

Title: Hydrothermal CO₂ reduction using biomass derivatives as reductants

Autors: M. Andérez-Fernández^a, E. Pérez^b, A. Martín^a, M.D. Bermejo ^{*a}

Affiliations: ^aHigh Pressure Process Group, Department of Chemical Engineering and
Environmental Technology, University of Valladolid (Spain)

^bTERMOCAL Research Group, Thermodynamics and Calibration, University of
Valladolid (Spain)

Hydrothermal CO₂ reduction using biomass derivatives as reductants

M. Andérez-Fernández^a, E. Pérez, A. Martín^a, M.D. Bermejo ^{*a}

^aHigh Pressure Process Group, Department of Chemical Engineering and Environmental Technology, University of Valladolid (Spain)

^bTERMOCAL Research Group, Thermodynamics and Calibration, University of Valladolid (Spain)

*Email: mbermejo@iq.uva.es

Abstract

A wide range of organic substances, potentially derived from biomass, were tested as reductants for CO₂ (added in form of sodium bicarbonate) in hydrothermal media. The reactions were carried out in batch reactors at 300 °C and 3h. All the substances reduced CO₂ to formic acid in yields up to ~~60~~65%. For ethanol and ethylenglycol, additional conditions were tested to study the dependence of the reaction with time and temperature. These results agree to the mechanisms proposed in literature that suggested that reduction is carried out by a primary or a secondary alcohol. However, some substances not containing these groups gave significant yields to formic acid so new mechanisms were proposed to explain them. 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.

Keywords: [NaHCO₃](#); [glucose](#); [HTW](#); [formic acid](#); [hydrogenation](#)

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 CO₂ by capturing at its source and storing it. As this technology develops, a great availability of CO₂ 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 CO₂ to the carbon cycle [1, 2].

Among the different processes for its conversion into chemicals, photochemical reduction, electrochemical reduction or hydrogenation of CO₂ are the most promising strategies [3]. However, CO₂ 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 CO₂ is using reaction in hydrothermal media [4-7] *i.e.* using liquid water as solvent at high temperatures. Another advantage of hydrothermal reduction of CO₂ in hydrothermal media is avoiding the use of gaseous H₂ as reductant. H₂ is still a derivative of fossil fuels so the environmental benefit would be lost. Moreover, H₂ utilization comprises safety issues due to its flammability and reactivity. The main product obtained from hydrothermal reduction of CO₂ 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 CO₂ 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 CO₂ 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 depolymerized 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-hydroxymethylfurfural (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 CO₂ reduction in one-pot reaction, would provide an attractive and sustainable approach for the valorisation of lignocellulosic residues and the decrease of CO₂ atmospheric emissions by integrating this process in the main CO₂ 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 CO₂ reductants and are oxidised 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 CO₂ 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 CO₂ reduction, primary alcohols are oxidised 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 (NaHCO₃) as source of CO₂ 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 CO₂ reduction and biomass conversion by hydrothermal processes.

2. Materials and methods

2.1. Materials

NaHCO₃ (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 (H₂SO₄, 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 0.05M and a molar ratio of organic/NaHCO₃ equal to 1:10 (NaHCO₃ concentration equal to 0.50M). 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 NaHCO₃ 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 ~~the desired reaction temperature~~ 300°C. Pressure generated should be 85.9 bar taking as reference the properties of pure water.[32] After ~~the required~~ 180 min reaction time, the reactor was rapidly quenched in a cold water/ethylene glycol bath and liquid samples were collected. In the cases of EtOH and ethylene glycol, different reaction times (30, 90 and 180 minutes) 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 0.45mm 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 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.

The yield to formic acid was calculated as shown below:

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

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 potential of reduction of different organic substances derived from lignocellulosic biomass 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 Figure 1.

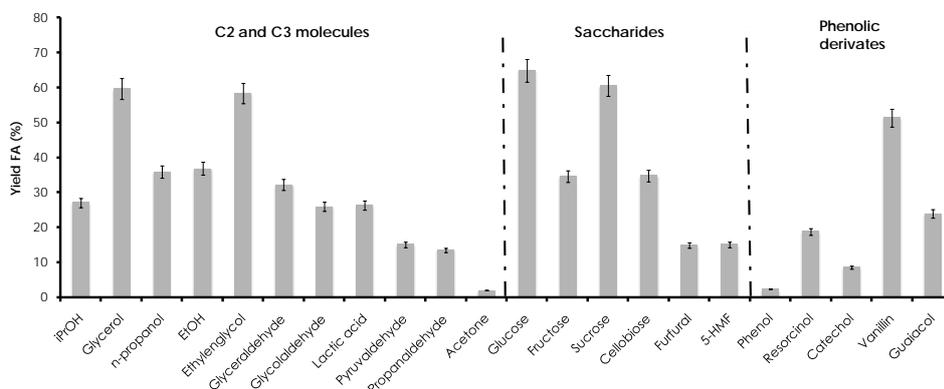


Figure 1. Yield to formic acid (%) from different organic compounds.

In order to verify that formic acid production was whether due to the CO₂ hydrothermal reduction, control reactions at 300°C for 180 min were carried out without the addition of NaHCO₃ but in presence of NaOH, as the former can partially decompose into the latter and this can catalyse formic acid formation from organic matter. In all these tests, NaOH 0.15 M was added. No formic acid or negligible amount was detected. Additional tests were carried out using only NaHCO₃ and water at 300°C during 180 min to check whether formic acid is produced without of an organic reductant. In these tests, again no formic acid was detected. Thus, formic acid was confirmed to be produced due to NaHCO₃ reduction in hydrothermal processes at 300°C.

[In most of the 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.](#)

Table 1. Main by-products obtained after the reaction using different organic compounds as reductants. In brackets are written those byproducts which

Entry	Organic compound	By-product(s)	Proposed mechanism(s)	Related references
1	EtOH	Acetic acid	Oxidation	[31]
2	Ethylene glycol	Lactic acid (glycolaldehyde, acetic acid)	Oxidation → Aldol condensation → keto-enol taut. → Retro-Aldol → Internal Cannizzaro	[31,33]
3	n-propanol	Propanaldehyde (Ethylenglycol)	Oxidation	[31]
4	<i>i</i> PrOH	Acetone	Oxidation	[6, 28, 31]
5	Glycerol	Lactic acid (Ethylenglycol)	Dehydration → Oxidation → Internal Cannizzaro	[4, 28, 29, 31]
6	Glyceraldehyde	Acetic acid (lactic acid)	Keto-enol taut. → Internal Cannizzaro → Oxidation	[4, 33]
7	Glycolaldehyde	Acetic acid (lactic acid)	Aldol condensation → keto-enol taut. → Retro-Aldol → Internal Cannizzaro	[30, 33]
8	Pyruvaldehyde	Acetic acid (lactic acid)	Internal Cannizzaro → Oxidation	[4, 33]
9	Lactic acid	Acetic acid (glyceraldehyde)	Oxidation → Rearrangement?	[39 40]
10	Glucose	Acetic acid, lactic acid, glicolaldehyde, EtOH	Retro-Aldol → Oxidation/rearrangement	[26, 35, 39 40]
11	Fructose	Acetic acid, lactic acid, glicolaldehyde, EtOH	Retro-Aldol → Oxidation/rearrangement	[26, 35, 39 40]
12	Cellobiose	Acetic acid, lactic acid, glicolaldehyde, EtOH	Hydrolysis → Retro-Aldol → Oxidation/rearrangement	[26, 35, 39 40]
13	Sucrose	Acetic acid, lactic acid, glicolaldehyde, EtOH	Hydrolysis → Retro-Aldol + Oxidation/rearrangement	[26, 35, 39 40]
14	5-HMF	Acetic acid, EtOH	Oxidation	[34]
15	Furfural	Acetic acid, EtOH	Oxidation	[34]
16	Catechol	MeOH, Lactic acid, (ethylenglycol)	Oxidation → ring opening	[40 41, 41 42]
17	Resorcinol	Propanaldehyde/acetone, acetic acid,	Oxidation → ring opening	[40 41]
18	Guaiacol	Methanol, catechol, lactic acid (acetic acid)	Hydrolysis → Oxidation → ring opening	[40 41, 41 42]
19	Vanillin	Methanol, catechol, (lactic acid, acetic acid)	Oxidation → Hydrolysis → Oxidation → ring opening	[40 41- 43 44]

concentration were between 5% and 10% of the initial concentration of the organic compound.

[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 studied belowdiscussed, as well as the influence of reaction time and temperature and NaOH concentration.](#)

[3.1.- C2 and C3 alcohols, aldehydes and ketones](#)

C2 and C3 alcohols, aldehydes and ketones, ~~whose~~ which molecular structures are shown in Figure 2, were tested using the conditions above described. Under these conditions, the yields to formic acid of *i*PrOH and glycerol were 27% and 60%, respectively, lower to those previously reported in literature [4, 6], which obtained maximum yields to formic acid equal to 70% from *i*PrOH and 90% from glycerol. However, these studies had also significant differences in the experimental set-up and operational parameters, *e.g.* different reaction time, different initial reactant concentrations and that in literature the reactors were shaken and the heating rate was higher.

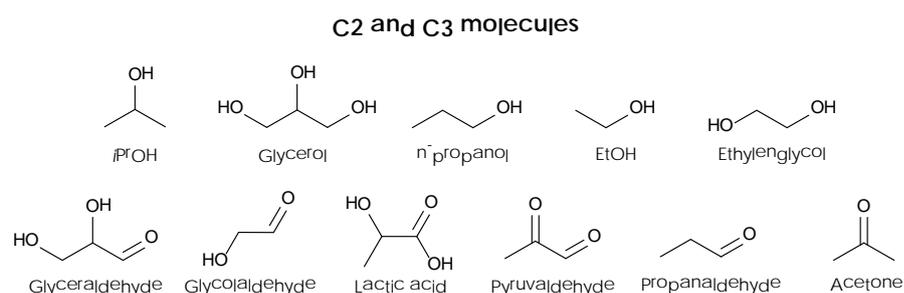


Figure 2. Molecular structure of C2 and C3 molecules.

Nonetheless, these results showed that NaHCO_3 can be reduced using several organic compounds as reductants in hydrothermal medium under the conditions studied (300 °C,

180 min). Interestingly, when using n-propanol, [a primary alcohol](#), as reductant, a yield to formic acid of 36% was achieved, slightly higher than the yield obtained from *i*PrOH, [which is a secondary alcohol](#), suggesting that the position of the -OH group in the molecule plays an important role in the reduction, probably due to steric effects. In the case of C2 alcohols, such as EtOH and ethylene glycol, similar yields to the analogous C3 alcohols were obtained (30% and 58%, respectively). These results are in agreement to the mechanism proposed by Jin and coworkers [4, 6] where the alcohol moiety is the main responsible of the reduction of CO₂. A H⁻ from the α-carbon of -OH moiety is transferred to the bicarbonate through a cyclic transition state as shown in Figure 3. The resulting HC(OH)₂O⁻ quickly dehydrates to formate.

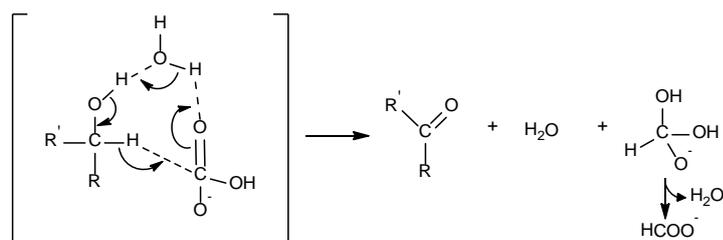


Figure 3. Mechanism for the reduction of bicarbonate to formate by a hydroxyl group.

[4, 6]

[Regarding to the by-products obtained due to the oxidation of these substances-organic compounds,](#) n-propanol and *i*PrOH mainly yielded propanaldehyde and acetone respectively, which was consistent to the mechanism proposed of oxidation of the -OH moiety [4, 6]. Ethanol, however, seems to be further oxidized to acetic acid. Reaction pathway of glycerine oxidation to lactic acid has been previously reported [33]: prior to -OH oxidation, the molecule undergoes a dehydration followed by a keto-enol tautomerization. After the oxidation, pyruvaldehyde re-arranges to lactic acid by an internal Cannizzaro reaction. [On the other hand,](#) ethylene glycol gives a particularly

high formic acid yield and surprisingly, apart from the expected glycolaldehyde, it yields lactic acid, which is a C3 molecule. That could be possible if, after the first oxidation to glycolaldehyde, this is converted to lactic acid or pyruvaldehyde, as suggested by other authors [31, 33], who propose an aldolic condensation to form an aldotetrose. After a C-C cleavage by a retro-aldol reaction and rearrangements a molecule of glycerlaldehyde and formaldehyde are formed. These can be further converted to lactic acid and formic acid.

Derivatives or intermediates from biomass processing, such as glycolaldehyde, glyceraldehyde, lactic acid and pyruvaldehyde were also tested for NaHCO_3 hydrogenation, obtaining yields to formic acid of 26%, 32%, 26% and 15%, respectively. The main difference between the yields to formic acid achieved by these compounds could be related to their molecular structures, which are displayed in Figure 2. Yield of glycolaldehyde is approximately half of ethylene glycol, which is reasonable because according to the mechanism proposed, the former would be generated from the

latter. [Lactic acid seems to be mainly degraded to acetic acid at long residence times. It has been previously suggested that lactic can be oxidized to acetic acid in hydrothermal media \[39\]. Reaction pathways, however, remain unknown. A small proportion of pyruvaldehyde was also obtained. Reaction of pyruvaldehyde to lactic acid in HTW via atom rearrangement has been reported \[33\] but not the reverse one. However in this work that seems to take place as well. Glyceraldehyde and pyruvaldehyde are both precursors of lactic acid. Glyceraldehyde can undergo a keto-enol tautomerization to give pyruvaldehyde and this can be further converted to lactic acid by internal Cannizzaro reaction. That is the reason why these three compounds are able to reduce \$\text{HCO}_3^-\$ while they are oxidized to acetic acid.](#)

When using molecules with carbonyl groups such as propanaldehyde and acetone, yields to formic acid were 13% and 2%, respectively. Such significant yield to formic acid when using propanaldehyde is surprising because it does not have hydroxyl groups.

This can be explained if aldehydes can undergo an aldol condensation in hydrothermal alkaline medium [33] or they can be further [oxidized](#) to acids.

[3.2.- Saccharides](#)

Monosaccharides (glucose and fructose) and disaccharides (sucrose and cellobiose) are also good CO₂ reductants, due to the yields obtained when using these compounds as reductants. Significant differences were observed when starting from glucose or fructose. Despite of their similar structures, which are shown in Figure 4, the yields to formic acid were 65% and 35%, respectively. It was reported that monosaccharides undergo a retro-aldol condensation to break down into smaller compounds or dehydration to form 5-HMF and furfural. These intermediates can be then oxidized [34].

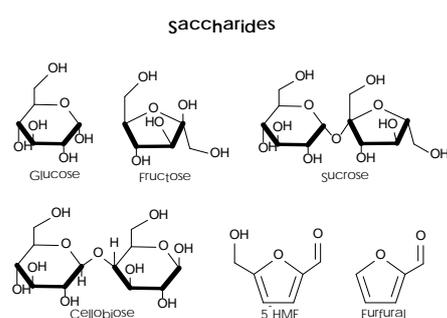


Figure 4. Molecular structure of saccharides.

The differences observed can then be related to the fact that glucose splits into three C₂ molecules (glycolaldehyde) whereas fructose splits into two C₃ molecules (glyceraldehyde and pyruvaldehyde) [26, 35-38], or dehydrates to one 5-HMF molecule. It can be noticed that three times the yield obtained for glycolaldehyde is significantly higher than the sum of the yields for glyceraldehyde and pyruvaldehyde (Figure 1). More surprising are the yields to formic acid when using the disaccharides sucrose (glucose – fructose) and cellobiose (glucose – glucose), 60% and 35% respectively, since they readily hydrolyze in HTW to their constituent monosaccharides. The explanation may be a different thermal stability of either sucrose or cellobiose. In the case of saccharides derivatives furfural and 5-HMF, both compounds reached a yield to formic acid of 15%.

The main by-product obtained from monosaccharides and disaccharides were acetic and lactic acids, in different proportions. That is in agreement to the mechanisms previously described [26, 35, 40]. However, the similarities in the composition of the by-products do not allow discerning differences in the reaction pathway.

3.3.- Lignin derivatives

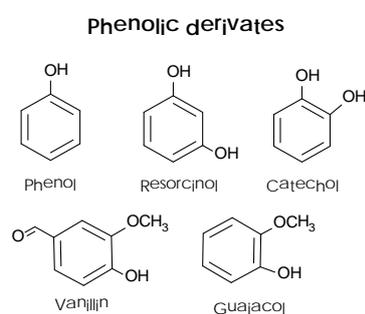


Figure 5. Molecular structure of phenolic derivatives.

When using phenolic lignin model compounds, a wide range of yields to formic acid was obtained. The molecular structures of the different tested compounds are shown in Figure 5. The lowest yield was obtained from phenol, achieving only 2%. Higher yields to formic acid were obtained by using resorcinol and catechol solutions (19% and 9%, respectively). The highest yield to formic acid was 51% when using vanillin solution, followed by guaiacol (24%). Su et al. [31] also reported low reactivity for phenol, which is expectable since the reduction of CO₂ is performed by primary or secondary -OH groups [4, 6]. However, the relatively high yields to formic acid achieved by the rest of the aromatic compounds tested are unexpected.

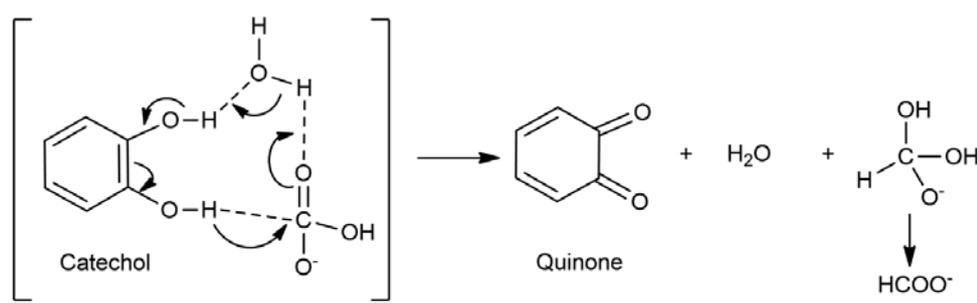
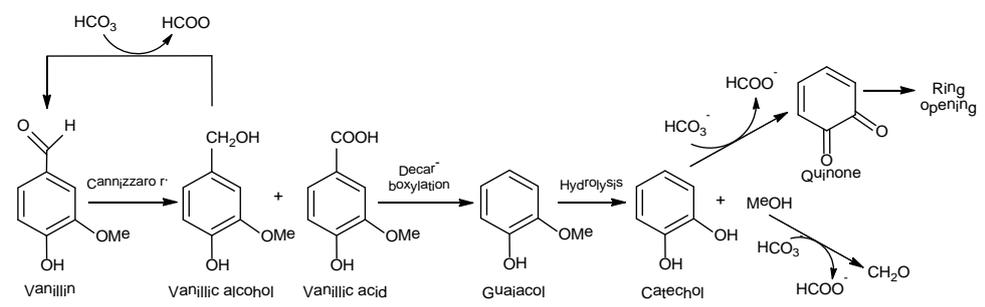


Figure 6. Proposed mechanism for the reduction of bicarbonate to formate by catechol.

By-products from resorcinol were propanaldehyde and/or acetone and acetic acid whereas that from catechol was lactic acid. These products can only be formed from a ring-opening mechanism. It should also be mentioned that the solutions obtained from aromatic compounds were reddish-brown coloured. In HTW, the aromatic rings can be oxidized to quinone groups, which are highly coloured and tend to undergo ring opening in water at high temperatures [41]. A proposed mechanism of CO₂ reduction by catechol is depicted in Figure 6. Oxidation takes place through a cyclic transition state similar to that reported in the literature with the exception that the H⁺ to be transferred is on the hydroxyl group at ortho position. The main by-products from guaiacol are

methanol and catechol most likely produced from a hydrolysis of the methoxy group.
However, yield to formic acid from guaiacol is higher than from catechol, indicating
that methanol has also a reducing role, and it may produce extra amount of formic acid.
On the other hand, oxidation of vanillin to vanillic acid can occur in the presence of
oxidants. Additionally, at high temperatures (>280 °C), the latter readily decarboxylates
to guaiacol [41-43]. That is the reason why the same by-products are observed when
starting from vanillin or guaiacol. However, yields to formic acid are higher than for the
former, which suggests again that the oxidation of the carbonyl accompanies the
reduction of CO₂. That can be possible considering that vanillin can undergo a
Cannizzaro disproportionation to vanillic acid and vanillic alcohol [44] and the latter
reduces CO₂.



Código de campo cambiado

Figure 7. Proposed sequential mechanism of HCO₃⁻ reduction with vanillin, guaiacol and catechol.

Figure 7 shows a proposed sequential mechanism of oxidation reaction. Each of these oxidations can be accompanied of a HCOO⁻ reduction, which explains that the Y_{FA} also follow a decreasing trend. Moreover, detected intermediate compounds (methanol and catechol) agree with the proposed pathway.

3.4.- Dependence of the reaction time and temperature

The dependence of formic acid yield with reaction time and temperature for ethanol and ethylene glycol is shown in Figure 8. The evolution of the reaction is positive with time for every condition tested. At 300 °C the reaction takes place mainly during the first 90 minutes while the rate decreases significantly at longer times. Temperature plays a more determinant role in the reaction rate as yields are much lower at 250 °C. This behaviour has been observed in previous reports for CO₂ reduction by glycerol [4] and isopropanol [6] indicating they proceed through similar reaction mechanisms. Reactions of these compounds at higher reaction temperature has not been tested since increasing the reaction temperature further than 300°C would not provide better yields to formic acid. Previous reports showed the degradation of formic acid at higher temperature than 300°C at short reaction times (<1m) [39] and, therefore, higher temperature would lead to a faster disappearance of it in the medium.

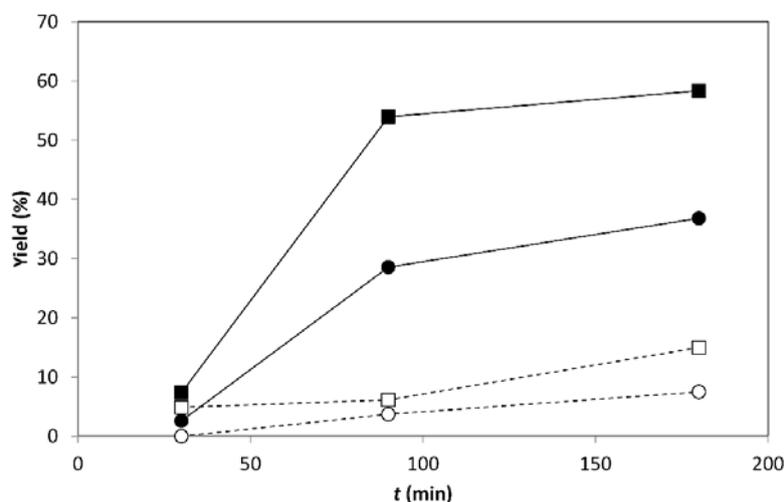


Figure 8. Dependence of formic acid yield with time and temperature for the reduction of NaHCO₃ using ethanol and ethylene glycol as reductants. (■):

Ethylene glycol, 300 °C; (□) Ethylene glycol, 250 °C; (●): Ethanol, 300 °C; (○): Ethanol, 250 °C.

3.5.- Influence of NaOH concentration

4. Conclusions

In this work, the hydrothermal reduction of NaHCO_3 to formic acid was achieved by the conversion of different lignocellulosic biomass model compounds. Yields to formic acid up to 65% were obtained by using the different organic solutions as reductants after 180 min at 300°C, being the yield to formic acid from glucose the highest yield achieved. Although the detailed reaction mechanism is still unknown and the operational parameters should be optimized, this study demonstrates the possibility to combine the CO_2 hydrothermal reduction with the lignocellulosic biomass conversion to obtain value-added chemicals and energy from renewable sources. This work should provide interesting information to further integrate the CO_2 reduction in biomass hydrothermal conversion at industrial scale, where glucose could be used as reductant due to the high yield to formic acid achieved and that can be selectively obtained from cellulose hydrolysis.

Acknowledgments

This project has been funded by MINECO through project ENE2014-53459-R. MAF acknowledges JCYL the predoctoral grant. EPV thanks JCYL for the postdoctoral fellowship. MDB thanks MINECO for Ramon y Cajal position.

References

- [1] M. He, Y. Sun, B. Han, Green carbon science: scientific basis for integrating carbon resource processing, utilization, and recycling, *Angew. Chem. Int. Ed.* 52 (2013) 2-16.
- [2] T. Sakakura, J.C. Choi, H. Yasuda, Transformation of carbon dioxide, *Chem. Rev.* 107 (2007) 2365-2387.
- [3] M. Mikkelsen, M. Jorgensen, F. C. Krebs, The teraton challenge. A review of fixation and transformation of carbon dioxide, *Energy Environ. Sci.* 3 (2010) 43-81.
- [4] Z. Shen, Y. Zhang, F. Jin, The alcohol-mediated reduction of CO₂ and NaHCO₃ into formate: a hydrogen transfer reduction of NaHCO₃ with glycerine under alkaline hydrothermal conditions, *RSC Adv.* 2 (2012) 797-801.
- [5] B. Wu, Y. Gao, F. Jin, J. Cao, Y. Du, Y. Zhang, Catalytic conversion of NaHCO₃ into formic acid in mild hydrothermal conditions for CO₂ utilization, *Catalysis Today* 148 (2009) 405-410.
- [6] Z. Shen, Y. Zhang, F. Jin, From NaHCO₃ into formate and isopropanol into acetone: Hydrogen-transfer reduction of NaHCO₃ with isopropanol in high-temperature water, *Green Chem.* 13 (2011) 820-823.
- [7] F. Jin, X. Zeng, J. Liu, L. Wang, H. Zhang, G. Yao, Z. Huo, Highly efficient and autocatalytic H₂O dissociation for CO₂ reduction into formic acid with zinc, *Scientific Report* 4 (2014) article number 4503.
- [8] A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, CO₂-"neutral" hydrogen storage based on bicarbonate and formates, *Angew. Chem. Int. Ed.* 50 (2011) 6411-6414.
- [9] S. Enthaler, J. Langermann, T. Schmidt, Carbon dioxide and formic acid - the couple for environmental-friendly hydrogen storage, *Energy Environ. Sci.* 3(2010) 1207-1217.
- [10] C. Federsel, R. Jackstell, M. Beller, State-of-art catalyst for hydrogenation of carbon dioxide, *Angew. Chem. Int. Ed.* 49 (2010) 6254-6257.
- [11] M. E. Berndt, D. Allen, W. E. Seyfried, Reduction of CO₂ during serpentinization of olivine at 300°C and 500 bar, *Geology* 24 (1996) 351-354.
- [12] H. Takahashi, T. Kori, T. Onoki, K. Tohji, N. Yamasaki, Hydrothermal processing of metal base compounds and carbon dioxide for the synthesis of organic compounds, *J. Mater. Sci.* 43 (2008) 2487-2491.

- [13] Y. Chen, Z. Jing, J. Miao, Y. Zhang, J. Fan, Reduction of CO₂ with water splitting hydrogen under subcritical and supercritical hydrothermal conditions, *International Journal of Hydrogen Energy* 41 (2016) 9123-9127.
- [14] F. Jin, Y. Gao, Y. Jin, Y. Zhang, J. Cao, Z. Wei, R. L. Smith Jr., High-yield reduction of carbon dioxide into formic acid by zero-valent metal/metal oxide redox cycles, *Energy Environ. Sci.* 4 (2011), 881-884
- [15] C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, Valorization of biomass: deriving more value from waste, *Science* 337 (2012) 695-699.
- [16] M. Stöcker, Biofuels and biomass-to-liquid fuels in the biorefinery: catalytic conversion of lignocellulosic biomass using porous materials, *Angew. Chem. Int. Ed.* 47 (2008) 9200-9211.
- [17] B. Kamm, Production of platform chemicals and synthesis gas from biomass, *Angew. Chem. Int. Ed.* 46 (2007) 5056-5058.
- [18] P. E. Savage, N. A. Rebacz, Water under extreme conditions for green chemistry, *Handbook of Green Chemistry* 5:11 (2010) 331-361.
- [19] N. Akiya, P. E. Savage, Roles of water for chemical reactions in high-temperature water, *Chem. Rev.* 102 (2002) 2725-2750.
- [20] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant. Properties and synthesis reactions, *J. Supercrit. Fluids* 39 (2007) 362-380.
- [21] D. A. Cantero, M. D. Bermejo, M. J. Cocero, Reaction engineering for process intensification of supercritical water biomass refining, *J. Supercrit. Fluids* 96 (2015) 21-35.
- [22] P. C. Veggi, R. N. Cavalcanti, M. A. A. Miereles, Production of phenolic-rich extracts from Brazilian plants using supercritical and subcritical fluid extraction: experimental data and economic evaluation, *J. of Food Engineering* 131 (2014) 96-109.
- [23] J. M. Prado, L. A. Follegatti-Romero, T. Forster-Carneiro, M. A. Rostagno, F. Mauger Filho, M. A. A. Miereles, Hydrolysis of sugarcane bagasse in subcritical water, *J. Supercrit. Fluids* 86 (2014) 15-22.
- [24] F. P. Cardenas-Tore, T. Forster-Carneiro, M. A. Rostagno, A. J. Petenate, F. Mauregi Filho, M. A. A. Miereles, Integrated supercritical fluid extraction and subcritical water hydrolysis for the recovery of bioactive compounds from pressed palm fiber, *J. Supercrit. Fluids* 93 (2014) 42-48.
- [25] F. Jin, X. Zeng, Z. Jing, H. Enomoto, A potentially useful technology by mimicking nature-rapid conversion of biomass and CO₂ into chemical and fuels under hydrothermal conditions, *Ind. Eng. Chem. Res.* 51 (2012) 9921-9937.

- [26] D. A. Cantero, A. Álvarez, M. D. Bermejo, M. J. Cocero, Transformation of glucose into added value compounds in a hydrothermal reaction media, *J. Supercrit. Fluids* 98, 2015, 204-210.
- [27] S. Kang, X. Li, J. Fan, J. Chang, Hydrothermal conversion of lignin: a review, *Renew. Sust. Energ. Rev.* 27 (2013) 546-558.
- [28] Z. Shen, M. Gu, M. Zhang, W. Sang, X. Zhou, Y. Zhang, F. Jin, The mechanism for production of abiogenic formate from CO₂ and lactate from glycerine: uncatalyzed transfer hydrogenation of CO₂ with glycerine under alkaline hydrothermal conditions, *RSC Adv.* 4 (2014) 15256-15263.
- [29] Y. Wang, F. Wang, C. Li, F. Jin, Kinetics and mechanism of reduction of CO₂ by glycerol under alkaline hydrothermal conditions, *Int. J. Hydrogen Energy* 46 (2016) 9128-9134.
- [30] F. Jin, Z. Huo, X. Zeng, H. Enomoto, Hydrothermal conversion of CO₂ into value-added products: a potential technology from improving global carbon cycle, *ACS Advances in CO₂ conversion and utilization* 4 (2010), 31-53.
- [31] J. Su, L. Yang, X. Yang, M. Lu, B. Luo, H. Lin, Simultaneously converting carbonate/bicarbonate and biomass to value-added carboxylic acid salts by aqueous-phase hydrogen transfer, *ACS Sustainable Chem. Eng.* 3 (2015) 195-203.
- [32] <http://webbook.nist.gov/chemistry/>
- [33] H. Kishida, F. Jin, X. Yan, T. Moriyac, H. Enomoto, Formation of lactic acid from glycolaldehyde by alkaline hydrothermal reaction, *Carbohydr. Res.* 341 (2006) 2619-2623.
- [34] F. Jin, Z. Zhou, H. Kishida, H. Higashijima, H. Enomoto, Controlling hydrothermal reaction pathways to improve acetic acid production from carbohydrate biomass, *Environ. Sci, Technol.* 39 (2005) 1893-1902.
- [35] D. A. Cantero, A. Sánchez Tapia, M. D. Bermejo, M. J. Cocero, Pressure and temperature effect on cellulose hydrolysis in pressurized water, *Chem. Eng. J.* 276 (2015), 145-154.
- [36] T. M. Aida, K. Tajima, M. Watanabe, Y. Saito, K. Kuroda, T. Nonaka, H. Hattori, R. L. Smith Jr, K. Arai, Reactions of D-fructose in water at temperatures up to 400°C and pressures up to 100 MPa, *J. Supercrit. Fluids* 42 (2007) 110-119.
- [37] M. Sasaki, K. Goto, K. Tajima, T. Adschiri, K. Arai, Rapid and selective retro-aldol condensation of glucose to glycolaldehyde in supercritical water, *Green Chem.* 4 (2002) 285-287.

[38] D. A. Cantero, L. Vaquerizo, C. Martínez, M. D. Bermejo, M. J. Cocero, Selective transformation of fructose and high fructose content biomass into lactic acid in supercritical water, *Catal. Today* 255 (2015) 80-86.

[39] [J.L. Yu, P.E. Savage. Decomposition of formic acid under hydrothermal conditions. *Ind Eng Chem Res.* 37 \(1998\) 2-10](#)

[40] F. Jin, Z. Zhou, A. Kishita, H. Enomoto, Hydrothermal conversion of biomass into acetic acid, *J. Mater. Sci.* 41 (2006) 1495-1500.

[41] E. Perez, J. Fraga-Dubreuil, E. García-Verdugo, P. A. Hamley, B. Thomas, D. Housley, W. Partenheimer, M. Poliakoff, Selective aerobic oxidation of para-xylene in sub- and supercritical water. Part 1. Comparison with ortho-xylene and the role of the catalyst, *Green Chem.* 13 (2011) 2389-2396.

[42] E. Perez, A. Davis, C. O. Tuck, M. Poliakoff, Quantitative analysis of products from lignin depolymerisation in high-temperature water, *Bioresource. Technol.* (submitted).

[43] G. González, J. Salvadó, D. Montané, Reactions of vanillic acid in sub- and supercritical water, *J. Supercrit. Fluids* 31 (2004) 57-66.

[44] I. A. Pearl, Reactions of vanillin and its derived compounds III. The Cannizzaro Reaction of vanillin, *The Journal of organic chemistry* 10 (1947) 79-48.