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Low temperature catalytic reforming of heptane to hydrogen and syngas

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M.E.E. Abashar *

Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

Abstract The production of hydrogen and syngas from heptane at a low temperature is studied in a circulating fast fluidized bed membrane reactor (CFFBMR). A thin film of palladium-based membrane is employed to the displacement of the thermodynamic equilibrium for high conversion and yield. A mathematical model is developed to simulate the reformer. A substantial improvement of the CFFBMR is achieved by implementing the thin hydrogen membrane. The results showed that almost complete conversion of heptane and 46.25% increase of exit hydrogen yield over the value without membrane are achieved. Also a wide range of the H_2/CO ratio within the recommended industrial range is obtained. The phenomena of high spikes of maximum nature at the beginning of the CFFBMR are observed and explanation offered. The sensitivity analysis results have shown that the increase of the steam to carbon feed ratio can increase the exit hydrogen yield up to 108.29%. It was found that the increase of reaction side pressure at a high steam to carbon feed ratio can increase further the exit hydrogen yield by 49.36% at a shorter reactor length. Moreover, the increase of reaction side pressure has an important impact in a significant decrease of the carbon dioxide and this is a positive sign for clean environment.

1. Introduction

The energy sector has been faced with major challenges of crude oil prices, diminishing of fossil fuel reserves, environmental quality, and the rapid growth of the industry. These challenges have imposed a strong demand for alternative fuels. Hydrogen had been recognized as an important alternative clean fuel that produces no pollution or greenhouse gases and has the highest energy content (Abashar, 2004; Abashar et al., 2007). The conversion of syngas (H_2,CO,CO_2) to clean liquid fuels free from sulfur such as gasoline and diesel is another promising route to alternative fuels (Mark, 1999; Olusola et al., 2010).

Hydrogen can be produced by different processes such as thermochemical and electrolysis processes. The thermochemical processes release hydrogen in the molecular structure of different resources such as natural gas and biomass, while the electrolysis processes release hydrogen from the molecular structure of water. Steam reforming of methane has been known as the main industrial thermochemical process that is widely used to produce hydrogen and syngas (Abashar, 1991; Elnashaie and Abashar, 1993).

Nomenclature

A_c	free cross-sectional area of the reactor for catalyst circulation, m^2
Ar	Archimedes number, [-]
d_{H2}	diameter of hydrogen membrane tube, m
d_c	diameter of catalyst particle, m
d_c^*	dimensionless diameter of catalyst particle
F_j	molar flow rate of component j, kmol/h
g	gravitational acceleration, m/s^2
k_i	rate coefficient of reaction i
$K_2, K_4,$	equilibrium constant of reactions (2) and (4), kPa^2
K_3	equilibrium constant of reaction (3), [-]
L	reactor length, m
N_{H2}	number of hydrogen membrane tubes
P	total pressure, kPa
P_j	partial pressure of component j, kPa
Q_{H2}	permeation rate of hydrogen, kmol/h
r_i	rate of reaction i, kmol/kgcat h
R	gas constant, kJ/mol K
Re_p	particle Reynolds number, [-]
T	temperature, K

T_f	feed temperature, K
u_o	superficial gas velocity, m/s
u^*	dimensionless gas velocity
z	dimensionless length of the reactor

Greek letters

δ_{H2}	thickness of hydrogen membrane, μm
ε	void fraction
μ_g	viscosity of gas, kg/m.s
ρ_c	catalyst density, kg/m^3
ρ_g	gas density, kg/m^3

Superscript

p	permeation side
r	reaction side

Abbreviation

CFFBR	circulating fast fluidized bed reactor
CFFBMR	circulating fast fluidized bed membrane reactor

The conventional processes of methane steam reforming are very expensive due to severe external heating and also suffer from destructive elevated temperatures for the catalyst and the reactors. For example, the production of syngas that was used as a feedstock for the gas to liquid processes (GTL) such as the Fischer–Tropsch (FT) process may cost about 70% of the capital and running costs of the total plant (Mark, 1999). This high cost and other technical factors have stimulated the research arena to develop cost-effective technologies of hydrogen and syngas processes and also to examine different aspects of improvement with respect to the thermal efficiency, catalyst properties, operations and new designs (Kaihu and Hughes, 2001; Venkataraman et al., 2003; Levent et al., 2003).

Recently, Elnashaie and co-workers have shown that circulating fast fluidized bed membrane reactors (CFFBMR) are versatile and efficient type of reformers for hydrogen production (Chen et al., 2003a,b; Prasad and Elnashaie, 2003; Abashar et al., 2007, 2008; Abashar, 2012). Among the advantages of circulating fluidized bed reactors are: effective gas–solid contact, uniform temperature distribution, elimination of high diffusion limitations, high gas throughputs per unit cross-section, and high steam-to-carbon ratio (Brereton and Grace, 1993; Kunii and Levenspiel, 1997, 2000). Moreover, the application of palladium-based membranes in the CFFBMR has a significant impact on shifting the thermodynamic equilibrium and separation of hydrogen (Shu et al., 1994, 1995; Dittmeyer et al., 2001; Hughes, 2001; Abashar, 2004; Abashar et al., 2007).n-Heptane is used by many investigators as a model compound for higher hydrocarbons such as gasoline and naphtha (Pant and Kunzru, 1996; Seiser et al., 2000; Puolakka and Krause, 2004; Ran et al., 2004). High hydrogen and syngas yields have been obtained by steam reforming of heptane (Chen et al., 2003a,b, 2004). Also, the required heat per carbon atom of heptane is less than methane and the heat duty will be less (Rostrup-Nielsen et al., 1998). Chemical kinetics of higher hydrocarbon such as n-heptane has been developed and used by many researchers (Phillips et al., 1969; Rostrup-Nielsen, 1973, 1977; Tottrup, 1982; Christensen, 1996; Nah and Palanki, 2009; Rakib et al., 2010). Surprisingly, there are only limited published studies in modeling and simulation of steam reforming of n-heptane in the CFFBMR (Chen et al., 2003a,b, 2004). This preliminary study is an extension to Elnashaie and co-workers (Chen et al., 2003a,b) to investigate the potential of production of hydrogen and syngas at a low temperature as an alternative to the costly conventional high temperature steam reforming processes. Also a thin layer of composite hydrogen membrane of 5 μm thickness is employed in this study to enhance the displacement of the thermodynamic equilibrium for further permeation of the hydrogen through the membrane, instead of relatively thick hydrogen membrane used by Chen et al. (2003a,b). Moreover, the factors affecting the H$_2$/CO ratio have been studied to achieve the desired recommended industrial range for the syngas suitable as a feedstock of the GTL processes.

2. Reactions kinetics

The main reactions of steam reforming of *n*-heptane over a nickel based catalyst are represented by (Chen et al., 2003a,b; Christensen, 1996; Nah and Palanki, 2009):

Heptane steam reforming reaction

$$C_7H_{16} + 7H_2O \rightarrow 7CO + 15H_2 \tag{1}$$
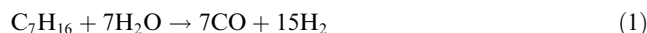
Methanation reaction (reverse of methane steam reforming reaction)

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{2}$$

Water gas shift reaction (WGS)

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$

Methane overall steam reforming reaction

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \tag{4}$$