

Reactive separation by pervaporation for valorisation of CO₂: application to carbonation of alcohols

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Highlights

- Reactive separation
- Innovative use of pervaporation
- Organic valorisation of CO₂

1. Introduction

Considering global warming effects on earth, the diminution of the emissions of CO₂ has become an essential objective. In addition, the rarefaction of fossil fuels leads us to develop a more sustainable chemistry by using CO₂. Indeed, in a circular economy perspective, CO₂ is no longer seen as a waste but as a source of carbon used to produce value-added chemicals. However, only a few examples are developed at the industrial scale.

In this context, our work is focused on the synthesis of organic carbonates by associating CO₂ with alcohols or diols. Figure 1 represents an example of the studied reactions: the synthesis of dimethyl carbonate. Because of their low toxicity, organic carbonates have many potential applications like fuel additive, solvent or monomer. Currently, they are produced by using some toxic and harmful components like phosgene. The synthesis via the route CO₂ + alcohol has proven to be the most interesting one concerning the environmental aspect and the sequestration of CO₂ [1].

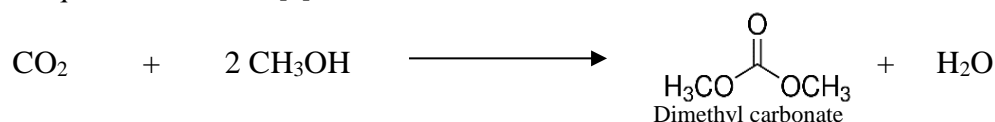


Figure 1. Methanol carbonation with CO₂

Many homogeneous and heterogeneous catalysts have been tested for this synthesis. Some of them give high selectivity but the yield is still low because of the unfavourable thermodynamics of the reaction [2]. The dehydration of the reaction medium can improve the yield by shifting the equilibrium towards the formation of carbonates. Some water-removal techniques have been tested in the literature, the reactive dehydration by using 2-cyanopyridine is the most efficient one with 99 % yield obtained [3]. However, this kind of dehydration raises some issues like the separation and the recycling of the dehydratant. In our work, a system of pervaporation is used [2]. It avoids the use of a new reactant and it is easier for the maintenance. The objective of this work is to combine the reaction with the system of pervaporation in our process, shown in Figure 2. Very few papers worked on the dehydration of this reaction by pervaporation [4-5].

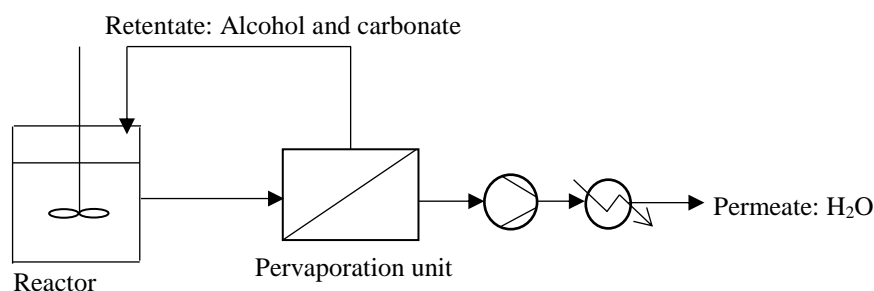


Figure 2. Circulation loop between the reactor and the system of pervaporation

2. Methods

The reaction took place in an autoclave with a capacity of 100 mL. 50 mL of the reactant were introduced in the reactor with a certain amount of an oxide catalyst like CeO_2 . The reactor was pressurised with CO_2 after 3 purges. Then, temperature was increased until the desired value. During the reaction, samples were taken to study the kinetics. At the end of the reaction, the reactor was cooled down and depressurised. The samples were analysed with a GC FID. A parametric study of the reaction was done with pressures up to 50 bar and temperatures until 150°C . The pervaporation was performed with a planar cell of pervaporation purchased by Sulzer Chemtech. Different DeltaMem's PERVAP polymeric membranes were tested and the influence of some parameters like the feed temperature, the water concentration and the feed rate was studied.

3. Results and discussion

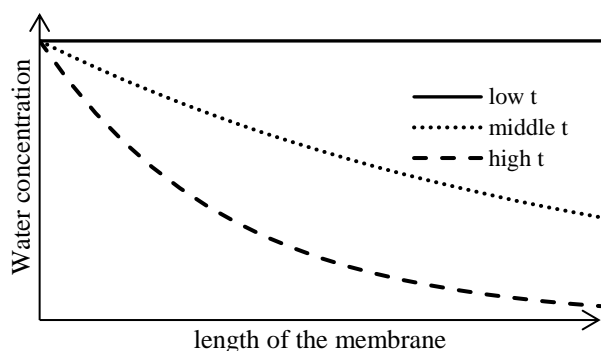


Figure 4. Variation of the water concentration of the mixture along the membrane for different residence times t

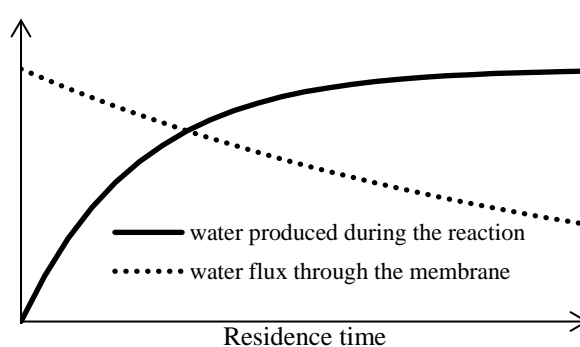


Figure 4. Amount of water produced during the reaction and water flux through the membrane against the residence time

After having studied the reaction and the performance of the membranes separately, the objective is to combine them both in a same process. The parameters that suit the reaction and the pervaporation the best have to be defined. In particular, the flow rate has an important impact on the performance of the process. Indeed, the pervaporation is more efficient if the residence time is shorter because the gradient of concentration will be higher all along the membrane, as we can see in Figure 4. On the contrary, the production of carbonate and water is higher when the residence time is higher. As shown in Figure 4, a compromise between the two residence times has to be found to optimize the yield of carbonate.

4. Conclusions

The originality of this work is the association of a CO_2 valorisation reaction with a pervaporation dehydration system. A parametric study of the reaction is performed and the best membrane for dehydrating the reaction medium is found. The best parameters to combine the reaction and the pervaporation system in a same process are defined.

Acknowledgments

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References

- [1] J. G. M.-S. Monteiro, O. de Q. F. Araújo, J. L. de Medeiros, *Clean Technol. Environ. Policy* 11 (2009) 459–472.
- [2] N. Diban, A. T. Aguayo, J. Bilbao, A. Urtiaga, I. Ortiz, *Ind. Eng. Chem. Res* 52 (2013) 10342–10354.
- [3] Y. Cao, H. Cheng, L. Ma, F. Liu, Z. Liu, *Catal. Surv. Asia* 16 (2012) 138–147.
- [4] M. Honda, M. Tamura, Y. Nakagawa, K. Tomishige, *Catal. Sci. Technol.* 4 (2014) 2830–2845.
- [5] A. Dibenedetto, M. Aresta, A. Angelini, J. Ethiraj, B. M. Aresta, *Chem. – Eur. J.* 18 (2012) 10324–10334.
- [6] C.-F. Li, S.-H. Zhong, *Catal. Today* 82 (2003) 83–90.

Keywords

CO_2 valorisation ; Organic carbonates ; Pervaporation ; Dehydration