CONVERSION OF SUCROSE TO ORGANIC ACIDS USING ALUMINUM NITRATE IN AQUEOUS MEDIUM

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INTRODUCTION

The term biorefinery is attributed to processes whereby renewable feedstocks are converted to fuels, platform chemical and value-added biobased materials, and this has a major role in sustainable chemical process development. Viability is an important aspect to the biorefinery concept, which means that feedstock provision must be stable and available at costs that are compatible with commercialization. In general, biorefinery developments have two strategic goals: the energy goal of replacing imported petroleum in favor of renewable, locally available raw materials, and the economic goal of establishing a strong bio-based industry for generations to come (Bozell and Petersen, 2010). Among biorefinery products, organic acids are considered building blocks with an important market share, and represent an important fraction of carbohydrate-derived compounds. Nearly two-thirds of building blocks based on renewable raw materials are made up of organic acids, showing the importance of these chemicals in establishing a renewable and sustainable industry (Serrano-Ruiz, West and Dumesic, 2010).

Levulinic and lactic acids are some of the biomass-derived chemicals with the greatest economic potential. Lactic acid has received great attention due to its use in biodegradable polymers such as poly(lactic acid) (PLA), a biodegradable and biocompatible high molecular mass polymer that plays an important role in replacing plastics derived from the petrochemical industry (Wang, Song, Huang, Liang, and Chen, 2014). New catalytic processes are sought for the synthesis of lactic acid from renewable raw materials, which are low-priced and widely profuse. In this work, organic acids were successfully produced from water-soluble carbohydrates using metal salts as catalysts in aqueous media.

The chemical conversion of carbohydrates is ruled by two main mechanisms: dehydration to furan derivatives and retro-aldol reaction to C3, C2 and C1 building blocks (Marianou, Michailof, Pineda, Iliopoulou, Triantafyllidis and Lappas, 2018). Dehydration converts hexoses to furan compounds such as 5-(hydroxymethyl)-furfural (HMF), which may undergo oxidation and/or rehydration to release levulinic and formic acids under acid conditions (Kruger, Nikolakis and Vlachos, 2012). By contrast, the retro-aldol mechanism starts from glucose with its isomerization to fructose, followed by retro-aldol processes resulting in glyceraldehyde and dihydroxyacetone (C3 building blocks). Finally, glyceraldehyde is dehydrated to pyruvaldehyde followed by intramolecular Cannizzaro reaction to produce lactic acid (Scheme 1) (van Putten, van der Waal, de Jong, Rasrendra, Heeres, and de Vries, 2013; Rasmussen, Sorensen and Meyer, 2014; Yang, Yang, Tian, Vattipalli, Fan and Lin, 2016).

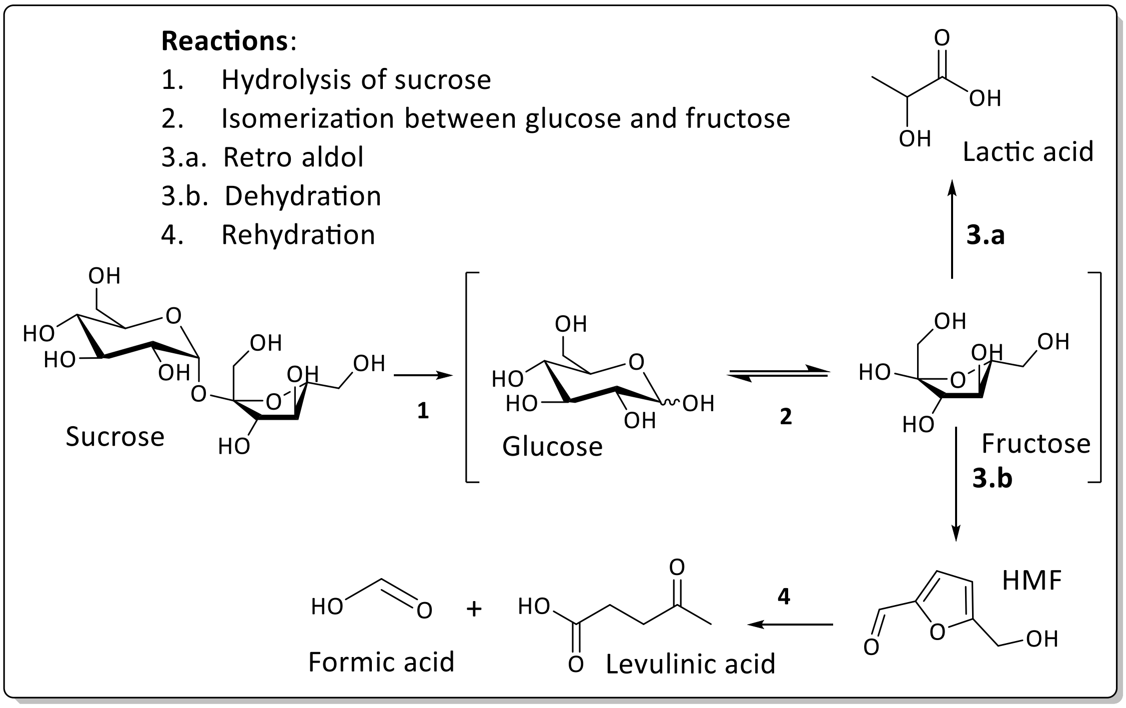

Figure 1. Proposed scheme for the chemical conversion of sucrose to lactic, formic and levulinic acids and 5-(hydroxymethyl)-furfural (HMF).

MATERIALS AND METHODS

Materials: Glucose, fructose and sucrose, standard of furfural (99%), acetic acid (>99,7%), levulinic acid (99%), lactic acid (99%), and 5-(hydroxymethyl)-furfural (99%) were obtained from Sigma-Aldrich Brazil (Jurubatuba, São Paulo). $Al(NO_3)_3{\cdot}9H_2O$ was purchased from Vetec® (Duque de Caxias, Rio de Janeiro).

Conversion of carbohydrates: experiments were performed in aqueous media containing sucrose (3,32 mmol) and 4% $Al(NO_3)_3{\cdot}9H_2O$ in relation to the total carbohydrate content. Experiments were performed in a CEM microwave reactor using a closed glass tube and in a stainless-steel (SS) reactor fitted with a poly(tetrafluoroethylene) (PTFE, Teflon®) tube using conventional heating. The reaction time was 90 min in both reaction systems, while temperatures varied from 170 to 215 °C in experiments under microwave heating. The reaction temperature in conventional heating increased gradually and was monitored until circa 215 °C was reached. The reaction products were analyzed by ion-exchange liquid chromatography (HPLC) and yields were based on stoichiometric calculations.

Conversion of carbohydrate in microwave using gradual heating: dehydration of sucrose (33,2 mmol·L-1) in aqueous media was carried out in the presence of $Al(NO_3)_3{\cdot}9H_2O$ as catalyst (9 % w/w). Experiments were performed in a microwave reactor and in a poly (tetrafluoroethylene) (PTFE, Teflon®) reactor with a stainless steel tube with conventional heating. The heating time was 120 min in both systems. A reaction was carried out in the Teflon® reactor with a stainless steel tube in an oven with gradual increase in temperature, which was monitored with a thermocouple. The reactor interior takes approximately 90 min to reach 200 °C. The second reaction was carried out in a microwave reactor and the temperature was manually increased to simulate oven heating. The third reaction was also carried out in a microwave reactor, however, with an operational heating time of 2 min to reach 200 °C. After the reaction time the samples were analyzed in HPLC and the yields based on the stoichiometric amount of each product.

Chromatographic analysis: carbohydrate and organic acid analyses were carried out by high performance liquid chromatography (HPLC) using a Shimadzu workstation that was equipped with two detection systems: diode array UV spectrophotometry (UV-DAD) and differential refractometry (RID). The chromatographic column was an Agilent Hi-Plex-H that was operated at 65 °C using H_2SO_4 8 mmol L^{-1} as mobile phase in a flow rate of 0.6 $mL.min^{-1}$. Quantification was carried out by external calibration using the concentration ranges 0.1 to 3.0 $mg{\cdot}L^{-1}$ for carbohydrates glucose, fructose, and sucrose for HMF and furfural, and organic acids lactic, levulinic, acetic and formic.

Organic acids and HMF yields were calculated with respect to the corresponding theoretical yield, which was based on the stoichiometric amount of given organic acid or HMF that could have been produced from the total carbohydrate content of the starting material. Eqs (1) and (2) show calculations for yields of HMF and organic acids from glucose, respectively, where HMF_{exp} and $OrgAc_{exp}$ are the amount of HMF or Organic Acid that were experimentally determined, m_{Glc} is the initial mass of glucose (Glc), and SF is the stoichiometric factor of glucose conversion into HMF, levulinic, formic, and lactic acids (OrgAc), respectively 0.70, 0.64, 0.25, and 0.50, being determined by dividing the molar mass of the compound to be quantified by the molar mass of the substrate used in the reaction.

$$HMF_{Glc}(mol\%) = \frac{HMF_{exp}(g)}{m_{Glc}(g) \times SF} \times 100 \tag{1}$$

$$OrgAc_{Glc}(mol\%) = \frac{OrgAc_{exp}(g)}{m_{Glc}(g) \times SF} \times 100 \tag{2}$$

RESULTS AND DISCUSSION

Reactions controls

Reaction controls were aimed at analyzing the behavior of sucrose under heating in the absence of any added catalyst. These experiments were carried out at 200 °C for 120 min in a microwave reactor, using 11.4 $g{\cdot}L^{-1}$ sucrose. **Figure 2** shows the thermal conversion sucrose under these experimental conditions. Fructose, produced by sucrose hydrolysis, was almost completely consumed (93%) during the thermal treatment, while only half of the glucose moiety (48%) was converted to 5-HMF and organic acids. In general, sucrose thermal conversion produced 27% 5-HMF by hexose dehydration, plus 2% formic and 7% levulinic acids by 5-HMF rehydration.

The same reactions described above were also carried out in a Teflon®-lined stainless steel reactor, heated in a muffle furnace. The maximum temperature reached in the reactor was 200 °C, but the heating took place gradually. **Figure 3** presents the results obtained for this heating system. In this reaction system, glucose (25%), as well as a small amount of fructose (3%) remained partially unconverted, with both being generated by sucrose hydrolysis. 5-HMF predominated in the reaction products (28%) with small quantities of the same organic acids mentioned above. The low conversion of sucrose to organic acids (mainly lactic acid) in the two reaction systems justified the need for an exogenous acid catalyst to improve conversion efficiency.

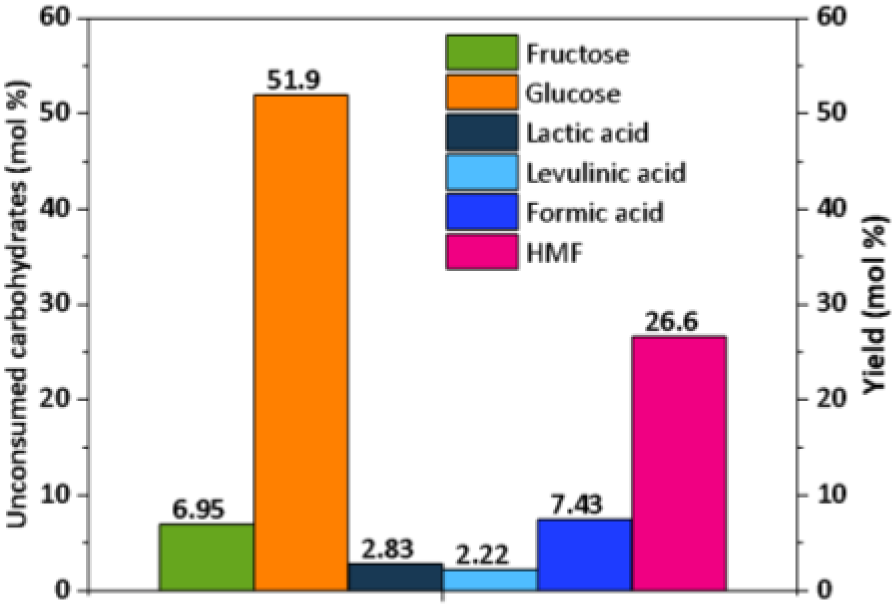

Figure 2. Unconsumed carbohydrates and products obtained from sucrose after 120 min at 200 °C in a microwave reactor, without any added catalyst.

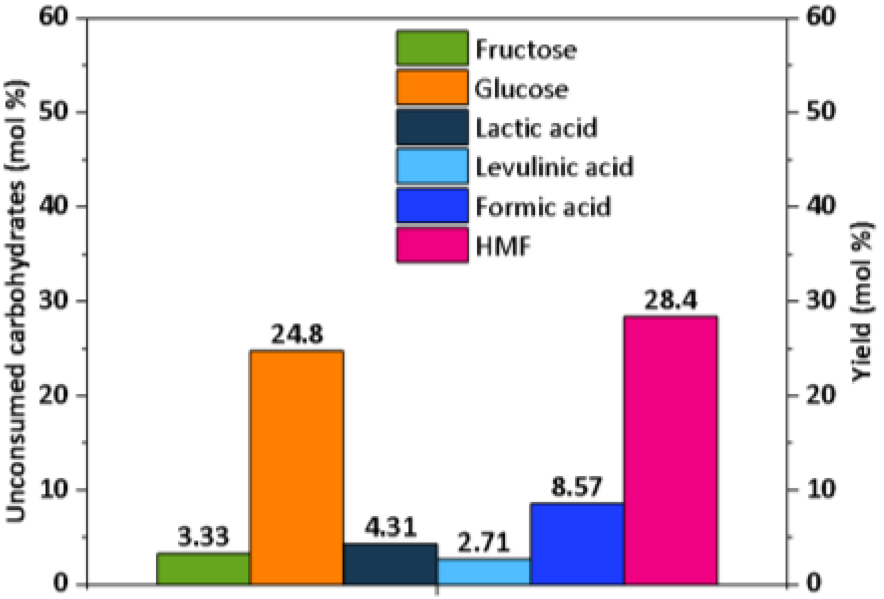

Figure 3. Unconsumed carbohydrates and products obtained from sucrose after 120 min using a 200 °C temperature set-point in a muffle and a Teflon®-coated stainless steel reactor, without any added catalyst.

Influence of temperature in fructose conversion using $Al(NO_3)_3$ as catalyst

The influence of temperature on the catalytic conversion of sucrose was evaluated using $Al(NO_3)_3 \cdot 9H_2O$ in a microwave reactor for 90 min at 170, 180, 190, 200 and 215 °C. **Figure 4** shows the product yields obtained from sucrose at different reaction temperatures.

The use of different temperatures in microwave heating shows that the retro-aldol (**Figure 1**) scheme prevails over dehydration in the lower temperature range, forming more lactic acid than any other reaction product. At temperatures higher than 180 °C, the yield of lactic acid decreases and that of levulinic acid increases, meaning that dehydration becomes the predominant reaction scheme (**Figure 1**). An atypical fact observed for this carbohydrate was the reappearance of fructose in the reaction medium at 200 °C, which had already been consumed at lower temperatures. This result suggests a possible analytical error due to the coelution of some yet unidentified reaction component. According to Choudhary, Mushrif, Ho, Anderko, Nikolakis, Marinkovic, Frenkel, Sandler, and Vlachos (2013), the selectivity to 5-HMF in fructose dehydration increases with increasing temperature, indicating that the apparent activation energy associated with the formation of 5-HMF from fructose is higher compared to parallel reactions such as the retro-aldol conversion to lactic acid. The presence of glucose decreased with increasing reaction temperatures, with formic and levulinic acids gradually becoming the main reaction products.

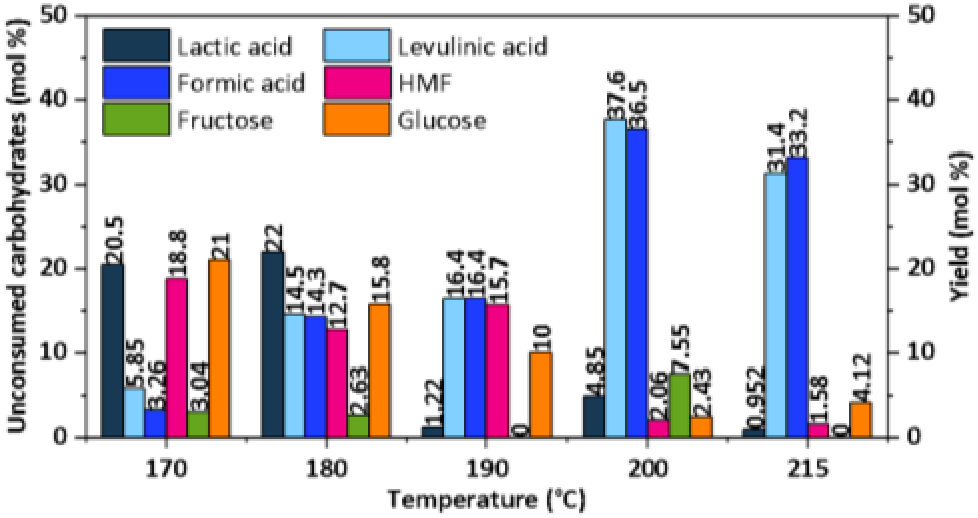

Figure 4. Conversion of sucrose in microwave heating using $Al(NO_3)_3$ as catalysts in different temperatures.

Comparison between gradual heating in conventional and microwave

The reaction systems used have different heating regimes. **Figure 5** shows that the microwave reactor reaches the desired temperature (200 °C) in 2 min, while the muffle furnace needs 90 min to gradually reach the same temperature, which was maintained unaltered until 120 min (isothermal reaction). To compare the effect of these two heating systems on reaction performance, the muffle furnace heating regime was simulated in the microwave reactor. For this, the temperature was increased manually at every 4 min to mimic the heating behavior of the muffle furnace (**Figure 5**). **Figure 6** compares the results obtained for sucrose conversion when reactions were carried out with gradual (in the muffle furnace using a Teflon®-lined stainless steel reactor) and fast (in a microwave reactor using a sealed glass tube reactor) heating regimes. The main product for the reaction carried out in the oven with gradual heating was lactic acid (65%), meaning that the retro-aldol prevailed under these experimental conditions (Holm, 2010). The same product profile was also observed for reactions carried out in a microwave reactor in which gradual heating was applied, but the lactic acid yield was much lower (48 %). Nevertheless, the gradual heating favored the retro-aldol mechanism as observed under conventional heating. Lewis acids promote the retro-aldol reaction, but exposure to higher temperatures for long reaction times changed the product profile in favor of dehydration. In this case, the main reaction products were levulinic and formic acids, formed by rehydration of 5-HMF in yields corresponding to 33.5 and 38.5%, respectively. Dehydration reactions are promoted by Brønsted-Lowry acid, and these acids come from the degradation of the Lewis acid at higher temperatures forming nitric acid and an aluminum aquo complex as demonstrated by Gomes, Rampon and Ramos (2017) using $AlCl_3·6H_2O$.

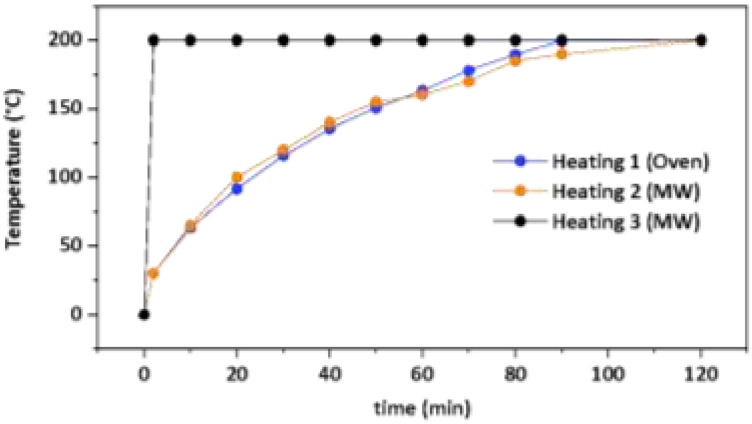

Figure 5. Temperature profile in the microwave reactor applying direct (fast) and stepwise (gradual) heating, compared to the heating profile of the muffle oven.

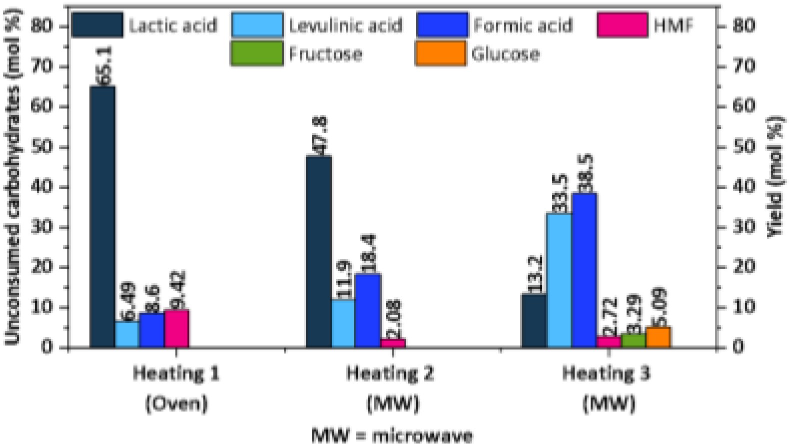

Figure 6. Products obtained in the conversion of sucrose carried out in the presence of $Al(NO_3)_3·9H_2O$ in three different heating regimes.

CONCLUSION

Lactic, levulinic and formic acids, and 5-HMF were produced from sucrose in aqueous medium in the presence of $Al(NO_3)_3$ using two heating systems: conventional heating in a muffle using Teflon®-lined stainless steel reactors and by microwave irradiation in a microwave reactor using sealed glass tubes. The use of catalysts is necessary for such reactions, since the yields of the products of interest were low in the absence of a catalyst.

When heating systems were compared, lactic acid production predominated for reactions carried out under conventional heating (muffle oven), with the best yield being 67 mol %. The results obtained for the microwave reactor can be divided into two parts: when the setpoint temperature was reached in a short time (2 min) and when temperature was raised gradually to mimic the heating regime of the muffle furnace. In the first case, the best lactic acid yield was 13 mol %. However, when the setpoint temperature (200 °C) was reached stepwise in the microwave reactor, the lactic acid yield was raised up to 48 mol %.

Regarding the catalyst used in this study, $Al(NO_3)_3$ are accessible and less toxic than other catalytic systems described in the literature, such as erbium-based catalysts (Lei, Wang, Liu, Yang and Dong, 2014). Furthermore, lactic acid was obtained in the absence of agitation, external pressure, or inert atmosphere. Taking these facts into account, the results obtained with $Al(NO_3)_3$ can be considered quite promising.

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