OPTIMALIZATION OF RECUPERATION PROCES WITH METHYL BROMIDE FOR STATIONARY QPS-TREATMENT FOCUSED TOWARDS MINIMAL ENERGY CONSUMPTION

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ABSTRACT

Desclean Belgium together with Vito, supported by the Flemish Government (IWT-Institute for the Promotion of Innovation by Science and Technology in Flanders), enrolled a project to investigate optimalization of recuperation of MeBr with fumigation of containers in the harbor of Antwerp (Quarantine and Pre-Shipment treatments - QPS). The objective of this investigation was to provide an answer towards the question if it was feasible to recuperate MeBr on a practice and mobile way by active carbon in order to reduce the emissions of MeBr towards zero (part of Montreal protocol). Practical stands for the dimensions and weight of the total systems. With mobile the daily appliance and substitution of the current approach is meant with minimum number of persons for proper execution. It was necessary to further investigate the process of recuperation of MeBr towards energy efficiency. Besides the improvements of the recuperation process of active carbon, alternative absorbents were evaluated. Thermal management (heating of active carbon and active fan control) had a significant roll within the process control. The results shows that is possible to recuperate MeBr on a practical and mobile way by combination of one or several steps, followed by an additional step that eliminates Me Br completely. The result is a feasible and economical process that allows large-scale introduction of emission free MeBr treatments for QPS. Furthermore the developed approach shows high potential for successful introduction into other applications like agriculture.

Key Words: Quarantine and Pre-Shipment treatments – QPS, Methyl Bromide – MeBr, Integrated Pollution Prevention and Control - IPPC

1. INTRODUCTION

The project consisted of several Work Packages (WP):

In WP 1, the process of recuperation of MeBr in active carbon was evaluated applying quantum chemical methods like chemisorptions, mass spectrometry, gas chromatography, thermo spectrometry, thermo graphical metrical analyze (TGA),

and Differential Scanning Calorimeter (DSC). In WP2 possible alternative materials for sorption were evaluated like zeolites, focused on minimum energy usage. In WP3 thermal management was further optimized to obtain minimum electric energy usage as well on peak power as total energy consumption to allow introduction of a battery power system.

2. PROCESS OF RECUPERATION OF MeBr

Four different types of Active Carbon (AC) were characterized towards adsorption (Table 1). Provided specifications were checked. All samples had a specific surface (BET) of 900 – 1000 m²/g and contained 5% tot10% water. Hydrafin CC8*30 is an AC derived from coconut fiber which, according to the literature should be very efficient for sorption of MeBr. No specifications were obtained from Organosorb 10-CO, a catalytic activated AC on basis of cupper. All materials were micro porous with an average dimension < 10 Å.

Table 1. Specifications and measured values of AC samples

Type	Specification		Measured		
				48 h Vacuüm	TGA
	BET (m²/g)	Conc H_2O (Wt%)	BET (m²/g)	Conc H_2O (Wt%)	Conc H_2O (Wt%)
Hydrafin 30N	900	5%	890	5,5%	1,7%
Hydrafin CC8 * 30	1000	10%	1160	18,9%	18,7%
Desorex K47	900	5%	950	4,8%	8,5%
Organosorb 10-CO	—	—	1140	2,8%	4,4%

The specific surface (BET) was determined with N_2 adsorption / desorption. Notice the relative small differences between specified and measured.

The amount of absorbed water on the samples was determined by the diminution of the weight after 48 hours of storage in vacuum at room temperature. Significant reduction in weight with ~100°C in the thermo gravimetric analyses of the samples were noticed. (see figure 1a). The TG analyses of all monsters were executed from room temperature up to 1200 °C (temperature rises of 5 °C/min) under constant flow (70 cm³/min) of argon. The results are given in table 1 (colon 5 and 6). Figure 2 compares the specifications. It is clear that hydrafin CC8*30 –with 20% – has the highest power to sorption for water. Given that the BET of Organosorb is almost the same as Hydrafin CC8*30, the sorption capacity for water is limited (~3 – 4 %). The reason lies within the catalytic activation. Within the DSC spectrum (figure 1b) it is clear to see that the desorption of H_2O is endothermic and –as expected– according the quantity of absorbed water. Above 600°C a possible degradation of the product is noticed.
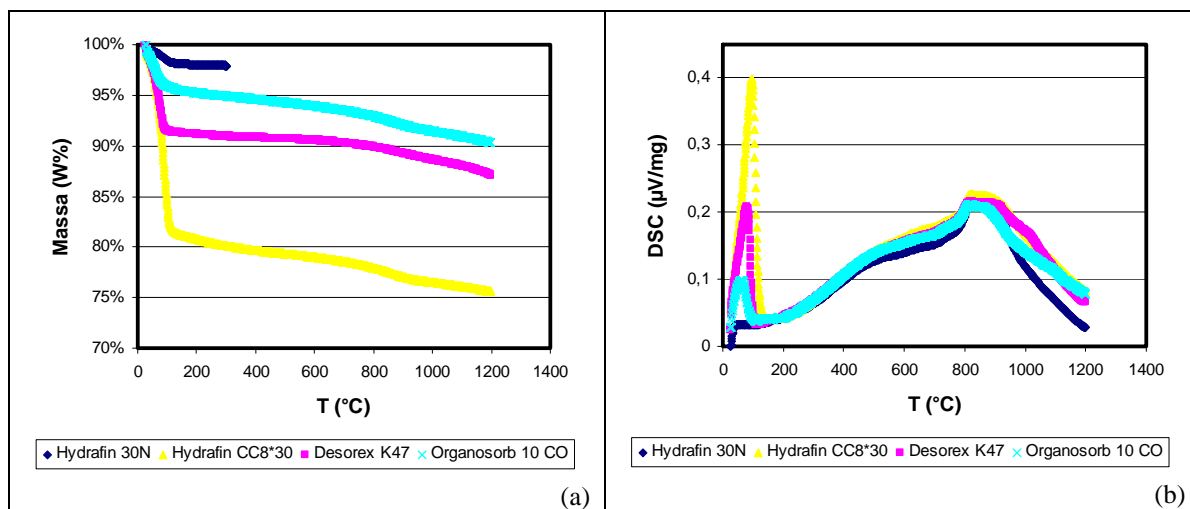
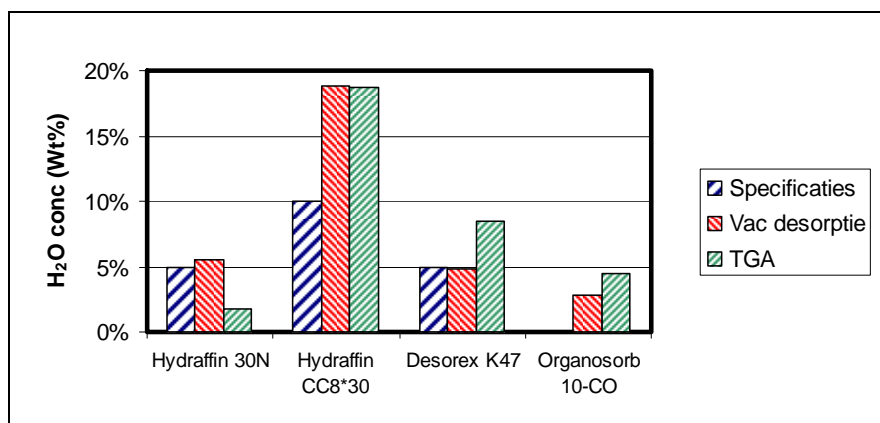Figure 1: TGA (a) en DSC (b) measurements of different types AC under inert (Ar) atmosphere

Figure 2: Concentration of H_2O for the different types of AC under vacuum desorption and TGA under inert (Ar) atmosphere compared to the provided specifications.
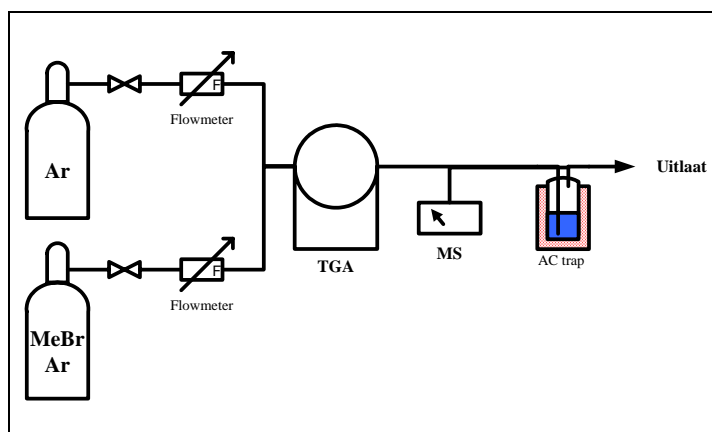
Figure 3: TGA: MeBr adsorption and desorption under inert (Ar) atmosphere
A significant difference is noticed between the 'pure' active carbon (Hydrafin en Desorex) and the catalytic active Organosorb (figure 5). The adsorption of MeBr on Organosorb is much faster (~14%/h) then for Hydrafin en Desorex (2 – 3.5 %/h) (table 2). Given that the adsorption time was not sufficient to achieve equilibration, a relative good estimation of the sorption capacity was obtained. The capacity of absorption of Organosorb is significant higher (> 20 %) then the other AC types. The capacity of absorption of Desorex is maximum ~10% while Hydrafin is lower.
The velocity of desorption is –with room temperature– like expected lower: about the 50%. With higher temperature the velocity increases significant. This phenomenal can also be obtained under vacuum conditions. The quantity of heath that is released with adsorption and required for desorption can normally retrieved from DSC signal. However this signal is given the materials to weak to allow any statement. A possible conclusion is that the amount of heath (per gram AC) will be limited.
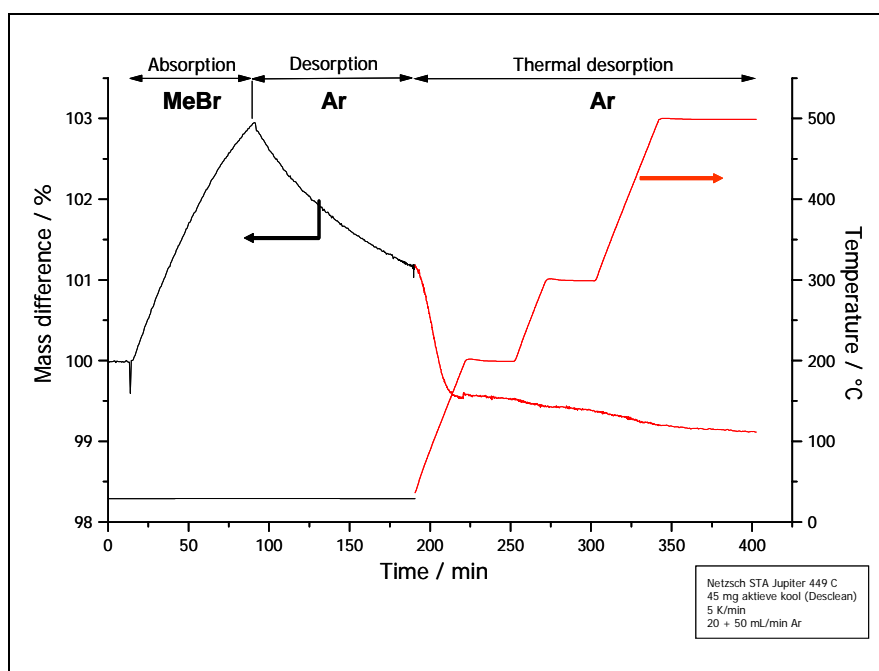

Figure 4: TGA measurement: MeBr adsorption and desorption under inert (Ar) atmosphere
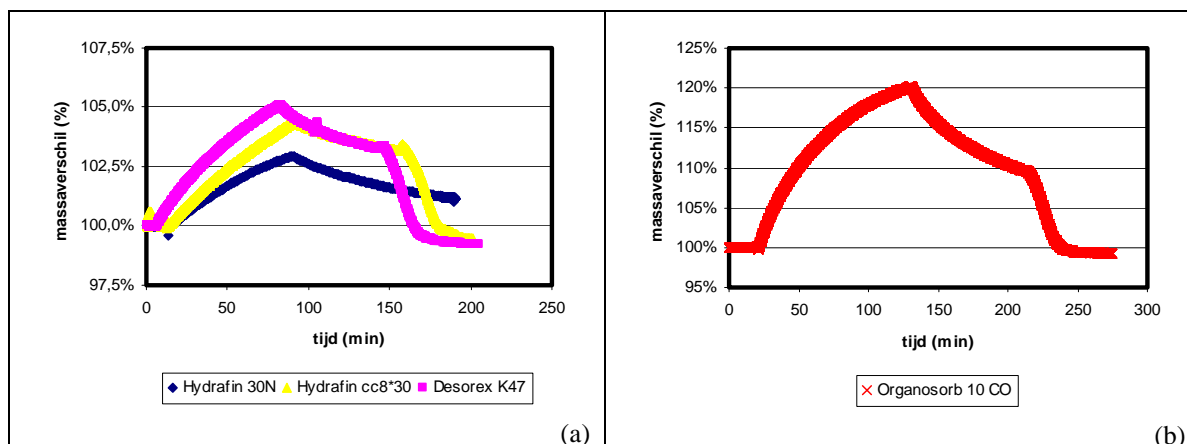
Figure 5: TGA for absorption and desorption of MeBr for the different AC samples

Table 2: Adsorption and desorption velocity of MeBr for different types of AC

Type	MeBr Sorptiesnelheid	
	adsorptie (Wt%/h)	desorptie (Wt%/h)
Hydrafin 30N	2.33	1.06
Hydrafin CC8 * 30	3.44	1.19
Desorex K47	3.65	1.84
Organosorb 10-CO	14.2	7.75

3. SIMULATION OF DE ENERGY DEMAND

Based on the article "Methyl Bromide Recovery on Activated Carbon with Repeated Adsorption and Electrothermal Regeneration" (J.D. Snyder & J.G. Leesch in Ind. Eng.Chem Res. 2001 p. 2925 ev – see References) statically and dynamical simulations related with the energy demand were executed. These simulations programmed in Engineering Equation Solver (EES).

The static simulation were based on the chemical equilibrium between the active carbon and the MeBr partly in the containers, partly absorbed by the AC. From these simulations the conclusions were made towards the distribution of mass of the MeBr in the different cartridges (sequence of cylinders used after each other to allow reduction of MeBr in multiple steps) and number of applied cartridges in function of the temperature, desorption and absorption.

The dynamic simulations were focusing on several time depending aspect of the process, like:
- the amount of required energy at each moment
- the temperature behavior of the AC during the process
- the absorption and desorption of MeBr

- the concentration of MeBr in the container

All simulations were executed for a container of a volume of 35 m³ with air temperature of 30 °C and atmospheric pressure of 1,013 bar. As assumption was take that the complete container department had to be filled from 0 to 15.000 ppm MeBr (about 2 kg MeBr). In reality less MeBr will be applied since the container will be filled when disinfection has to take place. On the other side the container will consists of material that will absorb MeBr (e.g. wood) resulting in more initial MeBr to obtain the required initial concentration of MeBr. Furthermore the effect of humidity was not taken into account.

For the obtained energy consumption the energy for the thermal management (heating/cooling) is only taken into consideration, exclusive the energy required for the ventilation. This is acceptable given the fact that the thermal energy demand is in general much larger.

4. THERMAL MANAGEMENT AND ENERGY CONSUMPTION

A test set-up (see Figure 6) was constructed to allow to understand the impact on thermal management and to capturing the energy consumption. Key question that had to be addressed was if it is possible to obtain a portable and practical system.

The following components were applied:
Cylinder: diameter 160 mm length 1 m filled with active carbon
Ventilator: VENPLAST Type P 282, 0.75 kW 3F 380V 50 Hz powered by an 3-phase inverter with frequency regulation for speed regulation
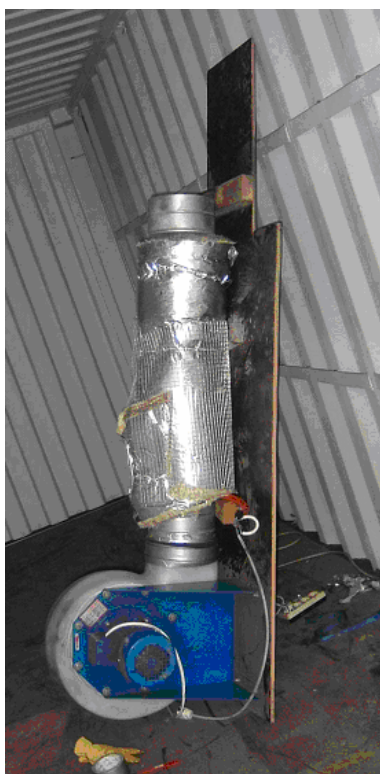**Heating**: 12 m heating ribbon, (120°C, 66W/meter) with 3 D metal grid

Figure 6: Test set-up

With this relatively simple construction it was easy to obtain a first step MeBr absorption of more then 60% (40000 towards 13500 ppm). With the addition of multiple steps (cartridges) almost fully absorption was obtained (40000 towards 5 ppm).

5. CONCLUSION

Major differences were found between the 'pure' active carbon (e.g.. Hydrafin en Desorex) and the catalytic active Organosorb. The absorption of MeBr on Organosorb is much faster (~14%/h) then for Hydrafin and Desorex (2 – 3.5 %/h). The adsorption capacity of Organosorb is significant higher (> 20 %) then the other types of AC. The adsorption capacity of Desorex is maximum (~10%) while Hydrafin is lower. The desorption velocity is –with room temperature– as expected significant lower (50%). With higher temperature this velocity increases rapidly. Similar effect can be obtained by applying vacuum. Besides the specific capacity, the size of the grain is important for the airflow and the required energy. Relevant information concerning the usage of MeBr and possible alternatives were studied.

From the simulation can be concluded that the time to achieve equilibrium is directly dependent of the airflow. A possible approach is the two step process, starting with the adsorption of MeBr with active carbon, followed by the destruction of the remaining fraction of MeBr via the chemical reaction of natriumthiosulfaat (NaS_2O_3). Although Hydrafin CC8*30-active carbon possesses relative good

absorption property and thermal stability with higher temperatures (150 °C), the less efficient Desorex K47 was restrained due the more compact packing.

Partially recuperation of MeBr (up 60%) is possible on a practical and mobile way. And with the introduction of the second step MeBr is no longer released and opens the door for emission free MeBr treatments on a practical way.

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