# Design of a true moving bed reactor for the direct synthesis of dimethyl carbonate

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## HIGHLIGHTS

- True moving bed reactor (TMBR) for the direct synthesis of dimethyl carbonate.
- A TMBR design algorithm was proposed based on a single objective function.
- Contour maps inside the separation region were computed to assess the TMBR.

## GRAPHICAL ABSTRACT
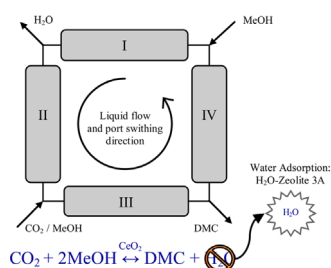
## ABSTRACT

In the present work is proposed the direct synthesis of dimethyl carbonate (DMC) using a true moving bed reactor (TMBR) to enhance the equilibrium yield. A methodology to design the TMBR is proposed, concerning the maximization of reaction conversion and DMC purity at the outlet stream, and the minimization of the desorbent consumption, together in a single-objective function. The design is supported by numerical simulation, which was based on the experimental data collected from our previous works: mass transfer, adsorption over zeolite 3A, reaction kinetics over cerium oxide, and reaction equilibrium. Besides, the design is also supported by the volume separation method and contour maps of relevant performance variables inside the separation region. In addition, the potentiality and weaknesses of a TMBR process, for the DMC production, are discussed. The TMBR here proposed allows a complete separation between water and DMC in extract and raffinate streams, together with a conversion of carbon dioxide around 6% at 30 MPa and 363 K.

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## 1. Introduction

Dimethyl carbonate (DMC) is the simplest linear organic carbonate, and due to its high versatility and low toxicity is considered an important chemical for future green processes. Indeed, DMC can be used as solvent (Schäffner et al., 2010), gasoline additive (Pacheco and Marshall, 1997), or building block for carbonylation and methylation reactions (Memoli et al., 2001). These two last applications are probably the most important because, if DMC market expands, it may become a sustainable alternative for phosgene and dimethyl sulphate. Nowadays, DMC is mainly produced by oxi-carbonylation of methanol (MeOH) (Romano et al., 1980), which uses hazardous reactants such as oxygen and carbon monoxide, and corrosive fluids to regenerate the catalyst.

However, DMC can be synthesized by other routes such as the direct synthesis from methanol and carbon dioxide ($CO_2 + 2MeOH \leftrightarrow DMC + H_2O$) (Sakakura et al., 1998; Dibenedetto et al., 2013; Tomishige et al., 2001, 2000). This route is considered very promising because it promotes the use of carbon dioxide and uses less toxic chemicals (Monteiro et al., 2009), although it is not considered readily feasible

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due to its high thermodynamic limitations. Several authors studied the direct synthesis assisted by dehydrating agents that react with water and shift the equilibrium towards DMC production (Sakakura et al., 1998; Eta et al., 2010; 2011a,b; Honda et al., 2009, 2013; Tomishige and Kunimori, 2002). In fact, this methodology showed successful results, reaching high yields of DMC. However, the addition of extra compounds to the reaction system results in more separations and reaction units, i.e., to extra energy needs.

In several other chemical processes, where the reaction equilibrium is also strongly limited, an excess of one reactant or/and recycling the non reacted species (Seider et al., 2008) is used. Other approach is the use of reactive separation technologies (Lutze et al., 2010; Stankiewicz and Moulijn, 2000). They are an excellent example of process intensification and consist in the integration of reaction and separation in the same unit, where one or more products are continuously separated during the reaction to shift the equilibrium towards product(s) formation. These technologies aim to reduce the process units, reduce wastes production and energy consumption, contributing in a sustainable way for the so called "green chemistry" (Anastas and Warner, 1998).

In this work a reactive chromatography process is proposed in order to shift the DMC reaction equilibrium. In our previous works we studied the reaction kinetics over cerium oxide (Santos et al., 2013), and the adsorption of water and DMC over a zeolite 3A surface (Santos et al., 2014). Now, based on the data collected so far, we present a design methodology for a true moving bed reactor (TMBR) for the direct synthesis of DMC, concerning the maximization of reaction conversion and DMC purity, together with the minimization of the desorbent consumption. This methodology can be easily extended to other reaction systems.

### 1.1. The true moving bed reactor

The true moving bed consists in a chromatograph where both fluid and solid (adsorbent) move countercurrently, enhancing the driving force and consequently the separation performance; when the reaction takes place simultaneously and the products are separated from the reactants, the reaction equilibrium is displaced towards the formation of more products to establish a new equilibrium. With this strategy it is possible to shift the overall conversion when compared to simpler reactors without in situ separation of the products.

In Fig. 1 is shown a sketch of a TMBR with its four zones for a (non-catalytic) reversible reaction $A \rightleftharpoons B + C$, where B is the more strongly adsorbed component, followed by A and C, respectively. First, Feed stream ($F$), containing the reactant A, is fed to the unit; then, in Zone II and III compound A is converted into B and C. Compound B, which is more strongly adsorbed, is pushed towards the Extract stream ($X$), while C is pushed towards the Raffinate stream ($R$). Zones I and IV are designed in order to avoid the accumulation of either B or C in the unit. In Zone I the fluid flow rate should be high enough to regenerate the adsorbent avoiding the contamination of Zone IV by compound B; an Eluent stream ($E$) is used to regenerate the adsorbent. In Zone IV the fluid flow rate should be low enough to force the adsorption of C, pushing it backwards.
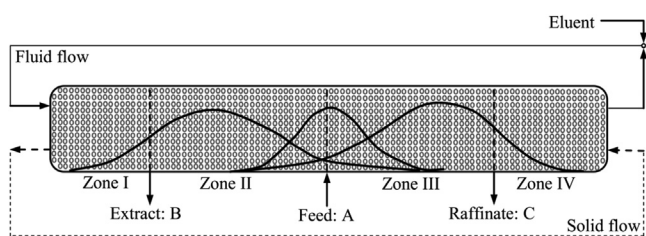


**Fig. 1.** Countercurrent reactive chromatography: TMBR for the reaction $A \rightleftharpoons B + C$.

Some operating restrictions should be obeyed in order to achieve the complete separation of the products. Let us define $\gamma_i$ as the ratio between liquid and solid flow rates in each zone $i$:

$$\gamma_i = \frac{Q_{liq,i}}{Q_{sol.}}, \quad i = \text{Zone I, II, III, or IV} \tag{1}$$

Considering the equilibrium theory (Ruthven and Ching, 1989; Zhong and Guiochon, 1996) (no mass transfer resistances) for linear isotherms ($q = K_{ads} \times C$), over an adsorbent with a certain particle porosity ($\varepsilon_p$), the following restrictions are imposed:

$$\text{Zone I}: \quad \varepsilon_p + (1 - \varepsilon_p)K_{ads,B} \leq \gamma_I \tag{2}$$

$$\text{Zone II}: \quad \varepsilon_p + (1 - \varepsilon_p)K_{ads,C} \leq \gamma_{II} \leq \varepsilon_p + (1 - \varepsilon_p)K_{ads,B} \tag{3}$$

$$\text{Zone III}: \quad \varepsilon_p + (1 - \varepsilon_p)K_{ads,C} \leq \gamma_{III} \leq \varepsilon_p + (1 - \varepsilon_p)K_{ads,B} \tag{4}$$

$$\text{Zone IV}: \quad 0 \leq \gamma_{IV} \leq \varepsilon_p + (1 - \varepsilon_p)K_{ads,C} \tag{5}$$

These restrictions are commonly represented in the so-called separation regions, which are the feasible regions of operating flow rate ratios ($\gamma_I, \gamma_{II}, \gamma_{III}$, and $\gamma_{IV}$) that allow a complete separation between compounds B and C. Other algebraic models for the separation regions were proposed, based on the same principles, for non-linear isotherms, such as Langmuir (Chiang, 1998; Mazzotti et al., 1994; Migliorini et al., 2000) or Toth isotherms (Sá Gomes et al., 2009). The introduction of the mass transfer resistances (Zhong and Guiochon, 1997) in the separation regions determination is much more complicated, because mass transfer depends on the physical properties of the compounds (viscosity, diffusivities, etc), velocity, and design. In order to obtain more precise separation regions (taking into account mass transfer resistances), successive simulations should be performed using realistic mathematical models.

The concept of separation volume was also proposed (Rodrigues and Minceva, 2005; Rodrigues and Pais, 2004; Azevedo and Rodrigues, 1999) to predict the effect of mass transfer resistances, not only on the restrictions of Zones II and III, but also on the restrictions of Zones I and IV, giving more information but also requiring more effort. In spite of the more accurate results obtained when realistic models are used, the equilibrium theory is a very useful tool for a first guess in TMB(R) design.

The major drawback of the TMBR is the difficulty of operating the solid stream: high energy demand, and challenging to ensure plug flow. Moreover, the movement of the particles can cause abrasion, which leads to a drop in the TMB efficiency. In order to overcome this drawback, a novel technology emerged: the simulated moving bed (SMB). Patented by Broughton and Gerhold (1961), the SMB simulates the movement of the solid by changing the positions of the inlet and outlet streams. In the end of each switching time ($t_{switch}^{SMBR}$), each stream moves forward for the next section. The SMB is similar to a TMB if the following equivalences are respected:

$$Q_{solid, \text{TMB}} = (1 - \varepsilon_b)\frac{V_{section}}{t_{switch}^{SMBR}} \tag{6}$$

$$Q_{fluid, \text{SMB}} = Q_{fluid, \text{TMB}} + Q_{solid, \text{SMB}} \tag{7}$$

where $Q$ is the flow rate, $\varepsilon_b$ is the bulk porosity, and $V_{section}$ is the volume of the section between each pair of inlet and outlet streams. Ruthven and Ching (1989) claimed that for a SMB with 2–4 columns per section the oscillation on Raffinate and Extract concentrations are smooth.

Nowadays, the SMBR is widespread for several reaction systems: enzymatic reaction for high-pure fructose (Hashimoto et al., 1983), synthesis of bisphenol A (Kawase et al., 1999), production of acetals (Silva and Rodrigues, 2005), sugar isomerisations (Da Silva et al., 2005, 2006).