Chemical Engineering & Processing: Process Intensification 120 (2017) 258–267

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

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

Utilising a radial flow, spherical packed-bed reactor for auto thermal steam reforming of methane to achieve a high capacity of H_2 production

Davood Iranshahi[a], Parisa Salimi[a], Zahra Pourmand[a], Samrand Saeidi[b,*], Jiří Jaromír Klemeš[c]

[a] Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), No. 424, Hafez Avenue, Tehran 15914, Iran

[b] Department of Wood and Paper Science, Research Institute of Forests and Rangelands, Agricultural Research, Education and Extension Organization (AREEO), Tehran, Iran

[c] Sustainable Process Integration Laboratory – SPIL, NETME Centre, Faculty of Mechanical Engineering, Brno University of Technology – VUT Brno, Technická 2896/2, 616 00 Brno, Czech Republic

ARTICLE INFO

Keywords:
Hydrogen production
Auto-thermal
Steam reforming
Synthesis gas
Spherical reactor
Packed bed reactor

ABSTRACT

Due to various problems associated with the use of conventional reactors (CR) in different units, such as pressure drop across the tube, high manufacturing costs and low production capacity, a novel radial flow spherical packed bed reactor (RF-SPBR) is proposed in the current study for auto thermal steam reforming of methane. As the RF-SPBR is considered to be a viable alternative to CR, their simulation results while performing auto thermal steam reforming, are compared in this manuscript. In this case, the developed mass and energy balance equations have been solved for both CR and RF-SPBR and the yield of products profile and conversion of reactants have been compared with both designs. The results indicate that pressure drops imperceptibly decreases from 3 to 2.97 bar in the spherical configuration, while in CR it drops from 3 to around 2.4 bar. Since more reactants can be used in the spherical design, the novel spherical reactor configuration is one of the most economically viable alternatives in comparison with tubular reactors in terms of both process enhancement and costs minimization and, thus, it can be considered as a remedy in reforming units.

1. Introduction

The mounting concern about the environmental consequences of using fossil fuels has been caused the development of alternative sources of energy [1,2]. By increasing the emission sources, there is a growing interest in the production of hydrogen, without environmental effects [3]. It is considered to be one of the most essential materials in chemical, oil and energy industry, as it serves as an important feedstock for the production of important chemicals, such as ammonia and methanol [4].

Pure hydrogen is considered to be the perfect fuel for proton-exchange membrane fuel cells (PEMFCs), which have a various variety of automotive and non-automotive applications [5]. The absence of CO is the most important features in the PEMFCs design. It can easily be adsorbed on the surface of the catalyst and thus, the needed sites for hydrogen reactions are blocked and poisoned [6]. Since such poisoning effect results in a drastic decline in performance, using ultra-pure hydrogen is vitally important [7]. Considering the difficulties related to both hydrogen storing and transporting, on-site generation of hydrogen from suitable hydrocarbon feedstock such as gasoline, natural gas and methanol seem to be much more feasible in comparison to powering PEMFC by hydrogen directly [8].

Steam reforming of light liquid or gaseous hydrocarbon is considered to be a commercially advanced technology and the main pathway for large-scale hydrogen generation [9]. It involves the reaction of steam with methane over supported nickel catalyst in packed-bed reactors and has various advantages including high hydrogen yield. However, this process has various drawbacks, such as requiring a massive amount of energy to keep the temperature high in the range of 850–900 °C and also producing a high pressure in the range of 15–40 atm [10]. Moreover, complicated process units are also required, including reformers, high and low temperature shift reactors (HTS and LTS) and a preferential oxidation reactor [11]. Another disadvantage of this process is the occurrence of hot spots along the reactor which can cause catalyst deactivation [12]. As a result, this process cannot be employed for decentralised synthetic gas production.

Although the steam reforming technology has been used for years, improvements can still be implemented. Partial oxidation is another thermochemical reforming technique which has been adopted to produce hydrogen, in which methane and sub-stoichiometric oxygen are fed into the reactor in the absence of water. This process has great advantages, including exothermicity, approximately 100% methane

* Corresponding author.
E-mail address: samrandsaidi@gmail.com (S. Saeidi).

http://dx.doi.org/10.1016/j.cep.2017.07.020
Received 4 October 2016; Received in revised form 19 July 2017; Accepted 21 July 2017
Available online 02 August 2017

Nomenclature

A_c	Cross section area (m^2)
C_i	Concentration of each component ($mol\ m^{-3}$)
C_p	Specific heat of the gas at constant pressure ($J\ mol^{-1}$)
D_e	Effective diffiusity ($m^2\ s^{-1}$)
d_p	Particle diameter (m)
k_i	Rate constant for the rate of reactions
K_{eff}	Conductivity of fluid phase ($W\ m^{-1}\ K^{-1}$)
K_{pi}	Equilibrium constant based on partial pressure for component i
M_i	Molecular weight of component i ($g\ mol^{-1}$)
P	Total pressure (bar)
Q	Volumetric flow rate ($m^3\ s^{-1}$)
r_1	Rate of reaction for reaction 1 ($mol\ kg\ cat^{-1}\ s^{-1}$)
r_2	Rate of reaction for reaction 2 ($mol\ kg\ cat^{-1}\ s^{-1}$)
r_3	Rate of reaction for reaction 3 ($mol\ kg\ cat^{-1}\ s^{-1}$)
R	Gas constant $kJ\ kmol^{-1}\ K^{-1}$
T	Temperature (K)
T_{ref}	Reference temperature (K)
Z	Length of reactor coordinate

Abbreviations

ATR	Auto-thermal reforming
CR	Conventional reactor
RF-SPBR	Radial flow spherical packed-bed reactor
FR	Flow rate ratio
PEMFCs	Proton-exchange membrane fuel cells
HTS	High-temperature shift reactors
LTS	Low-temperature shift reactors

Greek letters

η	Effectiveness factor (−)
μ	Viscosity of fluid phase ($kg\ m^{-1}\ s^{-1}$)
ρ	Density of gas phase ($kg\ m^{-3}$)
ρ_b	Density of catalytic bed ($kg\ m^{-3}$)
ε	Porosity (−)
ΔH_i	Heat of reaction ith ($kJ\ kg^{-1}$)
υ_i	Stoichiometric coefficient of component ith in reaction
ϕ_s	Sphericity

conversion and low contact time. However, various disadvantages including a lower H_2-to-CO ratio in comparison to SMR [13] and the high risk of hot spots formation along the reactor has hampered the use of this process in industrialised facilities [14].

A combination of adiabatic steam reforming and non-catalytic partial oxidation known as auto thermal methane reforming (ATR) has been introduced as a viable solution to resolve these dilemmas [15]. The required heat in conventional reforming is normally supplied from the outside reactor wall by combusting extra fuel. However, in ATR process air or pure oxygen is co-fed with water and methane, causing the internal combustion of a portion feed which provides adequate energy for endothermic reforming reactions. Running these reactions parallel to each other makes this process much more energy-efficient [16]. Compared to other reforming techniques, this thermal neutral process offers a wide range of advantages, including small reactor size, easier start-up and lower energy requirements [17]. A wide range of H_2-to-CO ratios can be obtained by manipulating the inlet concentration of oxygen. The ATR process is predicted to play an important role as an agent to restrict the level of CO_2 as a result of using pure oxygen instead of air, which can reduce the high cost of carbon capture from the flue [18].

One of the drawbacks of the tubular reactors is unfavourable pressure drop, which causes the decline of the reaction rates and conversions. Although this issue can be settled by utilising radial-flow tubular reactors, radial-flow patterns are not easily practicable in tubular reactors. Consequently, there is a growing interest toward in using spherical reactors in order to resolve the issues related the use of conventional reactors [19]. Using smaller catalytic pellets eliminating internal mass transfer, higher feed flow contributing to the productivity of the plant and significant reduction in the thickness of the reactor are among the advantages of spherical reactors [20]. Several studies have been conducted to demonstrate process enhancements resulting from using spherical reactors [21]. Shahhosseini et al. [22] developed a multi-stage spherical reactor (one-dimensional mathematical model) for auto-thermal reforming of methane to maximize synthesis gas and minimise CO_2. The optimised spherical configurations have several advantages compared to conventional reactors, including higher synthesis gas production, small pressure drop and low manufacturing cost. In another work, Viecco and Caram investigated the operational characteristic of spherical reverse flow reactors, in which the flow enters the reactor through one whole hemisphere then leaves the next one. High temperature can be reached in the centre of the reactor bed making it favourable for impossible feed streams to be processed in conventional unidirectional steady-state reactors without the addition of expensive auxiliary fuels [23].

Table 1
Kinetic rate expressions for methane combustion [30] and water-gas shift and steam reforming [35].

Rate constant parameters	A_i	$E_{a,i}$ (kJ/mol)
k_{1a} ($mol\ bar^{-2}\ kg_{cat}^{-1}\ s^{-1}$)	8.11×10^5	86
k_{1b} ($mol\ bar^{-2}\ kg_{cat}^{-1}\ s^{-1}$)	6.82×10^5	86
k_2 ($mol\ bar^{-0.404}\ kg_{cat}^{-1}\ s^{-1}$)	2.62×10^5	106.9
k_3 ($mol\ bar^{-2}\ kg_{cat}^{-1}\ s^{-1}$)	2.45×10^5	54.5
Adsorption parameters	K_i^o	ΔH_i (kJ/mol)
$K^{ox}CH_4$ (bar^{-1})	1.26×10^{-1}	−27.3
$K^{ox}O_2$ (bar^{-1})	7.87×10^{-7}	−92.8

Of prominent importance is modelling and simulating the ATR process since it can predict the trajectory of components profiles and the temperature profile [24]. A lot of researches have been performed on the modelling of autothermal steam reformer [25]. Avci et al. [26] simulated a series of bench scale and industrial scale reactors in order to investigate the effect of different catalyst bed and molar feed on the product distribution. Lin et al. [27] carried out the modelling of an experimental methane fuel processors and performed analysis in order to locate optimum operating point. Lattner and Harold [28] conducted a comprehensive study on the process feasibility of various reactor types for ATR for the production of hydrogen in PEM fuel cells. In another work, Hagh [29] used an atomic balance approach in order to develop a framework for theoretical interpretation of reforming reactions and deducted an optimisation strategy which can be applied to any ATR regardless of either size or feed flow rates.

In this study, by reducing energy use and increasing the production of desirable products, the efficiency of this process has been improved. Due to the radial flow of the feed in the RF-SPBR, the pressure drop is considerably lower and the results showed considerably higher yield and conversion of products profile in the radial configuration in comparison to the conventional reactor designs.

The aim of this work is to compare the spherical and tubular reactors while performing the auto-thermal reforming. Both reactors would be modelled by applying the mass balance, energy and, momentum balance. The performances of both designs are compared by