



Simultaneous formic acid production by hydrothermal CO₂ reduction and biomass derivatives conversion in a continuous reactor

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ABSTRACT

The reduction of CO₂ to obtain formic acid in hydrothermal media can contribute to the reduction and valorization of CO₂ emissions, but in order to apply it industrially, scalable continuous-flow reactors must be developed. In this work, a continuous flow reactor is developed that can process up to 1.2 L/h of bicarbonate solution. Glucose as model compound of the products of the hydrothermal decomposition of lignocellulosic biomass is used as reducing agent. Feed stream is suddenly heated at the inlet of the reactor by mixing it with a preheated water stream and instantaneously cooled after the reactor by decompression Joule-Thompson effect, allowing a precise control of the residence time and enabling to apply short residence times down to 1 s that are not feasible in batch reactors. Several operational parameters, as residence time, temperature and additives, were studied. Yields to formic acid up to 63 % were achieved at 300 °C with residence times lower than 1 min. In order to better understand the process, NaH¹³CO₃ was used in selected experiments to check if the origin of formic acid was the reduction of bicarbonate or the hydrolysis of glucose. It was found that almost 50 % of formic acid was produced due to the reduction of NaHCO₃ after 10 min of reaction, a proportion significantly higher than that observed in batch experiments at similar reaction times. Furthermore, experiments performed without NaHCO₃ or with other alkaline buffers demonstrate that NaHCO₃ also promotes the transformation of glucose into formic acid, increasing the overall selectivity of the process and facilitating downstream processing.

1. Introduction

There is currently an increasing effort in developing alternative energy and commodity sources that could replace petroleum-based chemicals, that have been exploited during decades, leading to a reduction of the reserves and the increase in the emissions of greenhouse gases, especially carbon dioxide (CO₂). Different strategies have been proposed to diminish the effects caused by the increasing concentration of CO₂ in the atmosphere, including carbon capture, storage, utilisation and conversion. The latter represents not only an opportunity to reduce the CO₂ emissions, but also an alternative to obtain fuels and chemicals, closing the carbon cycle [1,2].

Among the different options, the hydrothermal conversion of CO₂ into useful products, mainly formic acid (FA), stands out by the high yields of conversion of CO₂ (higher than 70 %) that can be achieved in

comparatively short reaction times (typically 1 – 2 h). The hydrothermal conversion consists of the reduction of CO₂ dissolved in a basic aqueous solution (such as those obtained by carbon capture by absorption into aqueous solutions of amines or sodium hydroxide), performed at high pressure and temperature (up to 300 °C and 200 bar). This process can use different reductants, including metals and organic substances, especially those bearing alcohol groups [3–5].

Hydrothermal technology can also be used for the pre-treatment and valorisation of lignocellulosic biomass, producing different platform chemicals [6]. In general, the first and main product of lignocellulose decomposition is glucose, together with other sugars and derivatives [7–10], compounds that contain alcohol groups and therefore are suitable reductants for the hydrothermal conversion of CO₂. Indeed, a previous work of the authors proved that most of these derivatives can be used as CO₂ reductants to obtain formic acid [5]. The use of these

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molecules in CO₂ reduction has the advantage of producing additional products from another renewable source, residual biomass, in “one-pot”. The products obtained in the combined process are platform chemicals: formic acid, acetic acid and lactic acid, which are of great importance for a wide range of applications, such as textile, leather, pharmaceutical, plastic and dyeing industries [11–13].

In some previous works dealing with the reduction of CO₂ using organic molecules, sodium bicarbonate ¹³C (NaH¹³CO₃) as CO₂ source has been used to verify by ¹³C NMR analyses that the origin of formic acid was the inorganic CO₂ and not (only) the organic reductant. It was found that while for simple molecules such as glycerol, all formic acid comes from bicarbonate [14], for more complex substances, such as algae, plastics or glucose, part of the formic acid was obtained throughout both reactions of biomass degradation and NaHCO₃ reduction [15–18]. The production of additional formic acid from biomass degradation instead of other compounds is an advantage, as it improves the selectivity of the whole process.

In a previous work of the authors [18], the batch hydrothermal reduction of NaHCO₃ with glucose and other organic reductants produced by hydrothermal decomposition of biomass was also analysed employing marked NaH¹³CO₃ to assess the origin of the formic acid obtained as the main product. Two different mechanisms of production of formic acid were observed: the first one, at short reaction times, consists on the decomposition of glucose into formic acid and other by-products, achieving a low yield to FA-¹³C (formic acid produced by reduction of the marked inorganic carbon), whereas at longer reaction times, the second reaction mechanism leads to a higher yield to FA-¹³C. Similarly, temperature plays an important role, being 300 °C the optimal for the conversion of inorganic carbon into formic acid. These results indicate that the reduction pathway of NaHCO₃ takes place by oxidation of the by-products rather than by the oxidation of glucose itself, needing comparatively long reaction times to achieve high ratios of FA-¹³C/total FA. A reaction mechanism comprising the decomposition of glucose into glyceraldehyde and glycolaldehyde, which are further decomposed into formaldehyde, which is the key intermediate that reacts with bicarbonate to produce formate, was proposed. Other final products of the reaction included acetic acid and lactic acid, which were alternative products of the decomposition of glyceraldehyde and glycolaldehyde.

In this previous work of the authors [18], as in most previous experimental studies, batch reactors were employed due to the simplicity of the procedure, that allows studying a wide range of operational parameters, such as type of feedstock (e.g., monosaccharides, disaccharides, lignocellulose fractions, or biomass residues), temperature, time and additives, in order to achieve a better understanding of the process and the kinetics of the reactions [14,19–21]. Nevertheless, discontinuous reactors have different disadvantages, as poor control of reaction variables (temperature, time, pressure), which reduces the selectivity towards target products, and large downtimes [22–24]. Although time can be easily controlled by introducing the reactor in the heating system and quenching it after a determined amount of time, the inner part of the reactor and reaction mixture are subjected to a heating ramp that may hinder the selectivity to target products, as side reactions could take place during the time until the desired reaction temperature is reached. In addition, due to the vast dimensions of the problem of CO₂ emissions, the industrial application of these processes normally seeks the capacity to process large quantities of reactants, and discontinuous operational systems are not able to accomplish this requirement. Thus, to turn this technology in a marketable and suitable industrial-wise process, further advances should be made by developing continuous reaction systems that allow an improved control over the process variables (resulting in a higher selectivity to products) and provide a higher production capacity.

Continuous set-ups for the hydrothermal upgrading of biomass have been developed in the past decades in a reduced size, to investigate the optimal conditions for different types of biomass as feedstock and selectivity to products as a previous step for an industrial size. From the

point of view of the control of process conditions, continuous setups allow analysing the operation with shorter reaction times than those achievable with batch systems, and also provide a very precise control of reaction time, as the reaction can be initiated heating the reaction mixture by direct injection of hot water and stopped by quenching or cooling the reaction effluent [25–27]. As in the studies performed with batch reactors, pilot plant studies have focused in the main constituents of lignocellulosic biomass as a previous step to develop a process for direct conversion of biomass [28–33]. However, equivalent studies using continuous flow reactors for the hydrothermal conversion of CO₂ with organic reductants have not been performed yet. There are favourable prospects for the integration of biomass conversion and reduction of CO₂ dissolved in an aqueous phase as bicarbonate into a single continuous reactor, because previous reports have demonstrated that the addition of alkaline salts (e.g. Na₂CO₃, K₂CO₃, KHCO₃) promote the hydrothermal treatment of biomass improving the yield to liquid products (especially bio-oil) [34,35].

In this work, a set up with a continuous flow reactor is used to study the hydrothermal reduction of bicarbonate using glucose and some of its main hydrothermal decomposition products as reductants. After the proof-of-concept test, a wide range of operational conditions are tested, including selected experiments with H¹³CO₃ that contribute to elucidate the origin of the organic products obtained and the different reaction pathways. The products obtained are carboxylic acids of great interest (e.g., formic acid, acetic acid and lactic acid), which are yielded in different proportions depending on the operational parameters. To the best of our knowledge, there are no previous works focused on formic acid production in a continuous reactor by combination of glucose hydrothermal treatment and CO₂ reduction.

2. Materials and methods

2.1. Materials

NaHCO₃ (100 %) was acquired from COFARCAS. D-(+)-glucose (99 %), glycerol (99.5 %), *n*-propanol (>99.7 %), glyceraldehyde (90 %), lactic acid (≥85 %), pyruvaldehyde (40 %), 5-HMF (99 %), furfural (99 %) and fructose (99 %) were purchased from Sigma Aldrich. Ethanol (EtOH, 99.5 %), acetone (99.5 %), isopropanol (*i*PrOH, 99.9 %), and sulfuric acid (H₂SO₄, 96 %) were obtained from Panreac, while propanaldehyde (99 %) was acquired from Acros Organics.

Some experiments and analysis were carried out using chemicals with ¹³C isotope. These chemicals were: NaH¹³CO₃ (99+%, 98 atom %¹³C), acetic acid-1-¹³C (99 %, 99 atom %¹³C) and formic acid-¹³C (95 wt% in H₂O, 99 atom %¹³C), which were purchased from Sigma Aldrich, and deuterated solvent (D₂O, 99.9 % D atom) from Cortecnet.

All reactants were used without further treatment of purification.

2.2. Experimental set-up

The set-up used for the continuous hydrothermal reduction of NaHCO₃ into formic acid is schematically depicted in Fig. 1 and photographed in Fig. 2. A solution of NaHCO₃ and organic model compounds is pumped to the operation pressure (200 bar) using a HPLC pump (Gilson, model 25.SC, P-01) at a rate 0.995–10.0 mL/min into the reactor (R-01), placed in an electric oven (Gallur, model MT-14, series 1115), and it is mixed with a preheated ultrapure water stream (preheated in E-01), pumped by another HPLC pump (Gilson, model 10.WSC, P-02), keeping a pumping ratio 1:1 v/v, in order to quickly achieve the desired reaction temperature. After leaving the reactor, the reaction is stopped by sudden depressurisation in valve V-07 (manufactured by Autoclave Engineers, model 30VRMM4812-HT), which produces an instantaneous cooling by Joule-Thomson effect, and effluents are further cooled down to room temperature using a concentric tube heat exchanger (E-02). Liquid products are separated from gas products in a flash vessel (VS-01), and liquids samples are collected for HPLC and

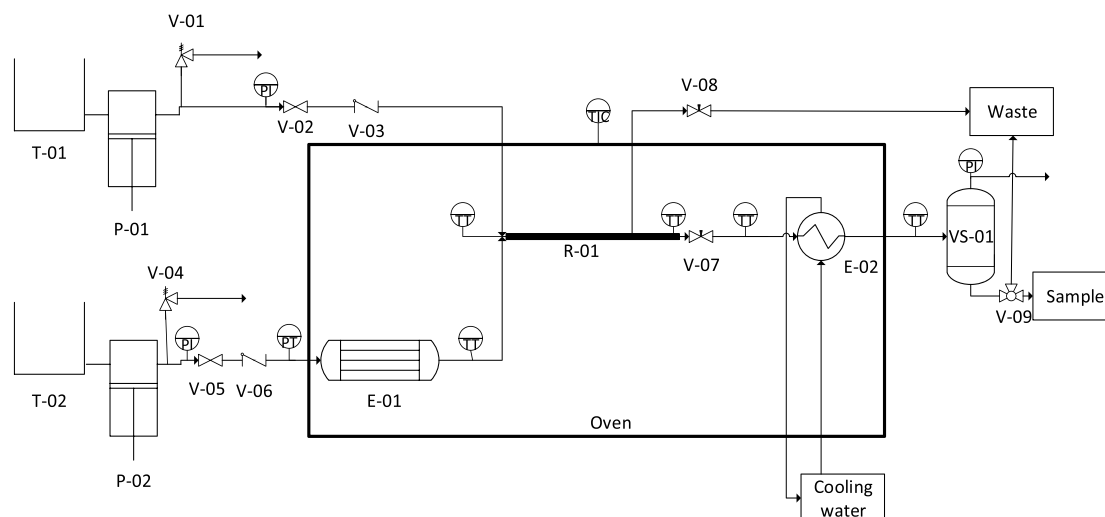


Fig. 1. Schematic diagram of the experimental set-up of hydrothermal CO₂ conversion in a continuous flow reactor. Legend: T-01: solution tank; T-02: water tank; P-01 and P-02: pumps; V-01 and V-04: pressure relief valve; V-02 and V-05: ball valves; V-03 and V-06: check valves; E-01 and E-02: heat exchangers; R-01: tubular reactor; V-07: high temperature valve; V-08: auxiliary valve; VS-01: flash vessel; V-09: three-way valve; PI: pressure indicator; PT: pressure transducer; TT: thermocouple.



Fig. 2. Photographs of the experimental set-up of hydrothermal CO₂ conversion in a continuous flow reactor. Tubular reactors are placed inside an electrical oven to facilitate the replacement of reactors of different residence times. In the photograph, reactor 3 of Table 1 is installed.

NMR analyses throughout a three-way valve (V-09). The gas separated in the flash vessel, presumably composed of vaporized water, desorbed CO₂ and hydrogen produced by the organic reductants, was obtained in quantities that were too small for collecting and analysing it.

In order to achieve different ranges of residence time (τ), three reactors with different volumes were built. Their dimensions are shown in Table 1. Residence time τ was controlled by the inner volume of the reactor and the flow set in the pumps. In addition, τ depends on the reaction temperature, as the density of the stream varies as expressed in Eq. (1):

$$\tau = V/Q_w = \left[\frac{(\pi D^2 L)}{4} \right] \cdot \frac{\rho_w}{Q_0 \rho_0} \quad (1)$$

where V is the reactor volume, Q_w is the volumetric flow occurring at reaction temperature and pressure, L is the reactor diameter, ρ_w is the density of the medium at the reaction temperature and pressure (obtained from the NIST database [36]), Q_0 is the volumetric flow at room temperature, and ρ_0 is the density of the medium at room temperature (obtained from the NIST database). At 300 °C, the residence time can vary from 1 s to 75 min by using the three different reactors and the flow rate ranges provided by the pumps.

2.3. Experimental procedure

At the beginning of an experiment, water was pumped through the system while heating the oven to the reaction temperature and keeping the pressure constant adjusting the opening of the decompression valve (V-07). After achieving a steady temperature inside the oven, water and solution streams were pumped at the target reaction flow for one hour after reaching steady state. This is assessed by verifying that temperature and pressure readings in the set up remain constant. During operation, inlet and outlet temperatures of the reactor remain constant within ± 5 °C; the outlet temperature was always lower than the inlet temperature by 5–20 °C depending on the flowrate (the higher the flowrate, the higher the variation of temperature), because the global reaction is endothermic. After reaching steady state, three consecutive samples of the reactor effluent were taken and stored for analysis. Flow was changed to establish a new residence time and steady state was reached again before taking the next set of samples.

2.4. Analytical methods

After being filtered through a 0.22 μ m Nylon filter, liquid samples were analysed by HPLC chromatography. The reactions carried out using NaH¹³C₃ were also analysed by nuclear magnetic resonance (NMR) techniques. The HPLC apparatus (Waters, Alliance separation module e2695) was operated with an Aminex 87H (Bio-Rad) column and two detectors: RI (Waters, 2414 module) and UV (210 nm, Waters, 2998 module). The mobile phase was 5 mM H₂SO₄ with a flow rate of 0.6 mL/min. The temperatures of the column and the detector were 60 °C and 30 °C, respectively.

Table 1
Reactors used in the hydrothermal CO₂ reduction experiments.

Reactor	\emptyset ext (in)	Length (cm)	Inner volume (mL)
Reactor 1	1/8	19.5	0.5
Reactor 2	1/4	22.8	3.7
Reactor 3	1/4	1220.0	200.0

The yield to products (Y_{product}) was calculated with respect to the concentration of the organic reductant (the limiting reagent) as shown in Equation (2):

$$Y_{\text{product}} = \frac{C_{\text{HPLC product, f}}}{C_{\text{organic, i}}} \cdot 100 \quad (2)$$

where $C_{\text{HPLC product, f}}$ is the molar concentration of the different products obtained at the end of the reaction and $C_{\text{organic, i}}$ is the initial molar concentration of the corresponding solution of the organic model compound.

Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR analyses were performed using a 500 MHz Agilent instrument equipped with One NMR probe in the Laboratory of Instrumental Techniques (LTI) Research Facilities, University of Valladolid. For the quantification of ^{13}C products, two different analyses of the sample were performed: one with samples without further treatment and another adding acetic acid- ^{13}C ($\text{CH}_3^{13}\text{COOH}$) as internal standard. In all cases, 600 μL of sample was transferred to a NMR tube and 50 μL of D_2O were added for internal lock reference. Samples analysed with $\text{CH}_3^{13}\text{COOH}$ as internal standard were prepared as follows: 2.5 mL of filtered sample were spiked with 5 μL of $\text{CH}_3^{13}\text{COOH}$, achieving a concentration of 34 mM $\text{CH}_3^{13}\text{COOH}$, 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 $^\circ\text{C}$, 70 s relaxation delay between transients, 45 $^\circ$ pulse width, and spectral width of 31250.0 Hz, a total of 512 transients and 1.048 s acquisition time. In order to obtain a decoupled spectrum without NOE enhancements, the inverse-gated proton decoupling method was used. The ^{13}C 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 64 K zero-filling was applied to improve the digital resolution of the final spectrum.

The yield to formic acid obtained from $\text{NaH}^{13}\text{CO}_3$ was determined as shown in Equation (3):

$$Y_{\text{FA, NMR}} = \frac{C_{\text{FA, f, NMR}}}{C_{\text{organic, i}}} \cdot 100 \quad (3)$$

where $C_{\text{FA, f, NMR}}$ is the molar concentration of formic acid ^{13}C obtained after the reaction, determined by quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR analysis, and $C_{\text{organic, i}}$ is the initial molar concentration of the organic model compound.

All experiments were performed at least twice in order to ensure reproducibility. The relative standard deviation (RSD) at every experimental condition was calculated as indicated in the Equation (4):

$$\text{RSD} (\%) = \frac{\sigma}{\mu} \cdot 100 \quad (4)$$

where RSD is the relative standard deviation expressed in %, σ is the standard deviation, and μ is the mean of the set of values. In the experimental results reported, RSD was lower than 10 %, as presented in the tables of numerical results provided as [Supplementary Information](#).

3. Results and discussion

3.1. Comparison between batch operation and continuous reaction: Proof of concept

In this section, the results obtained with the continuous reactor reported in this work using the reactor 3 described in [Table 1](#) and the batch reactor reported in a previous work [18] are compared. In order to determine not only the influence of the set-up in the FA production, but also the origin of FA ($\text{NaH}^{13}\text{CO}_3$ conversion, $\text{FA-}^{13}\text{C}$, or glucose degradation), $\text{NaH}^{13}\text{CO}_3$ was used as CO_2 source. In order to facilitate the

interpretation of results, these are presented in this section as graphics; numerical results can be found in the tables provided as [Supplementary Information](#). These tables present in detail the results obtained in replications of each individual experiment. As it can be observed, highly consistent results were obtained with these replications, which demonstrate the capacity to precisely control the experimental conditions which is one of the advantages of the continuous set-up used in this work over batch reaction systems. Tables in the [Supplementary Information](#) also provide the experimental inlet and outlet temperatures at the reactor determined at each experiment. As presented in these tables, temperature increases in all experiments, indicating that the global reaction is exothermic, which is favourable for the energy integration of the process. It can be also observed that variations between inlet and outlet temperature in experiments with the smaller reactors 1 and 2 are generally below 5 $^\circ\text{C}$, indicating a good control of temperature during the reaction, but that these variations increase to 10 – 50 $^\circ\text{C}$ in experiments with reactor 3. The longer variations in this case may be due to a higher conversion in the reactions of decomposition of glucose at longer residence times.

Total yields to FA (produced both by NaHCO_3 reduction and glucose degradation) and the yield to $\text{FA-}^{13}\text{C}$ in both set-ups are compared in [Fig. 3](#). As it can be seen in this figure, the results obtained with the batch and the continuous set up are comparable in absolute values, but show different trends, as the yield in batch reactors decreased from 47.5 % to 33.0 % mol total FA/mol glucose in reaction times between 10 and 60 min, whereas yield in continuous reactor increased from 31.3 % to 43.3 % mol total FA/ mol glucose in the interval from 10 to 45 min. Furthermore, in the continuous set-up the yield to $\text{FA-}^{13}\text{C}$ was almost constant, reaching a 15.2 % mol $\text{FA-}^{13}\text{C}$ / mol glucose after 10 min and varying scarcely at longer reaction times, whereas in the batch set-up, the yield to $\text{FA-}^{13}\text{C}$ increased from 7.5 % and 19.2 % in reaction times between 10 and 60 min.

The differences in the performance of both set-ups are also evident in the results of the ratio $\text{FA-}^{13}\text{C}$ / total FA presented in [Table 2](#). Using the continuous reactor, the proportion of FA produced by the reduction of $\text{NaH}^{13}\text{CO}_3$ remained constant in between 10 and 30 min of residence time, achieving a maximum ratio of 48.6 % $\text{FA-}^{13}\text{C}$ / total FA after 10 min of residence time, and decreased to 32.3 % after 45 min. In contrast, with batch reactors a ratio $\text{FA-}^{13}\text{C}$ / total FA of just 15.9 % is achieved

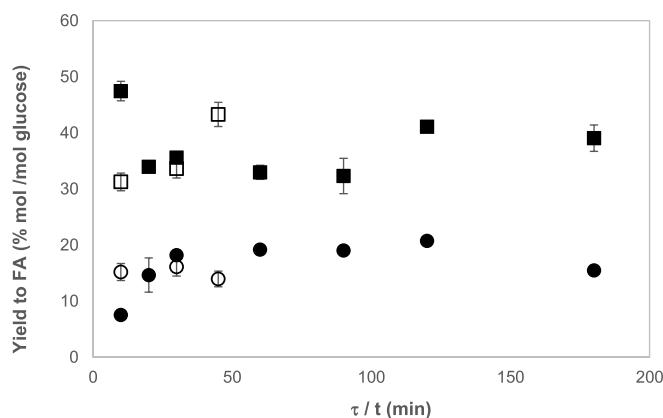


Fig. 3. Comparison between yield to total FA and $\text{FA-}^{13}\text{C}$ as a function of residence time using glucose as reductant in continuous plant and batch reactors. Symbols: (■): yield to total FA in batch reactor; (□): yield to total FA in continuous reactor 3; (●): yield to $\text{FA-}^{13}\text{C}$ in batch reactor; (○): yield to $\text{FA-}^{13}\text{C}$ in continuous reactor 3. Reaction conditions in both continuous and batch reactors: initial concentration of glucose: 0.05 M, initial concentration of $\text{NaH}^{13}\text{CO}_3$: 0.5 M, temperature: 300 $^\circ\text{C}$. All experiments were performed at least twice, and error bars indicate the deviations between replications of the experiment; in some cases, error bars are not visible because they are smaller than the symbols used in the diagram. Numerical results with the continuous reactor are reported in [Table S1](#) of supplementary information.

Table 2

Ratio FA-¹³C/total FA (%) as a function of reaction time in batch reactors (data obtained in a previous work [18]) and in the continuous reactor (reactor 3) at 300 °C.

Batch reactor t (min)	% FA- ¹³ C/total FA	Continuous reactor (reactor 3) t (min)	% FA- ¹³ C/total FA
10	15.9	10	48.6
20	43.2	30	47.9
30	51.1	45	32.3
60	58.2		
90	58.9		
120	50.4		
180	39.6		

after 10 min, and this ratio only starts to increase to 43.2 % FA-¹³C / total FA after 20 min.

Considering these results, it can be observed that the continuous reactor achieves a higher performance in the reduction of inorganic NaH¹³CO₃ than batch reactors: in batch reactors, the first burst of production of formic acid is due to the degradation of glucose, and FA-¹³C only starts to build up after relatively long reaction times of 30 – 60 min [18], but Fig. 3 and Table 2 demonstrate that in the continuous reactor, the conversion of inorganic NaH¹³CO₃ proceeds to high yields at short residence times of 10 min. This discrepancy clearly indicates a difference in the mechanisms of the reaction in the continuous and batch set-ups at short reaction times, and for this reason further experiments described in the following sections were focused on short residence times.

3.2. Effect of reaction residence time and reaction temperature on yield to FA

As indicated before, one of the advantages of continuous reactors from the point of view of the experimental study of the system is the possibility to operate with short residence times. In order to investigate the effect of shorter residence times on the evolution of glucose and on the yield to total FA and to analyse the reasons for the different behaviour of batch and continuous reactors in this residence time interval, continuous reactors 1 and 2 were used to operate between 1 and 10 s and 8–60 s, respectively. Reactions in these residence time ranges were also performed at different reaction temperatures (200 °C, 250 °C and 300 °C), as depicted in Fig. 4.

As presented in Fig. 3, a higher reaction temperature and a longer

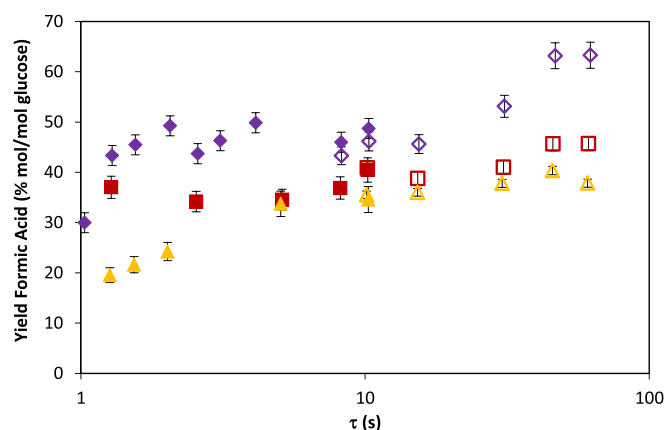


Fig. 4. Influence of reaction temperature and residence time on yield to total FA using glucose in continuous reactor 1 (full symbols) and 2 (empty symbols). Symbols: (◆,◇): 300 °C; (■,□): 250 °C; (▲,△): 200 °C. Reaction conditions: 0.05 M glucose, 0.50 M NaHCO₃. Horizontal axis (τ) is plotted in logarithmic scale. All experiments were performed at least twice, and error bars indicate the deviations between replications of the experiment; in some cases, error bars are not visible because they are smaller than the symbols used in the diagram. Numerical results are reported in Tables S2–S7 of Supplementary Information.

residence time led to a higher yield to total FA (analysed by HPLC), reaching a maximum yield to total FA of 63.3 % after 1 min at 300 °C, using the continuous reactor 2. It should be pointed that a yield to FA of 63.2 % was obtained after 45 s at 300 °C, showing that a further increase in residence time did not improve significantly the yield to total FA. It is remarkable that a yield to formic acid of 30 % was reached after only 1 s of residence time at 300 °C, and that the yield achieved after 1 min of residence time (63.3 %) is higher than yields obtained at longer residence times, reported in the previous section 3.1. This result is consistent with the results obtained in the study of the reaction with batch reactors [18], that showed two peaks in the yield: the first one at short residence times and the second one at longer residence times over 60 min, with a decrease in the yield at intermediate times that were attributed to degradation of formic acid and slow build-up of intermediates that prompt the conversion of bicarbonate. The high yields obtained in the continuous reactor at the residence time of 1 min correspond with the first peak observed in batch experiments, although due to limitations in the operation of a batch system, residence times as short as 1 min could not be tested in the previous study with batch reactors [18]. Furthermore, Table 3 presents a comparison of these values with the conversion yields reported in the literature for hydrothermal conversion of CO₂ using batch reactors and different reductants and operating temperatures. It can be observed that, as already indicated, the yields obtained with the continuous flow reactor at 1 min are higher than the yields achieved at longer residence times with batch reactors and glucose as reductant, and are comparable to the yields achieved at similar conditions by hydrothermal conversion using stronger (and more expensive) metal reductants. Regarding the comparability between the two reactors at different temperatures, it can be observed that the yield to total FA varied only up to 2 % employing different reactors but keeping constant temperature and residence time, demonstrating that there is consistency in the results of formic acid production with the two reactors employed.

Besides FA, other by-products in the liquid samples identified throughout HPLC analysis were mainly acetic acid, lactic acid, glycolaldehyde and glyceraldehyde (Fig. 5). The main by-product obtained due to the oxidation of the glucose was, in all the cases, acetic acid, whose production follows the same trend that that of FA as a function of residence time and reaction temperature, showing a related formation pathway between both products. Yields to acetic acid up to 42 % were reached after 45 s of residence time at 300 °C. The same relationship was observed in batch experiments [18]. A similar trend can be observed in the case of lactic acid, although achieving a lower yield (up to 25 % after 45 s of residence time at 300 °C). In this case, the hypothesized reaction pathway involves the isomerization of glucose into fructose, which undergoes a *retro*-aldol reaction to pyruvaldehyde and the subsequent isomerisation into lactic acid. This process is favoured by high pressure and temperature and alkaline reaction conditions [28]. In previous works, lactic acid was also obtained as by-product of the conversion of glyceraldehyde to glycolaldehyde in hydrothermal media [5]. Interestingly, the yield to glycolaldehyde and glyceraldehyde was not

Table 3

Comparison of the yields obtained in this work with the continuous flow reactor with literature results obtained using batch reactors.

Reactor type	Reductant	Temperature	Reaction time	Yield
Continuous flow reactor (this work)	Glucose	300°C	1 min	63 %
Continuous flow reactor (this work)	Glucose	300°C	45 min	43 %
Batch reactor [18]	Glucose	300°C	120 min	41 %
Batch reactor [39]	Glucose	150°C	15 min	27 %
Batch reactor [38]	Zn	300°C	120 min	79 %
Batch reactor [37]	Zn	300°C	120 min	54 %
Batch reactor [3]	Al	250°C	120 min	58 %

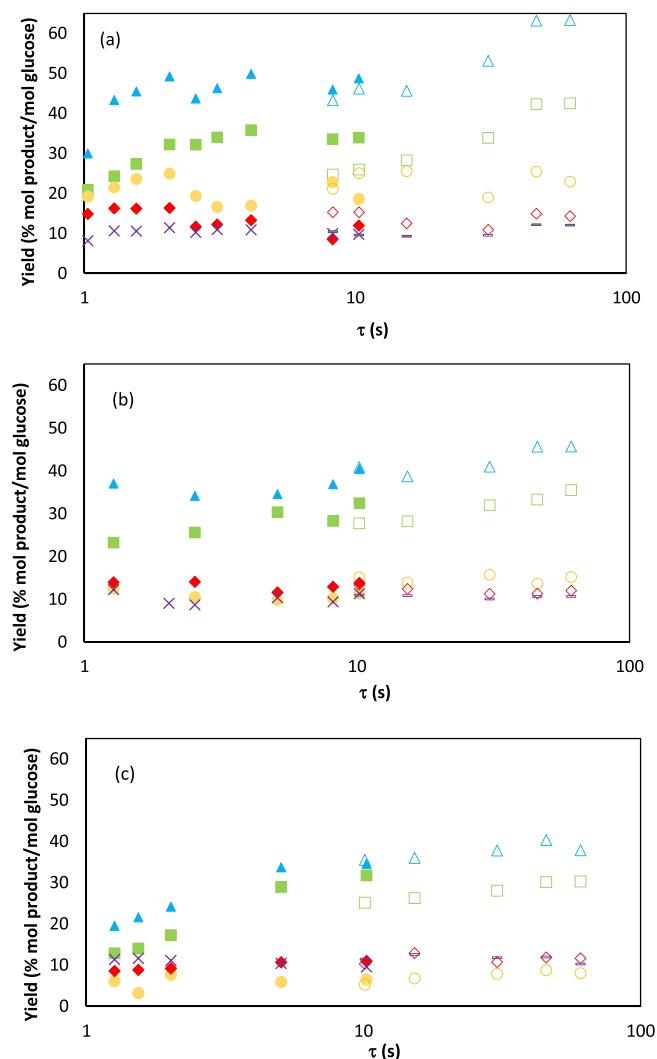


Fig. 5. Evolution of yield to formic acid (▲,△) and other by-products at 200 °C using glucose as reductant in the continuous reactors 1 (full symbols) and 2 (empty symbols). Main by-products identified: (■,□): acetic acid; (●,○): lactic acid; (◆,◇): glycolaldehyde; and (×, -): glyceraldehyde. Reaction conditions: 0.05 M glucose, 0.50 M NaHCO₃, (a) T: 300 °C, (b) T: 250 °C, (c) T: 200 °C. Horizontal axis (τ) is plotted in logarithmic scale. Numerical results are reported in Tables S2–S7 of Supplementary Information.

influenced by the reaction temperature or the residence time, showing a constant yield around 10 % in both by-products in all the cases. Their production mechanism may be related to the *retro*-aldol condensation of glucose and fructose, respectively. In this sense, the obtained by-products and the hypothesised reaction mechanisms agree with those observed in batch experiments [18], but these compounds are formed at much shorter reaction times than in batch experiments, indicating that the equilibrium of the corresponding formation reactions is achieved faster.

This difference in the behaviour of the continuous and batch reactors may be due to the differences in the mode of operation of both types of reactors. On the one hand, in the continuous reactor, a nearly instantaneous heating of the reaction mixture is achieved by direct injection of preheated water, whereas in batch reactors it is difficult to make heating faster than the reaction of conversion of glucose to formic acid, which already takes place at lower temperatures, down to 150 °C [39]; thus, during the minutes required to heat the batch reactor to a temperature high enough to initiate the reduction of NaHCO₃, a significant fraction of glucose can be already converted to formic acid and is not available to

perform the reduction of NaHCO₃, thus lowering the FA-¹³C / total FA ratio. Moreover, while in batch reactors pressure is generated autogenously, i.e. by the steam and gases produced by the reaction itself, in the continuous reactor pressure is imposed mechanically with the decompression valve. Therefore, while in batch reactors the small amounts of H₂ that are produced by the decomposition of glucose, that are hypothesised to participate in the reduction of NaHCO₃ [18], are in gas–liquid equilibrium with gaseous H₂, in the continuous reactor the pressure of 200 bar set by the decompression valve promotes the dissolution of H₂, increasing its concentration in the liquid phase and thus accelerating the reactions in which it is involved.

Regarding the concentration of the reductant, glucose was completely consumed within the first second of reaction at 250 °C and 300 °C. However, at 200 °C there is still a 14 % (7 mmol/L) of the initial concentration after 1.25 s of reaction, achieving full conversion after 5 s at 200 °C. It should be noted that fructose (an isomer of the glucose) appeared at 200 °C, following the same trend as glucose, indicating that part of the glucose is transformed into fructose and is converted afterwards. These results agree with those discussed above regarding the production of glyceraldehyde.

3.3. Study of the buffer effect of the NaHCO₃ on glucose conversion

Besides its role as inorganic carbon source, NaHCO₃ may participate in the formation of organic products by decomposition of glucose. Indeed, previous studies have demonstrated the possibility to obtain formic acid from organic molecules in high temperature processes, normally under alkaline conditions [5,40,41]. In order to analyze the effect of sodium bicarbonate in the first seconds of reaction, further experiments using glucose were performed at 300 °C using reactor 1 (residence time between 1 and 10 s) and different alkaline conditions.

The first experiment was performed employing a solution 0.05 M of glucose in the mixing point without further addition of NaHCO₃ or any other alkaline source (Fig. 6a). The maximum yield to FA obtained was 14 % after 5 s of reaction. Comparing the results of this experiment with the previously obtained when using NaHCO₃ (Fig. 5), that show much higher yields, it can be clearly observed that the addition of NaHCO₃ results in a different reaction mechanism. In addition, the proportions of the different by-products changed when no NaHCO₃ was added, being in this case lactic acid and glycolaldehyde the main products in the first 4 s of reaction, whereas at longer reaction times (5–10 s), the main by-products were lactic acid and formic acid, reaching their maximum yields of 28 % and 14 % at 5 s, respectively, and decreasing afterwards. It was also observed that glucose did not react as fast as in experiments with NaHCO₃, still having a concentration of 35 mM of glucose after the first second of reaction and achieving a 90 % of conversion after 5 s of residence in the reactor. In addition, fructose was identified in the liquid samples, achieving a maximum concentration 7 mM after 1.5 s of residence.

Another experiment was performed using a solution 0.05 M of glucose in a buffer solution (0.50 M Na₂HPO₄ and 0.05 M NaH₂PO₄), so that the same pH when employing NaHCO₃ (pH ~ 8) was achieved at room conditions. No further CO₂ source was added (Fig. 6b). The evolution of the products in this case was similar to the one observed when using NaHCO₃. Formic acid was the main by product (achieving a maximum yield of 30 % after 8 s of residence time), followed by acetic acid, lactic acid, glycolaldehyde and glyceraldehyde. However, the yield to formic acid is significantly lower than the yield achieved when using NaHCO₃. These results indicate that the production of formic acid is indeed prompted by the addition of alkaline media, but the maximum is much lower than when using bicarbonate as buffer due to the lack of the contribution of the formic acid generated by reduction of bicarbonate.

3.4. Glucose by-products as reductants

In order to have a better understanding of the reaction, further

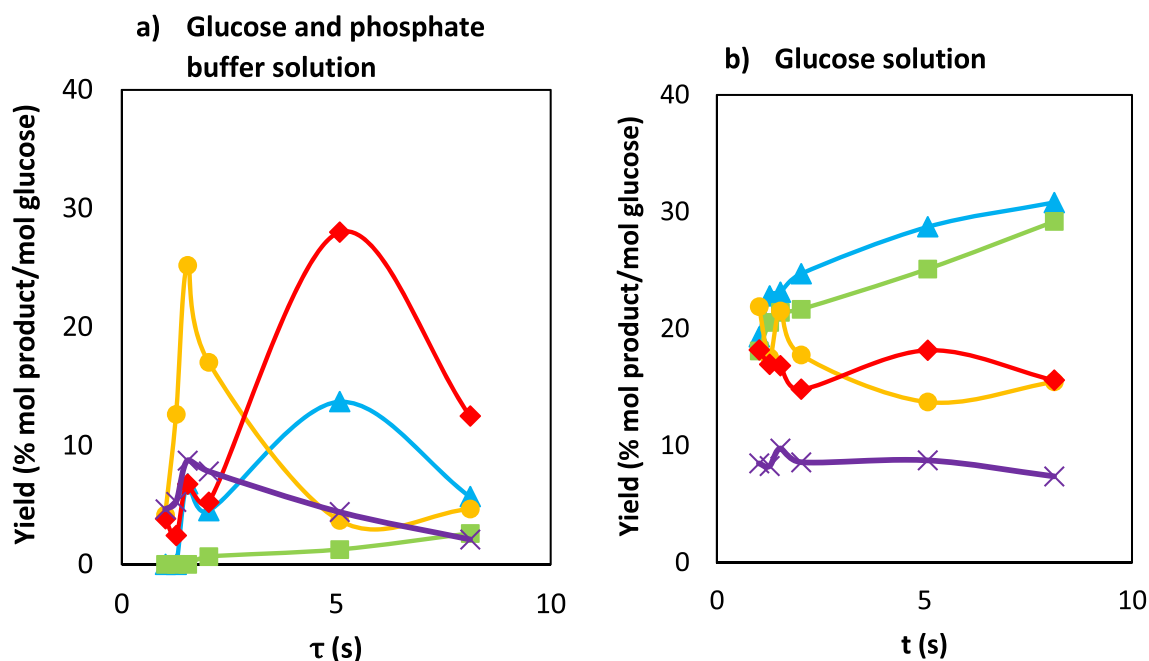


Fig. 6. Evolution of yield to FA (\blacktriangle) and other by-products at 300 °C in the continuous reactor 1 using (a) 0.05 M glucose solution; (b) 0.50 M of glucose, 0.50 M of Na_2HPO_4 and 0.05 M NaH_2PO_4 solution. Main by-products identified: (\blacksquare): acetic acid; (\bullet): lactic acid; (\blacklozenge): glycolaldehyde; and (\times): glyceraldehyde. Numerical results are reported in Tables S8 and S9 of Supplementary Information.

experiments were performed at 300 °C in the continuous reactor 1 ($\tau = 1$ –10 s) using the main by-products obtained with the glucose as reductants: acetic acid, lactic acid, glycolaldehyde and glyceraldehyde, in order to study their effect in the reduction of NaHCO_3 into formic acid, especially at short reaction times. The main results are reported in Fig. 7.

As reported in previous works [18], no formic acid was detected at short reaction times when acetic acid was used in presence of NaHCO_3 . In the case of lactic acid, no formic acid was obtained when reacting lactic acid with NaHCO_3 in the continuous reactor, despite that the previous work in batch reactors showed the ability of lactic acid to reduce NaHCO_3 into formic acid at 300 °C at relatively long reaction times in batch reactions [18]. A different trend was observed in the experiments employing glycolaldehyde and glyceraldehyde solutions as organic reactant. Previous studies have shown that these components can be obtained through glucose hydrothermal decomposition, and they were able to reduce NaHCO_3 into formic acid under hydrothermal conditions [18,23,25,42,43]. However, they required longer reaction times to reduce NaHCO_3 to formic acid.

Different reaction times were set using glycolaldehyde or glyceraldehyde as organic reactant in the continuous reactor. The distribution of products from glycolaldehyde hydrothermal treatment with and without NaHCO_3 in the continuous reactor is depicted in Fig. 7a and b. The presence of NaHCO_3 in the media resulted in an increase on the yield to the main products identified (i.e., formic acid, acetic acid and lactic acid). It is remarkable that the production trends of formic acid and acetic acid followed a similar pathway, reaching a maximum yield of 17 % and 10 %, respectively, after 5 s of reaction. In the case of lactic acid, the maximum yield was achieved at 1 s of reaction, achieving a yield of 8 %. Despite lactic acid is a C3 carboxylic acid and glycolaldehyde is a C2 aldose, the possible reaction pathway of glycolaldehyde conversion under alkaline hydrothermal conditions has been previously reported by Kishida et al. [44], being then this the plausible formation mechanism in presence of NaHCO_3 .

In the case of reactions carried out without the addition of NaHCO_3 , acetic acid was the predominant product, followed by formic acid, reaching maximum yields of 4 % and 2 %, respectively after 8 s of residence time. In addition, no lactic acid was detected under these

operational conditions, which agrees with previous investigations about the necessity of alkaline media for glycolaldehyde conversion. Furthermore, NaHCO_3 plays an important role in glycolaldehyde conversion. In the presence of NaHCO_3 , glycolaldehyde conversion was higher than 90 % after the first second of reaction (4 mM glycolaldehyde at 1 s), and it increased to 95 % after 10 s of reaction, reaching a minimum concentration of 2 mM glycolaldehyde at that time. However, without the presence of NaHCO_3 , glycolaldehyde conversion was lower, varying from 9 % to 33 % at residence times between 1 and 10 s, respectively.

Analogously, reactions of glyceraldehyde with or without the presence of NaHCO_3 followed similar trends as those achieved with glycolaldehyde (Fig. 7c and 7d). The addition of NaHCO_3 to the reaction media resulted in a higher production of formic acid, acetic acid and glycolaldehyde, following a similar trend in their production. The maximum yield achieved to formic acid and lactic acid were achieved after 5 s of retention time (22 % and 15 %, respectively), whereas the maximum yield to acetic acid was achieved after 8 s of reaction (17 %). Different distributions of products were achieved when no NaHCO_3 was present in the reaction media. The main product was lactic acid, which achieved a maximum yield of 62 % after 5 s of reaction. The other products were observed in lower yield than in experiments in presence of NaHCO_3 , achieving the maximum yield to formic acid and acetic acid (5 % and 2 %, respectively) after 10 s of residence time. In addition, no glycolaldehyde was detected in the reaction without NaHCO_3 addition, indicating that the reaction pathway of glycolaldehyde from glyceraldehyde is favoured in alkaline media.

Contrary to glycolaldehyde, the conversion of glyceraldehyde is not influenced by the addition of NaHCO_3 to the media. Whereas glycolaldehyde reaction without the addition of NaHCO_3 was hindered, in the case of glyceraldehyde, a 95 % of conversion was achieved in the first second of reaction with and without the presence of NaHCO_3 in the media, reaching in both cases a 99 % of conversion after 10 s of residence time.

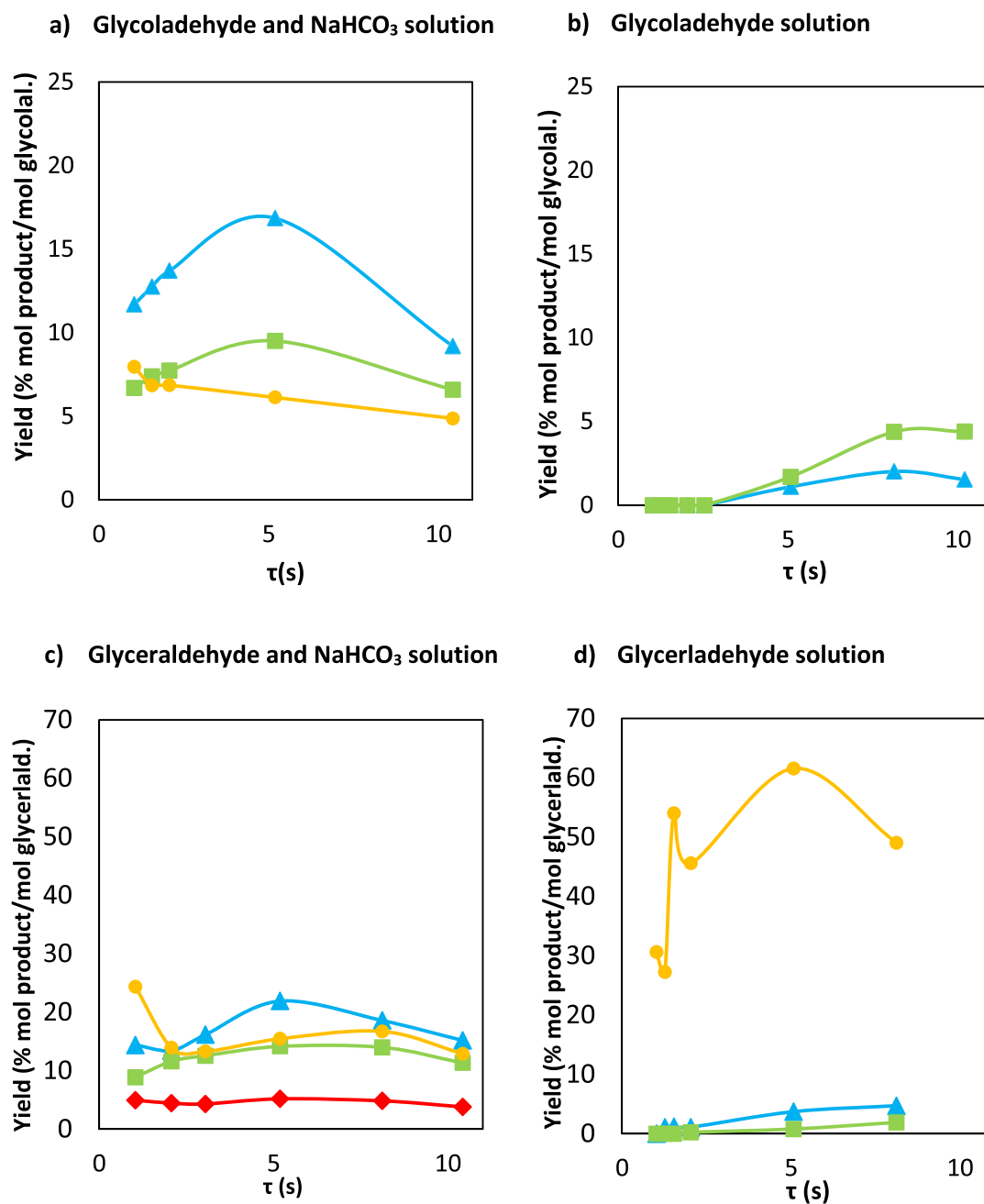


Fig. 7. Evolution of yield to formic acid (▲) and other by-products at 300 °C using a glycolaldehyde or glycerlaldehyde solutions in the continuous reactor 1. (a): 0.05 M glycolaldehyde and 0.50 M NaHCO₃ solution; (b): 0.05 M glycolaldehyde; (c): 0.05 M glycerlaldehyde and 0.50 M NaHCO₃ solution; (d): 0.05 M glycerlaldehyde. Main by-products identified: (■): acetic acid; (●): lactic acid; (◆): glycolaldehyde. Numerical results are reported in Tables S10–S13 of Supplementary Information.

4. Conclusions

In this work, the simultaneous glucose and NaHCO₃ hydrothermal treatment for the production of formic acid were carried out successfully in continuous flow reactors. For the first time, the NaHCO₃ reduction to formic acid using organic molecules in a continuous apparatus is reported.

Experiments using NaH¹³C₃ as CO₂ source determined that the faster heating ramp and the mechanically-set pressure that favours de dissolution of gaseous products, favoured the reduction of NaH¹³C₃. Although a lower production of total formic acid is achieved after 10 min of residence time in the continuous reactor compared with results previously reported in batch reactors [18], a considerably higher ratio FA-¹³C/total formic acid was obtained in the continuous reactor,

reaching a ratio of 48.6 % in the first 10 min of reaction. A maximum yield to formic acid of 63 % after 60 s of reaction was reached. In addition, the effect of sodium bicarbonate on the yield to formic acid and other by-products was also investigated, observing that the yield to formic acid was higher when NaHCO₃ was added to the medium. This synergistic effect of NaHCO₃ in the hydrothermal biomass conversion to formic acid with high yield and selectivity may prompt the development of the process in order to obtain a green source of chemicals and energy by converting residues into useful products.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Angel Martin reports financial support was provided by Spain Ministry of Science and Innovation. Angel Martin reports financial support was provided by Junta de Castilla y Leon Consejería de Educacion.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.139741>.

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