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## THE BTEX EMISSION FROM MOULDING SANDS WITH FURAN RESIN DEPENDENCE ON THE VOC CONTENT AND LOSS ON IGNITION

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The article contains the results of emission BTEX (benzene, toluene, ethylobenzene and xylenes) during thermal destruction (500 – 1 300 °C) of moulding sand with furan resin. This furan resin is with a high content of free furfuryl alcohol (about 80 %). Knowledge of emissions of these compounds allows the assessment the harmfulness of a given moulding sand. Quantitative analysis of BTEX is highly complex and requires using of modern equipment (e.g. gas chromatography – mass spectrometry). Therefore, an attempt to assess potential emissions of BTEX compounds from a given moulding sand based on measurements of total volatile organic compounds (VOC) emission and loss on ignition (LOI). These measurements are less time-consuming and do not require expensive equipment.

Key words: castings, furan resin, moulding sand, BTEX, VOC

#### INTRODUCTION

Organic dangerous substances constitute up to 96 % of all hazardous substances emitted by the typical cast iron foundry. Organic substances are emitted during making moulds and cores (preparation of moulding sands, cores production and storage), when organic binders are applied. However, the largest amount of dangerous organic substances is liberated during pouring, cooling and knocking out of moulding sands with bentonite and additions of lustrous carbon carriers or moulding sands with organic binders. In foundry plants applying moulding sands with bentonite and lustrous carbon carriers it can constitute even 90 % of the total emission of hazardous substances [1, 2].

Moulding sands with furfuryl resins found wide applications in foundry plants of ferrous alloys. However, due to probably carcinogenic properties of furfuryl alcohol the EU Directive (Regulation (EC) No. 1272/2008) limits this substance content (in a monomer form) in resin up to 25 %. Leading world companies producing binders for castings have been – since a couple of years – performing intensive investigations on developing furfuryl resins, which would meet the requirements of this Directive.

Volatile organic compounds (VOC) are organic chemicals that have a high vapor pressure at room temperature. Their high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air. A VOC is any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard atmospheric pressure of 101,3 kPa and can do damage to visual or audible senses [3].

Out of all substances generated when high temperatures are influencing binding materials applied for moulding sands, the special group, due to their extremely harmful influence, constitute polycyclic aromatic hydrocarbons (PAHs) and compounds from the BTEX group. Knowledge of emissions of these compounds allows the assessment the harmfulness of a given moulding sand [4-7].

A determination of the emission of the BTEX group substances - from the given moulding sand - on the bases of measuring the VOC emission and LOI is not only less time consuming but also does not require using expensive equipment and can provide bases for the preliminary assessment of the moulding sand harmfulness.

The results of measurements of emissions of substances from BTEX group for sands with additions of a reclaim and with furfuryl resin containing about 80 % of a furfuryl alcohol monomer, are presented in paper [8-12].

### METERIALS AND TESTING METHODO-LOGY OF INVESTIGATIONS

The aim of investigations was the determination the influence of the reclaim addition and the binder fraction (especial H/R: hardener to resin ratio) on the moulding sand harmfulness – in an aspect of the BTEX emissivity.

The following moulding sands were tested:

• M1 – matrix: 15 % fresh high-silica sand, 85 % reclaim, binder: 1 % resin, 0,5 % hardener – in relation to the moulding sand amount (H/R = 0,50);

S. Żymankowska-Kumon, AGH University of Science and Technology, Kraków, Poland

- M2 matrix: 15 % fresh high-silica sand, 85 % reclaim, binder: 0,9 % resin, 0,45 % hardener in relation to the moulding sand amount (H/R = 0,45);
- M3 matrix: 100 % fresh high-silica sand, binder: 1 % resin, 0,4 % hardener – in relation to the moulding sand amount (H/R = 0,40).

All moulding sand samples originated from the same cast iron foundry. The total VOC amounts were determined for temperatures: 500 - 900 °C.

The BTEX content was determined at the temperature range: 500 - 1300 °C.

The analysis of substances from BTEX group were carried out by the gas chromatography method with the application of the flame-ionising detector (FID). The identification was carried out by means of the system consisting of the gas chromatograph Trace GC Ultra, equipped with the capillary chromatographic column RTX 5MS (Restek) of a length 30 m and internal diameter 0,25 mm.

LOI and VOC content was determined by procedure AFS No. 117-87-S and No. 213-87-S [4].

### **RESULTS AND THEIR DISCUSSION**

# Determination of the VOC emission and LOI content

Analytical results of the content of VOC and LOI from moulding sand are listed in Table 1 and Table 2. When the temperature reached about 900 °C the total VOC content is constant. LOI were determined at a temperature of 950 °C.

In dependence on the matrix kind the VOC emission and LOI values are changing. When the reclaim is present in the matrix both parameters are significantly larger as compared with the moulding sand based on the fresh sand matrix (even twice).

The second criterion is the resin and hardener fraction, expressed by the H/R ratio, in the moulding sand. In case of M1 moulding sand the H/R value equals 0,50; while of M2 moulding sand it equals 0,45 (at the same matrix compo-sition). M2 moulding sand demonstrated the higher VOC emission and LOI value than M1 moulding sand. It was probably caused by the fact that the binder in M2 moulding sand was not fully hardened (too low hardener amount in relation to the resin).

Table 1 Analytical results of total VOC content / mas. %

Sample	VOC					
	500 °C	700 °C	900 °C			
M1	2,76	2,97	3,05			
M2	2,58	2,96	3,52			
M3	1,32	1,40	1,51			

#### Table 2 Analytical results of LOI content / mas. %

Sample	LOI		
M1	3,11		
M2	3,77		
M3	1,60		

## Measuring the content of compo-nents from the BTEX group

Quantitative data of the emissivity of components from the BTEX group are listed in Table 3.

#### Table 3 Results of the benzene and toluene content emitted from the moulding sands during the thermal decomposition

Sample	Temperature / °C						
	500	700	900	1 100	1 300		
Saı	Benzene content in emitted gases / mg/kg moulding sand						
M1	0,00*	3,26	6,65	14,52	296,01		
M2	0,00*	5,89	7,25	15,42	333,14		
M3	0,00*	1,25	3,65	9,86	170,81		
	Toluene content in emitted gases / mg/kg moulding sand						
M1	18,78	142,65	160,25	860,98	2,83		
M2	17,65	138,36	159,36	797,49	2,51		
M3	9,65	71,58	89,50	423,98	1,45		

\* below the limit of quantification

The tested moulding sands demonstrate differences in the emission of the BTEX group substances. The emission of benzene and toluene from all moulding sands, increases with a temperature increase. The toluene emission is at its maximum in a temperature of 1 100 °C, while the benzene emission in 1 300 °C. This is caused by the toluene decomposition into a simpler benzene structure.

## Correlation between the benzene emission and LOI content

The dependence of the generated BTEX substances (especial benzene) and LOI content from moulding sand is presented in Figure 1.

As can be noticed in the diagram the benzene emission increases when the LOI increase. The diagram described the linear equation character-rised by a high correlation coefficient R = 0.9934.

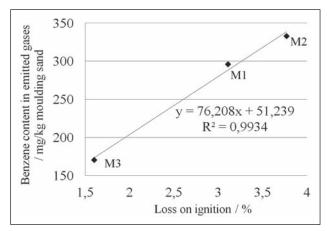


Figure 1 Dependence of the emission of benzene content and LOI

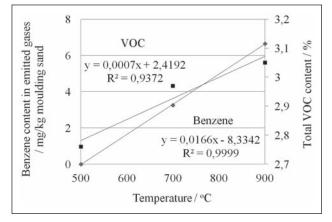


Figure 2 Dependence of the emission of benzene and total VOC emission (M1)

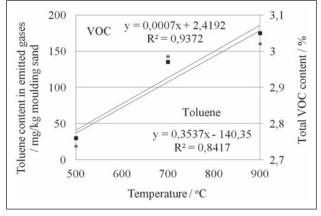


Figure 3 Dependence of the emission of toluene and total VOC emission (M1)

Thus, it can be assumed that at the preliminary ecological assessment of the given moulding sand – in respect of its probable benzene emission – the simplest parameter is the LOI.

## Correlation between the BTEX and VOC emission

The dependence of the benzene and toluene emission and total VOC content from moulding sand M1 is presented in Figures 2, 3; for moulding sand M3 is presented in Figures 4, 5.

As it results from diagrams there is a certain dependence between the benzene and toluene content and the VOC emission, in a temperature range: 500 - 900 °C. Both dependences can be described by linear equations of a high correlation coefficient (R > 0,9), regardless of the kind of matrix used or the H/R ratio value.

### CONCLUSIONS

As the result of the performed investigations, several conclusions, related to the thermal destruction of moulding sands with furfuryl resins, can be drawn.

1. There is a dependence between the benzene emission and the VOC emission and LOI amount, which can be determined by linear equations.

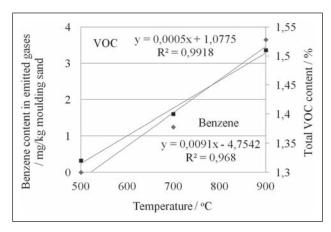


Figure 4 Dependence of the emission of benzene and total VOC emission (M3)

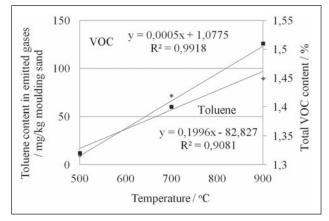


Figure 5 Dependence of the emission of benzene and total VOC emission (M3)

- 2. The higher LOI of the moulding sand the higher VOC and benzene emission.
- 3. Based on the LOI knowledge and the VOC emission it is possible to determine preliminarily the benzene emission from the given moulding sand at high temperatures.
- Moulding sands on the matrix with a reclaim addition exhibit higher LOI and higher VOC emission and thereby a higher benzene emission than moulding sands on the fresh high-silica sand matrix.
- 5. The moulding sand hardening degree, it means the H/R ratio, has an influence on LOI and the VOC emission.

The performed tests are less time-consuming and less complicated than the chromatographic analysis. They do not require the expensive equipment such as the gaseous chromatograph. This is an essential information since not all foundry plants have well equipped laboratories.

The determination of the benzene emission amount is important from the point of view of ecology and human health, since this is a carcinogenic compound and negatively influences living organisms.

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#### REFERENCES

- [1] M. Holtzer, M. Kubecki, R. Dańko, S. Żymankowska-Kumon, A. Bobrowski, 4th International symposium on high-temperature metallurgical processing, TMS 2013 Annual meeting & exhibition, San Antonio, 2013, ed. Tao Jiang et all, 643-650. DOI: 10.1002/978111 8663448. ch77.
- [2] A. Bobrowski, M. Holtzer, R. Dańko, S. Żymankowska-Kumon, Analysis of gases emitted during a thermal decomposition of the selected phenolic binders, Metalurgija International 18 (2013) 7, 259-261.
- [3] http://en.wikipedia.org/wiki/Volatile\_organic\_ compound#European\_Union, 2014-08-15, 20:45.
- [4] M. G. Ribeiro & W. R. P. Filho, Risk assessment of chemicals in foundries: The international Chemical Toolkit pilotproject, Journal of Hazardous Materials, A136 (2006), 432-437. DOI: 10.1016/j.-jhazmat.2006.01.019.
- [5] P. Scarbel, C. E. Bats & J. Griffin, Effect of mold and binder formulation on gas evolution when pouring aluminum casting, AFS Transactions 114 (2006), 435-445.
- [6] G. R. Crandell, J.F. Schifo, G. Mosher, CERP organic HAP emission mea-surements for iron foundries and their use in development of an AFS HAP guidance document, AFS Transactions 06-031 (2006) 10, 1-17.
- [7] D. Fabbri, I. Vassura, Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials

by analytical pyrolysis, Journal of Analysis and Applied Pyrolysis 75 (2006), 150-158.

- [8] H. W. Dietert, A. L. Graham, R. M. Praski, Gas evolution in foundry materials - its source and measurement, AFS Transa-ctions 84 (1976), 221-228.
- [9] J. F. Schifo, J. T. Radia, G. R. Crandell, G. Mosher, What we know and what we don't, AFS Transactions 111 (2003), 1193-1190.
- [10] G. Crandell, 13th CIATF International Conference on Environmental Protection, Leipzig, 2000, Paper 13.
- [11] V. A. C. Haanappel, Gas chromatographic mass spectrometric analysis of tar compo-unds formed during pyrolysis of rice husks, Journal of Chromatography 562 (1991), 531-545.
- [12] C. D. N Humfrey, L. S. Levy, S. P. Faux, Potential carcinogenicity of foundry fumes: a comparative in vivo-in vitro study, Food and Chemical Toxicology 34 (1996), 1103-1111. DOI: 10.1016/S0278-6915(97)-000-81-1.
- S. Ji, L. Wan, Z. Fan, The toxic compounds and leaching characteristics of spent foundry sands, Water, Air and Soil Pollution 132 (2001), 347-364. DOI: 10.1023/A: 1013207000046.
- Note: The responsible translator for English language is ANGOS Translation Office, Kraków, Poland