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Monolith and foam catalysts performances in ATR of liquid and gaseous fuels

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HIGHLIGHTS

- A preliminary study on catalyst geometry and configuration is proposed for CH_4 ATR.
- Foam and honeycomb monoliths are candidate as best supports.
- Noble metals on monoliths catalyst shows excellent activity.
- Catalyst temperature profile influence in reaction rate is observed.

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ABSTRACT

Hydrogen fuel cells seem the most viable solution to the pollution reduction and the energy growing demand. Very compact and small size production plant for distribute production may reduce hydrogen transport and storage difficulties. Due to the high reactor compactness and thermal self-sustainability, the auto-thermal reforming (ATR) reaction of gaseous and liquid hydrocarbons can be the optimal solution. Fossil hydrocarbons like methane, gasoline and diesel still remain the favourite feed for catalytic auto-thermal reformer, due to the widespread existing delivery pipelines and the high energy density. Unfortunately, due to the different characteristics of liquid and gaseous fuels, it is very difficult to realize a multi-fuel processor characterized by high performances in terms of thermal efficiency and hydrogen yield, and, up to now, very low number of papers dealing with multi-fuel reformers is present in the literature.

In this work, a catalytic reactor for the auto-thermal reforming of gaseous and liquid hydrocarbons was developed. An high pressure feed system, based on the “common rail” technology was adopted for liquid fuel, allowing the formation of micro-droplets, assuring a very quick liquid fuel vaporization, an uniform mixing with other reactants, avoiding the coke formation, and improving the hydrogen yield and thermal efficiency. A commercial monolith structured catalysts was used: the influence of catalyst configuration was analysed. In order to obtain a total self-sustainable process and a very compact system, a heat exchanger was integrated in the reactor to preheat water and air streams by exploiting the heat from exhaust stream. Process control is assured by monitoring temperatures and composition in up to 6 point along the catalytic bed.

Preliminary tests showed high thermal system efficiency, with a good hydrocarbon conversion at different operating conditions. The low start-up times makes the system extremely versatile, and suitable for batch operations.

1. Introduction

The antithetic problem of growing world energy demand focuses on research and optimization of alternative energy sources: hydrogen appears as an ideal clean and sustainable energy.

The hydrogen–fuel cells combination attracts the greatest interest from the scientific research world. Since the well-known difficulties in hydrogen transport and storage, distributed production of H_2 results as the most viable solution.

The two most diffused technologies for H_2 production are H_2O electrolysis and hydrocarbon fuels processing. The latter still has several limitations, as low process kinetic and very high operative costs. Therefore, despite the growing interest in renewable resources, due to the wide diffusion of fossil fuels and their costs relatively low, hydrocarbons fuel processing still remain the best solution in a period of transfer to a hydrogen based economy.

A fuel processor aims to convert a hydrocarbon fuel (natural gas, gasoline, diesel) in a H_2-rich stream to feed a fuel cell system.

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It consists in three main steps: a reforming unit, in which syngas is produced from hydrocarbons, a water gas shift unit to convert CO in further H_2, and a preferential oxidation unit, to remove any CO traces from syngas. In order to define the most suitable fuel processor system to couple with a fuel cell for electric energy production, the thermal energy management, the H_2 productivity required to load the fuel cell, the quick response to the load changes, as well as the start-up and shut-down procedure, are the main features to take in account in the choice.

There are three primary techniques used to produce hydrogen from hydrocarbon fuels: steam reforming (SR), partial oxidation (POX), and auto-thermal reforming (ATR). The choice of the proper reforming chemistry is the start point to design an effective reforming process.

The SR is a catalytic endothermic process in which a hydrocarbon (e.g. methane) reacts with steam to produce hydrogen and carbon monoxide:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad \Delta H_0^{reaz} = +206\ \text{kJ/mol}$$

Due to endothermicity of SR reaction, in order to achieve high methane conversion, very high reaction temperature is required. Despite SR needs to supply energy to the system, due to its high H_2 yield it is the main process for industrial hydrogen production. It requires very large reactors and plants and very long start-up and shut-down times, therefore it is the optimal solution for steady state operations.

The POX is an exothermic reaction in which hydrocarbon is oxidized in lack of oxygen, and can be conducted by catalytic or non-catalytic reactors:

$$CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO \quad \Delta H_0^{reaz} = -35.6\ \text{kJ/mol}$$

The exothermicity of the reaction allows the self-sustainability of the POX process, very compact plants and short transitory time. However hydrogen yield is lower than that of SR. This reaction may be conducted in catalytic conditions in order to improve selectivity toward desired products.

The ATR is a combination of SR and POX, in which hydrocarbon reacts both with steam and oxygen:

$$CH_4 + xO_2 + yH_2O \leftrightarrow aCO + bCO_2 + cCH_4 + dH_2O + eH_2 + fC_{(s)}$$

In principle, ATR may be considered as the sequence of the two previous reactions: POX and SR [1]: the oxidative reaction occurs as a first step of the process, while the steam reforming reaction starts when the process steam reaches a consistent temperature. It is a self-sustained catalytic process, in which the exothermicity of hydrocarbon oxidation reaction supplies to the system the heat needed for the SR reaction; therefore, as a typical ATR reactor behavior, along the catalytic bed the temperature quickly raises the first zone, and then slowly decreases until the end [2]. Exothermicity of the reaction as well as hydrogen yield depend strictly on feed ratio values x and y [3]. Auto-thermal operation point is the condition at which the energy requirements of the SR reaction are balanced by oxidation reactions [4].

By aiming to achieve a distributed H_2 production, simple, very compact and versatile systems, characterized by fast start-up time and very quick response to feed changes are required. To this goal, the chemical characteristics of ATR reaction, like high reaction rate, and the ability to work without any external heat sources, candidate the ATR of hydrocarbons as one of them most promising selections [5,6].

Since ATR reaction involves three different reactants, both liquid and gaseous, to obtain proper reactants mixing results an important step in the process. A non-uniform mixing of reactants may cause local incorrect feed ratio values x and y, with a decrease of yield and selectivity toward desired products, coke formation, and catalyst deactivation [7,8]. Therefore, a well reactants premixing may improve hydrocarbon conversion, as well as reduce coke deposition on the catalytic surface.

In order to improve system compactness, the auto-thermal reforming of a liquid fuel may be an interesting solution, due to the high energetic density. On the other side, methane is the hydrocarbon with the highest hydrogen-to-carbon ratio (H/C = 4). Therefore, an auto-thermal reformer for both liquid and gaseous fuels may be an ideal solution for a fully versatile system. Despite, due to the very different characteristics of liquid and gaseous fuels, it is very difficult to realize a multi-fuel processor. The main difficult consists in the mixing of a liquid fuel with other gaseous reactants (air and steam). To vaporize the liquid hydrocarbon needs an external heat exchanger that in the one side drastically increases the plant size, in the other side hydrocarbon overheating may causes cracking phenomena. In order to reduce these worsening, non-thermal vaporization of liquid fuels was explored. Two are the main methods to achieve a "cold vaporization" of liquid fuels: very high pressure injection [9] and ultrasound-assisted injection [10]. For both cases, the liquid fuel is atomized in micro-droplets that quickly vaporize on contact with the other pre-heated reactants. Since cracking phenomena strictly depend from the residence time of the droplets in the warm environment, the microdroplets diameter arrows great importance in the feed system efficiency. Another explored solution for liquid fuel atomization is the air-assisted injection [11], in which fuel atomization is enhanced by a high pressure air flux.

Despite ATR is a thermally self-sustained process, reactants temperature at the inlet of catalytic bed influences the thermal profile along catalyst, the outlet temperature and then the fuel conversion and the H_2 yield [12,13]. Higher reactants temperature assures higher hydrocarbons conversion. On the other side, products temperature was about 700–800 °C, while further purification stages, like Water Gas Shift (WGS) and CO Preferential Oxidation (PROX) need lower temperature, respectively about 300 °C and about 100 °C [14–19]. In order to reduce plant size and operating costs, very advantages may be achieved by heat transferring from products stream to fed streams [20,21].

In ATR process, the choice and the optimal setup of the catalytic system play a fundamental role in the plant design. Catalyst selection may greatly affect both the conversion degree and the selectivity of the reaction, so the presence of an active species rather than another one can lead to different reaction products. Obviously the catalyst selection should be made according to the defined operating conditions and based on the selected fuels. Since the ATR process may be considered as the synthesis of SR and POX [22], the catalyst must ensure simultaneously a high selectivity towards these two reactions, inhibiting other unwanted, such as hydrocarbon cracking. Several studies have demonstrated that nickel [23–25] as well as noble metals (Pt, Rh, Ru) [26–28] supported on Al_2O_3, CeO_2 or ZrO_2 show good activity toward reforming reactions [29–33]; improvements in stability and selectivity are achieved from bimetallic catalytic systems [34]. Great attention must be also devoted to the catalyst structure (e.g. powder, pellets, honeycomb, foams, etc.) [35]. Previous studies have demonstrated that high thermal conductivity supports allow a flat thermal profile along catalytic bed [36], and thus a higher average temperature at the outlet section of the catalytic bed, that leads to higher hydrocarbon conversion [37]. On the one hand, highly conductive supports assure a more uniform radial temperature, allowing to correctly exploit the whole catalyst section; on the other hand, the high thermal conductivity results in a reduction of hot-spot phenomena and in a mitigation of temperature peak typical in the first zone of the catalytic volume in ATR processes. Therefore the reduction in peak temperature is obtained by distributing heat on the whole catalyst, resulting in a sensible temperature increase