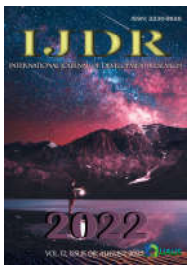
ISSN: 2230-9926

Available online at http://www.journalijdr.com

IJDR

International Journal of Development Research
Vol. 12, Issue, 08, pp. 58141-58147, August, 2022
https://doi.org/10.37118/ijdr.24858.08.2022



RESEARCH ARTICLE OPEN ACCESS

PURIFICATION AND CATALYTIC OXIDATION OF ENZYMATIC HYDROLYSATES OF PRETREATED SUGARCANE BAGASSE FOR GLUCONIC ACID PRODUCTION

Soares, I.B*[1]; Cunha, C.J.C.M.R[2]; Benachour, M[1] and Abreu, C.A.M[1]

[1]Laboratory of Catalytical Processes - Department of Chemical Engineering- Universidade Federal de Pernambuco, Recife-PE-Brazil; [2]Department of Nuclear Energy - Universidade Federal de Pernambuco, Recife- PE-Brazil

ARTICLE INFO

Article History:
Received 27th June, 2022
Received in revised form
17th July, 2022
Accepted 23rd July, 2022
Published online 27th August, 2022

Key Words:
Sugarcane Bagasse, Enzymatic Hydrolysis, Purification, Catalytic Oxidation, Slurry Reactor, Gluconic Acid.

Corresponding author: Soares, I.B,

ABSTRACT

Lignocellulosic Lignocellulosic wastes from agroindustry are sources of available carbohydrates to produce second-generation ethanol (E2G) and other high added values substances (as organic acids). Among these residues, sugarcane bagasse, which is obtained from grinding of sugarcane through the extraction of the juice and which is already applied for E2G production, emerges as one of the main wastes. In this work, enzymatic hydrolysates of samples of pretreated sugarcane bagasse were processed to purification with active charcoal and subjected to catalytic oxidation in a three-phase reactor (slurry), using Pd /Al_2O_3 as a catalyst, aiming production of gluconic acid (GA), a product with a high added value, used in the textile and food industries. The catalytic oxidation of the hydrolysates which were purified under these conditions yielded a conversion of 70% of glucose and produced GA in a yield close to 80% in 4 hours. A mathematical model (Langmuir-Hinshelwood) studied for the catalytic oxidation of glucose from enzymatic hydrolysates proved to be reasonably adequate with the experimental data and reveals that the presence of acetic acid from the buffer solution of enzymes did not change the reaction mechanism pathway. Also, it was made a brief economic discussion of the feasibility of the process steps studied in this work based on the raw material and final product. These results point out sugarcane bagasse as a very profitable raw material for gluconic acid.

Citation: ***Soares, I.B., Cunha, C.J.C.M.R., Benachour, M., Abreu, C.A.M.*** "Purification and Catalytic Oxidation of Enzymatic Hydrolysates of Pretreated Sugarcane Bagasse for Gluconic Acid production*", International Journal of Development Research*, 12, (08), 58141-58147.

INTRODUCTION

Lignocellulosic residues, such as those found in agriculture and the sugar and alcohol industries or derivate from wood industries, represent the most available sources of raw materials, and consequently cheaper for the production of E2G and other products with high added value (Cara *et al*. 2007; Sarkar *et al*. 2012; Sendelius 2005; Usmani *et al*. 2020). Among these residues, the sugarcane bagasse emerges as one of the main ones. It is a solid, fibrous and low-density residue produced shortly after grinding sugarcane for broth extraction and which is generally used as fuel to produce steam and electricity (Rudolph *et al*. 1999; Jackson de Moraes Rocha *et al*. 2011). In Brazil, it is estimated that the 2021/2022 harvest (according to a survey carried out in August 2021), will produce 530 million of tons processed, generating an amount of 148.4 million tons of solid waste (Forbes 2021).

However, according to the *Companhia Nacional de Abastecimento*, (CONAB)-Brazil, 90% of sugarcane bagasse is destined for burning, sufficient to supply the energy demand of sugar-alcohol plants and export energy (about 37.5% of the energy produced), while the rest is stored, being a risk due to possible spontaneous combustion of the material (Dos Santos *et al*. 2011; Lavarack Griffin, G. J., & Rodman, D 2000; Henrique M. Baudel, Zaror, and De Abreu 2005; Jackson de Moraes Rocha *et al*. 2011). The plant structure of sugarcane bagasse consists of cellulose, hemicellulose and lignin, being cellulose and hemicellulose representing about 80% of the dry mass of this biomass (Henrique Macedo Baudel 1999). These are potentially convertible to soluble carbohydrates via pre-treatment and enzymatic hydrolysis (Rudolf, Andreas; Baudel, Henrique; Zacchi, Guido; Hahn-Hägerdal, Barbel ; Lidén 2007) and, hence, can be processed chemically and biochemically for the production of high value-added species (E2G and organic acids, for example). Organic acids and aldehydes have great industrial interest, especially in the pharmaceutical and food areas (Besson, *et al*., 1995; Carvalho *et al*. 2021). Lignin, in turn, can be converted to other specialties through oxidation, such as vanillin, syringaldehyde and phenolics (Sales *et al*. 2007). Its depolymerization has also huge potential to produce biofuels, as phenolic oil or syngas (Halder *et al*. 2019)

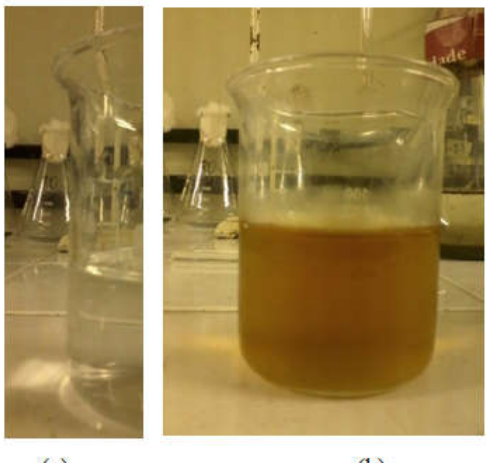
Specifically, the chemical oxidation or hydrogenation of mono and disaccharides (xylose, glucose and lactose) for the production of saccharinic acids (xylonic, gluconic and lactobionic by oxidation) or polyols (xylitol, sorbitol, lactitol by hydrogenation) has been developed aiming at the valorization of lignocellulosic vegetable biomass and residues from the milk industry (Cabral 2006; Soares 2013; Carvalho *et al*. 2021). One of these products is the gluconic acid (GA) and its derivatives, that can be found in food products, such as wine and honey. It is an acid that has low toxicity and caustic action and is therefore capable of forming complexes with divalent and trivalent metals in aqueous solutions, especially iron, aluminum, zinc and calcium. used as chelators in the metallurgical and paper industries(Mafra 2013; Ramachandran *et al*. 2006). Gluconic acid and its derivatives are considered safe by the Food and Drug Administration (FDA)(Wong, Wong, and Chen 2008). GA is a product obtained industrially especially by fermentation, using *Aspergillus niger, Zymomonas mobilis* and *Gluconobacter suboxidans* or enzymatic using glucose oxidase (Gogová and Hanika 2009; Liu and Cui 2007). However, another possibility of production of this compound is based on the oxidation of glucose solutions with oxygen or air via heterogeneous catalytic chemistry using palladium, platinum and gold catalysts(Lima and Poço 2017; Mirescu and PrüBe 2007). Several researchers have reported yields of gluconic acid above 95%, using such catalysts in tests with pure glucose solutions (Hermans and Devillers, 2002; Lima and Poço, 2017; Mirescu and PrüBe, 2007). The oxidation reaction occurs at a slightly alkaline pH, close to 9, which must be kept constant with the use of a base (for example NaOH) and at low temperatures (50ºC is often adopted) (Abbadi and van Bekkum, 1995; Hermans and Devillers, 2002).

The catalysts of palladium or palladium and bismuth are more selective to GA than platinum catalysts because they have lower activity in the oxidation of primary and secondary alcohols (Corma *et al*., 2007). However, the deactivation of these catalysts is the main limitation of the process and occurs with the increase of the conversion and consequent decrease of the pH caused by the very formation of the acids during the oxidation (Lima and Poço, 2017), especially during oxidation of non-pure solutions of glucose, since these impurities can be adsorbed on the catalytic surface, reducing the fraction of catalytic sites for the adsorption of glucose (Hermans and Devillers, 2002; Lima and Poço, 2017; Liu and Cui, 2007; Önal *et al*., 2004). In this context, it is possible to carry out a purification of the enzymatic hydrolysates, aiming to avoid the poisoning of the catalysts. Unfortunately, in the specialized literature, there are no references to the purification techniques of these hydrolysates, since there is no need to purify them for the production of E2G (a product of extreme interest in the vast majority of research in the area of lignocellulosic materials), since the content of these hydrolysates does not present toxicity to the glucose-fermenting microorganisms (Rudolf *et al*., 2007; Sendelius, 2005). Meanwhile, techniques for the purification of hydrolysates from the pretreatment step (hemicellulosic hydrolysate), are vast in the literature. The use of activated carbon, calcium hydroxide (overliming), ion exchange resin and treatment with enzymes (or a combination thereof) are necessary to avoid the poisoning of xylose fermenting microorganisms (Cardona *et al*., 2010; Chandel *et al*., 2007), whichis based on the results obtained in the literature (Marton *et al*., 2003; Palmqvist and Hahn-Hägerdal, 2000).

In this context, the term "detoxification" is used. In a preliminary study, Soares (Soares, 2013) performed purification experiments of enzymatic hydrolysate from pretreated sugarcane bagasse with active charcoal in a shaker using different levels of temperature, time and agitation, prior to catalytic oxidation for gluconic acid production. It was point out that, in conditions of temperature of 60°C at 200 rpm for 1 hour, 23% of acetic acid from the enzymatic hydrolysate (due to buffer solution) was removed and 90% of glucose was recovered. In this work, enzymatic hydrolysates of pretreated sugarcane bagasse were subjected to catalytic oxidation in a three-phase reactor (slurry reactor) with air and 2% Pd/Al_2O3 for GA production. In order to test the efficacy of the catalyst and the purification methods, the catalytic oxidation of natural hydrolysate (without purification) and purified with activated charcoal was performed, and the results were compared with the oxidation of pure glucose solution. Also, Langmuir-Hinshelwood model were applied to the experimental results, aiming to confirm the mechanism of oxidation reported in literature.

MATERIAL AND METHODS

Purification of enzymatic hydrolysates of pretreated sugarcane bagasse with active charcoal: Previously, 52g (dry basis) of sugarcane bagasse (pretreated with sulfuric acid diluted in an autoclave reactor) was subjected to enzymatic hydrolysis with buffer solution sodium acetate/acid acetic (pH 4.8), using commercial enzymes from Novozymes®, during 72 h at 50°C and 200 rpm in a shaker. The obtained liquor was vacuum filtered and diluted to 1L and it became as shown in Figure 1a. This hydrolysate was divided into 2 portions of 500 mL, one of which was treated with 10 g of active charcoal (this portion of 500 mL was divided in 10 Erlenmeyer flasks with 50 mL and 1g of active charcoal in each one) and subjected under stirring at 200 rpm for 60 minutes at 60°C (Soares, 2013) in a shaker, becoming the liquor solution shown in Figure 1b. The other 500 mL portion remained untreated. Both solutions (treated with activated charcoal and untreated) were analyzed by HPLC (Refraction Index Detector) for glucose and acetic acid content under the following conditions: Aminex BioRad HPX-87H column, mobile phase: 0.005 mol/L H_2SO_4 solution with flow rate 0.6 mL /min and oven at 50°C.



(a) (b)

Figure 1. Aspects of enzymatic hydrolysates from sugarcane bagasse: untreated (a) and treated with activated charcoal (b)

Catalytic oxidation of enzymatic hydrolysate purified with active charcoal: The hydrolysate purified with active charcoal was subjected to catalytic oxidation in a slurry reactor (PARR 4848), using 2% Pd/Al_2O_3 catalyst. The reactor has a maximum capacity of 2 L and it is equipped with temperature, pressure and agitation controller (Figure 2). The pH of liquor was adjusted to 9 with NaOH solution. An air flow rate of 100 L/h and a stirring of 500 rpm (sufficient to eliminate the effects of external diffusion resistance of the reactants to the catalyst surface) and a useful volume of 500 mL were used. The reaction was conducted at 50°C and at atmospheric pressure and performed in a time of 4 hours, where samples were taken every 40 minutes of reaction. The pH of the reaction (which should be between 8.5 and 9.5) was monitored every 10 minutes in order to correct this variable by adding the 2 mol/L NaOH solution. Each sample was filtered and analyzed by HPLC for glucose (Refraction Index detector) and gluconic acid (UV detector) contents analysis under the following conditions: Aminex BioRad HPX-87H column, mobile phase: 0.005 mol/L H2SO4 solution with flow rate 0.6 mL /min and oven at 50°C.

Figure 2. Slurry reactor PARR 4848 used for catalytic oxidations performed in this work

For comparison, it was performed catalytic oxidation of the hydrolysate untreated and pure glucose solution (20g/L) in the same conditions. In order to calculate the glucose conversion, and yield and selectivity in GA for the experiments, it was used the following equations:

Glucose Conversion: $X = \frac{C_{G0}-C_G}{C_{G0}} \times 100\%$ (1)

Yield in GA: $Y = \frac{C_{GA}}{C_{GA^*}} \times 100\%$ (2)

Selectivity in GA: $S = \frac{C_{GA}}{(C_{G0}-C_G)}$ (3)

Where:

C_{G0}: initial concentration of glucose (g/L);
C_G: glucose concentration at any time (g/L)
C_{GA}: GA concentration at any time (g/L)
C_{GA*}: maximum GA concentration (g/L), considering maximum conversion of initial glucose.

Mathematical modeling of glucose oxidation: For a batch reactor in a slurry reactor, some researchers(Nikov and Paev 1995; Önal, Schimpf, and Claus 2004) describe the reaction of catalytic oxidation of glucose as occurring in three steps (in Pd/Al_2O_3 or Au, for example), according to the Langmuir-Hinshelwood unique site kinetic model:

- Adsorption of glucose on the surface of the catalyst
- Surface reaction (glucose to gluconic acid)
- Desorption of the gluconic acid from the surface of the catalyst.

The authors concluded that the surface reaction step is the limiting step of the process, by ensuring the elimination of external diffusion (mass transfer) of glucose through the reaction system. Thus, considering adsorption and first order kinetics for the catalytic reaction, the reaction rate of the glucose oxidation process is given by Equation 4 (Nikov and Paev 1995; Önal, Schimpf, and Claus 2004).

$$r = \frac{kK_GC_G}{1+K_GC_G+K_{GA}C_{GA}} . \rho_C \quad (4)$$

Where:

r: reaction rate (mmol/L. s);
k: kinetic constant of the reaction on the surface (mmol/g. s);
K_G: Glucose adsorption constant (L/mmol);
K_{GA}: Adsorption constant of gluconic acid (L/mmol);
ρ_c: Concentration of the catalyst (g/L);
C_G: Glucose concentration (mmol/L);
C_{GA}: Gluconic acid concentration (mmol/L);

For a batch reactor, the reaction rate is given by Equation 5:

$$r = -\frac{dC_G}{dt} \quad (5)$$

Where t is the time of reaction. Since Equation 4 and 5 are equal, we have the Equation 6:

$$-\frac{dC_G}{dt} = \frac{kK_GC_G}{1+K_GC_G+K_{GA}C_{GA}} \cdot \rho_C \quad (6)$$

To solve Equation 6, it was admitted that for t = 0, $C_G = C_{G0}$. Then its solution is given by Equation 7:

$$t = \frac{1}{k'\rho_C}\left[ln\left(\frac{C_{G0}}{C_G}\right) + K_G(C_{G0} - C_G) + K_{GA}(C_{G0}ln\left(\frac{C_{G0}}{C_G}\right) - (C_{G0} - C_G))\right] \quad (7)$$

Where $k' = k.K_G$ (L/g.s).

The results of experiments of catalytic oxidation of pure glucose solution and enzymatic hydrolysates were validated using the Langmuir-Hinshelwood model. For the kinetic parameters k', K_G and K_{AG}, it was used the values adopted by Nikov and Paev (Nikov and Paev 1995) for glucose oxidation at 50°C with Pd/Al_2O_3, which are: 7.9 x 10^{-4} L/g.s , 0.0138 L/mmol and 0.0279 L/mmol, respectively.

RESULTS AND DISCUSSION

Enzymatic hydrolysis and purification with activated charcoal: Table 1 shows the glucose and acetic acid contents in the enzymatic hydrolysate untreated and treated with activated charcoal. The results show that, although the activated charcoal modified the color of the enzymatic hydrolysate, as shown in Figure 1, its composition was practically unchanged, since about 93% of glucose were recovered. Besides, the removal of such color is desirable, since it comes from the commercial enzymes concentrate and may have the potential to cause poisoning of the catalyst in the oxidation step. Thus, the activated charcoal utilized in this work proved to be a suitable purifying agent of enzymatic hydrolysates solutions prior to catalytic oxidation reactions.

Table 1. Concentrations of glucose and acetic acid in the Enzymatic Hydrolysate untreated and treated with active charcoal.

Enzymatic hydrolysate	Glucose(g/L)	Acetic acid (g/L)
Untreated	12.6	4.5
Purified	11.7	4.3

Catalytic oxidation of glucose solution and enzymatic hydrolysates: Figure 3 shows the conversion profiles of glucose, yield and selectivity in gluconic acid (GA) for the catalytic oxidation of pure glucose solution (20g/L), for the untreated enzymatic hydrolysate and for the same hydrolysate treated with activated charcoal (purified EH). Figure 3a pointed out that highest glucose conversion was obtained from the pure glucose reagent, which reached a value close to 92% and 70% for the hydrolysates (untreated and treated) after 4h of reaction. Literature reports glucose conversions above 98% for catalytic oxidation of glucose solutions (Deller *et al*., 1992; Besson *et al*., 1995). However, the conversion of glucose was greater for the hydrolysates up to the first 2 hours of reaction reaching similar values. The yield of gluconic acid was higher when the hydrolysates were oxidized, especially the hydrolysate treated with activated charcoal, practically in all the time intervals studied, which reached a maximum value of 80% (Figure 3b). The catalytic oxidation of the untreated hydrolysate reached a yield close to 90%. The selectivity in GA was also higher for the treated hydrolysate at all time intervals studied (Figure 3c), being it about two times higher than the selectivity for the untreated hydrolysate for the first 2 hours of reaction. This observation shows the importance of purifying the hydrolysate after saccharification of pulps of pretreated sugarcane bagasse by enzymes, prior to the catalytic oxidation of glucose to gluconic acid.

Modelling Mathematical of glucose oxidation: Figure 4 shows the profiles of glucose and gluconic acid concentrations obtained in the experiments performed in this work and its comparison with Langmuir-Hinshelwood model. Figure 4a shows that experimental data fitted reasonably to the Langmuir-Hinshelwood model in relation to glucose for the oxidation of pure glucose solution. However, for GA, experimental data stayed below of curve for the model. It can be explained by low selectivity in GA obtained for this experiment (Figure 3c), as a consequence of side reactions, eventually due to the lack of pH control in some period of the reaction (Hermans and Devillers 2002). However, the value of regression coefficient, R^2, in relation to the model for this reaction was 0.880 for glucose and 0.725 for GA, indicating reasonable agreement between experimental data and model. Figure 4b, which shows the comparison between model and experimental data for the oxidation of untreated enzymatic hydrolysate, points out also a reasonable fit for glucose and GA in relation to the model, with values of regression coefficients (R^2) of 0.892 and 0.723 for glucose and GA respectively. It means that the adopted values for k, K_G and K_{GA} constants were well fitted for untreated enzymatic hydrolysate, pointing out that the mechanism of glucose oxidation for this hydrolysate was not changed by the presence of enzymes or acetic acid in the reactional system. For the oxidation of enzymatic hydrolysate treated by activated charcoal, Figure 4c also shows an acceptable adjusting between Langmuir-Hinshelwood model and the experimental data, presenting values of regression coefficients (R^2) of 0.884 and 0.723 for glucose and GA respectively. Therefore, the adopted valued for the constants k, K_G and K_{GA} were well fitted for treated hydrolysate, showing that the presence of acetic acid in the reactional medium did not influence the reaction mechanism pathway.

Brief economic analysis in terms of raw material and final product: Taking into account the overall process, a brief economic analysis of its feasibility can be made in terms of the cost of the raw material (sugarcane bagasse) and the final product (gluconic acid). In this work, 52 g of pretreated sugarcane bagasse was processed by enzymes and became into two solutions of glucose with 12.6 g/L and 11.7 g/L (after treatment with active charcoal). Only half of these solutions were processed by catalytic oxidation (500 mL). After the process, it was obtained about 6.2 g of gluconic acid for untreated enzymatic hydrolysate and 5.1 g for treated enzymatic hydrolysate, totalizing 11.3 g of this product. Considering 1 ton of natural sugarcane bagasse, which, after pretreatment process (removing mainly hemicelluloses) provides about 70% of pretreated

sugarcane bagasse (Soares 2013; Sun and Cheng 2002), we have 700 kg of this raw material. In proportion, it would be equivalent to 152 kg of gluconic acid. The estimated price of sugarcane bagasse in the last harvest was about US$ 11.00/ton (Cana 2019) and the price of gluconic acid is estimated at US$ 35.00/kg on average (Alibaba 2020). Hence, without considering the cost of overall process, one can set a profit by ton of handled natural sugarcane bagasse of, approximately:

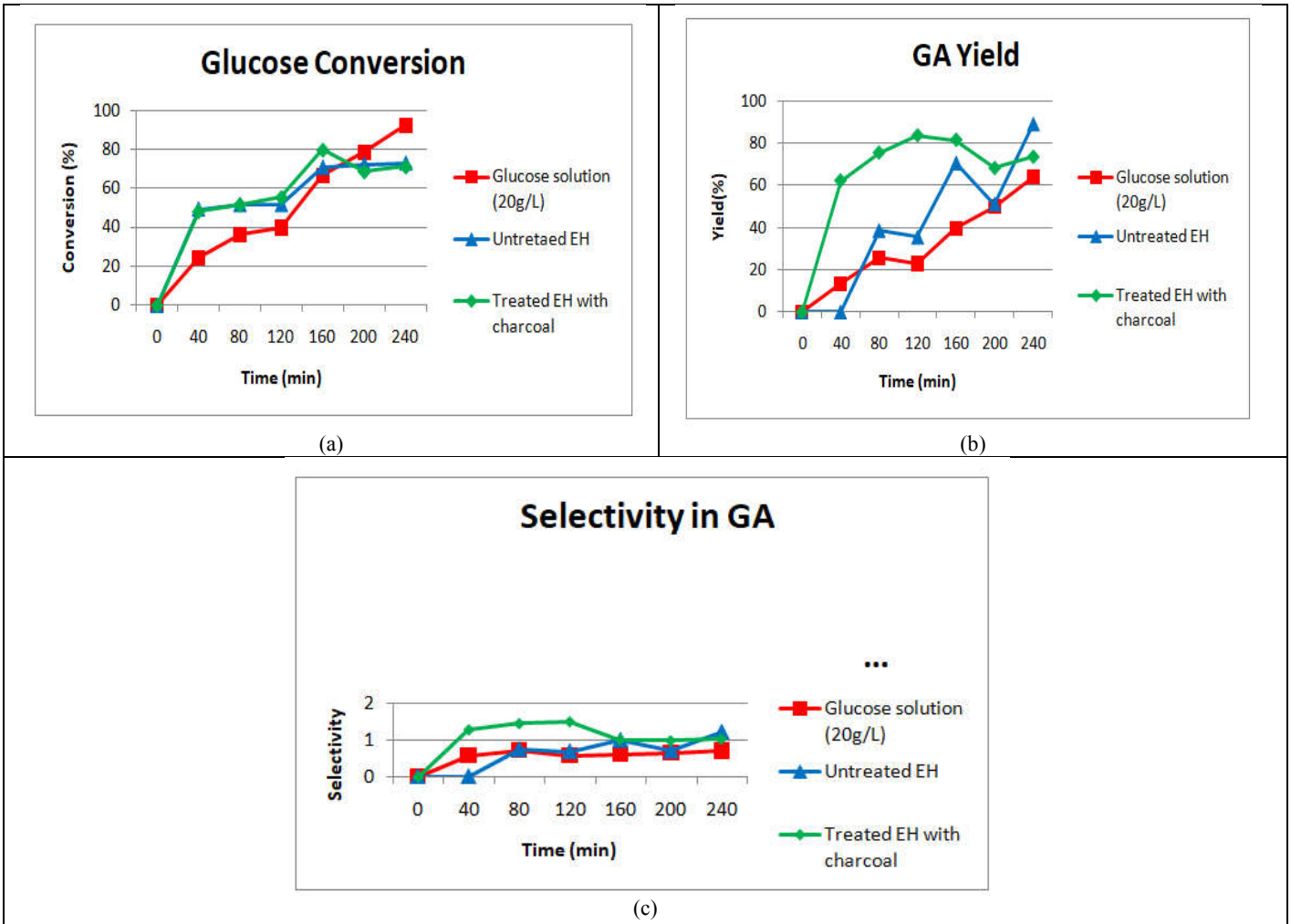
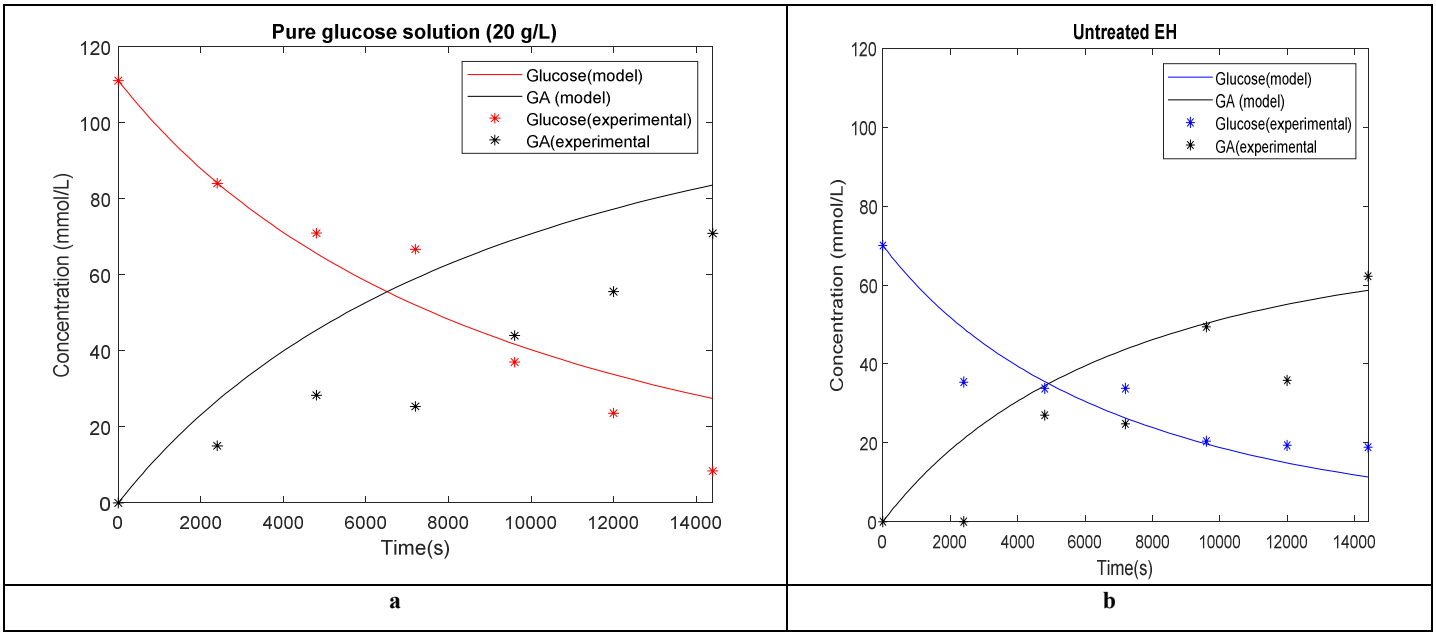
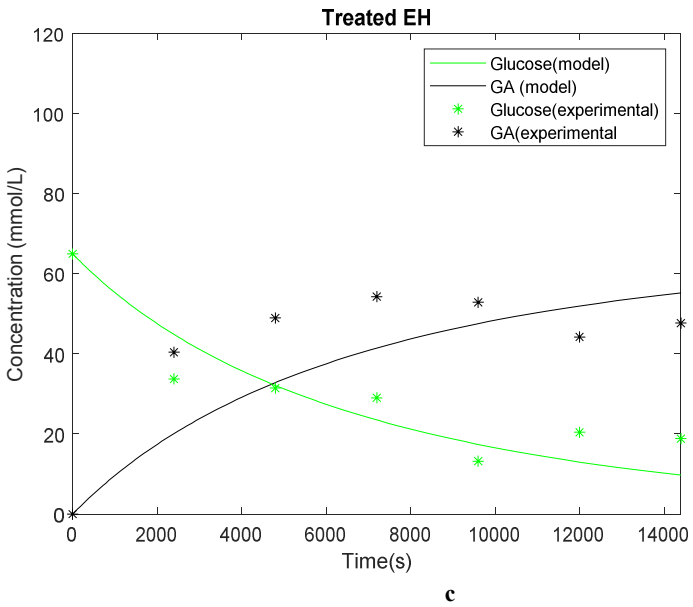


Figure 3. Conversion profiles of glucose (a), yield (b) and selectivity (c) in gluconic acid (GA) for the catalytic oxidation of pure glucose solution (20g/L) with 2% Pd/Al_2O_3 catalyst, for the untreated enzymatic hydrolysate (untreated EH) and for the same hydrolysate treated with activated charcoal (Treated EH with charcoal





c

Figure 4. Comparison between Experimental data and Langmuir-Hinshelwood model for (a) pure glucose solution; (b) untreated enzymatic hydrolysate and (c) treated enzymatic hydrolysate.

Profit = US$ 35.00/kg x 152 kg – US$ 11.00 = US$ 5,309.00.

This calculation takes into account the more costly acquisition of the raw material (sugarcane bagasse) and the cheaper sale of the product (gluconic acid). Hence, this presented profit can be much higher. This fact highlights a huge economic potential for sugarcane bagasse as feedstock to obtain gluconic acid. However, obviously, is necessary to evaluate the energetic and environmental costs of overall process. Other critical issue is the price of enzymes, which are often very costly for the process. Further studies may be done to reduce the dependence of enzymes in the process of obtaining glucose-rich solutions to obtain gluconic acid. For example, part of the hydrolytic process may be done using mineral acids (HCl or H_2SO_4) to convert cellulose into glucose, seeking to prevent the formation of considerable amount of glucose degradation products such as formic acid and 5 – hydroxymethylfurfural (HMF).

CONCLUSION

In this work, it was carried out catalytic oxidations of pure glucose and enzymatic hydrolysates from sugarcane bagasse (untreated and purified with activated charcoal) using 2% Pd/Al_2O_3 catalyst, aiming to produce gluconic acid. It was observed that these reactions presented high glucose conversion (above 70%) with reasonable selectivity towards gluconic acid, mainly the experiments performed with enzymatic hydrolysates. The experimental data were also consistent with the Langmuir-Hinshelwood kinetic model. A brief economic discussion of the process in terms of the raw material and final product, based on the amounts obtained in this study, pointed out the great potential of sugarcane bagasse as raw material for a very profitable production of gluconic acid.

Acknowledgments

The authors thank to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico,Brazil) and Capes (Coordenação de Aperfeiçoamento de Pessoal do Ensino Superior, Brazil) for their financial supports.

REFERENCES

Alibaba (2020). “Gluconic Acid Price, Gluconic Acid Price Suppliers and Manufacturers at Alibaba.” Gluconic Acid Price. 2020. https://www.alibaba.com/showroom/gluconic-acid-price.html.

Baudel, Henrique M., Claudio Zaror, and César A M De Abreu(2005). “Improving the Value of Sugarcane Bagasse Wastes via Integrated Chemical Production Systems: An Environmentally Friendly Approach.” *Industrial Crops and Products* 21 (3): 309–15. https://doi.org/10.1016/j.indcrop.2004.04.013.

Baudel, Henrique Macedo (1999). “Hidrólise-Hidrogenação de Hemiceluloses Da Biomassa Vegetal [Bagaço de Cana-de-Açúcar] Com Catalisador de Rutênio.” Universidade Federal de Pernambuco-UFPE.

Besson, M; Lahmer, F; Gallezot, P;Fuertes, P; Flèche, G (1995). “Catalytic Oxidation of Glucose on Bismuth-Promoted Palladium Catalysts.” *Journal of Catalysis*. https://doi.org/10.1006/jcat.1995.1065.

Cabral, Ana Cássia (2006). “Modelagem e Validação Do Processo Contínuo de Produção de Polióis Em Reator de Leito Gotejante.” Recife.

Cana, Jornal (2019). “Quanto Custa o Bagaço? Confira Aqui.” Jornal Cana. 2019. https://jornalcana.com.br/quanto-custa-o-bagaco-confira-aqui/.

Cara, Cristóbal, Manuel Moya, Ignacio Ballesteros, Ma José Negro, Alberto González, and Encarnación Ruiz (2007). “Influence of Solid Loading on Enzymatic Hydrolysis of Steam Exploded or Liquid Hot Water Pretreated Olive Tree Biomass.” *Process Biochemistry* 42 (6): 1003–9. https://doi.org/10.1016/j.procbio.2007.03.012.

Carvalho, Santulla Leide Bernardes Vasconcelos, Eliane Bezerra de Moraes Medeiros, Ayrton de Souza Wanderley, Luccas de Moura Ribeiro, Júlia Gabriela da Silva, Ivana Taciana de Almeida Simões, Nathalia Cecília do Rego Lemos, *et al* (2021). “Production of Xylitol from

Acidic Hydrolysates of Lignocellulosic Biomass by Catalytic Hydrogenation over a Ni–Ru/C Catalyst." *Chemical Engineering Research and Design* 174: 11–18. https://doi.org/10.1016/j.cherd.2021.07.025.

Forbes (2021). "Safra de Cana Do Centro-Sul Pode Cair a 530 Milhões de Toneladas, Com 'Viés de Baixa', Diz Unica - Forbes Brasil." 2021. https://forbes.com.br/forbesagro/2021/08/safra-de-cana-do-centro-sul-pode-cair-a-530-milhoes-de-toneladas-com-vies-de-baixa-diz-unica/.

Gogová, Zuzana, and Jiří Hanika (2009). "Dynamic Modelling of Glucose Oxidation with Palladium Catalyst Deactivation in Multifunctional CSTR: Benefits of Periodic Operation." *Chemical Engineering Journal* 150 (1): 223–30. https://doi.org/10.1016/j.cej.2009.02.020.

Halder, Pobitra, Sazal Kundu, Savankumar Patel, Adi Setiawan, and Rob Atkin (2019). "Progress on the Pre-Treatment of Lignocellulosic Biomass Employing Ionic Liquids." *Renewable and Sustainable Energy Reviews* 105 (January): 268–92. https://doi.org/10.1016/j.rser.2019.01.052.

Hermans, S., and M. Devillers (2002). "On the Role of Ruthenium Associated with Pd and/or Bi in Carbon-Supported Catalysts for the Partial Oxidation of Glucose." *Applied Catalysis A: General* 235 (1–2): 253–64. https://doi.org/10.1016/S0926-860X(02)00269-7.

Jackson de Moraes Rocha, George, Carlos Martin, Isaias Barbosa Soares, Ana Maria Souto Maior, Henrique Macedo Baudel, and Cesar Augusto Moraes de Abreu (2011). "Dilute Mixed-Acid Pretreatment of Sugarcane Bagasse for Ethanol Production." *Biomass and Bioenergy* 35 (1): 663–70. https://doi.org/10.1016/j.biombioe.2010.10.018.

Klaus Deller, Hainburg: Helmfried Krause, Rodenbach; Erik Peldszus, Hasselroth; Bertrand Despeyroux, Hanau (1992). Method for preparation of gluconic acid by catalytic oxidation of glucose, issued 1992.

Lavarack Griffin, G. J., & Rodman, D, B (2000). "Measured Kinetics of the Acidcatalysed of the Acidcatalysed Hydrolysis of Sugarcane Bagasse to Produce Xylose." *Catalysis Today* 63: 257–265. https://doi.org/10.1016/S0920-5861(00)00467-3.

Lima, Fabiana S, and João Guilherme R Poço (2017). "Obtenção de Ácido Glicônico Com Alta Seletividade a Partir de Uma Mistura de Glicose e Frutose ." Ouro Preto - MG.

Liu, Jianguo, and Zhanfeng Cui (2007). "Optimization of Operating Conditions for Glucose Oxidation in an Enzymatic Membrane Bioreactor." *Journal of Membrane Science* 302 (1–2): 180–87. https://doi.org/10.1016/j.memsci.2007.06.044.

Mafra, Agnes Cristina Oliveira (2013. "Produção de Ácido Glucônico e Xarope de Frutose a Partir de Sacarose Catalisada Por Enzimas Em Reator Airlift." *Universidade Federal de São Carlos* 84: 122.

Mirescu, Agnes, and Ulf PrüBe. 2007. "A New Environmental Friendly Method for the Preparation of Sugar Acids via Catalytic Oxidation on Gold Catalysts." *Applied Catalysis B: Environmental* 70 (1–4): 644–52. https://doi.org/10.1016/j.apcatb.2006.01.017.

Nikov, I., and K. Paev. 1995. "Palladium on Alumina Catalyst for Glucose Oxidation: Reaction Kinetics and Catalyst Deactivation." *Catalysis Today* 24 (1–2): 41–47. https://doi.org/10.1016/0920-5861(95)00011-4.

Önal, Y., S. Schimpf, and P. Claus. 2004. "Structure Sensitivity and Kinetics of D-Glucose Oxidation to D-Gluconic Acid over Carbon-Supported Gold Catalysts." *Journal of Catalysis* 223 (1): 122–33. https://doi.org/10.1016/j.jcat.2004.01.010.

Ramachandran, Sumitra, Pierre Fontanille, Ashok Pandey, and Christian Larroche. 2006. "Gluconic Acid: Properties, Applications and Microbial Production." *Food Technology and Biotechnology* 44 (2): 185–95.

Rudolf, Andreas; Baudel, Henrique; Zacchi, Guido; Hahn-Hägerdal, Barbel ; Lidén, Gunnar. 2007. "Simultaneous Saccharification and Fermentation of Steam-Pretreated Bagasse Using Saccharomyces Cerevisiae TMB3400 and Pichia Stipitis CBS6054." *Biotechnology and Bioengineering*, 1–21. https://doi.org/10.1002/bit.

Rudolph, V, M G Rasul, V Rudolph, and M Carsky. 1999. "Physical Properties of Bagasse Physical Properties of Bagasse" 2361 (June): 905–10. https://doi.org/10.1016/S0016-2361(99)00011-3.

Sales, Fernando G., Laísse C.A. Maranhão, Nelson M.Lima Filho, and Cesar A.M. Abreu. 2007. "Experimental Evaluation and Continuous Catalytic Process for Fine Aldehyde Production from Lignin." *Chemical Engineering Science* 62 (18–20): 5386–91. https://doi.org/ 10.1016/j.ces.2007.02.018.

Santos, Moacyr L. Dos, Omar J. De Lima, Eduardo J. Nassar, Katia J. Ciuffi, and Paulo S. Calefi. 2011. "Estudos Das Condições de Estocagem Do Bagaço de Cana-de-Açúcar Por Análise Térmica." *Quimica Nova* 34 (3): 507–11. https://doi.org/10.1590/S0100-40422011000300024.

Sarkar, Nibedita, Sumanta Kumar Ghosh, Satarupa Bannerjee, and Kaustav Aikat. 2012. "Bioethanol Production from Agricultural Wastes: An Overview." *Renewable Energy* 37 (1): 19–27. https://doi.org/10.1016/j.renene.2011.06.045.

Sendelius, Johan. 2005. "Steam Pretreatment Optimisation for Sugarcane Bagasse in Bioethanol Production." *Trials*, 8.

Soares, Isaías Barbosa. 2013. "Biorrefino Do Bagaço de Cana-de-Açúcar Com Produção de Sacarídeos via Processos Ácido e Enzimático e Conversões Catalíticas Em Ácido Glicônico Com Pd/Al2O3." Universidade Federal de Pernambuco-UFPE.

Sun, Ye, and Jiayang Cheng. 2002. "Hydrolysis of Lignocellulosic Materials for Ethanol Production : A Review q." *Bioresource Technology* 83 (1): 1–11. https://doi.org/10.1016/S0960-8524(01)00212-7.

Usmani, Zeba, Minaxi Sharma, Pratishtha Gupta, Yevgen Karpichev, Nicholas Gathergood, Rajeev Bhat, and Vijai Kumar Gupta. 2020. "Ionic Liquid Based Pretreatment of Lignocellulosic Biomass for Enhanced Bioconversion." *Bioresource Technology* 304: 123003. https://doi.org/10.1016/j.biortech.2020.123003.

Wong, Chun Ming, Kwun Hei Wong, and Xiao Dong Chen. 2008. "Glucose Oxidase : Natural Occurrence, Function, Properties and Industrial Applications," 927–38. https://doi.org/10.1007/s00253-008-1407-4.

****