

Natural Gas Odorants Desulfurization

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Abstract

This study investigates the use of activated carbon for the odorant removal from natural gas to be used for synthesis gas production for fuel cells. The odorants used in this study were dimethyl sulfide, tetrahydrothiophene, methyl mercaptan, and t-butyl mercaptan. It was concluded that only physical adsorption is contributing towards removal of sulfur species at lower temperatures, whereas the partial oxidation of organic sulfur and subsequent physical adsorption of low volatile oxidation product are the mechanisms for odorant removal at elevated temperatures. Pore size distribution of the activated carbon and vapor pressure of the sulfur species to be removed determine the removal capacity of activated carbon due to capillary condensation. Activated carbon modified with KOH to increase the adsorption of sulfur species as well as acid treated and KMnO₄ modified activated carbon to enhance the oxidation process were also the part of this study. The effect of GHSV and temperature on the sulfur species removal capacity of activated carbon was also studied.

Introduction

Natural gas as it occurs naturally has little or no perceptible odor. In order to make natural gas detectable without the use of instrumentation, the gas is odorized with one or more of a series of sulfur compounds. Odorants in common use include various mercaptans (methyl, ethyl, propyl, isopropyl, t-butyl), organic sulfides (dimethyl, methyl ethyl), thiophane (tetrahydrothiophene), and blends of these. However, the type of sulfur compounds used as odorants in natural gas depends on its geographical source. Table 1 provides the odorant composition used in US pipeline natural gas [1].

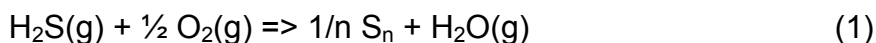
However, odorants may have detrimental effects on the reforming catalyst as well as on the fuel cell anode performance if natural gas is used as a reforming fuel for fuel cell applications. Thus, sulfur removal from natural gas is essential to ensure the long life of the reforming catalyst.

Table 1. Composition of odorants used in the US pipeline natural gas [1]

Natural gas odorant blend	Market share %	Composition breakdown
Mercaptans	40-55	100% mercaptans
Mercaptan/alkyl sulfide	40-55	sulfide content is typically 20-50%
Thiophane/mercaptan	5	thiophane content is typically 30-50%
Thiophane	1	100% thiophane

Desulfurization of natural gas depends on the type of sulfur compounds as well as the sulfur content. Adsorption processes using adsorbents such as activated carbon and zeolites are widely used to remove a wide range of sulfur compounds from gaseous emissions [2-4]. For continuous sulfur compounds removal, two similar beds are designed in parallel so that one is being used for adsorption while the other one is being regenerated.

In the literature, a number of studies have also been reported on the application of H₂S catalytic partial oxidation technology to the desulfurization of sour natural gas [5-9].



Thermodynamically, Reaction (1) has the potential to remove H₂S to the parts-per-billion level below 250 °C. Ghosh et al. [5] were the first to examine the applicability of Reaction (1) using an activated catalyst to sweeten natural gas. At National Energy Technology Laboratory, Gardner et al. [9] successfully demonstrated this technology in removing H₂S from a Texaco O₂-blown coal-derived synthesis gas.

The scope of this work was to determine the performance of the activated carbon or the modified activated carbon for the natural gas odorants removal. Physical adsorption method as well as selective oxidation of sulfur species was explored for odorant removal.

Experimental

The composition of the simulated natural gas used in this study is provided in Table 2. Two additional gas mixtures containing only sulfur species balanced by N₂ were also used in this study. The first gas mixture (Mix-A) contained 100 ppm of dimethyl sulfide (DMS), 100 ppm of tetrahydrothiophene (THT), and balance N₂, whereas the second gas mixture (Mix-B) had 100 ppm of methylmercaptan (MM), 100 ppm of t-butylmercaptan (TBM), and balance N₂. We decided to use higher concentrations of odorants (100 ppm) instead of normal concentrations (~10 ppm) present in natural gas so the effects are readily and accurately observable analytically.

Table 2. Composition of natural gas used in this study

Component	Composition	Component	Composition	Component	Composition
THT	96 ppm	N ₂	3.003 mole%	n-propane	2.998 mole%
DMS	99 ppm	O ₂	0.200 mole%	n-butane	1.253 mole%
H ₂ S	0.68 ppm	Methane	81.052 mole%	n-pentane	0.499 mole%
CO ₂	3.001 mole%	Ethane	7.994 mole%		

A fixed bed reactor system was used to conduct this series of experiments, which was operated continuously at temperatures up to 350 °C. A summary of reaction conditions is

given in Table 3. Exit gases including H₂S, COS, CS₂, SO₂, DMS, THT, thiophene, MM, and TBM were analyzed using flame photometric detector (FPD) in different GCs. The catalyst utilized in this study was F600 activated carbon obtained from Calgon Carbon Corporation. Physical properties of sulfur species of interest are listed in Table 4.

Table 3. Reaction conditions

Condition	Range	Condition	Range
Reactor temperature (°C)	25-350	GHSV (hr ⁻¹)	625-2500
Reactor pressure (psig)	10-50	Air flow rate	0-10 sccm
Natural gas flow rate	250 sccm		

Table 4. Physical properties of some sulfur species of interest

Sulfur species	Boiling point (°C)	Vapor pressure (bars) @ 25 °C	Vapor pressure (bars) @ 135 °C
Dimethyl sulfide	38	0.64	-
Thiophane	120	0.025	-
Thiophene	84	0.105	-
Dimethyl sulfoxide	189	0.0008	0.21
Methyl Mercaptan	8	-	-
Dimethyl disulfide	110	0.038	-
t-Butyl Mercaptan	63	0.55	-
Di-t-butyl disulfide	200	-	-

Results and Discussion

Effect of temperature

Fig 1 show the effect of temperature on the concentration of sulfur species in the reactor outlet at gas hour space velocity (GHSV) of 2500 hr⁻¹. At room temperature, a complete removal of THT from natural gas was observed over the time (2 hr) the experiment conducted. THT concentration in the reactor effluent slightly increased with an increase in temperature before further decreased to zero at elevated temperatures. At higher temperatures, dehydrogenation of THT to thiophene takes place and consequently the concentration of thiophene increased with increasing temperature. THT removal capacity of activated carbon decreased considerably with increasing temperature. While DMS removal from natural gas over activated carbon behaved completely different than the THT removal. DMS removal was 89% after 1 hr of run and 0% after 2 hr run at room

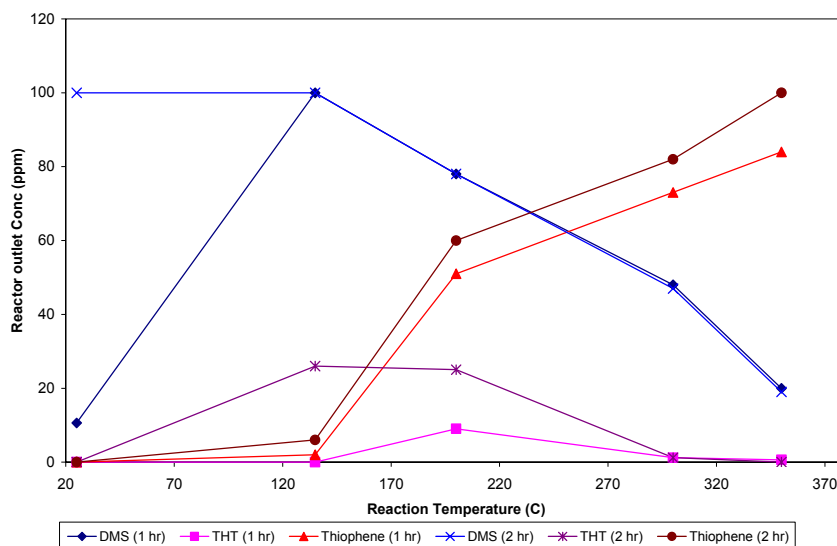
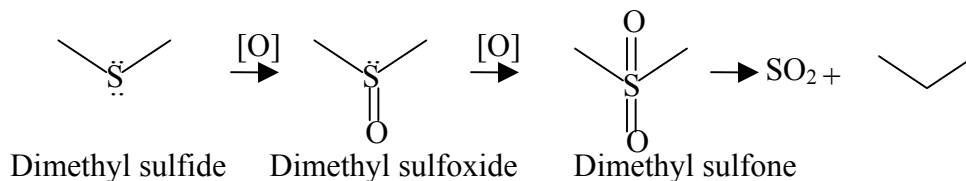


Fig 1. Effect of temperature on sulfur removal at GHSV of 2500 hr⁻¹ (Inlet: DMS = THT = 100 ppm)

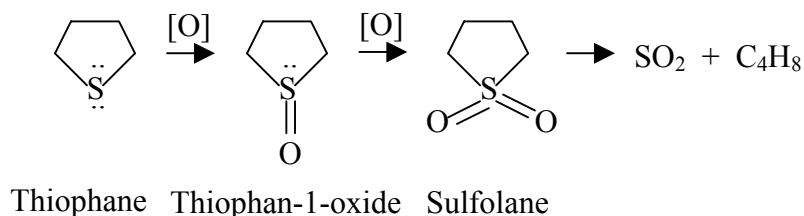
temperature. No DMS removal was observed at 135 °C, but concentration of DMS steadily decreased and, hence, DMS removal increased with increasing temperature.

Two lone pair electrons around the sulfide of DMS show a high nucleophilicity, hence, they are susceptible to attack by an electrophile. Oxidation products of DMS will be dimethyl sulfoxide (DMSO) or dimethyl sulfone, having been oxidized by the attack of one or two oxygen atoms respectively. The oxidation of sulfoxide to sulfone is relatively very slow and occurs comparatively higher temperatures because the electron-releasing ability of the sulfoxide sulfur is reduced considerably compared to sulfide sulfur. However, the decomposition of sulfones at elevated temperatures is expected which results in the formation of SO₂. The overall reaction occurs according to the equation:

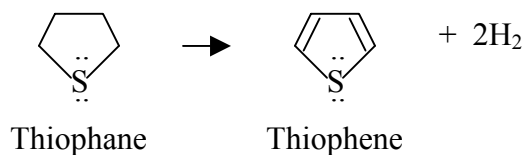


At higher temperatures (200-300 °C), the oxidation reaction as well as the adsorption phenomenon is responsible for DMS removal. Oxidation products of DMS (DMSO and dimethyl sulfone) have a considerably low volatility and can have retention through capillary action on micropores of activated carbon. At 350 °C, a significant amount (19 ppm) of final decomposition product SO₂ was observed in the reactor effluent. It is also interesting to note that the DMS removal rate after 2 hr of operation was the same as 1 hr operation except at room temperature.

Similarly, the oxidation of THT yields tetramethylene sulfone (or sulfolane):

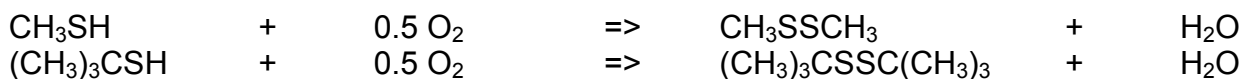


Dehydrogenation reaction of THT to thiophene dominates the oxidation reaction of THT.

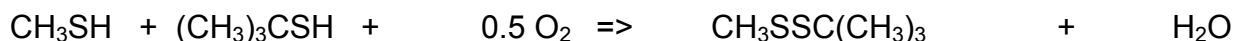


Sulfur's extra pair of electrons in thiophene molecule is involved in the π cloud as in an aromatic structure. These electrons are not readily available for nucleophilic reactions as of THT. Aromaticity provides high stability to thiophene molecule and, thus, it tends to undergo reactions in which the stabilized aromatic ring is retained.

A complete removal of mercaptans from the Mix-B was observed at room temperature for 25 hrs. However, mercaptans were converted presumably into disulfides at elevated temperatures as evident from shifted peaks in GC. Oxidation of mercaptans (thiols) yields less volatile disulfides,



Co-oxidation of the mercaptans is also possible if there are multiple mercaptans present,



However, we never confirmed the formation of oxidation products of DMS, THT, or mercaptans analytically. Extraction of the adsorbed sulfur species with methylene chloride was attempted in order to separate and to identify the adsorbed sulfur species using the GC-MS technique. But, the concentration of trapped sulfur species in activated carbon was not enough for GC-MS analysis. Similarly, the TGA study of used activated carbon could not differentiate the adsorbed sulfur species. It was expected that the sulfur species would desorb from the activated carbon at different temperatures in TGA based on the strength of physical adsorption of particular species. Formation of SO_2 at elevated temperatures in DMS removal experiment, however, is only possible through the chemical pathways (as shown above) involving low-volatile oxidized sulfur intermediates.

The possibility for sulfide to decompose into H_2S and hydrocarbon increases with an increase in temperature. In the gaseous phase alkyl sulfides decompose at 400-800 °C to H_2S and the corresponding alkenes. Cyclic sulfides such as THT are more stable than the aliphatic analogs; their decomposition occur relatively elevated temperatures.

Catalyst modification

The adsorption of sulfur species on activated carbon is determined by the pore structure and to a large extent by the presence of active groups of acidic or basic at the surface. Increase of the basicity of the activated carbon by impregnating with KOH or NaOH leads to increase of the sulfur adsorption. Activated carbon modified with 0.2 mmol KOH/g showed higher DMS removal capacity at room temperature compared to unmodified activated carbon (Fig 2). However, KOH modified is not effective for sulfur species removal at higher temperatures (Figs 3-4).

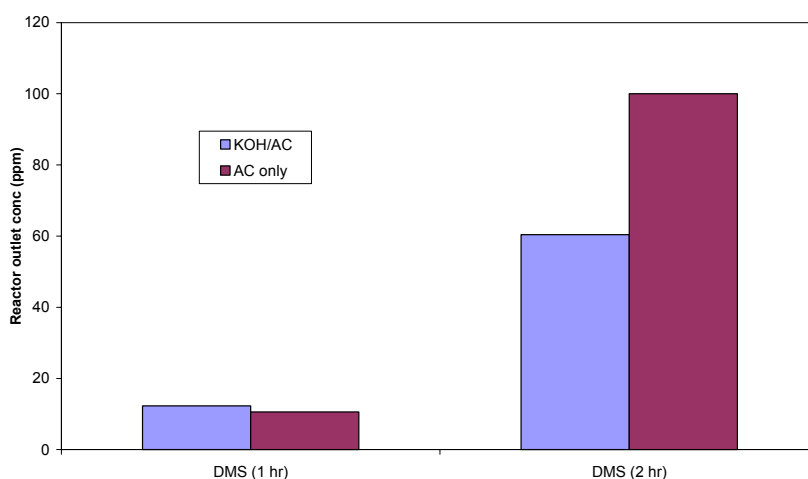


Fig 2. Effect of KOH modification of activated carbon (AC) at room temperature (Inlet: DMS = THT = 100 ppm)

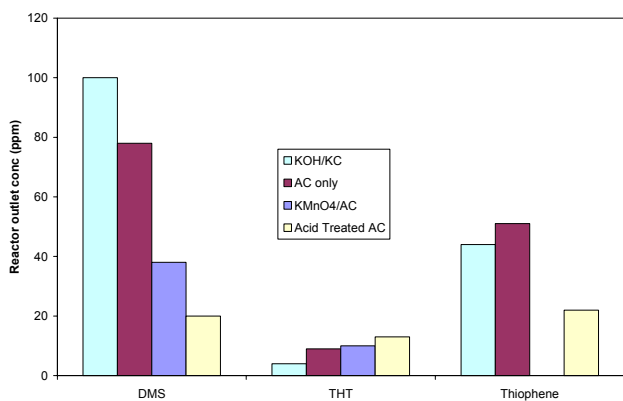


Figure 3. Effect of catalyst modification on sulfur removal at 200 °C (Inlet: DMS = THT = 100 ppm)

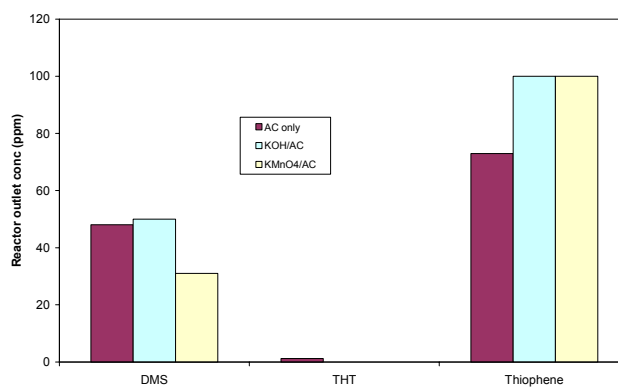


Figure 4. Effect of catalyst modification on sulfur removal at 300 °C (Inlet: DMS = THT = 100 ppm)

The chemical nature of the activated carbon surface can be modified by an oxidant treatment to enhance the oxidation process. Acid treated and KMnO_4 modifications significantly improved the performance of activated carbon for sulfur species removal at elevated temperatures (Figs 3-4). The oxidation of sulfur species greatly enhanced due to increased surface oxygen on acid treated activated carbons. At 200 °C, a significant decline in THT concentration was observed with acid treated and 0.2 mmol KMnO_4/g modified activated carbon. The oxidation reaction of THT dominated over the dehydrogenation reaction in the presence of oxidation environment on activated carbon.

Effect of space velocity

The effect of GHSV on the sulfur removal from the natural gas can be seen in Fig 5. The GHSV of the gas in the reactor was varied by changing the mass of the catalyst in the bed keeping the gas velocity through the bed constant. Removal of DMS at 200 °C was not affected by space velocity. However, a significantly higher DMS removal of 93% was observed after one hour of operation at GHSV of 1250 hr^{-1} and temperature of 300 °C. At the same temperature, only 52% DMS removal was observed at GHSV of 2500 hr^{-1} . Almost a complete removal (98%) of thiophenic sulfur was observed at GHSV of 1250 hr^{-1} and 200 °C, whereas at the same temperature it was only 40% removal at 2500 hr^{-1} . The increase in removal would be due to the fact that there would be more surface available per gas molecule and hence an increased number of collisions of the molecules with the surface thus enhancing the rate of adsorption of the molecules. However, no significant effect of GHSV on thiophenic sulfur was found at higher temperatures (300 and 350 °C).

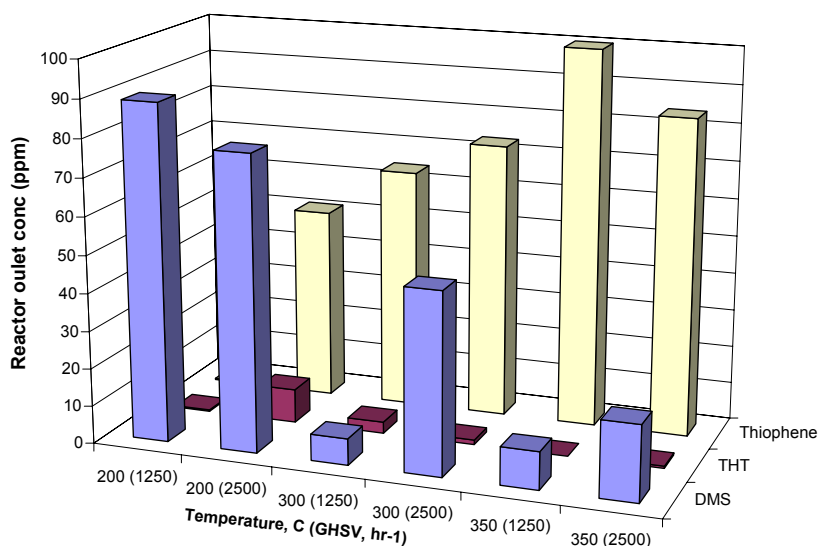


Fig 5. Effect of GHSV on sulfur removal at different temperatures (Inlet: DMS = THT = 100 ppm)

Effects of oxygen concentration in feed

Experiments were also conducted without feeding any air to the system. Comparison of concentration of sulfur species without feeding any air with air feed are shown in Fig 6. Removal performance of activated carbon was significantly down without any external air feed. That solidifies our assumption that the less volatile oxidized species of sulfur is formed at elevated temperature which is physically adsorbed on the activated carbon and thus can be removed from the natural gas. However, there was a small amount of oxygen was present in the simulated natural gas feed (Table 2).

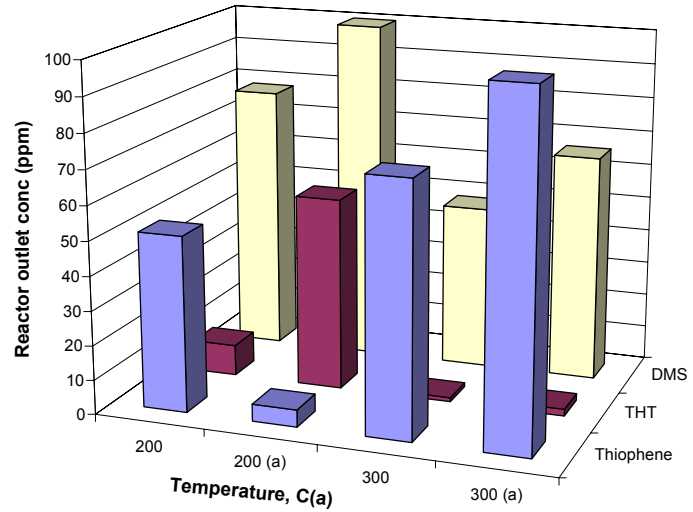


Fig 6. Effect of O₂ on the sulfur removal (a: without O₂) (Inlet: DMS = THT = 100 ppm)

Long-term studies

At room temperature, a complete removal of THT in natural gas was observed for the first 10 hrs (GHSV 2500 hr⁻¹) (Fig 7). However, THT removal capacity suddenly decreased after 11 hrs to 43% and no THT removal was observed after 15 hrs of experiment. The THT adsorption capacity of activated carbon was found to be 0.033 g of THT/g of activated carbon. At higher temperature (300 °C), as mentioned earlier, THT exclusively converted to thiophene and, therefore, no thiophenic sulfur removal was observed. Whereas, DMS conversion over activated carbon remained unchanged (~45%) over 9 hrs of run at 200 °C (Fig 8). Similarly, the yields of SO₂ and COS from DMS conversion remained the same over time (Fig 8).

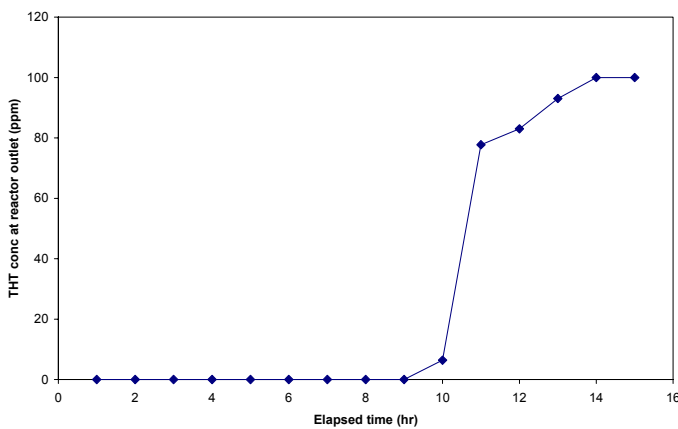


Fig 7. THT removal at room temperature and 2500 hr⁻¹ (Inlet: THT = DMS = 100 ppm)

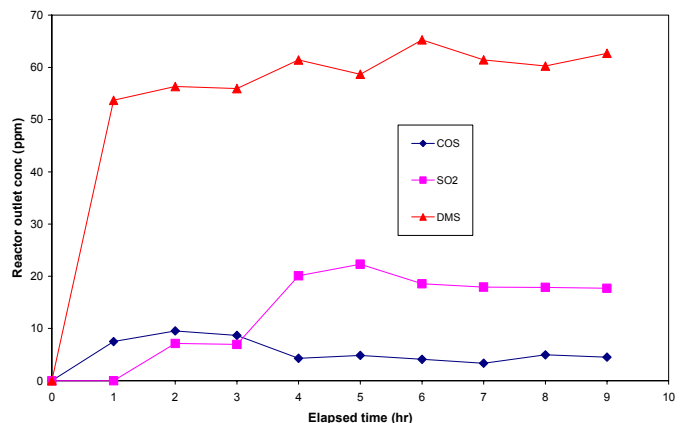


Fig 8. Removal of DMS at 200 C and 2500 hr⁻¹ (Inlet: DMS = THT = 100 ppm)

Competitive Adsorption

Sulfur capacity of activated carbon at room temperature was significantly increased when model sulfur species in N₂ used instead of a simulated natural gas mix as given in Table 2. Since, the competitive adsorption of higher hydrocarbons decreased the sulfur species adsorption capacity of activated carbon. Therefore, the presence of relatively higher hydrocarbons in natural gas would decrease the sulfur removal capacity of the activated carbon sorbent. A complete sulfur removal from Mix-A (DMS, THT, and bal N₂) and Mix-B (MM, TBM, and bal N₂) was observed over activated carbon for 25 hrs at room temperature and 1250 hr⁻¹.

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