**Effect of Process Conditions in The Reduction of CO2 Captured By Ammonia.**

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**Highlights**

* CO2 as ammonium carbamate can be reduced to formic acid in hydrothermal media with a yield up to 38%
* Catalyst content, temperature and time are the relevant variables
* The formic acid yield is indirectly proportional to the initial concentration of carbamate
* The aluminum-water splitting reaction is feasible for reducing capture CO2 without dry H2

**1. Introduction**

The rapid population growing is making necessary the use of fossil fuels for the production of electricity, as well as fuel in the automotive industry, and will be still extended for many years [1]. This situation have encouraged to put the efforts in finding solutions concerning the mitigation of CO2 emissions, such as CO2 capture and storage technologies (CCS), and the Carbon Capture Utilization (CCU). The amine based CCS technology is one of the most attractive solutions nowadays, but the high cost of the desorption step entails to consider further possibilities. For instance, the French Company Alston developed a technology known as “Chilled Ammonia” [2]. In this technology, combustion gases are absorbed into an ammonia aqueous solution (28%wt) at low temperature (2-10˚C), to absorb CO2 as carbonate, bicarbonate and carbamate of ammonia. Regeneration step consists also in desorption at temperatures between 100-150˚C, being less energetic than those from amines. Nevertheless, to completely avoid this step, our proposal is to reduce CO2 captured in aqueous media as a carbamate with or without gaseous hydrogen. The last is achieved by the implementation of an environmentally friendly and economical hydrogen production technology like Aluminum-water splitting, and other reducers like zinc or biomass derivatives, which have proven to be effective in reducing sodium bicarbonate in hydrothermal media with efficiencies of up to 60% [3]. In the present work, the main product of the absorption of CO2 in ammonia, the ammonium carbamate (AC), is transformed into formic acid in hydrothermal media, using metallic aluminum powder as reductant and Pd (5% wt) supported in activated carbon as catalyst, at temperatures from 80 to 200˚C and pressures above the saturation of water.

**2. Methods**

For stablishing the effect of the process variables on the production of formic acid (FA), several assays, under inert atmosphere of N2, varying the temperature (80-300˚C), time (0.5-5 h), Al:AC molar ratio (3-9), catalysts content (7.5-60 wt% with respect to carbamate), liquid filling (50-85% of the total volume of the vessel) and initial concentration of aqueous AC solution (0.5-2.0M) were conducted in an stainless steel stirred reactor from Parr instruments, with autogenic pressure. The variation of the variables was performed based on a central point of reaction conditions (120˚C, 2h, Al:AC ratio of 6, 15% catalyst, 70% filling and 0.5 M of AC). The concentration of AC and FA were determined by means of HPLC (Waters, Alliance separation module e2695), using an Aminex 87H (Bio-Rad) column and RI detector (Waters, 2414 module).

**3. Results and discussion**

As observed in figure 1 (selectivity and conversion not disclosed), the time positively affects the yield, reaching 27% after 4 h of reaction and tends to level off, but with the depletion of selectivity. The highest selectivity (72%) is achieved at 0.5 h, indicating that the FA is formed faster than other possible compounds. The increase of initial concentration appears to not have a positive impact, since we observed a drop in the yield from 25% (0.5M) to 12% (2.0M). The temperature (not shown) presents a maximum yield of 20% between 120-150˚C. The catalyst content behaves similarly than time, allowing to obtain a yield as high as 38%, with a high selectivity of 85%, and conversion of 40% (not shown).

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|  **Figure 1.** Effect of time and Initial concentration over Yield of FA |

On the other hand, the Al:AC molar ratio does not have a great impact on the process. The liquid filling level also plays a positive effect over the process as the final autogenic pressure increases.

**4. Conclusions**

In the process to obtain formic acid, from the capture of CO2 in aqueous ammonia solution, the variables that mostly affect the yield are the catalyst content, temperature and time. The reduction reaction can be achieved without the use of gaseous hydrogen with a yield up to 38% with an AC initial concentration of 0.5M. Scarce works have been found in the hydrothermal reduction of carbamates without dry hydrogen for producing value-added chemicals, representing a promising field of innovation.

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**References**

[1] T. Covert, M. Greenstone, C.R. Knittel, J Econ Perspect. 30 (2016) 117-138.

[2] E. Gal, Patent No. WO2006022885, (2006).

[3] M. Andérez-Fernández, E. Pérez, A. Martín, M. Bermejo, J Supercrit Fluid. 133 (2017) 658–664.