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Catalytic combustion of sulphur-containing methane lean emissions in a reverse-flow reactor with integrated adsorption

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HIGHLIGHTS

- Reverse flow reactor with integrated H_2S adsorption demonstrated experimentally.
- This device suppresses the effect of sulphur poisoning in methane combustion.
- Molecular sieve 5A is suitable for H_2S adsorption from methane lean gases.
- Adsorption equilibrium and packed-bed mass transfer determined.
- Parabolic temperature profile of the reactor enhances the adsorption/desorption.

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ABSTRACT

Lean methane emissions (0.15–0.5% CH_4) often contain low concentrations of sulphur compounds (e.g. H_2S). Regenerative catalytic oxidation is an efficient process for methane removal and upgrading of these streams, but the presence of sulphur compounds deactivates typical combustion catalysts. We propose in this work a new strategy for overcoming this problem, by using a reverse flow reactor provided with integrated adsorption beds. Therefore, it is possible to operate autothermically with low methane concentrations, as well as effectively separate the sulphur compounds before reaching catalytic bed. The working principle of this device has been experimentally demonstrated in a bench-scale reactor working at conditions typical for industrial emissions (GHSV = 1146 h^{-1}, 4300 ppm CH_4, 100–500 ppm H_2S). It has been found that molecular sieve 5A is a suitable adsorbent for this device. The influence of the main reverse flow reactor variables, switching time (200–400 s) and methane feed concentration (4000–4500 ppm), on the performance of the process has been studied. The integrated adsorption performs better at switching time 400 s, while methane concentration has negligible influence, provided that the reactor is maintained ignited.

1. Introduction

Methane lean emissions are released in many industrial activities, such as coal mines, natural gas distribution systems, coke ovens, landfills, wastewater treatment plants, etc. [1]. As a result, the global atmospheric concentration of methane has increased from a pre-industrial value of about 0.7 up to 1.8 ppm in late 2014 [2]. Methane is a powerful greenhouse gas, with a global warming potential 25 times greater than that of carbon dioxide [3]. For this reason, the combustion of anthropogenic methane to carbon dioxide before being released to the atmosphere is of great environmental interest.

The International Panel for Climate Change (IPCC) recommends two main strategies for mitigation of greenhouse gas emission from the waste sector (e.g. landfills): the enhancement of landfill methane recovery and utilization, and the optimization of methanotrophic methane oxidation in landfill cover soils and biofilters. The first strategy is the one considered in the present work [4,5]. Traditional landfill gas recovery technology may become less effective on future landfills, due to sites receiving mechanically-biologically pre-treated wastes with low gas generation potential [3]. The current EU Waste Framework Directive (2008/98/EC) encourages waste separation at source and biological treatment [6].

In the present work, the use of regenerative catalytic oxidation in reverse flow reactors is proposed for the treatment of methane lean emissions, which, due to their low energy density, are unsuitable for use in traditional valorisation technologies, such as gas

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turbines or engines [7,8]. The high thermal efficiency of regenerative catalytic oxidation allows the autothermal operation (without an external fuel or heat source), even for methane concentrations as low as 1500 ppm [9–11].

Conventional catalytic reverse flow reactor (RFR) consist of a packed bed formed by three successive layers of material (inert, catalyst and inert). The gas feed is introduced at ambient temperature and heated above ignition temperature by heat transfer from the inert beds. The feed flow direction is periodically reversed to trap heat inside the beds and maintained the reactor ignited. This reactor configuration has been proposed and experimentally tested for the treatment of methane lean emissions [12–16].

In many cases, emissions containing methane or other organic compounds contain also sulphur compounds (e.g. hydrogen sulphide, sulphur dioxide, etc.). Thus, natural gas can contain up to 5% H_2S before treatment, coke oven gas an average 0.3% H_2S [17], and in biological processes (landfills and water treatment plants) concentrations as high as 1% are also found, depending on the nature of the organic materials [18–20].

The presence of sulphur compounds in such emissions, even at low concentration, is an important problem for catalytic oxidation. Thus, it is well-known that most oxidation catalysts (based on Pd, some metal oxides like MnO_2, etc.) suffer important poisoning from sulphur compounds [21,22]. To overcome this issue, the reverse flow reactor with integrated separation, introduced by Bos et al. [23], is proposed here for the combustion of lean emissions containing sulphur compounds. The novelty of the present work is to extend this reactor concept to the separation of sulphur compounds, so that these compounds are prevented from reaching the catalyst.

Hydrogen sulphide will be used as model compound, since it is the sulphur compound most widely present, and at higher concentrations, in these emissions, but the process can be easily adapted to other sulphur compounds, by selecting the appropriate adsorbent and process conditions. The organic compound to be treated is methane, present very frequently in emissions, and one of the most difficult organic compounds to react, so most organic compounds will be destroyed at the conditions at which methane combusts.

In order to accomplish these scopes, an appropriate adsorbent material for hydrogen sulphide separation was firstly selected and tested at laboratory scale. The adsorption equilibrium and mass transfer were measured experimentally and modelled. Then, the working principle of the reverse flow reactor with integrated adsorption was experimentally demonstrated in a bench-scale device. Finally, the influence of the main operational variables on the performance of the reactor was studied.

2. Materials and methods

2.1. Materials

High purity gaseous reactants (0.5% vol. H_2S in nitrogen and 2.5% vol. CH_4 in air) were provided by Air Liquide, and air was supplied by a compressor equipped with a drying unit.

A commercial 5A molecular sieve (0.8 K_2O: 0.2 Na_2O: 1 Al_2O_3: 2.0 SiO_2: x H_2O) supplied by Sigma–Aldrich and shaped in pellets (diameter 3.3 mm, length 7 mm) was used as adsorbent. Its particle density, 1156 kg/m^3, and bed packing porosity, 43.2%, were measured experimentally. BET surface area and pore volume of the adsorbent, measured by nitrogen physisorption, are 436 m^2/g and 0.220 cm^3/g, respectively. Most of the surface area and pore volume of the material correspond to micropores: t-Plot micropore area, 403 m^2/g, and t-Plot micropore volume, 0.187 cm^3/g. This adsorbent is claimed by the supplier to be appropriate for the adsorption of hydrogen sulphide. Other commercial adsorbents (alumina and titania) were considered, but were discarded after observing that hydrogen sulphide reacted on them, forming sulphur dioxide and sulphur.

The catalyst used was a commercial mixed-oxide catalyst ($CuO–MnO_2/Al_2O_3$) supplied by Haldor-Topsoe as spheres of 4.2 mm diameter, with particle density 2162 kg/m^3 and bed packing porosity 53.7%. This catalyst, studied in a previous work [24], was found to be active for methane combustion and stable at high temperature (500–600 °C).

2.2. Experimental device

The adsorption of hydrogen sulphide in the molecular sieve 5A was studied first in a lab-scale fixed bed. The device consisted of a stainless steel tube of 0.009 m inside diameter and 0.440 m length. A weight of $0.3 \cdot 10^{-3}$ kg of adsorbent, grounded and sieved to 355–710 μm, was mixed with $0.3 \cdot 10^{-3}$ kg of 355–710 μm glass particles and introduced inside the tube. This bed was set in position using stainless steel foil. Upstream, the tube was filled with 1 mm glass spheres to achieve uniform gas flow and heating. The geometry of this bed is adequate to minimize axial dispersion and channelling: bed diameter/particle diameter = 17 > 10. Hence, a gas flow pattern close to plug flow inside the tube can be assumed. The external surface area of the adsorbent particles in this bed was estimated as 6580 m^2/m^3_{bed}.

Isothermal conditions were obtained by a temperature-controlled electric furnace. Temperature measured by a thermocouple placed inside the tube was used as set point of the controller.

The feed was prepared by mixing hydrogen sulphide-air synthetic mixture and air from the compressor in adequate proportions. The gas flow rate was measured and controlled by BRONKHORST mass-flow controllers. The concentration of the influent and effluent were analysed using a quadrupole mass spectrometer, PFEIFFER VACUUM OMNISTAR. This device analyses hydrogen sulphide every few seconds with a precision of ±1%. For each experiment, the device was re-calibrated to ensure reliable quantitative measurements.

A second experimental device, a bench-scale unit, was used for studying the adsorption of hydrogen sulphide in commercial-sized adsorbent particles (un-grounded), and the operation of the reverse-flow reactor with integrated adsorption. The piping and instrumentation diagram is depicted in Fig. 1. The reactor feed was prepared by mixing hydrogen sulphide-air and methane-air mixtures, as required, with air in adequate proportions. Gas flow rates were measured and controlled by BRONKHORST mass-flow controllers (FIC 01 to 03).

The reactor consisted of a stainless steel flanged tube of 0.050 m inside diameter and 0.700 m length. The tube housed a packed bed 0.400 m long, which was kept in place by means of a stainless steel support. The temperature of the gas inside the tube was measured in 7 positions along the axial coordinate by means of an array of thermocouples fixed to a stainless steel rod (TT 1-7). The tube was surrounded by an oven formed by 7 sections capable of heating (using electrical resistances) and cooling (using a flow of cold air from a blower) independently. This oven is designed to compensate radial heat losses from the tube in order to ensure near-adiabatic conditions. To accomplish this goal, the temperature inside the reactor is measured (TT 1-7) and passed as set-point to a set of controllers by a programmable logic controller (PLC 01). The controllers (TIC 01 to 07), feedback PID, act on the electrical resistances and control the temperature of the air in the oven section. Further details about the operation and performance of the compensating oven are given elsewhere [25,26].