

Formic acid production by simultaneous hydrothermal CO₂ reduction and conversion of glucose and its derivatives

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ABSTRACT

Background: The hydrothermal reduction of CO₂ using organic molecules such as alcohols can produce renewable fuels and platform chemicals, such as formic acid (FA). If the process is performed using glucose as reductant, the yield is especially high, because FA is selectively produced both by reduction of CO₂ and by degradation of glucose degradation in alkaline hydrothermal media.

Methods: This article analyzes the origin of formic acid using NaH¹³C₃O₃ as CO₂ source, assisted by HPLC and ¹³C-NMR to study the origin of FA.

Significant findings: Results show that two reactions pathways take place: the first one, at short reaction times, consists on the decomposition of glucose into formic acid and other by-products, achieving low yield to FA-¹³C, whereas longer reaction times lead to a higher yield to FA-¹³C. Similarly, temperature plays an important role, being 300°C the optimal. Further reactions were performed using the main by-products of previous reactions (acetic acid, lactic acid, glycolaldehyde and glyceraldehyde) as reductants to understand the reaction mechanisms. Results indicate that the reduction pathway of NaHCO₃ take place by oxidation of the by-products rather than by the oxidation of glucose itself, needing long reaction times to achieve significant high ratios of FA-¹³C/total FA.

1. Introduction

Due to the utilization of fossil sources as fuels and the CO₂ levels in the atmosphere related to the anthropogenic activity, several studies have proposed different processes for both CO₂ mitigation and fossil fuels replacement, at the same time that new energy sources are developed, such as biological, photochemical and electrochemical processes [1]. One approach is the replacement of fossil fuels by renewable sources for the production of fuels and platform chemicals. Biomass (especially lignocellulosic biomass, which is composed of cellulose, hemicellulose and lignin) is a promising alternative due to these characteristics, as it is a renewable, sustainable, inexpensive and world wide spread feedstock. In the last years, different processes have been proposed to fractionate and obtain value-added products from this raw material, such as biological, enzymatic, thermochemical and

hydrothermal processes [2–4].

On the other hand, the carbon capture, utilization and conversion represents an opportunity to reduce the concentration of CO₂ in the atmosphere, at the same time that this gas could be valorized by means of its utilization or conversion [5–8]. Besides the existing industrial applications of CO₂, further conversion processes that involves renewable energies have been developed, such as photochemical, electrochemical and biological methods [9–12]. Recently, hydrothermal processes have also been found suitable to transform CO₂ into useful products such as formic acid (FA) or methanol, regarded as Liquid Organic Hydrogen Carriers (LOHC), that can be dehydrogenated in order to obtain H₂ or be directly used as feedstock for power cells, playing an important role in the hydrogen economy [13–18].

Hydrothermal method uses water at high temperature and pressure (above 100°C and saturation pressure) In these processes, water can play

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different roles in the reaction, such as green solvent, hydrogen donor and catalyst. In this way, the use of gaseous hydrogen is avoided, resulting in a safer process with lower reliance in fossil fuels (for H₂ production) [13–15]. Previous studies have shown the possibility to reduce CO₂ under hydrothermal conditions using different metals (Fe, Mn, Al or Zn) or organic compounds as reductants, being FA the main product from CO₂ reduction. Besides as LOHC, FA can be used in different industries, such as textile, chemical, agricultural and pharmaceutical industries [13,19–27]. In many of these studies, the best results are obtained when CO₂ is in form of bicarbonate, which is the main product of capturing CO₂ using NaOH solutions [28–30]. In addition, hydrothermal processes are receiving attention not only for CO₂ conversion, but also for biomass valorization, obtaining value-added chemicals by its fractionation and conversion [27,31–34]. In fact, formic acid can be also produced by means low-temperature hydrothermal processes from biomass [35–39]. As biomass is a world-wide spread, sustainable and inexpensive feedstock (sometimes even considered as a residue), the production of commodity chemicals using the hydrothermal technology could result in an inexpensive and green method, solving in this way the conundrum caused by the shortage of fossil fuels and excessive levels of CO₂ in the atmosphere.

The reduction potential of different organic molecules has been previously investigated. C3 alcohol molecules such as isopropanol and glycerol were used as reductants obtaining significant yields to formic acid and concomitant production of acetone and lactic acid as oxidized products respectively [13,25]. In a previous report testing several biomass model compounds, the highest yield to formic acid was achieved using glucose as and sodium bicarbonate (NaHCO₃) as CO₂ source, being of high interest as glucose is the main product of the hydrothermal degradation of cellulose. As by-products, acetic and lactic among others were obtained. These latter compounds, however, are rather hydrolysis products (redox neutral reaction) since the oxidation number is the same than the starting glucose and they are also obtained when no CO₂ is present. Further exploratory investigations in the topic, using glycerol, algae and polyvinyl chloride, examined the origin of formic acid by using sodium bicarbonate ¹³C (NaH¹³CO₃) [40–42]. The main purpose of using NaH¹³CO₃ is to detect the origin of formic acid by ¹³C-NMR techniques in combination with HPLC analyses. Yang et al. tested algae and its main constituents as possible reductants of NaH¹³CO₃ at 300 °C during 2 h, showing that formic acid is produced (in different proportions) from both sodium bicarbonate and the organic molecules. In the case of glucose, it was observed that a 47.9% of the total formic acid was produced by NaH¹³CO₃ reduction (without further optimization of reaction conditions), indicating a concomitant production of formic acid from both reagents under hydrothermal conditions [40]. It is then proven that bicarbonate, C(IV) undergoes a reduction to formic acid, C(II), but the mechanism is still unclear because no oxidation by-products have been detected in significant amounts.

In this work, NaH¹³CO₃ is used as CO₂ source to study in detail the mechanistic effects of CO₂ reduction with glucose (a representative monosaccharide of carbohydrates and component of lignocellulosic biomass). The origin of FA is determined using marked NaH¹³CO₃ as inorganic carbon source, varying the operational conditions to determine the plausible mechanisms through which glucose hydrolyses and/or reduces bicarbonate. To do this, not only glucose was used as reductant as cellulose, but also its hydrolysis products, such as lactic acid, acetic acid, glyceraldehyde and glycolaldehyde.

2. Materials and methods

2.1. Materials

As reagents, NaH¹³CO₃ (99%, 98 atom %¹³C), D-(+)-glucose (99%), glyceraldehyde (90%) and glycolaldehyde dimer (99%) were used as reductants and standards, and they were obtained from Sigma Aldrich. For HPLC standards, the following chemicals were used: glycerol

(99.5%, Spain), n-propanol (> 99.7%), pyruvaldehyde (40%), 5-HMF (99%), furfural (99%), fructose (99%), rahmnose (99%), resorcinol (99%), glucuronic acid (> 98%), oxalic acid (≥ 99%), acrylic acid (99%), d-glyceric acid calcium salt (99%), catechol (99%) and guaiacol (> 99%) were bought to Sigma Aldrich. Ethanol (EtOH, 99.5%), acetone (99.5%), isopropanol (iPrOH, 99.9%), formaldehyde stabilized in MeOH (37–38% w/w) and propanoic acid (99%) were acquired from Panreac. Formic acid (98%) and galacturonic acid (≥ 97%) were purchased from Fluka. Methanol (MeOH, 99.99%) was obtained from Fisher Scientific. Ethylenglycol (≥ 99.5%) was obtained from Merck. All the chemicals were used without further treatment.

For ¹³C-NMR analysis, acetic acid-1-¹³C (99%, 99 atom %¹³C) and formic acid-¹³C (95 wt% in H₂O, 99 atom %¹³C) were purchased from Sigma Aldrich. Deuterated solvent (D₂O, 99.5% D atom) were purchased from Cortecnet

2.2. Experimental procedure

Solutions in MilliQ water (ultrapure water) were prepared using a concentration 0.50 M of NaH¹³CO₃, and 0.05 M of glucose, unless otherwise indicated. Experiments were performed in batch reactors, described elsewhere [28]. These reactors consist of tubes with a length of 12 cm; o.d. of ½” and 1.24 mm of thickness, made of SS 316 stainless steel with an internal volume of 15.6 mL. The solution was loaded in the reactor up to the 50% of the volume, and the reactor was sealed. Afterwards, the reactor was introduced in a preheated fluidized alumina bed, which allows a fast heating of the solution, reaching the temperature set point inside the reactor (300 °C) in less than 3 minutes. Considering the introduction of the reactors in the fluidized alumina as the initial time (t = 0 min), after the desired reaction time, the reactor was cooled down using an ice bath. Once cooled, the reactor was opened, and liquid products were collected. Reactions were performed at least twice to ensure reproducibility. Reactors were weighted before and after the reaction to check the correct sealing.

2.3. Analytical procedure

Liquid samples were collected and filtered through a 0.22 μm Nylon filter. Two different techniques were used to analyse and quantify the products distribution: high performance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR). HPLC analyses were carried out in a Waters Alliance separation module e2695, using a Rezex ROA-Organic Acid H+ (8%) LC column (300 × 7.8mm, Phenomenex) and a refractive index detector. The column temperature was kept at 40 °C and the detector temperature at 30 °C. The mobile phase was a 25 mM H₂SO₄ solution in MilliQ water, with a flow rate 0.5 mL/min under isocratic conditions.

Quantitative ¹³C{¹H}-NMR analyses were performed using a 500 MHz Agilent instrument equipped with OneNMR probe in the Laboratory of Instrumental Techniques (LTI) Research Facilities, University of Valladolid. For the quantification of ¹³C products, two different analyses of the sample were performed: one sample without further treatment and another adding acetic acid-1-¹³C (CH₃¹³COOH) as internal standard. In all cases, 600 μL of sample was transferred to a NRM tube and 50 μL of D₂O for internal lock reference were added. Samples analysed with CH₃¹³COOH as the internal standard were prepared as follows: 2.5 mL of filtered sample were spiked with 5 μL of CH₃¹³COOH, achieving a concentration of 34 mM CH₃¹³COOH, and then the mix was shaken in a vortex for 20 s to ensure the correct mixing. The acquisition parameters for quantitative measurements were: 25 °C, 70 s relaxation delay between transients, 45° pulse width, and spectral width of 31250.0 Hz, a total of 32 transients and 2.044 s acquisition time. In order to obtain a decoupled spectrum without NOE enhancements, the inverse-gated proton decoupling method was used. All the studies of ¹³C{¹H} experiments were recorded on 500 MHz Agilent instruments equipped with OneNMR probe, and ¹³C {¹H} chemical shifts (δ) were reported in part

per million (ppm) and referenced to tetramethylsilane (TMS). The final spectra were manipulated and processed using Mestrelab Research software (MNova 12.0) (Santiago de Compostela, Spain). Prior to NMR analysis, $^{13}\text{C}\{^1\text{H}\}$ data obtained were subsequently apodized with line broadening window function of 1 Hz and a value of 64K zero-filling was applied to improve the digital resolution of the final spectrum.

Yields reported in this work are calculated with respect to the organic reductant, which as indicated in Section 2.2 is the limiting reagent. Yields with respect to the inorganic carbon source NaHCO_3 can be obtained from the reported yields considering the NaHCO_3 :organic molar ratio, e.g. dividing by 10 for a concentration 0.50 M of $\text{NaH}^{13}\text{CO}_3$ and 0.05 M of glucose. The yield to total formic acid (total FA) and the rest of by-products was calculated as follows (Eq. 1):

$$Y_{\text{product, HPLC}} = \frac{C_{\text{Product, f, HPLC}}}{C_{\text{organic, i}}} \times 100 \quad (\text{Eq. 1})$$

Where $C_{\text{product, f, HPLC}}$ is the molar concentration of the different products after the reaction, determined by HPLC, and $C_{\text{organic, i}}$ is the initial molar concentration of the reductant.

The yield to formic acid obtained from $\text{NaH}^{13}\text{CO}_3$ was determined as shown in Eq. (2):

$$Y_{\text{FA, NMR}} = \frac{C_{\text{FA, f, NMR}}}{C_{\text{organic, i}}} \times 100 \quad (\text{Eq. 2})$$

Where $C_{\text{FA, f, NMR}}$ is the molar concentration of formic acid ^{13}C after the reaction, determined by ^{13}C -NMR analysis, and $C_{\text{organic, i}}$ is the initial molar concentration of the reductant. The comparative results between HPLC and NMR techniques are displayed in the Supporting Information (Section A1).

All the experimental data presented in this work have a relative standard deviation (RSD) lower than 10%.

3. Results and discussion

In order to test the validity of the RMN method, a primary set of reactions were performed using $\text{NaH}^{12}\text{CO}_3$ and $\text{NaH}^{13}\text{CO}_3$ as CO_2 sources and glucose as reductant at 300°C for 120 min (Fig. S1). It can be observed that, in the reaction using $\text{NaH}^{12}\text{CO}_3$, no signals in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum are detected, as expected for the low natural abundance of ^{13}C (1.1%) in the ^{13}C -NMR studies recording under quantitative conditions. However, reactions with $\text{NaH}^{13}\text{CO}_3$ resulted in the production of formic acid ^{13}C (FA- ^{13}C), which is observed at 173 ppm at reasonable acquisition times in the quantitative ^{13}C -NMR spectra. This demonstrates that CO_2 can be transformed into FA using glucose (or one of its hydrolysis products) as reductant. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of experiments carried out using $\text{NaH}^{13}\text{CO}_3$ as CO_2 source showed other significant peaks: The intense peak observed at 163 ppm is assigned to the unreacted $\text{NaH}^{13}\text{CO}_3$ that remained in the solution after the reaction. Due to the equilibrium of the unreacted $\text{NaH}^{13}\text{CO}_3$ in water, another weak signal is observed at 123 ppm, attributed to dissolved $^{13}\text{CO}_2$ [43,44].

3.1. Effect of time in the origin to formic acid

The effect of time on $\text{NaH}^{13}\text{CO}_3$ reduction using glucose as reductant was tested, as depicted in Fig. 1. As observed in this Fig., the yield to FA shows a complex behavior: it is high at short reaction times (10 min), decreases at intermediate times of 10-120 min and increases again after 120 min. Correspondingly, the yield to FA- ^{13}C is very low at short reaction times at increases in the time interval 10 min – 90 min. The highest yield to total FA (47.5%) was achieved after 10 min of reaction, but also the lowest yield to FA- ^{13}C (5.9%). Therefore, at short reaction times, a rapid FA production is mainly due to glucose decomposition. However, as the reaction proceeds the proportion of FA- ^{13}C increases, suggesting that the FA initially formed is being partially replaced by FA from bicarbonate. To explain these observations, it is necessary to

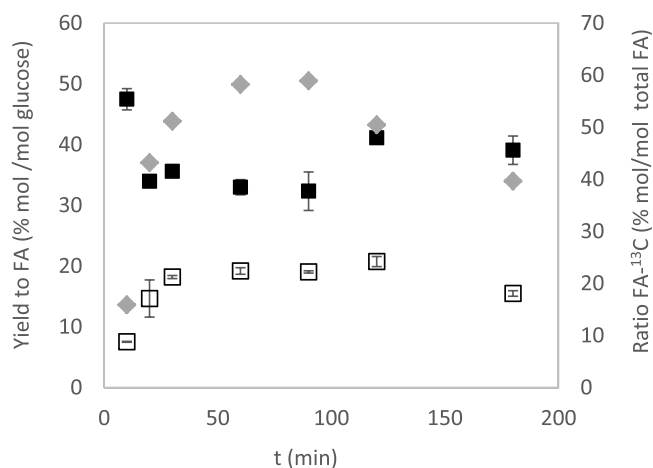


Fig. 1. Effect of reaction time on the yield to total FA and FA- ^{13}C . Legend: (■): yield to total FA; (□): yield to FA- ^{13}C ; (◆) ratio FA- ^{13}C . General reaction conditions: 0.50 M $\text{NaH}^{13}\text{CO}_3$; 0.05 M glucose; T: 300°C ; t: 120 min.

assume the existence of reversible reactions in the reaction mechanism. As the yield to total FA decreased at reaction times between 30 and 90 min, FA must partially decompose under the reaction conditions. FA- ^{13}C concentration increases to a plateau after 30 min, as well as the proportion FA- ^{13}C /FA. At 120 min the reaction seems to undergo into a new stage, as total FA yield increases again.

Besides FA, other products were identified after the reaction (Fig. S2), which were not detected in the ^{13}C -NMR spectra, indicating that were produced by the glucose degradation as they are not enriched in ^{13}C . No or negligible amount of glucose or fructose were detected in any of the samples. The main by-products obtained were acetic acid and lactic acid. The yield former one remains nearly constant along the whole reaction Lactic acid formation is also fast, reaching a maximum yield of 43% but starting from 120 min, it decreases, apparently being converted into glycolaldehyde (and probably FA). Acetic acid yield achieves values of ca. 40% in the first minutes of the reaction and remains almost constant throughout time, which suggests that is produced at the very early stages of the reaction by non-reversible reactions. In the case of lactic acid, its concentration increases very fast in the first 30 min of reaction to achieve a maximum yield of 43.1% at 90 min of reaction, decreasing afterwards, and apparently being converted into glycolaldehyde (plus probably FA). Glyceraldehyde was also detected by HPLC analysis, and its yield decreases with time to very small proportions.

3.2. Effect of reaction temperature on yield to formic acid

Fig. 2 depicts the yield to total FA and FA- ^{13}C , and the ratio FA- ^{13}C /total FA as a function of reaction temperature, observing that formic acid was produced at all the temperatures tested. However, at 200°C , all the FA produced was a result of glucose decomposition, as no FA- ^{13}C was detected by ^{13}C -NMR analysis. As temperature increases, both the total yield to FA and the proportion FA- ^{13}C /total FA increases, the latter significantly. At 325°C however, the total yield to FA decreases again. Despite at this temperature the ratio FA- ^{13}C /total FA was the highest at the temperatures tested, reaching a ratio FA- ^{13}C /total FA of 55.0%, this improvement is counterbalanced by the decrease in yield. This behaviour is consistent with a set of equilibrium reaction either being shifted to FA- ^{13}C (bicarbonate reduction) by effect of temperature of by speeding up their equilibrium kinetics. However, if the temperature is too high, decomposition reaction of FA to CO_2 and H_2 start getting importance [45].

The main by-products were acetic acid and lactic acid followed by glyceraldehyde and glycolaldehyde at all temperatures (Fig. S3).

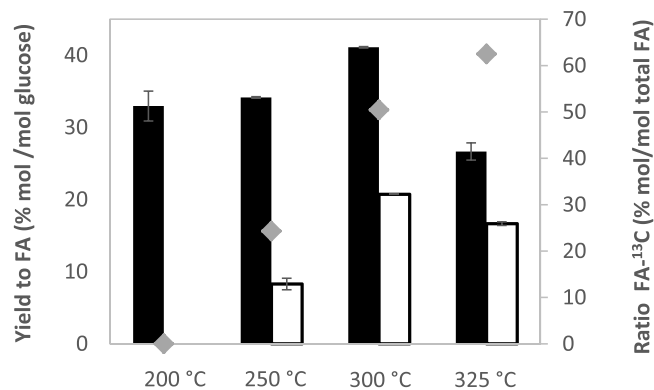


Fig. 2. Effect of temperature on the yield to total FA and FA-¹³C. Legend: (■): yield to total FA; (□): yield to FA-¹³C; (◆): ratio FA-¹³C; (◆): ratio FA-¹³C. General reaction conditions: 0.50 M NaH¹³CO₃; 0.05 M glucose; t: 120 min.

However, the trend of each by-product differs. Acetic and lactic acids yield slightly increased when the reaction temperature was higher, showing the results with lactic acid a peak at 250°C that can be attributed to experimental uncertainty. Interestingly, the yield to glyceraldehyde followed a trend opposite to total FA production. The yield to glycolaldehyde is greatly affected by temperature, when temperature is higher than 300°C it decreases *ca.* six-fold.

3.3. Effect of initial concentration of glucose on yield to formic acid

The influence of the initial concentration of glucose was tested for values between 0.025 and 0.5 M (Fig. 3). At low glucose concentrations of 0.025 M – 0.05 M, the performance of the reaction does not significantly vary. However, at higher concentrations of 0.05 M – 0.5 M, the higher the initial concentration of glucose, the lower the yield to total formic acid. The proportion FA-¹³C/total FA also decreases with the initial concentration of glucose but at a lower rate. Similar to the results presented in previous sections, the main by-products were lactic acid and acetic acid, followed by glyceraldehyde and glycolaldehyde (Fig. S4). In all cases, the higher the initial concentration of glucose resulted in the lower yield to by-products, reaching the maximum yield to these products using an initial concentration of glucose of 0.025 M and following a similar trend than the yield to formic acid. These results suggest that an excess of glucose has a detrimental effect on the production of formic acid

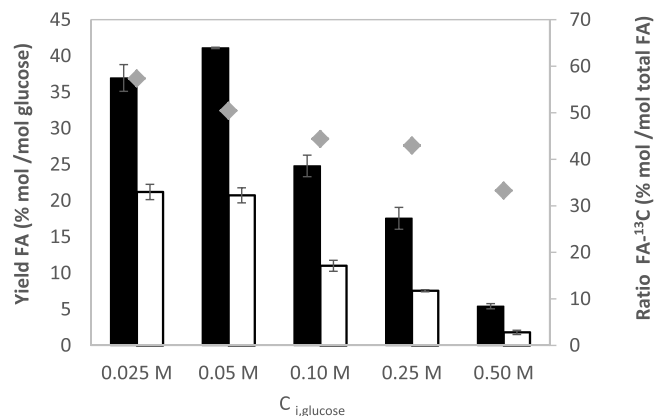


Fig. 3. Effect of initial glucose concentration on the yield to total FA and FA-¹³C. Legend: (■): yield to total FA; (□): yield to FA-¹³C; (◆): ratio FA-¹³C; (◆): ratio FA-¹³C. General reaction conditions: 0.50 M NaH¹³CO₃; T:300°C, t: 120 min.

3.4. Reduction of NaH¹³CO₃ using degradation products from glucose

In order to obtain a better understanding of the reaction mechanism and the substance that acts as direct reductant of NaH¹³CO₃, experiments were carried out using major by-products of glucose degradation, namely acetic acid, lactic acid, glycolaldehyde and glyceraldehyde.

In the case of acetic acid, no formic acid was observed neither in HPLC nor ¹³C-NMR analysis, detecting only unreacted acetic acid and NaH¹³CO₃ in the analyses. This molecule is stable enough to be produced after a non-reversible reaction of hydrolysis. On the other hand, formic acid was obtained when using lactic acid, glycolaldehyde and glyceraldehyde as reductant (Fig. 4). Employing the by-products as reductants, the maximum yield to total FA (26.1%) was obtained using glyceraldehyde after 10 min of reaction, followed by glycolaldehyde (21.8%, 60 min) and lactic acid (13.8%, 180 min). Similar to glucose, longer reaction times led to a higher yield to FA-¹³C in all cases.

It was also observed that the formic acid produced by the degradation of organic molecules followed a different production pathway with lactic acid than with glycolaldehyde and glyceraldehyde. The formation of FA from the lactic acid is slower than from the other two. While glycolaldehyde and glyceraldehyde are converted almost totally at all reaction times, *ca.* 82% of initial lactic acid remained unconverted after 180 min of reaction. It should be noted that the yield to FA reaches a maximum to decrease later with reaction time when glycolaldehyde and glyceraldehyde are used as reductants. Lactic acid then is a relatively stable hydrolysis product as it has been detected as a typical product from biomass hydrolysis, however, it can further proceed to FA at lower extent.

The evolution of by-products as a function of reaction time for the three different organic model compounds are shown in the Fig. S5. In the case of lactic acid, acetic acid and glyceraldehyde were detected as the main by-products, indicating a related production mechanism. When using glycolaldehyde or glyceraldehyde, the main by-products obtained were also lactic acid and acetic acid. They are produced in high yield at the first moments of the reaction and its proportion does not change much at longer times. It should be noted that lactic acid (a C3 molecule) was produced from glycolaldehyde, a C2 aldose. The production lactic acid from glycolaldehyde in alkaline hydrothermal reaction has been reported by Kishida et al. [46]. Glycolaldehyde seems to be an important intermediate in the hydrothermal glucose conversion. Similar mechanisms may be happening in this research, as the media is also alkaline caused by NaHCO₃. Glyceraldehyde (an intermediate of the proposed mechanism) was not detected as by-product in any case, indicating that this is a very reactive intermediate. It is also noticing that higher yields to acetic and lactic acid were obtained using glyceraldehyde, compared to those achieved with glycolaldehyde.

The ratio FA-¹³C / total FA of these reactions are shown in Table 1. In all cases, the same trend can be observed: longer reaction times resulted in a higher ratio; that is, there is an increasing replacement of FA generated directly from the reductant by FA from bicarbonate. Again, this strongly suggest a mechanism of reversible reactions. In the case of lactic acid, the ratio FA-¹³C/ total FA increases faster for reaction times up to 60 min. compared to the aldoses, probably because LA reacts more slowly to FA.

As reaction time is longer, a major proportion of FA-¹³C is produced out of the total FA detected by HPLC analysis, reaching the maximum ratio FA-¹³C /total FA of 76.5% and 80.5% after 180 min of reaction using glycolaldehyde and glyceraldehyde as reductant. Summarizing, these results indicate that: a) the intermediate products tested behave very similarly than glucose (except acetic acid, which is stable and lactic acid which reacts more slowly); b) the organic molecules quickly hydrolyse to produce FA (and other by-products); c) reduction of NaHCO₃ to formic acid requires of longer reaction times; d) the FA formed from reduction replaces that formed by hydrolysis by a mechanism of reversible reactions.

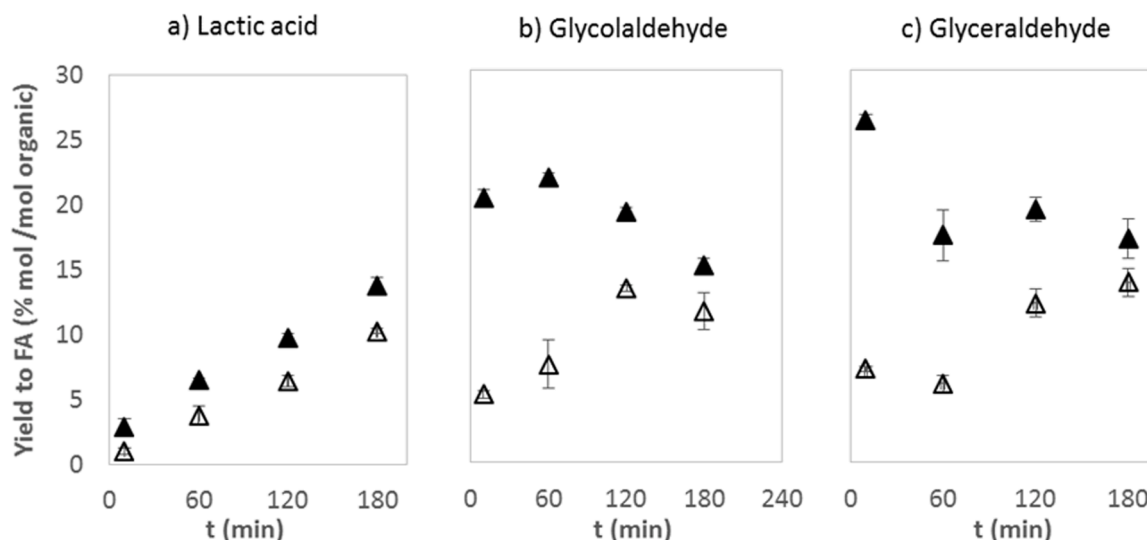


Fig. 4. Effect of reaction time on yield to total FA and FA-¹³C using lactic acid (a), glycolaldehyde (b) and glyceraldehyde (c) as reductant. Symbols: (▲): total yield to formic acid, determined by HPLC; (△): yield to formic acid ¹³C, determined by ¹³C-NMR analysis. Reaction conditions: 0.05 M organic model compound, 0.50 M NaH¹³CO₃, 50% filling, T: 300°C.

Table 1

Ratio FA-¹³C / total FA (%) as a function of reaction time using lactic acid, glycolaldehyde and glyceraldehyde as reductants. Reaction conditions: 0.05 M reductant, 0.50 M NaH¹³CO₃, 50% filling, T: 300°C

t (min)	% FA- ¹³ C / total FA		
	Lactic ac.	Glycolaldehyde	Glyceraldehyde
10	35.5	25.8	27.4
60	58.2	34.5	34.7
120	65.6	69.6	62.9
180	74.2	76.5	80.5

3.5. Proposed mechanism

The results described in the previous sections have been used to elucidate a mechanism of the reaction, based on the mechanism proposed in literature about the hydrothermal conversion of glucose and other organic compounds [47,48]. Fig. 5 depicts the plausible routes of glucose conversion under hydrothermal conditions (black) and the proposed mechanism for the obtention of formic acid by simultaneous conversion of CO₂ and glucose/glucose derivatives (green).

Under hydrothermal conditions, glucose may isomerize into fructose

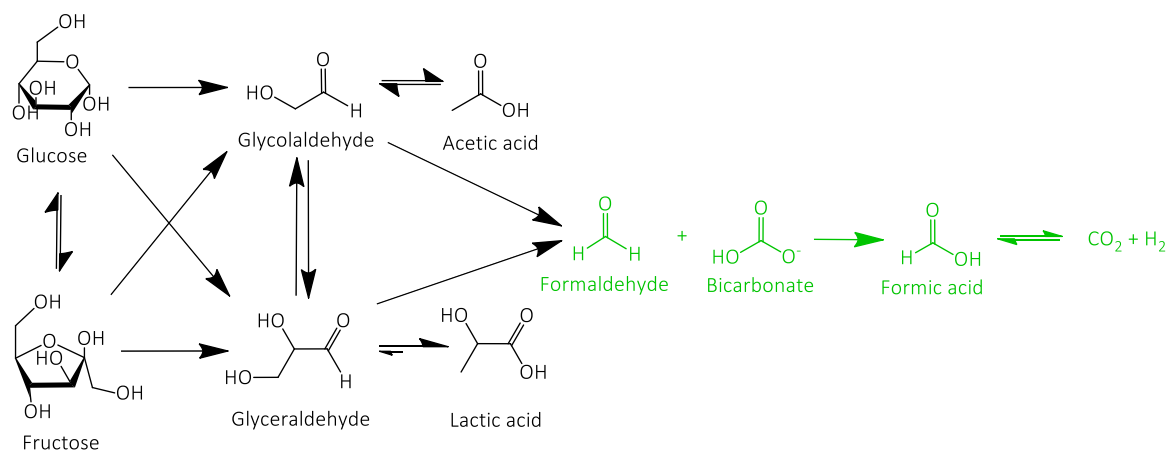
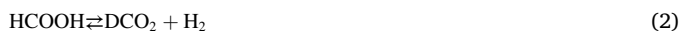
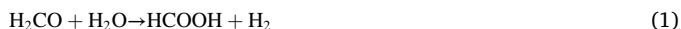


Fig. 5. Proposed mechanism for NaHCO₃ reduction using glucose as reductant. Black data were obtained from previous studies and green ones have been proposed using the data obtained in this work.

glucose and glucose derivatives degradation, especially at short reaction times (10-60 min), as the different aforementioned reactions take place within minutes, obtaining also glycolaldehyde and glyceraldehyde as by-products [35–39]. On the other hand, the formic acid produced from $\text{NaH}^{13}\text{CO}_3$ reduction, which is detected by ^{13}C -NMR analysis, requires of longer times (> 60 min), being reduced by the by-products (especially lactic acid, glycolaldehyde and glyceraldehyde) produced by the degradation of glucose in the first minutes of reaction, obtaining mainly acetic acid as by-product.

Although reduction of bicarbonate is a fact, none of the C2 or C3 intermediates mentioned so far seems to be the direct reductant of the C (IV) species because it has not been detected the corresponding oxidized molecule. Instead of that, we propose that formaldehyde, which can be produced by degradation of glyceraldehyde and glycolaldehyde, would be the reductant of NaHCO_3 to formic acid. Interestingly, the oxidized product is also formic acid, so the overall reaction would be a redox comproportionation of C(0), formaldehyde and C(IV), bicarbonate to yield C(II), formate. Formaldehyde is not detected by HPLC in our reaction products but that can be because it reacted effectively with water or because its free form is present in aqueous solutions in low quantities [58]. The ^{13}C -NMR analysis indicate that these reactions must be reversible. The detailed comproportionation mechanism cannot be determined with the experimental information available, but a plausible possibility is that it proceeds by H_2 as intermediate. H_2 can be released to solution to subsequently react with bicarbonate. The reduction of C(IV) with gas hydrogen has been widely reported [59]. Formaldehyde is known to thermally decompose into CO and H_2 at high temperatures. However, in aqueous media and moderate temperature, it can undergo decomposition via two mechanisms, a Cannizzaro reaction yielding formate and methanol or a dehydrogenation yielding formate and H_2 [58]. Both mechanisms are base-catalyzed, but since no methanol is detected in our tests, we can propose that in the latter the one that plays a role in this process. H_2 is partially soluble in high-temperature water so once released it can participate in the reaction bicarbonate (avoiding interphase mass transfer limitations). A proposed scheme of reaction is:



The observations are consistent with this reaction mechanism, at the first stages of the reaction, FA is directly produced from formaldehyde by dehydrogenation (reaction 1). Reversible reaction (2) explains how the ^{13}C -FA replaces FA as time proceeds. The addition of reaction (1) and reaction (2) reversed results in the comproportionation reaction proposed (reaction (3)).



Finally, in the last stages of the reaction or for high temperatures, decomposition of FA and formaldehyde into CO, CO_2 and H_2 happens to an extent enough to release these gases to the vapor phase thus decreasing FA total yield.

In summary, simultaneous hydrolysis of glucose and oxidation of bicarbonate can be achieved and we propose that these reactions proceed by a mechanism composed by a set of reversible reactions. The products obtained in highest be obtained directly from glucose hydrolysis products or by a comproportionation reaction between these and C (IV) added to medium. The importance of FA has already been discussed. The generation of the other two by-products seems difficult to avoid, but that is not a big drawback as they have also interesting applications: lactic acid for example is the monomer of the renewable polymer polylactic acid; acetic acid is an important chemical used in many industrial processes such as terephthalic acid or cellulose acetate production.

4. Conclusions

In this research, the hydrothermal reduction of NaHCO_3 using

glucose as reductant was achieved, studying a wide range of operational conditions that contributed to understand the reaction mechanism, concerning the use of glucose as reductant. As glucose may also decompose into formic acid under hydrothermal conditions, $\text{NaH}^{13}\text{CO}_3$ was used as CO_2 source, being thus possible to differentiate the formic acid produced by NaHCO_3 reduction from that obtained from glucose conversion by means of ^{13}C -NMR analysis.

Two different pathways for the production of FA were observed: at short reaction times, the FA detected was produced by the degradation of glucose, whereas at long reaction times, FA was mainly produced by the reduction of NaHCO_3 under hydrothermal conditions, reaching the maximum yield of 20.7 % mol FA- ^{13}C / mol glucose (yield to total FA of 41.1%) after 120 min. Further experiments using the by-products detected in reactions with glucose as reductants have contributed to shed a light on the plausible reaction routes, indicating that glucose degradation products are responsible of NaHCO_3 reduction to formic acid at long reaction times and that reaction mechanisms proceed through a set of equilibrium reactions in which formaldehyde is hypothesized to be a key reaction intermediate.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2022.104504.

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