



Structured catalytic substrates with radial configurations for the intensification of the WGS stage in H₂ production

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ABSTRACT

Weight and size reduction of fuel processing reactors is one of the key issues in the development of catalytic H₂ production and purification systems for distributed power plants. The search for innovative solutions is focused on the development of both catalyst formulations and geometries which could help to achieve an effective process intensification. Precious metals based structured catalysts in form of monolith or foam prepared from ceramic or metallic substrates could be a viable option to overcome heat transfer limitations, which typically characterize these systems. They allow high efficiency of fuel conversion even at high GHSV, and better stability and durability, a critical issue for industrial WGS catalysts. In this work we report on the development of an integrated kW-scale system, CH₄ fuelled, for H₂ production arranged with an autothermal reforming (ATR) and a WGS stage. Both reactors operated with noble metals based structured catalysts. Since in an adiabatic WGS reactor the reaction rates are not optimized throughout the reactor we employ noble metals foam structured catalysts assembled in such a way to perform inside the reactor axial or radial gas flow geometry. The aim of the work is to verify the influence of flow geometry on the reformer performance.

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1. Introduction

Fuel cells gained over the years more and more interest as power generation systems. In particular, polymer electrolyte membrane (PEM) based fuel cells, combined with cogeneration systems, are of great interest for residential applications [1–3]. Essential requirements for this kind of systems or fuel processors, which provides for an on site and real time generation of electricity with high efficiency, are the compactness and rapid response to load changes, high thermal efficiency, extremely low CO concentration in the exhaust stream [4]. Some of these aspects are strictly correlated to the thermodynamic and kinetics of the catalytic reactions involved as well as on construction and integration of the reactor units. Many literature works focus attention on the development of fuel processors based on different feeds such as natural gas [5,3,6], LPG [7], methanol [8], iso-octane [9], diesel [10], however natural gas is still the preferred solution, owing to the extensive distribution pipelines throughout the world. In order to realize very efficient fuel processors, great attention must be devoted to both reforming technology and catalyst choice. With regards to the first aspect, it must be observed that the peculiar characteristics of autothermal reforming (ATR) reaction may provide for a low energy duty, since an ATR reactor can be heated

up to the catalyst threshold temperature through the exothermic reaction of a portion of fuel. Furthermore, the reaction can be performed at space velocities higher than that employed in the more traditional steam reforming process, thus being more suitable and practical for medium and small fuel processors. With regards to the catalyst choice, attention must be paid to both chemical formulation and structure, since structured catalysts in form of honeycomb monolith or open cell foams may better perform at high space velocities with low pressure drops with respect to packed bed reactors [11]. Moreover, the necessity to avoid coke deposition when the reaction environment is oxygen poor, which is typical of Ni based catalysts, led to the study of innovative catalysts more resistant to deactivation [12]. Studies carried out on precious metal-based structured catalysts showed that they could be an effective option [13–15]. On the other hand, the exhaust stream at the outlet of a reforming reactor has a too high CO level to be fed to a fuel cell. Thus, a preliminary purification step, generally performed by water gas shift reaction, is necessary. From an industrial point of view the reaction is usually carried out in two stages: the first at high temperature on Fe₃O₄/Cr₂O₃ catalysts, the second at low temperature on Cu/ZnO/Al₂O₃ catalysts. 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 [16,17]. Moreover, the exothermic character of the WGS reaction provides for an opposite

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effect of temperature on the rate and equilibrium CO conversion. In fact, for adiabatic operation the reaction rates are not optimized throughout the reactor, since at the reactor inlet the reaction rate is limited by the relative low temperature, whereas at reactor outlet the approach to thermodynamic equilibrium slows the net reaction rate. For such a reason, in order to strive for isothermal operation, thus enhancing the overall reaction rate and lowering the required catalyst mass, van Dijk and van den Brink proposed a radial WGS reactor for diesel reforming showing the successful operation of the radial solution [18]. The same concept previously applied to other reactions such as the autothermal reforming [19] and partial oxidation of methane [20] or methanol [21], showed that a radial flow catalyst configuration enables the changing gas velocity to accommodate the different kinetic rates and heat release characteristics of these reactions. This allows a flat temperature profile and approach to equilibrium composition to be achieved in a single catalyst bed. The essential feature, however, is the choice of ceramic foam for the structure of the bed. Reticulated ceramic foams have important properties for catalytic activity such as high thermal stability, low pressure drop and enhanced heat transfer, in particular when materials with high thermal conductivity are employed [19]. Owing to their open structure foams may be especially effective in reactions where the radiation absorbing properties of the catalytic bed may allow more uniform temperatures throughout the structure [22].

In this work we report on the influence of structured catalytic substrates with radial configurations for the intensification of the WGS stage integrated with a kW-scale CH_4 -ATR reactor. In particular, the aim of the work is to verify the effect of flow geometry (axial and radial) on a WGS reactor behaviour in terms of CO conversion, temperature increase and selectivity.

2. Experimental

Catalytic activity tests were carried out with a thermally integrated system including an autothermal reforming and a water gas shift reactor, both depicted in Fig. 1.

Both reactors are built in stainless steel with an inside diameter of 36 and 44 mm, respectively for ATR and WGS stage. The ATR reactor is able to produce up to $5 \text{ m}^3(\text{STP})/\text{h}$ of H_2 and can be schematized in a lower section where, during the start-up phase, methane reacts 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 is located in the upper 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

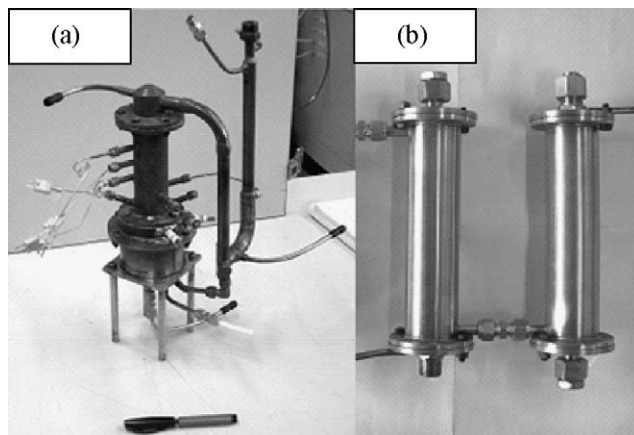


Fig. 1. Autothermal reforming (a) and water gas shift reactors (b).

only in the catalytic bed. The gas mixture flows through the catalytic bed where three thermocouples (T_L , T_M , T_H) are located 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 [23,24] is characterized by a very short start-up time (less than 3 min) and has been successfully operated with structured catalysts in form of honeycomb monoliths or open cell foams Ni [25] or noble metals based [15,19]. The WGS reactors are connected in series to the ATR reactor according to the integration scheme reported in Fig. 2.

It can be observed that the WGS reactors are placed at the outlet of the ATR reactor after the preheating of the reactants in such a way to reach a temperature suitable for this stage. Furthermore, one more heat exchanger for water heating is placed at the outlet of the WGS reactors in order to partially recover the heat released by the slightly exothermic WGS reaction. Previous studies carried out with noble metals based honeycomb monoliths for both the stages, showed that the optimization of thermal integration leads to improve the whole integrated system thermal efficiency by 72%, demonstrating also the feasibility of the integration without any external assistance both in terms of heat sources and extra steam addition [26]. It must be observed that owing to slow kinetics of WGS reaction with respect to the ATR, in some activity tests two WGS reactors assembled in parallel (Fig. 3b) were employed in order to increase the contact time in the WGS stage leaving unchanged the value in the ATR one.

Due to the very different kinetics performances of the ATR and WGS stages, to obtain the proper catalytic bed volume for the WGS reaction, shift reactors have been loaded with a two times higher catalyst volume with respect to the ATR reactor. NDIR analyzers (ADVANCE OPTIMA, 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 analyze alternatively the product distribution inlet and outlet the WGS stage. For both stages specific structured noble metals based catalysts provided by BASF (ex-Engelhard) were

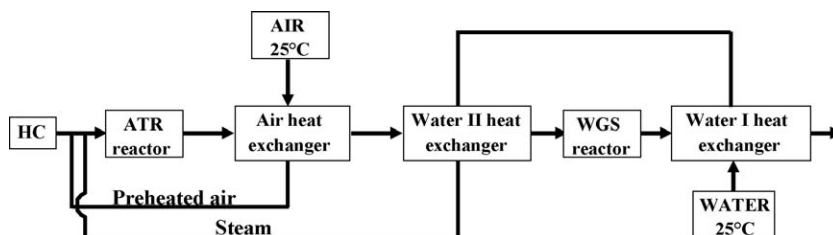


Fig. 2. ATR and WGS reactors integration scheme.

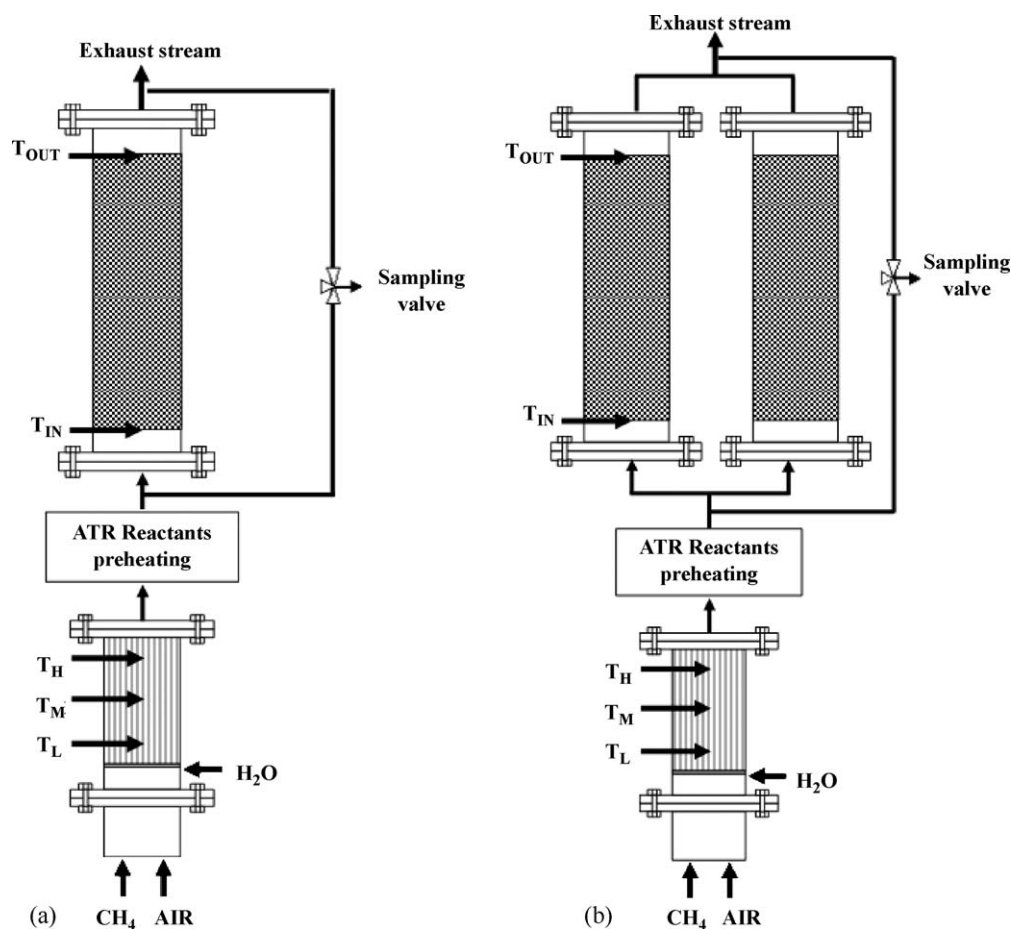


Fig. 3. Single WGS bed (a) or two WGS beds (b) assembly.

employed. In the ATR reactor, the catalyst was structured in the form of ceramic honeycomb monolith, whereas for WGS stage, a ceramic open cells foam SiC/Al₂O₃ based (Vesuvius Hi-Tech) was employed as catalyst carrier. A scanning electron microscopy image of the SiC based support is reported in Fig. 4 where it is possible to observe the peculiar network of the structure.

To provide axial or radial gas flow geometry, ten annular shaped catalyzed foam elements were assembled in each WGS reactor to realize the structured catalytic bed.

The different configurations with the relevant thermocouple positions for the temperature monitoring are reported in Fig. 5. It must be observed that the radial gas flow geometry can be

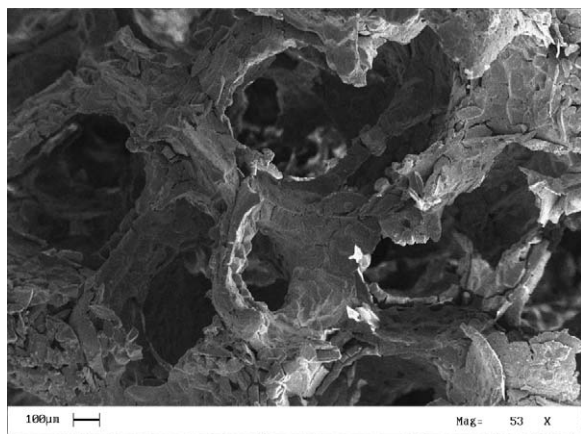


Fig. 4. SEM image of the SiC/Al₂O₃ based foam support.

classified depending on the reactor radial flow direction. In particular, in the centripetal-flow type the gas is fed to the distributing channel and travels radially from the outer screen to the center pipe. In the centrifugal-flow type the gas is fed to the center pipe and travels radially from the center pipe to the outer screen. From the literature it is well known that the operating efficiency of a radial flow reactor largely depends on the gas stream distribution over the catalyst bed height. In order to have an uniform flow distribution, the gas mass flow should be equally divided over the catalyst bed height, otherwise some parts of the bed will be under utilized [27,28]. Furthermore, a non-uniform flow distribution over the bed height affects the reaction conversion and selectivity and the temperature profile [27,29,30]. The optimum utilization of the catalyst mainly depends on the pressure distribution inside the reactor. An important design criterion for the radial flow reactor is to have the radial pressure independent of the axial coordinate [27,31]. In other words, the uniformity criterion means achieving a uniform flow distribution in a radial flow reactor by having the same pressure drop between the center pipe and the annular channel at any axial level. Under these considerations, in order to intensify the flow distribution, two porous sintered stainless steel tube were employed as gas distribution devices, respectively in the annular channel and the axial pipe.

For the axial assembly (Fig. 5a), the ATR exhaust stream flows through the catalytic WGS bed in an axial direction. To obtain this configuration the axial pipe is inhibited to the gas flow by filling it with quartz wool, whereas the catalyst monolith is placed into the reactor by using specific expanding insulating mat layer (3 M InteramTM), thus forcing the gas to flow into the annular cylindrical

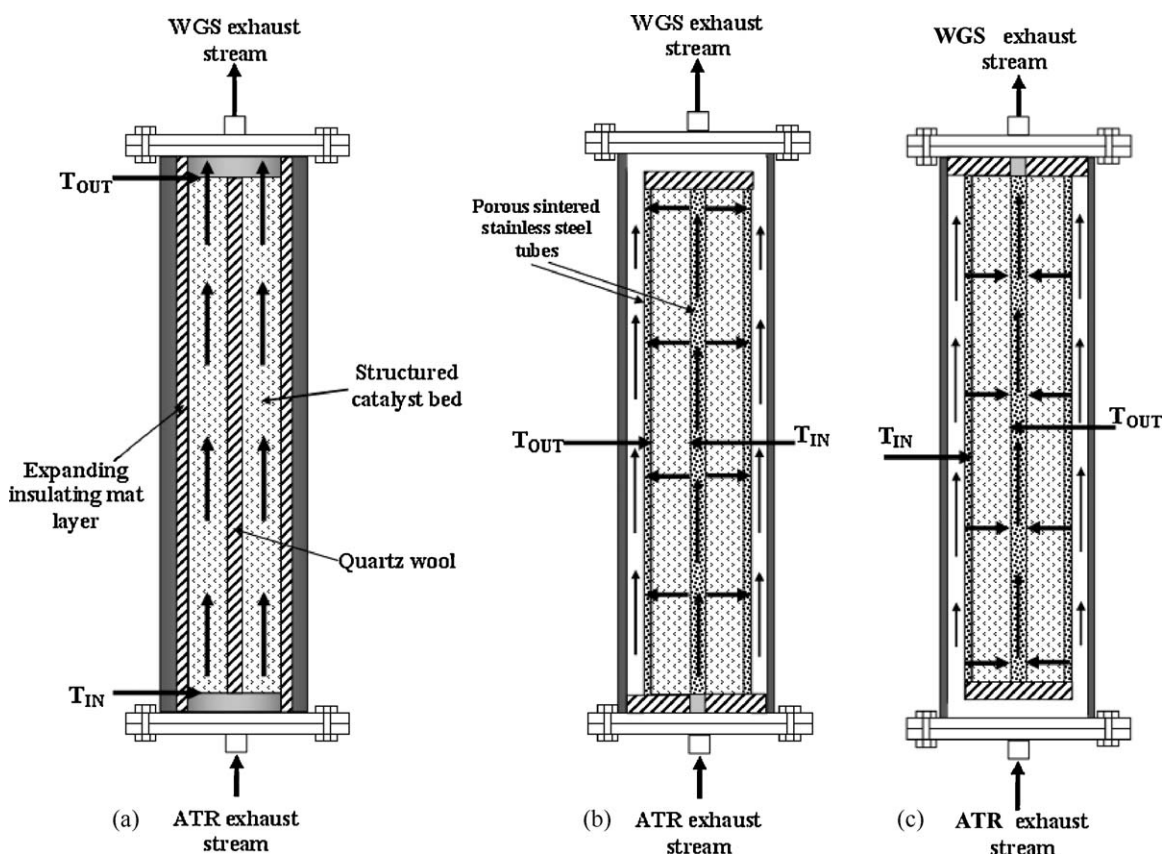


Fig. 5. Axial (a), radial centrifugal (b), radial centripetal (c).

catalytic bed volume. More complex are the assemblies in the radial schemes (Fig. 5b and c). In particular, for the radial centrifugal assembly, the gas is forced to flow in the axial pipe through the gas distributor crossing the catalytic bed in radial direction to the annular channel, where it flows through the second

gas distributor and finally it is collected outside the WGS reactor. Both the gas distributors are placed in order to ensure a homogeneous gas flow throughout the catalytic bed. For the radial centripetal case, a similar assembly is realized, with the opposite gas flow direction.

The catalytic activity tests were carried out by changing the gas hourly space velocity (GHSV) in the range 6700–15,000 h⁻¹, whereas the molar feed ratio H₂O/CO was kept equal to 1.8 and 2.6. These parameters refer to the operating conditions of the WGS stage. The operating conditions of the ATR stage were changed in such a way to ensure the above-mentioned operating conditions in the WGS reactor. Furthermore, it must be observed that the space velocity in the shift stage is evaluated as the ratio between the total gas volumetric flow rate (STP conditions) fed to the ATR reactor and the total WGS catalytic bed volume. In all the experimental tests the WGS reactor inlet temperature was kept at 370 ± 5 °C by a PID controlled heating tape wrapped all around the WGS reactor inlet, whereas the typical gas composition measured at ATR reactor outlet is the following (vol.%, d.b.):

CH ₄	CO	CO ₂	H ₂	O ₂	N ₂
0–0.5	10.0–13.0	5.7–8.0	31.8–34.0	n.d.	Balance to 100

3. Results and discussion

The results of catalytic activity tests carried out with different flow geometries at changing GHSV value and H₂O/CO molar feed ratios are reported in Fig. 6. The experimental CO conversion is compared with that provided by thermodynamic calculations carried out at shift reactor lowest outlet temperature. A general trend of CO conversion decreasing at increasing the space velocity

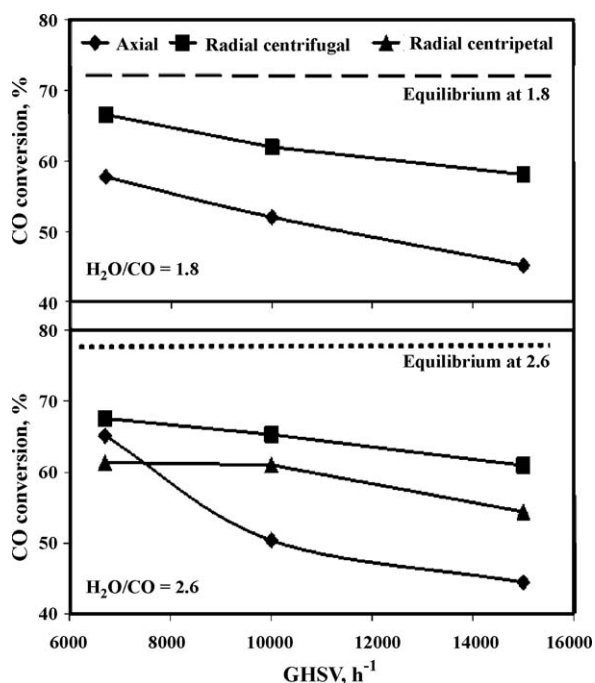


Fig. 6. Experimental and equilibrium CO conversion as a function of GHSV and H₂O/CO feed ratio values with different flow geometries.

is observed, however in this case it is very interesting to point out on the dramatic effect of the contact time on CO conversion. In particular, in the axial configuration, at higher $\text{H}_2\text{O}/\text{CO}$ molar feed ratio the CO conversion decreases from 65% to 50%. However, this catalyst showed not so remarkable catalytic activity in these conditions, in fact experimental results show that even at low GHSV values, the experimental CO conversion is quite far from the thermodynamic one. The effect of $\text{H}_2\text{O}/\text{CO}$ molar feed ratio is especially evident only at higher contact time, where an increased value of this parameter led to increasing CO conversion. At lower contact time the water gas shift reaction is inhibited to a great extent by the low kinetic constant, in such a way that the reactor performances are not so influenced by the thermodynamic parameters, and the effect of the feed ratio becomes of no consequence.

In the same figure are also reported results of catalytic activity tests carried out with radial centrifugal and radial centripetal flow geometry by changing GHSV value and $\text{H}_2\text{O}/\text{CO}$ molar feed ratios.

In the case of radial centrifugal configuration, the comparison with the axial configuration shows that the catalytic activity is higher at each space velocity. In particular, a CO conversion of about 66% is obtained already at a $\text{H}_2\text{O}/\text{CO}$ feed ratio of 1.8 and GHSV of 6700 h^{-1} , resulting in an experimental CO conversion value very close to that evaluated by the thermodynamic calculations of about 72%. At this operating condition the $\text{H}_2\text{O}/\text{CO}$ feed ratio increase is not so effective, whereas at higher space velocity a slight increase in CO conversion is observed by increasing the feed ratio.

However, the most interesting observation is that in the overall investigated range of space velocities a smaller dependence of CO conversion on the GHSV values is found with respect to the axial configuration.

For what concern the results of catalytic activity tests carried out with radial centripetal flow geometry, the experimental results presented in the same figure, show that by increasing the GHSV values the CO conversion decreases. In particular, the measured values are 61% at 6700 h^{-1} , and 54% at $15,000\text{ h}^{-1}$. Again, the experimental CO conversion is quite far from the thermodynamic one, even if for the higher GHSV values the CO conversion seems to be slightly increased with respect to the axial bed configuration.

Finally, by comparing the experimental results obtained for the three different flow geometries, it is possible to observe that for both molar feed ratios, and for the same operating conditions, the radial flow geometries allow to realize a higher CO conversion. In particular, this effect being more evident at higher space velocities indicates that in the radial configurations the negative effect of GHSV increase on the reactor performances is depressed. This behaviour can be explained considering that the dramatic effect of a low contact time in the shift reaction is compensated by the decrease of the gas linear velocity through the catalytic bed. In fact, for the radial assembly the cross-sectional area changes with the radial position and may allow a different local contact time and temperature profile enabling an optimal catalytic bed exploitation with a higher overall CO conversion. This result is very consistent with the literature results reporting that the different geometry, like radial flow reactor, or axial bed with very different aspect ratio, and the corresponding lowered linear gas velocity may result in different reactor performances, essentially due to the increase of the bed thermal conductivity [20,18,32].

Furthermore, when we compare the two different radial assemblies, we can observe that the centrifugal one better performs with respect to the centripetal one. This specific result may be likely due to the fact that in centripetal radial flow the temperature increases with radius decreasing and, accordingly, the most part of the catalytic bed operates at low temperatures. With centrifugal radial flow the situation is reversed, since the most part

of the catalytic bed operates at higher temperature, more similar to the outlet one. Thus, the results may be to a great extent influenced by the reactor operating conditions and by the intrinsic catalytic activity. Indeed, when we use a less active catalyst the possibility to operate at higher temperature may allow the attainment of higher CO conversion. On the other hand, when a more active catalyst is employed the thermodynamic limits may be reached by far also at lower temperatures, so that the operation at higher temperature may become disadvantageous.

The comparison of the temperature difference between outlet and inlet shift reactor in the different geometries are reported in Fig. 7 for the two $\text{H}_2\text{O}/\text{CO}$ feed ratios at GHSV value of $10,000\text{ h}^{-1}$.

From the data reported in Fig. 7 it is observed that for any bed configuration the increase in the $\text{H}_2\text{O}/\text{CO}$ molar feed ratio results in a lower temperature increase. This effect may be likely due to the different CH_4 selectivity due to CO methanation, as reported in Fig. 8. At a deeper analysis we can observe that the radial configuration gives a higher temperature increase with respect to the axial bed configuration. We can explain this result considering that in the radial tests we obtain a higher CO conversion with respect to the axial case.

In Fig. 8 the influence of flow geometry and $\text{H}_2\text{O}/\text{CO}$ feed ratio on the methanation reaction in the CO WGS reactor at GHSV = $10,000\text{ h}^{-1}$ is shown. The results confirm that the catalyst employed is characterized by a very low methanation tendency, with a CH_4 selectivity that is only about 2% also for the lowest value of the $\text{H}_2\text{O}/\text{CO}$ feed ratio, where for higher CO conversion, the methanation reaction may be more favoured.

In Fig. 9 the effect of the GHSV value on the temperature difference between outlet and inlet section is reported for two different $\text{H}_2\text{O}/\text{CO}$ molar feed ratios for the radial centrifugal bed configuration.

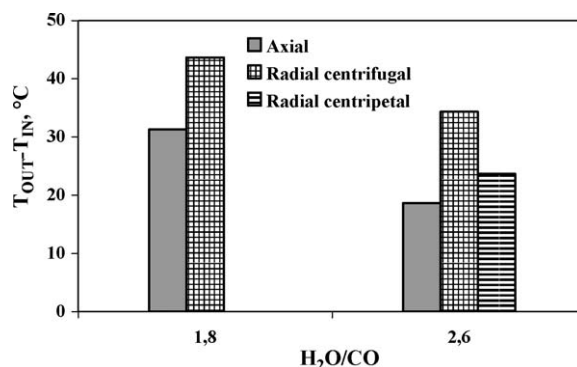


Fig. 7. Influence of flow geometry and $\text{H}_2\text{O}/\text{CO}$ feed ratio on temperature difference between the outlet and inlet shift reactor. GHSV = 10000 h^{-1} .

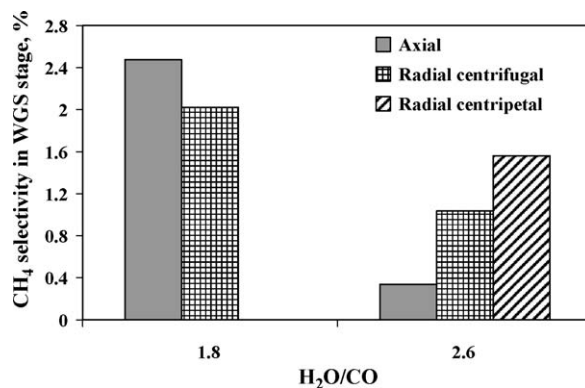


Fig. 8. Influence of flow geometry and $\text{H}_2\text{O}/\text{CO}$ feed ratio on the methanation reaction in the CO water gas shift reactor. GHSV = 10000 h^{-1} .

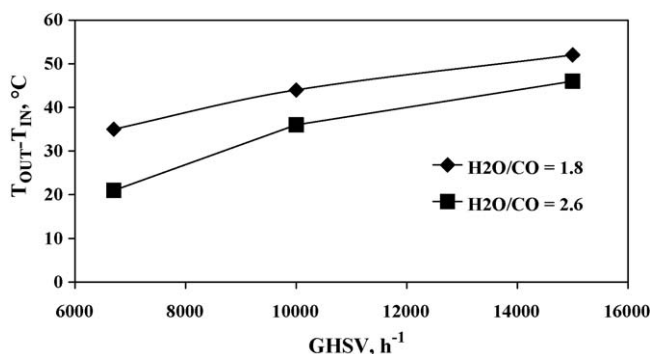


Fig. 9. Influence of GHSV on the temperature increase for the CO water gas shift reaction in the case of radial centrifugal bed configuration.

It is worth to note that at lower molar feed ratios the temperature differences are higher. Even if this result may appear not in very good agreement with the very similar CO conversion values measured and reported in Fig. 6, we can explain this peculiarity by considering the presence of a limited contribution of methanation reaction (see Fig. 8), due to very high reaction heat that is about five times higher than that of WGS reaction. In fact we estimate that to obtain a temperature increase of about 10 °C, a CH₄ selectivity of only about 2% is required.

For what concern the GHSV effect, at first look, the experimental results observed in Fig. 9 do not seem to agree with the CO conversion behaviour. Actually, as reported in Fig. 6, the CO conversion shows an opposite behaviour, increasing with the GHSV value decrease. In particular, at decreased gas linear velocity in the catalytic bed a corresponding decrease in the temperature difference between outlet and inlet of shift reactor is observed. This behaviour is consistent with literature studies [18], according to which the decrease of gas linear velocity leads to an increase of thermal conductivity, with enhancement of temperature redistribution phenomena in axial direction which is followed by a temperature profile flatness.

4. Conclusions

We found a remarkable difference of behaviour between the different reactor configurations investigated. In general, we can conclude that the radial configurations perform better than the axial one, by allowing higher CO conversion, especially when higher GHSV values are employed. This finding makes radial configurations good candidates for the intensification of WGS stage in small scale H₂ production plants. Moreover, the experimental results evidenced a remarkable difference between the two radial configurations, likely due to the possibility to generate a gas velocity profile inside the catalytic bed which allows a better reaction coupling with catalyst volume in dependence on the “reaction coordinate”, thus resulting in higher CO conversion, and, accordingly, in higher temperature difference between inlet and outlet shift reactor.

On the basis of the experimental results the choice of centripetal or centrifugal radial flow could be performed by considering the catalyst intrinsic activity and the reactor operating conditions. Indeed, if the catalytic activity is not very high the

overall reaction rate is not limited by the thermodynamic equilibrium and a temperature bed profile that allows the most part of the catalytic bed to operate at higher temperature and more similar to the outlet one may result in a more performing reactor. In the case of a very active catalyst it would be more convenient to have a higher inlet temperature to enhance the reaction rate, and a lower outlet temperature to avoid the equilibrium limitations.

It can be pointed out that these results were obtained under catalyst kinetic limitations, since the catalyst investigated was less active than the expected one. Thus, it would be very interesting to verify the influence of such configurations with a catalytic reactor operating at the outlet cross sectional area very close to the thermodynamic equilibrium.

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