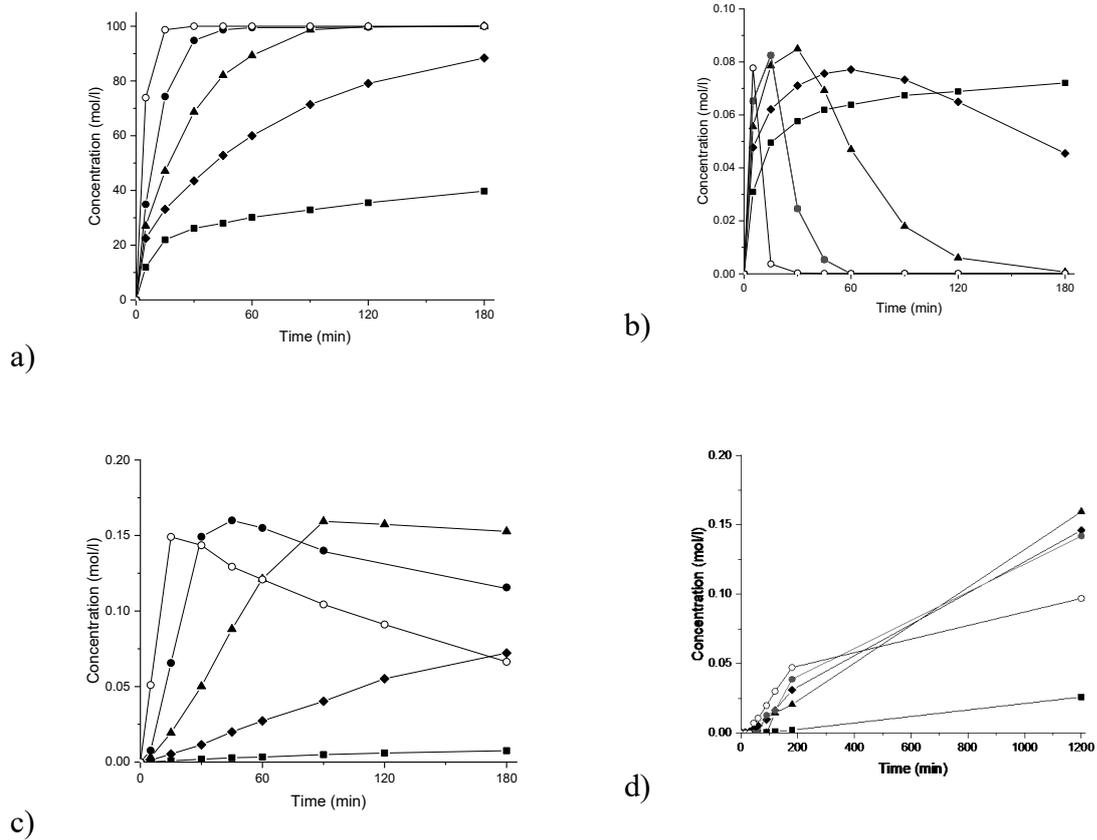
Table 2. Results from glucose transformation using different amounts of reactant, at different temperatures and pressures. The initial glucose concentration is 0.278 mol/l, total pressure 20 bar (if not else stated). The mass ratio between glucose and catalysts in all experiments was kept the same, i.e. : GLU:Ru/C:ZnO was 33 : 1: 2.7. Notation: SOR sorbitol, FRU fructose, EG ethylene glycol, GA glyceraldehyde, PA pyruvaldehyde, DHA dihydroxyacetone, HA hydroxyacetone, PG 1,2-propylene glycol

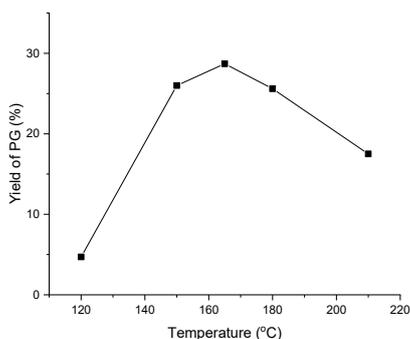
Entry	Temperature (°C)	Hydrogen pressure (bar)	Initial glucose concentration (mol/l)	Carbon balance (%)	Selectivity of SOR (%) at 70% conversion ^a	Selectivity of EG (%) at 70% conversion ^a	Selectivity of FRU (%) at 70% conversion ^a	Selectivity of PA+GA+DHA at 70% conversion ^a	Selectivity of HA (%) at 70% conversion ^a	Selectivity of PG (%) at 70% conversion ^a
1	120	18	0.276	83.3	11.2 (12.4)	1.3 (1.4)	23.3 (22.7)	13.1 (15.2)	0.0 (0.0)	3.9 (4.7)
2	150	15	0.276	83.8	8.0 (12.0)	1.6 (3.3)	26.7 (0.0)	15.0 (2.0)	7.0 (2.0)	1.7 (26.5)
3	165	13	0.278	53.5	4.1 (2.7)	1.3 (2.4)	30.0 (0.0)	11.4 (2.6)	9.7 (0.0)	0.0 (28.7)
4	180	10	0.277	64.1	5.4 (2.0)	1.6 (1.6)	43.1 (0.0)	18.1 (3.0)	14.6 (0.0)	0.0 (25.6)
5	210	5	0.277	35.1	3.1 (1.3)	0.6 (0.9)	26.6 (0.0)	13.4 (2.3)	8.7 (0.0)	0.0 (17.5)
6	180	5	0.280	41.3	2.9 (1.4)	0.5 (1.0)	28.5 (0.0)	10.9 (2.6)	9.4 (1.9)	0.0 (19.7)
7	180	20	0.276	51.9	4.1 (3.0)	1.0 (2.1)	28.1 (0.0)	12.0 (2.7)	9.3 (0.0)	0.0 (27.6)
8	180	10	0.056	84.0	5.0 (2.5)	1.2 (2.7)	45.2 (0.0)	17.3 (5.2)	11.8 (0.0)	0.0 (30.9)
9	180	10	0.138	79.9	8.1 (4.5)	2.1 (2.9)	42.8 (0.0)	17.4 (3.6)	13.0 (0.0)	0.0 (31.8)
10	180	10	0.410	65.7	3.7 (1.4)	1.2 (1.9)	45.1 (0.0)	17.3 (2.6)	13.9 (0.0)	0.0 (25.0)
11	180	10	0.551	62.0	7.1 (3.1)	2.3 (2.1)	41.8 (0.0)	20.5 (2.4)	13.8 (0.0)	0.0 (22.9)

^a after 1200 min

Influence of reaction temperature

The influence of the reaction temperature was studied at 120 – 210 °C. The total pressure was kept constant at 20 bar at different temperatures, except for 210 °C when it was increased to 25 bar to keep the total pressure above the steam pressure. The glucose concentration used in these experiments was 50 g/l corresponding to 5 wt% or 0.278 mol/l. The reaction time in all experiments was 20 hours, as for fructose, but for more clear visualization only the three first hours are shown for glucose conversion in Figure 6 and reported in Table 2.





e)

Fig. 6. a) Glucose conversion, concentration of b) fructose, c) hydroxyacetone and d) PG at different reaction temperatures, notation: 120 °C (■), 150 °C (◆), 165 °C (▲), 180 °C (●) and 210 °C (○), e) yield of PG at different temperatures after 180 min. Conditions: initial glucose concentration 0.276 mol/l, 0.15 g Ru/C, 0.41 g ZnO, 180 °C. Hydrogen pressure decreased with increasing overall pressure as follows: 18 bar, 15 bar, 13 bar, 10 bar and 5 bar. The total pressure was 20 bar, except at 210 °C it was 25 bar.

From Figure 6a it can be clearly observed that the reaction temperature has a major effect on the glucose conversion and complete conversion could be achieved within 3 h for the three highest temperatures. It was possible to obtain complete conversion at 150 °C within 20 hours while 120 °C was apparently too low temperature and not sufficient to achieve complete conversion for the tested catalyst loading. The time for full glucose conversion was linearly approximated to be 29.7, 19.4 and 13.5 min for the first 15 min for the runs at 165, 180 and 210 °C, respectively. The TOF at the different temperatures were 0.19, 0.28 and 0.41 min⁻¹, the calculations were based on the molar amount of ZnO used in the experiments. The activation energy for glucose transformation was determined to be 29.5 kJ/mol based on these values.

The carbon balance determined from HPLC analysis showed that at the two higher temperatures lower levels were obtained (Table 2, entries 1-4), most probably due to formation of gaseous products and oligomers, i.e. humins, which are not visible in HPLC analysis. The carbon balance at 180 °C with 0.277 mol/l initial glucose concentration was only 64% (Table 2, entry 4), while in ref. [10] with 0.05 mol/l initial glucose concentration the carbon balance was higher being 86.5 % at 180 °C and 4 bar hydrogen. It can, however, be seen from Table 2, entry 8 that

with 0.056 mol/l initial glucose concentration the carbon balance was nearly the same as reported by Hirano et al. [10]. Formation of gaseous products was confirmed over Ru/C- ZnO in glucose transformation at 180 °C under 4 bar hydrogen [10].

As discussed above glucose can react in several ways, e.g. by direct hydrogenation to sorbitol, or by isomerizing to fructose and further reacting to PG. In principle, mannitol can be also formed through hydrogenation of fructose, however, HPLC analysis did not show any shoulder of mannitol between the fructose and sorbitol peaks. Therefore, potential formation of mannitol was not considered in the current work.

Alternative pathways are also possible when after the retro-aldol splitting, C4 and C2 compounds are formed, and moreover, glyceraldehyde in principle can undergo the retro-aldol splitting.

Typical kinetic profiles in transformations of glucose highlighting the diversity of the products are illustrated in Figure 7.

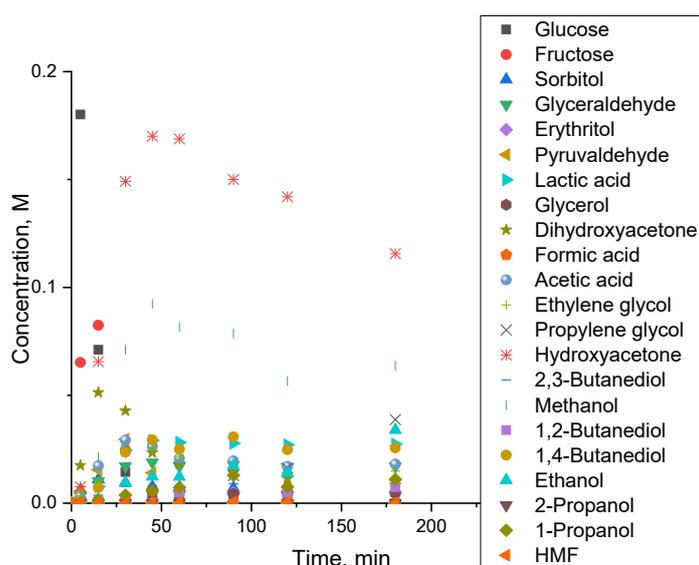


Figure 7. Concentration profiles in glucose transformations. Conditions: initial glucose concentration 0.276 mol/l, 0.15 g Ru/C, 0.41 g ZnO, 180 °C, hydrogen pressure 10 bar.

A detailed reaction scheme addressing the complexity of the reaction network is given in Figure 8.

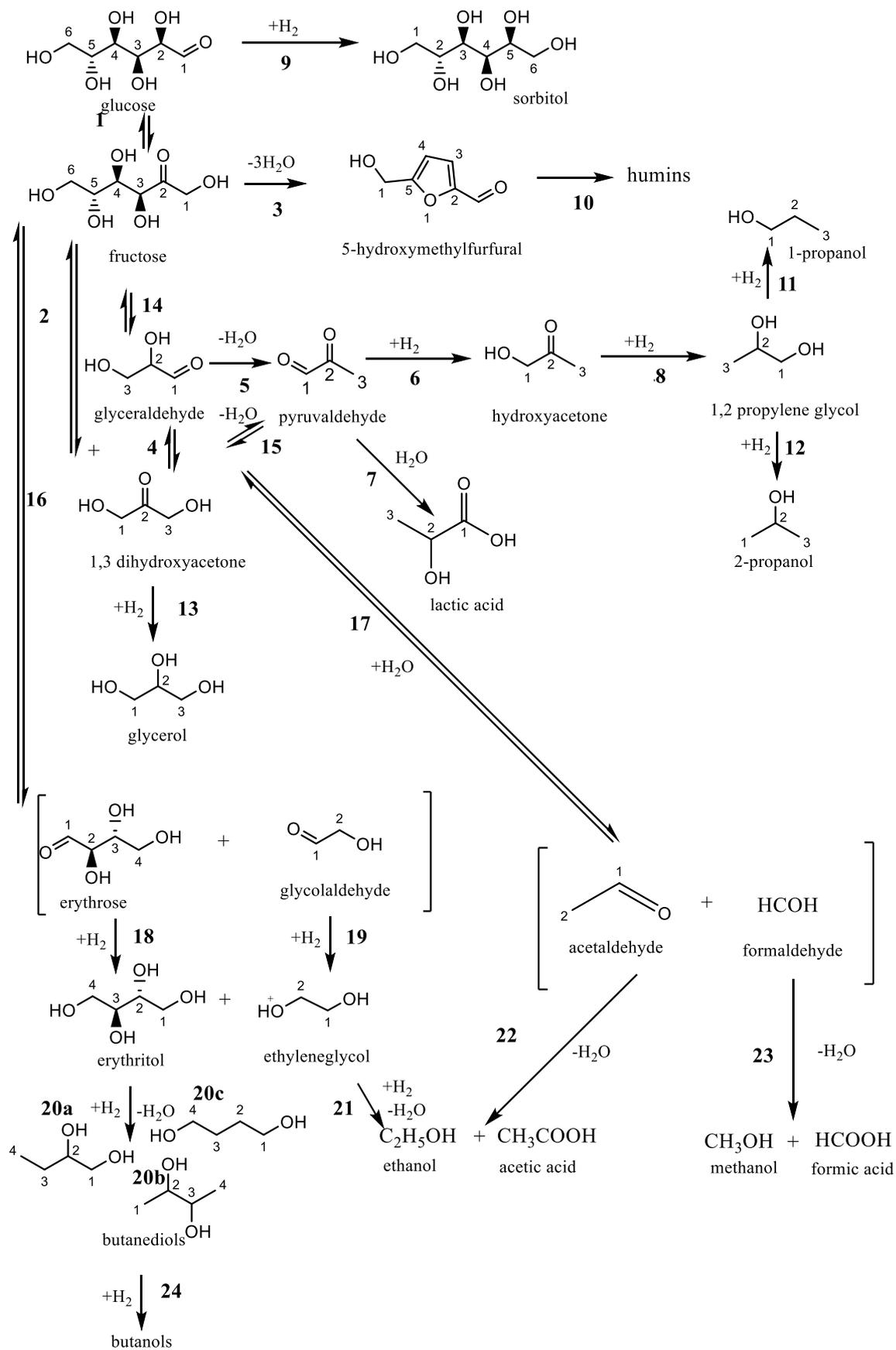


Figure 8. A detailed scheme of the reaction mechanism.

The first step in the glucose transformation to PG is isomerization to fructose (reaction 1). The concentration profiles of fructose at different reaction temperatures are shown in Figure 6b and in Table 2, entries 1-4, in which the temperature effect on both formation and consumption of fructose is clearly visible. As with the glucose conversion, formation and consumption of fructose are complete within three hours of the reaction at higher temperatures, while longer times are needed at 150 °C for full conversion. Interestingly, the concentration of fructose at 120 °C remained relatively constant after reaching the value shown in Figure 6a during the 20 hour experiment and did not react further. The curves in Figure 6a indicate that a high enough temperature is needed for the reaction to proceed further from glucose isomerization to fructose. Furthermore, dehydration of fructose forms 5-hydroxymethylfurfural (reaction 3), which in turn generates humins (reaction 10). Typically presence of Brønsted acid sites is considered to be important for dehydration of fructose and subsequently for formation of humins. It was, however, reported in the literature [27] that HMF can be formed in an aqueous solution of fructose through hydrothermal dehydration without any catalyst at temperatures between 120 and 140 °C. The same authors [27] did not observe formation of HMF using glucose as the starting material at 170 – 180 °C.

After the first step of glucose isomerization to fructose the C3-C4 bond in the latter is cleaved via a retro-aldol splitting. Two options are shown in the reaction scheme (Figure 8), i.e. reaction 14 giving directly two molecules of glyceraldehyde or alternatively dihydroxyacetone and glyceraldehyde are formed in stoichiometric amounts (reaction 2) as mainly proposed in the literature [28].

Dihydroxyacetone can in turn be tautomerized via a keto-enol mechanism to glyceraldehyde (reaction 4) or can be hydrogenated to glycerol (reaction 13). Dehydration of either 1,3-dihydroxyacetone (reaction 15) or glyceraldehyde (reaction 5) gives pyruvaldehyde.

The concentration profiles of 1,3-dihydroxyacetone and glyceraldehyde showing a rather slow disappearance of the aldehyde compared to the ketone suggests that the latter is more reactive.

It has been previously reported that for retro-aldolization the temperature should be higher than 160 °C [4], which is in agreement with the current work. The activation energy for retro-aldol condensation of sugars was reported to be ca. 140 kJ/mol, while for sugar hydrogenation (reaction 9) values close to 60 kJ/mol have been obtained [29-32]. The activation energy for the retro-aldol condensation of glucose was reported to be 148 kJ/mol over Ru/C-ammonium metatungstate [16], while for glucose hydrogenation it was 38.1 kJ/mol [16]. In another work [29], the activation energy for glucose retro-aldol condensation was over Ru/C-W 160.2 kJ/mol, while for glucose hydrogenation the activation energy decreased above 160 °C from 65.0 kJ/mol to 35.4 kJ/mol probably indicating presence of mass transfer limitations. The activation energy for fructose retro-aldol splitting was calculated using equation (3) to be 81 kJ/mol with a linear approximation of the maximal fructose concentration decrease rate shown in Figure 8b. The TOFs (based on the ZnO amount) used in the determination of the activation energy for fructose retro-aldol splitting were 0.17, 0.51 and 1.47 min⁻¹ at 165, 180 and 210, respectively.

The sum of the concentration of trioses (glyceraldehyde, dihydroxyacetone) and pyruvaldehyde, shown in Fig. S1 is the highest at 150 °C followed by 120 °C, while at higher temperatures these react further. It can, however, be seen from Fig. S2 that further transformations of trioses and pyruvaldehyde stagnated after 100 min at 210 °C. One reason for a low hydrogenation rate for these compounds is a low hydrogen partial pressure, 5 bar (Table 2, entry 5) and low hydrogen solubility. When the sum of the concentration of trioses and pyruvaldehyde was high at 120 °C and 150 °C, also low concentrations of hydroxyacetone were obtained (Fig. 6c).

Two reaction paths for further transformations of pyruvaldehyde are shown in Figure 8, one comprising dehydration to lactic acid, formed in small amounts (reaction 7) or hydrogenation on ruthenium catalyst to hydroxyacetone (reaction 6).

The concentration profiles for hydroxyacetone, which is formed through hydrogenation of pyruvaldehyde (reaction 6), at different reaction temperatures is presented in Figure 6c. As mentioned above, the key of obtaining a high PG selectivity is to produce significant amounts of hydroxyacetone. From Figure 6c one can see that reaction temperature did not influence the maximum concentration of hydroxyacetone at relevant temperatures (165-210 °C).

The maximum concentrations of hydroxyacetone were roughly double of the maximum fructose concentration, which is related to the stoichiometry of fructose retro-aldol splitting.

The last step in the glucose transformation to PG according to Figure 8 is, hydrogenation of hydroxyacetone. The concentration profiles of PG during the whole 20 hour experiments shown in Figure 6d confirm that similar final concentrations of PG were obtained at 150- 180 °C, while at the highest temperature of 210 °C this concentration was slightly lower, which can be related to the formation of other products not detected by HPLC, most likely humins as reported in ref [15]. The lowest temperature is clearly too low for the retro-aldol reaction of fructose as seen in Figure 6d resulting in the lowest PG concentration. Interestingly, the highest final concentrations of PG are roughly the same as the highest concentrations of hydroxyacetone, at 165 and 180 °C (Table 2, entry 3, 4). This finding illustrates the importance of achieving high concentrations of hydroxyacetone to maximize the yield of PG. The final yields of PG as a function of temperature are shown in Figure 6e.

Figure 9 shows the selectivity to PG as a function of the hydroxyacetone conversion at different temperatures.

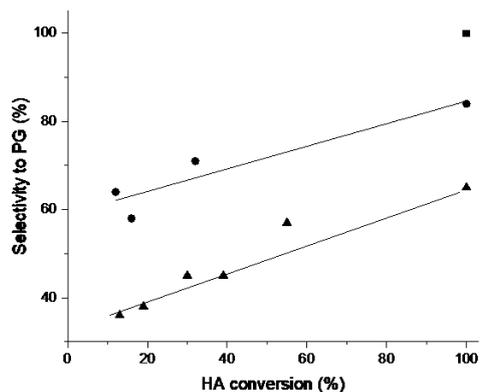


Fig. 9. Selectivity to PG as a function of HA conversion at different temperatures 165 °C (■), 180 °C (●) and 210 °C (▲).

It can be clearly seen that lower (165 °C) temperature gives better selectivity to PG compared to the higher temperatures. When comparing the current results with the literature data [10], it can be concluded that an optimum temperature giving the highest PG yields was found at 180 °C under 4 – 8 bar hydrogen over Ru/C-ZnO with slightly smaller Ru particles, 1.6 nm [10], while in the current case the average Ru particle size was 2.5 nm. The optimum temperature range of 227 – 247 °C giving ca. 24% yield of PG over 5 wt% Ru-3 wt% Sn/AC catalyst under 50 bar hydrogen was also observed in glucose transformation in [12]. In that work ruthenium formed an alloy with tin and the metal particle size was 2.7 nm.

Some PG hydrogenolysis to 1-propanol and 2-propanol was observed (reactions 11 and 12), especially at 180 °C and 210 °C analogously to the literature data [15]. The maximum yield of propanols in the current work was 7%.

Besides the formation of propylene glycol also ethylene glycol was observed in the reaction mixture, which can be explained by retro-aldol splitting of fructose to erythrose and glycolaldehyde (reaction 16). The latter is unstable and can be easily hydrogenated to ethylene glycol (reaction 19), which undergoes hydrogenolysis to ethanol (reaction 21).

To visualize the effect of temperature on PG and ethylene glycol formation in glucose transformations, the concentration of PG is plotted as a function of ethylene glycol (Fig. S1) at different temperatures. The results show that the retro-aldol splitting of glucose is the most prominent at 150 - 165 °C, while much lower amounts of EG are present at 120 °C and at 180-210 °C. In the current case at 180 °C the PG/EG ratio was after 1200 min ca. 10.9 over Ru/C-ZnO catalyst, while in the case of Hirano et al. [10] it was only 7.4 at the same temperature over Ru/C-ZnO. In the current work, the basicity of ZnO was 3.4 fold higher than reported in [10] pointing out the impact of strong basicity in the PG formation. The explanations for larger amount of basic sites determined using CO₂ – TPD in the current ZnO catalyst as compared to the reported in [10] can be the method of ZnO synthesis and different activation procedure such as calcination duration and temperature. In addition it was reported in ref. [10] that no ethylene glycol was formed in the presence of Ru/C without ZnO, giving, however, 9.3 % PG. In addition, small amounts of erythritol, butanol and butanediols were observed. They apparently are formed through retro-aldol splitting of fructose to erythrose and glycolaldehyde (reaction 16), further hydrogenation to erythritol (reaction 18) and subsequent hydrogenolysis to butanediols (reaction 20) and butanols (reaction 24).

The highest yield of erythritol was only 2 % indicating the erythritol reacted further to butanediols. The highest yield of butanediols was 11.5% at 165 °C after 1200 min with the highest yield found for 1,2-butanediol (5.3%). As a comparison in [10] the sum of 1,2-butanediol and 1,2-hexanediol was 11.9% over Ru/C-ZnO at 180 °C under 4 bar hydrogen Tomishige et al. [33] studied the hydrogenolysis of erythritol to butanediols over Ir-ReO_x/SiO₂ catalyst. The authors reported maximum selectivity to 1,4- and 1,3-butanediols to be 33% and 12% at 74% conversion at 100 °C. The yield of 1,2-butanediol was reported to be only 1% [32].

In the current case glucose hydrogenation (reaction 9) was observed in a minor extent, and the maximum sorbitol yield was 12% at 120 °C (Table 2). The highest concentrations of sorbitol

were obtained at the two lowest temperatures, 120 °C and 150 °C, and the highest hydrogen partial pressures, i.e. 18 bar and 15 bar, respectively. The maximum sorbitol yield was ca.12% after 1200 min (Fig. S3). It is known that hydrogenation is promoted at lower temperatures in comparison to glucose isomerization. Hexitol yield was only 3.4 % in [10] at 180 °C under 4 bar hydrogen, while the comparative yield of sorbitol in the current case was also small, only 2%. It is known that hydrogenation of sugars is promoted at lower temperatures, e.g. 140 °C [10] in comparison to glucose isomerization and its further transformation to PG. On the other hand, at 165 °C and above, the sorbitol concentration exhibited a maximum after which it declined to a plateau level at 180 °C.

The presence of formic and acetic acids along with methanol in the reaction products can be tentatively explained by retro-aldol splitting of trioses (reaction 17) with subsequent disproportionation of resulting aldehydes (i.e. reactions 22 and 23).

The reaction mixture was also analyzed after the reaction by ICP for possible leaching of zinc and ruthenium. It was found that significant leaching of zinc occurred with leaching values as high as 72.6% at 210 °C. Lower reaction temperatures resulted in lower leaching of zinc, however, the leaching of zinc was still considerable with leaching values of 16.2, 13.0, 52.1 and 69.7% at other temperatures (120-180 °C). Reuse of ZnO catalyst is thus not possible due to very severe leaching. The ruthenium content in the reaction mixture was also analyzed by ICP. The leaching of ruthenium was less than 0.5% of the initial content in all experiments performed at various temperatures, allowing to consider leaching of ruthenium negligible.

Based on the results presented above experiments at different hydrogen pressures and initial glucose concentrations were performed at 180 °C.

Effect of hydrogen pressure

The influence of hydrogen pressure was studied by conducting experiments at different pressures (Figure 10, Table 2, entries 4, 6, 7).

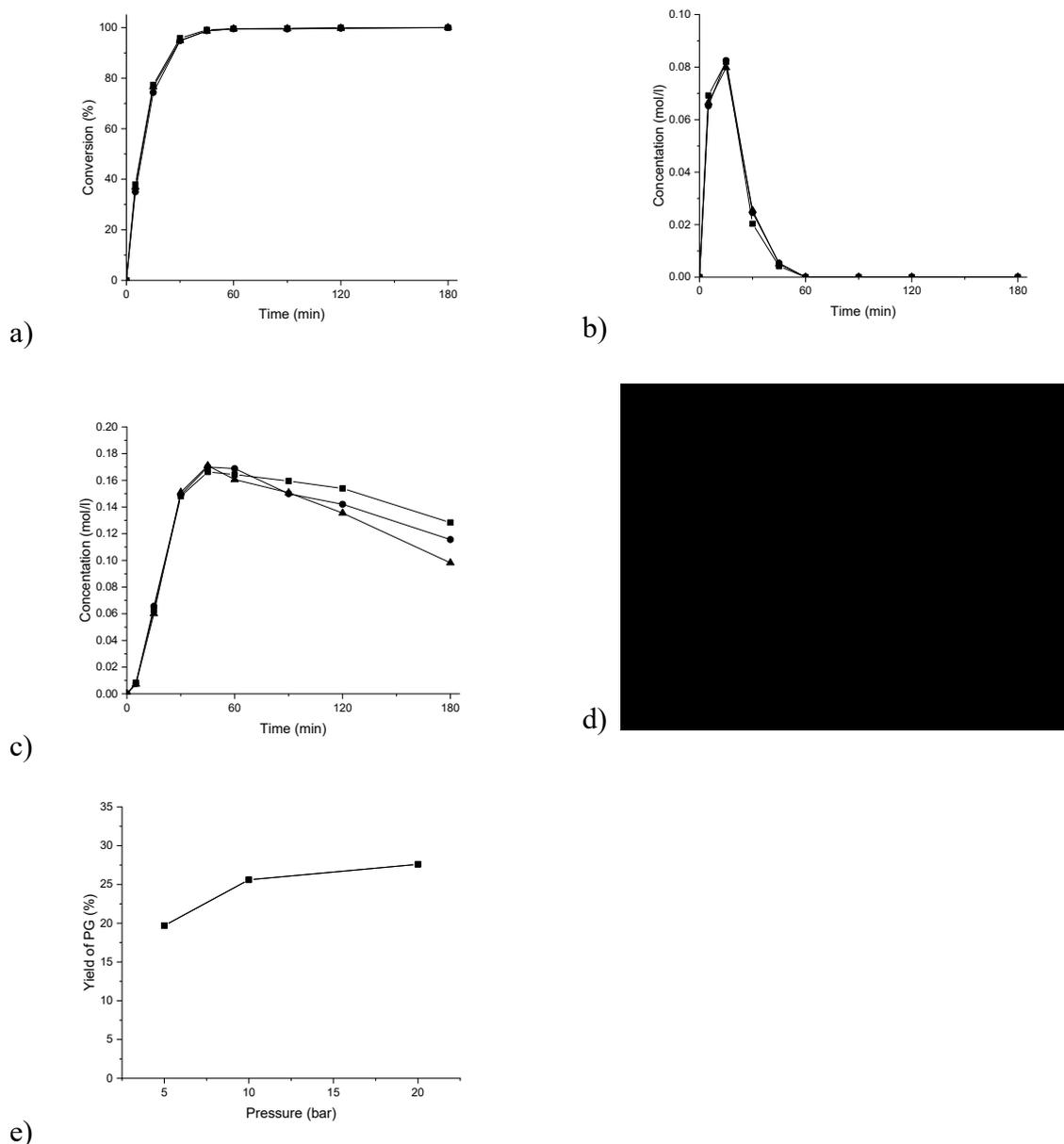


Figure 10. Effect of hydrogen pressure on a) glucose conversion, concentration of b) fructose, c) hydroxyacetone and d) PG at 180 °C, notation: 5 bar (■), 10 bar (●) and 20 bar (▲), e) yield of PG at different pressures after 180 min. Conditions: initial glucose concentration 0.276 mol/l, 0.15 g Ru/C, 0.41 g ZnO, 180 °C.

Figure 10a reveals that, within the pressure range investigated, the conversion of glucose was not dependent on the hydrogen pressure illustrating the zero order kinetics. The concentration

profiles of fructose at different hydrogen pressures are plotted in Figure 12b. As expected, since glucose conversion showed no influence of pressure, the concentration profiles for fructose are similar independently of hydrogen pressure.

The maximum concentration of hydroxyacetone determines the yield of PG. It can be seen from the concentration profiles for hydroxyacetone at different hydrogen pressures (Figure 10c) that the maximum concentration of hydroxyacetone is similar at all pressures, while further conversion is, however, slightly different. The conversion was lowest at the lowest pressure, increasing the pressure converted the hydroxyacetone faster. A complete hydroxyacetone conversion was achieved during the whole 20 h timespan for 10 and 20 bar hydrogen. The conversion at 5 bar was 93.6% after 20 hours.

The concentration profiles for PG at different hydrogen pressures are shown in Figure 10d. The final yield of PG (Figure 10e) increased with increasing pressure. Taking into account a reasonable high conversion of hydroxyacetone after 20 hours and a low PG yield at 5 bar hydrogen pressure it can be concluded that the hydrogen pressure should be high enough to enable selective hydrogenation of hydroxyacetone to PG. The selectivity to PG based on the maximum concentration of hydroxyacetone at the different pressures are 70.6%, 83.5% and 89.3% at 5, 10 and 20 bar of hydrogen.

Thermodynamic analysis for synthesis of 1,2-propylene glycol from glucose

The enthalpy (ΔH_r^0) and Gibbs free energy (ΔG_r^0) at standard conditions were calculated by following the thermodynamic approach [17], starting from the standard enthalpy (ΔH_f^0) and Gibbs free energy (ΔG_f^0) of formation from the elements estimated with the Joback approach [18-20] using the following equations:

$$\Delta H_{r,j}^0 = \sum_j \nu_{i,j} \cdot \Delta H_{f,i}^0 \quad (4)$$

$$\Delta G_{r,j}^0 = \sum_j \nu_{i,j} \cdot \Delta G_{f,i}^0 \quad (5)$$

The equilibrium constant of each reaction was calculated from its definition as follows

$$K_j^0 = \exp\left(-\frac{\Delta G_{r,j}^0}{RT}\right) \quad (6)$$

The dependence of free Gibbs energy of the reaction on temperature was included by implementing the Gibbs-Helmholtz equation in its approximated form valid at $P=1$ bar ($\Delta G_{r,j}^\phi$):

$$\frac{\Delta G_{r,j}^\phi(T)}{T} = \frac{\Delta G_{r,j}^0}{T^0} + \Delta H_{r,j}^0 \left(\frac{1}{T} - \frac{1}{T^0}\right) + \frac{1}{T} \int_{T_0}^T \Delta c_p^0 dT - \int_{T_0}^T \frac{\Delta c_p^0}{T} dT \cong \frac{\Delta G_{r,j}^0}{T^0} + \Delta H_{r,j}^0 \left(\frac{1}{T} - \frac{1}{T^0}\right) \quad (7)$$

Such approximation stems from absence of heat capacity values for several compounds, a similar nature of reactants and products with similar heat capacity and limited information on the heat of condensation for reactants. Nevertheless the applied approach gives a preliminary indication on the feasibility of different reactions, comprising a very complex reaction network. The calculated enthalpy and Gibbs free energy formation for each component (i) are reported in Table S1. The stoichiometric matrix was based on the reaction scheme reported in Figure 8. Starting from these values (Table S1), the enthalpy and Gibbs free energy for each reaction (j) at standard conditions, equilibrium constants at standard conditions (K_j^0), enthalpy and Gibbs free energy at different temperatures were estimated. A temperature range relevant for the experimental work of this study was investigated ($T_{min}=393.15$ K, $T_{max}=483.15$ K). The results of the calculations of enthalpy and Gibbs free energy at standard conditions are reported in Table S2 and Figure 11.

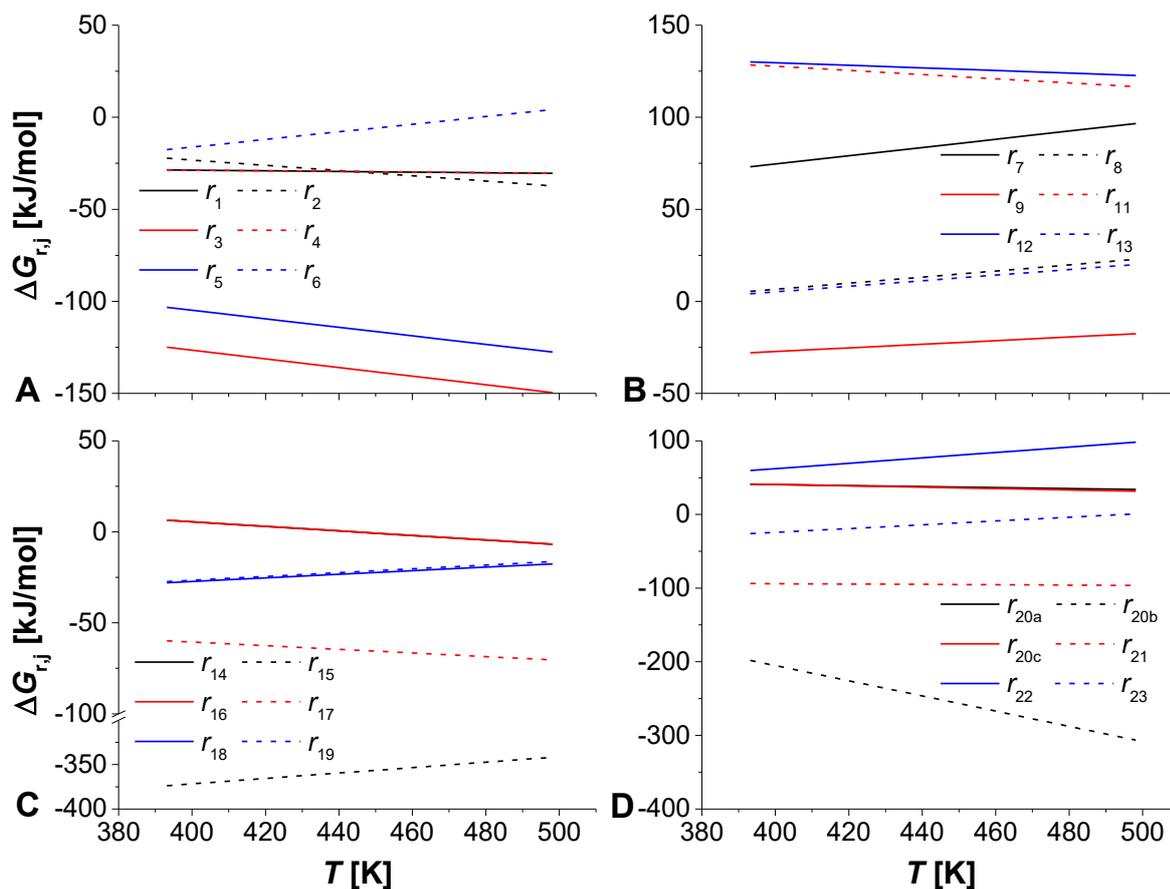


Figure 11 – Gibbs free energy for each reaction (j) as a function of temperature.

The calculations shown in Figure 11 for different temperatures correspond to hydrogen pressure of 1 bar. Figure 11 shows that isomerization reactions, i.e. transformations of glucose to fructose, and glyceraldehyde to dihydroxyacetone (reactions 1 and 4 respectively) display similar behaviors. This results can be understood by considering that such reactions involve molecules of the same molecular weight. The lowest Gibbs free energy values were calculated for reactions 3 and 5, representing the formation of 5-HMF and pyruvaldehyde. Reactions 7 and 6, i.e. the formation of lactic acid and hydroxyacetone from pyruvaldehyde show similar values but somewhat different trends. Lactic acid formation is a dehydration reaction, which has a negative ΔG , while ΔG for reaction 6, i.e. hydrogenation, becomes positive at high temperatures as expected. The intersection of the curves is given at 440 K, where the formation

of lactic acid is thermodynamically preferred to the same extent as hydrogenation to hydroxyacetone. It should be kept in mind however, that the calculations were done for the standard conditions, while experimental work is typically done at elevated pressures thus favoring the hydrogenation route. The Gibbs energy for the PG formation is slightly positive and thermodynamically not favored at these conditions (1 bar hydrogen in the temperature range of 393 -500 K), also because it is a hydrogenation reaction. On the other hand, typically PG synthesis is performed under higher hydrogen pressures, facilitating its formation [10, 15, 16]. Higher hydrogen pressure obviously shifts equilibrium making formation of PG feasible. It should be emphasized that other compounds present in minor amounts can be also formed as will be discussed in the kinetic modelling.

As expected sorbitol formation is thermodynamically favored, while generation of butanediol is only preferred in the case of 2,3-butanediol. The disproportionation reactions are favored only in the case of formaldehyde, as acetaldehyde leads to the positive values of Gibbs free energies.

Kinetic modelling

Kinetic modelling of glucose transformations was based on Figure 8 considering a possibility of reaction molecules to adsorb on the catalyst surface, e.g. the rates of reactions 1 and 9 r_1 and r_9 (mol/l/s) occurring respectively on ZnO and Ru/C are expressed as

$$r_1 = r_{+1} - r_{-1} = k_{+1} C_{glucose} / D_1 - k_{-1} C_{fructose} / D_1 \quad (8)$$

$$r_9 = r_{+9} = k_{+9} C_{glucose} P_{H_2} / D_2 \quad (9)$$

where k_{+1} is the rate constant of the forward reaction, $C_{glucose}$ is the concentration of glucose, P_{H_2} is hydrogen pressure. The denominators in eq. (8)

$$D_1 = 1 + K_{C=O,Ru} \sum C_{C=O} + K_{C-OH,Ru} \sum C_{C-OH} \quad \text{and (9)}$$

$D_2 = 1 + K_{C=O,ZnO} \sum C_{C=O} + K_{C-OH,ZnO} \sum C_{C-OH}$ comprise lumped adsorption terms for all compounds containing the carbonyl group $C_{C=O}$ or the hydroxyl group C_{C-OH} . Such compounds can be either adsorbed on Ru with the respective adsorption constant $K_{C=O,Ru}$, $K_{C-OH,Ru}$ or on ZnO ($K_{C=O,ZnO}$ and $K_{C-OH,ZnO}$).

The generation equations for different compounds can be easily written as shown below for glucose

$$\frac{dC_{glucose}}{dt} = -\frac{m_{cat,ZnO}}{V_L} (r_{+1} - r_{-1}) - \frac{m_{cat,Ru/C}}{V_L} r_{+9} \quad (10)$$

where m_{cat} is the mass of a catalyst relevant for a particular reaction, V_L is the liquid volume. It is assumed that all hydrogenation steps (e.g. 6, 8, 9, 11-13) proceed on Ru/C, while for the rest apart from a non-catalytic step 10 the mass of ZnO was considered in the rate equations. The experiments were conducted using the same amounts of Ru/C and ZnO.

In the model for the reactions occurring on metals, the adsorption constant of hydrogen was included in the denominator, while the rate constants of the hydrogenation steps are apparent containing the adsorption constant of hydrogen. As an example the rate of the step 6 is thus $r_6 = k_{+6} C_{pyruvaldehyde} P_{H_2} / D_1 / (1 + K_{H_2} P_{H_2})$.

The rate constants were presumed to obey the Arrhenius law. The modified Arrhenius equation was used to suppress the correlation between the pre-exponential factor and the activation energy,

$$k_i = k_{i,mean} \exp \left[\frac{-E_{act}}{R} \left(\frac{1}{T} - \frac{1}{T_{mean}} \right) \right] \quad (11)$$

where k_i , $k_{i,mean}$, E_{act} , R , T and T_{mean} denote the reaction rate constant, the reaction rate constant at the mean temperature (438 K), activation energy of the reaction, the universal gas constant, the temperature and the mean temperature, respectively.

The estimation of the kinetic parameters was performed for the experimental data generated for the mechanical mixture of two catalysts using the ModEst parameter estimation software [34]. The objective function (Q) for the residual sum of squares between the calculated and experimental values of concentrations for different time points was minimized during the parameter estimation to obtain the best-fit values using the Levenberg–Marquardt algorithm implemented in the software. The objective function was defined as

$$Q = \sum (c_{i(est)} - c_{i(exp)})^2 \quad (12)$$

where c and i denote the concentrations and the corresponding reactants.

The accuracy of the model description, comparing the model performance with the average concentrations was checked with the degree of explanation (R^2), which is defined in the following way

$$R^2 = \left(1 - \frac{\sum_{i=1}^n (C_{exp,i,j} - C_{mod,i,j})^2}{\sum_{i=1}^n (C_{exp,i,j} - \bar{C}_{exp,i,j})^2}\right) 100\% \quad (13)$$

where \bar{C}_{exp} is the average value of all data points.

Kinetic modelling was simplified taking into account that reactions 16-24 resulted totally in products the concentrations of which did not exceed 4 % of all determined reactants.

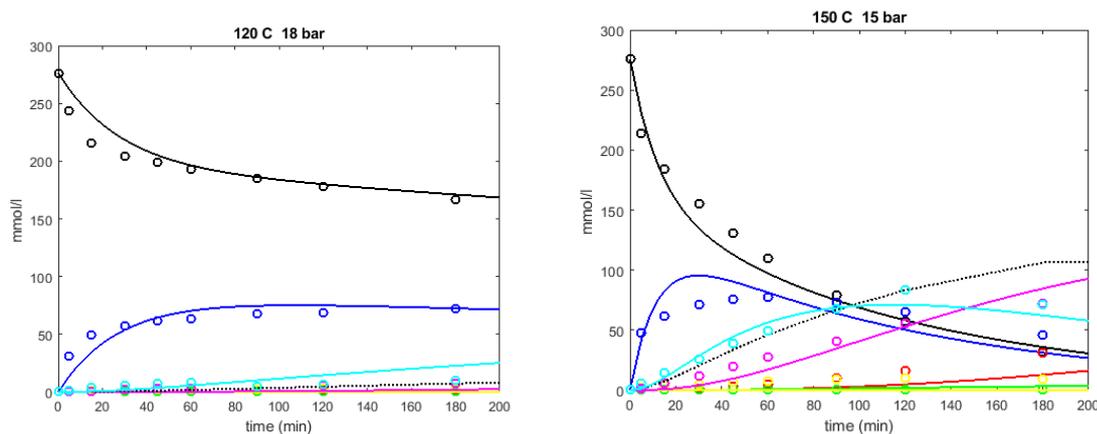
Preliminary calculations indicated that the estimated values of several parameters have large deviations, therefore the Monte Carlo Markov Chain (MCMC) method [35] was applied to improve the statistical analysis. In this method the samples are drawn randomly to approximate the probability distribution of parameter. The most probable values of constants given as maxima [36] allowed to simplify the model. All steps apart from step 1 can be considered as irreversible. Some of the adsorption constants (namely $K_{C-OH,Ru}$, $K_{C-OH,ZnO}$) could be neglected.

The estimated values of the rate constants and the activation energies along with the relative

standard errors for the final parameter estimation are listed in Table S3 having the degree of explanation of 95.5%.

A rather complex reaction network with several reversible steps was applied to describe transformations of glucose to 1,2 propylene glycol in a broad temperature range. This along with many reaction products and intermediates inevitably results in a large number of adjustable parameters which are difficult to estimate all of them simultaneously in a reliable way. Moreover, some of the products were formed in inferior amounts resulting in poor statistics for the corresponding constants as follows from Table S3. Application of the MCMC approach allowed to improve the statistics. In fact for some parameters, even if the standard error could be large, analysis of the parameters made by MCMC (Figure S4) indicate that the values are reasonably well determined. Based on the preliminary MCMC analysis the values of $K_{C=O,Ru}$ and $K_{C=O,ZnO}$ were fixed in the final parameter estimation.

Overall, a comparison between the experimental and calculated data for the main components (Figure 12) and statistical analysis of the relevant kinetic parameters demonstrate ability of the model to capture the main experimental observations in an adequate way. In agreement with the conventional mechanism of retro-aldol splitting of fructose, step 2 is more prominent resulting in a stoichiometric mixture of dihydroxyacetone and glyceraldehyde, while the formation of two molecules of glyceraldehyde was less important (reaction 14).



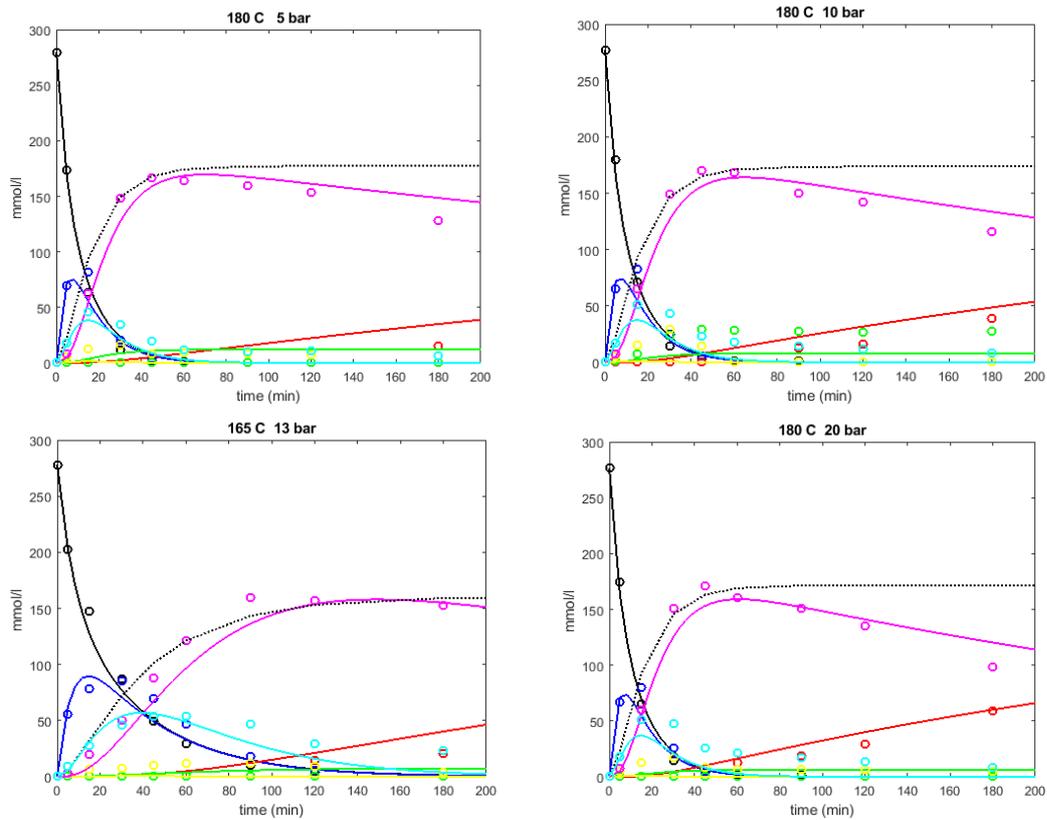


Figure 12. Comparison between the kinetic model and the experimental data . Legend: glucose –black, fructose- blue, 1,2 propyleneglycol – red, pyruvaldehyde-yellow, 1,3-dihydroxyacetone- cyan, hydroxyacetone- magenta; lactic acid -green, humins -black dotted.

Conclusions

The influence of reaction conditions was investigated in the transformation of glucose on a mixture of Ru and ZnO catalysts. The effect of temperature (120-210 °C) and hydrogen pressure (5-20 bar) was studied. It was found that the reaction temperature affected both the glucose conversion rate as well as the rates of the subsequent reaction steps. The activation energy for glucose transformation was calculated to be 29.5 kJ/mol and 81.1 kJ/mol for the subsequent fructose retro-aldol splitting. Moreover, the final yield of propylene glycol showed an optimum at 165 °C, which can be explained by inhibition of propylene glycol formation at low temperatures due to slow rates of preceding reactions while the highest temperature promoted side reactions, including the formation of humins. The overall mass balance closure for compounds detected by HPLC without considering humins and generation of gases ranged from 84 to 35% inversely depending on the reaction temperature.

The reaction order in hydrogen pressure was almost zero within the studied pressure interval 5-20 bar even if the lowest pressure gave a slightly lower propylene glycol yield.

A kinetic model was developed for the glucose transformation process. The model was capable to describe adequately the main features of the experimental observations.

Acknowledgements

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List of symbols

C	Concentration, mol/L
D	Dispersion, -
E_{act}	Activation energy, kJ/mol
ΔG_f^0	Gibbs free energy of formation at standard conditions, J/mol
ΔG_f^0	Gibbs free energy of formation at standard conditions, J/mol
ΔG_r^0	Gibbs free energy of reaction at standard conditions, J/mol
$\Delta G_{r,j}^\Phi$	Gibbs free energy of reaction at 1 bar and a chosen temperature, J/mol
ΔH_f^0	Enthalpy of formation at standard conditions, J/mol
ΔH_r^0	Enthalpy of reaction at standard conditions, J/mol
K_j^0	Equilibrium constant at standard conditions for reaction j
k	Rate constant
M	Mass, g
N	Number of atoms in a molecule, -
n	Amount of substance, mol
P	Pressure, bar
P^0	Standard pressure, bar
Q	Objective function, (mol/L) ²
R	Ideal gas constant, 8.3143 J/K/mol
R^2	Degree of explanation, -
r	Rate, the unit depends on the reaction order
S	Selectivity, -
T	Absolute temperature, K
T^0	Absolute standard temperature, K
t	Time, min
TOF	Turnover frequency, s ⁻¹
V	Volume, L
Y	Yield, -

Greek symbols

$\nu_{i,j}$	Stoichiometric matrix composed by i components and j reactions, -
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Abbreviations

EG	Ethylene glycol
HA	Hydroxyacetone
HMF	Hydroxymethyl furfural
PA	Puryvaldehyde
PG	Propylene glycol

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