

Development of method for identification of compounds emitted during thermal degradation of binders used in foundry

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Abstract

The aim of the research was to develop a method for identification of compounds emitted during thermal degradation of binders used in foundry. Research were performed with the use of Certified Reference Materials mixtures of semi-volatiles compounds with furfuryl alcohol and aldehyde. Furfuryl-urea resin samples were also used. Station for thermal degradation of materials used in foundry was designed and made. Thermal degradation process conditions and gas chromatograph coupled with high resolution mass spectrometry operating conditions were established. Organic compounds emitted during degradation were identified. The paper briefly represents the range of study and the results obtained for furfuryl-urea resin thermal degradation. Significant information about volatile and semi-volatile organic compounds emitted in different temperatures is also discussed.

Keywords: Foundry, Binders, Furan resin, Gas chromatography, Mass spectrometry

1. Introduction

Binders based on synthetic resins, the solvent for which are organic compounds, become more and more widely used in manufacturing of foundry moulds [1]. These resins in their initial state, pose a threat to human's health only to a minor extent, while products of their thermal decomposition, generated during hot metal pouring into moulds pose the most significant threat [2, 3]. As a result of temperature impact, noxious compounds, mainly representing the group of polycyclic aromatic hydrocarbons and volatile organic compounds may be formed and released into air. Some of the said compounds may condense in moulding sand and then be released to environment during mould cooling, castings

knock-out and used sand storage [4, 5]. Depending on the type of used resin (phenol – formaldehyde, urethane, furfuryl- urea) the following compounds may be formed: furfuryl alcohol, formaldehyde, phenol, as well as naphthalene and its methyl derivatives, biphenyl, fluorene, fenantrene or dibenzofurane, BTEX group compounds (benzene, toluene, xylene, ethylbenzene) and PAHs (polycyclic aromatic hydrocarbons) [6, 7]. Presence of these compounds was confirmed in laboratory tests conducted in Chemical Analyses Laboratory of the Institute for Ferrous Metallurgy as well as semi-industrial tests at the Faculty of Foundry Engineering, AGH University of Science and Technology [8]. These substances are toxic and excessive quantities thereof may pose a risk to human health. Even low concentration of their vapours has a negative impact on blood

composition and hemopoietic organs, leading to bone marrow impairment. High vapour concentration shows carcinogenic, narcotic and mutagenic effect [9, 10]. Due to a negative impact of the said compounds groups on human health and natural environment, both qualitative and quantitative identification is necessary of the composition of gases released during the resins exposition to high temperatures.

2. Material, scope and methodology of research

2.1. Unit for thermal degradation of selected materials

The designed station for thermal decomposition of selected materials used in foundry reflects temperature conditions at the boundary of phases: liquid metal – mould, as well as in the subsequent mould layers during mould pouring. Diagram of the designed station is presented in Figure 1. The main component of the unit is quartz tube reactor in form of removable quartz tube (B), the central part of which is installed in heating furnace (A). Station structure facilitates easy assembly of the reactor as well as its cleaning each time following decomposition of foundry materials' samples.

The second important component of the station is a port for sample introduction (C), which makes it possible to place the sample in reactor simultaneously with rinsing its inside with the flux of selected carrying gas. In order to facilitate sorption of volatile organic compounds formed during high temperature atmosphere impact on the materials examined in the tube reactor, a system of columns with adsorbent (XAD-2) ($E_{1,2}$) was installed at its opening. The first column constitutes measurement section, while the second one constitutes control section. Adsorbents from both columns are subject to analysis. The layer of adsorbent is rinsed with methanol, for the purpose of organic compounds extraction. Following proper preparation, extract sample is subject to analysis by means of gas chromatography combined with mass spectrometry (GC/MS).

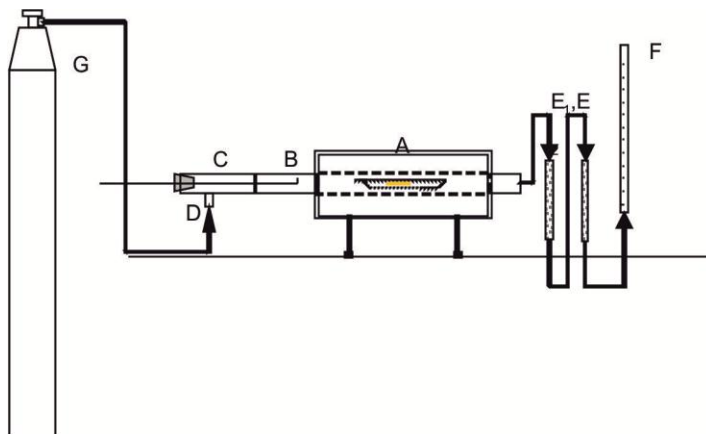


Fig. 1. Station for thermal decomposition of selected materials used in foundry (A – heating furnace, B – quartz tube, C – lock or sample loading, D – inlet of carrier gas, E_1, E_2 – columns with adsorbents, F – flow controller, G – gas cylinder)

The parameters which, primarily decide on achievement of the highest possible degree of recovery of compounds formed as a result of high temperature impact on the examined material include: carrying gas flow rate and reactor rinse time (duration). The above parameters were determined by means of experimental research with use of furan resin. Carrying gas flow rate was set at 3 l/h, while 10 minutes time was adopted as reactor rinse duration.

2.2. Determining retention times and identification of selected semi-volatile organic compounds

Analytical programmes used for identification and determination of volatile and semi-volatile organic compounds were prepared based on studies realized in Chemical Analyses Laboratory of the Institute for Ferrous Metallurgy in the period 2006-2008. The developed temperature programme for gas Trace GC ultra chromatograph (RTX 5MS chromatographic column, length: 30 m, inner diameter: 0.25 mm) facilitated correct distribution of standard reference mixture of semi-volatile organic compounds (Fig. 2).

Table 1. Retention times and primary ions of selected semi volatile organic compounds

Compound	Retention time (min)	Primary ion
Furfuryl aldehyde	2,50	96,0211
Furfuryl alcohol	2,67	98,0367
Phenol	4,48	94,0419
Cresol	6,78	108,0575
2,4-dimethylphenol	11,64	122,0732
2-methylnaphthalene	15,92	142,0782
Acenaphthalene	19,08	152,0626

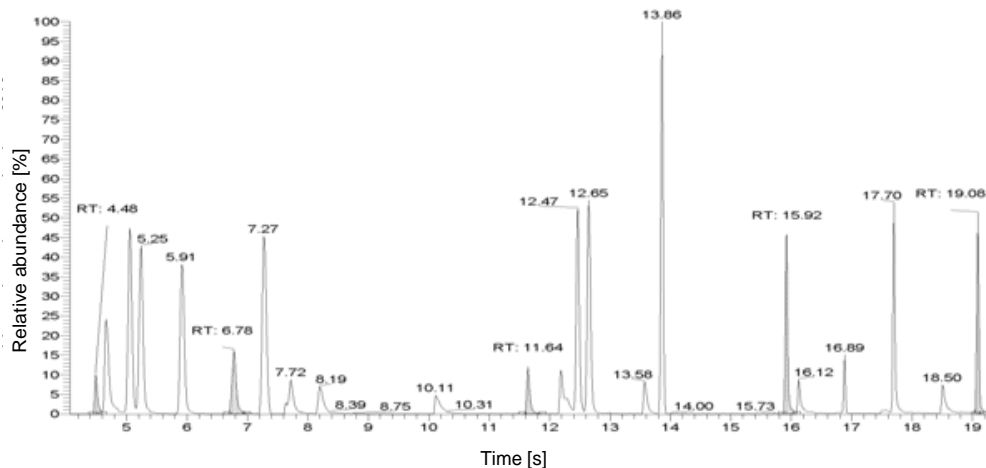


Fig. 2. Chromatogram of semi-volatile organic compounds standard mixture

3. Thermal decomposition of furan resin in the range from 100⁰C to 1300⁰C

By means of the station presented in Figure 1, as well as parameters of its operations determined as a result of the conducted research, decomposition of furan resin in temperature range from 100°C to 1300°C was effected. The research was conducted in argon atmosphere. The following samples of resin, weight: 10 mg were subject to shock heating at temperatures: 100°, 300°, 500°, 700°, 900°, 1100° and 1300°C. Methanol solutions achieved for particular tests were subject to analysis by means of gas chromatography coupled with mass spectrometry.

Sample chromatograms are presented in Figures 3-5.

In order to interpret the chromatograms, chromatograms obtained for particular solutions were compared to blank test chromatogram. Methanol solution obtained as a result of temperature impact on tray without resin addition constituted a

blank test. As a result of such comparison, all peaks from blank test were eliminated on chromatograms (red “X” sign).

Based on chromatograms obtained for standard reference solutions and retention times determined for particular compounds as well as the strongest ion peaks (Table 1), compounds released during temperature impact on the examined resin were identified (Table 2).

For the purpose of identification of the substances, the standard reference solutions of which were not available, NIST (*National Institute of Standards and Technology*) base of mass spectra was referred to, which constitutes a component of mass spectrometer software. The said base facilitates comparison of spectra with a specific probability only, and does not make it possible to confirm completely the presence of a given compound in the analyzed solution. In view of that, quantitative analysis was conducted only for the group of compounds, the presence of which in samples was confirmed according to the relevant standard reference mixture (Table 3).

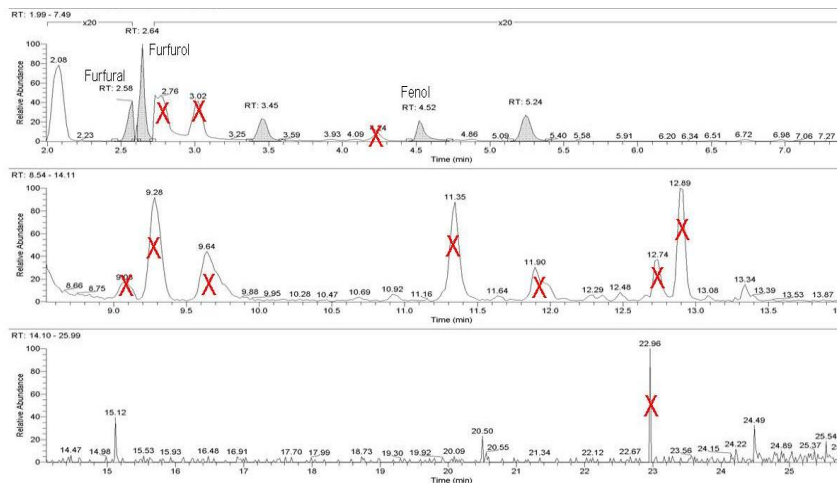


Fig. 3. Methanol extract chromatogram – resin heated at 100⁰C

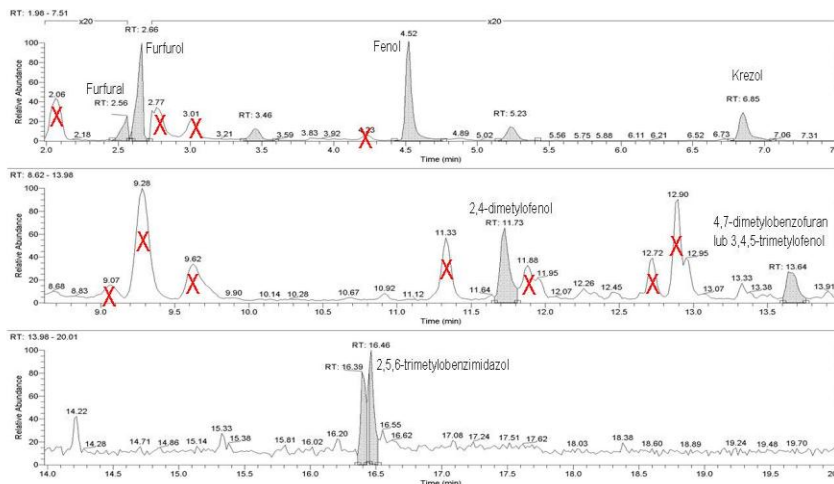


Fig. 4. Methanol extract chromatogram – resin heated at 500⁰C

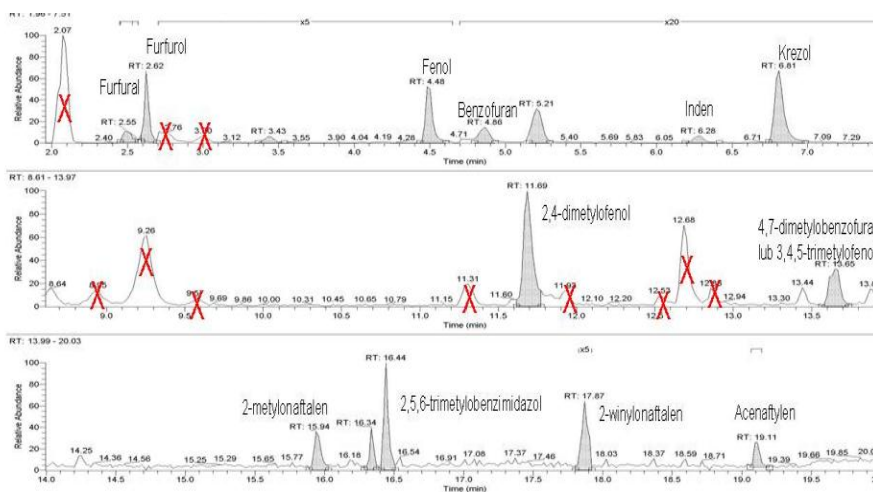


Fig. 5. Methanol extract chromatogram – resin heated at 900⁰C

Table 2.

Organic compounds generated as a result of selected temperature impact on furan resin

Compound	Retention time [min]	Process temperature [°C]						
		100	300	500	700	900	1100	1300
Furfuryl aldehyde	2,50	0	0	0	0	0	0	-
Furfuryl alcohol	2,67	0	0	0	0	0	0	-
Phenol	4,48	0	0	0	0	0	0	-
Benzofuran	4,86	-	-	-	-	0	0	-
Inden	6,27	-	-	-	-	0	0	0
Cresol	6,85	-	-	0	0	0	0	-
2,4-dimethylphenol	11,69	-	-	0	0	0	-	-
3,4,5-trimethylphenol	13,64	-	-	0	0	0	-	-
4,7-dimethylbenzofuran	13,64	-	-	0	0	0	-	-
2-methylnaphthalene	15,95	-	-	-	0	0	0	-
2,5,6-trimethylbenzimidazole	16,46	-	-	0	0	0	0	-
2-vinylnaphthalene	17,85	-	-	-	-	0	0	-
Acenaphthalene	19,11	-	-	-	-	0	0	0

“0” – presence of organic compound, “-” – absence of organic compound

Table 3.

Concentrations of organic compounds formed during decomposition of furan resin per its weight unit

Compound	P1 (100 ⁰ C) [mg/kg]	P3 (300 ⁰ C) [mg/kg]	P5 (500 ⁰ C) [mg/kg]	P7 (700 ⁰ C) [mg/kg]	P9 (900 ⁰ C) [mg/kg]	P11 (1100 ⁰ C) [mg/kg]	P13 (1300 ⁰ C) [mg/kg]
Furfuryl aldehyde	6,3*10 ⁻³	30,8*10 ⁻³	34,6*10 ⁻³	43,6*10 ⁻³	182,2*10 ⁻³	90,6*10 ⁻³	-
Furfuryl alcohol	90,2	221,6	207,2	294,5	16,7	5,9	-
Phenol	1,3	2,0	4,3	6,5	4,1	4,1	-
Cresol	-	-	1,9	3,4	2,1	1,4	-
2,4-dimethylphenol	-	-	1,4	2,5	1,8	-	-
2-methylnaphthalene	-	-	-	0,06	0,17	0,20	-
Acenaphthylene	-	-	-	-	0,20	0,02	0,02

Information presented in Table 3 may be depicted in form of a bar graph: change in the concentration of the emitted compound depending on temperature of the atmosphere where the resins were positioned. Graphs for selected compounds are presented in Figures 6-8.

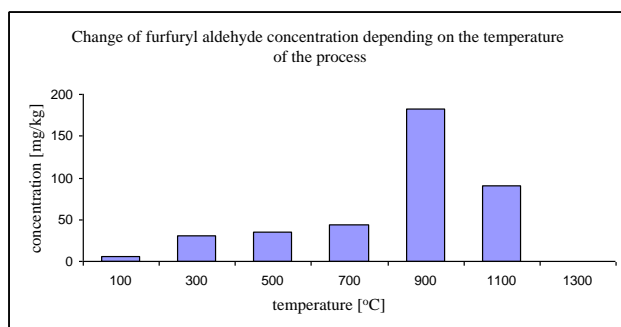


Fig. 6. Graph of the changes of furfuryl aldehyde concentration depending on the temperature of the atmosphere, in which the resin was placed

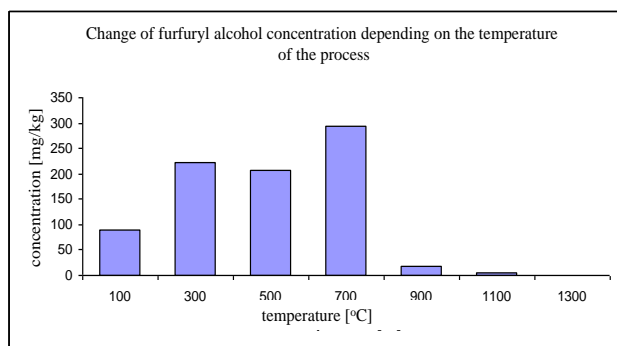


Fig. 7. Graph of the changes of furfuryl alcohol concentration depending on the temperature of the atmosphere, in which the resin was placed

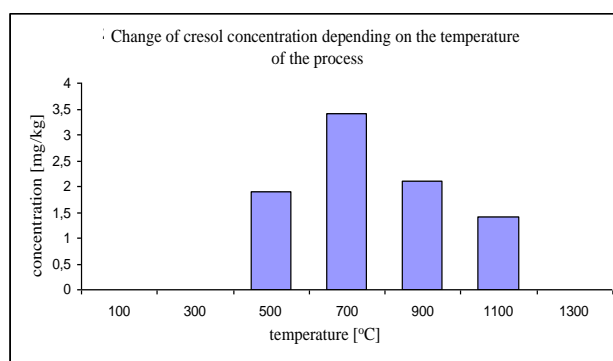


Fig. 8. Graph of the changes of cresol concentration depending on the temperature of the atmosphere, in which the resin was placed

4. Conclusions

1. The designed and constructed station for decomposition in laboratory conditions of the selected materials used in foundry, allows for conducting research in wide range of temperatures (100 °C – 1300 °C) and selected atmosphere of carrying gas.
2. A substantial part of compounds emitted during thermal destruction of the examined furan resin is regarded as detrimental and hazardous substances (Journal of Laws of the Republic of Poland - enclosure to no. 201, Item 1674 of October 14, 2005).
3. The largest diversity of organic compounds formed during thermal decomposition of furan resin occurs at the temperature of 900 °C.
4. The highest total concentration of the emitted organic compounds is observed at the temperature of 700 °C.
5. For the selected organic compounds identified within the conducted research, a temperature level exists at which the said compounds achieve the maximum concentration in gases.

Acknowledgments

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