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Removal of sulfur compounds from utility pipelined synthetic natural gas using modified activated carbons

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A B S T R A C T

Synthetic natural gas (SNG), which is produced from petroleum and distributed via pipeline in Honolulu by The Gas Company, was analyzed using a gas chromatograph equipped with a sulfur chemiluminescence detector (GC/SCD). Hydrogen sulfide (H_2S), methyl mercaptan (MM), ethyl mercaptan (EM), dimethylsulfide (DMS), dimethyl disulfide (DMDS), tetrahydrothiophene (THT), ethyl disulfide (EDS), and one unidentified compound (UN1) were detected. Among these sulfur compounds, THT is added as an odorant and was present in the highest concentration.

A commercial activated carbon (Calgon OLC plus 12X30) was modified by oxidation and impregnation methods and the resulting materials were evaluated for their ability to adsorb sulfur compounds present in SNG. The evaluation results indicate that all of the modification methods can improve the retention of individual sulfur compounds or the total sulfur capacity compared with the untreated virgin carbon. It is also found that activated carbons impregnated with metal impurities have different selectivity for sulfur compounds. Cu and Zn loaded carbons had the highest capacity for H_2S removal, Fe loaded carbon was more efficient for DMS removal (the most difficult S compound to remove), and carbon oxidized by HNO_3 was the best for THT removal.

Based on these findings, a composite sorbent consisting of Cu loaded and Fe loaded carbons was designed and tested. The test results indicate that the composite sorbent had improved performance in the removal of individual sulfur compound. A linear programming model was used to design a composite sorbent optimized to minimize the required sorbent mass based on a 1-kW scale fuel cell system service target. Validation tests showed that the optimized sorbent required less of the individual modified carbon components than when they were individually used for the same sulfur removal target.

1. Introduction

Pipeline gases, such as natural gas (NG) and synthetic natural gas (SNG), are composed of methane (CH_4), nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), water vapor (H_2O), trace amounts of higher hydrocarbons, and sulfur compounds. Due to their developed infrastructure and relatively abundant supply, NG and SNG will be preferred, near-term fuels for fuel cells in residential applications. The sulfur compounds, which are either naturally present or added intentionally as odorants for leak detection, include sulfides, mercaptans, disulfides and thiophenes. Typical sulfur odorants are tetrahydrothiophene (THT), tertiary butyl mercaptan (TBM), ethyl mercaptan (EM), and dimethyl sulfide (DMS). These sulfur compounds are strong poisons for reformer and fuel cell catalysts. Therefore, the removal of sulfur compounds from pipeline gas is a key component for fuel cell applications.

There are different sulfur tolerances reported in literatures for the catalysts used in the reformer and fuel cells anodes. If fuel gas contains 5 ppm of THT, it would produce reformate containing approximately 1–2 ppm of H_2S. The resulting sulfur content is high enough to adversely affect the performance of a proton exchange membrane (PEM) fuel cell; negative effect has been verified at H_2S concentration of as low as 0.2 ppm [1]. More strict limitations, sulfur concentrations of less than 10 or 20 ppb, have been reported [2,3]. In general, sulfur compounds should be removed to the lowest possible level prior to fuel processor and fuel cell use.

Fuel desulfurization is typically carried out using the following competing technologies: adsorption, selective catalytic oxidation (SCO) [4–6] and hydrodesulfurization (HDS). Compared with SCO and HDS technologies, adsorption can achieve sulfur removal at ambient pressures and temperatures, while SCO requires air addition and elevated temperature (150–280 °C), and HDS requires hydrogen addition/recycle and elevated pressure and temperature

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(300–400 °C). Therefore, an adsorption approach is attractive and practical to apply in a small-scale fuel cell system, e.g., in residential applications or a transportation system.

Activated carbons are porous sorbents that can be utilized in removing sulfur compounds [7,8], but offer relatively low sulfur-adsorption capacity at ambient temperature. The adsorption capacity of activated carbons is determined by their physical or porous structure, but is also strongly influenced by their chemical structure. To improve the sorbent performance, surface modification by oxidation [9] or metal impregnation [10] has been applied and verified. These methods can create large amounts of acid groups and more adsorption sites on the surface of activated carbon [9,11,12], which can increase sulfur capacity. It has been pointed out in the literature that modification by oxidation leads to the fixation of weakly acidic functional groups [13]. HNO_3 oxidation can produce a large number of acid surface groups, mainly carboxylic acid, anhydrides, lactones and phenol groups [9,11]. H_2O_2 oxidation usually generates less acidic groups than the HNO_3 treatment [14]. The use of inorganic metals in carbon modification can form catalytically active metals on the carbon surface that serve as adsorption active points. These different functional groups and metal ions on the carbon surface play important roles in the adsorption/oxidation of sulfur compounds, such as H_2S to sulfuric acid [15,16], and mercaptans to disulfides [12,17,18].

The purpose of the present work is to identify effective methods to modify activated carbons and improve their capacity to adsorb sulfur compounds present in SNG. This paper focused on the effects of modification methods, either by oxidation or impregnation, on sulfur adsorptive capacity of carbons. The effects of modification methods on the individual sulfur compound removal were also investigated. The results of this work were used to design a composite sorbent that improves the adsorptive selectivity for individual sulfur compounds while minimizing material requirements.

2. Experimental

2.1. Sorbents preparation and characteristics

A coconut shell activated carbon (OLC Plus 12X30, Calgon Carbon Corporation) was used as the parent material for all samples modified by impregnation or oxidation. Specifications and test methods for this material are presented in Table 1.

2.1.1. Impregnation

The selected metal impurities were from the Zn group ($Zn(NO_3)_2$ and $ZnAc_2$), Cu group ($Cu(NO_3)_2$ and $CuSO_4$), Fe group ($FeCl_3$), K group (KCl, KOH, and K_2CO_3), and Na group (NaOH and Na_2CO_3). The virgin carbon was impregnated by immersing 40 g in a 0.1N solution of the selected metal at 70–80 °C for 6 h. The modified carbons were then dried at 115 °C overnight. The loaded amount was around 0.4 mmol metal per gram virgin activated carbon.

2.1.2. Oxidation

Sorbent was prepared by mixing 40 g of the virgin activated carbon with 70 ml of 68–70% HNO_3 or 100 ml of 50% H_2O_2 at room temperature until there was no further gas evolution. The sample was washed with distilled water until no further change in pH was detected (around pH 5), and then dried overnight in an oven at 115 °C.

Table 1
Specifications and test methods for activated carbon (OCL Plus 12X30, data source: Calgon Carbon Corporation)

Test	Specification	Test method
Iodine number (mg/g)	1200	ASTM D 4607
Ash (wt.%)	2	ASTM D 2866
Apparent density (g/ml)	0.45	ASTM D 2854
Hardness number	97	ASTM D 3802
Particle size (mm)	0.6–1.7	ASTM D 2862

2.2. Testing procedure and apparatus

A stainless steel pipe 45.7 cm in length and 2.43 cm in inner diameter was used as the sorbent column. All of the components including the sorbent column and gas delivery lines were treated with a Sulfinert® coating or were made from Teflon to prevent sulfur compounds from being adsorbed on the working surfaces of the system. A Teflon insert with an inner diameter of 1.2 cm was packed with sorbent and placed in the column. A 4 g mass of sorbent was tested in all cases. The sorbent bed was about 8 cm long with the major axis oriented vertically. To distribute the flow evenly, 3 mm glass beads were packed into the container below and above the sorbent. SNG was supplied from a laboratory gas service valve to the sorbent column at a flow rate of 4.0–4.5 l/min using a pump. These conditions produced a gas hourly space velocity (GHSV) of $\sim$30,000 h^{-1} in the sorbent bed. After the SNG passed though the sorbent it was analyzed with a gas chromatograph (GC).

The concentrations of sulfur species were measured with a Shimadzu 2041 GC equipped with a capillary column (Rtx-1, 60 m × 0.53 m, 7 μm, Restek Corporation) and sulfur chemiluminescence detector (SCD) (Sievers Model 355). Helium (He) served as carrier gas and a six-port sampling valve was used to make automatic injections of samples from the gas exiting the sorbent bed.

In each analysis the GC column temperature was held at 50 °C for 1 min, ramped to 125 °C at 20 °C/min, ramped to 180 °C at 10 °C/min, held at 180 °C for 1 min, and finally cooled to 50 °C at 100 °C/min. Thus, effluent gas was sampled and analyzed with a cycle time of 13 min. Before and after the sorption test, SNG was analyzed for sulfur compounds from a gas line that by-passed the sorbent bed. Tests typically lasted 10 h.

The SCD is an equimolar response detector for sulfur independent of the host sulfur compound. Thus, a permeation tube device (Model CO395, Kin-Tek Laboratories) loaded with THT was used for sulfur calibration.

2.3. Evaluation of sorbents performance

The sulfur sorption capacity of candidate sorbents was determined by breakthrough testing under ambient conditions (typically 26 °C and 0.1 MPa). Because of the different concentration of the various sulfur compounds in the SNG, the breakthrough was defined as the first detection of sulfur compounds at different critical point: 0.2 ppm for THT, 0.02 ppm for the other S compounds, and 0.5 ppm for the total sulfur in the outlet gas, as shown in Fig. 1. These critical points are much higher than the minimum detection limit (MDL) of 0.05 pg sulfur/s determined with a 1.557-ppm THT calibration gas generated with the permeation tube device and a 125-μl sample loop on the GC's automatic sampling valve.

The sulfur capacity was calculated by using the following equation:

$$S_{\mathrm{cap}}\,(\mathrm{mg/g}) = \frac{Q\,(\mathrm{l/min}) \times t\,(\mathrm{min}) \times S_{\mathrm{conc}}\,(\mathrm{ppm}) \times 32{,}000\,(\mathrm{mg/mol})}{22.4\,(\mathrm{l/mol}) \times m_{\mathrm{sorb}}\,(\mathrm{g}) \times 10^6} \qquad (1)$$

where, S_{cap} (mg/g) is the sulfur capacity in milligram elemental sulfur per gram sorbent; Q (l/min) is the SNG flow rate; t (min) is the breakthrough time; S_{conc} (ppm) is the total sulfur concentration in SNG; m_{sorb} (g) is the mass of sorbent tested; and 32,000 (mg/mol), 22.4 (l/mol), and 10^6 are sulfur molar weight, molar volume

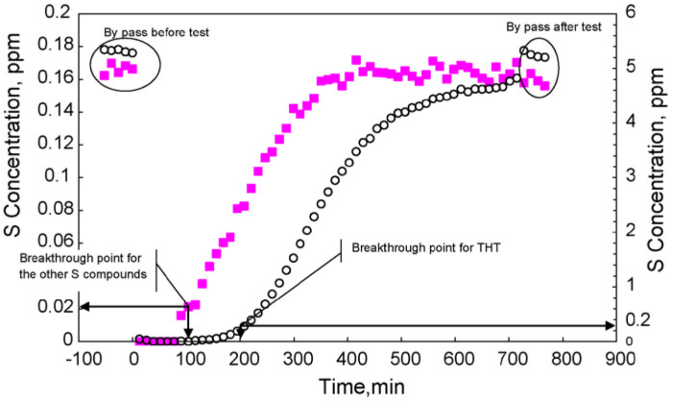

Fig. 1. Determination of breakthrough points for THT and the other sulfur compounds.

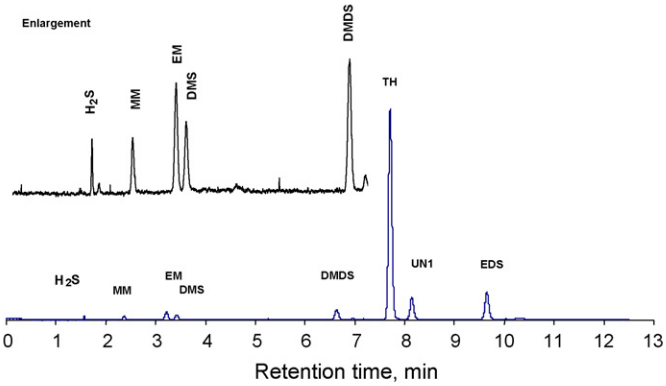

Fig. 2. Chromatogram plot of sulfur compounds in SNG.

of ideal gas, and unit conversion from ppm to molar concentration, respectively.

3. Results and discussion

3.1. Sulfur compounds in SNG

Fig. 2 is a typical chromatogram of sulfur compounds in SNG. Eight sulfur compounds were detectable as shown in the figure, including H_2S, methyl mercaptan (MM), ethyl mercaptan (EM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), tetra hydrothiophene (THT), ethyl disulfide (EDS) and one unknown compound, hereafter referred to as UN1. Among these sulfur compounds, THT is added as an odorant and is present in the highest concentration. The concentrations of sulfur compounds are presented in Table 2.

Table 2
Sulfur compounds and measured concentrations in SNG pipeline gas in Honolulu

Sulfur compounds	Concentration (ppm)
H_2S	0.06–0.15
MM	0.05–0.13
EM	0.1–0.4
DMS	0.06–0.22
DMDS	0.07–0.23
THT	4.2–7.8
UN1	0.3–1.0
EDS	0.13–0.18
Total	5.3–9.9

3.2. Evaluation of the sorbents performance

The performance of each sorbent was evaluated by breakthrough testing. Fig. 3 shows the breakthrough curves of each detectable sulfur compound in SNG using virgin coconut shell activated carbon as sorbent. Different breakthrough points indicate that the carbon surface has different selectivity for each sulfur compound. To compare the capacities of the various sulfur compounds among the tested sorbents, Eq. (1) was used to calculate the uptake capacity of virgin and modified activated carbons. Table 3 presents the calculated results based on elemental S (mg) per gram activated carbon for individual and total sulfur contents.

3.2.1. H_2S

Virgin carbon had the lowest capacity for H_2S (0.02 mg/g) out of all the sorbents tested. Both oxidization and alkaline impregnation improved sorption capacity up to 5.5 times greater than that of virgin carbon. Sorbents impregnated with Cu, Zn, however, did not experience breakthrough during the more than 10-h test showing that they have much greater H_2S uptake capacity.

Table 3
Sulfur compounds uptake capacity in virgin and modified activated carbon based on ~10-h sorbent tests (mg S/g activated carbon)

Sulfur compounds	H_2S	MM	EM	DMS	DMDS	THT	UN1	EDS	Total
Virgin AC	0.02	0.02	0.07	0.00	0.03	0.91	0.28	>0.17	1.32
Treated with oxidizer									
AC-HNO_3	0.03	>0.09	>0.23	0.00	0.29	3.43	>0.43	>0.26	4.80
AC-H_2O_2	0.04	>0.06	>0.16	0.00	0.13	2.05	>0.33	>0.15	2.90
Impregnated with Cu									
AC-$CuSO_4$	>0.17	>0.15	>0.33	0.00	0.11	1.55	0.37	>0.36	2.10
AC-$Cu(NO_3)_2$	>0.14	>0.06	>0.12	0.00	0.05	1.76	0.24	>0.33	2.30
Impregnated with Zn									
AC-$ZnAc_2$	>0.10	>0.13	>0.36	0.00	0.07	0.52	0.25	>0.33	0.86
AC-$Zn(NO_3)_2$	>0.08	>0.09	>0.22	0.00	0.11	2.14	0.42	>0.27	2.68
Impregnated with Fe									
AC-$FeCl_3$	0.02	>0.15	>0.45	0.03	0.29	2.40	>1.06	>0.75	3.50
Impregnated with alkaline									
AC-NaOH	0.04	0.03	0.09	0.00	0.07	1.24	>0.25	>0.20	1.77
AC-$NaCO_3$	0.03	0.03	0.12	0.00	0.13	1.58	>0.42	>0.31	2.25
AC-KOH	0.11	0.05	0.13	0.00	0.09	1.08	0.28	>0.35	1.70
AC-K_2CO_3	0.04	0.05	0.20	0.00	0.11	0.83	0.30	>0.46	1.43
AC-KCl	0.07	0.05	0.12	0.00	0.07	0.89	0.25	>0.22	1.15

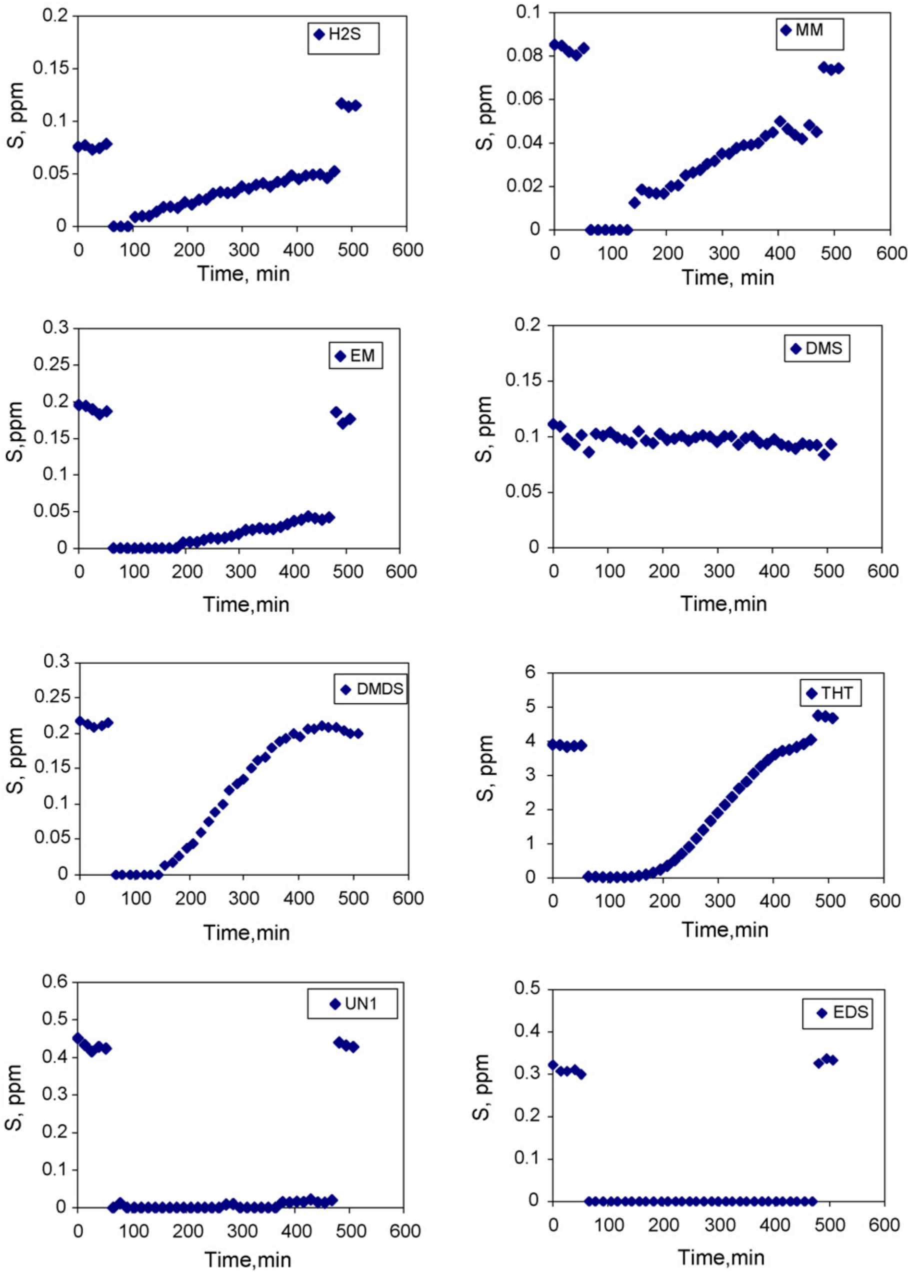

Fig. 3. Breakthrough curves of each sulfur compound for virgin activated carbon.

3.2.2. MM and EM

Virgin carbon also had the lowest capacity for MM (0.02 mg/g) and EM (0.07 mg/g). Sorbents impregnated with alkaline had a capacity up to 2.5 times greater for MM and nearly three times greater for EM when compared with virgin carbon. Breakthrough was not detected for the other sorbents indicating that oxidation and impregnation of Cu, Zn and Fe increased the AC sulfur adsorption capacity by at least 2–3 times for MM and EM, respectively. Moreover, MM is likely to be oxidized [7] on the carbon surface to DMDS that remains strongly adsorbed in the pore system, due to its larger size and higher boiling point.

3.2.3. DMS

DMS is regarded as the most difficult compound to remove [19] from pipeline gas. Breakthrough of DMS always occurred first, indicating that most sorbents having little or no uptake capacity. AC-$FeCl_3$ was the only sorbent which had any measurable uptake capacity (0.03 mg/g) under the test conditions.

3.2.4. DMDS

Virgin carbon had the lowest DMDS capacity (0.03 mg/g). The highest capacity was observed by the sorbents oxidized with HNO_3 or impregnated by $FeCl_3$, both showing nearly 10 times greater capacity. All other sorbents' uptake capacity for DMDS was improved 2–4 times. It was also found that virgin carbon and the sorbents impregnated with alkali had a higher capacity for DMDS than for MM, indicating that DMDS is more easily adsorbed than MM.

3.2.5. THT

Virgin carbon had an uptake capacity of 0.91 mg/g of THT. As was the case for DMDS, AC-HNO_3 and AC-$FeCl_3$ had the highest THT capacities with 3.43 and 2.4 mg/g, respectively. Three sorbents, AC-K_2CO_3, AC-KCl, and AC-$ZnAc_2$, had a THT capacity less than that of virgin carbon. All other sorbents had increased capacity, however, some only marginally so.

3.2.6. Unknown, UN1

This sulfur compound has not been identified. Virgin carbon had an uptake capacity of 0.28 mg/g. Cu, Zn and K impregnated sorbent reached breakthrough with a capacity similar to that of virgin carbon. Sorbents oxidized with HNO_3 and H_2O_2 or impregnated with NaOH, Na_2CO_3 and $FeCl_3$ did not experience breakthrough during testing which likely indicates higher capacity for this unknown sulfur compound.

3.2.7. EDS

This is the easiest sulfur compound to capture. None of the sorbents, including virgin carbon, experienced break through during the testing period.

3.2.8. Total sulfur

AC-HNO_3 had the highest total sulfur capacity of all tested sorbents but also had poor uptake capacity for H_2S and DMS. AC-$FeCl_3$, while having the second highest total uptake capacity, had a higher DMS capacity than AC-HNO_3. AC-$Zn(NO_3)_2$ had the third highest total sulfur capacity and an enhanced H_2S capacity. All other sorbents, except AC-$ZnAc_2$ and AC-KCl, were also improved by surface modification.

The sorbents display differences in adsorptive capacity and selectivity among the individual sulfur compounds present in SNG. These may be related to the disparity in concentrations of the sulfur compounds, the differences between the chemical structures of the sulfur compounds, physical differences in the pore sizes and distributions of the sorbents, and the chemical characteristics of the sorbent surfaces.

3.3. Evaluation and optimization of the composite sorbents

The evaluation of modified carbons indicated that competitive or selective adsorption of sulfur species occurred on the carbon surface. Sorbent beds using only one type of modified carbon would first exhibit breakthrough for the most recalcitrant sulfur compound, even though the sorbent had underutilized capacity for the other sulfur components. Due to the stringent requirements for fuel processing and fuel cell catalyst materials, early breakthrough of recalcitrant S compounds, even at low concentrations, could impact system performance. A composite sorbent for the removal of a suite of targeted sulfur compounds could be designed based on the sulfur removal capability of individual modified carbons.

Two modified carbons were used to prepare a composite sorbent consisting of 50% AC-$Cu(NO_3)_2$ and 50% AC-$FeCl_3$. AC-$Cu(NO_3)_2$ has a larger capacity for H_2S and a lower capacity of DMS, DMDS, and UN1 than AC-$FeCl_3$. The composite sorbent was expected to provide better performance, i.e. improved selectivity and capacity for the sulfur compounds present in the SNG. The test results were shown in Table 4. As expected, the composite sorbent was improved in H_2S, DMS, DMDS and UN1 capacities.

Table 4
Sulfur capacities for the composite sorbent (mg S/g activated carbon)

Sulfur compounds	AC-$Cu(NO_3)_2$ + AC-$FeCl_3$ (50:50)
H_2S	>0.08
MM	>0.17
EM	>0.57
DMS	0.07
DMDS	0.42
THT	2.31
UN1	>1.85
EDS	>1.31
Total	3.70

A mathematical (linear programming) model was formulated to optimize the design of the composite sorbent. Let x_i represent the mass of sorbent i in the composite and let c_{ij} represent the sulfur capacity of sorbent i for sulfur compound j. Thus x_i's are the decision variables for the model and the objective is to choose their values so as to minimize sorbent mass:

$$\text{Minimize}\, Z = \sum_{i=1}^{n} x_i \tag{2}$$

subject to the constraints that sufficient sorbent capacity be included for the removal of each individual S compound present in the SNG. Let Y_j represent the target mass (mg) of sulfur compound j to be adsorbed over the life of the composite sorbent bed, then the constraint equations are

$$\sum_{i-1}^{n} x_i c_{ij} \geq Y_j \quad \text{for} \quad j = 1\,\text{to}\, m \tag{3}$$

Because x_i cannot be negative, it is necessary to restrict the decision variables to be positive

$$x_i \geq 0 \quad \text{for} \quad i = 1\,\text{to}\, n \tag{4}$$

To apply the above mathematical model, two types of sorbents, AC-$Zn(NO_3)_2$ and AC-$FeCl_3$ were selected for sulfur removal from SNG in a 1-kW fuel cell application using SNG as fuel for H_2 generation. The composite sorbent bed would be required to remove sulfur from approximately 2500 m^3 of SNG (the fuel utilization efficiency is assumed as 75%), the amount required over 1 year of operation. Table 5 presents the assumed concentrations for sulfur species present in the SNG and the total amounts of sulfur species to be removed from the SNG during 1 year of operation. The sulfur capacity of each compound is listed in Table 3. In cases where no breakthrough occurred during a test, the sulfur capacity is shown as being greater than the amount of sulfur absorbed by the bed over the test duration. This value was used in the linear programming exercise.

According to the mathematical model, the following formulation is provided as an objective function:

$$\text{Minimize}\, Z = x_1 + x_2, \tag{5}$$

subject to the following constraints:

$$H_2S: \quad 0.14x_1 + 0.02x_2 \geq 357.1 \tag{6}$$

$$MM: \quad 0.06x_1 + 0.15x_2 \geq 285.7 \tag{7}$$

$$EM: \quad 0.12x_1 + 0.45x_2 \geq 714.3 \tag{8}$$

$$DMS: \quad 0.00x_1 + 0.03x_2 \geq 357.1 \tag{9}$$

$$DMDS: \quad 0.05x_1 + 0.29x_2 \geq 714.3 \tag{10}$$

$$THT: \quad 1.76x_1 + 2.40x_2 \geq 17857.1 \tag{11}$$

$$UN1: \quad 0.24x_1 + 1.06x_2 \geq 1071.4 \tag{12}$$

$$EDS: \quad 0.33x_1 + 0.75x_2 \geq 1785.7 \tag{13}$$

$$x_1 \geq 0 \tag{14}$$

$$x_2 \geq 0 \tag{15}$$

Table 5

Assumed sulfur concentration in the SNG and target sulfur removal per year based on a 1-kW fuel cell system consumed by 2500 m^3 SNG

Sulfur compounds	H_2S	MM	EM	DMS	DMDS	THT	UN1	EDS
S concentration in SNG (ppm)	0.1	0.08	0.2	0.1	0.2	5.0	0.3	0.5
S removal target (mg)	357.1	285.7	714.3	357.1	714.3	17857.1	1071.4	1785.7

where x_1 and x_2 represent the weights (g) of AC-$Zn(NO_3)_2$ and AC-$FeCl_3$, respectively.

The model was solved using MATLAB® software to yield:

$$x_1 = 850\,\mathrm{g} \tag{16}$$

$$x_2 = 11,903\,\mathrm{g} \tag{17}$$

$$Z = 12,753\,\mathrm{g} \tag{18}$$

The calculated results indicate that a sorbent composed of a mixture of 850 g of AC-$Zn(NO_3)_2$ and 11,903 g of AC-$FeCl_3$ would be sufficient to remove all sulfur compounds from SNG in a 1-kW fuel cell system during 1 year of operation. Using AC-$FeCl_3$ as a single sorbent to treat the same quantity of SNG would require 17,857 g of sorbent, 50% more material than the composite. It would not be possible to use AC-$Zn(NO_3)_2$ as a single sorbent because it has no capability to remove DMS.

4. Conclusion

Eight sulfur compounds in synthetic natural gas were quantified by GC/SCD: H_2S, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, dimethyl disulfide, tetrahydrothiophene, ethyl disulfide, and one unknown compound. The dominant sulfur compound was THT with a concentration in the range of 4–8 ppm. The remaining species were present in concentrations <1 ppm. To remove these sulfur compounds, a commercial activated carbon was selected as a sorbent and evaluated for its sulfur capacity. Oxidation and impregnation with metals were performed to modify the virgin carbon and improve sulfur capacity.

Results show that modified activated carbons can enhance the sulfur removal capacity of activated carbon significantly and produce different selectivity for sulfur compounds. Carbons loaded with Cu and Zn had the greatest capacity for H_2S removal; activated carbon oxidized by HNO_3 had the largest capacity for THT removal; Fe loaded carbon was more efficient for DMS removal, the most difficult compound to remove. By evaluating these modified activated carbons, one composite sorbent was proposed and verified to have an improved selectivity for sulfur compounds compared to the individual modified carbon components. Creating composite sorbents is a simple and effective way to remove sulfur compounds present in gaseous fuel with varied sulfur species and concentrations.

A mathematical model was developed to design optimized composite sorbents for removal of gas phase sulfur species. The objective of the optimization was to minimize the required amounts of sorbent materials while ensuring removal of all identified sulfur species based on a target gas volume (i.e. sulfur species concentration × gas flow rate × flow duration).

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