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Investigations of the Temperature Influence on Formation of Compounds from the BTEX Group During the Thermal Decomposition of Furan Resin

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Abstract

Organic binders applied in foundry plants based on synthetic resins, from the one side influence obtaining the required technological properties by the moulding sand and – in consequence – obtaining good quality castings, and on the other side are the source of volatile organic compounds (VOC). Together with synthetic resins their hardeners, which although added in very small amounts emit during their thermal decomposition substances negatively influencing the natural environment, are also used. Both, resins and hardeners only at the influence of high temperatures accompanying moulds pouring with liquid metal generate harmful volatile organic compounds including compounds from the BTEX group. Investigations of the temperature influence on the kind and amount of organic compounds formed during the thermal decomposition of selected binders and hardeners and their mixtures allow to determine temperature ranges the most favourable for emitting harmful substances as well as to compare their emission from the selected materials.

The aim of this study was the determination the temperature influence on formation substances from the BTEX group, during thermal decomposition of the selected binder, its hardener and their mixture. The BTEX group emission constitutes one of the basic criteria in assessing the harmfulness of materials applied for moulding and core sands and it can undergo changes in dependence of the applied system resin-hardener. Investigations were carried out on the specially developed system for the thermal decomposition of organic substances in the temperature range: 500°C – 1300°C, at the laboratory scale. The investigations subject was the furan resin, its hardener and hardened furan resin. The assessment of the emission degree of the BTEX group in dependence of the system subjected to the temperature influence was performed, within the studies. The temperature range, in which maximal amounts of benzene, toluene, ethylbenzene and xylenes were emitted from tested materials – was defined. The qualitative and quantitative analysis of the BTEX group were carried out with using the gas chromatography technique coupled with the mass spectrometry (GC/MS).

Keywords: Environment Protection, Moulding Sands, Synthetic Resins, BTEX, Thermal Decomposition

1. Introduction

A problem of organic compounds emission is essential in foundry industry, since these substances due to their harmful activities can be the direct cause of occupational diseases and also the source of the natural environment contaminations. During the whole casting production process employees are exposed to dangerous, harmful and uncomfortable factors related, among others, with emission of volatile organic compounds (VOC), which main source constitute organic resins and their hardeners applied at the moulding sands production. These substances subjected to high temperatures influences, in reducing atmosphere undergo thermal decomposition and as result of secondary reactions can generate harmful aromatic compounds. These substances are released into the environment already at the stage of mould pouring with liquid metal, but a part of them dyfunds into further parts of the mould, where it condensed on matrix grains and is released at the stage of cooling and knocking out of castings [1-7]. A part of these substances can be also rinsed out into environment during storing of spent foundry sands. Investigations carried out in the Faculty of Foundry Engineering AGH and in the Laboratory of Chemical Analyses, apart from confirmation of the VOC emission from foundry processes indicate also differences in amounts and kind of emitted VOC in dependence if the applied binder and hardener [8-11]. Within the frames of this study the investigations aimed at more thorough finding of differences between the BTEX emissions from three kinds of materials (resin, hardener, hardened resin) subjected to high temperatures influences. The applied system for thermal decomposition of materials can become a useful tool for comparing emissions from various binders and for facilitating the selection of proper materials in order to assure a compatibility with the regulations concerning the BTEX emission to the environment.

2. Methodology of investigations

2.1. Laboratory research stand for thermal decompositions of organic binders

The research stand for thermal decomposition of organic binders comprised two systems:

I) water cooled programmable furnace with radiant heating with the possibility of performing sample decompositions in a temperature range: 100°C – 700°C,

II) furnace with resistance heating, cooled by a forced air circulation allowing to perform sample decomposition in a temperature range: 700°C – 1300°C.

The basic element of each system was a reactor in a form of exchangeable quartz tube, in which the sample was placed and in which its thermal decomposition was performed. The application of such reactor allowed for its easy dismantling and cleaning after each experiment. Samples were introduced into this reactor through a special port enabling sample placement in the heated part of the reactor, at a simultaneous blowing-down its interior by a carrier gas stream (argon). This port consisted of a ferrule via which a carrier gas was introduced and of a silicone plug sealing

the system. A steel rod with a hook at the end was used for placing the sample in the heating zone. At the reactor outlet the system for adsorption of volatile compounds was situated. It consisted of two columns with adsorbents: the first (main) and the second (control). In addition these columns were equipped with two filtrating layers: preliminary – quartz-wool, main – MILLIPORE (symbol AQFA) filter of quartz fibres. Such solution was due to a significant amounts of dusts emitting from samples during their thermal decomposition at temperatures: 900°C - 1300°C. These dusts were deposited on adsorbent causing its partial deactivation.

Investigations performed on the system, designed in such way, allowed to simulate the shock process of an abrupt heating the tested material (the moulding sand component) occurring, e.g. at its contact with liquid metal, as well as to create conditions of its gradual heating in successive moulding sand zones. The schematic presentation of the stand is given in Figure 1.

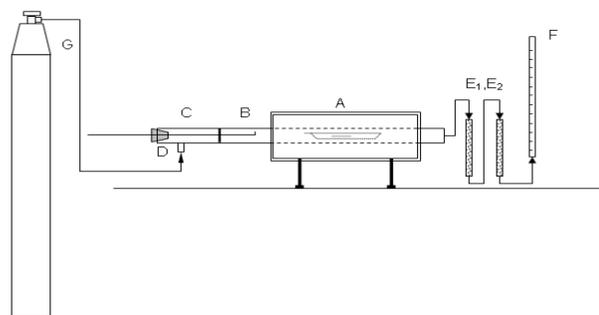


Fig. 1. Station for thermal degradation of binders used in foundry (A - furnace, B - quartz pipe reactor, C – lock for sample loading, D – inlet of carrier gas, E₁, E₂ – columns with adsorbents F – flow controller, G – gas cylinder)

2.2. Investigations

Investigation methodology allowing determining the temperature influence on organic compounds formation during thermal decomposition of binders was developed within preliminary works [11]. They comprised the selection of the most appropriate parameters of the experimental stand operations, such as:

- adsorbent mass,
- volume of a diluent used for extraction,
- carrier gas (argon and air),
- flow rate of a carrier gas via the tube reactor.

On the bases of preliminary tests, the main group of substances present in gases emitted during the thermal decomposition of furan resin, it means BTEX (benzene, toluene, ethyl benzene and xylenes), were singled out for quantitative analyses.

It was assumed, on the grounds of performed examinations, that for the complete adsorption of substances from the BTEX group formed from the decomposition of approximately 20 mg of furan resin on the laboratory stand, the adsorbent deposit (active carbon) of a mass of 200 mg should be used, while the diethyl ether volume sufficient for the extraction of BTEX adsorbed in a column with active carbon equals 10 ml.

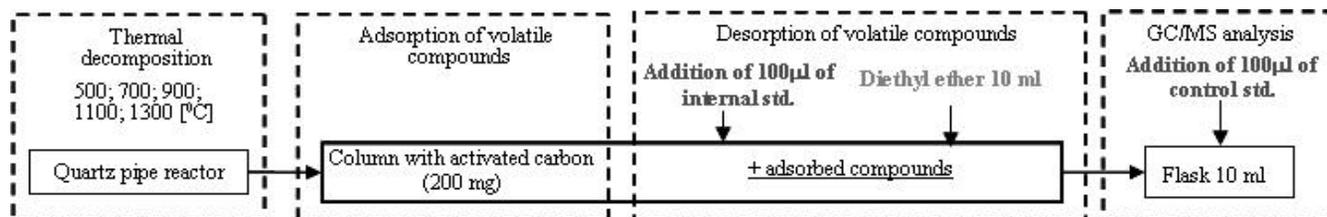


Fig. 2. Diagram of the process of determination BTEX compounds emitted during the thermal decomposition of furan resin, the hardener and hardened resin

In addition, the carrier gas flowing rate was determined at the level of 3 l/h and it was decided that this gas would be argon.

Finally the scheme presented in Fig. 2 was assumed for the detection process of the BTEX group in gases emitted during the thermal decomposition of furan resin. The current control of the BTEX extraction process was performed by feeding the column with adsorbent, before the desorption, by means of a diluent with 100 µl of internal standard – deuterated benzene (C_6D_6).

3. Thermal decomposition of the furan resin at temperatures: 500-1300°C

Examinations were performed in the argon atmosphere. Samples of the resin and hardener were in a liquid form. Whereas samples of the hardened resin, obtained for investigations in a form of rolls of a diameter 3 mm and height app. 8 mm, due to dimensions and mass required preliminary preparations. To decrease the sample mass and dimensions they were grinded in the cryogenic mill, cooled by liquid nitrogen and finally, the powdered samples were obtained. Samples of the resin, hardener and hardened furan resin were fed into the heated reactor in ceramic boats and subjected to shock heating at temperatures: 500°C, 700°C, 900°C, 1100°C and 1300°C. A heating time was for each temperature the same and equals 10 minutes. After this time the argon flow via the reactor was stopped and substances adsorbed on the active carbon column were extracted. Extracts – on the basis of diethyl ether – obtained for individual tests were analysed by the gas chromatography technique coupled with the mass spectrometry. The gas chromatograph was equipped with the chromatographic column, RTX 5MS (Restek), 30 m long and of an inner diameter 0.25mm. The mass spectrometer operated within the range of 30-450 amu at the photo multiplier voltage: 1.8 kV.

During the standard mixture analysis by the GC/MS technique, for each peak occurring in the chromatogram the complete mass spectrum of the substance leaving the chromatographic column was recorded. These spectra as well as retention times constitute the basis to assign to individual peaks the matching substances. The retention times determined in the study and the monitored ions for the BTEX group are presented in Table 1.

Table 1.

Retention times and monitored ions of BTEX compounds

Compounds	Retention time [min]	Monitored ion
Benzene	1,67	78,1118
Toluene	2,45	92,0626
Ethylbenzene	4,09	106,0783
m+p – xylenes	4,31	106,0783
o – xylene	5,09	106,0783

The quantitative determinations of the BTEX group substances formed during the thermal decomposition of the furan resin, its hardener and hardened resin were realised by means of pure substances (benzene, toluene, ethylbenzene, xylenes). The basic solutions contained app. 140 µg/ml of the given substance. On the basis of such solutions the series of calibration samples were prepared. Additionally into calibrating solutions the constant volume (100 µl) of internal and control standards were introduced. As the internal standard for the BTEX group deuterated benzene (C_6D_6) was used, while the control standard contained deuterated toluene ($C_6D_5CD_3$).

On the basis of standard diagrams the amounts of substances formed during the thermal decomposition of the furan resin, its hardener and hardened resin were determined and then recalculated for the sample mass used in individual experiments. The obtained results are presented in Tables 2-4.

Table 2.

The concentrations of BTEX compounds, emitted during thermal decomposition of furan resin

Compounds	ŻFURI	ŻFUR2	ŻFUR3	ŻFUR 4	ŻFUR5
	500°C	700°C	900°C	1100°C	1300°C
	[mg/g]	[mg/g]	[mg/g]	[mg/g]	[mg/g]
Benzene	0,1	0,2	97,5	62,1	47,1
Toluene	0,2	0,2	12,3	0,6	0,4
Ethylbenzene	0,0	0,0	1,9	0,9	0,5
m+p-xylenes	0,0	0,0	4,9	2,9	1,4
o-xylene	0,0	0,0	0,7	0,3	0,0
Total	0,3	0,4	117,3	66,8	49,4

Table 3.

The concentrations of BTEX compounds, emitted during thermal decomposition of furan resin hardener

Compounds	UTW 1	UTW 2	UTW 3	UTW 4	UTW 5
	500°C	700°C	900°C	1100°C	1300°C
	[mg/g]	[mg/g]	[mg/g]	[mg/g]	[mg/g]
Benzene	0,3	0,7	68,7	99,2	20,9
Toluene	74,1	75,9	115,5	18,6	0,2
Ethylbenzene	8,3	8,8	1,8	0,6	0,7
m+p-xylenes	62,1	67,8	25,9	2,9	1,9
o-xylene	3,0	4,4	2,6	0,3	0,2
Total	147,8	157,7	214,4	121,4	23,9

Table 4.

The concentrations of BTEX compounds, emitted during thermal decomposition of hardened furan resin

Compounds	UTWŹ1	UTWŹ1	UTWŹ1	UTWŹ1	UTWŹ1
	500°C	700°C	900°C	1100°C	1300°C
	[mg/g]	[mg/g]	[mg/g]	[mg/g]	[mg/g]
Benzene	0,2	1,1	15,2	53,9	29,0
Toluene	44,2	40,3	71,1	0,9	0,2
Ethylbenzene	0,1	0,2	0,9	0,4	0,4
m+p-xylenes	0,5	0,9	2,3	1,3	1,2
o-xylene	0,0	0,1	0,3	0,0	0,0
Total	45,0	42,6	89,7	56,5	30,9

Graphic results are presented in Fig. 3–7 where the concentration changes of the analysed substance in relation on the heating temperature and the kind of material are shown.

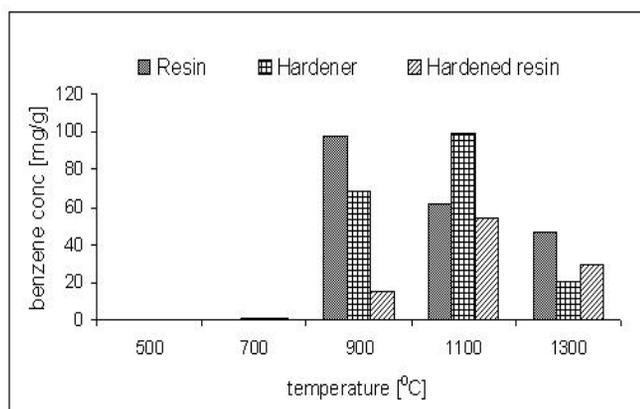


Fig. 3. Changes in the concentration of benzene in the gases emitted in the process of thermal decomposition, depending on the process temperature and the type of material being tested

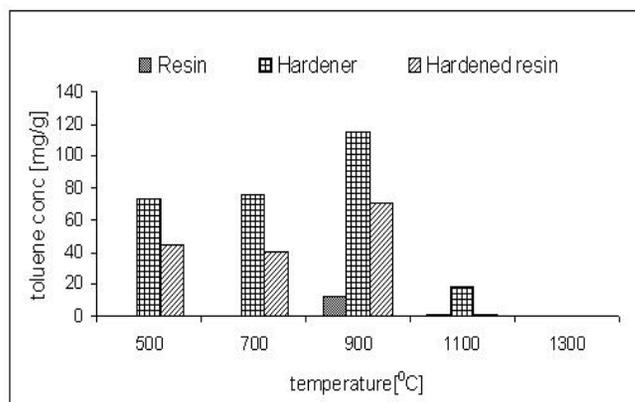


Fig. 4. Changes in the concentration of toluene in the gases emitted in the process of thermal decomposition, depending on the process temperature and the type of material being tested

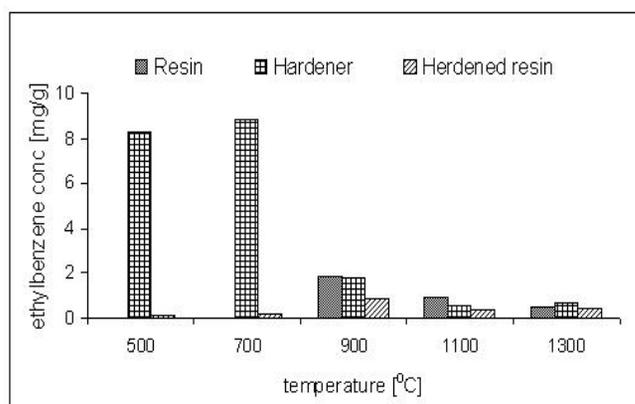


Fig. 5. Changes in the concentration of ethylbenzene in the gases emitted in the process of thermal decomposition, depending on the process temperature and the type of material being tested

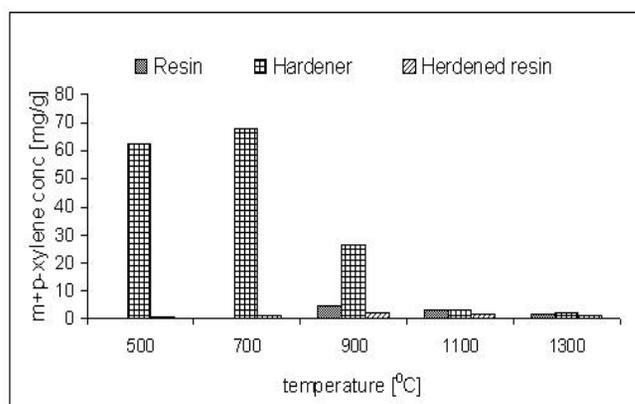


Fig. 6. Changes in the concentration of m+p-xylene in the gases emitted in the process of thermal decomposition, depending on the process temperature and the type of material being tested

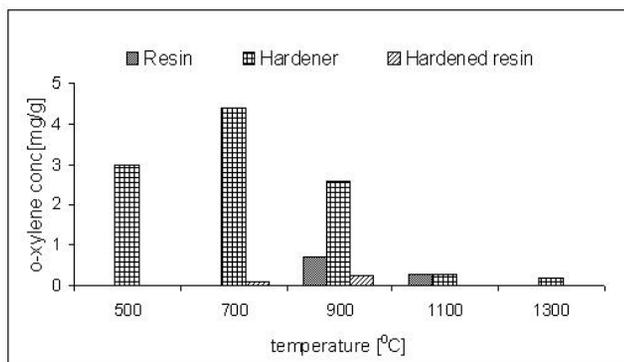


Fig. 7. Changes in the concentration of o-xylene in the gases emitted in the process of thermal decomposition, depending on the process temperature and the type of material being tested

4. Conclusions

1. There is the temperature range, within which individual substances from the BTEX group obtain the highest concentrations.
2. The highest total concentration of gases from the BTEX group emitted during the thermal decomposition of the resin, its hardener and hardened resin is observed at a temperature of 900°C.
3. Maximum concentration of benzene during the thermal decomposition of the hardener and hardened resin is observed at a temperature of 1100°C, and in case of the resin at a temperature of 900°C.
4. The highest toluene emission in case of the thermal decomposition of the hardener and hardened resin occurs at a temperature range: 500°C – 900°C and is larger from several dozen to a few hundred times than in case of the resin decomposition.
5. Toluene, ethylbenzene and xylenes indicate the highest concentrations in gases formed as the result of the hardener thermal decomposition in a temperature range from 500°C to 900°C.
6. The developed laboratory stand and methodology can be used for investigating thermal decompositions of other substances containing organic compounds.

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Badania wpływu temperatury na powstawanie związków z grupy BTEX podczas termicznego rozkładu żywicy furanowej

Streszczenie

Spoiva organiczne stosowane w odlewnictwie bazujące na żywicach syntetycznych, z jednej strony wpływają na uzyskanie przez masę formierską odpowiednich właściwości technologicznych a w konsekwencji tego otrzymania dobrych odlewów, a z drugiej w procesach odlewniczych stanowią źródło lotnych związków organicznych (LZO). Wraz z żywicami syntetycznymi stosowane są również ich utwardzacze, których dodatek stanowi wprawdzie niewielki procent w stosunku do masy żywicy, ale związki uwalniane w trakcie ich termicznego rozkładu mogą negatywnie oddziaływać na środowisko naturalne. Zarówno żywice jak i utwardzacze dopiero pod wpływem temperatury towarzyszącej zalewaniu formy ciekłym metalem generują szkodliwe lotne związki organiczne, w tym związki z grupy BTEX. Badania wpływu temperatury na rodzaj oraz ilość związków organicznych powstających podczas termicznego rozkładu wybranych spoiw i utwardzaczy oraz ich mieszanin, pozwalają określić zarówno zakres temperatur najbardziej charakterystycznych dla uwalniania szkodliwych związków, jak również dokonać porównania ich emisji z wybranymi materiałami.

Celem pracy było określenie wpływu temperatury na tworzenie się związków z grupy BTEX podczas termicznego rozkładu wybranego spoiwa, jego utwardzacza i ich mieszaniny. Emisja BTEX-ów stanowi jedno z podstawowych kryteriów oceny szkodliwości materiałów stosowanych do mas formierskich i rdzeniowych i może ulegać zmianie w zależności od rodzaju stosowanego układu żywica-utwardzacz. Badania prowadzono na specjalnie zaprojektowanym układzie do termicznego rozkładu substancji organicznych w zakresie temperatury 500–1300 °C w skali laboratoryjnej. Przedmiotem badań była żywica furanowa, jej utwardzacz oraz utwardzona żywica furanowa. W ramach badań dokonano oceny stopnia emisji BTEX-ów w zależności od układu poddawanego działaniu temperatury. Zdefiniowano zakres temperatur, w którym z badanych materiałów uwalniane są maksymalne ilości benzenu, toluenu, etylobenzenu i ksylenów. Analizę jakościową i ilościową BTEX-ów prowadzono z zastosowaniem techniki chromatografii gazowej połączonej ze spektrometrią masową (GC/MS).