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Design of a biogas steam reforming reactor: A modelling and experimental approach

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ABSTRACT

This paper covers the research activities performed at the CNR Institute for Advanced Energy Technologies "Nicola Giordano", aimed at developing and testing a biogas steam reforming reactor. A mathematical model has been developed in order to describe, the performance of the above-cited steam reforming reactor (packed bed). To study the effects on reaction performance, a parametric analysis was performed varying operating conditions such as inlet temperature and reagent molar ratio. The model was validated by comparing the calculated data with the experimental data obtained with a proprietary Ni/CeO_2 based catalyst in packet bed micro-scale reactor at different T = 700–900 °C, S/C = 1–5 and GHSV = 30,000 h^{-1}, showing a good agreement between the experimental and theoretical results.

Introduction

There is an urgent need in Europe to increase the use of renewable fuels to comply with the EU 20–20–20 objectives [1]. In this scenario biomasses and the derived biofuels represent a source of alternative energy.

The biogas, obtained from a variety of biomasses and processes such as degradation of urban and industrial waste, landfills, co-digestion of zootechnical effluents, agricultural waste and energy crops, can be considered as one of the most known and widespread renewable fuels [2]. At present, biogas is mainly used to produce electricity and heat using cogeneration systems; internal combustion engines (ICE) and gas turbines represent the most used technologies, this type of utilization is strongly influenced by the limits of the conventional engines: low electrical conversion, high levels of noise, maintenance and pollutant emissions, especially for small biomass gathering terminals [3–6].

More attention has been paid to an alternative use of biogas for hydrogen/syngas production. In this respect, there is an increasing interest for small scale locally distributed hydrogen production units, based on reforming processes, to serve as sources of hydrogen for fuel cells [7]. The production of syngas is important also for the utilization as a raw material for the production of synthetic fuels with low environmental impact (hydrogen, methanol, dimethylether and synthetic gasolines) [8].

The principal components of biogas are CH_4 and CO_2, therefore, the Dry Reforming (DR) process could be the most appropriate to produce hydrogen/syngas, but the severe

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Table 1 – Reaction equilibrium constants and Arrhenius kinetic parameters.

Reaction, j	Equilibrium constant, K_j	k_{oj} (mol/(kg_{cat} s))	E_j (J/mol)
1	$K_I = \exp\left(\frac{-26,830}{T_s} + 30.114\right)\left(bar^2\right)$	1.7×10^{15} $bar^{0.5}$	240,100
2	$K_{II} = K_I K_{III}(bar^2)$	2.3×10^{14} $bar^{0.5}$	243,900
3	$K_{III} = \exp\left(\frac{4.400}{T_s} - 4.036\right)$	5.43×10^{5} bar^{-1}	67,130

$k_j = k_{oj} \times \exp(-E_j/RT)$.
R is gas constant in J/(mol*K).

operating conditions (high reaction temperature and absence of steam) resulting in catalyst deactivation by coke deposition and/or sintering of the metallic phase and support [9]. This means that more efforts must be taken, especially for the development of active and stable catalyst formulations.

Actually, Steam Reforming of Methane (SRM) is the most common chemical process to convert methane into hydrogen. SRM is an endothermic reaction and the ratio of water and methane is 1:1 that is calculated from stoichiometry of SRM, however, excess steam is usually employed to suppress carbon formation (around more than 3 times of stoichiometry). Thus, the Steam Reforming of biogas in heterogeneous catalytic reactors, is expected to become a short-term viable method for the production of hydrogen/syngas [10,11]. Ni-based catalysts were investigated mostly for this reaction and are of potential for industrial application [12–14].

The design of a biogas reactor is the key aspect for the performance and efficiency of a hydrogen generator: weight and volume should be minimized and the heat management system optimized for different operating conditions. In this respect, the development of a biogas steam reforming reactor, has been carried out at the CNR/ITAE Institute. Particularly, a mathematical model has been developed in order to describe, the performance of the above-cited steam reforming reactor (packed bed). The aim of the model is to investigate the performance of the reactor in order to enhance optimization and control of the steam reforming unit. The model plays a key role in overcoming the issues of system design, by evaluating the temperature and the gas concentration profiles in the reactor. The model was validated by comparing the calculated data with the experimental data obtained with a proprietary Ni/CeO_2 based catalyst [14] in packet bed micro-scale reactor at different T = 700–900 °C, S/C = 1–5 and GHSV = 30,000 h^{-1}.

Computational methods

Reactor modelling

The simulation of the processes is achieved through the description of transport phenomena by Partial Differential Equations (PDEs), numerically solved using the Finite Element Methods. The model is able to couple heat and mass transport and chemical reactions occurring in the reactor. Energy and mass balances have allowed to define the temperature and the products profiles along the length of the reactor.

According to the literature the following reactions are the prevailing reaction routes [15]:

R_1: $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\quad \Delta H_{298} = 206.2$ kJ/mol

R_2: $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$ $\quad \Delta H_{298} = 164.9$ kJ/mol

R_3: $CO + H_2O \leftrightarrow CO_2 + H_2$ $\quad \Delta H_{298} = -41.2$ kJ/mol

As the first two reactions are highly endothermic, excessive amounts of heat have to be supplied to the reactor in order to maintain the desired high temperature.

The reactor is simplified and modelled as a non-isothermal plug flow reactor. Assuming a steady-state, the main equations of the model are presented below:

Species mass balance:

$$\frac{dF_i}{dV} = R_i \tag{1}$$

where F_i is the species molar flow rate (mol/s), V represents the reactor volume (m^3), and R_i represents the species net reaction rate (mol/(m^3 s)).

Reactor energy balance:

$$\sum_i F_i C_{p,i} \frac{dT}{dV} = w_s + Q + Q_{ext} \tag{2}$$

where $C_{p,i}$ is the species molar heat capacity (J/(mol·K)), and Q_{ext} is the heat added to the system per unit volume (J/(m3·s)). Q denotes the heat due to chemical reaction (J/(m3·s)).

$$Q = \sum_j H_j r_j \tag{3}$$

where H_j the heat of reaction (J/mol), and r_j the reaction rate (mol/(m^3 s)).

Table 2 – Van't Hoff parameters for species adsorption.

	K_{oi} (bar^{-1})	ΔH_i (J/mol)	K^C_{oi} (bar^{-1})	ΔH^c_i (J/mol)
CH_4	6.65×10^{-4}	−38,280		
CO	8.23×10^{-5}	−70,650		
H_2	6.12×10^{-9}	−82,900		
H_2O	1.77×10^{5} bar	88,680		

$K_i = K_{oi} \times \exp(-\Delta H/RT)$.
R is gas constant in J/(mol*K).