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CO2 valorization using epoxides under mild conditions



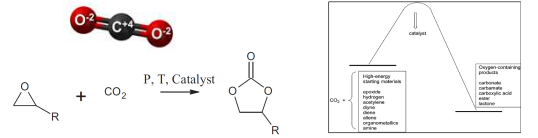
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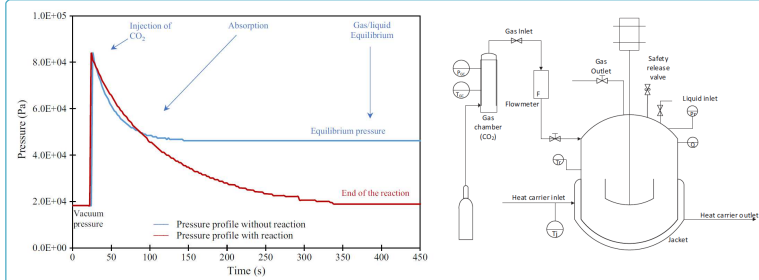
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Introduction

Carbon dioxide is the major greenhouse gas suspected to produce the climatic change. In order to reduce the emissions of CO₂, several ways have been studied like capture process, geological storage and valorization. Recently one of the most important studies is concentrated on chemical valorization of CO₂. This option offers a great potential to recycle CO₂ and to convert it in different high value products. One alternative consider the reaction between epoxides (products with high energy), with CO₂ to obtain cyclic carbonates. These kind of reaction are biphasic and not spontaneous requiring a catalyst. In order to model the system, the liquid/gas interaction between epoxides and CO₂ should be studied.



Experimental set-up



A calorimeter Reactor (Mettler RC1^M) was used to study gas/liquid equilibrium for several temperatures and pressures conditions.
 □ The isothermal method was used to measure CO₂ solubility.
 □ The injection of CO₂ is controlled by a gas chamber and a pressure sensor in the reactor.
 □ The pressure inside of the reactor is followed with the time to study the absorption and the liquid/gas equilibrium.
 □ A stirrer allows to keep the homogeneity in liquid phase and accelerate the mass transfer of the gas.

Thermodynamic equilibrium estimation

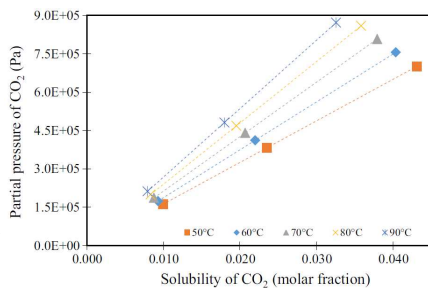
The solubility of CO₂ in ECH was studied at different temperatures and partial pressures of CO₂; The solubility data and Henry's law constant were estimated by using the pressure data. The gas chamber pressure (PR) and the equilibrium pressure in the reactor (Peq) were used respectively to calculate the total amount of CO₂ introduced in the reactor and the amount of CO₂ remaining in the gas phase

$$n_{CO_2}^{inj} = \frac{(P_{R1} - P_{R2})V_{CC}}{RT_{CC}}$$

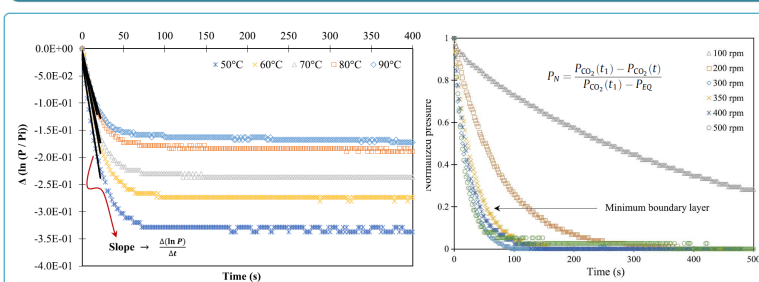
$$n_{CO_2}^{eq} = \frac{P_{eq}V_C}{RT_R}$$

$$X_{CO_2} = \frac{n_{CO_2}^{inj} - n_{CO_2}^{eq}}{n_{ECH}}$$

Henry's law constant has been obtained from the slope of the solubility curves between the partial pressure of CO₂ (PCO2) and the molar solubility of CO₂



Mass transfer without chemical reaction



Increase of the stirring speed improved the absorption rate

It is known that increasing agitation of the liquid increases the diffusion of the gas through the liquid film. As a matter of fact, increasing the stirring speed produces a reduction in the thickness of the contact film, which promotes the gas diffusion into the liquid and hence increases the absorption rate. After 300 rpm, the absorption rate was in fact not enhanced because the minimum boundary layer was attained

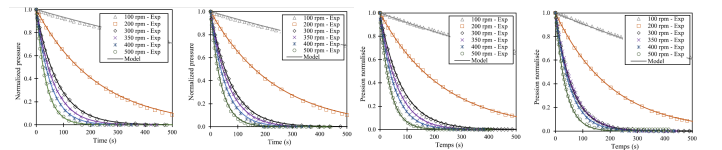
References

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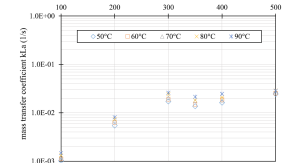
Mass transfer with chemical reaction

enhancement factor model with the experimental data when the catalyst was introduced into the system at (a) 50°C, (b) 60°C, (c) 70°C, (d) 80°C.

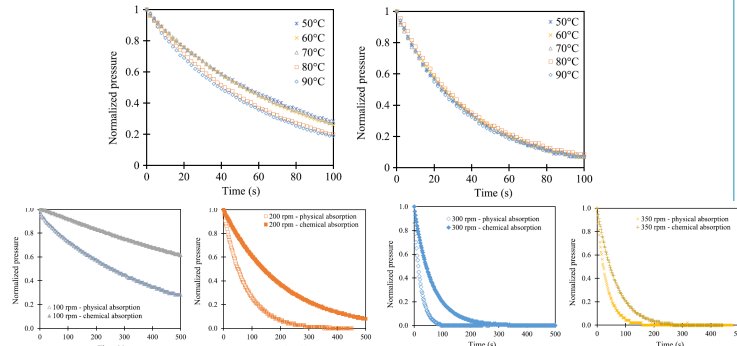
under hydrodynamic conditions, the minimum boundary layer was reached when the stirring speed was higher than 300 rpm, regardless of the temperature used during the absorption. This means that at this specific minimum, increasing turbulence did not have any influence on the mass transfer kinetics.



Variation of the mass transfer coefficient with the stirring speed at different temperatures. It can be seen that as the stirring speed increased, the mass transfer coefficient increased as well. This behaviour was due to the reduction in film thickness, which increased the transfer through the liquid film.



Chemical absorption profiles involving variation of normalised pressure against time at different temperatures and stirring speeds. It was noticed that at 300 rpm, the absorption rate increased as the temperature increased because of the occurrence of the reaction. However when the stirring speed was 500 rpm, a small effect of the temperature on the absorption rate was detected, because no appreciable changes in the pressure drop were observed. This means that the mass transfer kinetics at higher stirring speeds were faster than the kinetics of the chemical reaction. Therefore, even if the diffusion of gas through the liquid film was most important and the kinetic of the reaction was faster at high temperatures, the gas was not entirely consumed by the reaction.



Comparison of absorption rate with or without reaction

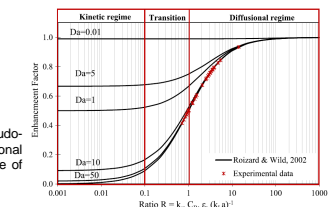
The absorption rates when the chemical reaction occurred in the system were lower than in the case of physical absorption. The pressure profiles at low stirring speeds (100, 200 rpm) presented the most important differences between physical and chemical absorption, because at low agitation, the effective film thickness of transfer was still not reached. Otherwise, when the stirring speeds were higher than 300 rpm, the physical and chemical profiles were closer, indicating the effective reduction of the film transfer.

$$P_{CO_2}(t) = P_{CO_2}(t_0) \exp\left(-\frac{RT_{CC}V_L k_1 a E}{V_R H e}\right) \quad R = \frac{k_1 C_{ECH} c_1}{k_1 a}$$

$$Da = \frac{k_1 a V_R}{Q_{CO_2}} \quad E = \frac{R + \frac{1}{Da}}{R + \frac{1}{Da} + 1}$$

Evaluation of R factor

For this study, R ratio took values between 0.1 and 100. Two pseudo-regimes were identified: a pseudo-regime in which the diffusional process interfered in the rate of the process and a pseudo-regime of transition between the kinetic and diffusional regime.



Conclusions & outlooks

- The influence of the mass transfer kinetics on the chemical valorisation of CO₂ by using ECH and a non-metallic catalyst was studied.
- In the absence of a catalyst, the mass transfer of CO₂ followed a purely physical profile and the stirring degree and temperature determined the absorption rate.
- Under the conditions employed in this work, the reaction between CO₂ and ECH was controlled by the reaction kinetics and not by the mass transfer