Methane Combustion in a Non-Premixed Catalytic Fluidized Bed Reactor

P. Ammendola (*), R. Chirone, M. Iamarino, R. Pirone, G. Russo, G. Tatta

Istituto di Ricerche sulla Combustione – C.N.R., Piazzale Tecchio 80, 80125 Naples - ITALY
Dipartimento di Ingegneria e Fisica dell’Ambiente, Università degli Studi della Basilicata - C.da Macchia Romana, 85100 Potenza – ITALY
Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II - Piazzale Tecchio 80, 80125 Naples - ITALY

ABSTRACT
The performance of a catalytic converter characterized by non-premixed feeding of methane and air, relevant to the combustion of mixtures within the flammability limits, has been characterized with reference to practical applications of fluidized bed boilers. Experiments were carried out in a 100 mm ID fluidized bed and using copper dispersed on γ-Al₂O₃ spheres (1mm diameter) as catalyst. Reaction temperature was controlled by means of a cooling coil wound up around reactor external surface. Effects of methane inlet concentration (in the range 4 – 9% vol.), gas superficial velocity (between 40 and 130 cm s⁻¹) and temperature (650, 700 and 750°C) on reactor performance have been investigated in terms of fuel conversion and unburned fuel emissions. Results indicated that heat generation up to 5.3 kW could be obtained with negligible emissions of CO, NOₓ and unburned methane in the exhaust gas.

INTRODUCTION
Fluidized bed catalytic converters represent a viable alternative to packed beds and monoliths for catalytic combustion applications. Despite the low attention by far received, considerable benefits may derive from catalytic combustion carried out in fluidized beds mainly due to their improved heat transfer properties, enabling, on one hand, an efficient heat recovery by means of external or submerged heat transfer surfaces and preventing, on the other, undesired overheating, related pollutant formation and catalyst thermal deactivation [1].

Among the open issues emerging from operating experience on bench- and large-scale fluidized bed catalytic converters, the loss of catalyst due to attrition [2,3] and the criticality of fuel/air mixing phenomena [4] are worth of consideration. Operation in the turbulent fluidization regime has been advocated as a way to overcome the onset of bubble-to-emulsion phase mass transfer resistances [2]. On the other hand operation at large gas superficial velocities brings about exceedingly large losses of catalyst as attrited material. Optimal trade-off between these conflicting requirements can only be achieved by decreasing catalyst attrition propensity and by careful optimization of hydrodynamics and gas mixing in the bed of fluidized catalytic converters.

It has been previously reported that a catalytic system based on copper supported on porous γ-alumina spheres can display good activity, low cost, excellent thermal and mechanical stability for use in fluidized bed catalytic combustion of light hydrocarbons [5]. Premixed fluidized catalytic combustion of methane and propane under fuel-lean conditions has been studied both experimentally and theoretically [6,7], highlighting how the use of coarse catalyst pellets could favourably affect the effectiveness of bubble-to-emulsion phase mass transfer. As a consequence, complete and stable hydrocarbons conversion was obtained at temperatures below 700°C, while the propensity to attrition and thermal deactivation of the
catalyst turned out to be fairly low. Nevertheless, the conditions at which the converter was operated (very low hydrocarbon concentration and premixed feeding) were of limited interest for practical applications.

The present work moves further to address the performance of catalytic converters characterized by non-premixed feedings of methane and air, relevant to the combustion of mixtures within the flammability limits, and hence to much more concentrated fuel/air mixtures. This extension is of increasing interest with reference to practical applications of gas fluidized bed boilers when considering the potentiality required and the problems related to a safety operation with boilers fed at methane concentrations inside flammability limits. The experimental facility used in this investigation is of a scale of practical interest when considering domestic application of boilers. The different operative conditions, the additional mixing limitations between directly injected methane and fluidizing air at the distributor level and the more applicative approach characterising the present study have requested a further detailed analysis, since no straightforward prediction of the reactor performances can be done in the light of the results previously obtained. Effects of methane inlet concentration, gas superficial velocity and temperature on reactor performance have been investigated in terms of fuel conversion and unburned fuel emissions.

EXPERIMENTAL

The catalyst consisted of copper dispersed on porous $\gamma$-$\text{Al}_2\text{O}_3$ spheres supplied by Sasol, characterized by high mechanical strength. The catalyst pellets lay at the borderline between groups B and D of the Geldart classification of powders [8]. Catalyst ageing at 800°C under reaction conditions yielded copper mainly as superficial spinel phase CuAl$_2$O$_4$, stable upon repeated thermal treatments. Preparation techniques and physico-chemical properties of catalyst are detailed in a previous work [5]. The experimental apparatus used in this work is reported in Fig. 1. The catalytic converter consists of a 100 mm ID stainless steel fluidized bed reactor, equipped with a porous plate as air distributor. Methane is injected in the bed 2 cm above the porous plate through a distributor consisting of a cross-shaped manifold, with
four branches 4 cm long. 4 holes of diameter $d_0 = 0.8$ mm were drilled along each branch, equally spaced and perpendicularly oriented with respect to the reactor axis. A similar device has been already used for the direct injection of gaseous fuels in non-catalytic fluidized bed reactors [9] and the discharge mode of methane at the distributor level is expected, for the experimental conditions of this work, to give rise to horizontal jets penetrating into the bed [10]. The reactor is equipped with a pre-packed bed, 60 cm height, consisting of Rasching rings of different sizes located below the porous plate to uniform inlet gas velocity profile. An electrical oven employed during reactor start up surrounds the packed bed. During steady state operation, the temperature is stabilized by removing the excess of heat generated by methane combustion by means of a cooling system consisting of a copper coil winded up around the external reactor surface for an height of 15 cm. Liquid water was used as exchange medium, subtracting heat from the reactor by complete vaporization. Vapour formed was then condensed and recirculated to the reactor. Temperature profile along the reactor axis is measured by means of 5 equally spaced thermocouples (form T1 to T5 in Figure 1), vertically inserted into the bed and located at 0.06, 0.145, 0.23, 0.315 and 0.4 m with respect to air distributor. Continuous monitoring of gas composition at the exhaust line was accomplished by on line analyzers (for CO, CO$_2$, O$_2$ and CH$_4$). A data acquisition unit was used to log on signals from the experimental facility. The bed consisted of 2100 g of catalyst with corresponding unexpanded bed heights of 0.30 m. Experiments were carried out at methane inlet concentrations ranging from 4 to 9% vol. The temperature range investigated was between 650 and 750°C. The upper limit of temperature range has been fixed with respect to the catalyst thermal deactivation threshold (800°C).

RESULTS AND DISCUSSION

The reactor was operated in conditions characterized by high methane conversion degrees, mostly above 0.99. Analysis of the exhaust gas only revealed products of complete methane oxidation, while neither CO nor NO$_x$ were detected. Catalytic activity was constant during the experimental campaign, as verified by reproducibility tests periodically performed at constant experimental conditions. Fragmentation and abrasion phenomena of catalyst particles did not occur in any significative extent. The reactor was almost isothermal for all combustion tests performed. Fig. 2 reports typical temperature profiles measured at fixed axial positions in experiments at 700°C and different fluidization velocities. For the lowest value of $u_0$ (40 cm s$^{-1}$), the temperature measured by the highest thermocouple (at 0.4 m above air distributor) is not reported since it hangs outside the fluidized bed, while at higher gas velocities all thermocouples resulted immersed in the bed due to its increased expanded height. Analysis of Fig. 2 indicates that temperatures differences along reactor axis are generally low and result, as expected, more appreciable at low fluidization velocities: at $u_0 = 40$ and 60 cm s$^{-1}$, temperature differences up to 10°C have been observed. In this case, higher temperatures are measured in the lower section of the bed, where most of the reaction takes place. Increasing $u_0$, temperature differences become smaller according to the improved solid
mixing and at 100 cm s\(^{-1}\) they do not exceed 1–2 °C. Due to small but possible temperature differences, experimental results of methane conversion are reported in the following discussion always with respect to the temperature measured by the first thermocouple in the bed, indicated as T1 in Fig. 1.

Fig. 3 reports methane concentration measured at outlet normalized with respect to inlet concentration, \(C_{\text{out}}/C_{\text{in}}\), as a function of the ratio between gas superficial velocity and the minimum fluidization velocity, \(u_0/umf\). According to previous findings [7], values of 21, 20 and 19 cm s\(^{-1}\) have been considered for \(umf\) at temperatures of 650, 700 and 750 °C respectively. Experimental data at constant temperature have been reported with the same symbol whatever the methane inlet concentration (in the range 4-9% vol.). Analysis of the figure shows that there is a range of gas velocities, \(u_0/umf < 2\), where full conversion of methane (\(C_{\text{out}}/C_{\text{in}} < 0.001\)) has been achieved regardless of reactor temperature. At \(u_0/umf > 2\), unburned methane increases and this effect is larger when decreasing operative temperature. In any case, very small amounts of methane were detected in the exhaust gas, methane outlet concentration remaining below 100 ppm for \(u_0/umf < 2\) at 650°C, for \(u_0/umf < 2.5\) at 700°C and for \(u_0/umf < 3\) at 750°C. Fig. 4 reports the maximum power that can be generated by the catalytic converter as a function of methane inlet concentration in respect of given standards for methane emission at the outlet. Data have been extrapolated from the experimental results of Fig. 3 obtained at reactor temperature of 750°C. For every inlet fuel concentration, maximum thermal power has been evaluated on the basis of the highest gas velocity (and hence of the highest gas flow rate) which allows to respect strict emission limits of 20, 100 and 200 ppm. For every given constraint, maximum thermal power increases, as expected, with increasing methane inlet concentration. For example, the severe standard at 20 ppm can be fulfilled, for methane concentrations ranging from 6 to 9%, with generation of thermal power between 2.75 and 3.6 kW. In respect of less severe emissions limits, i.e. 100 and 200 ppm, the converter increases maximum generable power up to 5.3 kW. In Fig. 5, outlet methane concentration has been reported with respect to reactor temperature for three different gas superficial velocities (40, 60 and 80 cm s\(^{-1}\)) and constant methane inlet concentration (6% vol.). At 40 cm s\(^{-1}\), almost complete methane conversion is reached in the whole temperature range and a negligible effect of reactor temperature is recognized.
The increase of gas velocity decreases methane conversion, according to a decrease of the residence time of the gas in the reactor. This effect can be partially compensated by an increase in reactor temperature: with respect to 40 cm s⁻¹, comparable reactor performances can be reached at 60 cm s⁻¹ by an increase of operative temperature up to 750°C. The favourable effect of temperature is nevertheless ineffective at 80 cm s⁻¹ where methane outlet concentration curve is not expected to level off to zero in the range of practical interest for the catalyst used.

Fig. 6 reports \( \frac{C_{\text{out}}}{C_{\text{in}}} \) as a function of the inlet fuel concentration in experiments performed at 750°C and \( u_0 \) of 60 (●), 70 (■) and 80 (▲) cm/s. Analysis of data shows that methane content at the outlet increases with increasing inlet fuel concentration. The effect of \( C_{\text{in}} \) has been analyzed in the light of a simple mathematical model of the reactor. As primary approximation, the catalytic converter has been described assuming plug-flow pattern for the gas through the bed and a reaction rate of \( m \)-th order with respect to fuel concentration. The resulting expression of \( \frac{C_{\text{out}}}{C_{\text{in}}} \) is:

\[
\frac{C_{\text{out}}}{C_{\text{in}}} = \left[1 + Da(m-1)\right]^{-\frac{1}{m}} \quad (1)
\]

Where Damköhler number, \( Da \), is:

\[
Da = \frac{kV_{\text{cat}}}{Q}C_{\text{in}}^{-m-1} \quad (2)
\]

where \( V_{\text{cat}} \) is the volume of catalyst, \( Q \) is the total gas flow rate and \( k \) and \( m \) are apparent kinetic constant and the apparent reaction order respectively. This model does not take into account the detailed physical and chemical mechanisms ruling the effective fuel conversion, but it lumps into the parameters \( k \) and \( m \) the effects of such phenomena.
Equation 1 was used to fit experimental data of methane conversion at constant temperature reported in Fig. 6 to obtain an evaluation of m. Good agreement with model prediction was found with $m = 0.94$ whatever the gas superficial velocity. This value is intermediate between $m = 0.7$, the intrinsic reaction order of the catalytic methane oxidation evaluated elsewhere [6], and $m = 1$, corresponding to first order phenomena with respect to methane concentration as interphase mass transfer. As a consequence, it can be concluded that the converter is not operating under a pure kinetic control, while the determination of the effective controlling mechanism affecting the methane conversion under the actual operative conditions needs a more detailed reactor modelling.

**CONCLUSIONS**

Catalytic combustion of methane in a fluidized bed of a copper-based catalyst has been investigated in a pilot scale reactor with non-premixed feeding of reactants.

The reactor has been operated in the bubbling regime of fluidization and temperature differences inside the bed are very limited. Moreover, stable reactor operation has been observed during the entire experimental campaign, indicating that catalyst thermal deactivation and loss of solid phase due to attrition did not occur in any significant extent.

Conversion of methane is complete at temperatures ranging from 650 to 750°C depending on the operative conditions in the reactor (inlet fuel concentration and fluidization velocity). As a consequence, under the conditions investigated, a maximum thermal power of about 5 kW can be produced in the reactor with fuel emissions lower than 200 ppm.

Experimental results indicate that both the effective catalytic kinetics and the mass transfer phenomena play a key role on methane conversion.

**REFERENCES**