

Influence of the Hardener on the Emission of Harmful Substances from Moulding Sands with Furan Resin in the Pyrolysis Process

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Abstract

The furan resin offers advantages such as high intensity, low viscosity, good humidity resistance and is suitable for cast different casting alloys: steel, cast iron and non-ferrous metal casting. For hardening furan resins are used different hardeners (acid catalysts). The acid catalysts have significant effects on the properties of the cured binder (e.g. binding strength and thermal stability) [1 - 3]. Investigations of the gases emission in the test foundry plant were performed according to the original method developed in the Faculty of Foundry Engineering, AGH UST. The analysis is carried out by the gas chromatography method with the application of the flame-ionising detector (FID) (TRACE GC Ultra THERMO SCIENTIFIC).

Keywords: Furan resin, Mould sand, Emission of gases, Pyrolysis; GC/MS, BTEX, PAH

1. Thermal destruction of furan binders of moulding sands

Casting furan resin offers advantages such as high intensity, low viscosity, good humidity resistance and is suitable for cast different casting alloys: steel, cast iron and non-ferrous metal casting. For hardening furan resins are used different hardeners (acid catalysts). The acid catalysts have significant effects on the properties of the cured binder (e.g. binding strength and thermal stability) [1 - 3].

Only a small number of acids (e.g. sulfonic, phosphoric and sulfuric acids) are practically used in production foundries due to operational and economic consideration (e.g curing rate, mould strength and catalyst price) [2, 3].

Specifically arylsulfonic acid (e.g. toluenesulfonic acid and xylenesulfonic acid) have been the most commonly used acid

catalysts, because they have suitable acidity and viscosity, excellent thermal degradability, and other properties that are important for foundry operations. In comparison, phosphoric and sulfuric acids are used only occasionally. This is because phosphoric acid is only suitable for curing furan resins that have a high urea component, whereas it is difficult to control the curing rate of sulfuric acid due to its strong acidity.

While the furan binders are beneficial for foundries to produce quality castings at low cost, they can produce considerable amounts of hazardous air pollutants (HAPs) e.g. benzene, toluene, and xylenes, that are categorized in Title III: HAPs of the 1990 Clean Air Act Amendments by the U.S. EPA, when they are thermally decomposed during metal casting processes [4, 5]. These HAPs may pose considerable threat to the environment and human health due to their high toxicity, carcinogenicity and mutagenicity [6, 7].

The harmful gases affect the health of workmen and nearby residents, and cause public protests. Foundries are therefore under increasing regulatory pressures to diminish their HAP emissions. These moulding sands are presently the most numerous within moulding sands with organic binders. However, due to probable carcinogenic properties of furfuryl alcohol, the EU Directive limits the content of this substance - in a monomer form - in resin to 25% [8]. The leading world companies, producers of binding materials for foundry engineering, are performing - since a couple of years - intensive studies to develop furan resins, which would meet the requirements of this Directive. However, it should be registered, that so drastic decrease of the furfuryl alcohol content in new resins in relation to the currently applied (which contain even up to 95% of furfuryl alcohol), must be accompanied with additional costs and - in consequence - must increase the price of such resin.

Moulding sands with furan resins, apart from undoubted technological advantages, indicate certain drawbacks, both within the scope of harmfulness and of castings quality. A special attention should be directed towards the sulfur presence in the applied hardeners, since it can transfer itself from moulding sands into the casting surface layer causing degeneration of modular or vermicular graphite.

The emission process of hazardous substances occurring during the pyrolysis of furan binders is investigated in various research centres since a couple of years. Admittedly the final products of pyrolysis such as: carbon monoxide, sulfur dioxide, carbon disulfide, benzene, toluene, ethylbenzene, xylene, thiophene and some substances from the PAH group, are known. [9 - 13].

However, the sources and formation pathways of HAPs are not well understood. It has been suggested that BTEX compounds are possibility formed from recombination reactions of the fragments (e.g. C₂ - C₄ radicals) that are generated from thermal cracking of furans [10].

However, the last papers [9, 14, 15] suggest, that BTEX are more likely derived from the benzene ring of arylsulfonic acids (e.g. paratoluenesulfonic acid). On account of this, the authors of the above paper investigated the pyrolysis process of two resins hardened by two different hardeners: paraxylenesulfonic acid (arylsulfonic acid) and methanesulfonic acid (alkylsulfonic acid). Both hardeners had similar properties and moulding sands prepared with them, on the bases of furan resin, had the required parameters, e.g. tensile strength. Although during the pyrolysis of both moulding sands similar substances from the HAP group were emitted, but their amounts were different.

The binder cured with methanesulfonic acid released okolo 67% less HAP emissions, than that cured with p-xylenesulfonic acid.

These results, as well as the results obtained by other researchers, indicate, that the acidic catalysts can influence the HAP composition emitted during pouring by liquid metal moulds of moulding sands with furan binder [4, 15, 16]. Benzene and toluene are two major products of heated reaction for each furan resin sand mold [10].

Moreover benzene was the most dominant HAP emission when benzenesulfonic acid was used as the catalyst, whereas toluene was the most abundant HAP species when p-toluenesulfonic acid was used. Haifeng Zhang [9] proposed the overall reaction pathways of BTX formation in pyrolysis of furan binders (Fig. 1),

when are cured with p-xylenesulfonic acid and methanesulfonic acid.

The BTX compounds can be formed when the bonds between the p-xylenesulfonic acid and the furan chains break, which produces aromatics and furans simultaneously (at temperature above 300°C). In addition, benzene may be formed from the fragments (e.g. C₃H₃, C₂H₂ and C₄H₄) that are derived from ring-opening reactions of furans (e.g. furan, 2-methylfuran and 2,5-dimethylfuran). As the temperature increase above 400°C, it decreases the amount of these two compounds, which can be attributed to the ring-opening of furans at elevated temperatures. Whereas in the temperature range: 460-650°C benzene is formed from the furan-derived intermediates.

For the binder with methanesulfonic acid, the BTX formation from the acid catalyst can be excluded because this acid does not have benzene ring. Thus, they are more likely produced from the fragments derived from thermal cracking of furans.

Starting from a temperature of 400°C the benzene amount significantly increases, which corresponds with the temperature range of the ring-opening reaction of furan.

On the other hand, the formation of toluene and xylenes in this temperature range from the furan-derived fragments is quite small. This is caused by the fact that furan can be easily formed from two furan-derived fragments (e.g. two propenyl radicals).

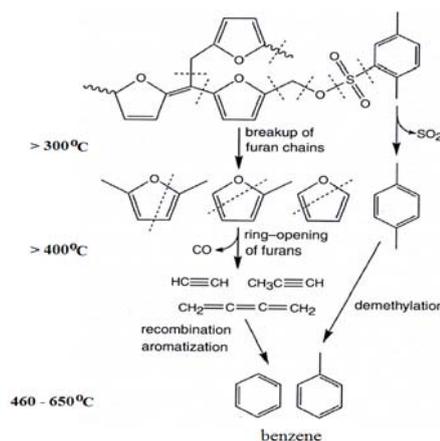


Fig. 1. Overall reaction pathways for the formation of aromatic HAPs in pyrolysis of the furan binder cured with p-xylenesulfonic acid [9]

The formation of toluene or xylenes requires usually reactions of more radicals (e.g. in case of toluene: two propenyl radicals and one methylene radical; in case of xylene and ethylbenzene the reaction of propenyl, butadienyl and methyl is necessary, and/or the reaction of two butadienyl radicals and two hydrogen atoms), which is much more difficult and less probable [10]. The comparison of the emission of substances from the HAP group in the pyrolysis of resin hardened by p-xylenesulfonic acid and methylsulfonic acids, indicated that in the first case three times more such substances were emitted than when methylsulfonic acid was applied as a hardener.

On the bases of these data it can be concluded that in case of furan resin hardened by p-xylenesulfonic acid aromatic substances from the HAP group are rather formed from the acid than from the

furan-derived fragments [9]. The formation of BTX compounds from the furan resin is much more difficult compared with the arylsulfonic acids. According to Liang [10] benzene is the main hydrocarbon product of furan resin with benzenesulfonic acid, but if the hardener is dimethyl benzenesulfonic acid or p-methyl benzenesulfonic acid, then toluene is the main hydrocarbon product. On the other hand, some ethylbenzene and small xylene are formed at 600 – 1100°C, when the dimethyl benzenesulfonic acid is used and some thiophen and small carbon disulfide are formed at same temperature range when using benzenesulfonic acid as a hardener.

About 1100°C is clear boundary line between the cracking and carbonization in the heated reaction of furan resin sand mold. It is believed that the cracking (or carbonization) of furan resin polymer yields various free radicals and/or atoms. Organic sulfonic acid was cracked to a thio and some alkyl and/or alkenyl radicals. The thio reacted with oxygen forming SO₂ or reacted with carbon forming CS₂. A thio with butadienyl yields thiophene.

As can be noticed from the above given references review, the kind of a hardener used for furan resins significantly influences the composition of gases emitted due to an influence of a high temperature of moulding sands. Therefore the subject of the hereby study was the comparison of the composition of gases from the PAHs and BTEX group emitted from moulding sands bound by two different furan resins (of a free furfuryl alcohol content 72% and <25%) hardened by 3 different hardeners. These hardeners were: of a normal sulfur content and high concentration of p-toluenesulfonic acid, of a low sulfur content and average

concentration of p-toluenesulfonic acid and without sulfur and arylsulfonic acids.

2. Applied materials and the investigation method

Moulding sands of the following composition were tested:

- Moulding no. 1: 1% resin F72 + 0.5% HS,
- Moulding no. 2: 1% resin F72 + 0.5% MS,
- Moulding no. 3: 1% resin F72 + 0.65% WS (H₃PO₄),
- Moulding no. 4: 1% resin F25 + 0.5% HS,
- Moulding no. 5: 1% resin F25 + 0.5% MS,
- Moulding no. 6: 1% resin F25 + 0.65% WS (H₃PO₄).

The characteristics of the applied resins and hardeners are given in Table 1 and 2.

Table 1.
The characteristics of resins [17]

Parameter	Furan resin	
	F72	F25
The content of free furfuryl alcohol, [%]	71.0 – 72.0	23.5 – 24.75
The total content of furfuryl alcohol, [%]	64 – 76	66.0 – 68.0
The content of free formaldehyde, [%]	0.03 – 0.06	0.15 – 0.20
The water content, [%]	9.0 – 10.0	10.0 – 12.5
The ethanol content, [%]	2.5 – 3.0	2.5 – 3.0
The nitrogen content, [%]	3.0 – 4.0	2.5 – 3.2
Density 20 °C, [g/dm ³]	1155 – 1165	1180 – 1190
Viscosity at 20 °C, [MPa s]	15 – 25	40 – 70

Table 2.
Properties of hardeners (high-sulfur, low-sulfur, H₃PO₄)

Parameters	Standard hardener HS	Low - sulfur hardener MS	Without sulfur hardener WS
Density, g/cm ³	1.22 – 1.24	1.21 – 1.23	1.58 – 1.70
Viscosity, mPa s	15	24 – 40	
Composition	p-toluenesulfonic acid (65% aqueous solution); sulfuric acid < 0.5 %	p-toluenesulfonic acid (36-41 % aqueous solution); lactic acid (30 – 35 % aqueous solution) sulfuric acid < 1 %	Orthophosphoric acid (52 % aqueous solution)

Investigations of the gases emission in the test foundry plant were performed according to the original method developed in the Faculty of Foundry Engineering, AGH UST [18].

A sample of the investigated moulding sand on the matrix of the standard high-silica sand of a roll shape of dimensions ϕ 50 x 50 mm, weight about 150 g, compacted by a moulder's rammer stroke, is poured with liquid cast iron of a temperature of 1350°C. The liquid metal mass was 9 kg. Gases emitting from the sample - after pouring it with liquid metal are led by means of a steel pipe via the drying system and the capsule with active carbon (during the BTEX measurement) or polyurethane foam (during the PAHs measurement) into pump. The whole mould (weight 24 kg) is made of green sand. The active carbon layer with adsorbed BTEX is extracted in diethyl ether. The analysis is carried out by the gas chromatography method with the application of the flame-ionising detector (FID) (TRACE GC Ultra THERMO

SCIENTIFIC). At the determination of compounds from the PAHs group a part of hydrocarbons was condensing on the formed dust particles and together with them was deposited on the filter placed in the capsule before the polyurethane foam. Therefore at determining the total amount of generated PAHs the polyurethane foam as well as the dust on the filter were analysed. Both, the filter and foam, were extracted by toluene and then separated from the matrix in hexane. Extracts obtained for individual samples were analysed by the high performance liquid chromatography (HPLC).

3. Results

Investigations of The results of the emission of gases from moulding sands with resin of the high content of furfuryl alcohol

(RF72) hardened by various hardeners are given in Table 3, while the analogous data for resin of the alcohol content <25% (RF25) are given in Table 4.

Table 3.

Amount and composition of gases emitted from moulding sands with furan resin RF72, after pouring with liquid cast iron (temperature: 1350°C)

Parameter	Hardener		
	HS	MS	WS
Contents of PAHs, mg/kg of mould sand	10.937	7.550	3.087
Contents of BTEX, mg/kg of mould sand	Benzene 561.8 Toluene 4.8 Ethylbenzene 0.01 Xylenes 0.02 Total 566.2	Benzene 542.4 Toluene 10.8 Ethylbenzene 0.0 Xylenes 1.0 Total 653.2	n.a.
Volume of gases, dm³/kg of mould sand	11.963	13.093	15.881
Loss on ignition of mould sand, %	1.18	1.24	1.39

Table 4.

Amount and composition of gases emitted from moulding sands with furan resin RF25, after pouring with liquid cast iron (temperature: 1350°C)

Parameter	Hardener		
	HS	MS	WS
Contents of PAHs, mg/kg of mould sand	10.411	6.870	2.843
Contents of BTEX, mg/kg of mould sand	Benzene 627.0 Toluene 18.3 Ethylbenzene 0.0 Xylenes 0.0 Total 645.3	Benzene 654.5 Toluene 10.1 Ethylbenzene 0.6 Xylenes 1.2 Total 665.2	n.a.*
Volume of gases, dm³/kg of mould sand	13.930	14.945	14.877
Loss on ignition of mould sand, %	1.32	1.30	1.27

* not analyzed

4. Discussion of results and conclusions

Investigations of BTEX and PAHs emissions from moulding sands with furan resins of different free furfuryl alcohol contents (marked F72 and F25), hardened by three hardeners of various sulphur and sulfonic acids contents (marked HS, MS and WS) confirmed the thermal destruction mechanism proposed in papers [9,10]. Conditions under which the discussed here experiments were performed, due to the way of their realisation (direct shocked influence of liquid cast iron on a moulding sand), correspond to conditions which are in the casting mould in the moulding sand layer directly adjusted to the casting (the so-called fast pyrolysis).

The given below conclusions can be drawn from the above studies.

1. Regardless of applying two different hardeners for both resins, the BTEX emissions were at the comparable level (within the limiting error, which in case of the BTEX analysis by means of gas chromatography method, with the FID excitation, equals 10%).
2. Benzene was the main component and in practice the only one from the BTEX group emitted from the tested systems. The content of toluene was lower by nearly two orders of magnitude.
3. In case of generating substances from the PAHs group the decisive is a hardener, and in consequence aromatic compounds present in its composition. The following relation was noticed: the smaller amount of arylsulfonic acid the lower PAHs content in the emitted gases. Concentration of these substances was decreasing in the sequence of the applied hardener: HS > MS > WS. When phosphoric acid (V) was used as the hardener (not containing arylsulfonic acids) the PAHs concentration was

nearly 4-times lower than for the hardener containing 65% of paratoluensulfonic acid (HS).

4. Naphtalene was the main component - often constituting up to 90% - of the PAHs group gases.
5. Volumes of the emitted gases were comparable, being within range: 12 – 16 dm³/ kg of moulding sand.
6. Losses on ignition of moulding sands prepared on a fresh sand were within limits: 1.18 – 1.39%.

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References

- [1] Shindo, A. & Izumino, K. (1994). Structural variation during pyrolysis of furfuryl alcohol and furfural-furfuryl alcohol resins. *Carbon*, 32, 1233-1243.
- [2] Coss, W W Richmond III. (1984). U.S. Patent No. 4,451, Catalyst composition and method for curing furan-based foundry binders. Patent and Trademark Office.
- [3] Akerberg, D.W. Huntley III. (1984). U.S. Patent No. 4,439. Catalyst system for furan resins. Patent and Trademark Office.
- [4] Tiedje, N., Crepaz, R., Eggert, T. & Bey, N. (2010). Emission of organic compounds from mould and core binders used for casting iron, aluminum and bronze in sand moulds. *J Environ Sci. Health A*, 45, 1866-1876.
- [5] Technikon # 1411-123 GJ, Baseline: PCS of furan cores, green sand without seacoal, iron. U.S. Army Contract DAAE30-02-C-1095 FY 2004 WBS #1.2.3.: 2005.
- [6] Man, YB., Kang, Y., Wang, HS. et al. (2013). Cancer risk assessments of Hong Kong soils contaminated by polycyclic aromatic hydrocarbons. *J Hazard Mater.*, 261, 770-776. Doi: 10.1016/j.jhazmat.2012.11.067.
- [7] Durmusoglu, E., Taspinar, F., & Karademir, A. (2010). Health risk assessment of BTEX emission in the landfill environment. *J Hazard Mater*, 176, 807-870.
- [8] Regulation EC No. 1272/2008.
- [9] Zhang, H., Zhao, H., Zheng, K., Li, X., Liu, G. & Wang, Y. (2014). Diminishing hazardous air pollutant emission from pyrolysis of furan no-bake using methanesulfonic acid as the binder catalyst. *J. Therm. Anal. Calorim.* 116, 373-381.
- [10] Liang, J. & Tsay, G. (2010). Composition and yield of the pernicious and stench gases in furan resin sand model founding process. *J. Environ. Eng. Manage.* 20(2), 115-125.
- [11] Holtzer, M., Bobrowski, A., Dańko, R., Kmita, A., Żymankowska-Kumon, S., Kubecki, M. & Górny, M. (2014). Emission of Polycyclic Aromatic Hydrocarbons (PAHs) and Benzene, Toluene, Ethylbenzene and Xylene (BTEX) from the furan moulding sands with addition of the reclaim. *Metallurgia* 53(4), 451-454.
- [12] Holtzer, M., Żymankowska-Kumon, S., Bobrowski, A., Dańko, R. & Kmita, A. (2014). The Influence of reclaim addition on the emission of PAHs and BTEX from moulding sands with furfuryl resin with the average amount of furfuryl alcohol. *Archives of Foundry Engineering*, 14(1), 37-42.
- [13] Holtzer, M., Dańko, R. (2013). *Harmfulness evaluation of binding material used for molding and core sands of the new generation*. Publishers "AKAPIT", Cracow.
- [14] Wang, YJ., Su, L., Li, XY, Duan, L., Wang, C. & Huang, T. (2011). Hazardous air pollutants formation from pyrolysis of typical Chinese casting materials. *Environ. Sci Technol.* 45, 6539-6544.
- [15] Xie, SZ., Li, F., Liu, CJ., Liang, JH. (2012). Development and application of furfuryl alcohol substitute materials furan resin for foundry. The 13th 21 provinces (cities, districts) 4 cities, casting and the seventh meeting of Anhui foundry technology conference proceedings Anhui: Mechanical Engineering Society in Anhui Province.
- [16] Cuoura, M., Belgacem, NM. & Gandini, A. (1997). The acid-catalyzed polycondensation of furfuryl alcohol: old puzzles unraveled. *Macromol Symp.* 122, 263 - 268.
- [17] Benz, N. & Froberg, K. (2013). Ecofriendly cold -hardening furane resins with a content of free furfuryl alcohol under 25%. *Lit. Proizv.* 6, 15 - 19.
- [18] Holtzer, M., Dańko, J. et al. (2.04.2012). No P-398 709. Station for research of the volume and harmfulness of gases compounds from the materials used in foundry and metallurgical processes. The Polish Patent Office.