**Catalytic carbonation reaction coupled with pervaporation for the production of diethyl carbonate from ethanol and CO2**

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**Highlights**

* Synthesis of DEC from ethanol and CO2 is promising concerning the environmental aspect.
* This study highlights the use of pervaporation to dehydrate the reaction mixture.
* A circulation loop is used to remove continuously water molecules.

**1. Introduction**

Because of its low toxicity and high biodegradability, diethyl carbonate (DEC) has many potential applications like fuel additive, solvent or monomer. Nowadays it is produced mainly by phosgenation of ethanol, which uses toxic and harmful chemicals [1]. Several new synthesis are developing but the most interesting one concerning the environmental aspect and the sequestration of CO2 is the carboxylation of ethanol with CO2 represented in figure 1 [2]. However, yields obtained in the literature for this reaction are still low whatever the catalyst used because of the unfavourable thermodynamics of the reaction [3]. To improve this yield, we can move the equilibrium toward the formation of the diethyl carbonate by removing water molecules produced during the reaction. Our work is focused on the utilisation of a physical way to dehydrate: the pervaporation. This method, which uses a hydrophilic membrane to dehydrate the reaction mixture, is slightly studied in the literature [4].

Figure 1. Ethanol carbonation with CO2

CO2

2 C2H5OH

H2O

+

+

Diethyl carbonate

C2H5OCOOC2H5

Membrane cell

Upstream pressure regulator

Pressure reducing valve

CO2

Tank

Reactor

T

T

P

P

T

P

Cold traps

Vacuum pump

Circulation pump

ethanol

 **2. Methods**

A 100 mL batch reactor was used to study the reaction of carboxylation of ethanol with CO2 with cerium oxide (CeO2) as catalyst. A membrane cell with a membrane PERVAP 4100 purchased from DeltaMem were used to study the dehydration of the solution. The permeate side pressure is maintained at 2 mbar with a vacuum vane pump and the permeate is condensed in two cold traps immersed in liquid nitrogen. The whole process used to study the dehydration of the reaction mixture in continuous is described in figure 2. As the reaction occurs at high pressure (between 20-50 bar), we used pressure reducing valves to ensure that the pressure on the membrane stays below 4 bar.

Figure 2. Scheme of the continuous process of dehydration of the reaction mixture of the carbonation of ethanol

**3. Results and discussion**

A parametric study of the reaction was performed in the reactor to develop a kinetic model. Temperatures from 95 to 125 °C, pressures from 10 to 60 bar and different compositions of water or DEC were tested. The thermodynamic equilibrium was defined based on these experiments. Different mechanisms like Langmuir-Hinshelwood or Eley Rideal were used to develop the kinetic models. The dehydration on the membrane PERVAP 4100 of different solutions was performed. We studied the influence of temperature, pressure and composition in the retentate on the selectivities and fluxes of the membrane. Figure 3 represents an example of the results obtained on the influence of the temperature on the reaction (left) and on the dehydration of an ethanol-water solution (right).

We performed a parametric study on the whole process (figure 2) to optimize the parameters of the continuous dehydration. With this parametric study we can work with a larger range of composition because the amount of DEC is continuously increasing while the amount of water is decreasing. Results obtained are slightly different from the results obtained from the study of the two equipments separately because of the circulation loop. Indeed, temperature and pressure change all along the loop to respect the equipment characteristics and the volume of the solution in the reactor is lower because of the volume of solution in the loop.

Figure 3. Left: production of DEC during reaction at different temperatures. Right: dehydration of 80 mL of an ethanol-water solution with 0.40% wt of water

**4. Conclusions**

This innovative work using pervaporation to dehydrate the reaction mixture of carboxylation of ethanol gives promising results. The circulation loop leads us to test the dehydration of the reaction mixture continuously. Temperatures, pressures and loop flow rate are the most important parameters to improve the performances and obtain better yields in DEC.

**References**

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