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Carboxylation of alcohol for CO₂ valorisation: thermodynamic and kinetic study

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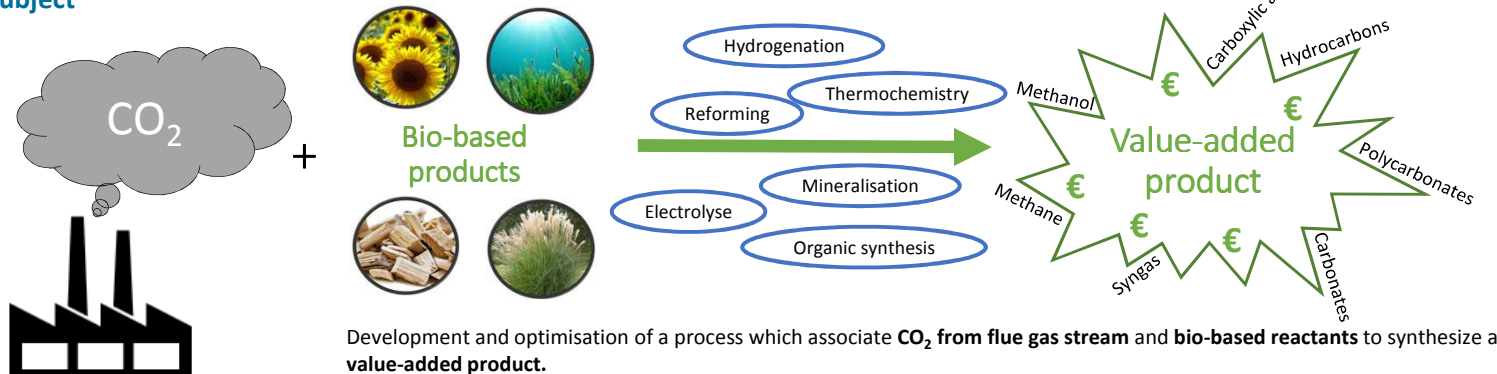
Context

- Considering **global warming** effect on earth, the diminution of CO₂ emissions becomes imperative.
- A new chemistry of CO₂ is developing to face up to the **rarefaction of fossil resources**.
- The **valorization of CO₂** using **bio-based products** creates a true **circular economy** by using CO₂ as a source of carbon to produce value-added products.

Objective

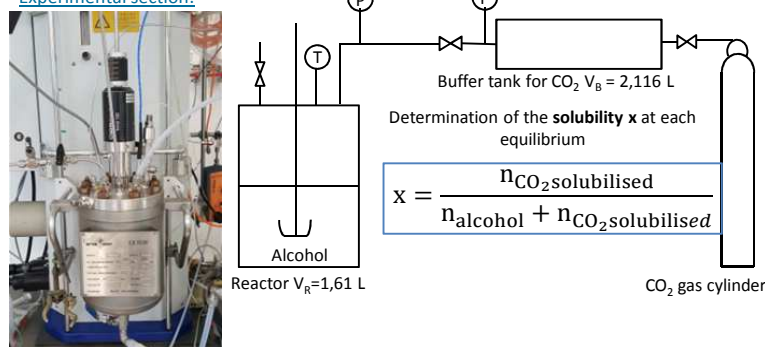
Transformation of CO₂ by
limiting the use of fossil energy

Subject



Study of the solubility of CO₂

Experimental section:



Calculation of the amount of CO₂:

Use of the equation of **Peng-Robinson (1976)** to simulate the behaviour of CO₂, real gas:

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

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

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

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2$$

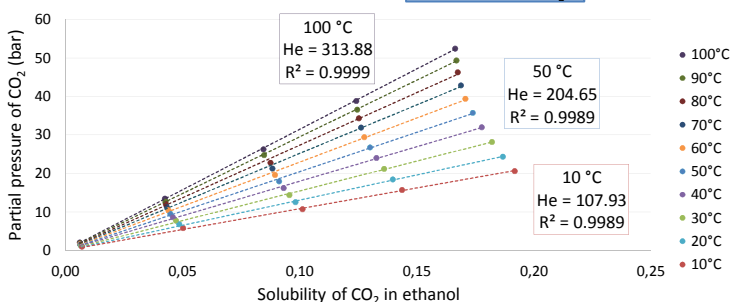
$$m = 0.374640 + 1.542260\omega - 0.26992\omega^2$$

$$\omega = 0.228; T_c = 304.8 \text{ K}; P_c = 73.8 \text{ bar}$$

Results for ethanol:

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

$$P_{\text{CO}_2} = \text{He} \cdot x_{\text{CO}_2}$$

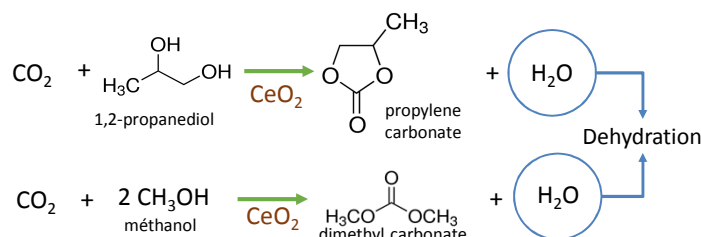


The solubility is proportional to the pressure of CO₂ for **ethanol, methanol, 1,2-propanediol and glycerol**. Results are in good agreement with the literature².

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

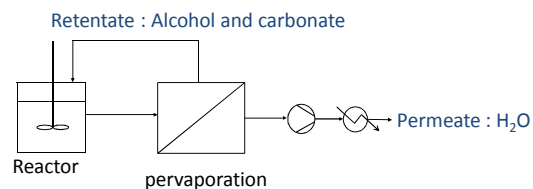
Examples of dehydrating systems¹:

- Use of a **dehydrating reagent**



- Use of a **molecular sieve**

- Use of a **pervaporation system**



Applications of carbonates:

- Fuel additive to reduce SO_x and NO_x emissions
- Low toxic solvent
- Starting materials for polycarbonates

Conclusion

- Study of the reaction of carboxylation of alcohols and diols with CO₂ to produce carbonates: study of **dehydration systems**.
- Measure of the solubility of CO₂ in **methanol, ethanol, 1,2-propanediol and glycerol**.
- Objective**: Development of a sustainable process which associate CO₂ and a **bio-based reagent** to produce **value-added chemical products**

¹M. 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; ²Gui et al. J. Chem. Eng. Data 56, 2420–2429, 2011