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To cite this version:

Alain Ledoux, Marie Décultot, Marie-Christine Fournier-Salauen, Lionel Estel. Carboxylation of alcohol for CO2 valorisation: thermodynamic and kinetic study. 10th World Congress of Chemical Engineering, Oct 2017, Barcelone, Spain. hal-02409753

HAL Id: hal-02409753

https://hal-normandie-univ.archives-ouvertes.fr/hal-02409753

Submitted on 13 Dec 2019

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Carboxylation of alcohol for CO_2 valorisation: thermodynamic and kinetic study

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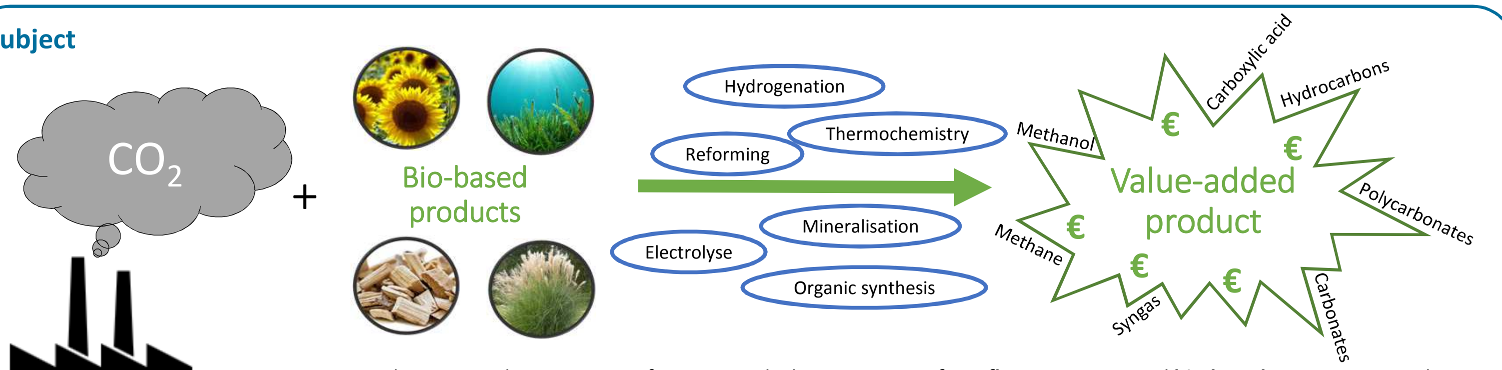
Context

- Considering **global warming** effect on earth, the diminution of **CO_2 emissions** becomes imperative.
- A new chemistry of CO_2 is developing to face up to the **rarefaction of fossil resources**.
- The **valorization of CO_2** using **bio-based products** creates a true **circular economy** by using CO_2 as a source of carbon to produce value-added products.

Objective

Transformation of CO2 by limiting the use of fossil energy

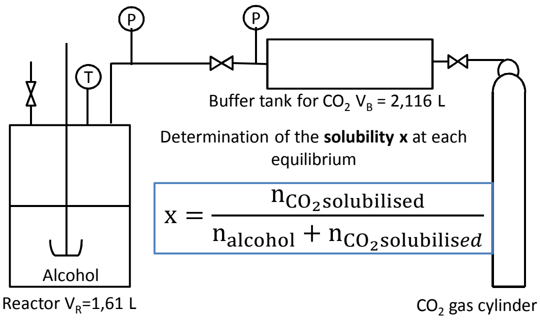
Subject



Development and optimisation of a process which associate **CO_2 from flue gas stream** and **bio-based reactants** to synthesize a **value-added product.**

Study of the solubility of CO_2

Experimental section:



$$x = \frac{n_{CO_2 solubilised}}{n_{alcohol} + n_{CO_2 solubilised}}$$

Calculation of the amount of CO_2:

Use of the equation of **Peng-Robinson (1976)** to simulate the behaviour of CO_2, real gas:

$$P = \frac{RT}{v-b} - \frac{a(Tc)\alpha(T)}{(v^2 + 2bv - b^2)}$$

$$a(T) = \Omega_a \frac{R^2T^2}{P_c} \qquad \Omega_a = 0.07780$$

$$b = \Omega_b \frac{RT_c}{P_c} \qquad \Omega_b = 0.457240$$

$$\alpha(T) = [1 + m(1 - T_r^{0,5})]^2$$

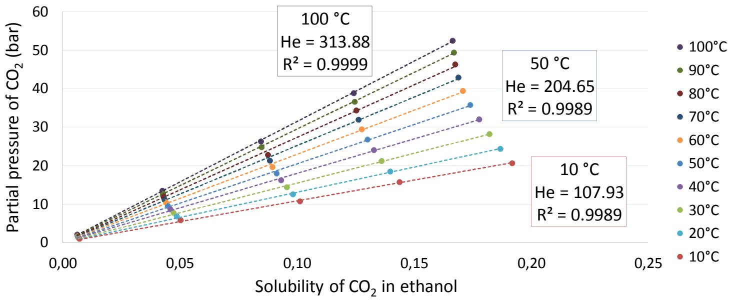
$$m = 0.374640 + 1.542260\omega - 0.26992\omega^2$$

$$\omega = 0.228 \; ; \; Tc = 304.8\ K \; ; \; Pc = 73.8\ bar$$

Results for ethanol:

Determination of the **Henry's law coefficient:**

$$P_{CO_2} = He.\,x_{CO_2}$$

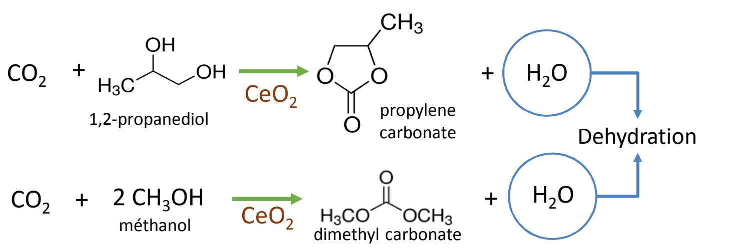


The solubility is proportional to the pressure of CO_2 for **ethanol**, **methanol**, **1,2-propanediol** and **glycerol**. Results are in good agreement with the literature[2].

Studied Reaction

Carboxylation of diols and alcohols to obtain **cyclic and linear carbonates** with the use of **cerium oxide catalyst.**

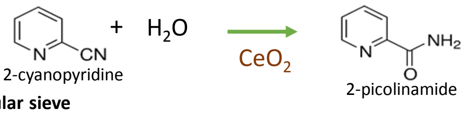
Synthesis of the main products:



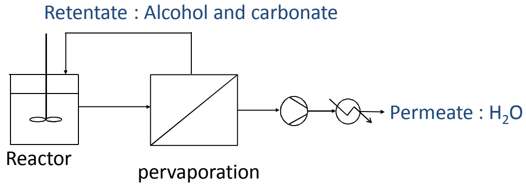
Study of **dehydrating systems** to shift the equilibrium toward the formation of carbonates

Examples of dehydrating systems[1]:

- ✓ Use of a **dehydrating reagent**



- ✓ Use of a **molecular sieve**
- ✓ Use of a **pervaporation system**



Applications of carbonates:

- ✓ Fuel additive to reduce SOx and NOx emissions
- ✓ Low toxic solvent
- ✓ Starting materials for polycarbonates

Conclusion

- Study of the reaction of carboxylation of alcohols and diols with CO_2 to produce carbonates: study of **dehydration systems**.
- Measure of the solubility of CO_2 in **methanol, ethanol, 1,2-propanediol and glycerol.**
- Objective : Development of a sustainable process which associate **CO_2** and a **bio-based reagent** to produce **value-added chemical products**

[1]M. Honda et al. J. Catal., vol. 318, pp. 95–107, 2014, M. Honda et al. ACS Catal., vol. 4, no. 6, pp. 1893–1896, 2014 ; [2] Gui et al. J. Chem. Eng. Data 56, 2420-2429, 2011

RÉGION NORMANDIE
ADEME Agence de l'Environnement et de la Maîtrise de l'Energie
LSPC Laboratoire de sécurité des procédés chimiques
INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES ROUEN NORMANDIE
UNION EUROPEENNE
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