



Research article

Direct synthesis of dimethyl ether in multi-tubular fixed-bed reactors: 2D multi-scale modelling and optimum design

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ABSTRACT

The scope of this work is to explore the viability of the direct synthesis of dimethyl ether (DME) over bifunctional catalysts, such as mixtures of CuO/ZnO/Al₂O₃ and γ -Al₂O₃ at industrial scale. To accomplish this purpose, the process is simulated using a phenomenological mathematical model considering momentum, mass and energy balances, applied to both the catalyst particles and reactor bed, which is solved in 2D axisymmetric coordinates. This constitutes a step beyond most of the available studies for the modelling of the DME synthesis reaction, based on simple 1D isothermal models.

The use of this detailed model revealed the importance of intraparticle mass and heat transfer, with effectiveness factors within the range 0.5–1.1. At the reactor scale, radial phenomena were found to be relevant. A design-sensitivity analysis of mass flux, catalyst fraction, pressure, feed temperature, cooling potential and tube diameter on the reactor performance was carried out. An optimized reactor design that provides 80% CO conversion operating at inlet temperature and pressure 245 °C and 40 bar, corresponds to 0.02 m diameter, 8.50 m length and 3600 h⁻¹ gas-hourly space velocity with a yield of dimethyl ether of 0.53.

1. Introduction

Industrial relevance of dimethyl ether (DME) has largely increased in the last years because it is environmentally friendly, has a wide range of applications, and can be manufactured from renewable resources. DME can be used directly as fuel, replacing LPG and conventional diesel fuel, with better combustion performance (lower gasses and soot emissions) [1], or as a fuel precursor and bioplatfrom molecule for the manufacture of other chemicals of interest, such as olefins, methyl acetate, formaldehyde or dimethyl sulfate, among others [2–5]. DME production has also an important role in the context of CO₂ valorization technologies. DME synthesis from CO₂-rich feeds could be an attractive route to recycle the greenhouse gas CO₂ by converting it into valuable products and thereby controlling its emission into the atmosphere [6]. Innovative reactor configurations, such as membrane reactors, are being developed to improve this reaction, typically with lower conversion and DME yield compared with the reaction from syngas [7,8].

The most mature route for DME synthesis from syngas consists of a two-step process: in a first reactor, methanol is synthesized in the presence of a metal catalyst, and in a second reactor methanol is dehydrated to DME over a solid acid catalyst. This manufacturing method requires high operation pressures, since methanol synthesis is limited by equilibrium. In order to overcome this limitation, a new one-step

synthesis process has been proposed and developed using bifunctional catalysts in a single reactor, with promising results, e.g. CO conversion in a direct DME synthesis reactor can be up to 80%, while a methanol synthesis reactor reaches only 20% [9].

Many of the published studies are focused in the development of new bifunctional or hybrid catalysts, being CuO/ZnO/Al₂O₃ and γ -Al₂O₃ the catalysts most commonly used as metal and acid functions, respectively. Several preparation methods have been studied, although physical mixing of both components seems to be the most suitable [10].

An important issue to be considered in direct DME synthesis is the reactor selection. Lu et al. [11] performed a comparison between fixed bed, fluidized bed and slurry reactors for this process, finding that fluidized beds are the best choice. However, this technology is not proven beyond small pilot plant scale, so its industrial suitability has not been demonstrated yet. Slurry reactors show slow mass transfer of reactants to the catalyst, and low solubility and diffusivity of reactants in the liquid phase. Therefore, the reactor type selected in the present work is the fixed bed reactor, in the form of cooled shell and tube, or sequences of adiabatic beds with intercooling [12].

Optimization of the operating conditions to increase DME yield and avoid paraffins formation is a key factor to increase the reaction performance. Another important factor is the formation of hot spots within the catalytic bed due to the large reaction exothermicity, this effect

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Nomenclature		z	axial coordinate (m)
<i>Latin symbols</i>		<i>Subscripts/superscripts</i>	
a	specific surface ($\text{m}^2 \text{m}^{-3}$)	O	inlet
c	molar concentration (mol m^{-3})	b	bulk
C_p	heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)	cat	catalyst
D, d	diameter (m)	e	effective
d_e	equivalent diameter (m)	G	gas
D_{ij}	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	i	compound
k	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	j	reaction
κ	hydraulic permeability (m^2)	P	particle
K	mass transfer coefficient (m s^{-1})	r	radial coordinate
k_j	kinetic constant per unit of catalyst mass ($\text{mol kg}_{cat}^{-1} \text{s}^{-1} \text{bar}^{-2}$)	R	reactor
K_{eqj}	equilibrium constant	ref	reference conditions
f_{cat}	catalyst weight fraction (–)	S	solid
f_i	fugacity (bar)	STP	Standard Temperature and Pressure
f_v	volume fraction (–)	w	wall
ΔH_j	reaction enthalpy (J mol^{-1})	z	axial coordinate
h	heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)	<i>Greek symbols</i>	
I	unitary matrix	β	approaching to equilibrium
L	length (m)	β_F	Forchheimer drag (kg m^{-4})
M_i	molecular weight (kg mol^{-1})	ε_{bo}	average bed porosity (–)
p	pressure (Pa)	ε_b	bed porosity (–)
Pr	Prandtl number, $Pr = C_{pG} \mu / k_G$ (–)	ε_{int}	internal porosity (–)
r	radial coordinate (m)	ϕ	sphericity (–)
r_j	reaction rate ($\text{mol kg}_{catj}^{-1} \text{s}^{-1}$)	η	effectiveness factor (–)
Re	particle Reynolds number, $Re = d_p \mathbf{u} \rho_G / \mu$ (–)	μ	viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
Sc	Schmidt number, $Sc = \mu / \rho_G D_{im}$ (–)	ν_{ij}	stoichiometric coefficient of compound i in reaction j (–)
T	temperature (K)	ρ	density (kg m^{-3})
\mathbf{u}	surface velocity, $ \mathbf{u} = \sqrt{u_z^2 + u_r^2}$ (m s^{-1})	τ	space time (s)
w_i	weight fraction (–)	τ_c	catalyst tortuosity (–)
y_i	molar fraction (–)		

leading to irreversible catalyst deactivation. As the catalyst behavior is strongly influenced by the reaction conditions, the development of a kinetic model for describing the system is essential to model and optimize the process. There are many studies on the kinetics of the integrated process, but most of them are based on kinetic equations obtained separately for the two involved reactions, methanol synthesis and methanol dehydration [8–10]. In a previous work of our group, an original kinetic model based on the simultaneous reactions involved in the process, working with a physical mixture of commercial CuO/ZnO/Al₂O₃ and γ -Al₂O₃ catalysts in a fixed bed reactor, was proposed and experimentally validated [13]. This model predicts the reactor behavior at a laboratory scale, with small catalyst particles, where mass and heat transport limitations are negligible. However, this is not necessarily true for industrial reactors. So, this model must be extended in order to be used for predicting the behavior of industrial reactors. The extended model should consider the spatial distribution of the catalyst components, and provide accurate information about temperature and composition profiles in the catalyst bed to allow the control of the process.

Some works on simulation of the direct synthesis process are available in the literature. Based on the process developed by KOGAS, Kim et al. [14] simulated a DME demonstration plant with Aspen Plus and used the results to propose modification of the process, but give very little details on the process conditions. McBride et al. [15] also simulated the process of DME synthesis in a fixed bed reactor using a layered arrangement of the two catalysts, finding that the physical mixtures of the catalysts gave better results. Vakili et al. [16] developed a steady-state one-dimensional heterogeneous model for a process consisting of two fixed bed reactors in series. The model was used to obtain the optimal reactors configuration and operating conditions.

Chen et al. [17] simulated the whole production process, considering the reactions at equilibrium, using Aspen Plus, and studied the energy integration through the pinch technology using the program Super-Target. Other study was performed by Manenti et al. [18], applying a systematic staging design to a system of two fixed-bed reactors in series used for methanol and DME synthesis, and performing a model-based integrated energy process optimization. They found that the integration of DME production with methanol synthesis increases notably the efficiency of the process. De Falco et al. [19] centered their simulation studies on the possibility of using CO₂ rich feeds for the DME direct synthesis, finding that water removal during CO₂ conversion is necessary.

Lee et al. [12] proposed a comprehensive one-dimensional steady-state model for the catalytic heterogeneous catalyst bed, considering heat and mass transfer between the catalyst pellets and reactants, and the effectiveness factor of the catalyst, together with the reactor cooling through the reactor wall. They compared a physical mixture of the 2 catalyst pellets and a hybrid catalyst. They found that the hybrid catalyst gave better CO conversion and DME productivity, but reactor temperature control was more difficult. They also reported strong pore diffusion effects. Song et al. [20] used a similar model, and compared simulation results with the obtained for a pilot reactor with good results. They found that the calculated effectiveness factor for the catalyst particles varied markedly along the reactor, and had unusual values. All these studies used 1D-models, where variations in the reactor radial coordinate are not considered, and then some potentially relevant mass and heat transfer phenomena involved are neglected.

The scope of this work is the development of a more accurate model for the direct synthesis of DME from syngas in a fixed bed reactor. The

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