



Modeling of synthesis gas and hydrogen production in a thermally coupling of steam and tri-reforming of methane with membranes



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ABSTRACT

In this novel study, tri-reforming process was used as a heat source to proceed steam reforming of methane in a two membrane hydrogen perm-selective Pd/Ag thermally coupled reactor. Results illustrated that H₂/CO ratio at the output of steam and tri-reforming sides reached to 6.1 and 0.9, respectively. Additionally the results showed that methane conversion at the output of steam and tri-reforming sides reached to 31% and 96%, respectively. By increasing the feed flow rate of tri-reforming side from 28,120 to 140,600 kmol h⁻¹, methane conversion and H₂ molar flow rate enhanced 40% and 28.64%, respectively.

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1. Introduction

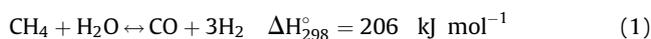
In recent years, there has been an increasing interest in hydrogen production because of its advantageous properties such as sustainability, high energy content, high efficiency (specifically when used in fuel cells), ease of storage and transportation and most importantly little or no impact on environment. Also hydrogen can be used as a chemical reactant in oil refining industry and production of ammonia, methanol or aniline [1–8].

One of the important hydrogen production processes that industrialized is steam reforming of methane [9,10]. For this purpose, methane is reacted with steam over an appropriate catalyst (usually Ni-based catalysts) under reactions (1)–(3) in a multi-tubular reactor and hydrogen rich syngas (H₂ and CO) is produced during this highly endothermic reaction. Methane conversion in this way is usually around 78% (with the operating parameters of: $T = 850\text{ }^{\circ}\text{C}$, $P = 1.6\text{--}4.1\text{ MPa}$, $\text{H}_2\text{O}/\text{CH}_4 = 2\text{ or }4$) [11–13].

Reaction equation of steam reforming process:

Steam reforming of methane reactions (SRM):

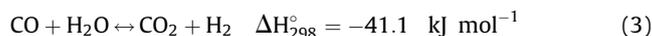
SRM 1:



SRM 2:



Water–gas shift (WGS) reaction:



Two main disadvantages were reported for these conventional steam reformers: firstly; is providing the necessary heat from huge fired furnaces to drive the highly endothermic steam reforming reactions. Secondly is low conversion of methane at moderate temperatures because the steam reforming reaction is inherently endothermic and thermodynamically favored by a high temperature [8,14].

Concept of thermally coupling of reactors suggests a solution for elimination of huge fired furnaces and thus energy saving. Coupled reactors are generally classified into direct, regenerative, and recuperative coupling [15]. Recently many researchers have studied recuperative coupling [16–20]. In these reactors, an appropriate exothermic process is coupled with endothermic one for supplying the required heat of endothermic reaction and so both reactions is proceeded simultaneously [15].

To proceed steam reforming of methane, Arab Aboosadi proposed an exothermic reaction of nitrobenzene hydrogenation as a heat source instead of methane combustion furnaces in conventional steam reformers [8]. Song proposed a new process called tri-reforming of methane that synergistically combined three processes of methane reforming; endothermic steam

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Nomenclature

a_p	specific surface area of catalyst pellet ($\text{m}^2 \text{m}^{-3}$)
A_c	cross section area of each tube (m^2)
C_p	specific heat at constant pressure (J mol^{-1})
d_p	particle diameter (m)
D_i	tube inside diameter (m)
D_{ij}	binary diffusion coefficient of component i in j ($\text{m}^2 \text{s}^{-1}$)
D_{im}	diffusion coefficient of component i in the mixture ($\text{m}^2 \text{s}^{-1}$)
F_t	total molar flow rate (mol s^{-1})
F_i	flow rate of component i (mol s^{-1})
h_f	Gas–solid heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
h_i	heat transfer coefficient between fluid phase and reactor wall in exothermic side ($\text{W m}^{-2} \text{K}^{-1}$)
h_o	heat transfer coefficient between fluid phase and reactor wall in endothermic side ($\text{W m}^{-2} \text{K}^{-1}$)
J_{H_2}	hydrogen permeation rate ($\text{mol m}^{-1} \text{s}^{-1}$)
k_i	rate constant of reaction i ($\text{mol kg}^{-1} \text{s}^{-1}$)
k_{4a}	first reaction rate constant for the fourth rate equation ($\text{mol kg}^{-1} \text{s}^{-1}$)
k_{4b}	second reaction rate constant for the fourth rate equation ($\text{mol kg}^{-1} \text{s}^{-1}$)
K_w	thermal conductivity of reactor wall ($\text{W m}^{-1} \text{K}^{-1}$)
L	reactor length (m)
M_i	molecular weight of component i (g mol^{-1})
N	number of components
P	total pressure (bar)
P_i	partial pressure of component i (Pa)
r_i	reaction rate of component i ($\text{mol kg}^{-1} \text{s}^{-1}$)
R_1	first rate of reaction for steam reforming of methane ($\text{mol kg}^{-1} \text{s}^{-1}$)
R_2	second rate of reaction for steam reforming of methane ($\text{mol kg}^{-1} \text{s}^{-1}$)
R_3	rate of reversed water–gas shift reaction ($\text{mol kg}^{-1} \text{s}^{-1}$)
R_4	rate of complete oxidation of methane ($\text{mol kg}^{-1} \text{s}^{-1}$)
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
R_p	particle radius (m)
Re	Reynolds number
Sc_i	Schmidt number of component
T	temperature (K)
u	superficial velocity of fluid phase (m s^{-1})
u_g	linear velocity of fluid phase (m s^{-1})
U	overall heat transfer coefficient between exothermic and endothermic sides ($\text{W m}^2 \text{K}^{-1}$)
v_{ci}	critical volume of component i ($\text{cm}^3 \text{mol}^{-1}$)
y_i	mole fraction of component i (mol mol^{-1})
z	axial reactor coordinate (m)

Greek letters

α	activity of catalyst (where $\alpha = 1$ for fresh catalyst)
$\Delta H_{f,i}$	enthalpy of formation of component i (J mol^{-1})
ε_B	void fraction of catalytic bed
η	effectiveness factor used for the intra-particle transport limitation
μ	viscosity of fluid phase ($\text{kg m}^{-1} \text{s}^{-1}$)

ρ	density of fluid phase (kg m^{-3})
ρ_b	density of catalytic bed (kg m^{-3})

Superscripts

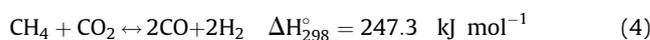
g	in bulk gas phase
s	at surface catalyst

Subscripts

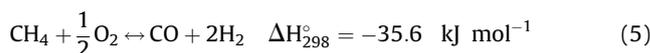
0	inlet conditions
i	chemical species
j	reactor side

reforming, carbon dioxide reforming (dry reforming), and exothermic oxidation of methane [21,22]:

Dry reforming of methane reaction (DRM):



Partial oxidation of methane (POM):



Complete oxidation of methane (COM):



Existence of methane oxidation reaction in tri-reforming process makes it to produce a large amount of heat as some of this heat will be spent for the endothermic processes of steam and dry reforming reactions.

One of the possible ways to overcome the equilibrium limitation and thus reach to a high methane conversion at lower temperatures is removing hydrogen from reaction zone by using of hydrogen perm-selective membranes [11,23]. Hydrogen removal prevents the steam reforming reaction to reach equilibrium [24] and thus hydrogen yield is improved at low temperatures.

Pd-based membranes are most promising for separation of ultra pure hydrogen from gaseous mixtures due to their high permeability, 100% selectivity relative to hydrogen, high stability at high temperatures and good resistance to corrosion and chemical solvents [25,26]. Also, palladium surface is so enough resistant against poisoning by hydrocarbons, steam and carbon monoxide. Many studies have been made on applying Pd/Ag membranes in packed bed reactors for improving conversion and selectivity. These membranes typical work in range of 300–600 °C and exhibit good mechanical properties [27–33].

One of the most significant discussions in thermally coupled reactors is applying membranes in the configuration of the reactor to reach more conversion in one step. Hence, many articles have made on thermally coupled membrane reactors [34–38].

In this paper, tri-reforming process is coupled with steam reforming reaction in a double concentric tube multi-tubular reactor. Actually, tri-reforming process has been considered as a heat source for driving endothermic steam reforming reaction instead of using huge fired furnace.

Elimination of a low performance fired-furnace and replacing it with a high performance tri-reformer reactor causes a reduction in full consumption with production of a new type of synthesis gas. Furthermore, hydrogen perm-selective Pd/Ag membranes are applied for both sides of tri- and steam reforming to attain pure hydrogen and adjust H_2/CO ratio as a feed gas for methanol synthesis at low reactant feed temperature.

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