

Removal of sulphur-containing odorants from fuel gases for fuel cell-based combined heat and power applications

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Abstract

Natural gas (NG) and liquefied petroleum gas (LPG) are important potential feedstocks for the production of hydrogen for fuel cell-based (e.g. proton exchange membrane fuel cells (PEMFC) or solid oxide fuel Cells (SOFC) combined heat and power (CHP) applications. To prevent detrimental effects on the (electro)catalysts in fuel cell-based combined heat and power installations (FC-CHP), sulphur removal from the feedstock is mandatory. An experimental bench-marking study of adsorbents has identified several candidates for the removal of sulphur containing odorants at low temperature. Among these adsorbents a new material has been discovered that offers an economically attractive means to remove TetraHydroThiophene (THT), the main European odorant, from natural gas at ambient temperature. The material is environmentally benign, easy to use and possesses good activity (residual sulphur levels below 20 ppbv) and capacity for the common odorant THT in natural gas. When compared to state-of-the-art metal-promoted active carbon the new material has a THT uptake capacity that is up to 10 times larger, depending on temperature and pressure. Promoted versions of the new material have shown potential for the removal of THT at higher temperatures and/or for the removal of other odorants such as mercaptans from natural gas or from LPG.

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1. Introduction

Natural gas (NG) and liquefied petroleum gas (LPG) are important feedstocks for the production of hydrogen for fuel cell-based (e.g. proton exchange membrane fuel cells (PEMFC) or solid oxide fuel cells (SOFC) combined heat and power (CHP)

applications. In densely populated areas, natural gas is a widely applied fuel for residential applications. For less inhabited areas and for leisure applications, LPG is the fuel of choice. LPG consists of a mixture of propane (s) and butane (s) in various ratios, depending on country and season. It is a versatile fuel that is used widely in de-centralised applications like heating (residential, industrial, agriculture, leisure, etc.). This broad range of applications is important for the development of the market for LPG-fuelled and fuel cell-based power and CHP applications.

A typical fuel cell-based CHP application may consist of several unit process steps [1–3] such as fuel pre-treatment (e.g. cleaning and preheating), catalytic partial oxidation or (steam or autothermal) reforming, high and/or low temperature water–gas shift, preferential CO oxidation (PROX), fuel cell and off-gas treatment in the afterburner. Fig. 1 presents a schematic drawing of a natural gas fuelled PEMFC-based CHP installation.

Natural gas and LPG contain sulphur components, either naturally occurring, or added deliberately as odorant. In cases where the fuel gas is to be used for residential purposes, naturally occurring sulphur species are first removed before adding (organo) sulphur compounds to odourise the otherwise odourless

Abbreviations: NG, natural gas; SNG, simulated natural Gas; LPG, liquefied petroleum gas; PEMFC, proton exchange membrane fuel cell; SOFC, solid oxide fuel cell; FC-CHP, fuel cell-based – combined heat and power; CPO, catalytic partial oxidation; WGS, water–gas shift; PROX, preferential oxidation (of CO); HDS, hydro desulphurisation; GC, gas chromatography; FPD, flame photometric detector; THT, tetrahydrothiophene; DMS, dimethyl sulphide; TBM, tertiary butyl mercaptan; EM, ethyl mercaptan; S, sulphur; NGDMI, natural gas desulphurisation material 1; BET, brunauer–emmett–teller (specific surface area); ppbv, parts per billion on volume basis; ppmv, parts per million on volume basis; ppmw, parts per million on weight basis; ppm, parts per million on a molar basis; vol.%, volume %; Mol.wt., molecular weight; bara, bar (absolute); barg, bar (gauge); US, United States; UK, United Kingdom; EC, European Commission

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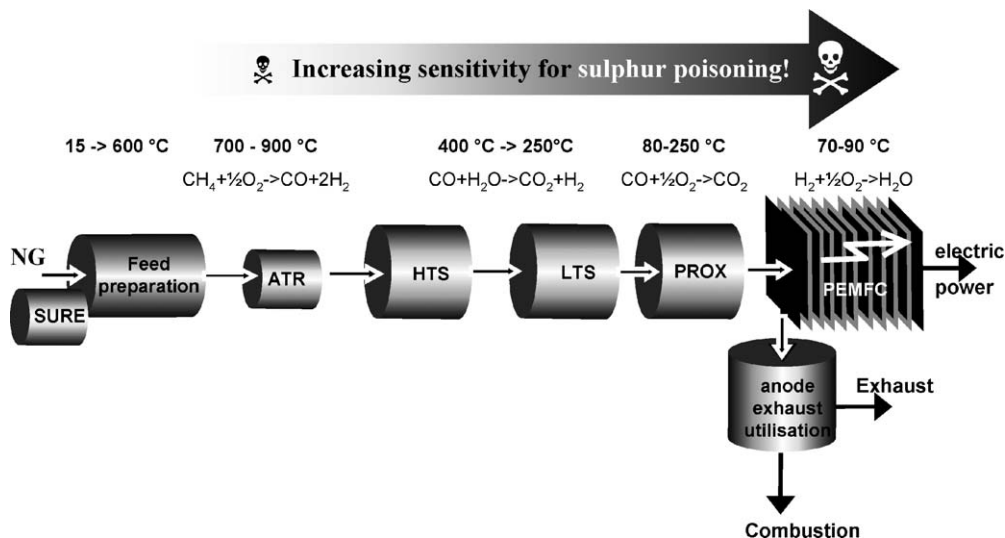


Fig. 1. PEMFC-CHP installation scheme.

gas. This is a legislated practice in order to be able to detect the gas by its scent in case of leaks. Typical sulphur containing odorants are TetraHydroThiophene (THT), mercaptans, like tertiary butyl mercaptan (TBM) and ethyl mercaptan (EM), and organic sulphides such as dimethylsulphide (DMS) or mixtures thereof. In The Netherlands, and in most of Europe, THT is used to odorise natural gas. In the United States and Japan, natural gas is commonly odorised with mercaptans and sulphides or with mixtures thereof. LPG is often odorised with ethyl mercaptan (EM). These sulphur containing components present in the fuel processor fuel, are likely to be converted to H_2S in the fuel processor section of the hydrogen generating system.

To prevent detrimental effects on the catalysts in a typical fuel cell-based combined heat and power installation, sulphur removal from the feedstock is mandatory. The sulphur removal task for LPG is more challenging than it is for natural gas. Propane, butane and heavier hydrocarbons are potential competitors for the sulphur compounds for adsorption sites, decreasing the adsorption capacity. Sulphur levels in LPG can be much higher when compared to natural gas; in the US levels can be as high as 120 ppmw. In Europe levels are generally less than 50 ppmw (EC legislation), depending on country of use and origin of the LPG.

From literature an ambiguous picture emerges on the sulphur tolerance of typical fuel processing catalysts. In general it seems that – due to the high operating temperature – low amounts of sulphur (typically below 10 ppm) do not seem to be a problem for platinum group metal based partial oxidation [4], autothermal reforming [5], or steam reforming [6] catalysts. This means that if sulphur removal is allowed to occur after CPO or autothermal reforming, the gas stream will be at elevated temperatures, which could enhance the opportunities for removing sulphur. While high temperature FeCr-based shift catalysts are not particularly susceptible to low levels of sulphur, low temperature CuZn-based shift catalysts are easily poisoned by even very low levels of H_2S [7]. Information on the sulphur

tolerance of alternative (e.g. noble metal based) shift catalysts or on the susceptibility of catalysts for the preferential oxidation of carbon monoxide is scarce. Considering the composition of PrOx catalysts and new generation WGS catalysts, it seems reasonable to assume that they will be poisoned by low levels of sulphur as well.

For the PEMFC it can be stated that sulphur compounds such as H_2S already at (sub) ppm levels lead to a significant degree of coverage on fuel cell anodes and that this coverage will poison its capability for oxidizing hydrogen, thus leading to lower fuel cell performance in terms of power output and cell efficiency. For PEMFC-based CHP installations the temperature level in the whole system is the lowest in the PEMFC itself and due to its catalytic composition, the influence of H_2S is expected to be largest of the PEMFC. Uribe and Zawodzinski of Los Alamos National Laboratory assessed the effect of fuel impurities on PEM fuel cell performance [8] using a PEMFC with a Pt/C anode. They found that concentrations as low as 0.2 ppmv H_2S adversely affect the performance of the fuel cell.

The effect appears to be cumulative and causes severe deterioration of the fuel cells' performance. Regardless H_2S concentration and running time, replacing the contaminated fuel stream with pure H_2 does not allow any recovery.

With respect to SOFC applications, Cunningham et al. [9] determined the sulphur tolerance of a reforming catalyst and two fuel cell anode formulations of the Rolls-Royce Integrated Planar Solid Oxide Fuel Cell. Both the reforming catalyst and the SOFC anodes suffered rapid and severe deactivation with H_2S concentrations similar to the sulphur content of UK natural gas (16 mg m^{-3}) of a mixture of ethyl mercaptan and diethyl sulphide. The susceptibility increases with sulphur concentration, but the safe concentrations of sulphur that result in little or no deactivation are far lower than the concentrations typically found in natural gas throughout Europe. To keep degradation due to sulphur poisoning at an economically sensible level, sulphur concentrations on ppbv level may be required at the fuel cell inlet.

As discussed above, the susceptibility of both fuel processing as fuel cell (anode) materials towards sulphur poisoning shows a clear need for desulphurisation of the fuel to be included in the fuel cell system. Hydro-desulphurisation (HDS) of the (organic) sulphur compounds, followed by scavenging the resulting H_2S on ZnO is the state of the art industrial sulphur removal technology [7]. However, HDS is not an attractive option for fuel cell systems, especially for relatively small-scale systems, since it requires high pressure, hydrogen, elevated temperatures and a complex (thermal) integration into the system. In addition, commercial – elevated temperature – adsorbents for sulphur contain heavy metals – often toxic, – requiring specific handling procedures according to guidelines for the use of hazardous substances. An ambient adsorption would be the preferred technology in view of system simplicity and costs. Although heavy metal activated low-temperature adsorbents are used, a wide choice exists in relatively harmless materials without toxic metals. Porous adsorbents like active carbons, zeolites or molecular sieves are candidates for ambient temperature sulphur removal technology [10]. Unfortunately, the use of low temperature adsorbents can be quite cumbersome and costly because of their relatively low capacity for sulphur. A large amount of adsorbent material may preclude its use as a sulphur filter for a CHP installation, because of size, weight and economic (material costs) constraints. Another drawback can be the adsorptive accumulation of toxic organic compounds from the fuel gas matrix (e.g. aromatics). Although the choice for a specific desulphurisation technology depends on many factors, the large scale aimed application of small-scale micro-combined heat and power primarily asks for a cost-effective desulphurisation technology that is simple to use without significant environmental objections. Within this scope this article describes the results of an extensive screening and testing programme of several low temperature adsorbents for their potential to desulphurise natural gas and LPG for fuel cell-based CHP applications.

2. Experimental

2.1. Experimental assessment sulphur tolerance of the PEMFC

The effect of 0.2 and 2 ppm H_2S in H_2 on the performance of a PEMFC with a 1:1 Pt:Ru containing anode has been investigated. Taking into account the dilution in the fuel processor by air, steam and expansion by conversion, a gas feed containing 5 ppmv of THT would lead to reformat containing approximately 1 and 2 ppm of H_2S when entering the fuel cell assuming no sulphur is scavenged in the fuel processor itself. The PEMFC voltage is monitored at a constant current density of 0.4 A cm^{-2} upon exposure to 0.2 and 2 ppm H_2S in H_2 . Cell temperature amounts to 65°C and gases are supplied at 1.5 bara. Anode and cathode contain 0.4 mg cm^{-2} PtRu and 0.4 mg cm^{-2} Pt, respectively. Only the cathode is humidified at 65°C . Nafion 112 has been taken as the proton exchange membrane. Exposure of the anode to H_2S starts after 24 h.

2.2. Benchmarking adsorbents for THT removal from natural gas

To identify potential adsorbent candidates for the removal of THT from natural gas, an experimental bench-marking study of several adsorbent materials has been conducted. The work focusses mainly on a functional screening of a number of adsorbents for their desulphurisation potential. An extensive physical characterization of the selected materials is therefore beyond the scope of this study. All adsorbents are commercially available and were selected from an extensive literature survey on materials for low-temperature desulphurisation. The materials have been tested as received from the supplier with commercial Dutch (North-Sea) natural gas under ambient conditions. Some adsorbents were also screened at 40°C . This higher temperature level was taken in view of potential system requirements. Considering system compactness and safety in case of gas leaks, the sulphur filter should be located inside the same housing as the – heat generating – fuel processor, and, consequently, be operated at slightly higher temperatures (e.g. at $30\text{--}40^\circ\text{C}$) than ambient. Table 1 contains an overview of the tested adsorbents, some of their physical properties, the composition of the feed gases and the test conditions of the conducted adsorption experiments.

2.3. Pilot-scale field test THT removal from natural gas at an industrial client

At a site of an industrial client, a 150 kW_e fuel processor has been operated with Dutch natural gas (see Table 1 for the composition) as feed (approximately $1 \text{ Nm}^3 \text{ min}^{-1}$ at full power). For this pilot-scale field test, a 60 l tubular filter bed has been filled with the NGDM1 adsorbent of an average particle size of 3 mm. Except for this slightly larger particle size, the physical characteristics are the same as those reported in Table 1. The adsorbent bed is operated at different throughputs and due to restrictions, at different operation pressures. The operation window of the adsorption bed is 2–8 barg. The adsorption bed is installed outdoor and therefore the operation temperature can vary from -10 to 30°C . At 1/3 and 2/3 of the bed length (maximum 200 cm), THT concentration can be monitored by means of an electrochemical THT detector (Odor Handy, manufactured by Axel Semrau, Germany). The filter bed of NGDM1 is exchanged when THT concentrations at 2/3 of the bed length exceed the detection limit (approximately 0.25 ppmv) of the THT detector. Upon exchange of the saturated bed of NGDM1, samples are taken at different bed heights to determine the loading of THT as function of the axial location in the bed. In the laboratory, these samples are destructed by wet chemical techniques, after which sulphur is determined by ICP. Fig. 2 presents a photograph of the experimental set-up with the 60 l filter tube.

2.4. Other odorants in natural gas and liquefied petroleum gas

Next to THT, the removal of other frequently used odorants from natural gas and LPG by low temperature adsorbents has been explored. Table 2 contains the structural formulae and some

Table 1
Tested adsorbent samples and general test conditions lab-scale experiments

Tested adsorbent materials			Physical characteristics				Test conditions	
Type of material	Code	Supplier	Shape	Size (mm)	BET area (m ² g ⁻¹)	Pore volume (ml g ⁻¹)	Feed gas	Temperature (°C)
Transition metal impregnated active carbon	RGM1	Norit b.v.	Cylindrical extrudate	1	1300	0.7	THT in NG	10
							THT in NG	Ambient
							THT in NG	40
							DMS/TBM in SNG	40
Non-impregnated active carbon	RB1	Norit b.v.	Cylindrical extrudate	1	1100	0.5	THT in NG	Ambient
							CuO/ZnO/alumina	R-12
Promoted nickel on oxide carrier	R-20	BASF	Cylindrical extrudate	1	280	0.4	THT in NG	Ambient
Promoted alumina	SAS6	Alcoa	Cylindrical extrudate	1	200	NA	THT in NG	10
							THT in NG	Ambient
							THT in NG	40
Zeolite	TOSPIX 94	Tokyo Gas	Cylindrical extrudate	1.5	700	0.4	THT in NG	10
							THT in NG	Ambient
							THT in NG	40
							DMS/TBM in SNG	40
							EM in LPG	40
Molecular sieve	13X	Aldrich	Cylindrical extrudate	1	540	0.3	THT in NG	Ambient
							EM in LPG	40
Natural gas desulphurisation material	NGDM1	SulphCatch b.v.	Particles	0.5–2	275	0.4	THT in NG	10
							THT in NG	Ambient
							THT in NG	40
							THT in NG	60
							DMS/TBM in SNG	40
							EM in LPG	40
X-promoted NGDM1			Particles	0.5–1	NA	NA	THT in NG	40
							DMS/TBM in SNG	40
							EM in LPG	40
Y-promoted NGDM1			Particles	0.5–1	NA	NA	THT in NG	40
							DMS/TBM in SNG	40
							EM in LPG	40
Y-NGDM1 + NGDM1 (6/4, v/v)			Particles	0.5–1	NA	NA	THT in NG	40
							EM in LPG	40

Reactor feed gas compositions

NG: North-sea natural gas (vol.%): 78.4 CH₄, 4.13 C₂H₆, 0.95 C₃H₈, 0.3 C₄H₁₀, 0.04 C₅H₁₂, 0.05 C₆H₁₄, 13.8 N₂, 2.21 CO₂, dewpoint –20 °C, THT content 18 mg m⁻³ at ntp (approximately 4.5 ppmv)

SNG: simulated natural gas (vol.%): 80.3 CH₄, 2.8 C₂H₆, 0.4 C₃H₈, 0.1 C₄H₁₀, 15.5 N₂, 0.9 CO₂, DMS content 1.4 ppmv, TBM content 4 ppmv

LPG: liquefied petroleum gas (vol.%): Approximately 70 propane and 30 butane (*n*- and *iso*-), EM content approximately 30 ppmv

Packed-bed reactor conditions

Parameter	Ambient temperature reactor	Temperature controlled reactor
Inlet pressure (bar (gauge))	0.1	0.1
Outlet pressure	Atmospheric	Atmospheric
Feed gas flow rate (l min ⁻¹)	3	0.5
Reactor diameter (mm)	25	15
Packed-bed height (mm)	150	60
Packed-bed sample volume (ml)	70	10
Packed bed weight sample weight (g)	30–70	4–10
Gas analysis	Gas chromatograph equipped with flame photometric detector hand-held electrochemical THT sensor	

physical and chemical characteristics of THT and the other odorants that have been used in this study.

A transition metal impregnated active carbon, a zeolite, NGDM1 and two promoted NGDM1 adsorbents have been tested for their potential to adsorb a mixture of DMS and TBM from simulated natural gas at 40 °C. Information on these adsor-

bents, the composition of the feed gas and the applied test conditions can be found in Table 1.

From literature and from the results of the adsorbents-benchmarking for natural gas, a zeolite, the NGDM1 adsorbent, two promoted versions of NGDM1 and a combination in series of a promoted NGDM1 and the non-promoted adsorbent were

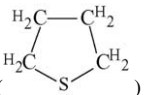
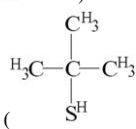
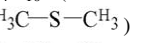
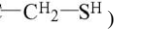


Fig. 2. Industrial scale desulphurisation filter for natural gas.

selected to assess their potential for LPG-desulphurisation at 40 °C. The adsorption tests have been conducted with commercial LPG from LP-gas containing ethyl mercaptan (EM) as the odorant (see Table 1 for information on these materials, the feed gas and the applied test conditions). The liquid-feed was vaporized, prior to submitting it to the fixed-bed reactor.

Adsorption tests were carried out in a lab-scale flow rig, equipped with fixed-bed tubular reactors, a liquid LPG feed line and LPG-vaporizer and a gas chromatograph with a flame-photometric detector for analysis of sulphurous components in the gas. Fig. 3 gives a schematic drawing of the flow rig. Table 1 presents an overview of all the tested adsorbent materials, the general test conditions that have been applied and the composition of the reactor feed gases.

Table 2
Characteristics of some common odorants for natural gas and LPG

Name and structural formula of the odorant	Physical and chemical characteristics		
	Mol. wt. [11]	Boiling point (°C) [11]	Vapour pressure (mbar at 20 °C)
Tetrahydrothiophene (THT), C ₄ H ₈ ()	88.17	121.1	19.3 [12]
Tertiary butyl mercaptan (TBM), C ₄ H ₁₀ S ()	90.18	64.2	190 [13]
Dimethylsulphide (DMS), C ₂ H ₆ S ()	62.13	37.3	532 [12]
Ethyl mercaptan (EM), C ₂ H ₆ S ()	62.13	35	590 [12]

3. Results and discussion

3.1. Sulphur tolerance of the PEMFC

Fig. 4 shows that exposing the fuel cell to the 2 ppm H₂S containing anode gas leads to an – almost instantaneous – and drastic decrease in performance. In about 65 h the performance of the fuel cell dropped to 50% of the original value. Recovery of the performance with pure hydrogen appeared to be impossible, while exposing the anodes to air during several minutes caused a significant restoration of the original performance (>90%). Anode gas containing 0.2 ppm H₂S does not lead to such a drastic performance loss during an exposure time of 100 h. However, after 400 h time-on-stream, the performance of the PEMFC is 20% lower when compared to the original activity. Comparing these results to those presented by Uribe and Zawodzinski [8] on Pt/C leads to the conclusion that the use of PtRu anodes does not lead to a lower sensitivity for H₂S, although it might be helpful for catalysing the recovery.

3.2. Benchmarking adsorbents for THT removal from natural gas

Fig. 5 presents an overview of the breakthrough curves at ambient temperature for removal of THT from odourised natural gas from the local grid. Adsorbent characteristics and experimental conditions can be found in Table 1. The outlet THT concentration in the purified natural gas has been plotted as a function of filtered natural gas per litre of the adsorbent material in the reactor. This amount is directly proportional to the uptake of THT by the adsorbent. Instead of using the full sulphur uptake capacity of the adsorbent, a breakthrough criterion for THT has been set at 0.1 ppmv S. This sulphur level would eventually lead to a sulphur content in a final reformat of less than 20 ppb. When the sulphur slip exceeds this criterion, replacement of the filter is necessary to prevent the downstream located fuel processing catalysts from exposure to even low sulphur levels. For all samples that have been tested, the pre-breakthrough concentration of the odorant appeared to be below the detection limit of the flame photometric detector of the GC (<20 ppbv).

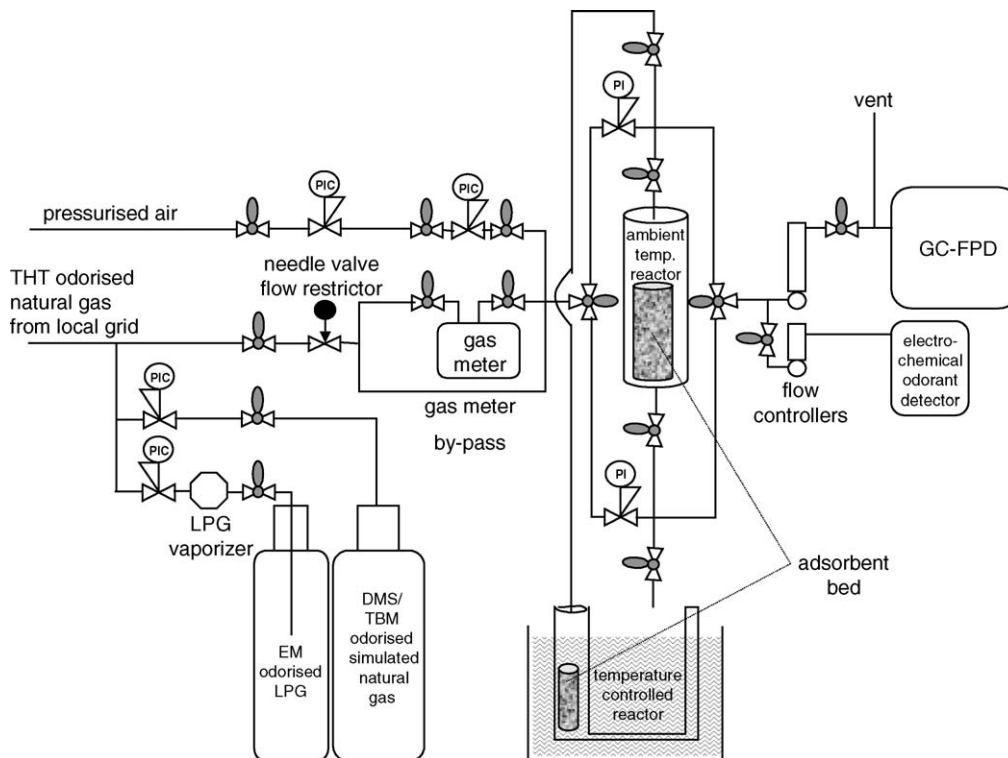


Fig. 3. Schematic set-up of laboratory-scale flow rig for adsorption experiments.

From Fig. 5 it is obvious that the zeolite, the molecular sieve and the NGDM1 material perform better than the active carbons and the metal/metal oxide based materials, with the active carbons showing the smallest THT uptake. The rather flat and irregular slope of the breakthrough curves for the zeolite and the molecular sieve might be due to micro-pore diffusion limitations for these materials. Among the active carbons, the transition metal impregnated carbon performs better than the non-impregnated sample. A significant increase in weight has been observed for all samples after THT breakthrough (4%–10%). This might be due to the co-adsorption of higher hydrocarbons

in the natural gas as indicated by an exothermic temperature effect at the beginning of the adsorption test. Especially for the zeolite a large temperature rise of more than 40 °C was observed at the beginning of the adsorption test. The commercial application of a material for a THT-filter is dependent on THT removal efficiency (i.e. residual THT concentrations in the filtered natural gas) and THT uptake capacity. The latter determines size and weight of the filter, that should be as small as possible in order to make the filter cost-effective for commercial applications.

In Table 3 the physical characteristics of the adsorbents and their determined sulphur uptake capacities at 0.1 ppmv S breakthrough are presented for the removal of THT from natural gas at ambient temperature. It should be noted that these effective

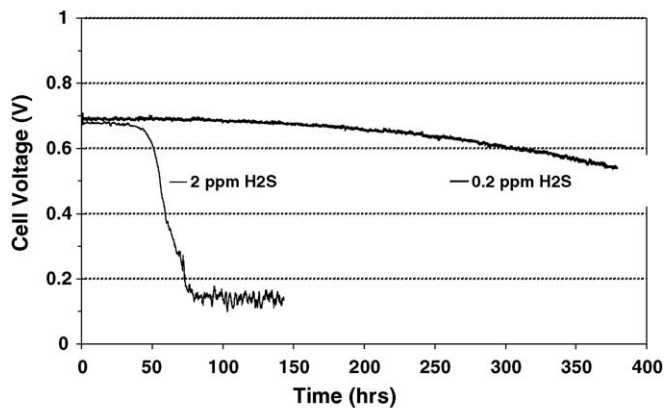


Fig. 4. PEMFC voltage at a constant current density of 0.4 A cm^{-2} upon exposure to 0.2 and 2 ppm H_2S in H_2 . Anode: 0.4 mg cm^{-2} PtRu; cathode: 0.4 mg cm^{-2} Pt, Nafion 112. $T_{\text{cell}} = 65^\circ\text{C}$. $P = 1.5 \text{ bara}$. Anode not humidified; cathode humidified at 65°C . Exposure to H_2S starts at 24 h.

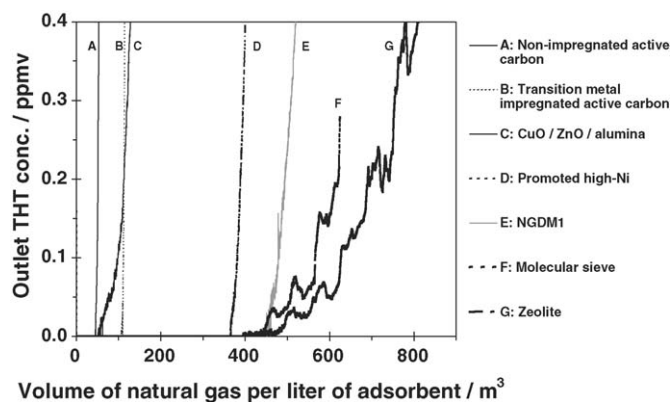


Fig. 5. Breakthrough curves of selected adsorbents for THT in commercial natural gas; measured in a packed-bed reactor at ambient temperature and 0.1 barg inlet pressure. Further conditions as in Table 1.

Table 3

Sulphur capacities of adsorbents for THT removal from NG at ambient temperature as function of specific surface (BET) area and pore volume

Adsorbent	THT uptake in g S l^{-1} (adsorbent) at ambient temperature	Physical characteristics			
		Shape	Size (mm)	BET area ($\text{m}^2 \text{g}^{-1}$)	Pore volume (ml)
Promoted alumina Alcoa SAS-6	4.9	Cylindrical extrudate	1	200	NA
Zeolite Tokyo gas TOSPIX94	4.0	Cylindrical extrudate	1.5	700	0.4
Molecular sieve Aldrich 13X	3.6	Cylindrical extrudate	1	540	0.3
NGDM1	3.0	Particle	0.5–2	275	0.4
Promoted nickel on oxide carrier BASF R-20	2.5	Cylindrical extrudate	1	280	0.4
Transition metal impregnated active carbon Norit RGM1	0.7	Cylindrical extrudate	1	1300	0.7
CuO/ZnO/alumina BASF R-12	0.7	Cylindrical pellet	3	125	0.3
Non-impregnated active carbon Norit RB1	0.3	Cylindrical extrudate	1	1100	0.5

capacities are in general lower than the maximum obtainable uptakes. Consequently, from the ambient temperature breakthrough curves in Fig. 5, it follows that the zeolite G has the highest THT uptake, but using the breakthrough criterion of 0.1 ppmv, the capacity of E, F and G are similar.

In general, a high specific surface area and pore volume might be beneficial for the adsorption of THT. From the results in Table 3 it is apparent that such a correlation does not exist for the tested adsorbents. Although the active carbon adsorbent RB1 has a relatively high specific surface area and pore volume (resp. $1100 \text{ m}^2 \text{g}^{-1}$ and 0.5 ml g^{-1}), its measured sulphur pick-up of $0.3 \text{ g (S) per liter of adsorbent}$ is lowest among the tested materials. On the other hand, the promoted alumina adsorbent SAS-6 has with a low surface area of $200 \text{ m}^2 \text{g}^{-1}$ the highest capacity for THT (4.9 g l^{-1}).

Apparently, other physico-chemical parameters of the adsorbents like pore texture (e.g. structure and diameter) and chemical composition (including type, amount and dispersion of chemical promoters) are more important in the THT adsorption process. The determination of these parameters requires an extensive physico-chemical characterization effort, that falls outside the scope of this study.

The relatively low sulphur capacity of 0.7 g l^{-1} for the CuO/ZnO/alumina adsorbent R-12 might be (partially) due to sub-optimal flow conditions in the packed bed due to the relatively large size of the pellet (3 mm) when compared to the reactor diameter (25 mm).

From Table 3 the promoted nickel adsorbent, the molecular sieve, the zeolite and NGDM1 are potential candidates for application within a residential power generator at ambient temperature. Assuming a 1 kW_e micro-combined heat and power installation, approximately $1200 \text{ m}^3 \text{ yr}^{-1}$ natural gas is needed to generate heat and power. In The Netherlands, this amount contains approximately 22 g of THT which is equivalent to 7.9 g of sulphur. This amount can be removed with 3.21 of the promoted nickel adsorbent, 2.61 of NGDM1 and 21 of the zeolite. However, the strong temperature rise at the beginning of the adsorption test with the zeolite is an important drawback for commercial application. Also, the high nickel load on the promoted nickel adsorbent is a serious disadvantage from a labour-hygienic point of view and because spent material might be difficult to dispose. NGDM1 has been obtained as a new adsorbent for THT. Compared to the other adsorbents, the material is environmentally safe, easy to use and possesses good activity (low residual sulphur levels) and sufficient capacity. The THT-saturated material was found to be partly (50%) regenerable with hot air ($60\text{--}80^\circ\text{C}$). The base material can easily be loaded with promoters to boost its sulphur uptake capacity (e.g. for application at higher temperatures and/or for other odorants). In addition, the material is available at an attractive price/performance ratio when compared to other candidates. This is especially important, because the development of a micro-combined heat and power generator is aimed at large scale residential use.

Table 4

Sulphur capacities of adsorbents for THT removal from NG

Adsorbent	THT uptake in g S l^{-1} (adsorbent)			
	10°C	Ambient temperature	40°C	60°C
Non-impregnated active carbon Norit RB1		0.3		
Transition metal impregnated active carbon Norit RGM1	0.7	0.7	0.5	
CuO/ZnO/alumina BASF R-12		0.7		
Promoted nickel on oxide carrier BASF R-20		2.5		
Promoted alumina Alcoa SAS-6	5.1	4.9	3.6	
Molecular sieve Aldrich 13X		3.6		
Zeolite Tokyo gas TOSPIX94	3.6	4.0	2.8	
NGDM1	4.0	3.0	1.2	0.8
X-promoted NGDM1			3.2	
Y-promoted NGDM1			4.5	

To investigate the effect of temperature on the adsorption, some adsorbent materials have been tested at different temperatures next to ambient temperature (see Table 1). Results are presented in Table 4.

From the tests at 40 °C it is obvious that the zeolite, the promoted materials and the promoted alumina are all candidates for application with a micro-CHP installation. On a yearly basis, only 1.81 of the Y-promoted adsorbent is needed to remove the THT from the natural gas. It should be noted that, the release of 10–20 ppmv hydrochloric acid was measured in our laboratory during the use of the promoted adsorbents. This is a serious drawback that has to be tackled by the use of specific guard beds and/or operation at lower temperatures. The results in Table 4 show that sulphur uptake capacities decrease with increasing temperature. This indicates the contribution of physical adsorption mechanisms such as capillary condensation to the overall adsorption process. Only TOSPIX 94 deviates slightly from this trend: its sulphur capacity at 10 °C (3.6 g l^{-1}) is a little bit lower when compared to its capacity at ambient temperature (4 g l^{-1}).

3.3. Pilot-scale field test THT removal from natural gas at an industrial client

Table 5 presents the results of the pilot-scale field test in which Dutch North-Sea natural gas (Table 1) was treated in a 60l adsorbent bed to remove the THT prior to entering the fuel processor. When using active carbon it was found that only some 30% of the predicted adsorbent capacity could be operated when sulphur penetrates through the adsorbent bed. In absolute terms this means that at the most some 4000 kg NG (approximately 5000 m^3 at a natural gas density of 0.8 kg m^{-3}) could be operated before a change out has to be carried out.

Table 5 shows that NGDM1 takes up more than 12 times the amount of THT when compared to the active carbon. The total amount of treated natural gas corresponds to approximately 409 g of sulphur (as THT), assuming a THT content in the natural gas of 18 mg m^{-3} . With 60l of NGDM1 the sulphur capacity is 6.8 g l^{-1} . This is significantly more than the sulphur pick-ups that have been measured in the laboratory tests. The reason for this higher sulphur uptake is a combination of two phenomena that are beneficial for physical adsorption; an average adsorption temperature below 10 °C and a relatively high natural gas pressure (3–9 bara). To double check this results and to establish the axial sulphur loading in the filter bed, samples were taken at different bed heights for sulphur analysis. Results are presented in Fig. 6.

Table 5
Sulphur take up with an industrial size odorant filter at ambient temperature and 3–9 bara system pressure

Adsorbent	Treated NG in m^3 (NTP) before breakthrough of THT at 2/3 of the filter bed length
Transition metal impregnated active carbon	5000
NGDM1	62500

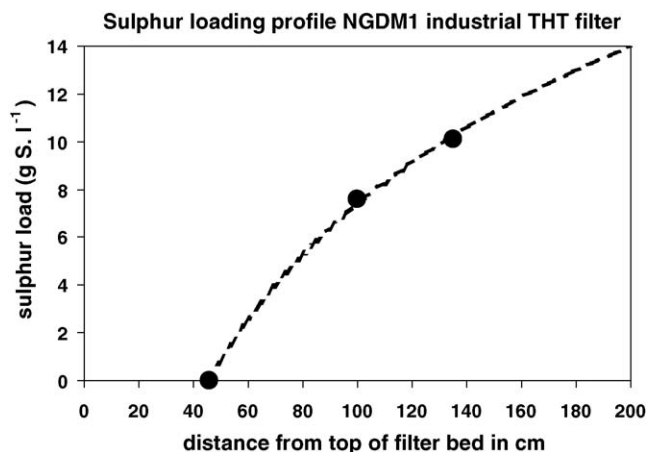


Fig. 6. Sulphur load as function of height in an industrial THT filter after saturation (total filter bed length 200 cm).

From Fig. 6 it is obvious that the 60l of NGDM1 are only partially sulphided with THT. Approximately 23% of the adsorbent inventory is still available for THT adsorption. The area below the sulphur loading profile corresponds to an amount of sulphur that is approximately 95% of the amount that has been calculated from the total volume of treated natural gas, assuming a THT content in the NG of 18 mg m^{-3} .

3.4. Other odorants in natural gas and LPG

In Table 6 sulphur uptake capacities at 0.1 ppmv S breakthrough are presented for the removal of a mixture of dimethyl sulphide and tertiary butyl mercaptan from simulated natural gas. Table 1 gives the composition of this simulated natural gas and the main characteristics of the adsorbents and applied test conditions. From Table 6 it is obvious that both the zeolite and the promoted materials are candidates for the removal of the common odorant mixture DMS/TBM. The impregnated active carbon and NGDM1 have a significantly lower DMS/TBM uptake. It is remarkable that the unpromoted NGDM1 has a four-fold lower pick-up capacity for DMS/TBM when compared to its behaviour for THT (0.3 g S l^{-1} versus 1.2 g S l^{-1} , see Table 3). But promotion with proprietary promoters leads to higher capacities as indicated by the 4.3 g S l^{-1} for the Y-promoted natural mineral. Recent research at Tokyo Gas in Japan has resulted in some specific, silver loaded zeolites with capacities up to 4 wt.% sulphur (as DMS/TBM) [14]. However, due to their high silver loadings (up to 25 wt.%) these materials are

Table 6
Sulphur capacities of adsorbents for DMS/TBM removal from NG at 40 °C

Adsorbent	DMS/TBM uptake in g S l^{-1} (adsorbent)
Transition metal impregnated active carbon Norit RGM1	1.1
Zeolite Tokyo gas TOSPIX94	>4.0
NGDM1	0.3
X-promoted NGDM1	2.9
Y-promoted NGDM1	4.3

Table 7
Sulphur capacities of adsorbents for EM removal from LPG at 40 °C

Adsorbent	EM uptake in g S l^{-1} (adsorbent)
Molecular sieve Aldrich 13X	0.2
Zeolite Tokyo gas TOSPIX94	7.3
NGDM1	<0.1
X-promoted NGDM1	1.5
Y-promoted NGDM1	1.8
Y-NGDM1 + NGDM1 (6/4, v/v)	2.5

likely to be very expensive and should be disposed of as chemical waste after saturation with sulphur, unless regeneration is possible.

In Table 7 sulphur uptake capacities at 0.1 ppmv S breakthrough are presented for the removal of ethyl mercaptan from liquefied petroleum gas (see Table 1 for tested adsorbents, feed gas composition and test conditions). The capacity results in Table 7 for the LPG odorant ethyl mercaptan indicates the superior performance of the zeolite that can accommodate almost three times more sulphur than the combination adsorbent. The adsorbent NGDM1 that has been developed for THT in natural gas, is clearly not a candidate for EM in LPG. The promoted versions of NGDM1 show somewhat better results.

The higher capacities are probably due to the promoter assisted conversion of the ethyl mercaptan into the larger diethyl-disulphide followed by adsorption [15,16]. The formation of the disulphide was detected by GC-MS analysis of the product gas after breakthrough. In previous work it has been found that this disulphide much more easily adsorbs on the unpromoted NGDM1 when compared to the ethyl mercaptan.

To boost the desulphurisation performance of the NGDM1 for LPG, this phenomenon was used by combining the Y-promoted NGDM1 with the unpromoted adsorbent in series in an attempt to convert the ethylmercaptan into the disulphide on the promoted NGDM1, followed by adsorption on the second bed of unpromoted NGDM1. The sum of the individual sulphur adsorption capacities of Y-promoted NGDM1 and NGDM1 for EM (in the ratio 6/4) is approximately 1.1 g S l^{-1} which is less than half of the 2.5 g S l^{-1} for the serial combination both adsorbents. This indicates the possibility to use NGDM1 for mercaptans too, by first converting them into the di-sulphides on an appropriate catalyst followed by adsorption on NGDM1.

Given the fact that the molecular sieve is a common state of the art adsorbent for mercaptans in NG and LPG, its measured capacity is surprisingly low. For a 1 kW_e LPG fuelled micro-combined heat and power installation, the yearly amount of LPG is approximately 400 m^3 containing 16 g S (as ethyl mercaptan). Approximately 80 l of the molecular sieve would be needed to desulphurise the fuel against only 2.2 l of the zeolite or 6 l of the promoted SulphCatch adsorbent. Within an estimated total system volume of 250 l the latter two adsorbent inventories are small enough to be incorporated in the installation. Despite the fact that the (commercial) zeolite takes up almost three times more sulphur than the combi-adsorbent, the latter is more cost-effective.

Table 8
Desulphurisation performance of selected adsorbents for odorant removal from NG and LPG at 40 °C for 1 kW_e PEMFC-based CHP applications

Adsorbent	Sulphur uptake in g S l^{-1} (adsorbent)	Minimum adsorbent change-out volume per year in liter
5 ppmv THT in 1200 m^3 NG		
Zeolite TOSPIX94	2.8	2.6
Promoted alumina SAS-6	3.6	2.0
NGDM1	1.2	6.0
X-promoted NGDM1	3.2	2.3
Y-promoted NGDM1	4.5	1.6
1.4 ppmv DMS/4 ppmv TBM in 1200 m^3 simulated NG		
Zeolite TOSPIX94	>4.0	<2.1
X-promoted NGDM1	2.9	2.9
Y-promoted NGDM1	4.3	2.0
30 ppmv EM in 400 m^3 LPG vapour		
Zeolite TOSPIX94	7.3	2.2
Y-NGDM1 + NGDM1 (6/4, v/v)	2.5	6.3

3.5. Concluding remarks desulphurisation at 40 °C

Table 8 presents an overview of adsorbents per fuel gas application in terms of sulphur pick-up capacities at 40 °C operation temperature and 0.1 ppmv breakthrough of sulphur. For comparison purposes, Table 8 also contains the amount per year of each adsorbent that would be needed to desulphurise the corresponding fuel gas for a typical 1 kW_e PEMFC-CHP application (assuming 3200 kWh power demand and an electric efficiency of 32% [17]).

For THT removal from natural gas the Y promoted NGDM1 has the highest sulphur capacity. Only 1.6–2 l of the material is needed to desulphurise the yearly amount of natural gas. However, Y-NGDM1 has a limited thermo-chemical stability which causes the release of gaseous trace components that can be harmful to catalysts when no precautions are taken. Operation at lower temperatures and/or the use of specific guard-beds is needed to counteract the effect. When size limits are not too stringent, the unpromoted NGDM1 is a good alternative, due to its ease of use, low cost and reasonable capacity; even at 40 °C, only 6 l are needed per year.

The removal of DMS/TBM from natural gas is best carried out with TOSPIX94; less than 2.1 l are needed per year. Also for LPG the zeolite shows the highest sulphur pick up. Only 2.2 l y^{-1} are needed for LPG desulphurisation. However, the use of the zeolite suffers from a strong exothermic temperature effect at the beginning of an adsorption run. In order to prevent this temperature rise, a special pre-treatment is necessary. Despite the fact that the (commercial) zeolite takes up almost three times more sulphur than the combi-adsorbent, the latter is more cost-effective.

4. Conclusions

To prevent detrimental effects on the catalysts in fuel cell-based power and CHP applications, sulphur removal from the feedstock is mandatory. From experimental bench-marking studies of adsorbents, several candidates for the removal of

sulphur containing odorants at low temperature have been identified.

Among these adsorbents a new material has been discovered that offers a economically attractive means to remove the main European odorant THT from natural gas at ambient temperature. The material is environmentally safe, easy to use and possesses good activity (residual sulphur levels below 20 ppbv) and capacity for the common odorant THT in natural gas. When compared to state of the art metal promoted active carbon the new material has a THT capacity that is two to six times larger, depending on temperature. Promoted versions of the new material have shown potential for the removal of THT at higher temperatures and/or for the removal of other odorants such as mercaptans from natural gas or from LPG.

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