

Analysis of the Compounds from the BTEX Group, Emitted During Thermal Decomposition of Alkyd Resin

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Abstract

Suitability of the given binding agent for the moulding sands preparation depends on the one hand on the estimation of technological properties of the sand and the mould made of it and the obtained casting quality and on the other hand on the assessment of this sand influence on the natural and working environment. Out of moulding sands used in the foundry industry, sands with organic binders deserve a special attention. These binders are based on synthetic resins, which ensure obtaining the proper technological properties and sound castings, however, they negatively influence the environment. If in the initial state these resins are not very dangerous for people and for the environment, thus under an influence of high temperatures they generate very harmful products, being the result of their thermal decomposition. Depending on the kind of the applied resin (phenol-formaldehyde, urea, furfuryl, urea-furfuryl, alkyd) under an influence of a temperature such compounds as: furfuryl alcohol, formaldehyde, phenol, BTEX group (benzene, toluene, ethylbenzene, xylene), and also polycyclic aromatic hydrocarbons (PAH) can be formed and released.

The aim of the study was the development of the method, selection of analytical methods and the determination of optimal conditions of formation compounds from the BTEX group. An emission of these components constitutes one of the basic criteria of the harmfulness assessment of binders applied for moulding and core sands. Investigations were carried out in the specially designed set up for the thermal decomposition of organic substances in a temperature range: 500^oC – 1300^oC at the laboratory scale. The object for testing was alkyd resin applied as a binding material for moulding sands. Within investigations the minimal amount of adsorbent necessary for the adsorption of compounds released during the decomposition of the resin sample of a mass app. 15 mg was selected. Also the minimal amount of solvent needed for the desorption of compounds adsorbed in the column with adsorbent was found. The temperature range, in which the maximal amounts of benzene, toluene, ethylbenzene and xylenes are released from the resin, was defined. The qualitative and quantitative analyses of compounds from the BTEX group were performed by means of the gas chromatography combined with the mass spectrometry (GC/MS).

Key words: moulding sand, binding, BTEX, thermal analysis, GC/MS.

1. Introduction

Foundry engineering belongs to braches of industry of an increased occupational risk. During the whole casting production process employees are exposed to hazardous, harmful and

uncomfortable factors related, among others, to the emission of volatile organic compounds. The main source of these compounds emission are resins – applied as binding materials – and hardeners based on organic substances, which at high temperatures of liquid metals are subjected to a thermal decomposition. Due to this process several more or less harmful organic compounds are

formed. Depending on the kind of the resin applied (phenol-formaldehyde, urea, furfuryl, furfuryl-urea, alkyd) under an influence of a high temperature such substances can be formed and released: furfuryl alcohol, formaldehyde, phenol, components of the BTEX group (benzene, toluene, ethylbenzene, xylenes), and also polycyclic aromatic hydrocarbons (PAH) [1-9]. These compounds are mainly generated when a mould is being poured with liquid metal. These compounds, to a significant degree, penetrate into further parts of a mould, condense on matrix grains and then release during moulds cooling and castings knocking out [6, 7]. Their part can be rinsed up into the environment during storing spent sands. The presence of these compounds in spent moulding sands and on the selected work stands in the foundry plant was experimentally confirmed in several laboratory examinations carried out in the Laboratory of Chemical Analysis of the Institute for Ferrous Metallurgy and in semi-industrial investigations in the Faculty of Foundry Engineering AGH [10-14]. On account of a harmful influence of these compounds - especially from the BTEX group - on the human health and on the natural environment, the investigations aimed at the in-depth knowledge of their formation conditions (among others: kind of an atmosphere, temperature range, kinetics) are necessary. They will allow, in future, for such controlling of the foundry process parameters, which will minimise amounts of emitted hazardous compounds.

2. Investigation methodology

2.1. Laboratory stand for the thermal decomposition of organic binders

The research stand for the thermal decomposition of organic binders consisted of two furnaces: the resistory furnace and radiator furnace, the horizontal tubular reactor and columns with an adsorbent (active carbon). In the first stage of examinations the system, allowing to perform the thermal decomposition in a wide temperature range (50-1300⁰C) and in the selected atmosphere of a carrier gas, was constructed. On the bases of the results obtained in the first stage of investigations, the examinations in the second stage were limited to the temperature range from 700⁰C to 1300⁰C. The aim of these investigations was the selection of the best work parameters of the research stand, encompassing:

- adsorbent mass,
- volume of the applied solvent,
- kind of the carrier gas (argon and air).

The subject of examination was the alkyd resin used as a binder of moulding sands.

As the result of preliminary tests, aimed at the determination of main groups of components present in gases emitted during the thermal decomposition of resins, for quantitative investigations of

compounds from the BTEX group (benzene, toluene, ethylbenzene and xylenes) were singled out. For the needs of the quantitative analysis the minimum active carbon mass, able to adsorb all these compounds from gases, was to be determined. To achieve this aim the alkyd resin was placed in the quartz tubular reactor heated to the chosen temperature from the range: 700⁰C - 1300⁰C, at simultaneous rinsing the system with the carrier gas (argon).

The equipment fragment responsible for the adsorption consisted of two columns with adsorbents: the first (specific) and the second (controlling). In addition, these columns were equipped with two filtration layers: preliminary - quartz-wool, specific - MILLIPORE filter (symbol AQFA) of quartz fibres.

The reason for the application of such solution were considerable amounts of dusts released from samples during their thermal decomposition in temperatures: 900⁰C - 1300⁰C, which caused dusts excessive settling on the adsorbent. In order to find the minimum amount of the adsorbent the series of experiments of the decomposition of 15 mg samples of the alkyd resin in temperatures: 700⁰C, 900⁰C, 1100⁰C, 1300⁰C were performed.

2.2. Investigations

200 mg of active carbon in the preliminary column and 100 mg in the controlling column was applied as the adsorbent. Diethyl ether was used for the extraction of compounds from the adsorption columns. As the result of the performed examinations 200 mg of active carbon was assumed to be sufficient for the total adsorption of compounds from the BTEX group formed during the decomposition of 15 mg sample of the alkyd resin. Chromatograms illustrating the results of the experiment realised in 900⁰C are presented in Figure 1.

The successive parameter needed verification was the amount of solvent necessary for a total desorption of compounds from the BTEX group adsorbed in the adsorption column after the thermal decomposition of the alkyd resin. To assess the amount of solvent, the known amount of gaseous benzene was supplied for the column with the adsorbent. To obtain this aim, 1 ml of solution of the known benzene concentration in diethyl ether was added to the washer in the water-bath of a temperature of 85⁰C. Then the washer was rinsed for 30 minutes with argon directing gas with benzene on the column with active carbon. After finishing the washing in order to desorb benzene, the column was washed by successive portions of diethyl ether of a volume of 2 ml. Before the measurement, into the vials with extracts the constant volume of p-xylene was added, which - in this case - constituted the reference point. Each portion was analysed and then the surface area below the benzene peak was determined. The obtained values of areas under benzene peaks were referred to the area under the reference standard peak (p-xylene). The obtained results are presented in Table 1.

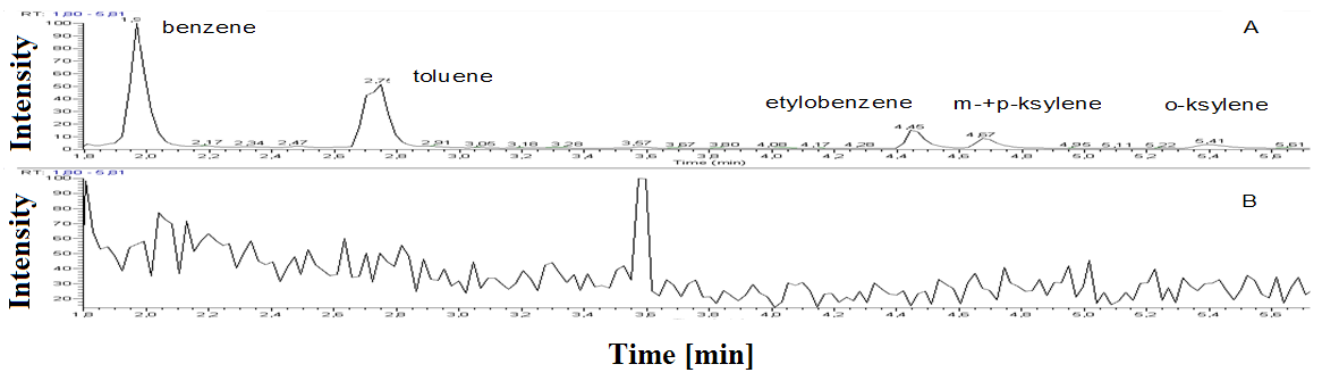


Fig.1. The fragment of the chromatogram for the diethyl ether solution obtained after the desorption of compounds formed during the thermal decomposition of the alkyd resin in a temperature of 900°C, **A**- adsorbed in the preliminary column, **B**- adsorbed in the controlling column (intensity of the peak is at the level of background noises).

Table 1. Ratio of the surface areas under the benzene peaks, of benzene desorbed from active carbon, to the surface area under the reference standard peak in successive portions of diethyl ether.

Extraction	Benzene / control pattern
1	1,77
2	0,72
3	0,33
4	0,25
5	0,18
6	0,17

Additionally the dependence of the ratio of benzene desorbed from the active carbon to the amount of the reference standard in successive portions of diethyl ether was illustrated in Figure 2.

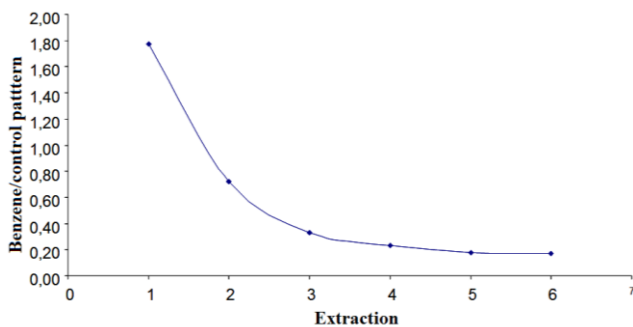
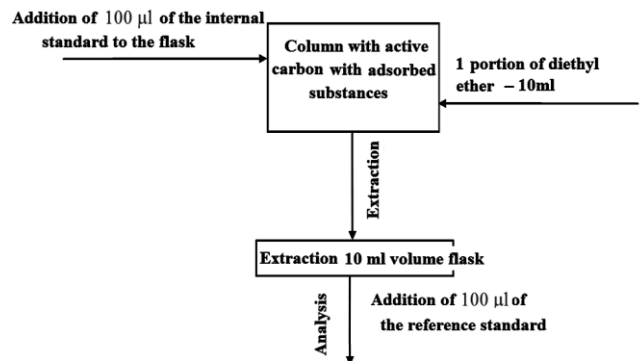


Fig. 2. Dependence of the benzene amount to the reference standard amount in successive portions of diethyl ether

As the result of the series of six extractions it was found, that in the sixth portion of diethyl ether the ratio of the surface area under the peak of the extracted substance (benzene) to the surface area under the peak of the reference standard (p-xylene) is not significantly decreasing. Thus, it can be concluded that after 5 extractions a certain state of equilibrium - between the adsorbate amount on active carbon and its amount in diethyl ether solution - was established. Further extractions do not increase the yield.

Therefore 10 ml of diethyl ether was assumed as the volume sufficient for the extraction. Finally the extraction process presented schematically in Scheme 1 was used for the compounds of the BTEX group desorption from the column with active carbon. A current control of this extraction process was performed by supplying 100 µl of the internal standard - benzene d₆ - on the column with the adsorbent before the desorption process by the solvent.



Scheme 1. Extraction process of compounds from the BTEX group from the column with active carbon

3. Thermal decomposition of the alkyd resin in the temperature range 500-1300 °C

On the grounds of the preliminary investigations, which allowed to determine the conditions of the thermal decomposition (temperature range) and to select the kind and amount of the adsorbate and extracting substance, the decomposition of the alkyd resin was performed in the temperature range from 500 to 1300°C. Examinations were performed in an argon atmosphere. Successive resin samples were abruptly heated to temperatures: 500°C, 700°C 900°C, 1100°C, 1300°C. The obtained extracts in

diethyl ether were analysed by means of the gas chromatography method coupled with the mass spectrometry method. The gas chromatograph was equipped with the chromatographic column RTX 5MS (Restek) of a length of 30 m and inner diameter equal

0.25mm. The mass spectrometer operated in the range of 30-450 amu (*atomic mass unit*) at the photomultiplier voltage of 1.8 kV. The example of the chromatogram obtained for the diethyl ether extract is presented in Figure 3.

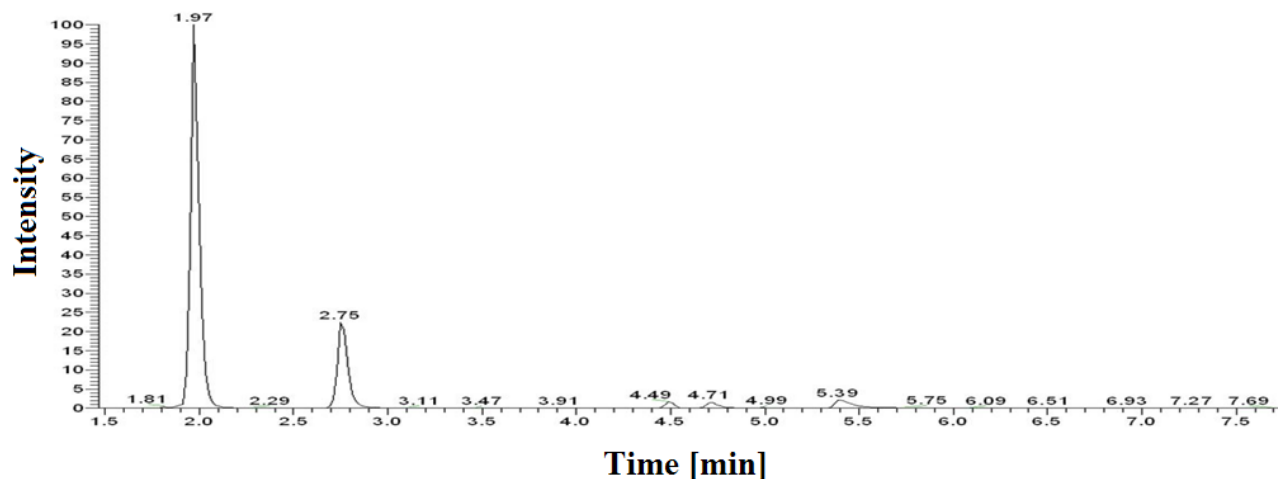


Fig. 3. Chromatogram of the diethyl ether extract – the alkyd resin decomposition process carried out in a temperature of 900°C

During the analysis of the standard mixture of compounds by the GC/MS techniques, for each peak occurring in the chromatogram the total mass spectrum of substance leaving the chromatographic column was recorded. These spectra as well as the retention times constitute the basis for assigning the corresponding compounds to individual peaks. The retention times and the strongest ionic peaks for the BTEX group are presented in Table 2.

Table 2. Retention times and the strongest ionic peaks of compounds from the BTEX group: compound, retention time, the strongest ion

Compounds	Retention times [min]	Strongest ionic peaks
Benzene	1,97	78,1118
Toluene	2,75	92,0626
Etylobenzene	4,49	106,0783
m+p - ksylene	4,71	106,0783
o - ksylene	5,39	106,0783

Quantitative determinations of compounds from the BTEX group generated during the thermal decomposition of the alkyd resin were carried out on the basis of pure substances (benzene, toluene, ethylbenzene, xylenes). The basic solutions contained app. 140 µg/ml of the given substance. On the grounds of such solutions the series of calibrating samples were prepared. In addition, a constant volume (100 µl) of the internal and reference standards were introduced into the calibrating solutions. As the internal standard for compounds from the BTEX group *benzene* d_6 was used, while the reference standard contained *toluene* d_8 .

On the basis of standard solutions the amounts of compounds formed during the thermal decomposition of the alkyd resin were determined and then recalculated into the sample mass in individual experiments. The obtained results are presented in Table 3.

Table 3. Concentrations of compounds from the BTEX group, formed during the decomposition of the alkyd resin

Compounds	Alk 1	Alk 2	Alk 3	Alk 4	Alk 5
	500°C [mg/g]	700°C [mg/g]	900°C [mg/g]	1100°C [mg/g]	1300°C [mg/g]
Benzene	1,2	4,4	105,6	91,8	5,9
Toluene	0,8	1,0	21,7	0,7	0,0
Etylobenzene	2,3	2,1	0,4	0,2	0,2
m+p-ksylene	5,5	5,7	2,3	0,7	0,7
o-ksylene	0,1	0,1	0,2	0,0	0,0
Σ	9,9	13,3	130,2	93,4	6,8

These results are presented graphically in Fig. 4 - 7, where the concentration change of the emitted compound in dependence on the resin heating temperature is seen.

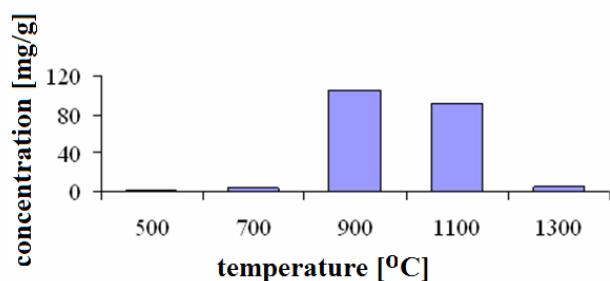


Fig. 4. Diagram of the benzene concentration changes in gases emitted during the thermal decomposition of the alkyd resin versus the process temperature

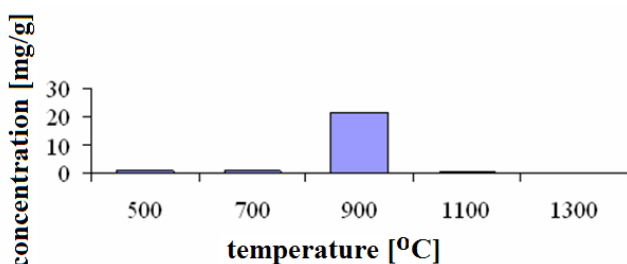


Fig. 5. Diagram of the toluene concentration changes in gases emitted during the thermal decomposition of the alkyd resin versus the process temperature.

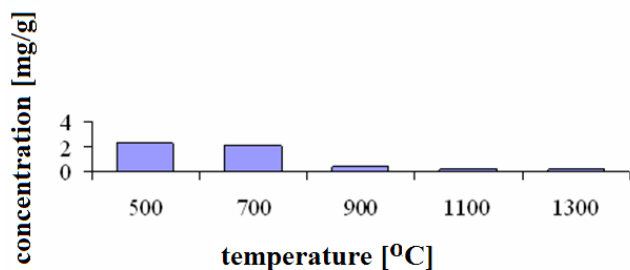


Fig. 6. Diagram of the ethylbenzene concentration changes in gases emitted during the thermal decomposition of the alkyd resin versus the process temperature.

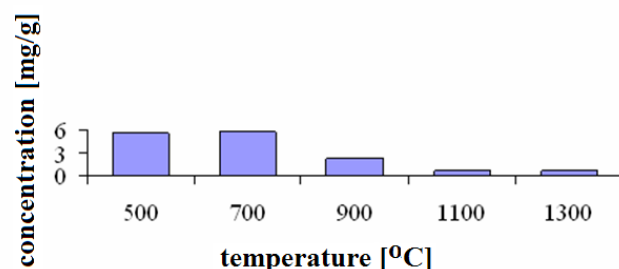


Fig. 7. Diagram of the concentration changes of the sum of meta- and para-xylene in gases emitted during the thermal decomposition of the alkyd resin versus the process temperature.

4. Conclusions

1. For the total adsorption of compounds from the BTEX group, generated during the decomposition of 15 mg of the alkyd resin at the laboratory stand, the active carbon deposit of a mass of 200 mg should be applied.
2. The volume of diethyl ether sufficient for the total extraction of the BTEX compounds, adsorbed in the column with active carbon, equals 10 ml.
3. The highest cumulative concentration of gases from the BTEX group emitted from the alkyd resin occurs at a temperature of 900°C.
4. There is a temperature range at which individual components achieve their highest concentrations. In the case of benzene the highest concentration is achieved during heating the sample in the temperature range: 900 -1100°C.
5. The developed laboratory stand and the methodology can be utilised for investigations of thermal decomposition of other substances containing organic compounds.

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