Synthesis of dimethyl carbonate and propylene glycol in a membrane-assisted reactive distillation process: Pilot-scale experiments, modeling and process analysis

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ABSTRACT

The simultaneous production of dimethyl carbonate and propylene glycol by transesterification of propylene carbonate with methanol is limited by several thermodynamic restrictions. The reactant conversion is limited by the chemical equilibrium, whereas the purification of dimethyl carbonate is hindered by the formation of an azeotrope with methanol thus necessitating an energy-intensive reference process to produce both products. Process intensification is a promising tool to increase the sustainability of chemical processes by using novel apparatuses and techniques. Therefore, an intensified, membrane-assisted reactive distillation process was investigated in this study allowing to overcome both limitations. Reactive distillation was used to overcome the chemical equilibrium, whereas vapor permeation was used to overcome the azeotrope. However, detailed experimental studies remain necessary to reduce the general industrial skepticism towards these processes and thus increase their use. Hence, a detailed pilot-scale experimental study was performed to quantify synergistic effects between both unit operations. The experimental results were applied to validate a process model that was used to analyze the process. In the future, the insights of the process analysis can be used to define the operating range of the process. This step is necessary to initialize the economic optimization of this process concept in industrial scale.

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1. Introduction

The gradually increasing ecological awareness of the society and the continuously decreasing fossil fuel reserves represent particular challenges to the energy-intensive chemical industry. According to a report of the "European Chemical Industry Council" [1], the energy consumption of the European chemical industry, including pharmaceuticals, was 67,200 kt oil equivalents in 1990. Due to several activities that have increased the energy efficiency of chemical processes, the energy consumption was lowered to 54,000 kt oil equivalents, although the overall production capacity increased by 75% over the same period of time. However, the crude oil price increased by a factor of 3.8 between 1990 and 2010, resulting in increased operating costs for chemical processes, even though energy demand decreased [2]. Hence, a general improvement in energy efficiency is necessary to increase sustainability and allow the chemical industry to contend with future challenges [3]. An effective lever to achieve this objective is the use of process intensification (PI). According to Lutze and Górak [4], "process intensification is a tool for the targeted enhancement of involved phenomena at different scales to achieve a targeted benefit. The four scales for these systems are the (i) process/plant level, (ii) the operation and equipment level, (iii) the phase and functional level and the (iv) fundamental and molecular level [3,5]". Górak and Stankiewicz [6] summarized several approaches to reach PI on a functional domain. Two promising examples that were mentioned are reactive and hybrid separation processes. Combining unit operations with different separation mechanisms results in a hybrid separation process that yields synergistic effects, which may increase energy efficiency and provide the ability to overcome the thermodynamic limitations of the stand-alone operations [7]. The best-known example of a hybrid separation process is the combination of distillation and membrane separation, the industrial applications of which have been presented in a review by Lipnizki et al. [8]. The combination of

Nomenclature

Latin letters

a_i	activity of component i
a_{ij}	UNIQUAC binary interaction parameter
b_{ij}	UNIQUAC binary interaction parameter (K)
DF_i	driving force for mass-transfer of component i (kPa)
J_i	permeate flux of component i (kg h^{-1} m^{-2})
K_a	activity-based chemical equilibrium constant
k_a	activity-based reaction rate constant (kg^3 s^{-1} kmol^{-2} m^{-3})
M_i	molar mass of component i (kg kmol^{-1})
$\dot{m}_i$	mass flow rate of flow i (kg h^{-1})
n_c	number of components
p	pressure (kPa)
p_d	dew point pressure (kPa)
p_i	partial pressure of component i (kPa)
Q_i	molar permeance of component i (mol h^{-1} m^{-2} kPa^{-1})
r_a	rate of reaction (mol h^{-1} m^{-3})
T	temperature (K)
T_d	dew point temperature (K)
V	volume of the liquid phase (m^3)
w_{cat}	mass fraction of catalyst (g g^{-1})
w_i	mass fraction of component i (g g^{-1})
y_i	molar fraction of component i in vapor phase (mol mol^{-1})

Greek letters

τ_{ij}	UNIQUAC binary interaction parameter
Φ	objective function
$\chi_{MeOH/PC}$	molar feed ratio between MeOH and PC (mol mol^{-1})
ψ	degree of vapor saturation

Subscripts

B	bottom
CF	column feed
D	distillate
F	feed
M	membrane module
Memb	membrane
MF	membrane feed
P	permeate
R	retentate
SH	superheating

Superscripts

sim	simulated value

reactive separations, such as reactive distillation (RD), with membrane separations can offer even more substantial benefits than conventional process alternatives [9]. Lutze and Górak [4] presented the recent developments and challenges of these so-called membrane-assisted RD processes, underlining their high potential in terms of PI.

Chemical reaction and distillation are superimposed in an RD column enabling PI [10]. This superimposition can result in the in situ removal of products from the reaction zone increasing the yield of chemical-equilibrium limited reactions [11]. Furthermore, RD enables to overcome azeotropes by chemical reaction depending on the investigated chemical system and the chosen operating conditions [12].

Membrane separations – in particular pervaporation (PV) and vapor permeation (VP) – operate independent of the vapor–liquid equilibrium (VLE) and offer the possibility of separating azeotropic mixtures [13]. However, their viability depends on the availability of a membrane material that can separate the given compounds, and these materials require extensive experimental investigations of their separation characteristics [14]. A crucial disadvantage of membranes is their high investment, which results in economically inefficient stand-alone membrane processes when high throughputs need to be processed or high purities need to be reached [15]. Hence, membrane separations are preferably combined with unit operations that can handle high throughputs (e.g., distillation) to constitute a hybrid separation process [16]. Nevertheless, these so-called membrane-assisted separation processes are sparsely applied in industry due to their complex process design and their difficult operability caused by the complex interactions between the combined unit operations [17].

To improve the industrial application of this promising PI concept, capable process design tools and detailed experimental process experience is necessary. In recent years, process design tools for membrane-assisted separation processes have been presented by various authors [18–21]. However, experimental results must be provided at a meaningful scale to prove the feasibility of the identified processes and to study the behavior of these highly integrated processes, i.e. in terms of impurities that can accumulate in the process due to recycle streams. In addition, these investigations provide a better understanding of the interactions between the combined unit operations but have poorly been emphasized in the literature. Steinigeweg and Gmehling [22] considered the transesterification of methyl acetate with n-butanol to produce butyl acetate and methanol. They performed simulation studies for a membrane-assisted RD process to integrate this reaction. However, an experimental investigation of this integrated process was not performed because only stand-alone RD and PV to separate the low-boiling azeotrope between methanol and methyl acetate were investigated. The membrane-assisted RD process was merely investigated by means of simulation studies. Buchaly et al. [23] experimentally investigated a membrane-assisted RD process for the production of propyl propionate by the esterification of propionic acid with n-propanol in pilot scale. Within this process, VP was applied to separate the by-product water from a heterogeneous, low-boiling azeotrope between n-propanol, propyl propionate and water. Lv et al. [24] studied the esterification of acetic acid with ethanol to produce ethyl acetate and water. They experimentally investigated a membrane-assisted RD process in pilot scale. In this process, a PV membrane was connected to the reboiler and separated water from the mixture.

All presented studies focused on the use of membrane-assisted RD processes for single-product systems. A hydrophilic membrane was used to either remove the by-product water or to remove one of the reactants that was not completely converted in the RD column. In addition, insights into the operation and behavior of the process were not given. Hence, this study will provide detailed experimental experience and results for a membrane-assisted RD process that simultaneously produces two valuable target products from one reaction. The transesterification of propylene carbonate (PC) with methanol (MeOH) to synthesize dimethyl carbonate (DMC) and propylene glycol (PG) was considered as a case-study. In contrast to the aforementioned studies, the membrane was applied to remove the organic compound MeOH and not water, whose separation is currently a state-of-the-art technology [25]. The membrane-assisted RD process was experimentally investigated in pilot scale with the objective to show the feasibility of the process concept. Special attention was paid to the interference of both unit-operations by performing experiments with and without a recycle