



A novel ZnO-based adsorbent for biogas purification in H₂ production systems

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ABSTRACT

The aim of this work, which was carried out as part of the BioH2Power project, was to identify a system for both the desulphurization and dehalogenation of landfill biogas at ambient temperature. Such a system should be capable of reducing, to less than 1 ppmv, the substances that are present in the biogas which are considered undesirable for both reforming and Molten Carbonate Fuel Cell (MCFCs) catalysts. The principal goal was to identify a multifunctional adsorption bed that would be able to purify the landfill biogas to sulphur and chlorine concentrations of below 1 ppmv, with a high removal efficiency (>99%). Two commercial activated carbons types were studied for this purpose. In addition, for the first time, activated carbon, functionalized by ZnO nanoparticles, was tested at ambient temperature for the simultaneous removal of H₂S and organochlorinated molecules. The biogas desulphurization results have shown that the 10% ZnO/ROZ3 synthesized material has a higher adsorption capacity than the commercial activated carbon material ROZ3, for H₂S removal, due to the presence of well dispersed ZnO nanoparticles on the surface of the activated carbon. Moreover, the biogas dehalogenation results confirm that the use of two adsorbent beds in series: RB4W + ZnO/ROZ3, is a good solution because not only does the removal capacity of H₂S remain but also because it improves the performance of the abatement of high molecular weight halogenated hydrocarbons.

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1. Introduction

Biogas is a valuable renewable energy carrier. It can be exploited directly as a fuel or as a raw material for the production of syngas and/or hydrogen. Biogas is principally composed of methane (CH₄) and carbon dioxide (CO₂), but, depending on its source (i.e., landfills, anaerobic digestion plants), it can also contain significant quantities of undesirable contaminant compounds, such as hydrogen sulphide (H₂S), halogenated hydrocarbons, ammonia (NH₃) and siloxanes. Their presence constitutes a major problem because (i) during the combustion process in thermal or thermo-catalytic conversion devices, hydrogen sulphide and halogenated compounds form corrosive acids, such as H₂SO₄, HCl and HF [1] and (ii) they generate harmful environmental emissions. It is therefore important to include biogas purification steps upstream from its final use processes.

The most frequently used technology for the purification of biogas produced by the fermentation of manure and small-to-medium landfills from sulphur species and volatile organic compounds is adsorption [2]. The removal of H₂S to ultra low concentrations is principally obtained with solid adsorbents at high temperatures,

ranging from 200 to 800 °C. Different sorbents like copper, iron, aluminium, zinc and titanium oxides, and their mixtures have been developed for this purpose [3,4]. Due to the high operative and investment costs of high temperature processes, which diminish the advantages of using a renewable fuel, the use of a low temperature purification systems is more appropriate. Low temperature processes for the removal of sulphur species from gaseous streams also exist, but in general these are low sulphur capacity processes. Moreover, some methods such as gas–liquid absorption, which usually uses amine solutions, are also used at a high scale, but offer the disadvantage of producing secondary contaminated waste water streams [3]. Activated virgin and impregnated carbons (ACs) are highly specific surface area adsorbents which are also well-known for their capacity to remove H₂S and volatile organic compounds at low temperatures [5–7]. However, these systems have low capacities that require large volumes of carbon beds which need to be replaced frequently and, in general, impregnated ACs are non-regenerable, and lead to secondary waste stream problems [8]. Therefore, the development of more efficient adsorbent materials that are able to remove all the injurious compounds present in biogas and which work at low temperatures (30–200 °C) is necessary.

The aim of this work, which was carried out as part of the BioH2Power project, was to identify a purification system for MSW landfill biogas [9]. Such a system should be capable of reducing, to less than 1 ppmv, the substances present in the biogas that are

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undesirable for both reforming and Molten Carbonate Fuel Cell (MCFCs) catalysts. This research work has focused on the study of biogas purification adsorption materials for the removal of both sulphur and halogenated compounds, at ambient temperature (25 °C). Our principal goal was to identify a multifunctional adsorption bed that would be able to purify the landfill biogas, with sulphur and chlorine concentrations below 1 ppmv, with a high removal efficiency (>99%). Two commercial activated carbons types were studied for this purpose. In addition, for the first time, an activated carbon, functionalized with ZnO nanoparticles, was tested at ambient temperature for the simultaneous removal of H₂S and organochlorinated molecules.

2. Experimental

2.1. Adsorbent materials

Two different commercial activated carbons, purchased from NORIT, were tested: Norit ROZ3 and Norit RB4W. The former is an impregnated AC (with a KI concentration of between 2 and 5 wt%) which is specifically used for the removal of hydrogen sulphide. The latter, instead, is a virgin AC, which is specifically used for halogenated compound removal. In addition, zinc oxide, supported on activated carbon ROZ3 (ZnO/ROZ3), was synthesized in our labs. This material was also used to remove sulphurated compounds. A comparison between the ZnO-supporting ROZ3 material sample and the non-supporting one was made. The adsorbents were pelletized to obtain a grain size of between 250 and 425 μm.

2.2. ZnO/AC synthesis

The adsorbent material AC ROZ3 supporting 10 wt% of ZnO was synthesized by means of the precipitation method. Zn(NO₃)₂·6H₂O and NaOH, purchased from Sigma Aldrich, were used as precursors and dissolved in ID water to obtain a 0.4 M and 1 M solution, respectively. 150 ml of the sodium solution was mixed with 250 ml of zinc nitrate solution until a homogenous solution was obtained. The support (54 g ROZ3) was then added and agitation was kept constant at ambient temperature for 30 min, in order to induce the precipitation of Zn(OH)₂ [10]. After this, the solution was heated to a reflux temperature of 80 °C and aged for 60 min. Next, the material was washed with ID water using a milipore vacuum filter system. The final material was calcined at 150 °C for 2 h, in order to allow the complete formation of ZnO without any activated carbon alteration.

2.3. Characterization of adsorbents

X-ray diffraction analyses were carried out by means of a PW3830 Philips diffractometer to verify the formation of ZnO on the support. Surface area and pore size distribution analyses were carried out by means of a Micromeritics ASAP 2020 BET analyzer. The microporosity distribution of the material was calculated using the Density Functional Theory Model: N₂ @ 77 K on carbon, slit pores. The morphology of the synthesized material was observed using a ZEISS Supra 40 Field Emission Scanning Electron Microscope (FESEM), equipped with standard and dedicated secondary (IN-LENS) and backscattered (Solid State) electron detectors, and a Oxford energy dispersive X-ray detector. The XPS spectra were recorded, over fresh and used samples, using a PHI5000 Versa Probe with a scanning ESCA microscope fitted with an X-ray source of Al monochromatic (1486.6 eV, 25.6 W), a beam diameter of 100 μm, a neutralizer at 1.4 eV 20 mA, and a FAT analyzer mode. All the binding energies were referenced to the C1s peak at 284 eV of the surface adventitious carbon.

2.4. Desulphurization and dehalogenation tests

The composition of the real biogas produced at the Montescarpino MSW landfill in Genoa (Italy) was taken as a reference for this work. The adsorption tests were focussed on the removal of the high concentration contaminant compounds which were present in landfill biogas: hydrogen sulphide and organochlorinated species [8]. The complete system, reported in [8], involves that the biogas conveyed from the substations passes through a first purification section made up of: a primary coalescer, where a first separation of the condensate takes place; a heat exchanger, with a glycol solution circuit connected to a chiller that brings the gas temperature down to approximately 0–4 °C; a secondary condensate separator; a dry filter to partially remove residual solids. After this treatment, the biogas, which is now at a lower temperature and purified of macroscopic pollutants (particles, acid gases, ammonia and humidity), passes through a multistage centrifuge blower and is conveyed to the desulphurization and dehalogenation beds.

A schematic diagram of the used lab test-rig is reported elsewhere [8]. Three different gaseous mixtures that simulate the principal contaminants present in the real biogas, were used for the tests at ambient conditions (28 °C, 1 atm). Desulphurization experiments were carried out using H₂S, with a similar concentration to the maximum value found in the reference biogas (nearly 200 ppmv), diluted in nitrogen (N₂) gas. Instead, for the dehalogenation tests, a mixture containing eight different organochlorinated hydrocarbons, diluted in CO₂, CH₄ and N₂ (see Table 1), was used in order to reproduce a total chlorine concentra-

Table 1
Composition of the simulated biogas used for desulphurization and dehalogenation tests.

Compound	Model biogas for dehalogenation test	Model biogas for desulphurization tests	Model biogas for multifunctional bed test
	Concentration (ppmv Cl)		
Chloromethane	8.4	–	8.4
Chloroethane	6.7	–	6.7
1,3-Dichloroprop-1-ene (cis)	3.8	–	3.8
1,3-Dichloroprop-1-ene (trans)	3.9	–	3.9
1,1,1-Trichloroethane	3.2	–	3.2
1,1,2-Trichloroethane	2.7	–	2.7
Trichloroethene	3.3	–	3.3
1-Chlorobutane	4.5	–	4.5
Total Cl	64.9	–	64.9
H ₂ S (ppmv S)	–	190.1	190.1
CH ₄	25%	–	25%
CO ₂	25%	–	20%
N ₂	Balance gas	Balance gas	Balance gas

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