

INVESTIGATION OF IMPREGNATED ACTIVATED CARBON PROPERTIES USED IN HYDROGEN SULFIDE FINE REMOVAL

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Abstract - The effects of relative humidity (RH), carbon dioxide (CO₂), methane (CH₄), oxygen (O₂) presence and gas hourly space velocity (GHSV) on H₂S adsorption dynamics of KOH/CaO impregnated activated carbon are investigated in this study. X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray detector (SEM-EDX), thermogravimetric analysis (TGA), and Fourier Transform Infrared Spectroscopy (FTIR) techniques are applied and nitrogen adsorption characteristics are determined for characterization. The presence of water, O₂ and lower GHSV has beneficial effects on the activated carbon performance. CO₂ decreases the adsorption capacity due to its acidic characteristics. Best adsorption capacity is obtained as 13 wt % in KOH/CaO impregnated activated carbon, in a CH₄ (60%)/CO₂ (38%)/O₂ (2%) gas atmosphere, at ambient temperature, RH 90 and 5000 h⁻¹ GHSV. Sulphur species formation was verified with the help of SEM-EDX, XRD, TGA, FTIR and nitrogen adsorption analysis on the exhausted samples.

Keywords: Adsorption; Activated carbon; Hydrogen sulfide; Humidity.

INTRODUCTION

Molten carbonate fuel cells (MCFC) are high temperature energy conversion systems, suitable for combined heat and power (CHP) production. The use of renewables, such as biomass or waste-derived fuels in MCFCs is essential to reduce fossil fuel dependence, to enhance energy security and to support environmental sustainability. Biogas is a renewable bio-fuel, which may be either landfill or anaerobic digestion gas. Its composition depends heavily on the feedstock, but mainly consists of methane (CH₄) (45-75%), and carbon dioxide (CO₂) (25-50%), with smaller amounts (ppm) of contaminants (hydrogen sulphide (H₂S), organic sulfur, ammonia, halogenated hydrocarbons, and siloxanes) saturated with water vapor. These contaminants, especially H₂S, decrease the activity of the catalysts in the fuel cell electrodes, and also can cause corrosion in metallic

peripheral equipments. Thus, H₂S in biogas has to be reduced to the MCFC tolerance limits (< 1 ppm) (Bove and Lunghi, 2005; Ciccoli *et al.*, 2010).

Common methods for H₂S removal involve biological desulfurization on a filter bed (Duan *et al.*, 2007), NaOH/water scrubbing (Üresin *et al.*, 2014), amine-based absorption (Ohtsuka *et al.*, 2009), adsorption (Seredych and Bandosz, 2007) and catalytic oxidation (Yasyerli *et al.*, 2004). Among these methods, H₂S adsorption/oxidation on activated carbons is preferred due to the lower cost of the material and the higher efficiency of the process. Activated carbon surface properties, i.e. pore volume, surface area and chemistry determine the overall adsorption performance. In order to enhance the specific adsorption and catalytic properties, impregnation with caustics (NaOH, KOH) (Bandosz and Lee, 1998; Yan *et al.*, 2002) and sodium and potassium carbonate (Wang *et al.*, 2006) are studied. Temperature, gas velocity, H₂S

concentration and gas stream humidity are known to be important parameters in the H_2S adsorption process (Xiao *et al.*, 2008).

The influence of relative humidity, CO_2 , CH_4 , O_2 concentration and gas hourly space velocity (GHSV) on H_2S removal over the commercial KOH and CaO impregnated activated carbon was investigated in the present study. The activated carbon samples were characterized in terms of X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray detector (SEM-EDX), thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and nitrogen adsorption analysis before and after desulfurization tests.

MATERIALS AND METHODS

Materials

Activated carbon used in the adsorption experiments was commercial wood-based KOH/CaO impregnated activated carbon pellets. This material was specially developed by the manufacturer for biogas desulfurization through adsorption. Its particle diameter, BET surface area and micropore volume were 4 mm, $878.1 \text{ m}^2/\text{g}$ and $0.4 \text{ cm}^3/\text{g}$, respectively. Bulk density of the sample was $460 \text{ kg}/\text{m}^3$.

Experimental Apparatus

The experimental apparatus shown in Figure 1

was used in the adsorption experiments. The test reaction system consisted of feeding gas system (gas cylinders and mass flow controllers), reactor, stainless steel impingers, hygostat and gas analysis systems. All the lines, as well as the lines from the reactor to the gas chromatographs, were constructed from Sulfinert[®] materials. The temperature was measured by thermocouples placed in the reactor. The activated carbon granules were packed in a vertical Sulfinert[®] fix-bed tube reactor, which was placed in a tube furnace. The outer and inner diameters of the tube reactor were 9.53 mm (3/8") and 6 mm (~1/4"), respectively.

For the adsorption experiments, standard H_2S gas of 1000 ppm in nitrogen (certified grade (± 0.21 mole % uncertainty), Air Products, Belgium) were diluted with nitrogen (ultra high purity, Habaş, Turkey). CH_4 (high purity, STG, England), CO_2 (high purity, Habaş, Turkey), and O_2 (high purity, Habaş, Turkey) gases were used to simulate biogas. In order to achieve wet gas conditions, portions of $\text{N}_2/\text{CO}_2/\text{CH}_4$ flows were directed to impingers, as shown in Figure 1. Relative humidity of the gases entering the reactor was measured by using a hygostat (HST, Kimo Instruments). Permanent (N_2 , CO_2 , CH_4 , O_2) and H_2S gases were detected on-line by gas chromatographs (GC) (6890N, Agilent Technologies) with thermal conductivity detector (TCD) and flame photometric detector (FPD), respectively. Analytical conditions of the gas chromatographs used in the gas composition analyses are given in Table 1. Gas samples were taken approximately every 8 min for the GC analyses.

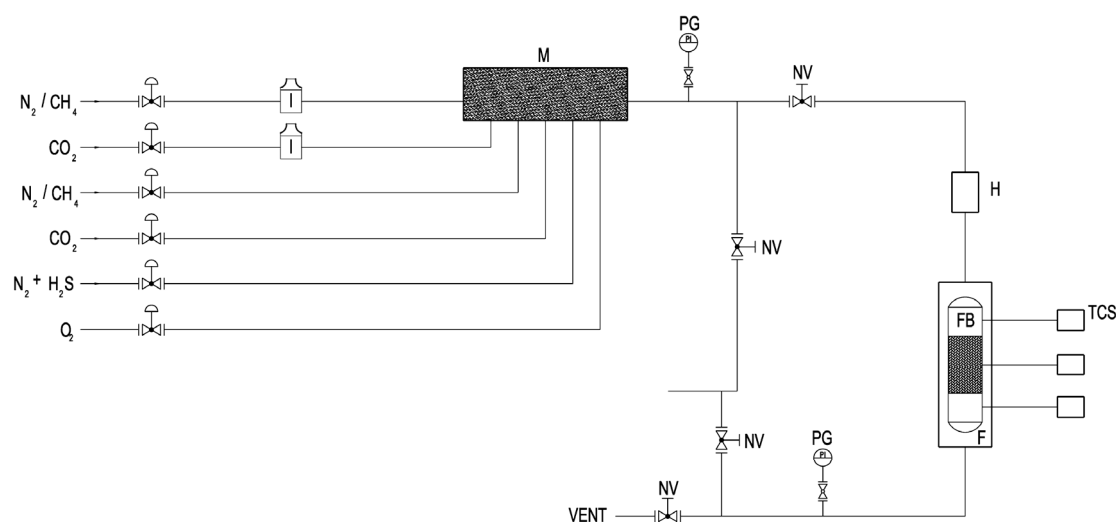


Figure 1: Schematic of the experimental set-up F: Furnace, FB: Fixed bed, GC: Gas Chromatographs, MFC: Mass flow control valves, I: Stainless steel impinger, M: Mixing manifold, NV: Needle valve, PG: Pressure gauge, TC: Thermocouple.

Table 1: Analytical conditions of gas chromatographs used in gas composition.

Detector type	GC parameters	
	TCD	FPD
Phase	Bonded polystyrene-divinylbenzene with molecular sieve PLOT	100% Dimethylpolysiloxane WCOT
Dimensions	75 m x 530 μ m x 40 μ m	105 m x 0.53 mm x 5 μ m
Oven	60 °C for 8 min.	60 °C for 3 min., 10 °C/min. ramp to 180 °C and hold for 5 min.
Carrier	Helium, 23.36 psig, 9.9 mL/min at 60 °C	Helium, 7.24 psig, 2.9 mL/min at 60 °C
Inlet temperature	94 °C	150 °C
Detector temperature	250 °C	250 °C

H₂S Adsorption Experiments

In the first part of the study, dynamic tests were carried out at ambient conditions (T= 25 °C) at three different relative humidities (RH) (0%, 35%, 70%) by using 2 cm³ (0.92 g) of activated carbon, with a GHSV of 15000 h⁻¹. The experimental matrix is shown in Table 2. The hydrogen sulfide amount was kept constant at 50 ppm in the experiments. In the second part, in order to investigate the effect of gas velocity on adsorption capacity, adsorption experiments were performed at ambient conditions (T= 25 °C) in 90% RH, by using 4 cm³ (1.84 g) of activated carbon, with two different GHSVs of 5000 h⁻¹ and 15000 h⁻¹ in a CH₄/CO₂/O₂ atmosphere. The hydrogen sulfide amount in the feed was kept constant at 400 ppm in the experiments. Table 3 shows the experimental matrix for these experiments. In order to fulfill MCFC requirements, dynamic tests were stopped at 1 ppm outlet H₂S concentration. H₂S sulfur removal capacities at 1 ppm were calculated by

Equation (i) (Cui *et al.*, 2009):

$$S_{cap} \left(\frac{\text{mg}}{\text{mg}} \right) \% = \frac{S_{conc} (\text{ppm}) Q \left(\frac{\text{L}}{\text{min}} \right) t (\text{min}) 32000 \left(\frac{\text{mg}}{\text{mol}} \right)}{22.4 \left(\frac{\text{L}}{\text{mol}} \right) m_{sorb} (\text{mg}) 10^6 \left(\frac{\text{ppm}}{\text{mg}} \right)} 100 \quad (i)$$

where S_{cap} (mg/mg) is the sulfur capacity, in elemental sulfur (mg) per gram sorbent (mg); S_{conc} (ppm) is total sulfur concentration in the gas mixture; Q (L/min) is the total gas flow rate sent to the reactor; t (min) is the breakthrough time; 32000 mg/mol is the molar weight of sulfur; 22.4 (L/mol) is the ideal gas molar volume, m_{sorb} (mg) is the mass of the activated carbon tested; and 10^6 is the conversion factor from ppm to molar concentration.

Table 2: Experimental matrix used in the adsorption experiments (T= 25 °C, 15000 h⁻¹, 50 ppm H₂S inlet conc.).

50 ppm H ₂ S	RH 0	RH 35	RH 70
CH ₄ / CO ₂ / N ₂ %	0 / 0 / 100	0 / 0 / 100	0 / 0 / 100
CH ₄ / CO ₂ / N ₂ %	0 / 37.5 / 62.5	0 / 36.7 / 63.3	0 / 36.2 / 63.8
CH ₄ / CO ₂ / N ₂ %	56.3 / 37.5 / 6.2	55.2 / 36.7 / 8.1	54.2 / 36.2 / 9.6
CH ₄ / CO ₂ / N ₂ / O ₂ %	-	0 / 36.7 / 62.3 / 1	0 / 36.7 / 62.3 / 1

Table 3: Experimental matrix used in the adsorption experiments (RH 90, T= 25 °C, 400 ppm H₂S inlet conc.).

400 ppm H ₂ S / RH 90	5000 h ⁻¹	15000 h ⁻¹
CH ₄ / CO ₂ / O ₂ %	60 / 38 / 2	60 / 38 / 2

Characterization

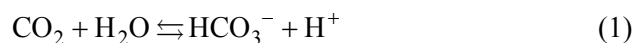
SEM analyses of the activated carbon samples were performed using a Jeol 6335 electron microscope. Relative sulphur content in exhausted samples determined with energy dispersive X-ray (EDAX) detector (Be channel, $t=90$ s). RIGAKU D/MAX 2500/PC X-ray diffractometer was used in XRD analyses, using $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation at 40 kV and 40 mA. The diffraction angle (2θ) was scanned from 2° - 50° at a scanning rate of $2^\circ/\text{min}$. TGA analysis was performed using a Mettler-Toledo TGA 851 between 20-900 °C in nitrogen atmosphere at 30 mL/min flow rate. FTIR spectra were monitored over a frequency of 500 to 4000 cm^{-1} (Perkin Elmer Spectrum 1 FTIR). Powdered activated carbon samples were mixed with KBr prior to analysis. The nitrogen adsorption on pristine and used activated carbons was measured using a Quantachrome Autosorb Automated Gas Sorption System. The specific surface area was determined by using the Brunauer-Emmett-Teller (BET) model and the pore size distribution was obtained from analysis of the desorption branch of the isotherms by the Barrett-Joyner-Halenda (BJH) method. Before the experiment, the samples were heated at 120 °C and outgassed at this temperature under a vacuum of 10^{-5} Torr to constant pressure.

RESULTS AND DISCUSSION

H_2S adsorption in N_2 gas with respect to relative humidity (RH) is shown in Figure 2 (a). It is seen that water presence enhanced the adsorption of H_2S . Previous results stated that water is very important in H_2S removal (Primavera *et al.*, 1998; Bandosz *et al.*, 2000; Yang *et al.*, 1998; Bagreev *et al.* 2005; Yan *et al.*, 2004; Flytzani-Stephanopoulos *et al.*, 2006; Li *et al.*, 2008; Klein and Henning, 1984; Mikhalovsky and Zaitsev, 1997). According to Primavera *et al.* (1998), water presence may affect the removal reaction path in two ways: (a) H_2S dissolution to HS^- ions occurs in the water film inside the adsorbent pores; thus, the removal reaction proceeds faster in water than on the catalyst surface; (b) water continuously removes sulfur from the active sites and promotes sulfur adsorption on different carbon sections (Xiao *et al.*, 2008, Primavera *et al.*, 1998; Klein and Henning, 1984). Hydrophilicity of activated carbon is believed to increase in the presence of oxygen-containing functional groups on the carbon surface (Choi *et al.*, 2008). Especially for higher relative humidities, water may be adsorbed when these func-

tional groups are present, thus, direct contact of HS^- with the carbon surface may be restricted. It was found that an increasing trend in sulfur deposition occurred until 60% relative humidity for activated carbons (Primavera *et al.*, 1998; Le Lauch *et al.* 2003).

H_2S adsorption in a N_2/CO_2 gas mixture with respect to RH is shown in Figure 2 (b). GC studies revealed that the outlet CO_2 concentration did not change and COS was not observed during the experiments. According to the figure, the presence of CO_2 in the gas mixture negatively effects the H_2S removal. Adsorption capacities of the activated carbon samples decrease, both in dry and wet conditions, due to the competition in adsorption between CO_2 and H_2S on the basic sites of activated carbon. It is known from the literature that the following reactions may occur if two acidic gases, mainly CO_2 and H_2S , are present in wet conditions.



As observed in the reactions, CO_2 transport is facilitated by bicarbonate ions, and H_2S is similarly transported in the form of bisulfide ions. In sufficiently thin films, diffusion times are so short that negligible amounts of CO_2 are converted via the slow reactions (1) and (2). However, steady-state carbonate, bicarbonate and hydrogen ion concentrations are affected by the presence of carbon dioxide, and the extent of reaction (4) is a function of pH. Thus, even when reactions (1) and (2) have negligible effects upon CO_2 transport, its presence affects the permeation of H_2S because of the influence of these reactions upon pH (Meldon and Dutta, 1994). Additionally, Bandosz (2002) and Bouzaza *et al.* (2004) stated that high-valent sulphur compound formation is promoted and H_2S dissociation is limited in an acidic environment, thus sulphur removal capacity decreases.

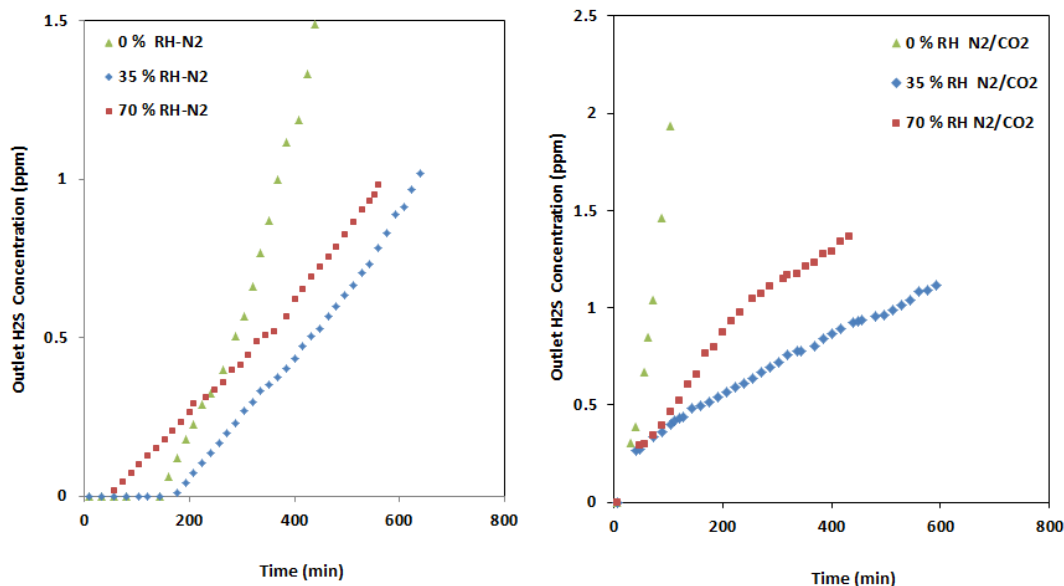


Figure 2: Effect of relative humidity on the outlet H₂S concentration in (a) N₂ gas (b) N₂/CO₂ (63.3% N₂/36.7% CO₂) gas mixture at T= 25 °C, 15000 h⁻¹ 50 ppm H₂S inlet conc.

Figure 3 shows breakthrough curves of the samples for a CO₂/CH₄ gas matrix. Especially at high RH, GC interferences were observed in H₂S measurements in gas mixtures with CH₄, but adsorption capacity was observed to increase in the presence of humidity as seen in N₂ and N₂/CO₂ gas mixtures.

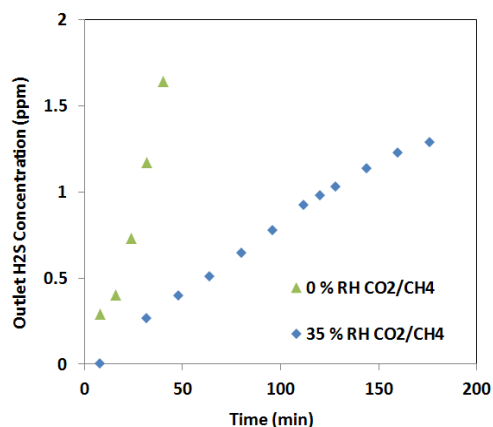


Figure 3: Effect of relative humidity on outlet H₂S concentration in CO₂/CH₄ (36.7% CO₂/55.2% CH₄/8.1% N₂) gas mixture at T= 25 °C, 15000 h⁻¹, 50 ppm H₂S inlet conc.

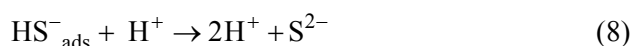
Sulfur removal capacities of KOH/CaO impregnated activated carbon in different conditions are calculated using Equation (1) and given in Table 4. Since the MCFC limit for H₂S is < 1 ppm, the breakthrough time is taken where 1 ppm H₂S concentration is determined at the reactor outlet by GC analysis.

Table 4: Adsorption capacities of samples with respect to moisture and gas composition (T= 25 °C, 15000 h⁻¹, 50 ppm H₂S inlet conc.).

Gas Matrix	Relative Humidity (RH)	Scap [w/w %] @ 1 ppm
N ₂	0	1.4
	35	2.5
	70	2.2
N ₂ /CO ₂	0	0.28
	35	2.10
	70	1.04
CH ₄ /CO ₂	0	0.12
	35	0.52
	70	-
N ₂ /CO ₂ /O ₂	35	4.32
	70	4.46

The mechanism of H₂S removal on KOH/CaO impregnated activated carbons consists of the following steps according to the literature (Leon *et al.*, 1992, Bagreev and Bandosz, 2005):

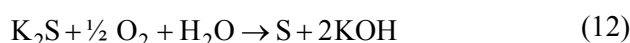
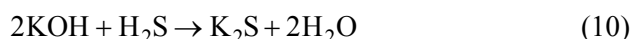
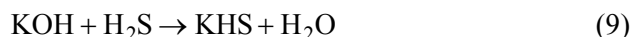
(1) Physical or ionic adsorption of H₂S on a porous carbon surface in dry or wet conditions:



As indicated by Adib *et al.* (1999), a basic environment favors the formation of S²⁻, which may pro-

mote the oxidation process and formation of elemental sulfur and partial conversion into sulfuric acid.

(2) Chemical adsorption of H₂S on metal oxides with sulfur formation:



If CO₂ is present, reactions between KOH and CO₂ may also occur that may weaken the catalytic activity of the impregnated activated carbon.

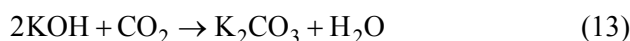
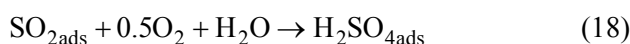


Table 4 shows that the activated carbon adsorption capacity is observed to depend highly on oxygen presence. Sulfur adsorption capacities of the samples in the N₂/CO₂/O₂ gas matrix are higher than in the others. This result suggested that, in addition to the reactions (6)-(14), oxygen and H₂S adsorb on the free active sites of the carbon surface (C_f) and then react catalytically with formation of elemental sulfur, sulfur dioxide or sulfuric acid, as seen in Reactions (15) through (18) (Choi *et al.* 2008; Puri 1970).



The effect of gas hourly space velocity (GHSV) on H₂S adsorption performance at constant temperature, H₂S concentration and RH was also investigated. According to Table 5, it is seen that the adsorption capacity is highly GHSV dependent. Break-through capacity is observed to increase with the decrease in GHSV, admitting that kinetic factors are crucial for this type of activated carbon.

Table 5: Adsorption capacities of samples in different moisture contents and gas compositions.

Gas Matrix	Relative Humidity (RH)	GHSV (h ⁻¹)	Scap [w/w %] @ 1 ppm
CH ₄ /CO ₂ /O ₂	90	5000	13.0
		15000	0.5

Characterization Experiments

SEM-EDX results in Figure 4 (a) (b) and Table 6 confirmed K and Ca metallic elements in pure activated carbon. After H₂S exposure, as shown in Figure 4 (b), a flaky phase was observed on the external surface of the carbon particles. Sulfur was detected in the EDX analysis of exhausted samples, which was in agreement with the adsorption experiments.

Table 6: SEM-EDS analyses results of pure and exhausted activated carbon in a N₂/CO₂/O₂ (62.3% N₂/36.7% CO₂/1% O₂) gas mixture at RH 70, T= 25 °C, 15000 h⁻¹, 50 ppm inlet conc.).

Element	Pure AC	Exhausted Sample
	Weight %	
C	79.1	79.5
O	11.3	12.4
K	5.4	5.5
Ca	4.2	1.9
S	-	0.7

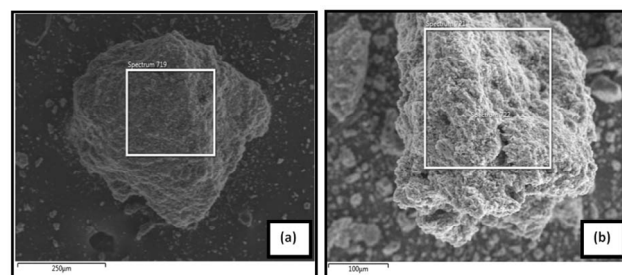


Figure 4: SEM images of (a) fresh and (b) exhausted activated carbon in N₂/CO₂/O₂ (62.3% N₂/36.7% CO₂/1% O₂) gas mixture at RH 70, T= 25 °C, 15000 h⁻¹, 50 ppm inlet conc.

Figure 5 shows the XRD patterns of pure activated carbon and exhausted samples. Especially in the samples used in the presence of humidity, some finger peaks attributed to fresh activated carbon disappeared, which might be caused by mass dilution effect of the sulfur species. Previous studies indicated that most of the deposited sulphur has an amorphous state (Xiao *et al.*, 2008; Bagreev and Bandosz, 2005). According to the Rietveld analysis of powder diffraction patterns, CaSO₄ was observed in used acti-

vated carbons, which exhausted H₂S in humid conditions (red and black lines in Figure 5, corresponded to samples N₂/CO₂-RH 35 and N₂/CO₂/O₂-RH 70, respectively). No CaSO₄ or any other sulphate formation was observed in pure and used activated carbons in dry conditions (N₂/CO₂-RH 0, green line in Figure 5).

In the presence of both oxygen and humidity, the proposed formation of CaSO₄ can be seen Eqs. (19) and (20) (Seredych *et al.*, 2008).

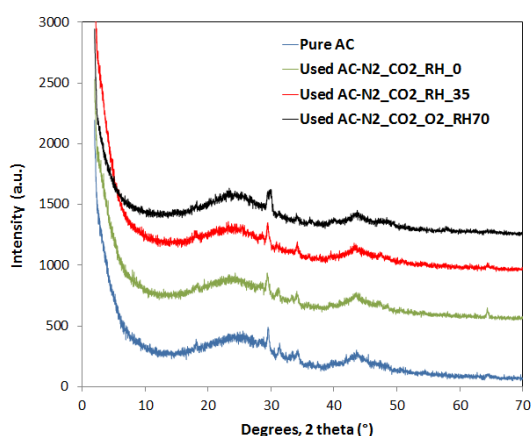
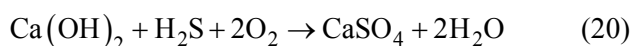
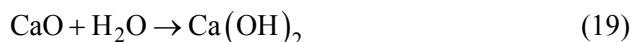


Figure 5: XRD patterns of fresh and exhausted activated carbons in different conditions ($T = 25\text{ }^\circ\text{C}$, 15000 h^{-1} , 50 ppm inlet conc.).

Thermal analysis results of the activated carbons in a nitrogen atmosphere are given in Figure 6. Differential thermal gravimetry (DTG) peaks of all the samples were observed to be stable at ambient temperatures, eliminating self-ignition risk of the materials studied. All the samples presented a weight loss around $85\text{ }^\circ\text{C}$, due to the desorption of water. DTG thermograms of the H₂S exhausted samples showed peaks at around $345\text{--}385\text{ }^\circ\text{C}$ in the presence of oxygen as a feed gas, unlike pure activated carbon. Peaks between 300 and $500\text{ }^\circ\text{C}$ are attributed to SO₂ formation from sulphur species in various studies (Bagreev *et al.*, 2005; Sreeramamurthy and Menon, 1975). The peaks at $845\text{ }^\circ\text{C}$ are associated with S-bearing species since they do not appear in pure activated carbon, which thermally desorbed at higher temperatures.

Even though there are some technical difficulties in recording the spectra of activated carbon samples, FTIR studies were conducted to characterize the samples. Figure 7 shows the FTIR spectra of pure

and exhausted AC in a N₂/CO₂ gas matrix with a RH of 35.

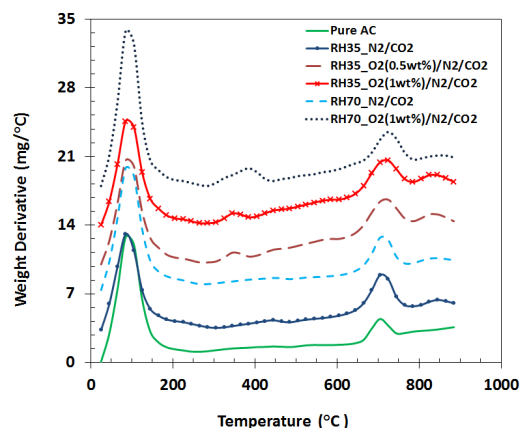


Figure 6: First derivative of weight loss of the fresh and exhausted (RH 35, RH 70, $T = 25\text{ }^\circ\text{C}$, 15000 h^{-1} , 50 ppm inlet conc.) activated carbon samples in nitrogen as a function of temperature.

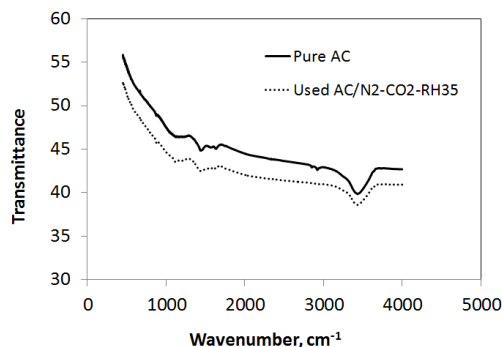


Figure 7: FTIR spectra of fresh and exhausted activated carbon in N₂/CO₂ (63.3% N₂/36.7% CO₂) gas mixture at RH 35, $T = 25\text{ }^\circ\text{C}$, 15000 h^{-1} , 50 ppm inlet conc.

For the pure activated carbon, the bands at 1680 cm^{-1} and 1492 cm^{-1} are related to the C \cdots O and C–O bond vibrations, indicating the presence of various oxygen groups. Additionally, C=C aromatic skeletal stretching of the carbon is observed as 1640 and 1444 cm^{-1} bands (Sreeramamurthy and Menon, 1975). A broad OH stretching at 3500 cm^{-1} was detected for both pure and treated samples. A new peak was detected at 1124 cm^{-1} in the exhausted sample, which may be assigned to C=S stretching (Sreeramamurthy and Menon, 1975). At 1124 cm^{-1} , SO₃²⁻ vibrations are also possible (Zawadzki, 1989).

Figure 8 shows the nitrogen adsorption isotherms for the pure and exhausted activated carbons. The shapes of the isotherms and hysteresis loops show that both samples have mixed micro- and mesoporous structures (Bagreev and Bandosz, 2004). For the exhausted activated carbon, it is seen that the

adsorption capacity decreases. The structural parameters calculated from the isotherms are listed in Table 7. BET surface areas, micropore areas, average pore diameters, total pore volumes and external surface areas are decreased significantly after desulfurization, if compared with unused activated carbon. The results are in accordance with the adsorption capacities of these samples given in Table 4. The sulfur or sulfurous products of catalytic oxidation may deposit in the pores and decrease surface area.

Table 7: Physical properties of fresh and exhausted activated carbons at T= 25 °C, 15000 h⁻¹, 50 ppm inlet conc.

Parameters	Pure AC	AC-N ₂ CO ₂ RH0	AC-N ₂ RH35
BET surface area (m ² /g)	878.1	824	826
Average pore diameter (Å)	21.05	19.64	15.96
Micropore area (m ² /g)	7.31 x 10 ²	7.05 x 10 ²	8.01 x 10 ²
Total pore volume (cm ³ /g)	4.62 x 10 ⁻¹	4.04 x 10 ⁻¹	3.29 x 10 ⁻¹
External surface area (m ² /g)	1.47 x 10 ²	1.18 x 10 ²	2.45 x 10 ¹

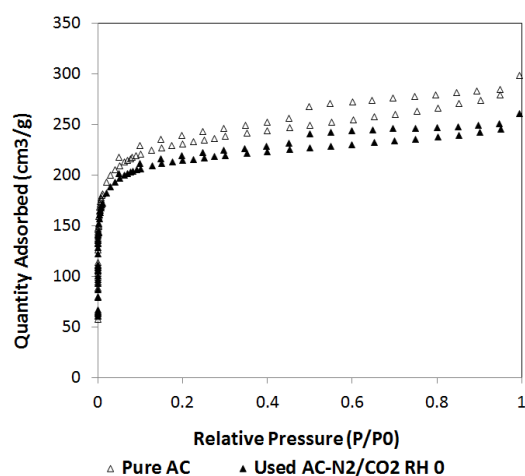


Figure 8: Nitrogen adsorption isotherms of (a) fresh (b) exhausted activated carbon in N₂/CO₂ (62.5% N₂/37.5% CO₂) gas mixture at RH 0, T= 25 °C, 15000 h⁻¹, 50 ppm inlet conc.

CONCLUSIONS

The study focused on the adsorption dynamics of a KOH/CaO impregnated activated carbon for H₂S removal under a biogas atmosphere. The effects of relative humidity, CO₂, CH₄ and O₂ presence and GHSV were investigated at ambient temperatures.

The presence of water, oxygen and a lower GHSV had beneficial effects on the activated carbon performance. CO₂ decreased adsorption capacity due to its acidic characteristics. Best adsorption capacity was obtained for 13% in KOH/CaO doped activated carbon, in a CH₄ (60%)/CO₂ (38%)/O₂ (2%) gas atmosphere, at ambient temperature, RH 90 and 5000 h⁻¹ GHSV. Sulphur species formation was verified with the help of SEM-EDX, XRD, TGA FTIR and BET analysis in the exhausted samples.

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