



Coal mine ventilation air methane combustion in a catalytic reverse flow reactor: Influence of emission humidity



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ABSTRACT

The role of the humidity content on the performance of catalytic reverse flow reactors (RFRs) for the abatement of methane emissions from coal mines is studied in this manuscript. It has been demonstrated that this technique is very useful for the abatement, and even upgrading, of these emissions. However, the effect of humidity on the reactor performance has not been addressed yet, in spite of being well known that water is an inhibitor in catalytic combustion.

Experimental studies in a lab-scale isothermal fixed bed reactor demonstrated that water decreases the activity of a palladium on alumina catalyst for the combustion of methane, but this inhibition is entirely reversible, results fitting well to a Langmuir–Hinshelwood kinetic model. Then, the influence of water was studied in a bench-scale RFR operating at near adiabatic conditions at different switching times (100–600 s) and methane feed concentrations (2700–7200 ppm). Finally, a mathematical model for the reverse flow reactor, including the kinetic model with water inhibition, has been validated using the experimental results. This model is of key importance for designing this type of reactors for the treatment of mine ventilation emissions.

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1. Introduction

In the last decades, environmental problems related to global warming have gained importance. Coal mining is an activity with great influence on greenhouse emission, because of the huge amount of methane emitted to the atmosphere during coal extraction through the ventilation system (concentration 1000 to 10,000 ppm). Ventilation air methane represents the main contribution (approximately 78%) to the carbon footprint of coal mining [1].

In the atmosphere, methane is accumulated and slowly oxidised with average lifetime of around 12 years. Nevertheless, the effect of methane as greenhouse gas is 21 times higher than that of carbon dioxide. For this reason, the combustion of methane to carbon dioxide before release has a great interest to reduce the net warming potential [2–4].

One suitable option for the treatment of ventilation air methane in coal mining is regenerative oxidation, and in particular regenerative catalytic oxidation (RCO) in a reverse flow reactor [5,6]. Catalytic oxidation is an interesting alternative to thermal oxidation, since the use of a catalyst significantly decreases the ignition temperature and, as a consequence, the size and thermal requirements of the combustion device. Moreover, the formation of NO_x is negligible [7,8].

Reverse flow reactors (RFRs) consist of a catalytic fixed bed reactor in which the feed flow direction is periodically reversed. RFRs present

great potential advantages for the combustion of hydrocarbon emissions. By selecting the appropriate switching time (t_{sw} , defined as the time elapsed between two consecutive flow reversals), most of the combustion heat is stored inside the reactor in consecutive cycles, so that autothermal operation is possible even for very slightly exothermic reactions. Hence, RFRs allow the efficient treatment of very lean emissions of volatile organic compounds (VOC) (e.g., originated from the use of organic solvents) or methane (e.g., coal mine vents) in air [9–11].

RFR advantages are a consequence of its forced unsteady state operation. However, this can also be a drawback to maintain ignited operation in the presence of disturbances in the feed flow rate or concentration. For example, if the feed becomes too lean, there is a risk of extinction, because the amount of heat released by the reaction is very low; in these situations, the RFR regeneration capacity is crucial to maintain autothermal operation. Under rich feed conditions, the heat released and accumulated in the reactor can overheat the catalyst bed, leading to catalyst thermal deactivation. Such issues have limited the industrial use of this type of reactors, and encouraged research in the development of suitable control systems [12–15].

The catalyst performance is affected by the presence of side compounds (different of methane) in the ventilation air. Among these compounds, water stands out because it is commonly present at high concentration in these emissions (near to saturation at ambient temperature). It is well-known that water has a negative effect on the activity of supported precious metal catalysts. The oxidation of methane on palladium-supported catalysts has been studied by different authors,

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with a general agreement on the existence of a reversible inhibitory effect [16–18]. Models based on Mars–van Krevelen or Langmuir–Hinshelwood kinetics have been found to agree with the observations [17].

The combustion of methane in reverse flow reactors has been studied experimentally, and also by means of simulations. Previous studies have been centred in the influence of operating conditions [19,20], optimization [21], model validation [20,22], control of ignition state [13, 23], or heat recovery [14,24]. Although water is present in high concentration in coal mine ventilation air (20,000–50,000 ppm) and the performance and stability of reverse flow reactors can be highly affected by the decrease of the catalyst activity caused by water, to the best of our knowledge, this aspect has not been studied. The main objective of this work is to fill this gap and assess the influence of water in the oxidation of methane in catalytic reverse flow reactors.

For accomplishing this purpose, the effect of water on the reaction kinetic is firstly studied, and an appropriate kinetic model is proposed. Then, the influence of water on the performance of reverse flow reactors is analysed in a bench-scale device. Finally, a detailed mathematical model of the reverse flow reactor is proposed and validated with the experimental data. This model is suitable to be used in the design and optimization of commercial-scale devices for the treatment of methane emissions in the presence of water.

2. Methodology

2.1. Catalyst characterisation

The catalyst used in this work, representative of catalysts commonly used for methane combustion, is a commercial palladium-based monolith supplied by BASF (reference FP-CPO-5M). The monolithic catalyst is formed by an inert support (cordierite) with a cell density of 390 cpsi (cell size $1.02 \cdot 10^{-3}$ m, open porosity 65 vol.%) and a washcoating (average thickness $8.1 \cdot 10^{-5}$ m, fraction 20 vol.%) impregnated with the active phase (0.39 wt.% palladium). Catalyst geometry was measured directly using the images from a stereomicroscope (Stemi 2000-C, ZEISS).

Solid density (2300 kg/m^3) was measured experimentally, and the solid heat capacity (900 J/kg K) and thermal conductivity (0.8 W/m K) were taken from the literature for cordierite-based monoliths.

Textural characteristics (specific internal surface area and pore volume) were measured by nitrogen adsorption at 77 K in a Micromeritics ASAP 2020 surface area analyser. Obtained data have been used for estimating internal porosity (12 vol.%) and porous structure properties (mean pore diameter 12 nm), needed for the mathematical modelling of the reactor.

2.2. Isothermal lab-scale reactor

Catalyst stability and reaction kinetics for methane oxidation have been studied in an isothermal fixed-bed reactor (0.6 m length and $9 \cdot 10^{-3}$ m internal diameter). The monolith was ground and sieved to 100–250 μm , and then mixed with ground glass (355–710 μm) to avoid deviations from plug-flow behaviour (tube diameter/particle diameter > 10).

The required feed methane/air mixture was prepared by mixing an air–methane mixture of 25,000 ppm methane, from a cylinder, and purified air from a compressor (Ingersoll-Rand), using two mass flow regulators. Inlet and outlet streams were analysed in an Agilent gas chromatograph (GC).

Water was introduced in the air stream with the help of a bubbler. The concentration of water was regulated using a temperature control system formed by a heating blanket and a temperature controller. The water content is analysed using a hydrometer (VATSAIA HMI 32).

2.3. Adiabatic bench-scale reverse flow reactor

The bench-scale reverse-flow reactor used in the present work consists of a 0.8 m long 0.05 m internal diameter 316 stainless steel tube. The tube contains three monolithic beds: one catalytic (0.15 m long) situated in the middle, and two inert (0.125 m long each) situated at both ends. The beds are surrounded by a glass wool layer, in order to avoid gas bypass near the reactor wall. The temperature of the bed is measured in 5 points along the reactor axis using a multipoint thermocouple array. The flow reversal is accomplished by using two pairs of solenoid valves (Parker-Lucifer 121K46E), acting on the reactor inlet and outlet streams.

Reactor feed, consisting of methane–air mixtures with different methane concentrations, is set using two mass flow meters (Bronkhorst F201C). The analysis of methane concentration at the inlet and outlet streams is performed on-line (each 5 s) using an infrared spectrometer (ABB-PIR3502). The reactor tube is surrounded by an oven, equipped with a dynamic temperature-control system able of compensating the heat transfer through the reactor tube, and hence allowing a reactor operation close to adiabatic [20,25,26].

The following protocol has been followed for each test. First, the reactor was fed with hot air, in order to pre-heat the beds above the ignition temperature of the air–methane mixture ($T_{pre} = 400 \text{ }^\circ\text{C}$). Then, the methane/air mixture was fed to the reactor (0.15 m/s n.t.p.) at room temperature ($20 \text{ }^\circ\text{C}$), and the flow reversal was started. The reactor was then operated until pseudo-steady state or extinction.

2.4. Reverse flow reactor model

Based on previous experience on modelling reverse flow reactors [20,27–29], in this work, a 1D heterogeneous dynamic model has been selected (see equations in Table 1). The meaning of the symbols is indicated in the list of symbols. The physical and transport properties appearing in the equations of Table 1 must be specified or calculated by means of appropriate correlations, as indicated in a previous work [22]. Danckwerts boundary conditions (see Table 2) have been used to solve the model in MATLAB using the method of lines (ode15s) [20, 22]. The switch of the feed direction is modelled by shifting the boundary conditions at both sides of the reactor.

3. Results and discussion

3.1. Catalyst stability

Catalyst stability at reaction conditions has been determined in the absence and presence of water. Tests have been carried out in the isothermal fixed-bed reactor at $475 \text{ }^\circ\text{C}$ and WHSV $1.22 \text{ m}^3 \text{ (n.t.p.) kg}_{\text{cat}}^{-1} \text{ min}^{-1}$ with methane feed concentration 1000 ppm. Results are depicted in Fig. 1. In the absence of water, methane conversion decreases during the first 1.5 h and then remains constant. Water is introduced in the reactor at $t = 7 \text{ h}$ with a concentration of 16,000 ppm, causing a sudden drop in conversion from 28% to 21%. Then, conversion remains nearly constant upon time. Finally, when the water feeding is discontinued at $t = 13 \text{ h}$,

Table 1

Summary of the main equation of the mathematical model proposed for the modelling of the reverse flow reactor.

Mass balance to the gas phase

$$\frac{\partial y_G}{\partial t} = -\frac{u_0}{\varepsilon_b} \frac{\rho_{\text{cat}}}{\rho_G} \frac{\partial y_G}{\partial z} + D_{\text{ax}} \frac{\partial^2 y_G}{\partial z^2} - \frac{aK_G}{\varepsilon_b} (y_G - y_S)$$

Mass balance to the solid phase

$$\frac{\partial y_S}{\partial t} = \frac{aK_G}{(1-\varepsilon_b)} (y_G - y_S) + \frac{\rho_S \Gamma_{\text{CH}_4}}{C_G}$$

Energy balance to the gas phase

$$\frac{\partial T_G}{\partial t} = -\frac{u_0 \rho_{\text{cat}}}{\varepsilon_b \rho_G} \frac{\partial T_G}{\partial z} + \frac{k_{\text{cat}}}{\rho_G C_{pG}} \frac{\partial^2 T_G}{\partial z^2} + \frac{ah}{\rho_G C_{pG} \varepsilon_b} (T_S - T_G)$$

Energy balance to the solid phase

$$\frac{\partial T_S}{\partial t} = \frac{k_s}{\rho_S C_{pS}} \frac{\partial^2 T_S}{\partial z^2} + \frac{ah}{\rho_S C_{pS} (1-\varepsilon_b)} (T_G - T_S) + \frac{\rho_S \Gamma_{\text{CH}_4} \Delta H}{\rho_S C_{pS}}$$

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