CHEMICAL ENGINEERING RESEARCH AND DESIGN XXX (2014) XXX–XXX

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Methanol synthesis from CO_2 and H_2 in multi-tubular fixed-bed reactor and multi-tubular reactor filled with monoliths

Sofiane Arab, Jean-Marc Commenge, Jean-François Portha, Laurent Falk*

Laboratoire Réactions et Génie des Procédés, 1 rue Grandville, BP 20451, 54000 Nancy, France

ABSTRACT

This work investigates the impact of catalyst structuring into particles or monoliths on methanol production from only CO_2 and H_2 at a large scale. Methanol synthesis in multi-tubular reactors is evaluated using packed-bed and monolithic reactors by modeling heat and mass transfer in each reactor. The obtained simulation results show that, at low gas hourly space velocity (GHSV = 10,000 h^{-1}), the performances of both reactor technologies are similar. In this case, the packed-bed reactor technology is the most appropriate technology due to its simplicity of installation and operation. At high GHSV (25,000 h^{-1}), the packed-bed reactor technology is limited by a considerable pressure drop that causes an important loss in productivity due to thermodynamic equilibrium, whereas the monolithic reactors exhibit negligible pressure drop and achieve far better performances.

Keywords: Methanol synthesis; Monolith; Packed bed; Reactor modeling; Carbon dioxide; Hydrogen

1. Introduction

The production of electricity from renewable sources such as wind or sun rises the issue of production irregularity and the gap between production and consumption. Conversion of the excess of produced electricity to valuable chemicals may be an interesting alternative to its storage in batteries which is generally not viable from an economic standpoint (Beaudin et al., 2010). Production of hydrogen by electrolysis of water can be the first step for the conversion of the excess of electricity. The storage of large amounts of hydrogen under high pressure is expensive and requires high safety precautions (Sakintuna et al., 2007). Therefore, the second step of the electricity conversion process can be the use of the synthesized hydrogen to hydrogenate CO_2, stemming from industrial sources, to valuable and safer chemicals such as methanol (Mignard et al., 2003).

Methanol is a key chemical intermediate that can be used to produce alternative fuels such as dimethyl ether (DME) (Olah, 2005). Currently, methanol synthesis is achieved at industrial scale in multitubular packed-bed reactors that operate at high pressure (50–80 bar) and intermediate temperature (200–300 °C).

Methanol synthesis from carbon oxides and hydrogen is usually achieved over copper and zinc oxides catalysts ($CuO–ZnO–Al_2O_3$) according to the following main reactions:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (A)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (B)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (C)$$

Abreviations: CPA, cubic-plus-association; DME, dimethyl ether; GHSV, gas hourly space velocity, h^{-1}; PC-SAFT, perturbed-chain statistical associating fluid theory; SRK, Soave–Redlich–Kwong; WHSV, weight hourly space velocity, h^{-1}.

* *Corresponding author*. Tel.: +33 383175104; fax: +33 383175086.
E-mail addresses: sofiane.arab@univ-lorraine.fr, sofiane.arab@live.fr (S. Arab).

Received 14 June 2013; Received in revised form 17 December 2013; Accepted 6 March 2014
http://dx.doi.org/10.1016/j.cherd.2014.03.009
0263-8762/

List of symbols

ΔH_r°	heat of reaction, J mol^{-1}
a_{sf}	interfacial area, m^2 m^{-3}
C	concentration, mol m^{-3}
$\mathbb{C}_p$	molar heat capacity of gas species, J mol^{-1} K^{-1}
d	half thickness of the monolith wall, m
d_h	hydraulic diameter of the channel, m
D_{ax}	coefficient of axial dispersion, m^2 s^{-1}
d_t	tube diameter, m
$\mathcal{D}_{m,i}$	molecular diffusivity of species i in the gas mixture, m^2 s^{-1}
$\mathcal{D}$	diffusivity, m^2 s^{-1}
e	coating thickness, m
e_t	tube thickness, m
f	fugacity, bar
$\mathcal{F}$	friction factor
h	heat-transfer coefficient between the fluid and the internal wall of the tube, W m^{-2} K^{-1}
k'	reaction rate constant
k_d	coefficient of interphase mass transfer, m s^{-1}
K	adsorption equilibrium constant, bar^{-1}
K_p	equilibrium constant based on partial pressures
L_t	tube length, m
l	hydraulic diameter of the channel, m
M	mass, kg
N_t	number of tubes
P	total pressure, Pa
$\mathcal{Q}$	power per unit of length generated by the reactions, W m^{-1}
R	ideal gas constant, J mol^{-1} K^{-1}
r_j	rate of reaction j, mol kg$_{cata}^{-1}$ s^{-1}
$Re_{d_h} = \frac{\rho u d_h}{\mu}$	Reynolds number
S	surface, m^2
$Sc = \frac{\mu}{\rho \mathcal{D}}$	Schmidt number
$Sh = \frac{K d_p}{\mathcal{D}}$	Sherwood number
T	temperature, K
u	fluid velocity, m s^{-1}
$\hat{u}$	fluid superficial velocity, m s^{-1}
U	global heat-transfer coefficient, W m^{-2} K^{-1}
v	molar volume, m^3 mol^{-1}
V	reactor volume, m^3
V_p	volume of a single catalyst particle, m^3
x	depth in the solid phase, m
z	axial position, m
Z	compressibilty factor

Greek letters

α	global efficiency of the catalyst
β	volume ratio
ε	porosity of the catalytic bed
Γ	denominator of the kinetics rates
λ	thermal conductivity, W m^{-1} K^{-1}
μ	viscosity, Pa s
ν	stoichiometric coefficient
Ω	open cross section offered to the fluid in the reactor, m^2
ρ	density, kg m^{-3}

Subscripts

ax	axial
A, B, C	reaction
$cata$	catalyst
eff	effective
i	chemical species number
j	reaction number
m	mixture
p	particle
t	tube
w	internal wall of the tube

Superscripts

ce	center of the solid
f	fluid
int	internal
s	solid
su	surface of the solid

The methanol synthesis process is globally exothermic. Skrzypek et al. (1995) carried out thermodynamic and kinetic studies of gas mixtures containing CO, CO_2 and H_2. They show that conversion of carbon oxides to methanol is promoted by high pressures and low temperatures (150–200 °C) while the reaction kinetics are promoted by high temperatures.

The use of monolithic reactor technology observed an important growth during the last two decades, and they will have increasing applications in mass production of chemicals. Through a state of the art study, (Tomašić and Jović, 2006) pointed out that the monolithic reactors are widely used for NO_x abatement, CO oxidation, and fine chemicals production. It seems worth to know to which extent this reactor technology may be advantageous for methanol synthesis from only CO_2 and H_2.

The present work investigates the impact of catalyst structuring on the performances and the size of methanol synthesis reactors. The conventional packed-bed reactors are compared to monolithic reactors for methanol production at a large scale. A parametric study is carried out in order to get more insight on the optimal operating conditions and geometry of both reactors. More than a traditional performance comparison of these technologies, these types of reactors both exhibit advantages and drawbacks with respect to operational and maintenance criteria that must be considered for proper evaluation of the potentials of each technology.

2. Modeling of reactors

To perform a reliable comparison of both technologies, in conjunction with a parametric study, a detailed model of the system first must be developed.

2.1. *Description of technologies*

Cooled multi-tubular reactors are considered in the present work, this reactor technology is well-established and widely used in chemical industry. The reactors are cooled by a counter-current stream of liquid water on the shell side.

The tubes of the packed-bed reactor are filled with spherical catalyst particles while those of the monolithic reactor contain several pieces of cylindrical monoliths with square

Please cite this article in press as: Arab, S., et al., Methanol synthesis from CO_2 and H_2 in multi-tubular fixed-bed reactor and multi-tubular reactor filled with monoliths. Chem. Eng. Res. Des. (2014), http://dx.doi.org/10.1016/j.cherd.2014.03.009