

# Potential Explosion Risk Discovered from Creation of Extremely Low Auto-Ignition Components by Neutralization of Alkaline Mercaptan Waste with HCl in the Presence of Methanol over Activated Carbon

Karl-Jan Erstad<sup>1\*</sup>, Michiel Makkee<sup>2</sup>

<sup>1</sup>Consultative Agronomists, Norway

<sup>2</sup>Catalysis Engineering, Chemical Engineering Faculty Applied Sciences, Technical University of Delft, Netherlands

\*Corresponding author: Karl-Jan Erstad, Consultative Agronomists, Norway. Tel: +4757737790; Email: karl-jan.erstad@raadgi-vande-agronomar.no

**Citation:** Erstad KJ, Makkee, M. (2018) Potential Explosion Risk Discovered from Creation of Extremely Low Auto-Ignition Components by Neutralization of Alkaline Mercaptan Waste with HCl in the Presence of Methanol over Activated Carbon. Int J Pollut Res: IJPR-102. DOI:10.29011/IJPR-102.000002

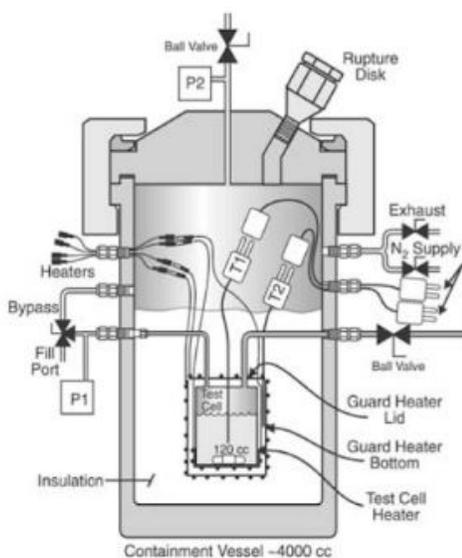
**Received Date:** 04 July, 2018; **Accepted Date:** 10 August, 2018; **Published Date:** 20 August, 2018

### Abstract

The Vest Tank accident May 24, 2007 raised the need to find the causes of the explosion in one of their storage tanks T3 containing sodic mercaptan waste and at that time unknown octane boosters as methanol, ethanol, and MTBE. HCl had been added to neutralize the excess of NaOH in the presence of large amounts of methanol. Laboratory experiments demonstrated a small-scale transformation of methanol (less than 1% in total) into Dimethyl Ether (DME), Chloromethane (CM) and Dimethoxymethane (DMM), nearly independent of the Methanol Concentration. Additional investigation with a calorimetric bomb showed that the adiabatic adsorption of Methyl Mercaptan (MM), CM, and DME to active coal in air led to a temperature increase of approximately of 700°C, whereas when purging with N<sub>2</sub> the temperature raised only 130-150°C. Under practical conditions in a coal filter canister, there will be energy losses, but the occurrence of trace amounts of DME together with MM with auto-ignition temperatures of 235 and 360°C, respectively, had led to an extraordinary risk of explosion.

### Introduction

In this study, attention is drawn to the circumstances of the Vest Tank accident in Slövaag, Norway, May 24 2007 [1]. Among the storage tanks, Tank T3, which was the first of two exploding tanks, measured a volume 3000 m<sup>3</sup>, height 18 m and contained around 50 m<sup>3</sup> caustic wastes enriched with mercaptans (thiols) after a washing of high sulphur loaded gasoline. The explosion in the storage tank occurred by a fire or smoldering in the active coal canister (0.5 m<sup>3</sup>) after adding 18 m<sup>3</sup> conc. HCl to neutralize the caustic waste. The fresh active coal bed was installed to capture all possible high smelly and extremely toxic mercaptans preventing emission to the environment under normal filling and emptying of the storage or breathing of the storage tank by day and night temperature fluctuations. A parallel to the canister fire could be found in the Savannah accident [2,3] where CST (Crude Sulfate Turpentine) containing beta-pinene, which was most susceptible to oxidation and fire by overheating in a newly-installed active coal filter, ignited as air was drawn in during evening cooling. Two years after the explosion and fire in the Vest Tank operation large quantities of methanol were found by the Norwegian police



**Figure:** TOC/Abstract art.

in different tanks (FFI report no. 2009/01119, Norwegian Defense Research Establishment). The source of methanol in the different tanks is still unrevealed. Most likely methanol could be added as an octane improver to the raw gasoline before the sulphur removal washing step, but the presence of methanol was unknown at the time of the explosion. Therefore, the potential risks for chemical reactions with methanol in the performed neutralization with concentrated hydrochloric acid of the alkaline waste were neither considered nor assessed. The alkaline waste resulted from the upgrading of gasoline by the removal of sulphur compounds with an alkaline washing in combination with a kind of “Mercox” operation. Prior to the full-scale neutralization in the tanks of Vest Tank one neutralization experiment was performed in the laboratory, with the real waste of tank T3 with concentrated hydrochloric acid addition, a kind of pilot plant experiment. During this HCl addition, severe gas evaluation was observed, but the composition of the gas

bubbles was not analyzed. Based on the presence of large amounts of mercaptans in the waste there were risks of smell from gas-phase mercaptans, but these gas bubbles would contain only very small concentration of lower mercaptans because of their high-water solubility. Some other unknown compounds had to be present. In the extensive literature search no references could, however, be found for the chemistry that might have taken place during the Vest Tank operation. Due the complexity of the reaction mixture under those reaction conditions (room temperature and extremely alkaline aqueous conditions), no chemical product will be made with high yield, such as DME (Dimethyl Ether). The Williamson’s synthesis in the classical literature is the closest approach of understanding [4]. It is specifically stated that a halide has to be the starting reactant and that in principle  $\text{MeOH} + \text{HCl}$  will not produce any DME or related products.

### A Proposed Reaction Chain for The Production of DME Was:



In organic chemistry, if one wants to have DME and DMM (Dimethoxymethane) from pure methanol then high yields are aimed for, i.e. high conversion coupled with high selectivity in the absence of water (product inhibition) and a base (etherification is normally an acid catalyzed reaction). However, it does not mean that other routes should be excluded. For the commercial production of DME, Chloromethane and Dimethoxymethane, other production routes are practiced and commercially applied. The fate of mercaptans on activated coal filters is only described in a few publications. The oxidation mechanism of  $\text{H}_2\text{S}$  (hydrogen sulfide), MT/MM (Methane Thiol, Methyl Mercaptan), and DMS (Dimethyl Sulfide) on wet ACF (Activated Carbon Fiber) in air at room temperature was investigated in flow system experiments using a packed column with single and mixed gas supplies [5]. Oxidation of MT (/MM) and DMS in mixed gases with  $\text{H}_2\text{S}$  was explained by the occurrence of a hydroxyl radical ( $\cdot\text{OH}$ ) generated from the ferrous cation (presence of Fe in the AC) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) through oxidation of  $\text{H}_2\text{S}$  on the wet ACF. Activated carbons of different origins were studied as Methyl Mercaptan adsorbents in wet, dry, and oxidizing conditions [6]. The materials were characterized using adsorption of nitrogen, Boehm titration, and thermal analysis. The results showed relatively high capacities of carbons for removal of  $\text{CH}_3\text{SH}$ . The amount adsorbed depended on the surface features. Methyl Mercaptan, in general, was oxidized to disulfides, which, depending on the chemistry of the carbon surface, could be converted to sulfuric acid due to the presence of water and active radicals. The formation of disulfides was found to be enhanced by the presence of water, as a result of dissociation of Methyl Mercaptan [7]. Disulfides, when formed, were expected to be stronger adsorbed on the surface of activated Carbon than in water (due to low disulfide solubility in water). In another study, four activated carbons were tested for their adsorbent capacities due to physical and chemical properties [8].

Their abundance of small pores, less than 10 Å, was decisive for sorption of Methyl Mercaptan. A major drop of surface pH of two of the carbons from 7.4 to 3.8-5.9 was related to a possible formation of sulfuric acid via dimethyl disulfide in the inner pores. In this study, we wanted to demonstrate the potential reactivity of methanol in alkaline conditions upon the addition of concentrated HCl and the effect of the generated components on the oxidation of mercaptans in the activated carbon bed and the involved risks of commercial operations (temperature runaways and potential explosions).

### Experimental Section

In the first study, performed at the Technical University of Delft in the Netherlands, formation of gases from methanol in reaction with hydrochloric acid, sodium hydroxide (NaOH) of Sigma Aldrich (part number 36175, 37 % hydrochloric acid (HCl) of Sigma Aldrich (part number 259148), methanol (>99.5%) VWR ProLab and demi water were used without any additional purification. Mercaptans were excluded due to their terrible smell and toxicity. The analyses were performed using a Hewlett Packard gas chromatograph, equipped with a Flame Ionization Detector (FID). 0.5  $\mu\text{L}$  liquid phase sample was injected on an AB-INOWAX, 60 m  $\times$  0.32mm  $\times$  0.50  $\mu\text{m}$  with temperature program: 40°C (6 min), ramp of 20 °C/min to 250°C with a dwell of 1 min. Detector temperature was: 200°C, injector 200°C. For gas chromatograph peak identification, a gas chromatograph coupled with a Mass Spectrometer (MS) (Shimadzu GCMS-QP2010S) was used. Liquid samples were injected on a Factor Four VF wax-ms, 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  with temperature program: 35°C (6 min), ramp of 70°C/min to 240°C with a dwell of 4 min. Injector

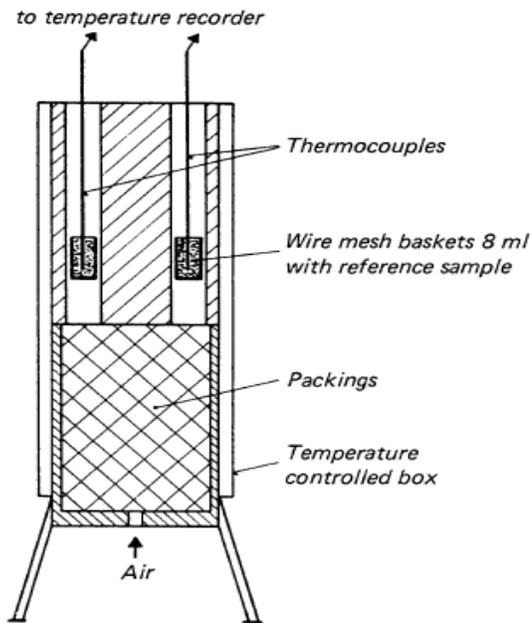
temperature was 250°C, ion source 200°C, interface 200°C. NIST library was used for MS peak identification. Closed plastic vials of 1.4 ml with a cap were used. In (Table 1) the initial composition in each vial is given. The vials were placed on a shaker with a frequency of 500 revolutions·min<sup>-1</sup> at ambient temperature (15-18°C). Samples were taken at the selected time intervals by placing the vial in the auto-sample tray of the GC. After injection, the vial was replaced in the shaker.

Sample	Methanol (μl)	HCl (μl)	H <sub>2</sub> O (μl)
25% methanol	250	500	250
10% methanol	100	500	400
5% methanol	50	500	450
Alkaline 25% methanol	250	500	250
Alkaline 10% methanol	100	500	400
Alkaline 5% methanol	50	500	450
Reference I	2000	2000	0
Reference II	1000	1000	0
Reference III	500	500	0

**Table 1:** Experimental setup for testing gas development from methanol in reaction with HCl.

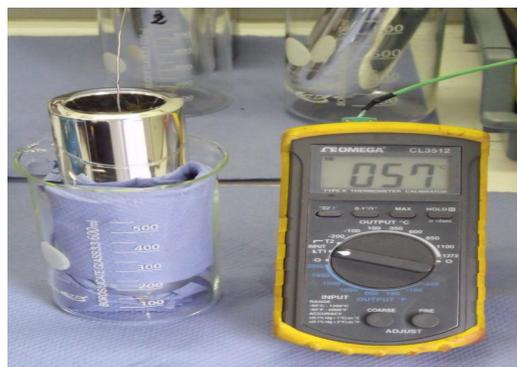
In the second study, conducted at Consilab, Frankfurt a.M. in Germany, experiments were done with a calorimetric bomb with an active carbon (Airpel 10) exactly weighed (about 45 g), and in 2-3 replicates. Firstly, the temperature increase in an adiabatic calorimeter (VSP2) was measured for Chloromethane (CM), Dimethyl Ether (DME), and Methyl Mercaptan/Methane Thiol (MM/MT), with pressure and de-pressure, using N<sub>2</sub> as a purging gas.

The experiments were performed in steps, shifting between purging and depressing. Start temperature was 30 °C, pressurizing to 0.7-1 barg, kept for a short while, depressurizing to 0 barg, measuring the temperature decrease, and cooling down to 30°C. Repetitions were done as long as any net temperature increases occurred. The active coal was weighed including the adsorbed gas compounds at each interval, and temperature increases over all test steps were calculated. Secondly, tests of possible self-ignition until 400°C were conducted with the active coal in a Grever oven, as presented in (Figure 1).



**Figure 1:** Grever oven for tests of self-ignition of active coal.

Thirdly, having observed a continued heating after transfer of MM saturated coal from the calorimeter into a Dewar vessel, as shown in (Figure 2), flows of air instead of N<sub>2</sub> with MM were added to the calorimeter containing active coal.

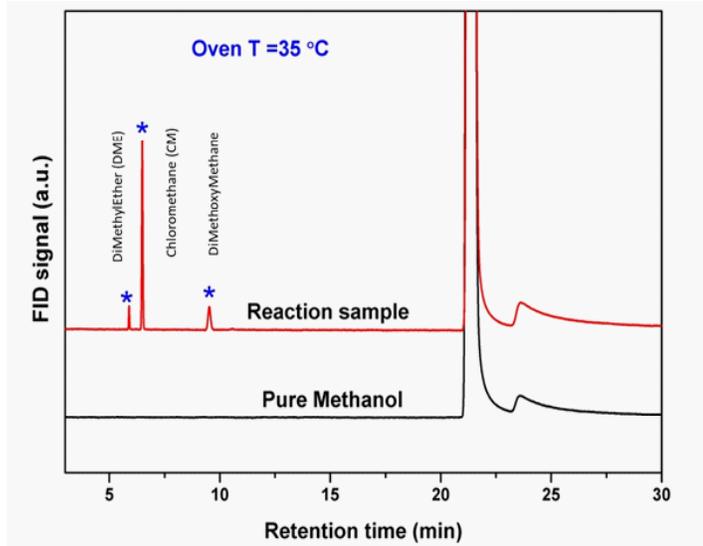


**Figure 2:** A distinctive temperature increase after the transfer of MM saturated active coal into a Dewar vessel when exposing to ambient air.

## Results

### Liquid-phase reaction (methanol, water, and concentrated HCl)

(Figure 3) gives a typical gas chromatogram of the liquid phase from the first study, formation of gases from methanol in HCl reaction.



Component	Retention Time (min)	Distribution
DME	5,44	6
H <sub>3</sub> CCl (CM)	6,04	71,5
Dimethoxymethane	9,07	22,5
Methanol	22,5	
Methanol conversion in the liquid phase of 0.65%		

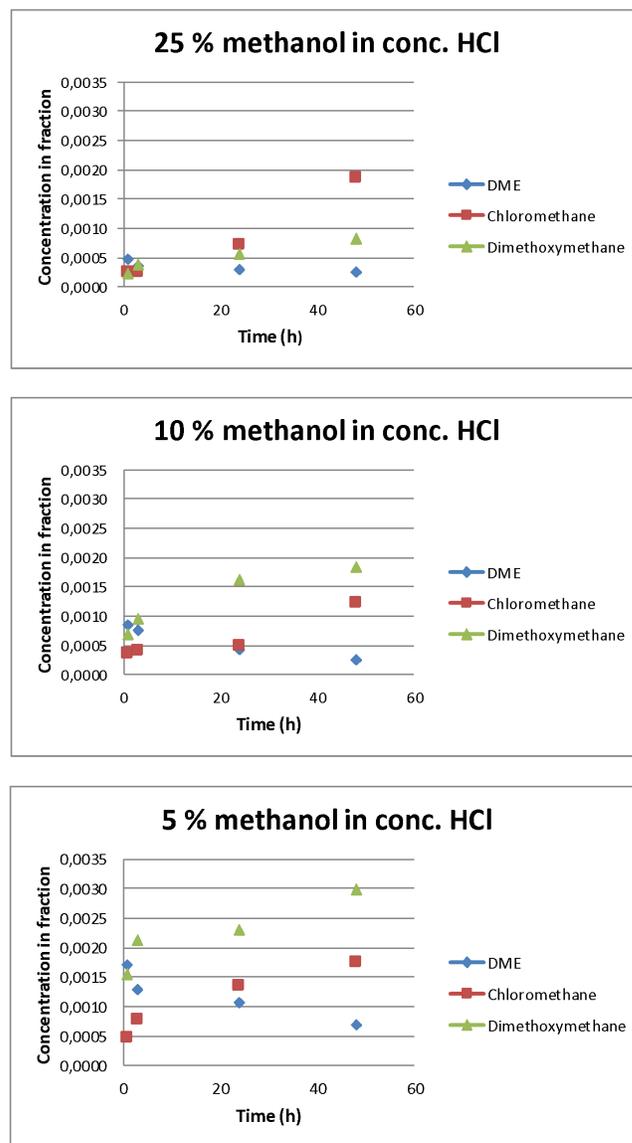
**Figure 3:** Typical gas chromatogram of the liquid phase of a mixture of methanol and concentrated hydrochloric acid, with methanol as dominant peak.

Besides methanol only DME, CM (Chloromethane), and DMM (Dimethoxymethane) were identified by the combination of gas chromatography and mass spectrometer. The recorded mass spectra were compared with the NIST library. A 100% match with DME, CM, and DMM was found. The NIST library gave also some trace amounts of trimethoxymethane or 1-ethoxy, 1,3, 3-trimethoxypropane. After detailed analysis of the fragment spectrum, the trace component was assigned to trimethoxymethane. Since the amount of trimethoxymethane was that low it was not taken into account in the conversion and selectivity calculation. More than 99% of the methanol remained not converted. However, the relative portion reacting with HCl slightly increased as the methanol was diluted with water and/or alkaline. (Table 2) presents the data from the reference experiments.

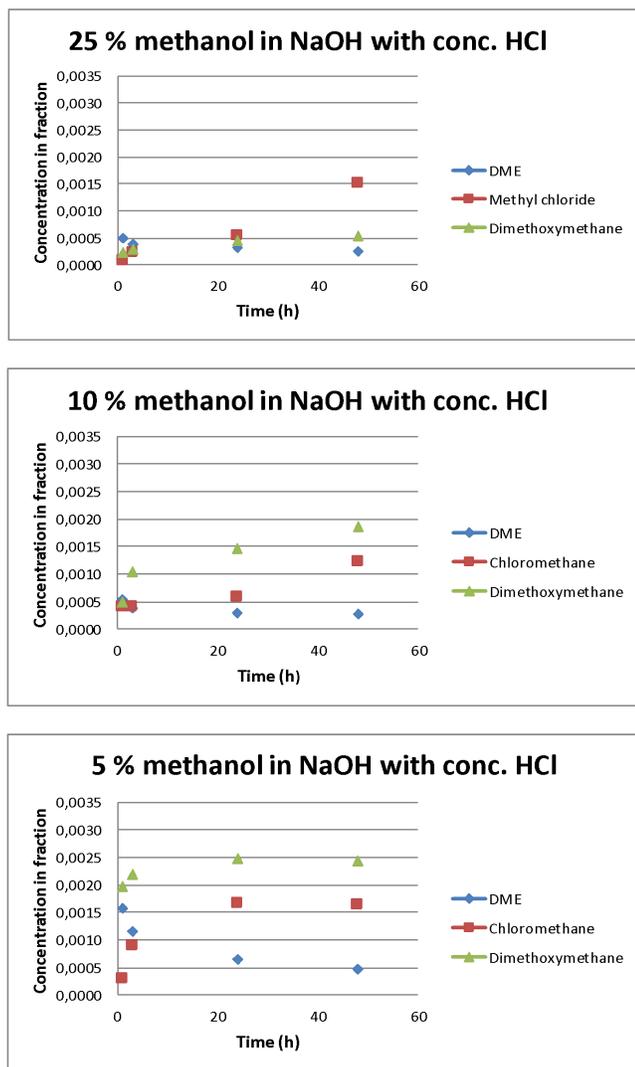
Ref.	Time, h	DME, %	CM, %	DMM, %	Methanol, %
I	24	0.042	0.483	0.132	99.443
II	28	0.038	0.449	0.142	99.37
III	26	0.051	0.504	0.174	99.27

**Table 2:** Methanol conversion of the samples of the reference experiments over time, with decreasing amounts of methanol and HCl as given in Table 1.

(Figure 4) shows the conversion of methanol for the different samples as a function of time on stream when no NaOH (sodium hydroxide) is present, (Figure 5) with NaOH.



**Figure 4:** Product development of the reaction of methanol in water solution and concentrated HCl at room temperature as a function of time on stream in a closed vial.



**Figure 5:** Product development of the reaction of methanol in an aqueous 0,1 M NaOH solution and concentrated HCl at room temperature as a function of time on stream in a closed vial.

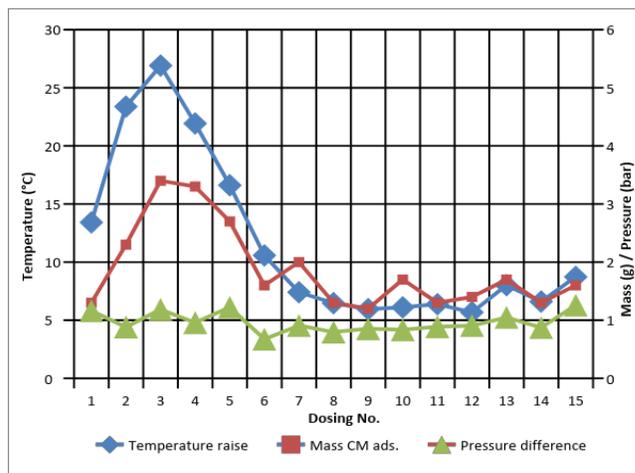
The conversion and the rate of conversion was almost independent of the initial methanol concentration and the presence or the absence of NaOH. In the presence of NaOH more DMM was formed and in the absence of NaOH more CM. The distribution between the components was calculated and a methanol conversion of 0.5 % was determined after 24 hours reaction time, as mentioned indifferent of the methanol concentration. The order of reaction in the homogeneously catalyzed conversion was first order with respect to methanol, i.e. the rate of the methanol conversion appeared linear to the methanol concentration. At high initial methanol concentration, CM was the main product after 48 hours. At low methanol concentration (5 %) mainly DME and to some extent DMM were formed after 1 hour. In time, DME concentration decreased and DMM and especially CM increased. Based on the performed experiments it could not be decided

whether the decrease of DME would result in an increase of either DMM or CM. Although the conversion levels were very low, the repeatability and the reproducibility of the experiments were very high. Almost the same conversion level with the same selectivity towards the mentioned products was measured. In a separate experiment the gas bubbles evolution in a larger vessel of 100 ml with a magnetic stirrer was followed with time on stream (10 ml methanol, 40 ml water, and 5 ml concentrated 37% HCl). The composition of the gas bubbles showed that besides methanol, DME and CM were the main products. The composition was analyzed by mass spectrometer. It should be noted that the boiling point of methanol is 64.6°C, whereas boiling point of CM, DME, and DMM are -24°C, -25°C, and 41°C, respectively. Due to the higher boiling point of DMM and its lower concentration, the found composition of the gas bubbles (DME and CM) is logical.

The methanol found in the gas phase is due to entrainment of the methanol with the low boiling components DME and CM. The experiments with MS as analysis detector were repeatable and reproducible. The quantification of the gas phase was outside the scope of the research, only the composition changes in time were measured.

#### Gas-phase adsorption experiments (mercaptan, dimethyl ether with either nitrogen or air)

In the second study, when CM (Chloromethane), DME (Dimethyl Ether), and MM (Methyl Mercaptan) were fed into the calorimeter with the active coal, they demonstrated quite equal temperature increases, which indicated merely an energy release by adsorption on coal filter surface. The recorded temperature profiles showed a high reproducibility. (Figure 6) shows the data for CM, with stepwise temperature increases without the lowering effect of depressurizing, quite high at the beginning, declining at the end by coal saturation. With about 45 g active coal the CM adsorbed was 11.8 g, by a feed of 28.1 g CM. The total adiabatic temperature increase was 174.1°C without depressurizing, and 151.3°C with depressurizing.



**Figure 6:** Pressure increase when feeding CM together with N<sub>2</sub> into the calorimeter, temperature increase without depressurizing.

The behavior of DME is presented in (Figure 7). The adsorption of a temperature increase by DME was a little slower in the start as compared with CM. With approximately the same mass of 45 g active coal the DME adsorbed was 10.9 g, by a feed of 17.8 g DME. The total adiabatic temperature increase was 130.6°C without depressurizing and 126.2°C with depressurizing.

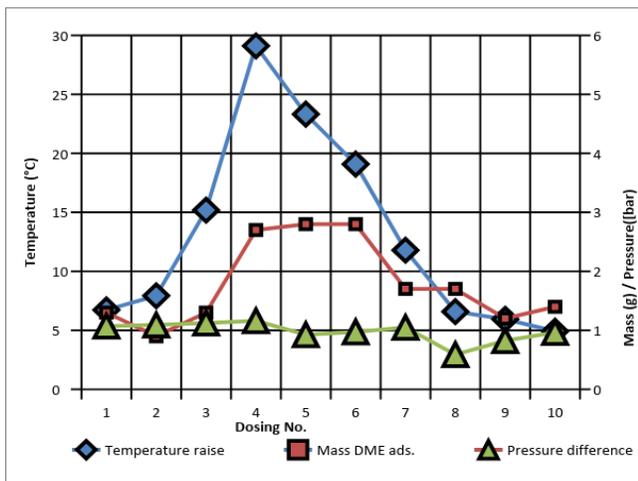


Figure 7: Pressure increase when feeding DME together with N<sub>2</sub> into the calorimeter, temperature increase without depressurizing.

(Figure 8) shows the corresponding results of MM into the calorimeter. The adsorption and temperature increase came promptly, and then fell rapidly by saturation on the active coal filter. Again, the mass of active coal was around 45 g and the absorbed MM was 14.9 g of a total feed of 21.9 g MM. The total adiabatic temperature increase was 187.4°C without depressurizing, and 152.7 °C with depressurizing.

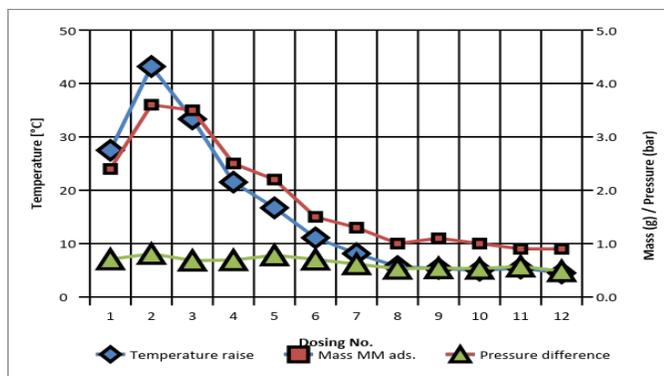


Figure 8: Pressure increase when feeding MM together with N<sub>2</sub> into the calorimeter, temperature increase without depressurizing.

In summary, the heating of active carbon in the Grewer oven until 420°C led to no sign of self-ignition of the adsorbed species, as the temperature evolution of the active carbon mixed with an inert reference material was almost identical under a nitrogen atmosphere. However, when transferring MM (Methyl Mercaptan) saturated coal from the calorimeter into a Dewar vessel, a continued heating occurred in contact with air, as shown in (Figure 9).

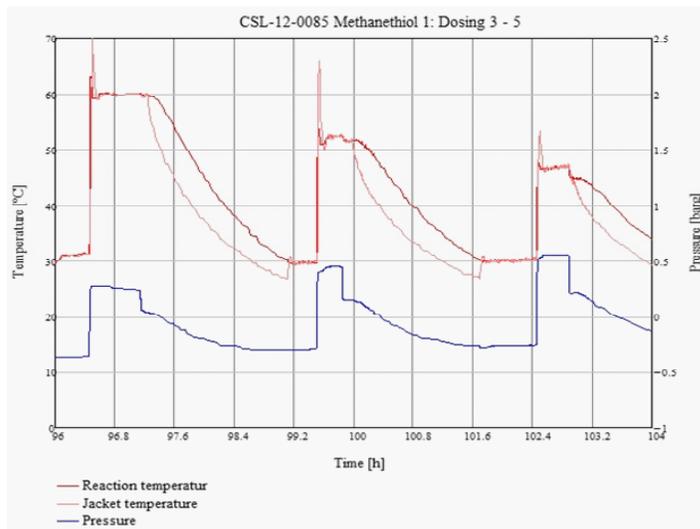


Figure 9: Pressure increase when feeding MM together with N<sub>2</sub> into the calorimeter and gradual reduction of increase in temperature by each feed step as the active carbon became saturated with MM.

This induced a new set of experiments, using air instead of N<sub>2</sub> as carrier gas, and a dramatic increase of temperature was observed, as illustrated in (Figure 10). This temperature increase is related to the oxidation of the adsorbed Methyl Mercaptan reported by Bashkova *et al.* [8].

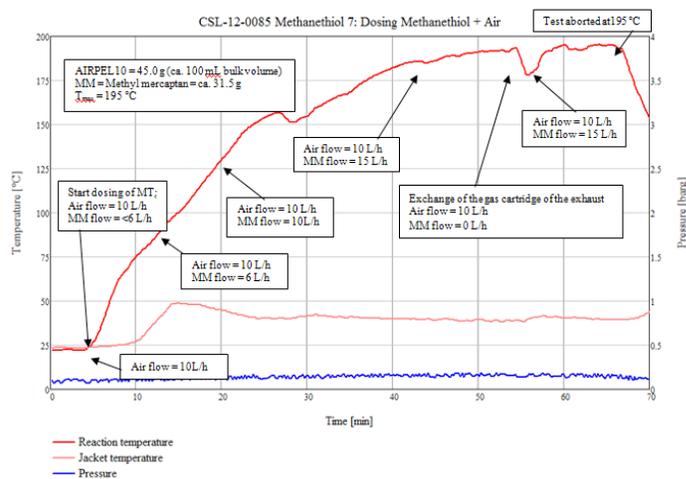
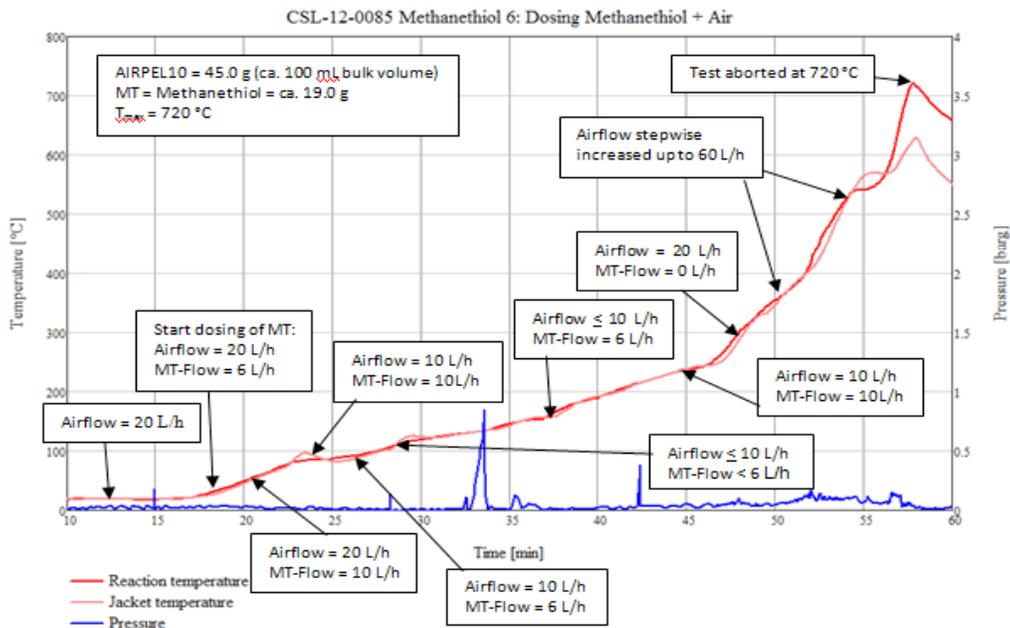


Figure 10: Pressure level when feeding various flows of MM together with air at steady flow into the calorimeter and with a distinct rise in jacket and in particular reaction temperature as the active carbon started to oxidize (experiment stopped at 195°C to check the endurance of the calorimeter).

When feeding various flows of MM and air into the calorimeter a distinct increase in both jacket and reactor temperature were observed as the activated carbon started to oxidize the MM. Tests were aborted when the reactor temperature reached 720°C (Figure 11).



**Figure 11:** Pressure fluctuations when feeding various flows of MM and air into the calorimeter and with a distinct rise in both jacket and reaction temperature as the active carbon with MM started to oxidize with the test continuing until 720°C.

Initially the first test was stopped at 195°C in order to check the condition of the calorimeter and verify that the equipment could withstand this strong heat generation by the oxidation of MM (Methyl Mercaptan) with air. Afterwards the purging of MM together with air was repeated and continued, and it was allowed to an elevated temperature of 720°C before it was stopped, as shown in (Figure 11). This indicated that this oxidation of MM in air over activated carbon is reproducible and perhaps is catalyzed by the impurities such as iron in the active carbon. MM was purged together with air into the calorimeter over almost 60 minutes. After the experiment the calorimeter was opened and we observed that the activated carbon had numerous hotspots indicated severe smoldering as demonstrated in (Figure 12).



**Figure 12:** Smoldering of active coal in hot spots (granules in ashes) following a strong oxidation when simultaneously MM and air were fed into the calorimeter over almost 60 minutes.

## Discussion

As pointed out in the introduction, scientific literature is very scarce with experimental results proving that MM saturated active coal could oxidize simultaneously with air flowing through the active carbon loaded filter. In the real world's practical industrial life, this oxidation of both MM and active carbon is not known. Hence, producers of active coal are not aware to warn about these risks. On the contrary, they recommended their active coal products. The activated carbon should even be impregnated with NaOH in order to double their capacity especially for the usage for mercaptans emission abatement.

However, by our experiments, a thermal runaway was observed when mimicking an active carbon filter system loaded with MM in a breathing air sequence, and most likely, the reactions are catalyzed by iron as a natural compound of the active coal, especially for the oxidation of MM. These temperature runaways are obtained when the energy loss of the active carbon canister to the environment is small, and most pronounced with fresh, dry coal material. A development of hot spots is more probable by increasing size of coal filter canister, in line of the theory of Frank-Kamentskii [9]. In this study, activation energy was assessed to approximately 80 kJ/mole and the preliminary factor to  $3.63 \cdot 10^4$  K/s (thermal diffusivity of the bulk:  $2 \cdot 10^{-7} \text{m}^2/\text{s}$ ). If the system had no energy loss, a worst-case scenario was that a hot spot in the middle of the active carbon bed could develop from 150°C below any ignition point, because of the trapping of heat. On the other hand, in a practical situation, there will be energy losses, by gases flowing through and humidity acting as energy sinks, consuming and taking heat away by boiling and vaporization. Under actual reaction conditions as in Vest Tank T3 in the presence of methanol (even in the range of 5 to 10 %) in alkaline solution the addition of concentrated hydrochloric acid will lead to the formation of CM, DME, and DMM. The formation of especially DME will increase the risk of an explosion due to its very low auto-ignition temperature of 235°C, together with its boiling point of -24°C. This must be compared with the properties of MM, with an ignition temperature of 360°C and a boiling point of -6°C. The ambient temperature in the morning of the accident was 10°C. The presence of CM and methanol would not increase the risks to that extent due their quite high auto-ignition temperatures of 625 and 455°C, respectively.

## Conclusion

The adsorbed MM in breathing active coal filter is able to be oxidized. The neutralization of the alkaline waste with concentrated hydrochloride acid in the presence of methanol will result in the formation of CM, DMM and especially DME (with its low auto-ignition temperature). The combined effect of temperature increase of the oxidation of MM and the auto-ignition of DME will lead to

hot spot and even a fire in the active carbon canister (no flame resistor was installed). This was the ignition source (spark) to initiate the subsequent explosion of the (explosive) gas mixture in the T3 storage tank. In other words, the other unexpected gases increased the risks dramatically as well at the Savannah as the Vest Tank accidents. In the former case, it was the presence of beta-pinene, in the latter methanol transformed to DME.

## Author Contributions

These authors contributed equally.

## Notes

The authors declare no competing financial interests.

## Acknowledgment

We thank Consultative Agronomists, Norway for funding these investigations. We are also grateful to three anonymous reviewers for useful comments on an earlier version of this manuscript.

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