Structured catalysts for intensificated integration of kW-scale AutoThermal Reforming and WGS reactors

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Introduction

The increasing interest of the last years towards the research of an effective option for clean energy supply in distributed applications pushed the worldwide attention to the development of H_2 based fuel processors. The key requirements of a fuel processor to reach good performances are the efficiency and low cost, rapid start-up, small size and weight and very high thermal integration [1]. Several studies are reported in literature dealing with their development [2] and though steam reforming is the widely industrially recognized process to produce synthesis gas, the self sustainment characteristic of the autothermal reforming reaction (ATR) seems to well accommodate the fuel processor requirements. However, in order to achieve a high fuel processor efficiency, it must also be given attention to catalyst formulation and structure (honeycomb monolith and open cell foams), as very high active catalysts should lead to high throughputs with very small reactor volume [3,4].

This work reports the integration of a kW-scale (up to 5 m^3 (stp)/h of H_2) CH_4-ATR reactor with a catalytic water gas shift (WGS) reactor for the CO abatement without any external assistance both in terms of heat source and extra steam addition, discussing the results also in terms of economic evaluation relevant to production costs.

Materials and Methods

Both ATR and WGS reactors are built in stainless steel (Figure 1a) with the WGS stage connected in series to the ATR reactor (Figure 1b) and with internal diameters respectively of 36 and 44 mm.

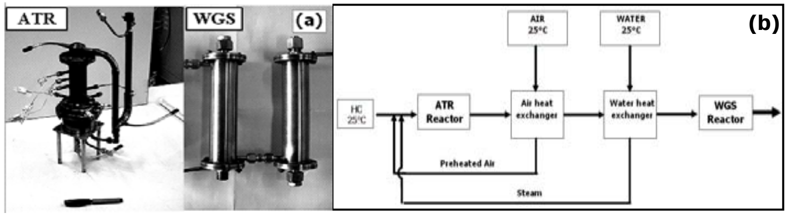

Figure 1. ATR and WGS reactors (a) and thermal integration scheme (b).

The WGS stage is realized by assembling two reactors in parallel in order to realize higher GHSV values in the shift stage with respect to those of the ATR stage. In the ATR stage, CH_4 and air are mixed and burned only during the start-up phase; after that H_2O is added and the operating condition are changed to the ATR ones. The mixture flows through the catalytic bed where three thermocouples are placed at 25, 50 and 75% of the bed height. The fed air and liquid water are preheated by the hot exhaust entering in the WGS reactors where two thermocouples are positioned at inlet and outlet bed. In order to achieve a better performance with higher amount of water to be fed at ATR stage inlet, a further thermal integration was realized, by partially recovering also the heat released by the slightly exothermic WGS reaction. A sampling valve allows to analyse the product distribution inlet and outlet the WGS stage, alternatively. A modified version of ATR reactor has been also designed for liquid fuel. For both ATR and WGS stages, specific noble metals based ceramic honeycomb monolith catalysts, were provided by Engelhard Co.

Results and Discussion

Typical results of catalytic activity tests are reported in Table 1.

Table 1. Catalytic activity tests results

Run	O_2/C	H_2O/C	GHSV, h^{-1}	T_H, °C	H_2O/CO	GHSV, h^{-1}	H_2, vol%	CO, vol%	CO_2, vol%	CH_4, vol%	T_{IN}, °C	T_{OUT}, °C	CO_{eq}, vol%
ATR					SHIFT								
1	0.64	1.2	45,600	825	2.0	6,700	45.0	2.1	14.2	1.0	291	369	2.6
2	0.60	1.2	68,000	803	1.9	10,000	46.5	2.8	14.2	1.0	292	375	3.0

The coupling of autothermal reforming and water gas shift reactions is quite difficult and requires an effective thermal integration and recovery, since the ATR requires elevated temperatures for high CH_4 conversion, while the WGS reaction is exothermic and thus low temperatures are necessary to achieve high CO conversion. Moreover, in contrast to the reforming reactions, temperature causes an antagonistic effect on the rate and equilibrium of CO conversion in the WGS reaction due to the exothermic character of the reaction. With regards to the operating conditions, the WGS reaction requires a H_2O/CO ratio as high as possible. This implies high H_2O/C molar feed ratios also in the ATR stage which results in a lower outlet temperature and in a higher duty for water vaporization, which in turns leads to a lower temperature at the inlet of the WGS stage. On the other hand, a suitable O_2/C ratio is necessary (at least equal to 0.6); it has to be high enough to guarantee a high temperature at the ATR reactor outlet, but not so high to result in reduced efficiency. Moreover, the assembly of two WGS reactor allows to operate at high GHSV values in the ATR stage, thus enhancing the H2 throughputs. The use of very active catalysts in both stages allows to reach equilibrium CO concentration with an overall system efficiency of about 72%.

Significance

The integration of a self sustained methane ATR reactor with a WGS reactor for CO abatement has been realized. The very high compactness as well as the good efficiency makes this system a good candidate for small scale applications such as distributed power generation. An economic comparison between steam and autothermal reforming has been performed.

References

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