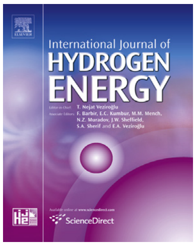
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 13811–13819

Available online at www.sciencedirect.com

ScienceDirect

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



# Phenomenological evaluation of industrial reformers for glycerol steam reforming

*Diego Rúa, Liliana Hernández*[*]

*Department of Chemical Engineering, Universidad de Bogotá Jorge Tadeo Lozano, Bogota, Colombia*

## ARTICLE INFO

*Article history:*
Received 18 November 2015
Received in revised form
17 February 2016
Accepted 22 April 2016
Available online 20 May 2016

*Keywords:*
Glycerol
Steam reforming
Packed bed reactor
Mass and heat transfer
Multiphysics modeling

## ABSTRACT

Methane steam reforming remains the most attractive route for synthesis gas and hydrogen production. However, glycerol, a byproduct from biodiesel production, now is proposed as a greener alternative that could permit the production of such gases with a lower environmental impact using a renewable source. In this work two types of industrial reformers, used commercially for methane steam reforming (i.e. Side-Fired and Top-Fired reformers), were simulated for glycerol steam reforming from phenomenological point of view using a 1D heterogeneous model built in COMSOL Multiphysics®. These calculations were made considering the catalyst internal and external mass and heat transfer resistances inside the packed bed reactor. The behavior of the reactors under adiabatic condition and the effect of catalyst particle size and shape on the performance of the reactor were also studied. From the results it was found that the internal and external mass transfer processes are the controlling resistances in the overall reaction process. The internal resistance is the most significant one, causing values for the internal effectiveness factor of even 0.02. Moreover, the formation of internal temperature gradients for catalyst particles is negligible for all cases. The use of Side-Fired reformers could be more convenient with respect to Top-Fired reformers, because the temperature gradients through the reactor wall are lower for the first one by 10 °C approximately. This is noteworthy in terms of heat transfer efficiency and thermal stresses that can affect the reactor framework, being this an important issue for highly endothermic reactions as the steam reforming of glycerol.

## Introduction

Several political, environmental and economic reasons have addressed the research about energy generation from renewable sources, including biofuels. One of the most known biofuels is biodiesel, whose sales reached the 7.4 billion gallons last year [1]. The most common procedure to get biodiesel is from transesterification of vegetable oils, which produces crude glycerol as a byproduct. There are other routes like high pressure splitting of fats, saponification in soap manufacturing, propylene oxidation, etc. [2]. Crude glycerol can contain water, organic and inorganic salts, small amounts of esters, alcohols, traces of glycerides, among other compounds [3]. It has a low commercial value and is toxic, its refining is expensive and the large amounts generated could be an environmental problem, because it should not be disposed directly to the environment [4].

---

[*] *Corresponding author*. Department of Chemical Engineering, Universidad de Bogotá Jorge Tadeo Lozano, Cra 4 No. 22-61, Bogotá, Colombia. Tel.: +57 1 2427030x1443.

E-mail addresses: diegoj.ruag@utadeo.edu.co (D. Rúa), lilianac.hernandezb@utadeo.edu.co (L. Hernández).

http://dx.doi.org/10.1016/j.ijhydene.2016.04.177

However, glycerol could be a renewable and environmentally friendly alternative for the production of syngas and hydrogen because its steam reforming is the most promising alcohol reforming since theoretically it can produce up to 7 mol of molecular hydrogen per mole of glycerol reformed [5]. The general reaction for the production of hydrogen through glycerol steam reforming is [6]:

$$C_3H_8O_3(g) + 3H_2O\ (g) \rightarrow 3CO_2(g) + 7H_2(g)\Delta H_{rxn@25^\circ C} = 128 kJ/mol \tag{1}$$

On the other hand, methane is the most important feedstock for syngas and hydrogen production [7], because such compound and the process used for its transformation are the cheapest [8]. In this sense, the most important process for syngas and hydrogen production is methane steam reforming performed usually on nickel supported on alumina catalysts [9]. For this reason, it will always be a referent for new technologies.

In this context, one way to evaluate the potential of glycerol steam reforming at industrial level is to study its behavior in a classical methane steam reformer, with the aim of finding some critical design parameters or operational conditions. In this sense, some studies have been made modeling a segment of packed bed reactor using a one dimensional pseudohomogeneous [10] heterogeneous model [11] but without including the physical configuration of reformer heating. Also, the rigorous simulation of a fluidized bed reactor is reported [12], however, packed bed reactors are the most utilized devices for similar objectives.

Very recently, a pseudohomogeneous model was proposed [13]. Such work was validated against the work of other authors giving satisfactory results. Nevertheless, their validation was performed from the data obtained in a microreactor, whose operating conditions and transport phenomena differ greatly from those of an industrial reactor.

Such works also consider isothermal or adiabatic conditions, which are opposite to the common operating conditions found in industry. There are few of these phenomenological models available in the literature [13], which makes this work attractive for a better understanding of this kind of mathematical models, and future works regarding industrial steam reforming of glycerol.

For the previous reasons, the aim of this work is to evaluate the behavior of two types of industrial reformers commercially used for methane steam reforming (i.e. Side-Fired and Top-Fired reformers) in a packed bed reactor from a phenomenological point of view.

To the date, there is no information available in the open literature regarding the performance of industrial reactors carrying out glycerol steam reforming taking into account external heat transfer, so this study could represent an interesting starting point for the design of these devices.

## Theory/calculation

The methane steam reforming at industrial scale usually is carried out in Side-Fired or Top-Fired reformers, for this reason, these two kinds of reformers will be modeled and their results will be compared with an adiabatic case.

To evaluate the behavior of reformers proposed above, a heterogeneous unidimensional model was implemented to describe mathematically mass and heat transfer for catalyst shaped in spheres and Raschig rings, as well as the pressure drop in the tubular reactor. This type of model implies that process conditions such as temperature, pressure, composition, etc. vary only along the length of the reactor i.e. they are the same in any cross section of the packed bed [14]. The reaction fluid was assumed as a mixture of ideal gases.

Furthermore, under the assumption that the fluid is well mixed, it can be considered that there are no axial mass or heat dispersion effects [14], and the behavior of one tube, is representative of any other in the reformer [14,15].

The mass and energy conservation equations used for modeling are described as follows [16,17]:

For the fluid phase:

$$-\frac{d(\upsilon\, C_i)}{dz} = k_{gi} a_v \left(C_i - C_{ip}^s\right) \tag{2}$$

$$\frac{d\left(\upsilon\, \rho_f\, c_p\, T\right)}{dz} = h_f a_v \left(T_s^s - T\right) - \frac{4h_w}{d_t}\left(T - T_t^{wi}\right) \tag{3}$$

For the catalyst particle:

$$-D_{ie}\frac{d^2 C_{ip}}{dx^2} = R_i^p \tag{4}$$

$$-\lambda_e \frac{d^2 T_p}{dx^2} = -\Delta H_{rxn} R_i^p \tag{5}$$

$$R_i^p = \rho_p r_i\left(C_{ip}, T_p\right) \tag{6}$$

For spheres and Raschig rings the catalyst-fluid mass transfer film coefficients ($k_{gi}$) were estimated with Thoenes–Kramers correlation (Equations (7)–(9)) [18] and J-factors for mass transfer (Equations (10) and (11)) [16] were respectively:

$$Sh' = (Re')^{1/2}(Sc)^{1/3} \tag{7}$$

$$Re' = \frac{Re}{(1-\varepsilon)} \tag{8}$$

$$Sh' = \frac{Sh\ \varepsilon}{(1-\varepsilon)} \tag{9}$$

$$J_D = \frac{k_g}{\nu}(Sc)^{2/3} \tag{10}$$

$$J_D = \frac{0.458}{\varepsilon}\left(Re_p\right)^{-0.407} \tag{11}$$

For estimating the catalyst-fluid heat transfer film coefficients ($h_f$) J-factors for heat transfer were used (Equations (11) and (12)) [16]:

$$J_D = J_H = \frac{h_f}{\rho \nu C_p}(Pr)^{2/3} \tag{12}$$

For estimating the tube inner surface-fluid heat transfer film coefficient ($h_w$) Leva's correlation was used [17]. The transport properties (Heat capacities, viscosities, thermal