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Research article

Studies on work of a prototype installation with two types of catalytic bed in the reactor for oxidation of methane from mine ventilation air

Barbara Kucharczyk [a,*], Beata Stasińska [b], Stanisław Nawrat [c]

[a] Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże S. Wyspiańskiego 27, 50-370 Wrocław, Poland
[b] Faculty of Production Engineering, University of Life Science in Lublin, Akademicka 13, 20-950 Lublin, Poland
[c] Faculty of Mining and Geoengineering, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

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ABSTRACT

This work presents results of the use of an installation for catalytic oxidation of methane from coal mine ventilation air and a possibility of its energy recovery. It presents studies carried out on a quarter-technical scale. It reports the work conditions of the catalytic flow reactor cooperating with a heat exchanger allowing auto-thermal operation of the process and production of thermal energy. For the concentration of methane in air 0.5–0.6% and ventilation air flow rate 3000–3500 $m^3 \cdot h^{-1}$ the methane oxidation installation worked without any supply of external energy (auto-thermally). At the same time heat was recovered and used to heat up the building housing the mine's main fans. Conducting the methane oxidation process at the concentration of methane in the air 0.48% and the ventilation air flow rate 2500 $m^3 \cdot h^{-1}$ shows a difficulty in obtaining auto-thermal work of the installation.

1. Introduction

Hard coal mines emit methane into the atmosphere, because it has to be removed from the mine for safety reasons. The total methane volume emitted to the atmosphere with mine ventilation air in Polish mines in 2011 amounted about 662 million m^3 [1]. Methane is a greenhouse gas that causes climate changes becoming more prominent in recent years. For comparison reasons the emission of each greenhouse gas is specified in an amount equivalent to carbon dioxide emission. Methane can trap about 20–25 times more heat than carbon dioxide [2–3]. Thus, despite the low methane concentration in air, its contribution to the greenhouse effect is quite substantial.

Protection against the climate change is important and it influences the need of development of methods for removing methane from mine ventilation air. In addition, oxidation of methane is an exothermic process and it can be a source of electrical energy, heat or cold. The difficulty in developing an economically viable technology for this purpose. Too low concentration of methane in mine ventilation air, which for safety reasons cannot exceed 0.75%, makes developing of an economically viable technology for this purpose difficult. Methane from mine ventilation air is often emitted into the atmosphere, because there is a problem with its removal due to its low concentration. Utilization of methane from ventilation air is a global problem. In recent years, concentration methane in the atmosphere has shown upward trend. Concentrations of methane in the atmospheric air have increased from 715 ppbv in the pre-industrial epoch to 1778 ppbv nowadays [2]. It is estimated that by the year 2020 methane emission will have increased by about 12 to 16% in such sectors as coal mining and agriculture [3].

Since the nineties numerous works have been conducted and their aim was to design an installation for combustion of methane from mine ventilation air and use the generated in this process heat. Due to a very low methane concentration in ventilation air (0–1%), heat recovery from hot combustion gases should be employed to make the process of removing methane economically viable. Heat recovery makes applying either recuperative or regenerative oxidizer possible. Currently there are three main technologies for reducing methane concentration using regenerative oxidizers [3,4,5]. In two technologies Thermal Flow Reverse Reactor (TFRR) and Catalytic Flow Reverse Reactor (CFRR) are used to transfer the heat of combustion to a flow-reversal reactor. They differ only in not using or using a catalyst, respectively. The developed commercial applications include thermal combustion in a reversal reactor Vocsidizer designed by Megtec System as well as catalytic oxidation in reversal reactors carried out by Canmet (Canada). In the third technology Catalytic Monolithic Reactor (CMR) of a honeycomb-type monolithic reactor is applied. Ceramic bed, most often in a form of a ceramic monolith, is used to recover heat from hot combustion gases in these technologies. Two chambers with such a bed are applied. Hot combustion gases pass through the first (cold) bed heating it. The gases before entering the combustion chamber are heated in the second bed (hot). After a certain time, the control system changes the direction of the gas flow. This causes that the first bed (cold) is heated by hot

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* Corresponding author.
E-mail address: barbara.kucharczyk@pwr.edu.pl (B. Kucharczyk).

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combustion gases and the second bed (hot) is cooled heating cold gases entering the combustion chamber. This type of system has a very high thermal efficiency 90–95%, which allows for fuel savings and finally reduces operating costs. However, it is difficult to maintain the desired temperature stable, especially when the reactor volume is large and the amount of combusted contaminants changes in time.

Methane from mine ventilation air can also be removed by catalytic oxidation with the use of recuperative catalytic oxidizer. In this technology, the counter-flow heat exchanger, in which the gas is heated by clean hot gases from methane combustion, is used to heat methane–air mixture before its entering the catalytic reactor. Zheng et al. [6] studied removal of 1% methane in air in a catalytic reactor at ventilation air flow rate 1000 $m^3 \cdot h^{-1}$ using this technology. Pd deposited on a ceramic monolith was used as a catalyst. They determined an influence of the startup flow coefficient and the startup power on process of commissioning the installation. They also studied an impact of operating conditions (space velocity, concentration of methane and average temperature of catalytic bed) on catalytic oxidation of methane.

There are also works carried out on mitigation and utilization of VAM. They include works on: lean burn catalytic gas turbine, recuperative gas turbine, power station air intake, combustion air for gas turbines and engines, catalytic combustion with drying, heating and cooling, desalination and methods increasing concentration of methane in so-called concentrators [3,4]. So far, the known solutions have been difficult to apply to the disposal of methane from coal mine shaft ventilation air, due to relatively low concentration of methane in ventilation air (0.1–0.3% in most mines) changing over time.

Catalytic oxidation of methane is the best method of removing methane from ventilation air and removal of volatile organic compounds (VOC) with waste gases. The heat released in the process can be used for generation of thermal or electric energy. Noble metals: Pt and Pd are most often used as catalysts in oxidation of VOC, including methane. Pt and Pd differ in catalytic activity in oxidation of various organic compounds. In oxidation of CO, CH_4 and olefins Pd is more active than Pt [7]. Pt is more active than Pd in oxidation of higher aliphatic hydrocarbons [8]. The activity of both metals in oxidation of aromatic hydrocarbons is substantial [7]. Lower activity, but higher resistance to poisoning and higher thermal resistance are exhibited by oxides of such metals as Co, Fe, Cr, Mn, Ni, Cu or their mixtures [14–15] or perovskite-type oxides with general formula ABO_3 such as $LaMnO_3$, $LaCoO_3$ $LaFeO_3$, $LaCrO_3$ [14–21]. The activity of perovskites in oxidation of VOC increases when the metal is substituted in the perovskite position B or A by a metal with different valence.

Pd [9–12] and bimetallic catalysts Pd-Pt [8], Pd-Ru [13] have the highest activity in oxidation of methane. $Pd(NO_3)_2$, $PdCl_2$, H_2PdCl_4 [9–12] or palladium organic salts dissolved in various solvents [10] are most frequently used as Pd precursors. It is not clear what amount of palladium in the catalyst is optimal, and it still remains unclear whether PdO, metallic Pd, or a mixed phase Pd/PdOx is the active form of palladium in methane oxidation [9–10]. The Pd content for Al_2O_3 support varies from 0.5% to 2%. The activity of Pd/Al_2O_3 catalysts increases with the increase in Pd content from 1% to 2% [12]. Because of the synergistic interaction of Pd and Pt, Pd-Pt-SAPO catalyst shows higher activity in oxidation of methane than that of Pd-SAPO-5 and higher thermal stability than those of Pd/Al_2O_3 and Pd/zeolite catalysts [8]. An addition of Ru to Pd at the ratio Ru/Pd = 1.5/3 mass% increases catalytic activity of Pd even if the catalyst is poisoned by H_2S. However, Rh addition does not increase the activity of Pd catalyst [13].

Palladium in the catalyst can be spread on standard granular or monolithic supports. Catalysts on the monolithic supports show many advantages over conventional catalysts on the ceramic granular supports. Their advantages include: lower gas flow resistance and a small pressure drop on a monolithic catalyst bed at a high gas flow rate ($>10^5$ h^{-1}), a high catalyst efficiency per active phase mass unit (whereby smaller reactors can be employed), high work safety, high thermal and chemical stability and the ease of placing the catalyst in a reactor and removing it for deactivation [22].

The aim of this work was to design an installation (and verify its operation) for oxidation of methane from mine ventilation air. This installation enables reducing emission of methane to the atmosphere and auto-thermal operating, i.e. the heat released from combustion of methane is sufficient to heat up the gas supplied to the catalyst to the ignition temperature of methane and the excess heat can be used for power generation purposes. A system consisting of a counter-flow tubular heat exchanger and a reactor is the most important part of the installation. The amount of methane removed from ventilation air and the amount of recovered heat can be increased by combining several such systems. The novelty of this work is operating a large installation, designed to remove methane from mine ventilation air with simultaneous heat recovery, studied under real conditions in a mine.

2. Materials and methods

2.1. Prototype of installation for oxidation of methane from ventilation air

A prototype of the installation for oxidation of methane from ventilation air was built near the Jas VI air shaft of the Jas Mos mine belonging to the Jastrzębska Spółka Węglowa SA [23]. This installation was designed by members of the Consortium to which AGH University of Science and Technology, Wroclaw University of Science and Technology and Maria Curie-Skłodowska University of Lublin belong.

While designing the installation we assumed that it would work continuously with the gas flow rates included in the range 3000–3500 $m^3 \cdot h^{-1}$ and allow getting up to 100 kW heat output. The installation should also work without additional heat from outside at low concentration of methane in the inlet gases. The installation works in the system under atmospheric pressure at low hydraulic resistance.

Fig. 1 presents the scheme of the installation. Methane from ventilation air taken by a tube from the outlet of Jas-VI shaft, after condensation of excess steam and removal of carbon dust in mechanical filters, passes through the fan regulating the flow rate through the system. Due to the variable and low content of methane in the ventilation air (0.1–0.3%), it is mixed with methane from the methane drainage network in the gas mixer. This protects the installation against fluctuations in methane concentration in mine ventilation air and allows examining its work at different fixed concentrations of methane in the air. Enrichment of the ventilation air in methane occurs when the concentration of methane in ventilation air taken from the mine and the required concentration of methane in the air supplying the installation differ from each other. Then the ventilation air is heated to the temperature required to initiate oxidation of methane on a catalytic bed by exhaust gases emerging in the reactor after combustion of methane, in a counter-flow tubular heat exchanger. A tubular heat exchanger of 6.6 m length and 0.71 m diameter and the heat exchange surface 180.8 m^2 is used.

The hot ventilation air with methane is introduced to a flow reactor, which contains two types of catalysts: a monolithic palladium catalyst on a heat-resistant foil and a palladium catalyst deposited on a granular Al_2O_3 ceramic support.

Hot exhaust gases from the catalytic reactor heat ventilation air before its entering the catalytic reactor in a counter-flow gas-gas heat exchanger. Next, the exhaust gases are introduced into a gas-water heat exchanger in which the remaining exhaust gas heat is used to heat water.

The installation can be controlled by a computer or manually from the installation control board panel. All the control parameters are automatically saved in the computer, which allows their archiving and graphical visualization of the work of individual elements of the installation during their work.

The installation includes technical measures disabling it in the event of its malfunctioning. Due to the used in the reactor construction materials, the temperature in the reactor should not exceed 650 °C. For safety