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# Removal of sulfur compounds from natural gas for fuel cell applications using a sequential bed system

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ABSTRACT

The development of an adsorbent system and process conditions for the removal of sulfur-compounds from natural gas at ambient conditions of temperature and pressure to meet the purity specifications required for use in the fuel processor of a PEM fuel cell is described. The sulfur compounds to be removed from the natural gas were $H_2S$, dimethyl sulfide (DMS), carbonyl sulfide (COS), ethyl mercaptan (EM) and tertiary butyl mercaptan (TBM). The water content of natural gas was 120 ppmw. Metal-exchanged zeolites (Ca–X and Na–X) and mixed metal oxides (of Cu–Mn and Fe–Mn) supported on alumina were used as adsorbents. Even though some of the adsorbents were active for the removal of particular sulfur compounds (Ca–X, for example, for the removal of DMS), none of them could remove all the sulfur impurities simultaneously. Multiple adsorbents are necessary. The choice of the combination of adsorbents depends on the type and relative amounts of the various sulfur compounds. The latter vary with the origin and source of the natural gas feedstock. The sequential location and quantity of the individual adsorbents in the total adsorbent bed is also a critical parameter. A sequential bed system comprising of Ca–X followed by Fe–Mn oxides had significant desulfurization capacity at 38 °C, 15 psig, and a natural gas space velocity of 6000 $h^{-1}$. This combination of adsorbents was also tolerant to the presence of water, aromatics, $CO_2$, higher hydrocarbons and other such impurities sometimes present in the pipeline natural gas.

## 1. Introduction

Fuel cells convert hydrogen and oxygen directly into water and electricity. Water and heat are the only byproducts during the process. Hence, fuel cells are a more environmentally friendly alternative to combustion-related turbines for power generation and gasoline-powered internal combustion engines for transportation applications both of which produce combustion-related pollution, such as $NO_x$, CO and unburned hydrocarbon emissions [1a,1b]. In general, fuel cells have a fuel efficiency that is two to three times that of an internal combustion engine. Among the various types of fuel cells, the polymer electrolyte membrane fuel cells (PEMFC) has received considerable attention for relatively small-scale stationary and transportation applications due to its high power density, absence of corrosive liquid electrolytes, ambient operating pressures, relatively low operating temperatures (80–90 °C) and lack of moving parts (which greatly reduces maintenance needs). A critical aspect of the commercialization of PEMFC's is the ability to produce hydrogen that is sufficiently free of residual sulfur and CO. In addition to poisoning or deactivating the catalysts at the anode, even trace levels (above about 10 ppbw) of sulfur in the hydrogen that is produced by the sequence of fuel-reforming, water-gas shift, and preferential oxidation processes can greatly hinder the reaction kinetics of the fuel cell electro-catalysis.

Removal of sulfur from hydrocarbon streams is typically carried out using either (1) passive adsorption on solid adsorbents at ambient temperatures and pressures (2) catalytic hydrodesulphurization over solid catalysts and adsorbents at elevated temperatures (300–400 °C) and pressures (30–40 bar) followed by $H_2S$ removal or (3) selective catalytic oxidation with $SO_x$ removal. While passive adsorption offers "plug and play" operation, sulfur adsorption capacities are relatively low (typically less than 2–5 g sulfur per 100 g of adsorbent). This calls for large adsorbent inventories and frequent changeouts. On the other hand, catalytic desulfurizations with higher sulfur removal capacities and longer cycle times, requires greater capital investments and must be thermally integrated into fuel cell systems.

In this paper, we describe recent results in our attempts to develop solid adsorbents for the removal of sulfur from natural gas. The primary requirements were that these adsorbents (1) operate at ambient temperatures and pressures, (2) remove a wide variety of sulfur compounds (supplied in various combinations) in the presence of typical impurities, like $H_2O$ and hydrocarbons that are found in all natural gases and (3) be economically competitive with the existing adsorbents on the market (typically active carbon).

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**Table 1**
Composition (% V/V) of natural gas at different locations.

| | North America #1 | North America #2 | Europe #1 | Europe #2 | Asia #1 |
|---|---|---|---|---|---|
| Compound | | | | | |
| Methane (%) | 95.0 | 95.0 | 89.0 | 67.0 | 89.0 |
| Ethane | 3.0 | 3.0 | 5.0 | 0.5 | 5.0 |
| Propane | 0.4 | 0.4 | 2.0 | 0.5 | 3.5 |
| Butanes | 0.1 | 0.1 | 0.5 | 13.0 | 2.5 |
| Carbon dioxide | 1.0 | 1.0 | 1.0 | 0.5 | 0.0 |
| Nitrogen | 0.5 | 0.5 | 2.5 | 14.5 | 0.0 |
| Oxygen | 0.0 | 0.0 | 0.0 | 4.0 | 0.0 |
| DMS (ppm) | 0.0 | 2.0 | 0.0 | 0.0 | 6.0 |
| TBM | 3.0 | 4.0 | 0.0 | 0.0 | 5.0 |
| THT | 0.0 | 0.0 | 8.0 | 8.0 | 0.0 |
| COS | 0.0 | 1.0 | 2.0 | 2.0 | 0.0 |
| $H_2S$ | 0.0 | 1.0 | 0.5 | 0.5 | 0.0 |
| Other Mercaptans | 1.0 | 0.0 | 0.1 | 0.1 | 0.0 |

There is extensive journal and patent literature on adsorptive desulfurization. However, the number of studies that address, simultaneously, all the three issues mentioned above are not many. U.S. patent 6,579,347 [2] to Matsushita Electric describes a process using multiple adsorbents (zeolites) at ambient conditions, for removal of dimethyl sulfide (DMS) and tertiary butyl mercaptan (TBM) from “city gas”. The first bed was an ultrastable Y zeolite and the second bed contained a MFI or faujasite zeolite. The zeolites were found to be regenerable. U.S. patent application 2005-271913 [3] to Idemitsu Kosan claims the use of ceria ($CeO_2$) combined with metals selected from Ag, Cu, Fe and Mn and containing in addition, at least one oxide selected from $Al_2O_3$, $SiO_2$, $TiO_2$, $ZrO_2$, and MgO for removal of sulfur compounds from hydrocarbon gaseous feeds for fuel cells. U.S. patent application 2006-0058565 [4] also describes sequential beds with a sepiolite-based adsorbent in the first bed and a clay, zeolite or alumina in the second bed for the removal of sulfur compounds for fuel cell applications. A three step process wherein (1) the first adsorbent, a hydrophobic zeolite exchanged with one or more transition elements removes organic sulfur (except carbonyl sulfide, COS), (2) hydrolysis of COS occurs in the second bed and (3) $H_2S$ is adsorbed in the third bed over ZnO, is claimed by UOP [5]. Pipeline natural gas from Pittsburgh, PA, USA, was used by Israelson [6] to screen various adsorbents. This gas contains a total of 6 ppmv sulfur including dimethyl DMS, iso propyl mercaptan (i-PM), TBM and tetrahydro thiophene (THT). Adsorbents were screened at 50 psig, ambient temperature for physical adsorbents and elevated temperatures (100–350 °C) for chemical adsorbents. Space velocities varied from 156 to 2000 $h^{-1}$. For all catalysts tested, DMS was always the first sulfur compound to break through. The best adsorbent was a proprietary adsorbent (probably a Ag-exchanged Na–Y). The next in merit was a Cu–Y zeolite. The latter removed 100 times more DMS than activated carbon at a space velocity of 1621 $h^{-1}$ at ambient conditions. In the desulfurization of a city gas containing 2.4 ppm DMS and 2.4 ppm TBM at ambient conditions, Wakita et al. [7] reported that the efficiency of some alkali/alkaline ion – exchanged zeolites decreased in the order Na–Y ∼ Ca–X > Na–X. When the metal ions were exchanged for protons, the activity decreased in the order H-beta > H-USY > H–Y. Ag–exchanged Na–Y zeolites were tested [8] in a pipeline natural gas containing 1.8 ppm DMS and 1.2 ppm TBM with 10 and 1000 ppm water, respectively, at ambient temperature and pressure and a space velocity of 60,000 $h^{-1}$. Addition of water lowered the capacity for sulfur pick-up. DMS breakthrough occurred before TBM. However, as TBM breakthrough occurs subsequently, the concentration of DMS in the exit gas increased to levels higher than that in the inlet gas. Satokawa concluded that the interaction between TBM and Ag–Na–Y is stronger than that between DMS and the zeolite.

**Table 2**
Desulfurization – adsorbent screening conditions for Louisville natural gas.

| Temperature | Ambient |
|---|---|
| Pressure | 5 psig (1.3 bar) |
| Space velocity | 10,000 $h^{-1}$ |
| Sulfur feed gas | LG&E (TBM, DMS, $H_2S$, COS each <2 ppm) |
| Hydrocarbon feed | Natural gas approx (96% $CH_4$, 2%$C_2H_6$, 0.3% $C_3H_8$, 0.1% $C_4H_{10}$, 0.5%$N_2$, 1%$CO_2$, and 40–80 ppm benzene) |

In most of the earlier studies, the possibility of the reaction of two or more sulfur compounds present in natural gas to produce a new compound had not been investigated adequately. An additional factor was the ‘one material can remove all sulfur compounds’ approach adopted in many earlier studies. This approach was fairly successful with petroleum liquid feeds, particularly gasoline, wherein most of the sulfur compounds were thiophene derivatives and where nickel-based adsorbents removed all the individual sulfur compounds and were therefore, universal in application [9]. Water is also, usually, absent in such petroleum streams. Single catalyst beds containing prior-art, nickel-based adsorbents were, however, not successful when applied to adsorptive desulfurization of natural gas containing water.

The composition of natural gas is not consistent and varies with location (Table 1) and gas supplier where different odorants are added. Hence, a sequential bed approach with multiple adsorbents will be more advantageous. Our strategy was to develop two or more new materials which, when combined, would remove all the sulfur compounds in an average pipeline natural gas feed. Ideally, the sequential bed would be resistant to water, aromatics, $CO_2$, higher hydrocarbons and other such impurities present in a typical pipeline natural gas. The sequential location and quantity of specific adsorbents in the adsorption system would be determined based upon the sulfur composition of the inlet feed.

## 2. Experimental

### 2.1. Materials

The composition of Louisville, KY, USA, natural gas used in the present study is shown in Table 2 including the screening test conditions. The solid adsorbents were prepared by conventional wet-chemical procedures.

### 2.2. Test unit and analytical systems

The testing units, comprising 4 reactor tubes, are completely automated utilizing computer software obtained from Argonaut