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Elimination of Odours in Off-Gases from Food Production by Means of Ozone

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Introduction

Odorous compounds emitted in off-gases originating from food production industry and municipal management are a major part of the natural environment pollution, specially in the areas of urban agglomerations and intensive animal production. Chemical characteristics as well as biological activity of these substances bring about serious dangers for both lower organisms and humans. On account of severe harmfulness, the most worth mentioning, among others, are cyclic organic compounds which characterize with carcinogenic properties.

The development and implementation of effective methods of odours removal from food production facilities can greatly contribute to limiting the discomfort of the inhabitants. In particular, the inhabitants of bigger cities are affected by this problem which sometimes poses a significant nuisance for them. The contentment of the inhabitants and the lack of odour nuisance are also important for municipal authorities in taking investment decisions.

Among numerous techniques for gas purification from odours, in recent years there has been an intensive development of biological methods [Monani et al., 2007, Tymczyna et al, 2007], especially biofiltration which characterizes with low unit costs [Monani et al., 2007; Rappert & Muller, 2005, Tymczyna et al, 2007], yet it is not all-purpose.

As an alternative for biofiltration an ozonation in gas phase can be applied. Ozone in gaseous phase exhibits strong oxidizing and disinfecting properties, thus, in comparison to other methods its use is more advantageous, particularly when employing to fight unpleasant smell and decontaminate surfaces. Generally, it is more efficient than other disinfecting and bactericidal agents. Ozone can be produced on site, hence the problems connected with transport and storage can be neglected. Moreover, during the ozonation process no chlorinated by-products are formed and the excess amount of ozone can be decomposed to oxygen.

The methods for deodorization by means of ozone can, in the main, be applied when contaminated air or effluent gases cannot be treated with conventional oxidation techniques or biological methods. It should be noted that ozone being one of the strongest oxidizers allows to conduct gas purification processes together with bothersome odours removal in a relatively effective way. Oxidation of organic compounds included in odours proceeds with the formation of intermediate products which thereafter are subject to conversion to aldehydes and organic acids. During the oxidation of aromatic compounds a ring breaking mechanism is involved. The desirable effect can be often achieved by performing only partial oxidation which removes the functional group or locally modifies the molecular structure in a different way.

The effective use of ozone in eliminating odours contained in post-production gases is, however, still not fully examined in relation to the process. It occurs in spite of the attempts made to explain the "mechanisms" of these processes, which is proved by many papers [Jenkin & Haymann, 1999; Kim-Yang et al., 2005].

This article presents laboratory research on the ozone oxidation of benzene, cyclohexane and toluene which are the main components of odours originating from food and agriculture industry. The influence of the most meaningful parameters on the deodorization efficiency was analyzed.

Materials and methods

The ozonation experiment of selected odorants was carried out on the setup shown schematically in Fig. 1. It consists of ozonizer, power supply system, standard gas mixture generator, reaction chamber and analytical system. The change in ozone concentration was obtained through the control of the voltage supplied to the ozonizer.

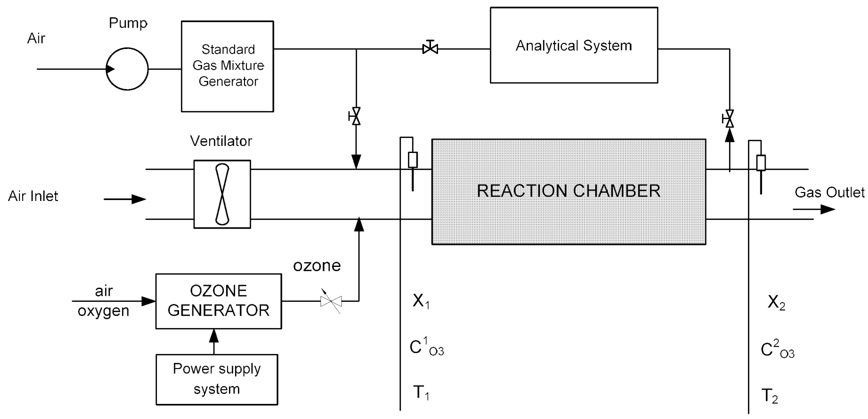

Fig. 1. Schematic of the experimental setup

In turn, along with changing the air flow rate through the reaction chamber it was possible to obtain different contact times τ:

$$\tau = \frac{V_R}{\dot{V}} \text{ , sec} \tag{1}$$

where: V_R – deodorization chamber capacity, $\dot{V}$ - volumetric gas flow rate.

Basing on the concentration measurement of the odorants before and after the reaction chamber, the deodorization efficiency η was evaluated as:

$$\eta = \frac{C_1 - C_2}{C_1} \tag{2}$$

where: C_1, C_2 – concentration of odorous substance in the inlet and in the outlet, respectively.
The measurements of the concentration of odorous compounds were made with the use of SPME-GC-MS method which was previously applied by Cai et al [2006, 2006a], Turkmen [2004] and Popp et al. [1999].
Exact parameters of GC-MS system are given in table 1.

Table 1. Conditions of analytical procedure

Isolation of analytes		
SPME	*100µm PDMS (Supelco)*	
Isolation time	*10 min*	
Desorption time	2 min at the temperature of injector	
The operation conditions of the chromatograph (TRACE ULTRA):		
Injector:	*constant temperature PTV (splitless mode) @ 270°C*	
Capillary column:	RTx 5 (Restek) 60m x 0.25mm d_f=0.25µm	
Oven temperature programming:	45°C (2 min hold) ramp 5°/min to 270°C, 10 min hold	
Carrier gas:	He (99,9996%) @ 40 cm/s	
The MS operating conditions (POLARIS Q):		
Ion source temperature	250°C	
Transfer line temperature	300°C	
Scanning mode I: *Full Scan*	42.0 - 270.0 amu	
Data aquisition	Excalibur 2,2	
Library	NIST '05 and Wiley 8th Edition	
SIM:	Quantitation ion	Qualification ions
Trimethylamine	58	59
Triethylamine	86	101
N,N-dimethylacetamide	87	72, 44
1-Propenethiol	73	74
Benzene	78	77
Toluene	91	92
Ethylbenzene	106	91
Xylenes	106	91
Cumene	120	105
Mesithylene	120	105
Trichloroethylene	130	132
Tetrachloroethylene	166	168, 164
Dichlorobenzenes	146	148, 111
Trichlorobenzene	180	182

According to literature review and the results obtained for the gas phase ozonation of the odour representatives originating from food and agriculture industry (Table 2), the ozonation process appears to be effective and promising technique of the deodorization of effluent gases. Applying high excess of ozone allows to remove almost 80% of odorous compounds.

Table 2. Degradation of selected odorous compounds in the gas phase ozonation [%] , contact time τ= 20 sec

Compound	Ozone concentration [gO_3/m^3]		
	0.062	0.125	0.187
benzene	NC	30	62
cyclohexane	NC	77	72
toluene	15	50	80

Due to satisfactory results obtained for degradation of compounds in a gas standard mixtures, this method was applied for degradation of organic compounds contained in real samples from food industry. Figure 2 depicts chromatograms of the degradation of the real sample.

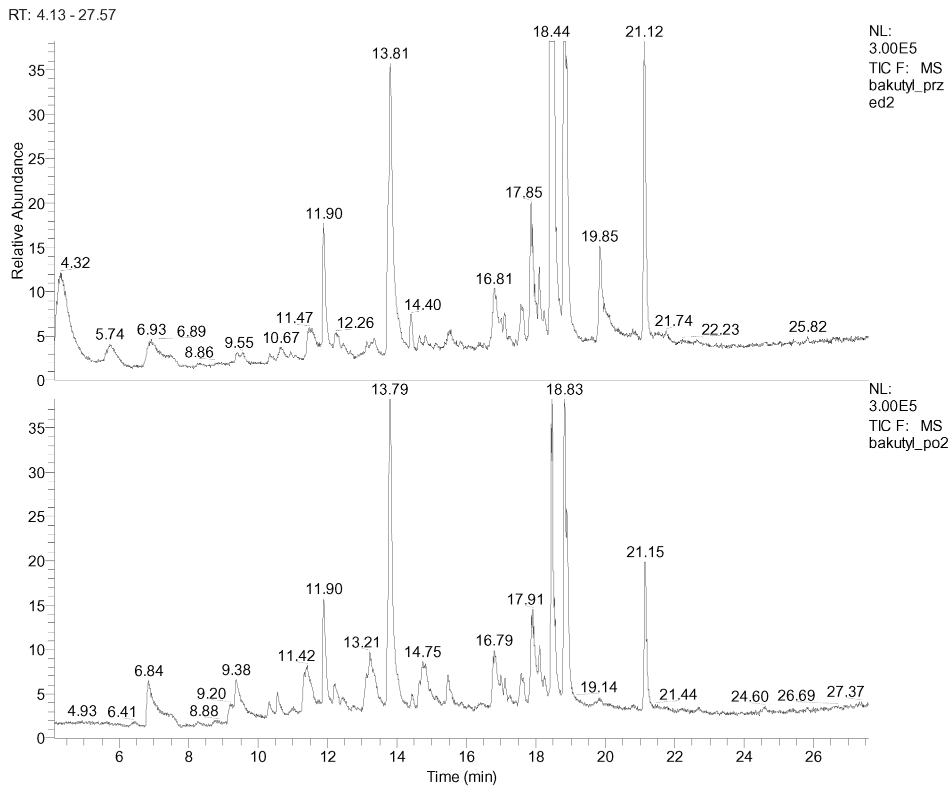

Figure 2 Degradation of real sample a stack gas from meet waste real sample

Degree of degradation of odorous compounds in the real sample is presented in Table 3.

Table 3. Degradation of compounds in natural sample off gases from met factory

Name of compounds	CAS	Concentration [ppm]	Percent degradation	Remarks
Trimethylamine	75-50-3	27	99	
Triethylamine	121-44-8	52	97	
N,N-Dimethylacetamide	127-19-5	7	increase	
Phenol	108-95-2	91	35	
Dichlorobenzene	95-50-1	104	57	
1-Propenethiol	925-89-3	23	97	
Quinone	106-51-4	4	increase	Degradation product of benzene ring containing compounds
Trichloroetene	79-01-06	72	7	degradation product of tetrachloroethene
Tetrachloroethene	127-18-4	96	75	
Dibutyhyl phthalate	84-74-2	17	65	
Dihexylphthalate	84-75-3	9	78	

The highest degradation was achieved for the organic compounds containing heteroatoms such as N and S. Degradation of trialkylamines amounted to 99%, similarly high for 1-propenethiol (97%). In case of chlorine-substituted compounds a significant decrease of tetrachloroethene concentration and an increase of trichloroethene concentration was observed. It can be presumed that trichloroethylene is an intermediate product of the oxidizing degradation of tetrachloroethene.

Conclusions

The gas phase ozonation is an effective and fast method for the deodorization of off-gases.

Applying ozone has many advantages such as low running costs, easy cleaning of the installation, no waste, elimination of bacteria, ability of increasing the efficiency of odour removal process through combining with other methods (ozone in aqueous solutions, exploitation of catalysts).

Conducted research on gas phase ozonation has proved a high effectiveness of this process. The method is particularly recommended for treating gases containing hardly biodegradable substances which prevent from using biological methods for degradation/elimination of these contaminants.

The obtained results confirm the fact that deodorization with ozone can be applied only to specific conditions, after carrying out detailed preliminary research determining the parameters of the process and fully identifying the reaction products formed.

Degradation of trace contaminants contained in generated standard gas mixture allows to conclude that this method could be employed with success for the purification of effluent gases in real, industrial conditions.

Acknowledgements

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