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Odor fading in natural gas distribution systems

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ABSTRACT

Since natural gas is odorless, to assure the customer safety, odorants are added to it to alarm the consumer in the case of a gas leak. Although the odorization is a common practice in natural gas distribution systems, odor fading has been reported in pipelines, which is a great safety risk. This paper summarizes results of experiments conducted to investigate possible chemical and physical mechanisms responsible for odor fading. In these experiments, X-ray photoelectron spectroscopy (XPS) and gas chromatography were used to check the possible interactions of tertiary butyl mercaptan (TBM) as odorant with the pipe material. Evidences of chemisorption, adsorption and desorption of TBM on the iron oxide inside the pipe were observed. It was found that by increasing pressure, rusted surface of the pipe, and temperature or by decreasing the gas flow rate and odorant concentration the mercaptan removal was increased.

1. Introduction

In the beginning of the 20th century, the natural gas used to contain byproducts, which contributed to a "gassy" odor (Usher, 1999). However, the progress in the production of natural gas resulted in eliminating these byproducts and consequently a gas leak was not detectible to human nose anymore (Usher, 1999). In 1937, this lack of safety proved fatal in the disaster at the New London Elementary school in Texas (Usher, 1999; Parrott, 2004). After this tragedy, US and Canada legislated the use of odorants in natural gas distribution systems (Ivanov et al., 2009). Based on these regulations the gas distributed to consumers must be detectable at one-fifth of its lower explosive limit (LEL), which is 1% of natural gas in air (Ivanov et al., 2009). The odorants that are frequently used for this purpose are blended alkyl mercaptans, such as tertiary butyl mercaptan (TBM) and isopropyl mercaptan (IPM), dimethyl sulfide (DMS), and thiophane.

Despite the usual odorization of the natural gas, odor fading has been reported in several cases in the pipelines. This is a major safety issue, since a gas sufficiently odorized still could lose its odor and in the case of a leakage could be undetectable and hazardous to the consumer (Usher, 1999). Odor fading is reported to happen mostly in the new pipelines and both chemical and physical mechanisms are suggested to affect its progress. Among these mechanisms adsorption and absorption of the odorants to the pipe material have been suggested to play a key role (Jacobus and Yaeger, 2008).

Upon commissioning a new gas pipeline, the pipeline itself will absorb and react with the odorant until it is saturated with it (Ivanov et al., 2009). Even in plastic pipes odor fading could happen due to the odorant adsorption and/or absorption (Usher, 1999). In case of steel pipes, a chemical reaction also occurs causing the formation of an iron sulphide layer, called patina on the inner surface (Usher, 1999).

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The chemical mechanisms suggested for the odor fading involve reactions of odorants with iron oxides and formation of less odorous and volatile compounds. Andreen and Kroencke (1964) first reported the evidence of reaction between iron oxide compounds and mercaptans that cause odorant loss in gas streams. They conducted experiments using a flow reactor and rusted steel spheres at ambient temperature and 5 psig pressure. Little (1978) also studied odorant loss using teflon tubing packed with Kel-F beads coated with α-FeO(OH). His studies showed α-FeO(OH) as the most effective of all the compounds for reacting with mercaptans.

It has been suggested that the odor fading happens due to the adsorption of the odorant on the pipe walls and also oxidation of the mercaptan compounds to alkyl disulfide by iron oxide in the pipe (Moran et al., 1993). While Moran et al. (1993) have shown evidence about the relation between odor fading and the iron oxide compounds, it is unclear if the odor fading occured mostly due to adsorption of the sulfur to the iron oxide layers or due to chemical reactions.

Odor fading also can be related to a number of physical parameters. Some physical parameters attributed to odor fading are pressure, temperature, gas velocity, the type of iron oxide compound, and thickness of iron oxide layer in pipes (Moran et al., 1993). One study has suggested that increasing pressure results in higher absorption of TBM. Lowering the temperature was found to initially result in higher TBM removal from the gas stream by the iron oxide compounds. After a longer exposure time, however, more TBM was removed from the gas at higher temperature (Moran et al., 1993).

In addition to the above literature, there is a large body of work on the adsorption processes in gas systems that could provide valuable insights into the possible mechanisms involved in the kinetics of mercaptan removal in the natural gas pipelines. In adsorption processes, one or more components of the gas are adsorbed on the surface of the adsorbent and a separation is achieved (Geankoplis, 2003). A simple theoretical model for this process has been proposed by Yoon and Nelson (1984) that describes the decrease in the adsorbate concentration as a function of time (Yoon and Nelson, 1984; Zeinali et al., 2010):

$$\ln\left(\frac{C}{C_0 - C}\right) = k_{YN}\,(t - \tau) \tag{1}$$

where k_{YN} is the rate constant ($\min^{-1}$), τ is the time required for 50% adsorbate breakthrough (min), C is the sample concentration, C_0 is the initial concentration and t is the breakthrough or sampling time (min). In this work, breakthrough is defined as the outlet concentration of mercaptan over its initial concentration over a period of time. To calculate breakthrough curves for a system, k_{YN} and τ for the adsorbate of interest must be determined based on the experiments (Yoon and Nelson, 1984; Zeinali et al., 2010).

Another model that can explain the diffusion of adsorbates through fixed beds of adsorbent is the diffusion model developed by Rounds and Pankow (1990). They found that the shape and position of the normalized breakthrough curve which is the plot of normalized concentration of adsorbate versus time, is related to the relationship between the rate of equilibrium mass transfer and the rate of intra-particle diffusion. This relation is represented by two time constants T_M and T_D, defined as:

$$T_M = \frac{K_p M_p}{f} \tag{2}$$

$$T_D = \frac{L_D^2}{D_{\mathrm{eff}}} \tag{3}$$

where K_P is sorption equilibrium constant, M_P is mass of particle, f is volumetric flow rate of gas, L_D is diffusion length, and D_{eff} is the effective diffusivity. To understand adsorption and desorption kinetics, Ko et al. (2003) conducted experiments on $CuSO_4$ film-surface diffusion and found that the position and shape of the breakthrough curve depended on the contact time between the sorbent and sorbate. Singh and Pant (2006) also evaluated the effects of concentration and flow rate on the shape of breakthrough curves. Their results showed that the higher the concentration and flow rate, the sooner the breakthrough would occur. This finding was further confirmed by Koh et al. (1998).

Even though odor fading is recognized as a safety concern, it is still largely an unsolved problem. Accordingly, the objective of this research was to obtain Enbridge system specific information and understand possible chemical and physical mechanisms responsible for odor fading in natural gas pipelines.

2. Experimental

A continuous gas flow reactor was designed to mimic the gas pipelines continuous flow. Enbridge's natural gas is usually odorized using a blend of 75% TBM and 25% DMS. However, for simplicity a blend of methane and TBM was used in this study to represent the odorized natural gas.

2.1. *Materials*

A mixture of 50.9 ppm TBM in methane (standard deviation: ±1 ppm), and also a grade 4.0 pure methane cylinder were purchased from Linde Canada and were used for the experiments. Additionally, liquid TBM (99%, Sigma Aldrich) was used to prepare calibration standards. The pure methane cylinder was used to adjust the concentration of TBM by adding it to the odorized gas stream in the experiments. For the experiments, ferric (III) oxide nanopowder, a stainless steel sample, a polyethylene pipe sample, and a 4.5 in. steel pipe were used. The polymer and steel samples were obtained from a 1/2 in. pipe (15.9 mm × 2.28 mm) and a 4.5 in. steel pipe, respectively, provided by Enbridge Gas Inc. The inner surface of the steel pipe was rusted. Therefore, both the rusted surface and also the polished surface of the steel were used for the XPS measurements. Table 1 shows the specifications of the samples.

2.2. *Experimental set-up*

The main part of the reactor was a 60 cm long glass lined steel tube with a 12.7 mm (0.5 in.) OD and 9.5 mm (0.37 in.) ID. The tubing was obtained from SGE Analytical Science. The glass lining was used to minimize the possibility of any chemical or physical reaction of TBM with the reactor itself and interfering with the measurements. To control the flow of the gases inside the reactor and also adjust the concentration of TBM, gas flow controllers were used. The possible leakage of the