Experimental and economical approach to the integration of a kW-scale CH$_4$-ATR reactor with a WGS stage

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Over the last years, fuel processors for H$_2$ production appears an attractive option for decentralized power supply. In this work we discuss on the integration of a self sustained CH$_4$-ATR reactor with a WGS stage both operating in the absence of any external energy source and extra steam addition. Several parameters such as ATR reactor operating conditions, WGS reactors assembly, thermal integration were investigated discussing the results in terms of system efficiency and economical aspects

1. Introduction

In the last years big research efforts have been carried out in the field of development of integrated fuel processors for hydrogen generation (Qi et al., 2007). A fuel processor is composed by the reformer reactor itself and devices dedicated to remove the carbon monoxide, which is frequently performed by catalytic reactions such as water gas shift and preferential oxidation. Actually, natural gas is still considered to be among the most attractive fuels for hydrogen production due to its relatively large existing reserves, potential for attaining high conversion efficiencies and suitability for distributed power system due to the existing transportation infrastructure throughout the world. Several examples in literature report the performance of fuel processors fuelled with diesel (Sopeña et al., 2007), natural gas (Seo et al., 2006, Lee et al., 2007, Britz and Zartenar, 2004), LPG (Cipitì et al., 2006), methanol (Liu et al., 2008) and iso-octane (Moon et al., 2008). The key requirements of fuel processors to be considered, in particular when they are employed in decentralized power supply, include rapid start-up, fast response to load changes, high fuel conversion efficiency, compactness, thermal integration and safety, simple design with low cost, stable performance for repeated start-up and shut-down (Ahmed and Krumpelt, 2001). To this purpose high attention must be devoted to process intensification technologies both relevant to the choice of the proper reforming technology and to the use of engineered catalysts which can help to optimize the operating conditions and consequently improve overall efficiency and reduce the requirement for materials and capital investment. Among the reforming technologies, the autothermal reforming (ATR) process attracts much attention primarily due to the low energy requirement, since an ATR based fuel processor can be heated up internally

relatively quickly by exothermic reaction of fuels, and also due to the fact that the reactor can be operated at high space velocity, thus being more dynamic than steam reforming systems and more practical for small or medium size fuel processors. With regards to catalyst formulation and structure, the autothermal reforming one must be carefully formulated to resist to high temperatures, to coke deposition and sulphur poisoning in particular when liquid hydrocarbons are employed and it must be highly active to well perform at high space velocity. Precious metals based catalysts structured in form of honeycomb monolith and open cells foam may represent an innovative and viable option (Giroux et al., 2005, Farrauto et al., 2003, Palo, 2007, Ciambelli et al., 2007). On the other hand, conventional low-temperature ($Cu/ZnO/Al_2O_3$) and high-temperature (Fe_3O_4/Cr_2O_3) catalysts are industrially employed in the water gas shift (WGS) stage. However, the high sensitivity to oxygen or pyrophoricity of Cu-based catalysts as well as the need for a long-term activation step, make them inappropriate for application characterized by repeated start-up and shut-down. Thus many researchers pointed out on the use of noble metals such as Pt (Panagiotopoulou, 2007, Jacobs, 2004).

This work reports the integration of a self sustained kW scale CH_4-ATR reactor with a catalytic WGS reactor for the CO conversion without any external assistance both in terms of heat source and extra steam addition. Both reactors operated with structured precious metals based catalysts. The influence of ATR reactor operating conditions (H_2O/C, O_2/C feed ratios and GHSV, the last one for both ATR and WGS reactors), WGS reactors assembly and thermal integration was investigated. Moreover, some engineering and economical aspects are reported.

2. Experimental

Both ATR and WGS reactors are built in stainless steel (Figure 1) with an inside diameter respectively of 36 mm and 44 mm.
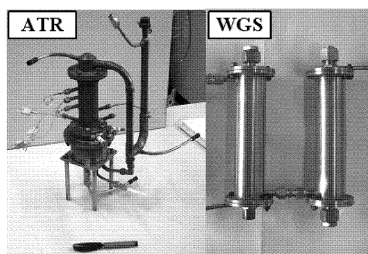

Figure 1 ATR and WGS reactors

The thermally self sustained ATR reactor, able to produce up to 5 m^3(STP)/h of H_2 consists of two main parts, a lower section where, only during the start-up phase, does methane react with air at a fixed O_2/CH_4 ratio (1.36) and an upper section where reforming reactions occur in the presence of the catalyst. Due to the specific O_2/CH_4 ratio employed in the start-up phase, the hydrocarbon oxidation occurring in the lower section produces heat which is transferred to the reforming section heating the catalytic bed up to the ATR catalyst threshold temperature. Methane and air are fed at the bottom of the reactor and premixed in a mixing chamber at the top of which a SiC foam is placed in order to obtain a well distributed and homogeneous flame. The catalyst bed (64 cm^3) is located in the upper (reforming) section, supported by a metallic gauze at the bottom of which water is fed to the reactor. CH_4 and air are mixed and burned only during the start-up phase; after that H_2O is added and the operating conditions are changed to the ATR ones and all the reactions occur simultaneously in the catalytic bed. The gas mixture flows through the catalytic bed

where three thermocouples (TL, TM, TH) are placed at 25, 50 and 75% of the bed height. The reactor is integrated with two heat exchangers to preheat the air and the water by the hot exhaust stream. The ATR reactor previously assembled and optimized (Palo, 2007) is characterized by very short start-up time (less than 3 minutes) and has been successfully operated with precious metals based monolith and foams (Ciambelli et al., 2007). The WGS reactors are connected in series to the ATR reactor according to the scheme shown in Figure 2a. Moreover, 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 (Figure 2b). All the integrated system is thermally insulated to avoid heat losses.
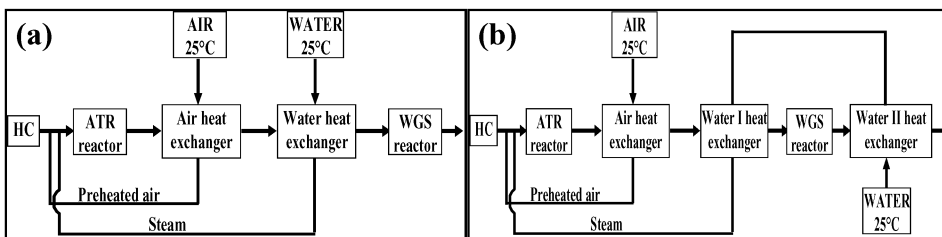

Figure 2 Thermal integration scheme before (a) and after improvement (b)

Owing to slow kinetics of WGS reaction with respect to the ATR, in some activity tests two WGS reactors assembled in parallel were employed in order to increase the contact time in the WGS stage leaving unchanged the value in the ATR one. Moreover, it must be observed that each shift reactor has been loaded with around three times higher catalyst volume with respect to the ATR reactor. In the WGS reactor two thermocouples (TIN and TOUT) measured the temperature at inlet and outlet bed. NDIR analyzers (ABB) were employed for real-time CH_4, CO, CO_2, O_2 and H_2 measurements on dry basis. A sampling valve allowed to analyse the product distribution inlet and outlet the WGS stage, alternatively. For both ATR and WGS stages, specific ceramic honeycomb monolith catalysts, provided by BASF (ex-Engelhard), were employed. The energy efficiency of the integrated system was calculated using the following equation:

$$Efficiency(\eta, LHV) = \frac{n_{H2}}{n_{CH4}} x \frac{\Delta H_{H2}}{\Delta H_{CH4}} \tag{1}$$

where n_{H2} is the H_2 throughput (mol h^{-1}), n_{CH4} is the CH_4 feed rate (mol h^{-1}) to the ATR reactor, ΔH_{H2} and ΔH_{CH4} are respectively the lower heating value (LHV) of H_2 and CH_4.

3. Results and discussion

The inlet and outlet temperatures measured as function of time in the WGS catalytic bed are reported in Figure 3. The first step is relevant to the WGS catalyst heating and any catalytic activity was observed. At the catalyst threshold temperature (around 300°C) an inversion in the temperature profile was observed with the WGS reactor outlet temperature higher than the inlet one, owing to the exothermicity of shift reaction. The experimental results obtained with a single WGS reactor are reported in Table 1.
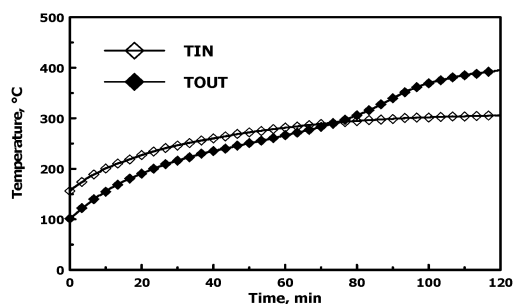
Figure 3 WGS inlet and outlet temperatures as function of time

These results show that the CO conversion in the WGS stage is very affected by thermodynamic (TOUT) and kinetic parameters (TIN, catalyst threshold temperature and GHSV). In fact, while the high endothermicity of reforming reaction requires elevated temperatures for high CH_4 conversion, the exothermicity of shift reaction requires very low temperatures to achieve high CO conversion.

Table 1 WGS gas composition at different ATR operating conditions with a single WGS reactor

	ATR				SHIFT								
Run	O_2/C	H_2O/C	GHSV, h^{-1}	TH, °C	H_2O/CO	GHSV, h^{-1}	H_2, vol%	CO, vol%	CO_2, vol%	CH_4, vol%	TIN, °C	TOUT, °C	COeq, vol%
1	0.64	0.8	45,600	834	1.3	13,400	41.4	8.6	8.9	1.0	302	343	3.5
2	0.63	1.0	68,000	788	1.4	20,000	44.5	8.0	9.6	0.0	292	337	3.1
3	0.64	1.0	68,000	926	1.5	20,000	44.0	5.1	11.9	0.9	315	379	3.5
4	0.64	0.9	68,000	939	1.4	20,000	44.0	4.5	12.5	1.0	333	410	4.6
5	0.64	1.0	90,000	998	1.5	26,500	43.4	5.9	11.7	1.0	331	397	3.9

Moreover, the temperature causes an opposite effect on the rate and equilibrium CO conversion in the WGS reaction due to the exothermic character of the reaction (Lee et al., 2007), since a higher operating temperature could avoid the kinetic limitations of WGS reaction but in turn could affect the thermodynamic CO conversion. On the other hand, the WGS reaction requires high H_2O/CO ratios. However, this condition implies high H_2O/C molar feed ratios in the ATR stage, resulting in a lower outlet temperature, higher duty for water vaporization and a lower temperature WGS stage inlet. A suitable O_2/C ratio is also necessary; it has to be high enough to guarantee a high temperature at the ATR reactor outlet, but not so high to cause a decrease in system efficiency (Roychoudhury et al., 2006). The operating conditions employed in all the runs can assure the threshold temperature for WGS catalyst, however the WGS inlet temperature reached in the runs 1 and 2 was not so high to avoid kinetic limitation. In fact, in these runs, the experimental CO concentration was quite far from the thermodynamic one. In the runs 3 and 4 the higher GHSV in the ATR stage allows a little increase in the shift reactor inlet temperature, corresponding to a better approach to the equilibrium composition, particularly for run 4. Unfortunately, a further GHSV increase (run 5) may become again a kinetic limitation. The obtained results show that the optimal value of GHSV in the ATR stage is around 68,000 h^{-1} which corresponds to about 20,000 h^{-1} in

the CO WGS stage. The system efficiency evaluated in the operating conditions of run 1 was about 61%. A sensible improvement of the integrated reactors performances in the runs 1 and 2 was achieved by lowering the GHSV value in the shift reactor with two WGS bed assembled in parallel (Table 2). In fact, a decrease in CO concentration was observed in both experimental tests from about 9 to 4 vol% and 8 to 4 vol%, respectively at ATR GHSV values of 45,600 and 68,000 h^{-1}. It must be observed that in both cases, the CO concentration reached at the outlet of the WGS reactor approaches the thermodynamic one. Moreover, the increase of contact time allowed to operate with a lower WGS inlet temperature, which was respectively 292 and 285°C. An increase in the system efficiency in the run 1 was also observed. The evaluated efficiency was 68%.

Table 2 Shift experimental composition with single or two WGS reactors

Run	CH_4, vol%	CO, vol%	CO_2, vol%	H_2, vol%	CH_4, vol%	CO, vol%	CO_2, vol%	H_2, vol%
	Single WGS reactor				Two WGS reactors			
1	1.0	8.6	8.9	41.4	1.0	3.9	13.5	43.8
2	0.0	8.0	9.6	44.5	0.9	3.9	13.8	45.1

Finally, in order to realize an improvement of the system efficiency, the higher thermal integration allowed a higher amount of water to be added to ATR reactor, thus enhancing the H_2O/CO feed ratio in the shift stage. The results are reported in Table 3.

Table 3 Influence of H_2O/CO feed ratio on system performance in the case of two WGS reactors

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 increase of H_2O/CO feed ratio in the shift stage causes a remarkable efficiency improvement. In fact, the comparison with the previously reported catalytic activity test, carried out at H_2O/C (ATR stage) of 0.8, shows that the heat recovery enhancement allows to reach the same WGS inlet temperature, though an higher amount of water is fed leading to an higher H_2 production in the operating conditions of run 1 and resulting in an overall efficiency of 72%.

4. Engineering and economical aspects

The compactness and the simplicity of the proposed design integration have an impact at different levels: a minimization of the heat loss, which increases the overall thermal efficiency of the system, a better plant stability adverse environmental conditions are going to have a minimum impact on the operation and a reduction of the capital investment. It is important to stress that the plant investment represents the main parameter determining the H_2 production cost for relative small units (Ciambelli et al., 2007), then any technical solution which reduces the requirements for plant materials and controls is making such technology more attractive. Inserting the process air preheater and the steam generator between the two catalytic beds, in a sort of sandwich,

and the BFW preheating just downstream the WGS reactor, should allow to install both reactors and the three exchangers in one common container with a sensible weight reduction of the interconnecting piping and of the shell. A preliminary analysis is showing that a savings of 30% of the material costs can easily be achieved which translate into a reduction of the production costs of 10-15%, depending of the plant capacity.

5. Conclusions

The integration of a self sustained CH_4-ATR reactor with a WGS reactor for CO abatement has been realized. The catalytic activity tests showed that good performance of the WGS stage may be obtained even operating at high GHSV in the ATR reactor. Higher H_2O/C ratio in the ATR stage and improved thermal integration of the reactors to recovery the higher energy required to vaporization and superheating of the liquid water allow to enhance the system efficiency with reduction of the production costs.

Acknowledgements

References

Ahmed, S. and M. Krumpelt, 2001, Int. J. Hydrogen Energy 26, 291.

Britz, P. and N. Zartenar, 2004, Fuel Cells 4, 269.

Ciambelli, P., V. Palma, E. Palo and G. Iaquaniello, 2007, AIDIC Conference Series 8, 67.

Cipitì, F., V. Recupero, L. Pino, A. Vita and M. Laganà, 2006, J. Power Sources 157, 914.

Farrauto, R., S. Hwang, L. Shore, W. Ruettinger, J. Lampert, T. Giroux, Y. Liu, and O. Ilinich, 2003, Annu. Rev. Mater. Res. 33, 1.

Giroux, T, S. Hwang, Y. Liu, W. Ruettinger and L. Shore, 2005, Appl. Catal. B 55, 185.

Jacobs, G., A. Crawford, L. Williams, P.M. Patterson and B.H. Davis, 2004, Appl. Catal. A 267, 27.

Lee, D., H.C. Lee, K.H. Lee and S. Kim, 2007, J. Power Sources 165, 337.

Liu, N., Z. Yuan, C. Wang, L. Pan, S. Wang, S. Li, D. Li and S. Wang, 2008, Chem. Eng. J. 139, 56.

Moon, D.J., J.W. Ryu, K.S. Yoo, D.J. Sung and S.D. Lee, 2008, Catal. Today 136, 222.

Palo, E., 2007, PhD Thesis, University of Salerno.

Panagiotopoulou, P., J. Papavasiliou, G. Avgouropoulos, T. Ioannides and D.I. Kondarides, 2007, Chem. Eng. J. 134, 16.

Qi, A., B. Peppley and K. Karan, 2007, Fuel Process. Technol. 88, 3.

Roychoudhury, S., M. Lyubovsky, D. Walsh, D. Chu and E. Kallio, 2006, J. Power Sources 160, 510.

Seo, Y.T., D.J. Seo, J.H. Jeong and W.L. Yoon, 2006, J. Power Sources 160, 505.

Sopeña, D., A. Melgar, Y. Briceño, R.M. Navarro, M.C. Álvarez-Galván and F. Rosa, 2007, Int. J. Hydrogen Energy 32, 1429.