



Research article

Demonstration of mitigation and utilization of ventilation air methane in a pilot scale catalytic reverse flow reactor



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ABSTRACT

The mitigation and utilization of ventilation air methane was demonstrated in a pilot scale catalytic reverse flow reactor. A kind of non-noble metal oxide catalyst of 1.8 m^3 was loaded and lean methane with a concentration of 0.2–1.0 vol% and a maximum feed flow rate of $800 \text{ m}^3/\text{h}$ was processed. The schemes of reactor control and heat recovery, viz., a simple logic-based controller plus hot gas withdrawal from reactor center, as proposed previously by simulation, were verified in this pilot scale reactor. The results prove that the autoregulative time to switch the gas flow direction will drop quickly to zero if a large amount of hot gas is withdrawn from the reactor by using the traditional method. The switching time has a great influence on the heat recovery efficiency, whereas the amount of hot gas removed out of the reactor impacts significantly on the reactor stability. All these experimental observations are in line with the simulation results. The long term operation proves the feasibility of hot gas withdrawal with a heat recovery efficiency of about 56% and the reliable performances of the non-noble metal catalyst in lean methane oxidation with a methane conversion over 90%. These results prove that the catalytic reverse flow reactor and control schemes used in this work are quite effective in the mitigation and utilization of lean methane.

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1. Introduction

Methane is the second most significant greenhouse gases after carbon dioxide. Coal mining contributes 8% of anthropogenic methane emissions, which is projected to increase through 2020, with an estimate as high as 793 Mt. CO_2 by 2020 [1]. 70% of coal-related methane comes from ventilation air methane (VAM) with a concentration of 0.1–1.0 vol%. However, the amount of VAM mitigated at present is almost negligible, as this methane resource is very dilute and variable in concentration and output. The mitigation of VAM requires either treatment in its dilute state, or concentrating up to levels that can be used in conventional methane fueled engines, but now the latter technology is not available in practice [2]. Since methane has a global warming potential of 21 times higher than that of carbon dioxide [3], the oxidation of methane into carbon dioxide is in favor of environmental protection and heat recovery. One approach uses VAM as combustion air, which was well-demonstrated in Australia [4].

Recently, great progresses have been made in thermally or catalytically oxidizing low concentration methane by reverse flow reactor

(RFR). A RFR works under forced unsteady state conditions by periodical switching of the feed flow direction. Owing to the velocity difference between the flowing gas and the thermal front, heat generated by the exothermic reaction can be trapped inside the reactor by selecting an appropriate switching interval, which makes the auto-thermal operation of an RFR possible even under very lean feed conditions [5]. Non-catalytic thermal flow reversal reactor (TFRR) works under a much higher temperature above $1200 \text{ }^\circ\text{C}$ without using any catalyst, but it was criticized for higher construction cost, possible formation of NO_x and extreme sensitivity to bed temperature [6]. Nevertheless, some thermal flow reversal reactors have been proven at full-scale demonstration [7].

Meanwhile, a catalytic reverse flow reactor (CRFR) may possess the merits of both catalytic oxidation and RFR. Catalytic oxidation can significantly reduce the ignition temperature and thus produce fewer NO_x pollutants; moreover, it allows better control of reaction over a wider fuel/air ratio without concerning the flammability [8]. Among various catalyst materials used, noble metal catalysts, especially supported palladium, exhibit high activity in the catalytic combustion of lean methane at a temperature as low as $400 \text{ }^\circ\text{C}$ [9–11]. Simulation and experimental study performed within a European Project showed that the operation temperature of CRFR might be too high (up to $800 \text{ }^\circ\text{C}$) for the noble metal catalyst like $0.5\% \text{ Pd}/\gamma\text{-Al}_2\text{O}_3$, suggesting that the large-scale

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implementation of this technique may encounter certain problems [6]. To overcome the drawbacks of noble metal catalysts, transition metal (Ni, Cu, Mn, Co, Fe, etc.) oxides have been considered as practical alternative materials for the catalytic combustion of lean methane [12–15]. Matros, Kolios, Zagoruiko and co-workers have made some detailed reviews on this kind of reactors [16–18].

Even though RFR has advantage of auto-thermal operation, it is hard to operate due to its hybrid and forced unsteady-state nature as well as the extensive variation in the methane concentration and flow rate [17, 19,20]. A great deal of effort has been made on the control of the RFR recently, including feed forward control [21], model predictive control (MPC) [19,20,22–25], linear quadratic regulator (LQR) control [26,27], robust control [28], logic control [5,29–34] and fuzzy logic control [35].

Besides operating the RFR auto-thermally, recovering part of heat is also very tempting due to the huge emission of VAM. Generally, heat can be recovered by two ways: one is central cooling, by which a heat exchanger is buried in the center of the reactor; the other is termed hot gas withdrawal, where a fraction of hot gas is removed out of the reactor to feed the boiler. Gosiewski and co-workers pointed out that heat extraction by central cooling could only guarantee stable operation for moderate heat recovery efficiency [36]; an increase in the heat recovery may lead to the extinction of the reaction or harm the heat recovery system. In the case of hot gas withdrawal from reactor center, on the contrary, a smooth bed temperature profile can be sustained and a stable symmetrical cyclic state can be achieved [37]. Marin and co-workers claimed that withdrawing part of hot gas from the catalyst end rather than from the center of the reactor may achieve the most stable operation [38]. By simulation, we also found that hot gas withdrawal from the middle of the reactor influenced the reactor behaviors greatly: the autoregulative switching time will drop quickly to zero if large amount of hot gas is withdrawn from the reactor; constant switching time has little effect on reactor stability in a broad range, but it exhibits great influence on the heat recovery efficiency and methane conversion [5]. Although many researches concerned bed temperature control and heat recovery schemes of a RFR for the mitigation and utilization of VAM, very few experimental works, especially in pilot-scale, were reported.

In this work, the mitigation and utilization of ventilation air methane was demonstrated in a pilot scale reverse flow reactor using a kind of non-noble metal catalyst. About 1.8 m³ of catalyst was loaded in the reactor and a maximum feed flow rate of 800 m³/h with a concentration of 0.2–1.0 vol% was processed. The schemes of reactor control [34,35] and heat recovery by hot gas withdrawal, proposed previously by simulation [5], were verified in the pilot scale reactor. The effects of switching time, feed content and feed volumetric flow rate on the reactor stability, methane conversion and heat recovery efficiency were investigated. Finally, the performance of this pilot scale reactor in a relative long term operation was reported. The insight shown in this work should be great benefit of to the development of efficient measures in the mitigation and utilization of VAM and other lean gaseous fuel streams.

2. Experimental

2.1. Setup of the pilot scale RFR

The RFR designed for the abatement and utilization of lean methane from VAM or tail gas of Fischer-Tropsch process was built in the Pilot-plan Base of Institute of Coal Chemistry (ICC), Chinese Academy of Sciences, Taiyuan, China. As shown in Fig. 1, it contains mainly three divisions: reaction system, heat recovery system and data acquisition and control system; other auxiliary facilities such as air compressor and storage tank of methane are not included in this picture. The reactor is composed of two parallel sections with an internal side length of 1.0 m mounted side by side and connected by a vault. The two sections are packed up with inert Al₂O₃ monolith and porous non-noble metal catalyst from bottom to top with heights of 2.0 and 1.0 m, respectively. Main operation conditions and properties of the catalyst and inert beds

of the RFR are listed in Table 1. A four-way valve at the bottom of the reactor was used to change flow direction. Heat recovery was achieved by withdrawing part of hot gas from the reactor center, and then flowing through a heat exchanger by an induced draft fan. Air was supplied to the reactor by a compressor with a capacity of 1200 m³/h. Air flow rates (in the range of 100–1000 m³/h) of the main pipe and the pipes for cooling the bed (<200 m³/h) were measured by pressure differential orifice meter, whilst the methane flow rate (<10 m³/h) was measured by using a mass flowmeter.

To initiate the oxidation reaction, the catalyst bed was preheated to about 500 °C by hot gas from the combustion chamber. The combustion chamber is at the bottom of the reactor, which ensures the preheating of the catalyst bed and meanwhile avoids sintering the catalyst by the flame. Flow direction was periodically reversed in the preheating stage to keep balance heating of the two catalyst sections. The entire preheating process took about 5 h. After reaching the ignition temperature in the catalyst bed, the simulated VAM (methane and air with designed flow rates) was supplied to the reactor and the flow direction was reversed regularly to sustain the oxidation of lean methane.

2.2. Non-noble metal catalyst

The catalyst used in this work is a kind of non-noble metal oxide supported on porous Al₂O₃. Briefly, the porous Al₂O₃ support was first coated with alumina sol and calcined at 650 °C for 5 h; the modified Al₂O₃ support was then coated with aqueous solution of zirconium nitrate and calcined at 750 °C for another 5 h. After that, the active species of Cu, Ce and Mn with a loading 10 wt% were loaded through multiple coating with the mixed aqueous solution of cupric nitrate, cerium nitrate and manganese nitrate. Finally, the catalyst was calcined at 700 °C for 5 h. The density of the compacted catalyst is 500 kg/m³, with a porosity of 70%. The porous structure favors the transport/diffusion of the reactants and can reduce the bed pressure drop. As shown in Fig. 2, the ignition temperature (with methane conversion of 50%) of this type of catalyst is around 500 °C and a complete conversion of methane can be achieved at about 625 °C.

The long term performance of the non-noble metal catalyst was tested in a bench-scale tube reactor for over 1500 h with the increase of bed temperature stepwise from 650 to 850 °C. In all cases, the conversion of methane upon oxidation exceeds 93% and the catalyst can tolerate a temperature as high as 850 °C; no obvious deactivation was observed even at this temperature for 500 h, showing its good resistance to high temperature. As a result, the maximum allowable temperature for the catalyst was set to 850 °C in the controller design.

2.3. Control and data acquisition system

The control and data acquisition were achieved by the software package SIMATIC Wincc. All the control points including air/methane flow rates, bed/fluid temperatures, switching time, water level in the water tank and actions of valves were displayed and recorded automatically. The valves were powered by compressed air. Air can be supplemented at the entrance of the catalyst bed, which is considered more powerful in cooling the catalyst beds.

The concentration of methane in the feed and effluent was monitored with a gas sensor (GJC4) and accurately analyzed with a gas chromatograph (Shimadzu GC-2014C, equipped with a column packed with carbon molecular sieve and a FID detector), through sampling at the entrance and exit of the reactor. Bed temperatures were measured by using 28 thermocouples, 12 of which were placed along the inert beds and others were located in the catalyst beds. Thus, the radial temperature distribution in the catalyst bed can also be concerned.

A logic-based controller was adopted for the regulation of bed temperature and optimization of heat recovery [34,35]. Since the maximum temperature that the catalyst can tolerate is set at 850 °C and the ignition temperature for lean methane is 500 °C for this type of non-noble

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