Journal of Power Sources 193 (2009) 338–341

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

New concept for soot removal from a syngas mixture

A. Raimondi, D. Fino*, G. Saracco

Department of Materials Science and Chemical Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

ARTICLE INFO

Article history:
Received 10 October 2008
Received in revised form 30 December 2008
Accepted 1 January 2009
Available online 24 January 2009

Keywords:
Syngas
Soot removal
TPOX reformer
Trap

ABSTRACT

A new concept for soot removal from inside a syngas environment has been studied. Particulate emissions are retained in a soot trap downstream from a thermal partial oxidation (TPOX) reformer, while the syngas atmosphere itself is utilized as a gasification agent to achieve continuous and passive trap regeneration. This work analyses the performances of the loading and the regenerating phases of a wall flow soot trap in a syngas environment in an ad hoc developed test rig. A balance point between filtered and removed soot was actually reached at trap temperatures in the 800–1000 °C range with soot abatement efficiencies above 95 wt%. The particulate is obtained from a TPOX reactor operating in very rich fuel conditions, using methane as fuel. The final application of the reactor and trap assembly is a micro CHP system, based on an SOFC fed by a TPOX reformer. However, application to larger contexts (e.g. biomass gasification plants) can be envisaged.

1. Introduction

Innovative technologies based on hydrogen as the carrier to produce energy, like solid-oxide fuel cells (SOFCs), seem particularly interesting for future civil and industrial applications, in a scenario of improved efficiency and reduced emissions. Fuel cells produce direct electricity while combined heat and power (CHP) applications can increase the global efficiency by a significant percentage, and be very promising for domestic applications [1]. An interesting opportunity regarding SOFCs is related to the opportunity by combining this technology with gas turbines to build new highly efficient power plants [2]. In comparison with the other fuel cells at the present on the market, SOFCs offer the great advantage of being a very robust system that is able to work over a wide range of syngas and at relatively high temperatures (600–1000 °C) [3,4].

The syngas necessary to feed the SOFC can be produced from biomasses or using fossil fuel reforming processes, such as thermal partial oxidation (TPOX), steam reforming (SR) or autothermal reforming (ATR). The TPOX reforming is a very interesting technology because of the relatively robust and compact setup and the related low costs. For TPOX reactors, there is neither the need for an external heat source (due to the exothermic behaviour of the process) nor for catalysts to obtain the reaction products [5]. Unfortunately, the hydrogen percentage obtainable with this technology is considerably lower than that obtainable by SR or ATR [3–5].

The hydrogen yield can be maximised with a TPOX reformer working at very low air-to-fuel ratios. In spite of this condition, the system leads to the production of very high quantities of soot, thus increasing the risk of carbon deposition over the fuel cell anode and consequent deactivation [6]. A trap located immediately downstream from the TPOX reformer, is surely a simple solution to obtain a soot free environment at the anode and preserve the SOFC efficiency for a long time as well as to guarantee the particulate emissions requested by the legislations in force [7,8].

Nevertheless, soot removal can become seriously problematic in these plants due to the absence of oxygen in the syngas. Traditional processes for soot trap regeneration such as the technologies adopted for diesel engines [8,10,11], cannot be used in passive regeneration system since they are based on combustion.

The syngas produced by POX reforming is mainly constituted by H_2, CO, H_2O, CO_2 and a non-negligible percentage of C_2H_2 (considered a major soot precursor) [6]. The possibility of gasifing the soot in this specific environment can be reached by operating continuously at high temperatures inside the trap, according to the most important gasification reactions for the carbon reported in the literature [12–14]. In particular, the presence of water and CO_2 in the syngas shows an interesting activity to gasify carbon at temperatures above 800 °C [12,14] according to the following reactions:

$$C + CO_2 \rightarrow 2CO \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 \quad (2)$$

In particular, reaction (1), which is also called the reverse Boudouard reaction [15], presents interesting carbon gasification properties at the common operating temperatures of the actual systems based on SOFC technology, even in the absence of catalysts [14,16].

* Corresponding author. Tel.: +39 011 5644710/4699; fax: +39 011 5644710/4699.
E-mail address: debora.fino@polito.it (D. Fino).

0378-7753/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2009.01.036

The present work has investigated, with an experimental plant, the feasibility of the removal of particulate trapped in a soot trap directly using the syngas produced by a TPOX reaction at a sufficiently high temperature. The experimental analysis reported in this work did not consider the adoption of catalysts to improve the gasification process, but focused on the chance of finding a possible new idea for soot removal in syngas mixtures.

2. Experimental

2.1. System set-up

The experimental investigation has been performed using an alumina insulated reactor with a soot trap fitted on its top. This reactor, where the reforming reaction takes place, is used as a soot generator to bring the system to rich fuel operating conditions. An iron grid has been used at the entrance of the reactor as a flame arrester, in order to avoid the flash back of the flame outside the reformer. The two different components were welded to avoid undesired air leakages at the entrance of the soot trap. An electrical pre-heater sends the air at a constant temperature of 600 °C to a premixing zone, where methane is added just before entering the reactor. Bronkhorst mass flow meters are used to send the air and methane to the premixing zone, while Swagelok steel pipes and fittings are provided to guarantee safe connections because of the high temperatures. An off-gas burner was placed after the trap to burn out most of CO for safety reason. A simplified scheme of the experimental set-up is presented in Fig. 1.

Two electric spark plugs, immediately outside the reforming reactor, ignite the mixture, while the flame front gets stabilized inside the reactor. The exact position of the flame should be defined as function of the different lambda, defined as the mass of the current air-to-fuel ratio over the stoichiometric air-to-fuel ratio. In particular, the flame front finds a stable position at lower lambda in the upper zone up to the risk of blow-off, whereas for higher lambda the risk is correlated to the possibility to have flash backs outside the entrance of the reactor.

Thermocouples are provided to measure the main temperatures of the system. One thermocouple controls the preheating air, while another has been placed immediately downstream the reactor; other two thermocouples measure the temperatures at the inlet and outlet of the soot trap.

The syngas composition is sucked by the gas analyzer pump before the soot trap in order to analyse the gas concentration produced by the reactor. During the regeneration process the syngas composition is alternatively measured upstream and downstream the soot trap, using a valve, for the purpose of finding some evidence of what happens in the expected chemical reactions, e.g. during regeneration. The ABB analyser is composed of the following modules: Caldos17 (thermal conductivity analyzer module) for H_2, Uras14 (infrared analyzer module) for CO, CO_2, CH_4 and Magnos106 (paramagnetic oxygen analyzer module) for O_2. The percentages of CO, CO_2, CH_4 and H_2 are measured in order to define the syngas mixture, while the oxygen is just measured with the purpose to ensure its absence to indicate the correct progress of partial oxidation. The concentration of water is not directly measured, can be calculated from the mass balance.

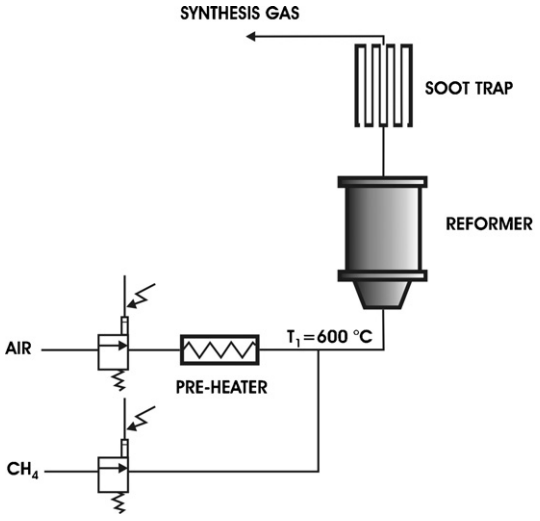

Fig. 1. Schematic diagram of the experimental set-up.

A soot trap was mounted immediately next to the outlet of the reformer. It is particularly important to have the soot trap close to the reformer to reach the highest possible temperatures in order to ensure the trap undergoes carbon gasification and self regeneration in the specific syngas environment [11–15]. The trap was made by the Stobbe Tech Ceramics A/S of SiC, to resist to the high operating temperatures [9,17,18] and is characterized by a diameter of 144 mm, a length of 108 mm and 150 cells per square inch (CPSI). The maximum pressure drop allowed within the wall flow trap, as recommended by Stobbe Tech Ceramics A/S, was set at 10 mbar. As a consequence of this specification a very sensitive differential pressure transducer was required to continuously monitor the pressure drop between the inlet and the outlet of the trap. The chosen instrument was a Bourdon Haenni differential pressure transmitter, operating in a range between ±60 mbar, connected by two flexible pipes to the entrance and the exit of the filter. The pressure drop measured is an indirect index of the soot loading, all other conditions being equal (flow rate, temperature, etc.). When the soot is loading the soot trap, a rise of the pressure drop is monitored, while during the regeneration process the decreasing of the pressure drop is expected because of the carbon gasification.

Particular attention has been paid to the insulation in all the system, to reduce as much as possible the heat losses and to reach the highest temperatures needed to regenerate the soot trap.

2.2. Testing procedure

Before starting, pre-heated air is sent at 600 °C for approximately 30 min, to bring the reactor to a homogeneous temperature condition that is ideal to obtain a fast ignition of the feed mixture. The initial lambda to start the reactor operation is approximately in the range of 0.65–0.70. When the process starts the lambda is progressively decreased to the lower operative values.

The lambdas studied during this experiments were in a range of 0.45 to 0.52. Lower lambda produces a considerable quantity of soot, but it takes a significant time to obtain the temperature conditions where carbon gasification can occur. A higher lambda produces less soot but on the other hand is significantly faster in reaching the expected temperatures. For lambda lower than 0.45 the combustion could be unstable and difficult to manage because of the more distant condition from the stoichiometric one whereas lambda above 0.52 produces a rather negligible quantity of soot. As mentioned above, the lower the lambda the higher the yield of hydrogen produced.

Lambda 0.45 has been used at the beginning of the test to load the soot trap. When the system reaches sufficiently high temperatures, close to the theoretical range to start the gasification, the lambda has been increased to 0.52 in order to raise the temperatures and decrease the quantity of soot produced, until the regeneration reaches. The lambda is then progressively decreased to 0.50 till 0.47 to analyze the trend of the pressure drop in higher soot production conditions. During all the experiment a constant total flow (CH_4 and air) is maintained at the value of 60 Nl min^{-1} in order to minimize

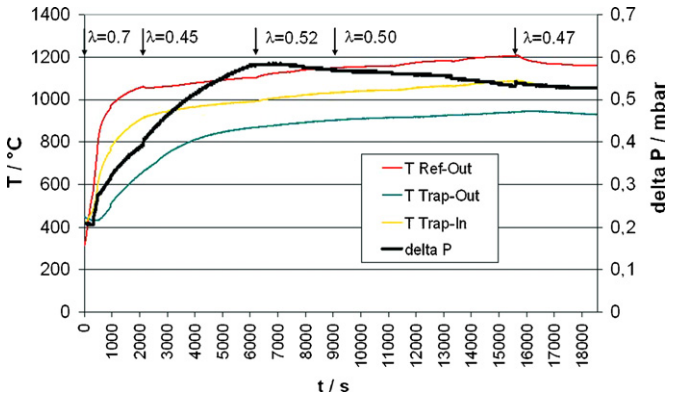

Fig. 2. Evolution of the pressure drop across the soot trap and of the temperatures at the reformer outlet, the trap inlet and the trap outlet as a function of time during loading and regeneration phases (air pre-heated at 600 °C).

Table 1
Gas components concentrations measured at the inlet of the filter.

Species concentration (%)	Lambda			
	0.52	0.50	0.47	0.45
H_2	14.06	15.45	18.87	20.63
CO	10.01	10.44	11.02	11.66
CO_2	4.83	4.56	4.12	3.59
CH_4	0.18	0.27	0.43	0.98

the effect of this parameter on the pressure drop. Other operating conditions being equal, the pressure drop is an indirect sign of the soot present in the trap. A determination of the exact amount of soot present in the trap would require reactor periodic dismantling which is a costly and rather difficult operation since the reactor set-up is suited to withstand temperatures as high as 1000 °C.

A run was also performed with subsequent loading and regeneration cycles carried out at 0.45 and 0.52 lambda values, respectively, with step changes between these two values, in order to prove the effectiveness of the devised regeneration route.

3. Results and discussion

Fig. 2 shows the temperature at the outlet of the reformer (red curve) from the ignition of the reaction, as well as the constant preheating air value of 600 °C. A fast initial rise due to the beginning of the reaction is presented in the first phase until temperatures up to 1000 °C are quickly reached, also owing to the high insulation, then a steady increase trend starts. The small fall of the outlet reformer temperature at the end of the graph is due to the less quantity of energy supplied from the process for lower lambda during the regeneration phase, induced by moving away from the stoichiometric condition.

Syngas has been analyzed when the reaction arrived to stable condition of reforming. Tables 1 and 2 list the gas composition analysed before and after the soot trap at different operating lambda values.

Table 2
Gas components concentrations measured at the outlet of the filter during regeneration.

Species concentration (%)	Lambda		
	0.52	0.50	0.47
H_2	14.34	15.89	19.53
CO	10.09	10.59	11.36
CO_2	4.76	4.46	4.00
CH_4	0.16	0.26	0.39

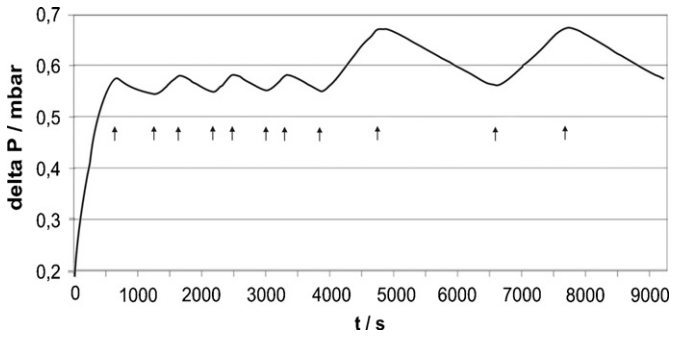

Fig. 3. Pressure drop variation resulting from repeated loading (λ = 0.45) and regeneration (λ = 0.52) cycles with two different cycle frequencies (air pre-heated at 600 °C). The arrows indicate the times at which step changes between the two λ values were accomplished.

As expected a general increase of H_2 and CO production is shown from lambda 0.52 to 0.45. The increase of H_2 yield is particularly evident presenting an increase of ca. 6% over the operating range of lambda studied. On the other hand, a constant reduction of the CO_2 concentration is monitored while lowering the lambda values. The CH_4 concentration is also increasing as long as the operating conditions of the system get farer and farer from the stoichiometric ones.

The data in Table 2 do confirm the actual progress of the devised regeneration mechanism, showing indeed a relative increase for H_2 and CO as well as a decrease of the CO_2 concentration, as referred to the values before the filter. These effect are more evident for the lower lambda, where harsher conditions in terms of soot production are present. It may be guessed that either CO_2 or eventually the water present boosts soot gasification.

Fig. 2 shows also the pressure drop trend during the experiments in comparison to the temperatures monitored at the inlet and the outlet of the trap. An initial steady increase of the pressure drop is evident. It is caused by the temperature rise and because of the soot produced at very rich fuel condition, to aim the fast trap loading of the filter. The ignition of the mixture was obtainable for lambda 0.65/0.70 and progressively decreased till 0.45, where a considerable amount of soot was produced by the reactor. When relatively long time was passed and a corresponding amount of soot was filtered, the lambda was increased to 0.52 to reduce the quantity of particles produced and increase the system temperature for the sake of starting the regeneration process. Analyzing the temperatures in the soot trap the end of the loading phase can be detected and the relative beginning of the regeneration approximately when 1000 °C at the inlet and 850 °C at the outlet of the trap are reached. It appears also important to have a high temperature all over the trap, which is in part favoured by the high thermal conductivity of SiC. After the self-regeneration of the filter for lambda 0.52 was performed for several minutes, the lambda was progressively decreased to 0.5 and 0.47. The trend of the pressure drop between inlet and outlet of the soot trap was decreasing for a 0.5 lambda value and reached a sort of balance point for a 0.47 lambda value where it can be inferred that the amount of soot filtered equalise that of soot undergoing gasification.

Finally, Fig. 3 proves that the loading/regeneration cycles can be effectively repeated, which represents an additional proof of the effectiveness of the proposed trap regeneration method.

4. Conclusions

A soot regeneration strategy for the soot trap, inside a syngas environment has been studied in this work. The characteristic

of the pressure drop in the wall flow, related to the soot emissions, has been analyzed in the range of lambda between 0.45 and 0.52.

The regeneration of the soot trap by carbon gasification by reaction with the gases produced by the thermal partial oxidation, was remarkable when the trap temperatures higher than 900 °C were obtained inside the trap. This specific test, performed using a simple reactor operating with very low air-to-fuel ratios, showed the possibility to obtain a regeneration process of the filter directly with syngas at high temperatures. The increase of the lambda from 0.45 to 0.52 finally induced a reduction of the pressure drop, an indirect sign of the lowering of the soot remaining in the trap.

The idea to have a continuously carbon gasification using syngas as gasification agent, taking care to have high temperatures inside the trap, has been experimentally proved. The durability of the materials working continuously at these temperatures is now being assessed to set up proper bases to export this idea in a post-research field.

Acknowledgement

The authors would like to thank the European Commission for the financial support of this work within the 6th framework program, project FlameSOFC, contract no. 019875 (SES6).

References

[1] I. Staffel, R. Green, K. Kendall, J. Power Sources 181 (2008) 339–349.
[2] A. Musa, M. De Paepe, Int. J. Hydrogen Energy 33 (2008) 4665–4672.
[3] K. Kordesch, G. Simader, Fuel Cells and Their Applications, VCH, Weinheim, 2003, pp. 133–141.
[4] R. O'Hayre, S. Won-Cha, W. Colella, F.B. Prinz, Fuel Cell Fundamentals, Wiley, New York, 2006, pp. 244–246.
[5] H. Pedersen-Mjaanes, L. Chan, E. Mastorakos, Int. J. Hydrogen Energy 30 (2005) 579–592.
[6] G. Vourliotakis, G. Skevis, M.A. Founti, Z. Al-hamamre, D. Trimis, Int. J. Hydrogen Energy 33 (2008) 2816–2825.
[7] D. Fino, V. Specchia, Powder Technol. 180 (2008) 64–73.
[8] M. Scheffler, P. Colombo, Cellular Ceramics, Wiley-VCH, Weinheim, 2005, pp. 416–438.
[9] A.G. Kostandopoulos, E. Kladopoulou, The optimum cell density for wall-flow monolithic filters: effects of filter permeability soot cake structure and ash loading, SAE Technical Paper No. 2004-01-1133.
[10] N. Russo, S. Furfori, D. Fino, G. Saracco, V. Specchia, Appl. Catal. B: Environ. 83 (2008) 85–95.
[11] A. Renzullo, A. Tarabocchia, G. Villata, A. Raimondi, D. Mescia, N. Russo, D. Fino, G. Saracco, V. Specchia, Delafossite based catalysts for diesel soot removal for passenger cars and light duty vehicles, SAE Technical Paper No. 2007-24-0095.
[12] A. Tomita, Catal. Surv. Jpn. 5 (1) (2001).
[13] A. Golovin, V.R. Pesochin, High Temperature 39 (2001) 80–84.
[14] M. Haghighi, Z. Sun, J. Wu, J. Bromly, H.L. Wee, E. Ng, Y. Wang, D. Zhang, Proc. Combust. Inst. 31 (2007) 1890–1983.
[15] K. Nagase, T. Shimodaira, Y. Itoh, M. Zheng, Phys. Chem. Chem. Phys. 1 (1999) 5659–5664.
[16] T. Osaki, T. Mori, React. Kinet. Catal. Lett. 89 (2006) 333–339.
[17] J. Zimmermann, G.E. Hilmes, W.G. Fahrenholtz, Mater. Chem. Phys. 112 (2008) 140–145.
[18] L.N. Kang, D.S. Fox, N.P. Bansal, J. Eur. Ceram. Soc. 25 (2005) 1705–1715.