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Hydrothermal CO_2 reduction using biomass derivatives as reductants

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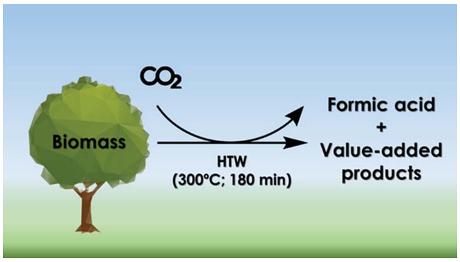
GRAPHICAL ABSTRACT



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ABSTRACT

A wide range of organic substances, potentially derived from biomass, were tested as reductants for CO_2 (as $NaHCO_3$) in hydrothermal media. The reactions were carried out in batch reactors at 300 °C and 3 h. All the substances reduced CO_2 to formic acid in yields up to 65%. These results agree to the mechanisms proposed in literature that suggested that reduction is carried out by primary or secondary alcohols. However, some substances without these groups gave significant yields to formic acid so new mechanisms were proposed. Out of all the compounds tested, glucose gave the highest yield to formic acid, probably due to its particular reaction pathways at the studied conditions. Effect of NaOH in the reaction using glucose was investigated to assure that formic acid is produced from bicarbonate. For ethanol and ethylenglycol, additional conditions were tested to study the dependence of the reaction with time and temperature.

1. Introduction

Carbon dioxide is one of the most concerning greenhouse gasses because of its increasing atmospheric level due to anthropogenic activity, e.g. fossil combustion and industrial processes. Different methods have been proposed to diminish the atmospheric CO_2 by capturing at its source and storing it. As this technology develops, a great availability of CO_2 is expected, then new opportunities arise to valorise it by transforming it into useful chemicals. This attractive approach is highly desirable since, apart from the economic benefits, it would bring a positive environmental impact because of the reincorporation of CO_2 to the carbon cycle [1,2].

Among the different processes for its conversion into chemicals, photochemical reduction, electrochemical reduction or hydrogenation of CO_2 are the most promising strategies [3]. However, CO_2 owns a great thermodynamic stability, which requires for its transformation high external energy substances, e.g. hydrogen, unsaturated compounds, organometallic compounds and small-membered ring compounds [4]. Another option for overcoming the high stability of CO_2 is using reaction in hydrothermal media [4–7] i.e. using liquid water as solvent at high temperatures. Another advantage of hydrothermal reduction of CO_2 in hydrothermal media is avoiding the use of gaseous H_2 as reductant. H_2, is still a derivative of fossil fuels so the environmental benefit would be lost. Moreover, H_2 utilization comprises safety issues

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due to its flammability and reactivity. The main product obtained from hydrothermal reduction of CO_2 is formic acid [4–7], that is an important chemical feedstock with a wide range of industrial applications such as storing hydrogen and to release it to power fuel cells and obtain energy. [8–10] Industrial formic acid production by CO_2 reduction would be an attractive approach to valorise this gas at the same time that its emissions are reduced. Zero-valent metals have proposed as reductants in hydrothermal media [7,11–14]. However, despite of obtaining acceptable yields, the metals should be reduced again in order to recycle them. Therefore, there is an increasing interest in obtaining an alternative CO_2 reductant.

Biomass is a world-wide spread, sustainable and inexpensive feedstock and, sometimes, considered as a residue [15]. Due to the depletion of fossil fuel reserves and the environmental problems attached to their consumption, several technologies are being developed in order to obtain value-added chemicals and biofuels [15–17]. Biomass is mainly composed of cellulose, hemicellulose and lignin. These biopolymers can be isolated and depolymerised into its monomeric units such as monosaccharides and phenols. Hydrothermal routes have been intensively studied to process biomass due to the outstanding properties that hot compressed water exhibits such as lower dielectric constant and higher ion product than ambient liquid water [18–21]. Water can act as acidic and basic catalyst as well as environmentally benign solvent. Following this approach, biomass has been converted into a wide range of intermediates and/or valuable products, such as lactic acid, acetic acid, 5-hydrozymethylfurfural (5-HMF), phenol and vanillin, among others [22–27], and many of these reactions involve oxidations. Therefore, the combination of both hydrothermal processes, biomass conversion and CO_2 reduction in one-pot reaction, would provide an attractive and sustainable approach for the valorisation of lignocellulosic residues and the decrease of CO_2 atmospheric emissions by integrating this process in the main CO_2 producers, such as power and industrial factories.

Despite the undeniable advantages of this approach, there are not many reports in literature about it. Most of them are focused on reduction of bicarbonate with isopropanol and glycerol [4,6,28,29]. According to these reports, primary or secondary −OH groups acts as CO_2reductants and are oxidized to the corresponding aldehydes or ketones. However, additional mechanisms are present because the oxidation of glycerine yields lactic acid. Jin et al. also demonstrated that glucose can act as reducing agent to convert bicarbonate as source of CO_2 into formic acid [30] but the mechanisms could not be resolved. Su et al. [31] tested some other hydroxylic compounds at 240 °C with heterogeneous Pd-based catalysts. They also obtained that along with CO_2 reduction, primary alcohols are oxidized to the corresponding carboxylic acid, secondary alcohols to the ketone, tertiary alcohols did not react and polyols yielded lactic acid.

However, there are still a lot of model compounds derived from lignocellulosic biomass that have not been tested. In this work, the ability of diverse compounds to reduce sodium bicarbonate ($NaHCO_3$) as source of CO_2 in hydrothermal medium is investigated. Particularly monosaccharides, disaccharides and lignin-derived phenols, but simple C2 and C3 alcohols and ketones are also tried to better understand the reactions pathways underlying. The main aim is to identify a potential compounds that makes possible to integrate both CO_2 reduction and biomass conversion by hydrothermal processes.

2. Materials and methods

2.1. Materials

$NaHCO_3$ (100%) was acquired from COFARCAS (Spain). Glycerol (99.5%), *n*-propanol (> 99.7%), glyceraldehyde (90%), lactic acid (≥85%),pyruvaldehyde (40%), 5-HMF (99%), furfural (99%), fructose (99%), D-(+)-glucose (100%),D-(+)-cellobiose (≥98%), resorcinol (99%), catechol (99%), guaiacol (> 99%) and vanillin (99%) were purchased from Sigma Aldrich (Spain). Ethanol (EtOH, 99.5%), acetone (99.5%), isopropanol (*i*PrOH, 99.9%), sucrose (100%) and sulfuric acid (H_2SO_4, 96%) were obtained from Panreac (Spain), while propanaldehyde (99%) and phenol (99%) were acquired from Acros Organics. Ethylenglycol was purchased from Fluka. The reactants were used without further treatment of purification.

2.2. Experimental procedure

Solutions in ultrapure (MilliQ) water of each organic compound were prepared with a concentration of 0.05 M and a molar ratio of organic/$NaHCO_3$ equal to 1:10 ($NaHCO_3$ concentration equal to 0.50 M). Experiments were carried out in batch reactors (length: 12 cm; o.d.: ½", with 1 mm of thickness) made of SS 316 stainless steel with an internal volume of 15.6 mL.

The $NaHCO_3$ and reductant solutions were loaded in the reactor, filling the 50% of its total volume. The reactor was placed then in an electric oven previously heated to 300 °C. Pressure generated should be 85.9 bar taking as reference the properties of pure water [32]. After 180 min reaction time, the reactor was rapidly quenched in a cold water/ethylene glycol bath and liquid samples were collected. In order to test the influence of NaOH addition, different reactions were carried out at 300 °C during 180 min using solutions of 0.05 M glucose varying the amount of NaOH (0–2 M) in both absence of $NaHCO_3$ and at a concentration of 0.50 M of the latter. In the cases of EtOH and ethylene glycol, different reaction times (30, 90 and 180 min) and reaction temperatures (250 °C and 300 °C) were tested, as well

Reactions were performed at least twice to assure reproducibility. In order to check the correct closure of the reactor and the no existence of leaks, the reactors were weighted before and after the reaction.

2.3. Product analysis

After being filtered through a 0.45 mm filter, liquid samples were analysed by HPLC (Waters, Alliance separation module e2695) using 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 H_2SO_4 with a flow rate of 0.6 mL/min. The temperatures of the column and the detector were 60 °C and 30 °C, respectively.

The yield to formic acid was calculated as shown below:

$$Y_{FA} = \frac{C_{FA,f}}{C_{org,i}} \times 100 \tag{1}$$

Where $C_{FA,f}$ is the molar concentration of formic acid obtained at the end of the reaction and $C_{org,i}$ is the initial molar concentration of the corresponding solution of the organic compound.

3. Results and discussion

The possibility of different organic substances derived from lignocellulosic biomass for CO_2 reduction was tested. The reductants were classified in three categories: saccharides; phenolic derivatives, which are model compounds from lignin depolymerization and simple molecules such C2, C3 alcohols and aldehydes that may be obtained from hydrothermal decomposition of the former compounds [18,21,26]. The yields to formic acid obtained from the different solutions of organic compounds are shown in Fig. 1.

In most cases, oxidized by-products obtained from the starting organic molecule were identified. The presence of these molecules gives clues to determine possible reaction mechanisms. Table 1 gathers the main by-products obtained for the different reactions along with proposed reaction pathways.

In the following sections, the yields to formic acid using different biomass derivatives as reductants divided in the three categories above named and their corresponding mechanisms are discussed, as well as