Conversion of Carbohydrates to Organic Acids in Aqueous Medium Using Aluminum Nitrate as the Catalyst Precursor

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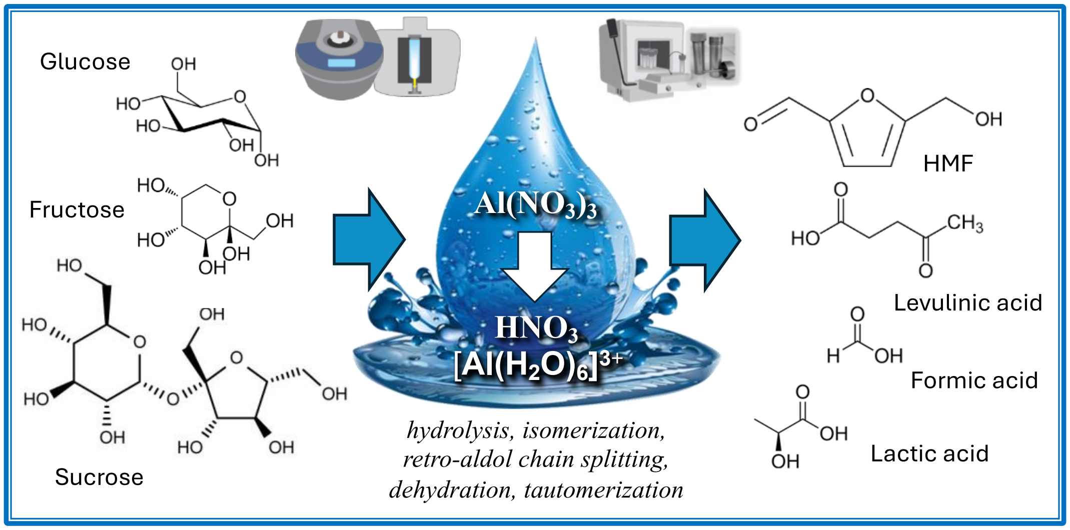
GRAPHICAL ABSTRACT



Conversion of Carbohydrates to Organic Acids in the presence of Aluminum Nitrate in Aqueous Medium

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Fructose, glucose, and sucrose were converted to organic acids in the presence of aqueous aluminum nitrate ($Al(NO_3)_3$) to develop a technically viable route for upgrading sugarcane molasses. Reactions were carried out in a microwave reactor and a muffle oven with conventional heating (convective heat transfer) using a sealed glass tubes and a hydrothermal stainless-steel autoclave as reaction vessels, respectively. Conversion was evaluated for different reaction times and temperatures. Lactic acid predominated as the product from the retro-aldol chain splitting of fructose, reaching a 67.5 % molar yield using 2.67 $mmol \cdot L^{-1}$ $Al(NO_3)_3$ (4 wt% based on the carbohydrate dry mass) in a stainless-steel reactor with conventional heating. Sucrose required hydrolysis, glucose isomerization, retro-aldol chain splitting, dehydration, tautomerization, and 1,2-H migration to produce lactic acid in molar yields approaching those obtained from fructose (65.5 %). Besides lactic acid, formic and levulinic acids were produced in variable amounts through a fructose dehydration pathway, having 5-(hydroxymethyl)-furfural (HMF) as reaction intermediate. The use of a stepwise heating regime was a critical parameter to achieve high product yields and good lactic acid selectivity in these reaction systems.

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INTRODUCTION

The biorefinery converts renewable feedstocks to biofuels, bioenergy, sustainable platform chemicals, and value-added biobased materials, and this can play a major role in sustainable process development (Takkellapati *et al*. 2018). Biorefineries have two strategic goals: the energy goal of replacing petroleum derivatives in favor of widely available sustainable (preferably renewable) raw materials, and the economic goal of establishing a strong biobased industry to support the upcoming transition to a low-carbon bioeconomy (Bozell and Petersen 2010; Igbokwe *et al*. 2022). Among a range of valuable biorefinery products, organic acids represent an important market share of technically viable carbohydrate derivatives. Nearly two-thirds of biobased building blocks are made of organic acids, showing the importance of these chemicals to improve the sustainability footprint of our chemical industry (Serrano-Ruiz *et al*. 2010).

Lactic and levulinic acids are some of the biomass-derived chemicals with the greatest economic potential (Dutta and Bhat 2021; Li *et al*. 2022). Lactic acid has received great attention due to its use in the synthesis of poly(lactic acid) (PLA), an industrially compostable and biocompatible high molecular mass biopolymer that plays an important role in replacing plastics derived from the petrochemical industry (Djukić-Vuković *et al*. 2019; Megías-Sayago *et al*. 2021). Also, lactic acid can be used in other areas for environmental, ecological, medical, and pharmaceutical applications. For instance, in the latter case, the (*S*) isomer can be used to produce cosmetics, ointments, anti-acne solutions, humectants, and controlled-release medications (Hofvendahl and Hahn-Hägerdal 2000; Ramot *et al*. 2016; Ojo and de Smidt 2023). Levulinic acid can be used as a precursor to produce herbicides such as aminolevulinic acid, pesticides, pharmaceuticals, green solvents, plasticizers, cosmetics, and intermediates (Bozell and Petersen 2010; Bazoti *et al*. 2023).

Sustainable conversion processes preferably based on low-price, widely available catalytic systems have been sought to produce organic acids such as lactic and levulinic acids from water-soluble carbohydrates. For instance, lactic, levulinic, and formic acids have been used as sources to produce glucose, fructose, and sucrose using different homogeneous and heterogeneous Brønsted-Lowry and Lewis acid catalytic systems (Table 1).

Table 1. Examples of Brønsted-Lowry and Lewis Acid Catalysts for the Conversion of Carbohydrates to Levulinic and Lactic Acids

Carbohydrate	Catalyst concentration	T (°C)	Product	Yield (mol %)	Reference
Fructose	3.6-7.2 % HCl	95	Levulinic acid	81	Kuster *et al*. (1977)
Fructose	Zn(SO_4)	300	Lactic acid	86	Bicker *et al.* (2005)
Fructose	50 wt% $ErCl_3$ in relation to fructose	240	Lactic acid	84.8	Lei *et al*. (2014)
Fructose and glucose	2.5 mmol·L^{-1} $VOSO_4$ in N_2 atmosphere	160	Lactic acid	58 and 56, respectively	Tang *et al.* (2014)
Fructose and glucose	18 wt% $AlCl_3$/$SnCl_2$ in relation to fructose	190	Lactic acid	90 and 81, respectively	Deng *et al*. (2018)
Glucose	18.6 mmol·L^{-1} $CrCl_3$ in 0.1 mol·L^{-1} HCl	140	Levulinic acid	46	Choudhary *et al.* (2013)
Glucose	5 % H_2SO_4	170	Levulinic acid	80	Chang *et al*. (2006)
Glucose	10 mmol·L^{-1} $ZnCl_2$/HCl or $AlCl_3$/HCl	180	Levulinic acid	47 and 41, respectively	Gomes *et al*. (2017)
Glucose	5 mmol·L^{-1} $ZnCl_2$, $ZnSO_4$, $CrCl_2$, $CrSO_4$, $AlCl_3$, or $Al_2(SO_4)_3$	140	Lactic acid	25, 25, 22, 25, 30, and 35, respectively	Rasrendra *et al*. (2010)
Glucose	Y-β and Yb-β zeolites	190	Lactic acid	45.3 and 43.6, respectively	Shen *et al.* (2022)
Sucrose	Surface-aminated Sn-β zeolite	190	Lactic acid	58	Kong *et al.* (2018)

Sucrose is extracted from either sugarcane or sugar beet and is available all year-round in the form of molasses, particularly in tropical countries, while glucose and fructose can be found in the form of starch (corn and other starchy syrups) and inulin hydrolysates (agave syrups), respectively. Cellulose may also be a valuable and widely available carbohydrate source for organic acid production, but its high recalcitrancy requires harsher reaction conditions to release glucose in high yields for catalytic conversion (Tang *et al.* 2014; Deng *et al.* 2018; Tallarico *et al.* 2019; Xu *et al*. 2020; Yan *et al*. 2023).

When sucrose is used as the starting reagent, the reaction begins by its hydrolysis to glucose and fructose (Fig. 1). Since hydrolysis depends on the protonation of the glycosidic oxygen, Brønsted-Lowry acids are normally used as catalysts. However, sucrose hydrolyses can take place under mild reaction conditions because fructose is a good leaving group due to its conformational instability. Next, glucose is isomerized to fructose, a step that is accelerated by the presence of a Lewis acid catalyst (Binder and Raines 2009). Then, fructose is converted to organic acids in two different reaction pathways: dehydration to 5-(hydroxymethyl)-furfural (HMF) followed by its rehydration to formic and levulinic acids (Bozell and Petersen 2010; Serrano-Ruiz *et al*. 2010; Osmundsen 2013; Gomes *et al*. 2017), and retro-aldol chain splitting forming glyceraldehyde and dihydroxyacetone (C3 building blocks) in tautomeric equilibrium, followed by glyceraldehyde dehydration to pyruvaldehyde and an 1,2-H migration (intramolecular Canizzaro reaction) to yield lactic acid (Orazov and Davis 2015; Albuquerque *et al*. 2017; Tang *et al*. 2018, 2019). This retro-aldol reaction pathway works best in the presence of a Lewis acid catalyst (Marianou *et al*. 2018; Hossain *et al*. 2021).

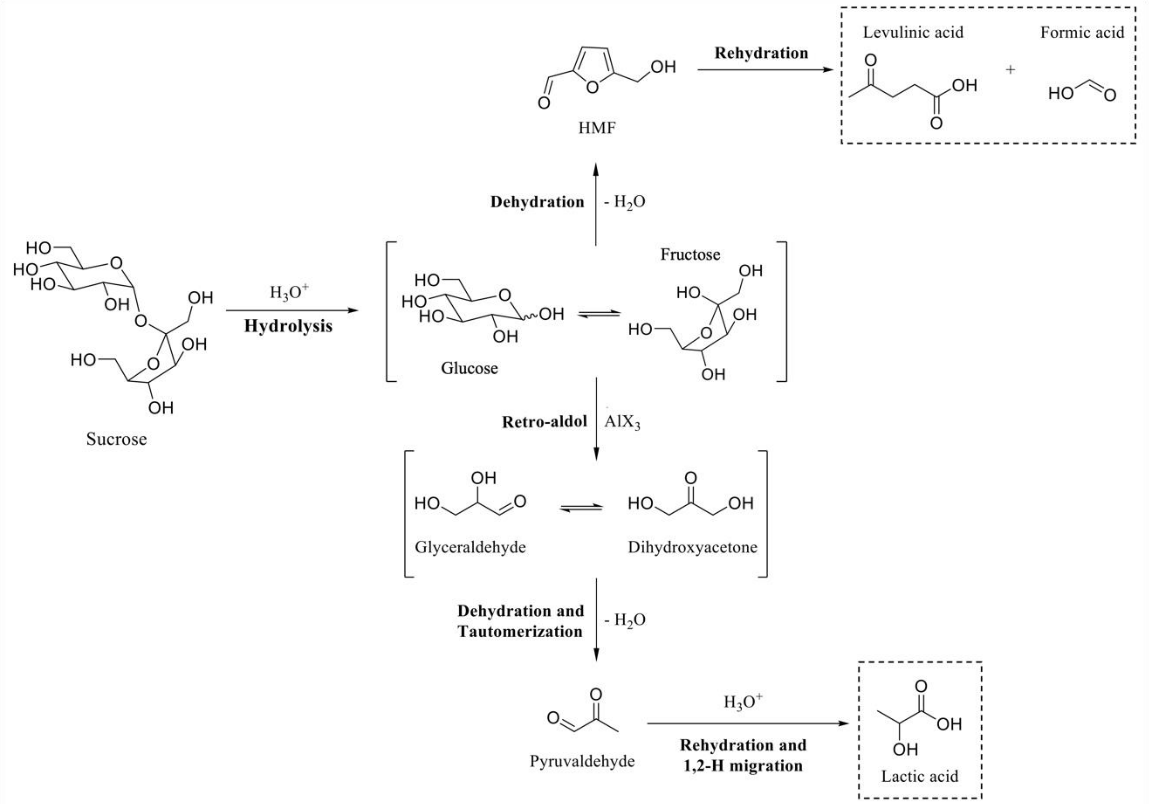

Fig. 1. Proposed steps for sucrose conversion to organic acids

In dehydration, water molecules are eliminated from fructose to form HMF in a mechanism that involves cyclic intermediates or ring opening reactions (Ståhlberg *et al.* 2010). HMF rehydration begins with the breakdown of the furan ring aromaticity and the formation of a carbocation (Osmundsen 2013; Zhang *et al.* 2015). Subsequently, successive steps involving the addition and elimination of water molecules occur until the structure is completely opened. In the final stage of this mechanism, formic acid is eliminated, and levulinic acid is formed in equimolar moieties. In total, two water molecules are incorporated to form levulinic and formic acids (Zhang *et al.* 2015). Such dehydration and rehydration reactions occur at high temperatures in aqueous media even in the absence of an acid catalyst. However, better yields and faster reaction kinetics are obtained in the presence of a strong Brønsted-Lowry acid catalyst (Osmundsen 2013; Zhang *et al*. 2015).

Metal salts of the M_qA_x type, after encountering water, dissociate and immediately hydrate, forming $M(H_2O)_n^{x+}$ species plus hydronium ions (H_3O^+). With this, Brønsted-Lowry acids are formed *in situ*, and their acidity depends on the strength of the anion. Meanwhile, aluminum halides such as $AlCl_3$ dissociate in water forming hydrochloric acid (HCl, pKa = –6.3), $Al_2(SO_4)_3$ and $Al(NO_3)_3$ release sulfuric (H_2SO_4, pKa_1 = –3.0) and nitric acids (HNO_3, pKa = –1.4), respectively. Hence, hexose dehydration depends on the Brønsted-Lowry acid strength released *in situ*. On the other hand, hydrolysis of the aluminum ion can generate numerous mononuclear (*e.g.*, $Al(H_2O)_{n-1}(OH)^{2+}$ and $Al(H_2O)_{n-2}(OH)_2^{1+}$) and polynuclear (*e.g.*, $Al(OH)_2^{4+}$, $Al_2(OH)^{5+}$, and $Al_3(OH)_3^{6+}$) species, whose formation depends on the metal concentration and reaction pH (Akitt 1989). At pH close to 3, hydrolysis of the aluminum ion mainly generates the mononuclear hexaaquo aluminum(III) species $[Al(H_2O)_6]^{3+}$. As the pH rises, species such as $[Al(OH)(H_2O)_5]^{2+}$, $[Al(OH)_2(H_2O)_4]^+$ and $Al(OH)_3$ are formed, as well as polynuclear species (Baes and Mesmer 1976). However, $Al(OH)_3$ flocculates because it is moderately soluble in water and, depending on the pH and Al^{3+} concentration, side reactions may occur, generating less stable polymeric and colloidal species (Martell and Motekaitis 1992). Among the abovementioned species, the $M(H_2O)_n^{x+}$ ion has the greatest Lewis acid character, presenting a hydrolysis constant K equal to 1.1 ($K_{1.1}$). The $pK_{1.1}$ value of Al^{3+} varies between 4.9 and 5.5 (Richens 1997; Akitt 1989).

According to Fang *et al.* (2023), the Lewis acid strength is not the only factor influencing carbohydrate conversion to lactic acid, but also the formation of intermediate complexes with metal cations derived from homogeneous catalysts. It has been hypothesized that small cationic radii favor the binding capacity of metal ions and fructose hydroxyl groups, facilitating the cleavage of carbon bonds and splitting the molecule to form lactic acid.

Hossain *et al*. (2021) hypothesized that cationic hydroxyl-aluminum complexes formed *in situ*, with the general formula $[Al(OH)_h]^{(3-h)+}$, are the actual catalytic species in reactions involving aluminum salts due to their strong Lewis acid character. For instance, $[Al(OH)_h]^{(3-h)+}$ were critical for the conversion of dihydroxyacetone to lactic acid *via* pyruvaldehyde in aqueous medium.

In this work, fructose, glucose, and sucrose were converted to organic acids in the presence of $Al(NO_3)_3$ in aqueous media under both conventional (convective) and microwave heating systems. Both retro-aldol chain splitting and dehydration pathways were evaluated in the presence and absence of a catalyst or a catalyst precursor under different temperatures, reaction times, and heating regimes. The working hypothesis was that, compared to other aluminum-based Lewis acids such as $AlCl_3$ and $Al(NO_3)_3$ would be more selective for lactic acid production through the retro-aldol chain splitting pathway. In addition, the use of microwave heating would accelerate the reaction kinetics without interfering with the reaction mechanism (Szabolcs *et al.* 2013).

EXPERIMENTAL

Materials

Fructose, glucose, sucrose, furfural (99 %), acetic acid (>99.7 %), levulinic acid (99 %), lactic acid (99 %), HMF (99 %), and $Al(NO_3)_3{\cdot}9H_2O$ were obtained from Sigma-Aldrich Brazil (Jurubatuba, SP, Brazil). Other reagents and organic solvents were purchased from local suppliers in analytical and chromatographic or spectrometric grade, respectively. All chemicals were used as received without any further treatment.

Methods

Thermal conversion

The thermal conversion of fructose (66.7 $mmol{\cdot}L^{-1}$), glucose (66.7 $mmol{\cdot}L^{-1}$), and sucrose (33.2 $mmol{\cdot}L^{-1}$) was assessed in a CEM microwave reactor (North Carolina, US) using a 10 mL sealed glass tube and a series of 50 mL hydrothermal stainless-steel autoclaves with a removable inner polytetrafluoroethylene (PTFE) chamber (SS-PTFE reactor) that were placed inside a muffle oven. Reactions were performed at 200 °C for 120 min and product analyses were carried out by HPLC at 65 °C using H_2SO_4 8 $mmol{\cdot}L^{-1}$ as the mobile phase as described below.

Effect of gradual heating on carbohydrate conversion using $Al(NO_3)_3{\cdot}9H_2O$

Dehydration of carbohydrates in aqueous media was carried out in the presence of 2.67 $mmol{\cdot}L^{-1}$ $Al(NO_3)_3{\cdot}9H_2O$ as the catalyst precursor, which initially corresponded to 4 wt % based on the carbohydrate dry mass. Experiments were performed with fructose, glucose (both at 66.7 $mmol{\cdot}L^{-1}$), and sucrose (33.2 $mmol{\cdot}L^{-1}$) using the CEM microwave reactor (MWR) and the SS-PTFE reactor described above. In the latter situation, heating was based on convective heat transfer, and the temperature profile was determined outside and inside one of the SS-PTFE reactors using a thermocouple. The reaction time was 120 min in both systems. However, the MWR took only 2 min to reach the setpoint temperature of 200 °C, whereas the heating time for the SS-PTFE lasted approximately 90 min. For this reason, one additional experiment was carried out in which the temperature was increased manually in the MWR to simulate the heating ramp of the muffle oven. Once the proposed reaction time was reached, the reaction vessels were cooled down to ambient temperature and aliquots were withdrawn, diluted with ultrapure water to approach 3 $mg{\cdot}mL^{-1}$ in relation to theoretical yields, filtered to pass a 0.45 μm PTFE syringe filter, and analyzed by high performance liquid chromatography (HPLC). Reaction yields were calculated based on the stoichiometric amount of each product (see below for details). When the reaction was carried out in duplicates, the results were reported as the mean value with the corresponding experimental error.

Influence of time on reaction conversion in the presence of $Al(NO_3)_3$

The influence of reaction time on carbohydrate conversion was investigated in the SS-PTFE reactor and in sealed glass tubes heated by microwave irradiation using 2.67 $mmol{\cdot}L^{-1}$ of the catalyst precursor. Fructose, glucose, and sucrose concentrations were the same as used previously and all reactions were carried out at 180 °C for 5 to 90 min in the microwave oven. The SS-PTFE reaction system was only used for fructose and the reaction times ranged from 30 to 240 min.

Kinetic study

Kinetic studies were performed using the two first-order equations (Eqs. 1 and 2) to adjust the reaction profiles,

$$C_t^A = \left(C_0^A - C_{inf}^A\right) \times e^{\left(-k_{obs}^A t\right)} + C_{inf}^A \tag{1}$$

$$C_t^B = \left(C_{0(1)}^B - C_{\mathrm{inf}(1)}^B\right) \times e^{\left(-k_{obs(1)}^A t\right)} + C_{\mathrm{inf}(1)}^B - \left(C_{\mathrm{inf}(2)}^B - C_{0(2)}^B\right) \times (e^{\left(-k_{obs(2)}^B t\right)} - 1) + C_{0(2)}^B \tag{2}$$

where C_t is the product concentration at a given reaction time, C_0 is the initial reagent concentration, C_{inf} is the infinite concentration, k_{obs} is the observed rate constant for pseudo-first order reactions, and *t* is the reaction time. Equation 1 was used for reagent consumption, while Eq. 2 was used for products that behave as intermediates (*e.g.*, HMF is produced by dehydration and later converted to formic and levulinic acids). For this reason, both C_0 and C_{inf} values are duplicated in Eq. 2, indicating two reaction stages: subscript 1 for product formation and subscript 2 for product consumption. Data were processed with the OriginPro 2018 software (version 95E).

Chromatographic analysis

Carbohydrate and organic acid analyses were carried out by HPLC using a Shimadzu (Kyoto, Japan) LC-20AD HPLC workstation equipped with a SIL-10AF autosampler and two detection systems: differential refractometry (Shimadzu RID-10A) and diode array detector for UV spectrophotometry (Shimadzu SPD-M10AVP). The chromatographic column was an Hi-Plex-H (Agilent, 300 × 7.7 mm; 8 mm) 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 calibration curves ($R^2 > 0.99$) ranging from 0.1 to 3.0 mg·L^{-1} for the following analytes: fructose, glucose, sucrose, HMF, furfural, lactic and, levulinic acid, acetic acid, and formic acid. Carbohydrates and organic acids were quantified by differential refractometry (RID-10A, Appendix Fig. S1), while furan compounds were monitored by UV spectrophotometry at the 280 nm wavelength (SPD-M10AVP). In some cases, the HPLC oven was turned off and analyses were carried out at ambient temperature (around 25 °C) to prevent sucrose hydrolysis. For this, reactions were carried out with sucrose (33.2 mmol·L^{-1}) under microwave heating without adding an exogenous acid catalyst for 90 min at 180 °C (thermal treatment). Then, reaction aliquots were taken and analyzed by HPLC. In addition, standard solutions containing sucrose, and a mixture of sucrose, glucose, and fructose were also analyzed for comparison. Organic acids and HMF yields were calculated with respect to their corresponding theoretical yield, which was based on the stoichiometric amount that could have been produced from the total carbohydrate content of the starting material. Equations 3 and 4 show how HMF and organic acid yields were calculated from carbohydrates (fructose, glucose, and sucrose),

$$\mathrm{HMF(mol\ \%)} = \frac{\mathrm{HMF_{exp}(g)}}{m_{\mathrm{Carb}}\mathrm{(g)} \times \mathrm{SF}} \times 100 \tag{3}$$

$$\mathrm{OrgAc(mol\ \%)} = \frac{\mathrm{OrgAc_{exp}(g)}}{m_{\mathrm{Carb}}\mathrm{(g)} \times \mathrm{SF}} \times 100 \tag{4}$$

where $\mathrm{HMF_{exp}}$ and $\mathrm{OrgAc_{exp}}$ are the amounts of HMF or organic acid that were determined experimentally, m_{Carb} is the initial mass of fructose, glucose or sucrose, and SF is the stoichiometric factor of carbohydrates conversion into HMF, levulinic, formic, and lactic acids (0.70, 0.64, 0.25, and 0.50, respectively). These factors were determined by dividing the molar mass of the analyte by the molar mass of the carbohydrate used for conversion.

RESULTS AND DISCUSSION

Sucrose Analytical Stability

Sucrose undergoes hydrolysis under relatively mild acidic conditions (Steinbach *et al*. 2018). Since reaction aliquots were analyzed by HPLC at 65 °C using a cation-exchange resin as the stationary phase and H_2SO_4 8 mmol·L^{-1} as the mobile phase, it was important to demonstrate that glucose and fructose release in the reaction medium was not due to acid hydrolysis during HPLC analysis, a behavior that was observed already in the authors' earlier studies (data not shown). This was resolved by performing HPLC of a sucrose standard solution at ambient temperature (25 °C), using otherwise identical analytical conditions. The blue line in Fig. 2 demonstrates that sucrose remained stable, since glucose and fructose were not detectable in the HPLC profile. Then, sucrose (33.2 mmol·L^{-1}) was thermally treated in the MWR at 180 °C for 90 min, and the product was subjected to the same analytical procedure. The red line in Fig. 2 shows that sucrose was almost completely hydrolyzed even in the absence of any reaction catalyst (that is, under thermal conversion). Hence, as observed later in this research, the absence of sucrose in the reaction products could not be attributed to hydrolysis during HPLC, using a mild acid mobile phase. This condition had to be used because it delivered the best resolution among sugars, furans, and organic acids, allowing for a more accurate qualitative and quantitative analyses of reaction products (see Fig. S1 in the Appendix).

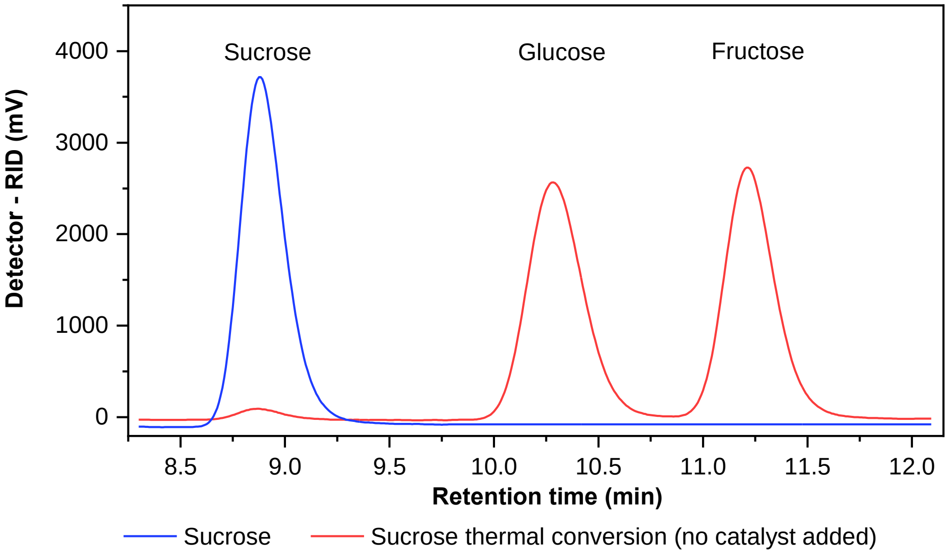

Fig. 2. HPLC analysis of sucrose at ambient temperature before and after thermal treatment at 180 °C for 90 min under microwave irradiation

Thermal Conversion

The thermal conversion of fructose (66.7 mmol·L^{-1}), glucose (66.7 mmol·L^{-1}), and sucrose (33.2 mmol·L^{-1}) was assessed in the MWR at 200 °C for 120 min, and the results are shown in Table 2. As expected, sucrose was not detected in any of the reaction products because it was hydrolyzed to fructose and glucose. Fructose, either pure or released by hydrolysis, was almost completely consumed during the heat treatment, while glucose remained partially unconverted in the reaction medium. Sucrose generated 26.61 mol % HMF by hydrolysis and dehydration, while HMF acid catalyzed rehydration released 7.43

mol % formic acid and 2.22 mol % levulinic acid. Also, the retro-aldol/1,2-H migration pathway yielded 2.83 mol % lactic acid from sucrose.

Table 2. Conversion, Product Yields, and Selectivities for the Thermal Treatment of Fructose, Glucose, and Sucrose *

Parameter	Fructose		Glucose		Sucrose	
	MW	SS-PTFE	MW	SS-PTFE	MW	SS-PTFE
Conversion (mol %)	98.41	100	46.23	93.98	100	100
Carbohydrates remaining (mol %)						
Fructose	1.59	n.d.	4.16	n.d.	6.95	3.33
Glucose	1.89	n.d.	53.77	6.02	51.91	24.76
Product yields (mol %)						
Lactic acid	2.64	4.01	2.21	2.02	2.83	4.31
Levulinic Acid	6.97	7.86	n.d.	1.94	2.22	2.71
Formic acid	13.44	12.39	n.d.	n.d.	7.43	8.57
HMF	36.12	20.21	19.12	14.27	26.61	28.38
Selectivity (%)						
Lactic acid	4.32	9.02	8.67	11.04	2.89	5.98
Levulinic Acid	11.42	17.67	n.d.	10.60	2.26	3.76
Formic acid	22.01	27.86	n.d.	n.d.	7.58	11.89
HMF	59.15	45.45	75.01	78.36	27.17	39.38
Fructose	-	-	3.10	n.d.	7.10	4.62
Glucose	16.32	n.d.	-	-	53.01	34.36

n.d., not detected; * Reactions were carried out for 120 min under microwave (MW) irradiation and in a SS-PTFE reactor system using a setpoint temperature of 200 °C.

The same reaction control was also carried out in the SS-PTFE reaction system, in which the setpoint temperature was 200 °C. Compared to MWR, both glucose and fructose were more extensively consumed, generating slightly higher yields of the three organic acids mentioned above. However, carbohydrate conversion to organic acids remained relatively low, justifying the need for addition of an exogenous acid catalyst. Also, the thermal treatment turned the reaction medium darker as time went by, showing that carbohydrates were gradually lost to side reaction forming humins. Such dark water-insoluble polymeric materials are known to arise from condensation reactions involving dehydration co-products such as furan compounds and organic acids (Deng *et al*. 2018).

Influence of Temperature on Carbohydrate Conversion

The influence of temperature on carbohydrate conversion using $Al(NO_3)_3$ as the catalyst precursor was investigated using MWR at 170, 180, 190, 200, and 215 °C for a fixed reaction time of 90 min. Table 3 shows the yield of products derived from fructose at different reaction temperatures, while Fig. 3 provides the HPLC profile of MWR reaction products at 180 °C using the Agilent Hi-Plex-H column and detection by differential refractometry.

At 170 °C, fructose was not completely consumed, with 25.9% remaining unreacted in the reaction medium (Table 3). At 180 °C, the selectivity for retro-aldol increased, resulting in the identification of at least one reaction intermediate (glyceraldehyde) and increased lactic acid yields (Fig. 3). However, at temperatures above 190 °C, the dehydration pathway was favored, with HMF acting as a reaction intermediate to produce levulinic and formic acids in almost equivalent molar yields. According to Choudhary *et al*. (2013), the selectivity for fructose dehydration increases with increasing reaction temperatures, indicating that the apparent activation energy for HMF formation is higher than that of the retro-aldol pathway. In addition, once produced, HMF was rapidly consumed due to its high reactivity and thermal instability (Lei *et al*. 2014). The presence of glucose was also observed in all reaction temperatures, and this was a result of the glucose/fructose isomerization equilibrium under the applied experimental conditions.

Table 3. Fructose Conversion at Different Temperatures for 90 min Using Microwave Heating and 2.67 mmol·L^{-1} $Al(NO_3)_3 \cdot 9H_2O$

Parameter	Set-point Temperature (°C)				
	170	180	190	200	215
Conversion (mol %)	74.1	98.4	100	100	100
Products yields (mol %)					
Lactic acid	29.2	36.6	23.6	18.2	15.8
Levulinic Acid	5.84	12.8	34.6	34.3	31.5
Formic acid	2.17	12.1	35.2	31.9	27.4
HMF	20.8	14.4	2.11	1.92	2.21
Glucose	1.80	2.18	0.70	n.d.	n.d.
Selectivity (%)					
Lactic acid	48.8	46.9	24.5	21.1	20.5
Levulinic Acid	9.75	16.4	35.9	39.7	40.9
Formic acid	3.62	15.5	36.6	36.9	35.7
HMF	34.8	18.4	2.19	2.22	2.87
Glucose	3.00	2.79	0.73	n.d.	n.d.

n.d., not detected.

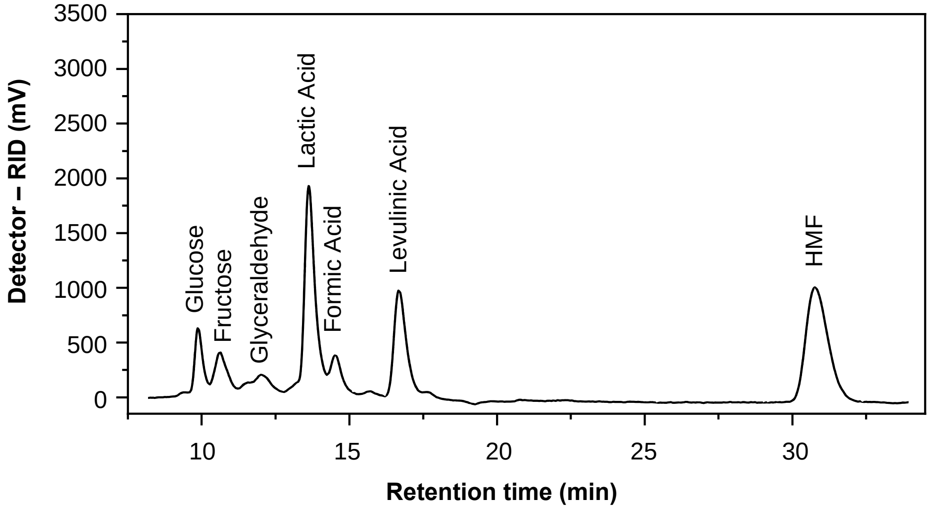

Fig. 3. HPLC analysis of MWR reaction products using the Agilent Hi-Plex-H chromatographic column at 65 °C, 8 mmol·L^{-1} H_2SO_4 as the mobile phase, and detection by differential refractometry. Reactions were carried out for 90 min at 180 °C using $Al(NO_3)_3$ as the catalysts precursor.

Bicker *et al.* (2005) studied the conversion of fructose in stainless steel tube reactors at 260 °C using $Zn(SO_4)$ as catalyst. Fructose was almost completely consumed in 140 s, yielding lactic acid as the main reaction product, followed by HMF in much lower yields. Glucose formation by fructose isomerization was also observed, along with the release of reaction intermediates such as glyceraldehyde, dihydroxyketone, and pyruvaldehyde. Hence, the retro-aldol mechanism prevailed over dehydration, probably due to the use of high temperatures and short reaction times. Also, it seems that HMF rehydration did not occur because both levulinic and formic acids formation was not reported.

Choudhary *et al.* (2013) studied the kinetics of fructose conversion in thick-walled glass vials using conventional heating in an oil bath and $CrCl_3$ as catalyst at 140 °C. Fructose conversion was complete after 160 min, but no lactic acid was formed, meaning that the reaction pathway was dominated by dehydration to HMF followed by rehydration to levulinic and formic acids. Fructose isomerization was also observed in this reaction system forming glucose and mannose in equimolar amounts.

The same trend was observed for glucose conversion at different temperatures (Table 4). However, glucose was not completely consumed in any of the applied reaction temperatures. While the highest temperatures (*e.g.*, 215 °C) led to the best levulinic and formic acids yields from glucose, fructose required lower temperatures (190 °C) to produce these organic acids predominantly. Incomplete conversion and low reaction yield from glucose demonstrate the greater stability of its pyranosidic ring compared to the furanosidic ring of fructose (Zhang *et al*. 2015). For this same reason, glucose must undergo isomerization to fructose prior to its dehydration to HMF (Rasmussen *et al*. 2014) or retro-aldol conversion to lactic acid (Marianou *et al*. 2018).

Table 4. Glucose Conversion at Different Temperatures for 90 min using Microwave Heating and 2.67 mmol·L^{-1} $Al(NO_3)_3 \cdot 9H_2O$

Parameter	Set-point Temperature (°C)				
	170	180	190	200	215
Conversion (mol %)	60.0	75.8	79.9	84.9	91.7
Products yield (mol %)					
Lactic acid	8.87	8.36	0.69	0.13	0.40
Levulinic Acid	1.16	9.04	10.4	31.9	35.1
Formic acid	13.1	9.91	13.4	31.4	37.1
HMF	16.7	16.9	18.1	4.42	n.d.
Fructose	5.82	2.41	0.98	n.d.	0.93
Selectivity (%)					
Lactic acid	19.4	17.9	1.58	0.18	0.54
Levulinic Acid	2.53	19.4	23.7	47.1	47.8
Formic acid	28.7	21.3	30.8	46.3	50.4
HMF	36.6	36.2	41.6	6.51	n.d.
Fructose	12.8	5.18	2.25	n.d.	1.26

n.d., not detected.

Table 5 shows the effect of temperature on sucrose conversion. The observed trends in product formation were very similar to that of fructose (Table 3), except for the presence of glucose from sucrose hydrolysis. The two main reaction pathways competed at the lowest temperature range (170 to 180 °C), with lactic acid being the main reaction product at yields lower than those obtained directly from fructose. HMF and its rehydration derivatives (formic and levulinic acids) became predominant at 190 °C, while the selectivity for the latter increased considerably at temperatures above 200 °C. Once again, this was expected because HMF is thermally unstable, and its gradual disappearance is related to its rehydration to formic and levulinic acids (Fig. 1) (Lei *et al*. 2014). Hence, HMF is rapidly formed and gradually consumed during the reaction course to produce organic acids plus water-insoluble humins. Glucose remained present in the reaction mixture even at the highest reaction temperature, while fructose was almost completely consumed as already observed in Table 3.

Table 5. Sucrose Conversion at Different Temperatures for 90 min Using Microwave Heating and 2.67 mmol·L^{-1} $Al(NO_3)_3·9H_2O$

Parameter	Set-point Temperature (°C)				
	170	180	190	200	215
Conversion (mol %)	100	100	100	100	100
Products yield (mol %)					
Lactic acid	20.4	21.6	4.22	1.85	0.95
Levulinic Acid	5.85	14.5	16.4	37.6	31.4
Formic acid	3.26	14.3	16.4	36.5	33.2
HMF	18.8	12.7	15.7	2.06	1.58
Fructose	3.04	2.63	n.d.	n.d.	n.d.
Glucose	21.1	15.7	10.1	2.43	4.11
Selectivity (%)					
Lactic acid	28.2	26.5	6.72	2.31	1.34
Levulinic Acid	8.06	17.8	26.1	46.7	44.1
Formic acid	4.51	17.5	26.1	45.3	46.6
HMF	25.9	15.6	25.1	2.56	2.21
Fructose	4.19	3.23	n.d.	n.d.	n.d.
Glucose	29.1	19.3	16.1	3.02	5.81

n.d., not detected.

It was observed in other studies that the use of higher temperatures (200 to 220 °C) under microwave irradiation produces good lactic acid yields from fructose and glucose in the presence of a Lewis acid catalyst (Zhang *et al*. 2015). The use of Brønsted acids, in combination or not with Lewis acids, led to the production of 49 mol % levulinic acid at 170 °C for 30 min using the same reaction system (Kumar *et al*. 2015). This is aligned to the fact that $Al(NO_3)_3$ dissociates in aqueous medium, releasing HNO_3, particularly at high temperatures, with the catalytic conversion becoming primarily governed by its Brønsted acidity (Fringuelli *et al*. 2001). Also, this would explain why, compared to lactic acid, levulinic and formic acids were produced in higher yields when reactions were carried out above this temperature setpoint.

Considering that 5 mL of 2.67 mmol·L^{-1} $Al(NO_3)_3·9H_2O$ contain 1.33×10^{-5} mmol of the Lewis acid, and that 4×10^{-5} mmol HNO_3 (1:3 stoichiometry) are released in the reaction medium when $Al(NO_3)_3$ is dissociated in water, enough Brønsted acid strength would be available to direct the reaction mechanism to fructose dehydration. To check this hypothesis, fructose was exposed to $4·10^{-5}$ mmol HNO_3 (8.01 mmol·L^{-1}) for 90 min at 180 °C under microwave irradiation (MWR) and products were analyzed by HPLC (Table 6). Indeed, HMF and its rehydration co-products (formic and levulinic acids) predominated in the reaction mixture, while lactic acid was produced in much lower quantities. Also, for reaction carried out with 2.67 mmol·L^{-1} $Al(NO_3)_3·9H_2O$, the medium pH dropped from 3.8 to 2.0 after 90 min.

The decrease in pH was due to the release of Brønsted-Lowry and Lewis acids from the catalyst precursor, in addition to the formation of organic acids during the reaction course. The former contributed to hexose dehydration to 5-HMF and its subsequent conversion to levulinic and formic acids, whereas the latter catalysed the retro-aldol reaction pathway. Also, the built up of organic acids in the reaction medium boosted the Brønsted-Lowry acidity, favoring dehydration as opposed to retro-aldol chain splitting.

In general, temperatures around 180 °C were best for lactic acid formation, while formic and levulinic acids predominated at temperatures above 200 °C. Fructose provided the best selectivity for lactic acid, whereas glucose and sucrose resulted in high selectivities for formic and levulinic acids. In all cases, HMF behaved as a reaction intermediate.

Table 6. Products Obtained in Aqueous Media from Fructose after 90 min at 180 °C in a Microwave Reactor and SS-PTFE, in the Presence of 8.01 mmol·L^{-1} HNO_3

Parameter	Fructose	
	MW	SS-PTFE
Conversion (mol %)	97.5	100
Product yield (mol %)		
Lactic acid	2.31	6.23
Levulinic Acid	21.4	38.2
Formic acid	24.8	39.2
HMF	6.21	1.76
Selectivity (%)		
Lactic acid	4.21	7.28
Levulinic Acid	39.1	44.7
Formic acid	45.3	45.9
HMF	11.3	2.06

n.d., not detected.

Kong *et al.* (2018) produced lower lactic acid yields (58%) from sucrose in the presence of a surface-aminated Sn-Beta Lewis acid catalyst. The reactions were also carried out in Teflon-lined stainless-steel reactors at 190 °C for 4 h. However, some catalytic systems described in the literature showed lactic acid yields higher than those described in the present work. Lei *et al*. (2014) reached 84.8% lactic acid from fructose in the presence of $ErCl_3$ using conventional heating. However, the percentage of catalyst used was 50 wt% in relation to the carbohydrate mass and the reaction occurred under a 2.0 MPa N_2 atmosphere and stirring at 600 rpm. Deng *et al*. (2018) achieved lactic acid yields close to 90% from fructose using 18 wt% $AlCl_3/SnCl_2$ in relation to the carbohydrate mass. The reaction also had to be carried out under N_2 atmosphere at 2.0 MPa. In relation to the catalyst precursor used in this study, $Al(NO_3)_3$ is much more accessible, inexpensive, and less toxic than other catalytic systems described in the literature, such as erbium-based catalysts. Furthermore, lactic acid was obtained in the absence of agitation, external pressure or inert atmosphere, using a maximum of 4% of catalyst in relation to the carbohydrate mass. Taking these facts into consideration, the results obtained in this work can be considered quite promising.

Influence of time on reaction conversion using $Al(NO_3)_3$ and microwave heating

Fig. 4 shows the results obtained from fructose at different reaction times (5 to 90 min) at 180 °C, under microwave irradiation. Fructose consumption (>95 %) levelled off after 25 to 30 min, and so did the concentration of lactic acid in the reaction medium. The lactic acid yield in 35 min was 37.6 mol % and, from this point on, its concentration showed no significant variation over time. Levulinic and formic acids were formed in lower yields, but their concentration increased continuously, reaching 12 mol % in 90 min.

Glucose conversion in the presence of $Al(NO_3)_3{\cdot}9H_2O$ is shown in Fig. 5 as a function of time. Lactic acid yields increased over time and reached its maximum (8.4 mol

%) in 90 min, although the system may have come to a *quasi*-equilibrium in 25 to 30 min. HMF prevailed as the main reaction product, indicating that dehydration was the preferred reaction mechanism, particularly at short reaction times. By contrast, the kinetics of levulinic and formic acids formation from HMF was almost linear, with both reaching yields around 8 mol % in 90 min. Once again, incomplete conversions and lower reaction yields from glucose demonstrated its higher stability over fructose and that glucose must isomerize to fructose prior to both reaction pathways described in Fig. 1 (Zhang *et al.* 2015).

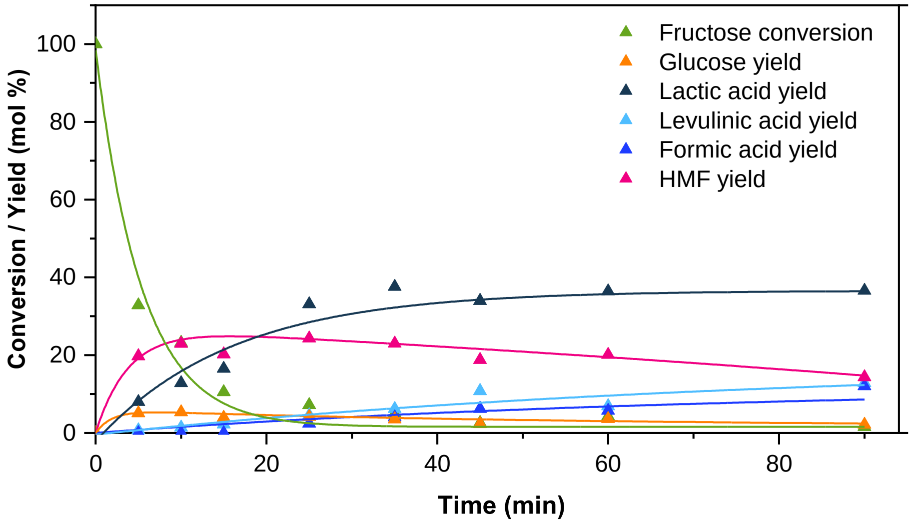

Fig. 4. Fructose conversion in aqueous media under microwave irradiation at 180 °C, in the presence of 2.67 mmol·L^{-1} Al(NO$_3$)$_3$·9H$_2$O

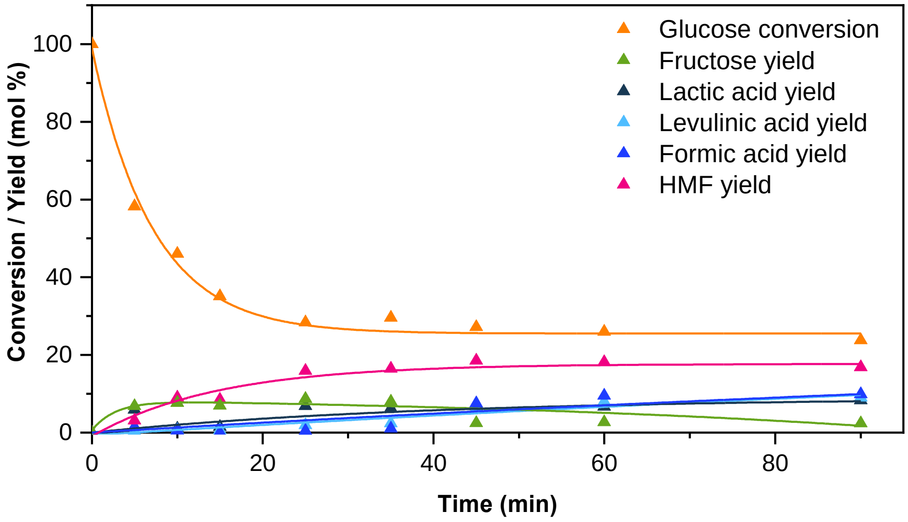

Fig. 5. Glucose conversion in aqueous media under microwave irradiation at 180 °C, in the presence of 2.67 mmol·L^{-1} Al(NO$_3$)$_3$·9H$_2$O

Fig. 6 shows the sucrose conversion profile under microwave irradiation at 180 °C in the presence of Al(NO$_3$)$_3$ as the catalyst precursor. As expected, sucrose was completely converted to glucose and fructose in the reaction beginning, and these monosaccharides were gradually consumed as already observed in Figs. 4 and 5, respectively. Fructose (Fig.

4) and sucrose (Fig. 6) displayed a similar behavior, mainly until 60 min of reaction time. However, yields were lower for sucrose since glucose, formed by acid hydrolysis, has a much lower conversion rate than fructose. This was confirmed by the higher concentration of unconverted glucose after 90 min, compared to that of unconverted fructose. For the same reason, sucrose reaction yields were higher than those obtained from glucose.

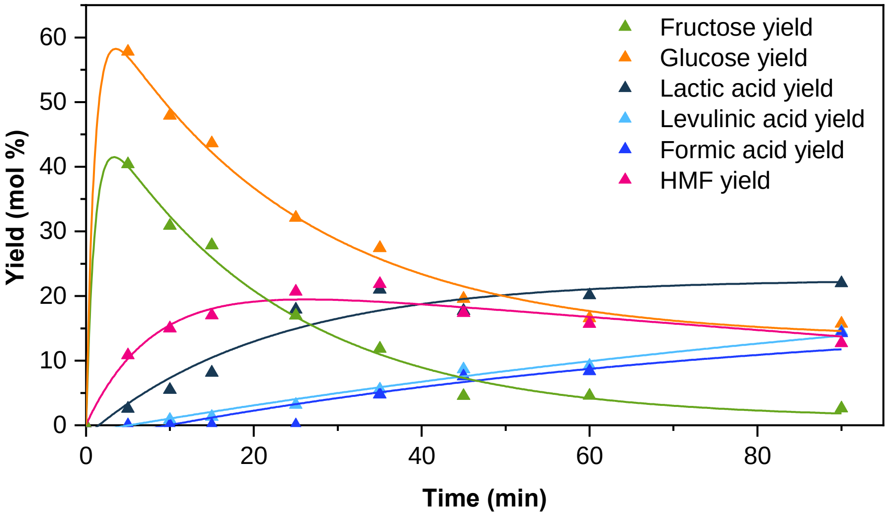

Fig. 6. Sucrose conversion in aqueous media under microwave irradiation at 180 °C, in the presence of 2.67 mmol·L^{-1} $Al(NO_3)_3·9H_2O$

From the adjusted kinetic profiles of Figs. 4, 5, and 6 using Eqs.1 and 2, the pseudo-first order rate constants for fructose, glucose, and sucrose conversion at 180 °C were calculated (Table 7).

Table 7. Rate Constants (k_{obs}) (min^{-1}) for Pseudo-first order Reactions, Obtained for the Conversion of Fructose, Glucose, and Sucrose at 180 °C in the Presence of 2.67 mmol·L^{-1} $Al(NO_3)_3·9H_2O$ using a MWR

Product	k_{obs} (min^{-1}) for the following reagents:		
	Fructose	Glucose	Sucrose
Lactic acid	0.057 ± 0.007	0.025 ± 0.003	0.046 ± 0.011
Levulinic acid	0.023 ± 0.004	0.004 ± 4 x 10^{-4}	0.007 ± 5 x 10^{-4}
Formic acid	0.013 ± 0.002	0.0044 ± 7 x 10^{-4}	0.013 ± 0.002
HMF	0.248 ± 0.081 (k_{obs}^A)[1] 1.149 x10^{-6} ± 0.02 (k_{obs}^B)[2]	0.067 ± 0.009	0.141 ± 0.081 (k_{obs}^A) 0.017 ± 0.06 (k_{obs}^B)
Fructose	n.d.[3]	0.06 ± 0.01 (k_{obs}^A) 0.04 ± 0.002 (k_{obs}^B)	0.722 ± 0.042 (k_{obs}^A) 0.05 ± 0.001 (k_{obs}^B)
Glucose	0.053 ± 0.01 (k_{obs}^A) 0.018 ± 0.034 (k_{obs}^B)	n.d.	0.364 ± 0.004 (k_{obs}^A) 0.04 ± 0.007 (k_{obs}^B)

[1] k_{obs}^A, pseudo-first order reaction constant for product formation
[2] k_{obs}^B, pseudo-first order reaction constant for product consumption.
[3] n.d., not detected.

Glucose conversion to lactic acid had the lowest k_{obs} value (0.025), while fructose conversion had the highest (0.057) because it did not require an acid hydrolysis or an isomerization step to undergo the reaction pathways described in Fig. 1. Sucrose presented a k_{obs} of 0.046 in its conversion to lactic acid. As fructose reacts faster than glucose, the k_{obs} for sucrose was expected to fall in-between. Levulinic and formic acids showed the same behavior as lactic acid. However, the identical k_{obs} for formic acid formation from sucrose and fructose indicated that, in reactions carried out with sucrose, this compound was being formed from fructose and not from glucose.

Figs. 4 and 6 demonstrate that fructose was almost completely consumed in a short reaction time and that its consumption rate was higher than that of glucose (Fig. 5). In the case of sucrose, the two rate constants $k_{obs}^{A}\ and\ k_{obs}^{B}$ (production rate and conversion rate, respectively) for fructose were higher than those of glucose, confirming that fructose is more rapidly produced and more rapidly consumed after it is released from sucrose by acid hydrolysis, respectively.

The kinetics of HMF production from fructose and sucrose had two rate constants ($k_{obs}^{A}\ and\ k_{obs}^{B}$) because HMF behaves as a dehydration product and a rehydration reagent (Table 1). Glucose had a single k_{obs} value for HMF formation because Eq. 1 fitted the experimental data; therefore, in this case, HMF behaved as a dehydration product most of the time. However, after 60 min, there was a slight drop in HMF yield, indicating its gradual consumption by rehydration with the concomitant formation of levulinic and formic acids.

The k_{obs}^{A} values for fructose conversion were always higher than those of sucrose and glucose because its conversion did not require additional steps such as hydrolysis and isomerization. Finally, the k_{obs}^{A} value for fructose isomerization to glucose was close to that of the reversed pathway, indicating that both reactions occurred in similar extents. However, k_{obs}^{B} values for fructose conversion were lower because glucose must isomerize before it undergoes dehydration or retro-aldol chain splitting.

Influence of time on fructose conversion under conventional heating

Figure 7 shows that the muffle furnace (using the SS-PTFE reactor with conventional heating) required no less than 60 min to reach the setpoint temperature of 180 °C. Therefore, the heating efficiency of the muffle furnace was much lower than that of the MWR, in which the temperature setpoint was reached in only 2 min (blue line in Appendix Fig. S2). Hence, it seemed that the gradual heating of the SS-PTFE reactor influenced the selectivity for the retro-aldol reaction, decreasing dehydration to HMF and the subsequent formation of levulinic and formic acids. The selectivity for lactic acid formation can be visualized in the HPLC profile of Fig. 8 for experiments carried out at 180 °C for 90 min in the SS-PTFE reaction system.

Appendix Fig. S2 confirms that SS-PTFE and MWR had different heating regimes. In the latter reaction system, the mixture remained at the setpoint temperature (180 °C) during most of the reaction time, whereas for the SS-PTFE, this time was considerably lower, with more than 90% fructose remaining unreacted until 30 min when the reaction temperature was still very low. Also, in this latter reaction system, the reaction temperature continued to rise, reaching 200 °C in roughly 120 min. Although this may have affected the reaction yields, it seems that other factors may have been influential, such as differences in the activation energy of intermediate reactions (Ramot *et al*. 2016). Nevertheless, fructose-to-lactic acid yields in the SS-PTFE reactor were much higher compared to microwave irradiation (67.5 and 38.5 mol %, respectively).

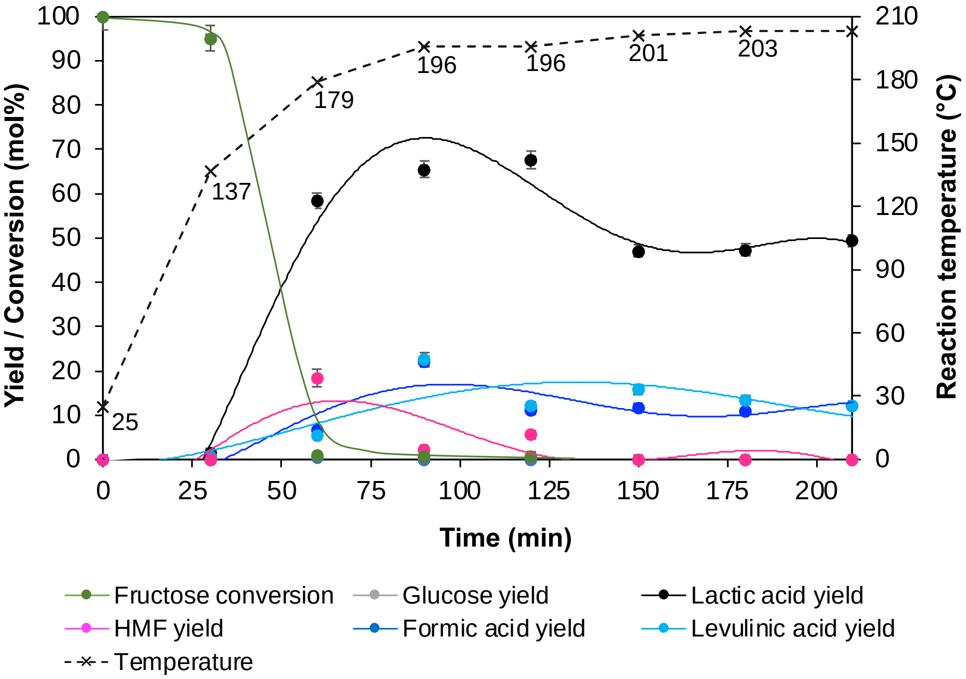

Fig. 7. Fructose conversion in aqueous media using a SS-PTFE reactor under conventional heating and a setpoint temperature of 180 °C, in the presence of 2.67 mmol·L^{-1} Al(NO$_3$)$_3$·9H$_2$O

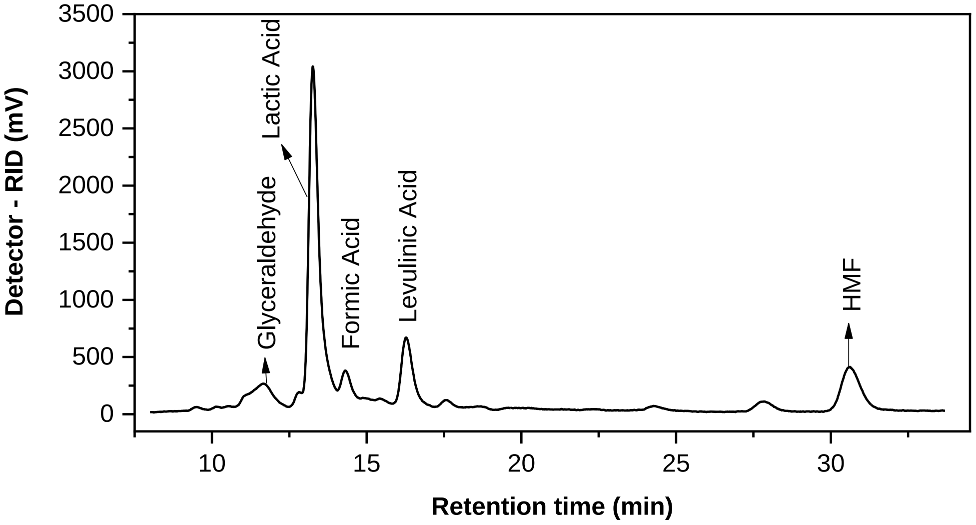

Fig. 8. HPLC profile of SS-PTFE reaction products using the Agilent Hi-Plex-H chromatographic column at 65 °C, 8 mmol·L^{-1} H$_2$SO$_4$ as the mobile phase, and detection by differential refractometry. Reactions were carried out for 90 min at 180 °C using 0.03 mmol Al(NO$_3$)$_3$·9H$_2$O as the catalysts precursor.

Influence of the heating ramp on sucrose conversion

Sucrose conversion was carried out in SS-PTFE reactors under conventional heating (muffle furnace), and the results were compared to those obtained under microwave irradiation using a fast and a slow (stepwise) heating strategy (Table 8). Reactions were carried out for 90 min in the presence of 2.67 mmol·L^{-1} Al(NO$_3$)$_3$·9H$_2$O with the setpoint temperature at 180 °C. The highest lactic acid yield was obtained with the conventional (convective) heating system, in which all carbohydrates were completely consumed (see the stepwise heating profile of SS-PTFE reactors in Table 8). By contrast, when the reaction was carried out under microwave irradiation, the selectivity for lactic acid was much lower, with formic and levulinic acids becoming the main reaction products (see fast heating of MWR in Table 8). To compare the impact of these different heating regimes on reaction performance, experiments were carried out in the MWR using the same heating ramp of the muffle furnace. For this, temperature was increased manually at every 4 min to mimic the SS-PTFE heating ramp (1.80 °C/min), as shown by the orange line of Fig. S2.

Table 8. Sucrose Conversion in the Presence of 2.67 mmol·L^{-1} $Al(NO_3)_3 \cdot 9H_2O$ for 90 min using Two Different Reaction Systems (SS-PTFE and MWR) and Two Different Heating Regimes (MWR with Slow and Fast Heating)

Product (mol %)	SS-PTFE[1]	MWR[2]	
	Slow heating	Slow heating	Fast heating
Lactic acid	65.5 ± 3.7	58.3 ± 3.2	13.2 ± 1.4
Levulinic Acid	13.5 ± 3.5	14.5 ± 2.8	33.5 ± 1.7
Formic acid	21.6 ± 3.7	22.4 ± 2.7	38.5 ± 1.5
HMF	2.4 ± 1.4	2.4 ± 1.1	2.7 ± 1.1
Fructose	n.d.[3]	n.d.	3.3 ± 1.5
Glucose	n.d.	n.d.	5.1 ± 1.9

[1] SS-PTFE, stainless-steel reactor with a PTFE liner.
[2] MWR, CEM microwave reactor.
[3] n.d., not detected.

Sucrose conversion in the MWR using stepwise heating (to simulate the muffle furnace heating rate) led to a product profile like that of the SS-PTFE reactor, in which lactic acid predominated (see slow heating in Table 8 for both SS-PTFE and MWR). However, lower lactic acid yields were obtained in the MWR, compared to the use of SS-PTFE autoclaves in the muffle furnace (58.3 and 65.5 mol %, respectively). In general, the retro-aldol mechanism seemed to prevail when gradual heating was applied, regardless of the reaction system. By contrast, a completely different product profile was obtained for reactions carried out with fast heating in the MWR. In this case, the highest yields were obtained for formic and levulinic acids (33.5 and 38.5 mol %, respectively), with low HMF recovery and some detectable unconverted monosaccharides (see fast heating in Table 2 for the MW reactor). Hence, the fast-heating rate, only achievable in the MWR, favored the carbohydrate dehydration pathway followed by HMF rehydration.

CONCLUSIONS

Lactic, levulinic, and formic acids as well as HMF were produced from fructose, glucose, and sucrose in aqueous medium containing aluminum nitrate as the catalyst precursor using two heating systems: conventional in a muffle oven using a stainless-steel reactor with PTFE coating and by microwave irradiation in a CEM reactor using sealed glass tubes. Lactic acid predominated in the reaction products under conventional heating, with the best yield being 67.5 mol % at the setpoint temperature of 180 °C. By applying the muffle oven heating ramp in the microwave reactor (MWR), the same product profile was obtained in slightly lower yield, which can be explained by the difficulty in reproducing manually the same temperature profile. However, when high temperatures were reached in a short heating time (2 min) using microwave irradiation (fast heating rates), the product profile changed considerably with a decline in lactic acid yield. Regarding the use of aluminum nitrate as the catalyst precursor, $Al(NO_3)_3{\cdot}9H_2O$ is relatively inexpensive, widely available, and less toxic than other catalytic systems already used for the same purpose (*e.g.*, $ErCl_3$ and $AlCl_3/SnCl_2$). Also, this catalyst precursor presented a good selectivity for the retro aldol reaction pathway, producing lactic acid in high yields.

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APPENDIX

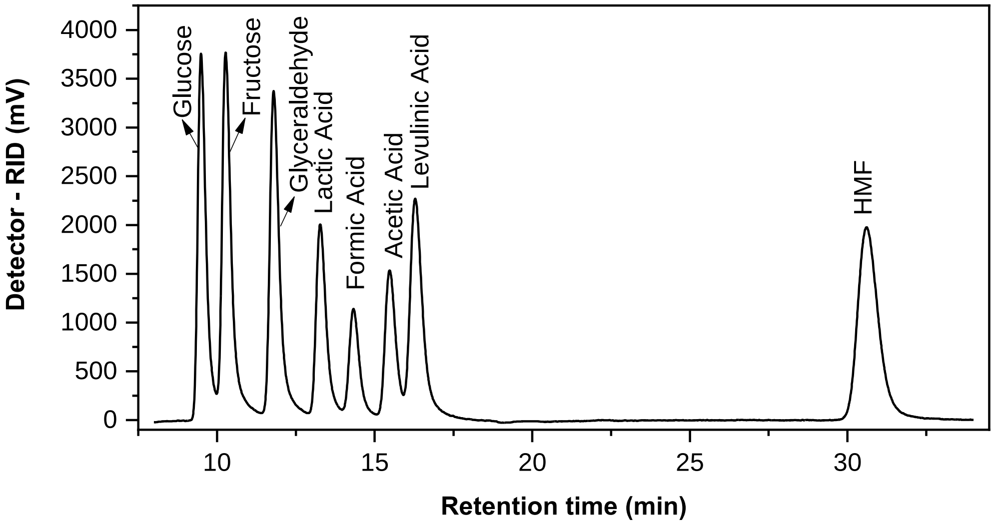

Fig. S1. HPLC profile of carbohydrate standards using the Agilent Hi-Plex-H chromatographic column at 65 °C, 8 mmol·L^{-1} H_2SO_4 as the mobile phase, and detection by differential refractometry.

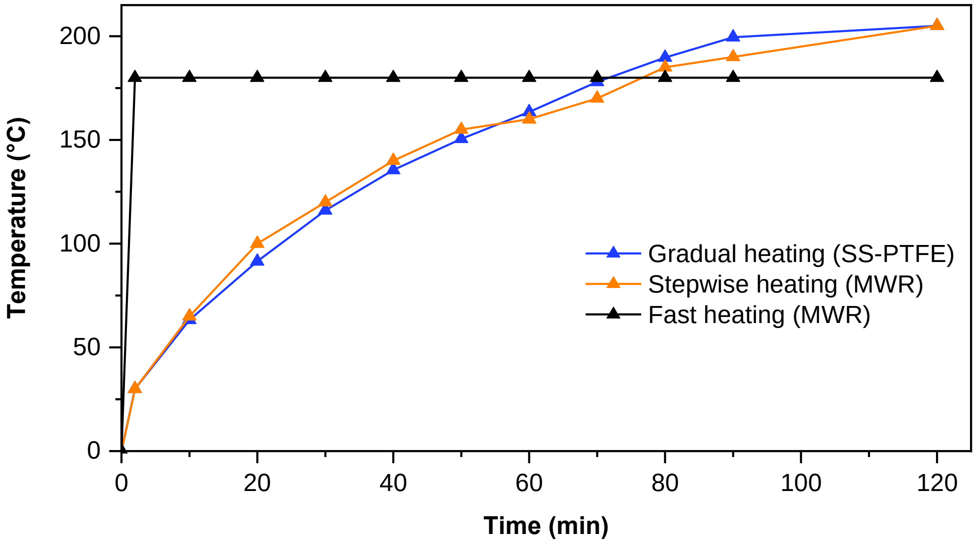

Fig. S2. Temperature profile under fast and gradual heating using the microwave reactor (MWR) and the SS-PTFE reactor in a muffle oven. The setpoint temperature in all cases was 180 °C.