

# Hydrogenolysis of Bagasse and Straw to 1,2-PDO: Feasibility of Conceptual Designs

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In the last few years, the need to substantially lower anthropogenic greenhouse gas emissions has boosted efforts to design biorefineries, where all parts of biomass are used to produce fuels and chemicals. 1,2-propanediol (1,2-PDO) has gained attention for its many, industry-relevant uses and for the success of the commercialization of the glycerol-based route. In face of the many uncertainties on the future bioeconomy, new routes for 1,2-PDO production are encouraged as a way to both diversify supply and add value to other products. That is the reason why catalysts for its production from cellulose have been developed over the last years. To provide a process-based perspective on that subject, this study presents a simulation-based analysis of the process, providing valuable information to fill in the gaps in present knowledge on the use of cellulose and sugars to produce 1,2-PDO. Thermodynamic simulations developed in Aspen Plus® v9 explored glucose hydrogenolysis to produce 1,2-PDO as a model compound representing cellulose.

## 1. Introduction

1,2-propanediol (1,2-PDO) has been evaluated as one of the most promising chemicals for renewable production due to its mature market volume – having application in many industries either alone or as a building block – and to the success of the glycerol-based route (Biddu et al., 2016). The commercialization of glycerol (GLY) hydrogenolysis, however, has been driven by the production of low-value glycerol as a by-product of the developing biodiesel industry, and a strong motivation to operationalize new routes for bio-1,2-PDO production is the risk that government subsidies for this industry may cease and that biodiesel production may shift toward a different route, decreasing glycerol availability (Biddu et al., 2016).

Some alternatives have been studied, such as the hydrogenation of pure cellulose, which can be obtained from low-value by-products of many existing and developing biorefineries and, therefore, benefit from their infrastructure to consolidate bio-1,2-PDO market. That is the reason why some catalysts have been developed and tested in the last ten years, and, even though cellulose is a highly stable molecule, yields as high as 42.6 wt.% (Xiao et al., 2013) have been achieved. Since it allows adding value to many developing biorefineries and is a route for bio-1,2-PDO production with an alternative raw material to glycerol, it is a benefit to the market and to a biobased economy to explore this route more thoroughly.

The reaction network involved in cellulose and sugars hydrogenolysis is very diverse (Beine et al., 2016) and, therefore, no efforts have been made yet to kinetically model or conceptually design and assess the feasibility of cellulose hydrogenolysis. Glucose can be used as a model compound for preliminary studies on this process since it can represent its complexity in a more manageable way. Table 2 shows the process parameters related to the best results in glucose catalysis for 1,2-PDO production so far.

Conceptual designs can help enlighten both bench-scale laboratory researchers and the industry on the implementation potential, costs and environmental implications of a process in such an early stage of development. They can also indicate improvement opportunities and possible design solutions for process bottlenecks, setting the direction for the development of new catalysts.

In this context, this study aims to present the first simulation-based analysis of 1,2-PDO production from glucose (GLU), a model compound for cellulose, by hydrogenolysis. A thermodynamic analysis of the reaction network makes it possible to preliminarily assess the use of pure cellulose, bagasse, and straw from the sugarcane industry to produce 1,2-PDO via hydrogenolysis. Different reaction routes from glucose were tested and compared to literature data, and their feasibility was discussed. This is a first step in understanding the possible practical issues and possibilities of this proposed route.

## 2. Methodology

### 2.1 Reaction networks proposed for GLU hydrogenolysis

The mixture of a component with a hydrogen gas stream in the presence of catalysts initiates a large number of reactions collectively named hydrogenolysis (Beine et al., 2016). Since this is a novel study on the system, cellulose hydrogenolysis will be better understood using GLU as a model compound. Figure 1 shows the reaction network that will be used according to mechanisms proposed in recent publications in the area.

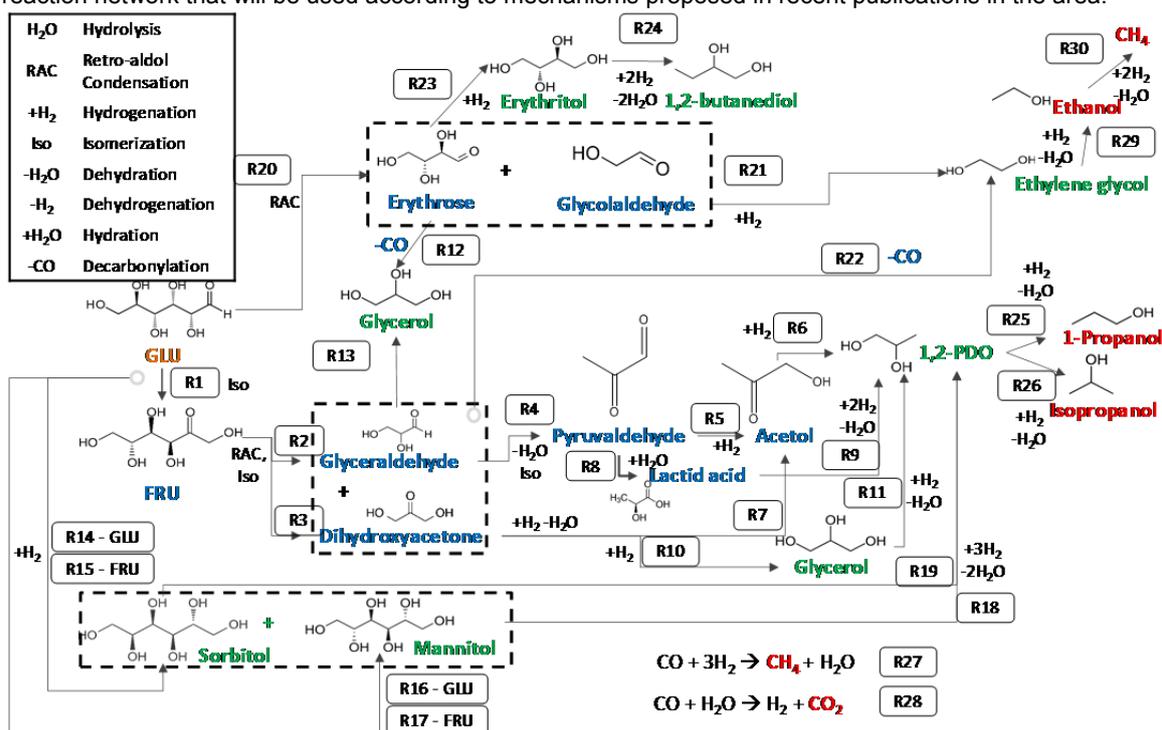


Figure 1: Reactions considered for conversion of cellulose to 1,2-PDO and by-products. The networks consider different categories of products: Green: main products found in experiments. Blue: intermediate products. Red: very stable, degradation products. FRU = fructose.

Source: (Beine et al., 2016; Zheng et al., 2017)

The reactions in Figure 1 and their equilibrium constants in Figure 2 are a guide based on the literature review used to define each network in Table 1. In the thermodynamic analysis, different networks were considered based on Figure 1, as shown in Table 1, since in Network 1a the glycols and polyols have selectivities in orders of magnitude below  $10^{-30}$  and this would make it hard to assess the impact of parameter changes. Also, by manipulating the reaction networks, it is possible to investigate which paths the catalysts favor in the system.

Table 1: Description of subdivisions of simulated networks 1 and 2.

Id	Products considered	Product assessed
1a	All products	CH <sub>4</sub>
1b	All products except CO, CO <sub>2</sub> and CH <sub>4</sub>	Ethanol and propanols
2a	Only main and intermediate products	1,2-butanediol
2b	Only main and intermediate products except for 1,2-butanediol	1,2-PDO
2c	Only sorbitol, mannitol and products in the ethylene glycol and glycerol routes	EG and GLY

## 2.2 Process simulation

The GLU hydrogenolysis reactions depicted in Figure 1 were simulated in ASPEN PLUS® V9. The thermodynamic models used were the UNIFAC model for reactions occurring under 10 bar and the PSRK model for pressures over 10 bar. Both erythrose and glyceraldehyde were not present in the software databank and thus had to be defined by the user by drawing their molecular structure and inserting their chemical formula and their Joback group parameters for the estimation of standard ideal gas Gibbs free energy of formation and standard ideal gas enthalpy of formation. The UNIFAC functional groups were also inserted for these components, as well as for dihydroxyacetone, erythritol, and mannitol for the estimation of binary interaction parameters.

Firstly, the reactions were set in equilibrium model reactors, which calculate simultaneous phase and chemical equilibrium, using the mean values found in the literature (Table 2) as the base case (BC) parameters for temperature, pressure, glucose weight fraction in the feed ( $w_{\text{GLU}}$ ) and  $\text{H}_2/\text{GLU}$  ratio in the feed ( $\text{H}_2/\text{GLU}$ ). Their chemical equilibrium constants were obtained as a function of temperature.

Then, the Gibbs free energy minimization reactor model was used to perform the sensitivity analysis (SA) described in Table 2 considering the products of the networks presented in Table 1. An upgraded case (UC) was defined by first varying temperature and pressure (SA1) and defining their values for maximum 1,2-PDO selectivity ( $S_{1,2\text{-PDO}}$ ) and then using these values to define the  $w_{\text{GLU}}$  and  $\text{H}_2/\text{GLU}$  (SA2) that result in the maximum  $S_{1,2\text{-PDO}}$  on network 2b. Selectivity (S) is defined as  $S = (\text{weight of product}/\text{weight of reactant feed})$  and conversion is calculated as  $\text{weight of all products}/\text{weight of reactant feed}$ . The reactor was considered isothermal.

Table 2: Main parameters found in literature and those of the base case (BC), upgraded case (UC), sensitivity analysis (SA) performed. <sup>a</sup>Pang et al 2018; <sup>b</sup>Hirano et al 2015; <sup>c</sup>Xiao et al 2014; <sup>d</sup>(Liu et al., 2016); <sup>e</sup>(Liu et al., 2015); <sup>f</sup>(Wang et al., 2015).

Parameter	Ref1 <sup>a</sup>	Ref 2 <sup>b</sup>	Ref 3 <sup>c</sup>	Ref 4 <sup>d</sup>	Ref 5 <sup>e</sup>	Ref 7 <sup>f</sup>	BC	SA1 [step]	SA2 [step]	UC
T (K)	513	453	413/493	453	453	523	460	300-600[20]	300	300
P (bar)	50	4	60	40	40	60	40	1-10[1], 10-100[10]	100	100
$\text{H}_2/\text{GLU}$	10	4	2.6	30.1	22.6	8.6	10	10	10-100[5]	10
$w_{\text{GLU}}$ (wt %)	10	0.9	30	5	5	7	10	10	1-9 [2] 20-60[10]	0.6

## 3. Results and discussion

The temperature dependence of the equilibrium constants of each reaction given in Figure 1 is presented in Figure 2, which shows that most network reactions are exothermic except for fructose retro-aldolization to dihydroxyacetone and glyceraldehyde (R2 and R3) and glucose retroaldolization to erythrose and glycolaldehyde (R20). Sorbitol and mannitol hydrogenation (R18 and R19) to 1,2-PDO have the highest equilibrium constants, followed by 1,2-butanediol (1,2-BDO) (R24) and  $\text{CH}_4$  formation reactions (R27 and R30).

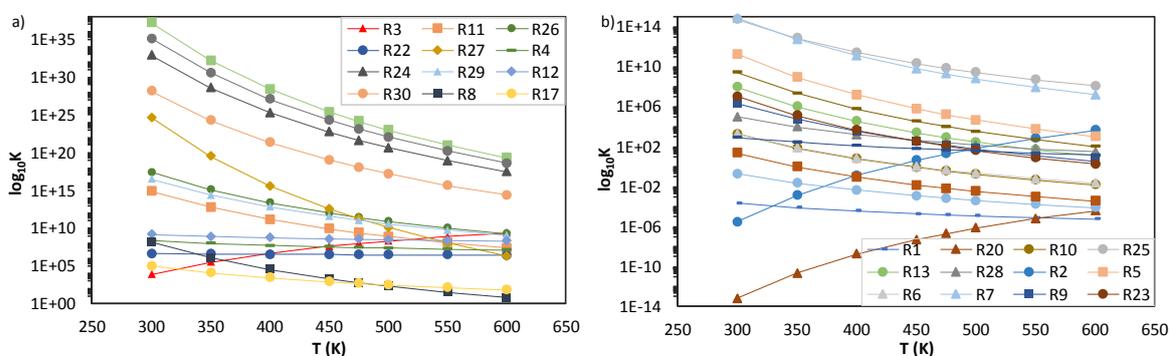


Figure 2: Reaction equilibrium constants versus temperature. (a) Highest equilibrium constants; (b) Lowest equilibrium constants.

All simulations had 100 wt % conversion. Typical product selectivity of the simulated networks (Figure 3), with hugely different orders of magnitude, is explained by the chemical equilibrium constants. Network 1a's product distribution shows that, as expected, the system preferably yields its most stable products, in this order: CH<sub>4</sub> (R27, R30), CO<sub>2</sub> (R28), CO (R12, R22), ethanol (EtOH) (R29) and propanols (PrOH) (R25, R26), (degradation products) all having high formation equilibrium constants (Figure 2). They are object of concern in many research areas. A wide variety of other products could also be formed, but since it has not been registered in traceable amounts in the literature, they were not considered in the models.

The Gibbs free energy minimization method used in this work reflects product stability and not necessarily reactions occurred in the reactor, so product distribution on Figure 3a could be explained by many reactions other than the ones in Figure 1. When compounds were excluded, some products changed position on the list of increasing selectivity, which happens because it is a rather complex network and variations on each path cause the equilibrium to rearrange (Zheng et al., 2017). That is why when network 1b was simulated, propanols were more produced than ethanol, and these could be evaluated simultaneously. 1,2-PDO and 1,2-BDO have also shifted positions.

Maximum and minimum selectivity values found on the sensitivity analysis are on Figure 3b, showing equilibrium limitations depending on which paths are hindered in the network, and values of the parameters for them are on Table 3. This is an important general guide to catalyst development, although each catalyst favors different reactions. A more detailed study of the networks for each catalyst is encouraged for more specific conclusions.

Table 3: Parameters for for maximum and minimum selectivities of main products. EG = ethylene glycol.

Parameter	CH <sub>4</sub>		PrOH		EtOH		1,2-BDO		1,2-PDO		EG		GLY	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
T (K)	300	300	300	300	600	300	300	300	300	600	300	600	300	600
P (bar)	100	100	100	100	1	100	100	100	100	1	100	1	100	1
H <sub>2</sub> /GLU	10	10	10	100	10	100	10	100	10	10	10	10	10	10
W <sub>GLU</sub> (wt %)	60	1	60	1	10	1	60	1	60	10	60	10	60	10

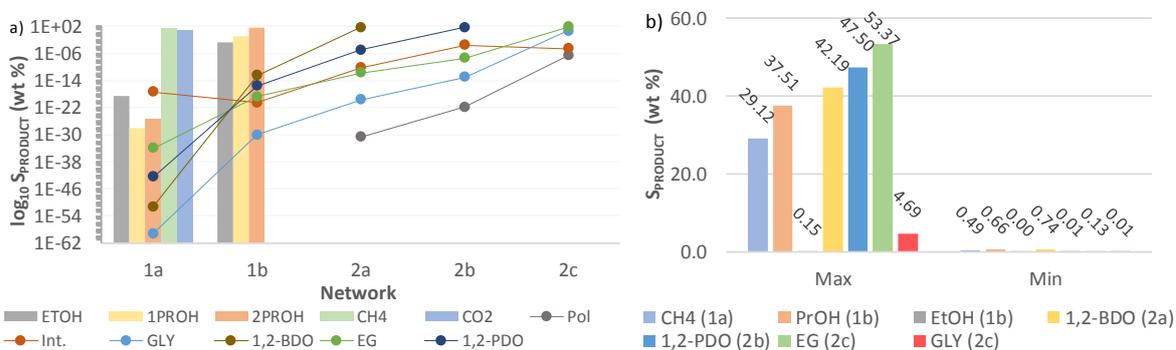


Figure 3:  $S_{\text{PROD}}$  for each network. a) Typical product distributions using the upgraded case; b) Maximum and minimum  $S_{\text{MAIN PRODUCTS}}$  found. Pol = sorbitol, mannitol and erythritol; Int = intermediate products; EG = ethylene glycol.

Operational costs are mainly influenced by the energy spent on purification. Water and hydrogen are introduced in the system in large quantities to improve flow conditions and to promote the reaction, but their weight fractions in the product stream,  $w_{\text{H}_2}$  and  $w_{\text{H}_2\text{O}}$ , should be minimized to lower their separation costs. Figure 4a shows how water is by far the predominant compound on the product stream, because the reactions mostly produce it. Hydrogen, on the other hand, is largely consumed by all reactions in the network, and thus has lower weight fractions than the main products on Figure 3 on the upgraded case, although some of the maximum  $w_{\text{H}_2}$  values (Figure 4b) exceed them. Figure 4a and Figure 4b show a decreasing and an increasing trend in  $w_{\text{H}_2\text{O}}$  and  $w_{\text{H}_2}$ , respectively.

Since most reactions are exothermic, lower temperatures should lower  $w_{\text{H}_2}$  and increase  $w_{\text{H}_2\text{O}}$ , but they have shown not to change much with temperature or pressure within the studied ranges. As expected, maximum and minimum H<sub>2</sub>/GLU values lead to maximum and minimum  $w_{\text{H}_2}$  and minimum and maximum  $w_{\text{GLU}}$  values lead to maximum and minimum  $S_{\text{H}_2\text{O}}$ , respectively. An increase in  $w_{\text{H}_2}$  and  $w_{\text{H}_2\text{O}}$  notably lowers the rest of the products' selectivities. Water selectivity, however, appears to significantly decrease with increased H<sub>2</sub> feed,

especially for higher  $w_{\text{GLU}}$ , as shown in Figure 4d. The values  $\text{H}_2/\text{GLU} = 100$  and  $w_{\text{GLU}} = 60$  wt % represent lower  $w_{\text{H}_2\text{O}}$  (31.11 wt %) and higher  $w_{\text{H}_2}$  (38.56 wt %), which are values that might be manageable from a process perspective.

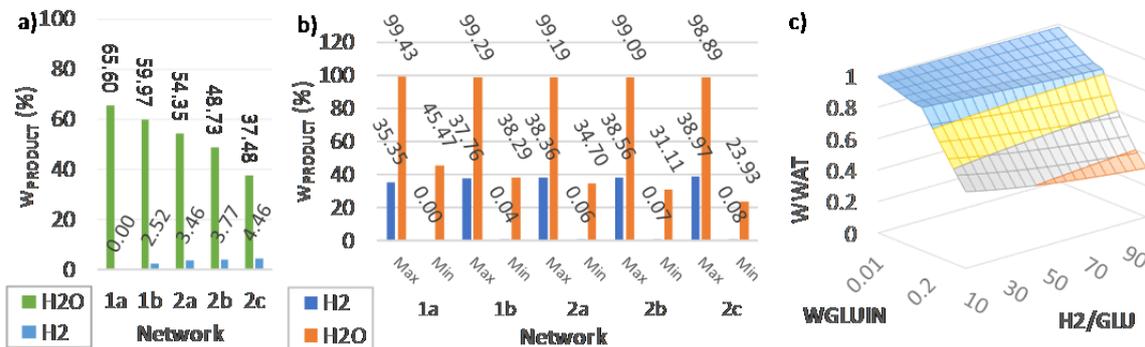


Figure 4: Variables that influence production costs. a) Upgraded case values for  $w_{\text{H}_2\text{O}}$  and  $w_{\text{H}_2}$ ; b) Maximum and minimum values of  $w_{\text{H}_2\text{O}}$  and  $w_{\text{H}_2}$  found during SA1 and SA2; c) SA2 to assess  $w_{\text{H}_2}$  on Network 2b.

Temperature and pressure seem to have little effect on the selectivity of degradation products. In scenario 2a (main products found in catalytic research on GLU hydrogenolysis), 1,2-BDO has by far the highest selectivity, explained by its second-highest equilibrium constants. It has been found in significant amounts amongst experimental product streams (Zheng et al., 2017) and that indicates the need to design catalysts that prevent its formation from occurring when targeting 1,2-PDO formation. In network 2a, its selectivity is lowered very slightly at high temperatures and low pressures.

Network 2b disregards its production to analyse  $S_{1,2\text{-PDO}}$  in the system. Figure 5a shows that low temperatures and high pressures greatly favor 1,2-PDO formation, which could be completely hindered on adverse conditions. There is a considerable region where its selectivity is close to its maximum, which has much lower temperatures than those found on literature for catalyst development (Table 2). Figure 5b exemplifies how sensitive  $S_{1,2\text{-PDO}}$  is to  $w_{\text{GLU}}$ , which is reported in very low values in the literature. Liu et al. (2016) have succeeded in reaching  $S_{1,2\text{-PDO}}$  of 55.8 wt %, which indicates that the specific network for each catalyst has to be studied for more accurate equilibrium predictions. Even so, this study shows that promising results might be achieved from operating at lower temperatures and higher  $w_{\text{GLU}}$  and research efforts should be focused on that.

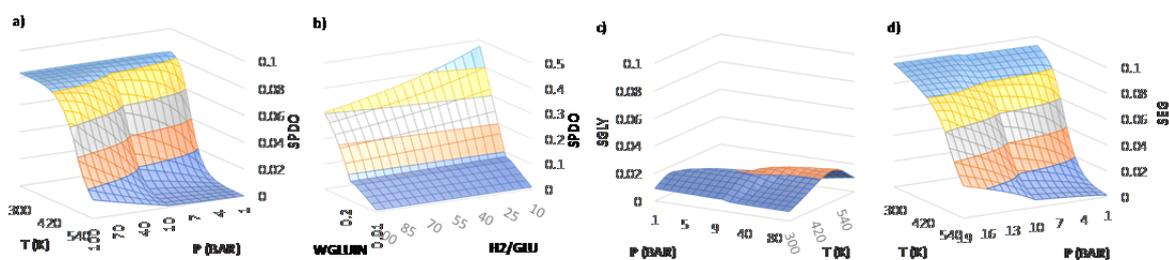


Figure 5: Sensitivity analysis of glycols production on Network 2b. a) SA1 to assess  $S_{1,2\text{-PDO}}$  on Network 2b; b) SA2 to assess  $S_{1,2\text{-PDO}}$  on Network 2b; c) SA1 to assess  $S_{\text{GLY}}$  on Network 2b; d) SA1 to assess  $S_{\text{SEG}}$  on Network 2b.

These conditions would also increase some byproducts and degradation products, especially high  $w_{\text{GLU}}$ . This was discussed before and reiterated by the analysis of network 2c, where only ethylene glycol (EG) and GLY routes and results are considered. Figure 5c and 5d indicates that low temperature lowers  $S_{\text{GLY}}$  and increases  $S_{\text{SEG}}$ .

#### 4. Conclusions and suggestions

This study provided the first thermodynamic analysis of the complex reaction network involved in GLU hydrogenolysis to form 1,2-PDO by simulating the chemical equilibrium of the most commonly proposed

mechanisms yielding the main products reported in the literature. Water is the most concerning compound present in the outlet stream, because its weight fraction usually ranges from 40 to 65 wt %, but can amount to 99 wt %, making purification costs extremely high. Degradation products ( $\text{CH}_4$ ,  $\text{CO}_2$ , CO, ethanol and propanols) were found not to be much affected by temperature or pressure. 1,2-BDO has high selectivity over other diols, explained by its highest equilibrium constants. 1,2-PDO production is favored by low temperatures and high pressures, which also promote EG, while low temperatures hinder GLY production.

Experiments published on the literature indicate that the equilibrium simulations in this study present the real trends observed with developed catalysts for 1,2-PDO production, with hexitols and tetrutols being produced in smaller amounts and diols being favored when the stable, degradation compounds are hindered. Therefore, this study can help enlighten the impacts of using bagasse and straw in the future for the same process. Interesting approaches for new catalysts are to explore lower temperatures and higher  $w_{\text{GLU}}$ . For equilibrium and kinetic simulation studies, the reaction network should be more thoroughly investigated to understand which paths occur with each catalyst and the consequences for product selectivity and operation costs. Kinetic data and more detailed mechanistic studies could help make better equilibrium and process predictions for a more detailed and correct design and assessment of this route.

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