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Phenolic Binders Based on Resole Resins for the Foundry Industry - Thermal Characteristics

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Abstract

The composition of gases emitted from commercial resin-based binders, under the influence of high temperatures of liquid metal (up to 1500°C), is determined in this summary with a view to assessing the potential harmfulness of these gases to the environment and workers. Mesaurements have been carried out using coupled analytical techniques, such as e.g. HS-GC/MS (Headspace/Gas Chromatography/Mass Spectrometry) or TG/DCS/FTIR (simultaneous Thermogravimetry/Differential Scanning Calorimetry coupled with Fourier Transform Infrared spectroscopy), which allow the simulation of conditions during casting production. A review of the existing literature indicates that the thermal decomposition of commercial resin-based binders is typically characterized by a multi-step process involving a series of sequential reactions, depending on the type of atmosphere. The process of decomposition has been observed to result in the release of various compounds, including water, carbon monoxide, carbon dioxide, phenol, BTEX (benzene, toluene, ethylbenzene and xylenes) and PAHs (polycyclic aromatic hydrocarbons) groups and others, from the tested binders. The composition and quantity of these gases have been found to be contingent on the type of binder, the temperature, and the heating rate of the sample. The decomposition of the binder has been demonstrated to occur through different mechanisms, which depending on the heating rate of the samples.

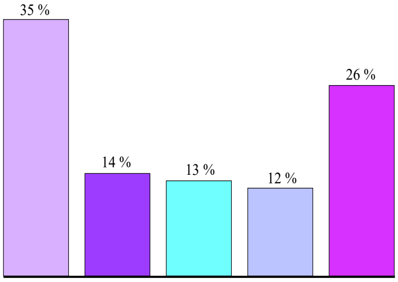
Keywords: Phenolic resin, Thermal decomposition, Foundry industry, Emission, Environmental protection

1. Introduction

Phenolic resins were the first completely synthetic polymeric materials synthesized. Until today they are the most widely used as binders and adhesives in the production of wood-based panels, moulds and cores technologies, heat-insulating materials, laminated plastics, paints and varnishes and abrasive, refractory, and other materials (Figure 1) [1, 2]. They are formed during the synthesis of phenol and formaldehyde. Depending on the nature of the environment in which the synthesis of the resin has taken place, we obtain (Figure 2) either novolaks (acidic environment and excess of formaldehyde over phenol) or resols (basic environment, with excess of phenol over formaldehyde), which can be cured by a gaseous or liquid curing agent [3, 4]. The polymerisation process of resols, takes place with an alkaline catalyst/curing agent [1-13]. Due to the presence of various reactive functional groups, the resins are capable of crosslinking under heat and in the absence of crosslinking agents (one-step resins) [3-14].

In the case of industrial-grade resins, manufacturers frequently incorporate additions [3-11] into the formulation eg. to reduce the viscosity of the liquid polymer or slows the reaction kinetics and prolongs sedimentation times [12] which affect the economics of the production process [3-12].

However, some functional properties, especially strength properties, of phenol resin are weak, and for their strengthening additions of other resins are introduced. In this way are obtained phenol-formaldehyde (PF) resins, phenol-formaldehyde-furan (PFF) resins, which meet the requirements of users [3, 4, 5, 13,14]. Another way of improving properties of PF resins is the addition of polymers. These polymers are widely used in structural adhesives, coatings an advanced composite matrices in aerospace and electronic industries, because they offer high fire resistance, high char yield, and solvent resistance [1, 4, 14-18] The above investigations concern tests of PF within the temperature range of up to 1000 °C, whereas only not much data concern their behavior at high temperatures, above 1000 °C.



35% - Woodworking industry (production of plywood, fiberboard, chipboard, etc.)
14% - Injection molding products
13% - Thermal insulation materials
12% - Laminated plastics (fiberglass, ect.)
26% - Others (production of paintwork materials, foamed plastics, ect.)

Fig. 1. Application of phenol - formaldehyde resins [based on 1, 2]

The basic feature of phenol resin is its resistance to high temperatures under conditions of mechanical stresses at minimal deformations. Hardened phenol resin has the required dimensional and structural stability. Because of their excellent ablative properties and structural integrity they can be used as high-temperature polymers [19]. Therefore thermal degradation of PF resins is an important research topic specifically their heat resistance, thermal stabilization and degradation kinetics [16, 20-24].

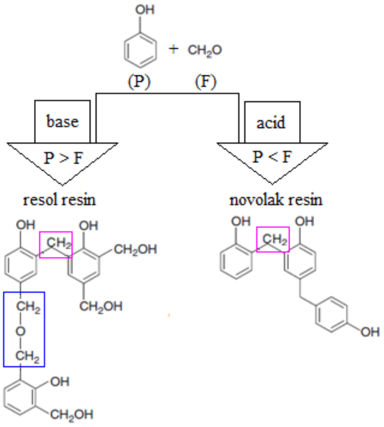


Fig. 2. Diagram of phenol-formaldehyde resin formation: resol and novolak type [based on 14]

Using PF resin as a binding element is its main application. Phenol resin easily penetrates and adheres to structures of several organic and inorganic fillers and reinforcements. A short thermal exposition, in order to finish the cross-linking or thermo-hardening process, causes obtaining final properties. The unique ability of PF resin to wetting and cross-linking of fillers and reinforcements provides means for obtaining needed mechanical, thermal and chemical properties. Such properties as hardness and thermal and chemical resistance of phenolic resins is utilised in production of grinding wheels, abrasive lining, refractory materials and other elements formed and used at high temperatures or in aggressive environments [1, 14, 25-27]. Since many years, PF resins with cellulose feelers have been used in productions of chipboards, plywoods, fibreboards. Also composites needed for demanding applications, such as drilling rig platforms, elements of rackets and thermal coatings are produced with the usage of phenolic resins. Liquid phenolic resins penetrate and saturate paper and other bases, providing good mechanical strength, electric properties and filtrating abilities. Typical examples of such applications are: electric and decorative laminates, papers, clutches and gears as well as filtration products. The above mentioned applications of PF resins are proceeding at temperatures of several dozen to maximum 200 - 300 °C. These resins are well known within this temperature range [3, 28, 29]. Products based on PF resins find applications as binders of moulding and core sands at the production of metal castings. Moulding sands with PF resins based binders constitute a significant fraction in the group of sands with chemical binders. Data concerning the share of individual technologies of the casting moulding sands with chemically hardened binders in EU are shown in Table 1 (sands with binders based on phenol-formaldehyde resin are separated) [3, 28, 30].

Table 1.
Comparison of the share of individual technologies of the casting moulding sands used in the EU [based on 3, 4, 30]

Individual technologies of the casting moulding sands	**UE, %**
Furan No-Bake	44
Phenol - urethane cold - box (gas amine)	32
Phenol hardened by ester no-bake (Alphaset)	14
Phenol –urethane no-bake (liquide amine)	3
Croning process	3
Inorganic binders	2
Hot – box system	2
Other	1

Along with the industry development and new technologies, especially automotive and cosmic industries, the demand for phenol-formaldehyde resins able to work at high temperatures is growing. Therefore investigations at temperatures above 1000 °C are so important. Difficulties are mainly consisting in the access to the equipment able to operate at such temperatures. The results of investigations of the thermal destruction process of PF resins at a temperature range up to 1100 °C are presented in the hereby study (including several studies performed by M. Holtzer et al. and A. Kmita et al. [4, 6-8, 24, 31, 32-35]). As the forecasts indicate the market of phenol resins in 2026 will reach 14.4 billion USD in relations to 11.7 billion USD in 2021 [36]. One of the faults of PF resins is toxicity of some main initial components [37, 38], which either can directly release from resins at surrounding temperature or can be forming at high temperatures (e.g. formaldehyde). Therefore a high caution should be exercised when working with these resins. In order to improve a stability of PF resins at high temperatures, thus to widen their application range, investigations of their thermal degradation in different atmospheres (eg. nitrogen or air), at temperatures near the ones at which they will operate, are necessary. An important indicator of the resin thermal stability is the final amount of ashes in tested samples. The higher amount of solid remains the more stable is the given resin. Main investigations on products of resin thermal degradation were performed in the air and/or inert (nitrogen, helium) atmospheres as well as in the vacuum [3, 4, 8, 16, 34, 35, 39-44]. Results of wide investigations of the thermal degradation effects of PF resin performed in the air and in inert atmosphere at temperatures up to 1100 °C as well as the kinetics of the thermal decomposition of these processes, are presented in a further part of this study. Production of metal castings is the practical example of PF resins application under the specified above conditions.

2. Phenol-formaldehyde (PF) resins in the moulding sand technology

In the field of moulding sand technology, the chemical character of binders is a key differentiating factor. These can be broadly classified into three main categories: inorganic binders (e.g. water glass, aluminosilicates), organic binders (e.g. PF resin, urea formaldehyde resin, phenol-furan resin) and materials of a natural origin (bentonite). Hardening can be achieved through the application of chemical or physical factors [4, 45]. The necessity to maintain high dimensional stability is becoming increasingly important in the production of castings with increasingly complex shapes. Consequently, modern foundries are increasingly utilising moulding and core sands with synthetic resins that are chemically bonded, due to the advantageous characteristics they possess, including ease of formation, the attainment of a superior final surface quality for castings, and their malleability [4, 45]. The type of bonding material used will determine the dimensional stability of the final product. It can be observed that the application of chemically bonded sands ensures a higher degree of fulfilment of the aforementioned parameters than that achieved with sands containing bentonite [4, 45]. A significant attribute of synthetic resins is their capacity to withstand elevated temperatures and the diverse range of gases produced under such conditions. The production of castings from metal alloys, including aluminium, copper and iron (iron casting and steel casting), provides examples of the use of resins at high temperatures (up to 1500°C) [4, 45]. To optimise the properties of resins, their mixtures are employed, thereby widening the range of their application. This includes the enhancement of high-temperature resistance, increased strength, and the limitation of the generation of harmful gases. The compositions of moulding sands bonded by PF resins are listed in Table 2 [4, 45].

Table 2.
Phenolic resins used in foundry industry [based on 4, 45]

Process	Phenolic resin	Hardener/Catalyst
• Croning Process; • Shell sands; • Hot-box.	Novolak	HMTA (hexamethylenetetramine) + heat
• Phenolic ester no bake (Alphaset).	Resol	Esters - liquid
• CO_2 resol/Betaset proces.		Gas hardener (CO_2/methyl formate)
• Phenolic urethane; • Cold-box (Ashland process).		Two-component binder e.g. with polyisocyanate, hardener - amine

3. Thermal characteristic of organic foundry binders

The rate of thermal decomposition of polymers depends on many factors, including the structure of the polymer, the type of atmosphere (oxidising, reducing or anaerobic) and many others [3, 4, 6, 11, 16, 46-55]. Typically, the end products of polymer degradation are char and small molecule compounds such as CO, CO_2, H_2O, toluene and its derivatives, phenol and its derivatives and others [7, 8, 11, 31].

Figure 3 shows a general decomposition scheme for polymeric materials [46], which essentially consists of two stages.

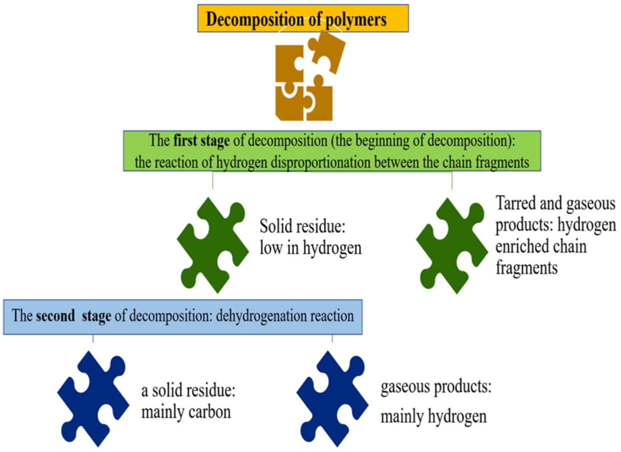


Fig. 3. Diagram of the thermal decomposition of the polymer, [based on 11, 46]

In the field of moulding sand technology, binders based on organic resins are the most commonly used method for binding matrix grains next to bentonite. Phenolic resins (resols or novolaks) are among the most frequently used. This is primarily due to the favourable technological properties of the moulding bounded by them [4, 44, 45]. However, the selection of a binder should also consider the potential risks associated with the formation of harmful pollutants [34, 35, 44, 56-59]. The results of the analysis of the primary sources of industrial emissions indicate that these originate primarily from industrial parks. The highest volatile organic compounds (VOCs) emissions were identified in the foundry production (approximately 60%), refractory production (approximately 25%) and printing production (approximately 20%) sectors. The identification of VOCs in casting, refractory and printing processes has been widely documented [4, 60]. Xylenes, amines, phenols and esters have been identified as the main VOCs species in these processes, respectively [60]. The generation of gaseous pollutants has been observed at virtually every stage of casting production, including mould making, casting and knock-out cast, as evidenced by numerous studies [4, 5, 7, 8, 30, 31, 35, 38, 44, 61].

Two distinct categories of operations can be distinguished during the metal casting process, which pose inherent risks to both human health and the environment [4, 11]:

a) at room temperature: the process of mould and core production during which, for example, evaporation of the volatile components of the moulding sand occurs;
b) in high-temperature processes: which include pouring, cooling and knock-out. During these stages, gaseous compounds such as benzene, phenol and dust are often emitted [4, 5, 7, 8, 11, 14, 16, 19, 24, 31, 38, 62].

It is therefore important to recognise the quantity and quality of the compounds produced in order to protect human health and the environment.

Thermal analysis technologies are widely employed for the determination of thermal stability and the investigation of thermal decomposition kinetics, mechanisms, and interactions in a multitude of materials, including foundry binders. The continuous advancement of these techniques enables an ever-wider range of research, including the assessment of gas-formation reaction kinetics, the analysis of the qualitative composition and quantity of gases released under ambient conditions and at elevated temperatures. As demonstrated by the findings of the studies referenced in [5, 6, 14, 19, 31, 38, 62], the casting production process gives rise to the formation of a number of harmful gaseous products at various stages. The formation of these compounds is dependent on temperature, with the resulting compounds exhibiting varying degrees of toxicity.

Among these gaseous products, polycyclic aromatic hydrocarbons (PAHs) or compounds from the BTX group (benzene, toluene and xylenes) are by-products of incomplete combustion of organic components (from the moulding sand) that may be carcinogenic and/or mutagenic [8, 31, 34, 35, 43, 44, 52, 56].

The aim of this summary is to provide a concise overview of the thermal characteristics of phenolic binders based on resol resins utilised in metal casting for mould production, as determined through thermal analysis technologies. The results of the research are presented, including the composition of the gaseous products emitted from binders at room temperature and at elevated temperatures. Moreover, the evolution volume and rate of these binders were also examined. In particular, thermogravimetric analysis (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been employed extensively to assess the thermal behaviour of foundry binders and to investigate the kinetics of thermal decomposition.

Conversely, coupled thermoanalytical techniques, including headspace-gas chromatography/mass spectrometry (HS/GC/MS), thermogravimetry/gas chromatography/mass spectrometry (TG/GC/MS), thermogravimetry/Fourier transform infrared spectroscopy (TG/FTIR), and pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) was employed to ascertain the composition of the gaseous products emitted from binders at room temperature and elevated temperatures [3-8, 11, 28, 31-35, 43, 44, 61, 63-73]. The aforementioned tests were conducted as part of an evaluation of the potential harmfulness of the applied binders, specifically those based on PF resins.

3.1. Volatilization gases of resole resin-bonded sands at ambient temperature

From point of view casting production the emission of gaseous air pollutants occurs at the moulding and pouring process. Therefore, it is important to identify both qualitatively and quantitatively the emitted major sources of air pollutants from industrial parks has practical significance in emission gases over the entire temperature range from the environment to the pouring temperature of the moulds. As it is known, at ambient temperature, at the stage of making foundry moulds, volatile components of the binder may evaporate, e.g. from a resin and/or a hardener. The HS-GC/MS technique was used to analyze gases emitted at ambient temperature from resin bonded sand [63, 68, 74]. Headspace (HS) it consists in collecting volatile gaseous products through volatilization and their analysis, e.g. with the use of GC/MS. In the work of Qian et al. [44] studied gas evolution and composition of the gaseous products emitted from 3 kind of foundry binders: furan resin; phenolic urethane and alkaline phenolic no-bake resin-bonded sands at room and high temperature. Research by HS-GC/MS conducted in [44] showed that the gaseous products of alkaline PF and furan no-bake resin-bonded sands showed no gas volatilization. Whereas in the case of phenolic urethane no-bake resin-bonded sands among voltalization gases have been identified such compounds as: monocyclic (MAH) and polycyclic aromatic hydrocarbons (PAHs) and heterocyclic aromatic compounds (HAC). Comparative studies have shown that alkaline PF no-bake resin-bonded sand are more environmentally friendly.

3.2. Thermal decomposition of binders -resole resins under flash pyrolysis conditions

The pyrolysis temperature depends on the kind of foundry alloy. This temperature varies from 700 ºC (aluminium alloys) to 1550 ºC (ferrous alloys). Results of investigations of the flash pyrolysis (Py) of a commercial binder based on PF resin, hardened by a mixture of organic esters at temperatures 500, 700, 900 and 1100 ⁰ C, are presented in papers [6-8, 31, 35, 75]. The obtained pyrolysis products were evaluated by Py/GC/MS method and are shown in Table 3 [7]. The presence of acetic acid or acetone is the effect of the thermal decomposition of organic catalyst/hardener [7, 76-82]. Moreover, it is known that certain catalyst/hardener components such as dimethyl ester are not – in practice - undergoing a thermal decomposition under analysed conditions, which is manifested by their high fraction in pyrolysis products. CO_2 was formed only at a lower temperature of the pyrolysis (500 °C), while above this temperature it was not present among products. Phenol and its methyl derivatives, nitrogen-containing compounds and small amounts of acetic acid were detected within the whole tested temperature range. At 500 °C the o-cresol fraction was equal nearly 22% and this was the highest fraction among released compounds (Table 3) [7]. At 700 °C phenol and its methyl derivatives dominated among pyrolysis products but also other products occurred, e.g. toluene [7]. At the pyrolysis temperature of 900 °C acetone and nitrogen compounds were still identified [7]. Carcinogenic and mutagenic compounds such as benzene and benzofuran were observed at the pyrolysis temperature of 900 °C [7]. An increase of the pyrolysis temperature to 1100 °C caused, among others, an increase of the presence of such substances as: benzene, toluene and phenol (Table 3) [7]. Additionally, compounds containing two aromatic rings such as fluorene were detected. The presence of this type of substances was also confirmed in studies of other scientists [7, 82-93]. The presence of nitrogen compounds is the most likely a result of the urea or amine addition during production of PF resin [3, 4, 7].

On the bases of the performed studies it can be stated, that the temperature of pyrolysis essentially influences the composition of generated gases. Within the tested temperature ranges of pyrolysis the effect of forming benzene and its methyl derivatives occurs. It is possible to determine the temperature range at which certain substances are forming. This provides the eventual possibility of controlling the pouring process of moulds by liquid metals in such a way as to avoid the most dangerous temperatures (e.g. 900 °C) [3, 4, 7, 11].

The described above investigations constitute the part of wide studies concerning thermal destructions of casting binders, including nanocomposites, carried out in AGH University of Science and Technology in a context of assessing their harmfulness [3, 4, 7, 8, 11, 24, 61, 69, 72, 73, 94-97].

Table 3.
Pyrolysis products of PF resol binder at selected temperature, identified by GC/MS method [7]. Table reprinted from Journal of Analytical and Applied Pyrolysis, 129, A. Kmita et al. "Pyrolysis of organic ester cured alkaline phenolic resin: Identification of products., 6-12, 2018, with permission from Elsevier.

Retention Time [min]	**CAS no.**	**Name of compound**	**Molecular weight**	**Temperature [°C]/ Fraction [%]**			
				500	**700**	**900**	**1100**
2.06	17344–99–9	2-amino-propionic acid ethyl ester ($C_5H_{11}NO_2$)	117			1.42	1.68
2.09	124–38–9	carbon dioxide (CO_2)	44	2.43			
2.11	37143–54–7	2-propanamine. 1-methoxy- ($C_4H_{11}NO$)	89				1.37
2.12	75–31–0	2-propanamine (C_3H_9N)	59			0.97	
2.13	6168–72–5	1-propanol, 2-amino- (C_3H_9NO)	75		3.78		
2.26	2919–23–5	cyclobutanol (C_4H_8O)	72		0.71		
2.67	67–64–1	acetone (C_3H_6O)	58		2.13	1.51	1.30
2.75	542–92–7	cyclo-penta-1,3-dien (C_5H_6)	66				1.07
2.90	593–75–9	methyl isocyanide (C_2H_3N)	41	1.24	0.54	0.40	
4.23	64–19–17	acetic acid ($C_2H_4O_2$)	60	1.74	0.66		
4.61	71–43–2[b]	benzene (C_6H_6)	78			1.80	4.56
7.77	108-88-3	toluene (C_7H_8)	92		1.37	3.30	5.20
11.63	95–47–6	benzene 1,2 dimethyl/ oxylene (C_8H_{10})	106		4.90	4.48	4.54
14.23	79–16–3	acetamide N-methyl (C_3H_7NO)	73	3.49			
15.23	526–73–8	benzene,1,2,3 trimethyl (C_9H_{12})	120		8.15	5.95	4.76
17.62	108–95–2 [b]	phenol (C_6H_6O)	94	16.28	13.11	19.94	11.70
17.86	271–89–6	benzofuran (C_8H_6O)	118			1.23	
18.39	1758–88–9	2-ethyl-1,4-dimethyl benzene ($C_{10}H_{14}$)	134		1.86	1.40	
20.03	95–48–7	phenol, 2-methyl/ o-cresol (C_7H_8O)	108	21.63	20.79	16.38	12.52
20.65	106–44–5	phenol, 4-methyl/ p-cresol (C_7H_8O)	108	14.80	9.90	6.35	9.26
21.68	95–87–4 [b]	phenol, 2,5-dimethyl ($C_8H_{10}O$)	122	12.00	10.01	10.42	5.66
22.45	620–17–7	phenol, 3-ethyl ($_8H_{10}O$)	122		1.25	1.73	
22.84	105–67–9	phenol, 2,4-dimethyl- $C_8H_{10}O$	122	15.78	11.61		
22.92	526-75–0 [b]	phenol,2,3-dimethyl/ 2,3Xylenol ($C_8H_{10}O$)	122			14.02	18.50
23.43	123-07-9	phenol, 4-ethyl ($C_8H_{10}O$)	122			2.01	2.50
23.97	3855-26-3	phenol, 2-ethyl-4 methyl ($C_9H_{12}O$)	136		1.42	2.48	1.65
24.43	2416-94-6	phenol, 2,3,6-trimethyl ($C_9H_{12}O$)	136				6.44

24.45	527-60-6	phenol, 2,4,6-trimethyl ($C_9H_{12}O$)	136	10.56	7.73	8.25	
25.43	1123-94-0	Phenol, 4-ethyl-3-methyl-($C_9H_{12}O$)	136				2.17
25.96	627-93-0 [a]	adipic acid, dimethyl ester ($C_8H_{14}O_4$)	174				
27.16	1901-26-4	3-buten-2-one, 3-methyl-4-phenyl-α-methylbenzylideneacetone ($C_{11}H_{12}O$)	160			2.29	
27.29	106-61-6 [a]	1,2,3-propanetriol, 1-acetate ($C_5H_{10}O_4$)	134				
27.51	102-76-1 [a]	1,2,3-propanediol-triacetate/ triacetin ($C_9H_{14}O_6$)	218				
29.54	102-62-5 [a]	glycerol 1,2-diacetate ($C_7H_{12}O_5$)	176				
35.56	86-73-7	fluorene ($C_{13}H_{10}$)	166				2.04
37.74	721-45-9	1,4-dimethyl-2-[(4-methylphenyl) methyl] benzene ($C_{16}H_{18}$)	210				3.45

[a] These compounds were not included in the analysis of the degradation products.

[b] Carcinogenic and mutagenic effect.

3.3. Thermal decomposition of PF binders under slow pyrolysis - the influence of the atmosphere

As the effect of the heat transfer into casting in further parts of the mould the moulding sand is slowly warming and the process atmosphere can be changing from inert via oxidizing to reducing [4]. As it is well known, the character of the atmosphere influences essentially the decomposition process of PF binders and in consequence influences the quantitative and qualitative composition of gases formed under the temperature influence [3, 7, 8, 31, 97-102]. Therefore it is essential in investigations of the thermal resistance of casting binders based on PF resin, to take into consideration not only the heating rate but also the influence of the atmosphere. Thus, for a complete process description investigations under inert, reducing and oxidizing conditions are recommended [3, 4, 7, 8, 31, 97-102].

3.3.1. Inert atmosphere

Studies of the team A. Kmita and M. Holtzer [3, 4, 31, 7, 8, 97, 98] are presenting systematic investigations of the slow pyrolysis process of PF binder, hardened by the mixture of organic esters (no-bake), by TG/DSC/FTIR or TG/GC/MS method. The applied FTIR and MS methods are complementary ones and provide fuller picture of achieved results. Investigations [7] performed by TG/DTG method within the temperature range from 25 to 1100 °C pointed out that the slow pyrolysis process of PF binder can be divided into 7 stages, in which mass losses occurred [7]. Observed mass losses are related to a gradual thermal degradation of the binder. The identification of gases emitted from the sample, as the temperature function, were carried out by means of the FTIR method (Figure 4) [7]. Correlation the released product identity with the onset, maximum and end-set temperatures of its release, and the corresponding mass loss (%) and mass loss rate (%/min), established from the TGA curve were presented in work [7].

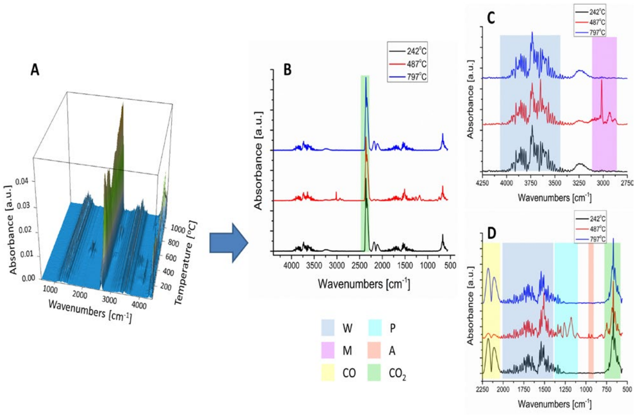


Fig. 4. FTIR spectra collected during decomposition of the PF resol binder: A) 3D chromatographic plot; B) FTIR spectra at temperature; C), D) spectra at different spectral ranges. W (water); M (methane), CO_2, CO, P (phenol), A (ammonia) [7]. *Figure reprinted from Journal of Analytical and Applied Pyrolysis, 129, A. Kmita et al. "Pyrolysis of organic ester cured alkaline phenolic resin: Identification of products., 6-12, 2018, with permission from Elsevier.*

Significant losses of the sample mass were observed at temperatures from approximately 100 °C to 550 °C. Heating the PF binder sample in the initial stage (from 113 °C to app. 330 °C), is associated with the thermal effect corresponding with the reaction of an exothermal character [7]. At a further heating of the sample several reactions, also of the exothermic character, were occurring one after another [3, 7, 8]. Above a temperature of 800 °C to approximately 1100 °C the recorded TGA slope became more gradual, no variations in the DSC curve were observed associated with a carbonization of organic residues [7, 103-106]. Within the low temperature range to approximately 300 °C the Authors identified, among the slow pyrolysis products, such compounds as: H_2O, CO_2, CO and ammonia [7]. The presence of ammonia indicates that nitrogen-containing substances were utilised during the production of the PF resin [4, 7, 8, 11, 24, 31]. Often urea is applied, which in the temperature range 200 to 400 °C undergoes decomposition with evolving ammonia. However, heating PF binder above 300 °C causes additionally releasing of phenol and its derivatives and also methane [7]. On the bases of the achieved TG/FTIR results the hypothesis can be stated that the slow pyrolysis leads to a total thermal degradation of resin, which in effect constitutes relatively low emission of harmful substances [7]. Probably a small abrupt temperature jump provides time for reactions in between these substances, leading to more complete decomposition process via slow pyrolisis [7].

It is, however, worth to note that FTIR is far less sensitive than the MS and as such it would not have been able to detect all of the trace compounds revealed via e.g. TG/GC/MS. Therefore, on purpose of obtaining a wider knowledge concerning the thermal decomposition of binders, complementary investigations utilising mass spectrometer are often performed (TG/GC/MS) [31].

Systematic investigations of the thermal decomposition of 2 kinds of PF resins originated from different producers performed by TG/GC/MS method, are presented in paper [31]. Samples were heated (TG) with a constant rate and emitted gases were condensed and divided on the GC column and identified by MS. The identification of individual gaseous substances emitted during the slow pyrolysis was carried out with utilizing the Library of Mass Spectra of the National Institute of Standards Technology (NIST MS, 2000). Results of the MS analysis are shown in Table 5 [31].

Table 5.
Slow pyrolysis products identified via MS analysis in cryo trap mode [31]. *Table reprinted from Arabian Journal of Chemistry, 11(3), A. Kmita et al. "Thermal decomposition of foundry resins: A determination of organic products by thermogravimetry-gas chromatography-mass spectrometry (TG-GC-MS)." 380-387, 2018, with permission from Elsevier.*

Retention time, min.	**Database hit**	**CAS No**	**Proba-bility, %**
99.832	Acetic acid	64-19-7	90
102.195	column material	--	--
103.037	Benzene, 1,3-dimethyl	108-38-3	97
	p-Xylene	106 -42-3	95
104.813	Benzene, 1-ethyl-3-methyl	620-14-4	83
104.935	Benzene, 1,2,3-trimethyl	526-73-8	97
105.194	Phenol	108-95-2	95
106.462	Phenol, 2-methyl	95-48-7	97
106.528	Benzene, 4-ethyl-1,2-dimethyl	934-80-5	90
	Benzene, 1,2,4,5-tetramethyl	95-93-2	90
	Benzene, 1-ethyl-2,3-dimethyl	933-98-2	90
106.792	Phenol, 4-methyl	874-41-0	96
107.312	Phenol, 2,6-dimethyl	576-26-1	97
107.795	No clear identification	--	--
107.955	Phenol, 3,5-dimethyl	108-68-9	97
108.808	Phenol, 2,4,6-trimethyl	527-60-6	95

CAS - number of chemical substance in Chemical Abstracts Service Registry

Among identified compounds the Authors [31] found, with a high probability, such gaseous products as: acetic acid, xylene, phenol and its derivatives and benzene methyl derivatives.

In addition performed investigations of the PF resin sample by means of the TG-GC/MS method in a quasi-continuous mode, which allowed to determine the temperature range and composition of emitted substances (Table 6) [31].

Table 6.
Slow pyrolysis products identified via MS analysis in quasi-continuous mode [31]. *Table reprinted from Arabian Journal of Chemistry, 11(3), A. Kmita et al. "Thermal decomposition of foundry resins: A determination of organic products by thermogravimetry-gas chromatography-mass spectrometry (TG-GC-MS)." 380-387, 2018, with permission from Elsevier.*

Retention time, min.	**Database Hit**	**CAS No**	**Proba bility/%**
45.072	Toluene	108-88-3	91
45.134	p-Xylene	106 -42-3	97
	Benzene, 1,3-dimethyl-	108-38-3	97
45.229	Benzene, 1,3,5-trimethyl	108-67-8	95
45.330	Phenol, 2-methyl	95-48-7	94
45.364	Phenol, 4-methyl	874-41-0	93
	Benzene, 1-ethyl-3,5-dimethyl	934-74-7	74
45.470	Phenol, 2,3-dimethyl	526-75-0	95
45.549	Phenol, 2,4-dimethyl	105-67-9	93

As the Authors indicate [31] the first mass loss of the sample, observed on TG curve is related to releasing of water (to 300 °C) and some organic compounds including acetic acid and CO, CO_2. The presence of carbon compound is justified by the fact that one of the binder component was propylene carbonate, which is decomposed above 240 °C [31, 76, 80, 81]. Further heating of the sample caused 2 successive weight losses in the range to app. 600 °C and 1000 °C, which are related to further emitting of CO and CO_2.

However, the main thermal decomposition of resin occurred in the second stage (with mass loss equal app. 22%) it means in the temperature range from app. 300 °C to 600 °C [31]. Among products of the slow pyrolysis such substances as: benzene, phenol and their derivatives (Table 5) were identified [31]. Phenol and its methyl derivatives can be forming due to breaking of bonds between the aromatic ring and methylene group together with a hydrogenation of this group [4, 31, 77, 84-86, 88]. On the bases of the investigation results obtained by the TG/FTIR method as well as by the complementary TG/GC/MS technique it can be stated, that in order to decrease amounts of emitted harmful substances during the thermal decomposition of PF binders the attention should be focused on decreasing amounts of moulding sands, which reach a temperature above 400°C [8, 9, 24, 31, 83]. It is imperative that the contact time of the casting with the moulding sand is kept to a minimum. Consequently, the casting should be knocked out from the sand mould as expeditiously as is technologically feasible [4, 31].

3.3.2 Reducing and oxidizing atmosphere

In order to fully reflect conditions occurring in the mould after its pouring with liquid metal, it is necessary to perform the degradation in reducing and oxidizing atmospheres. The Authors [3, 8] performed systematic studies of the influence of atmosphere kind on the pathway of the thermal destruction reaction of commercial binders (based on PF resin) applied in foundry practice. It was proven that the atmosphere, in which samples were heated, had a very essential influence on DSC and TG curves (Figure 5) as showed Authors in [8]. In all tested samples, regardless of the atmosphere kind, the mass loss as a temperature function can be divided into 5 main stages [8]. The highest loss was recorded for the sample heated in the oxidizing atmosphere (in practice it was a total combustion). In the reducing atmosphere the mass loss was app. 30%, while the smallest loss was recorded for the sample heated under the inert conditions [8]. In dependence of the atmosphere kind the shapes of TG/DSC curves were different, which indicates that mechanisms of the thermal degradation of tested samples were also different. The degradation temperature of PF binder also depends on the atmosphere [8]. All thermal effects observed on the DSC and TG plots, supplemented with corresponding FTIR information are presented in [8]. Investigations performed by TG/FTIR method [8] indicated that kind and amount of gases emitted during the thermal decomposition of binders based on PF resin to a high degree depend on a temperature and atmosphere [8]. These are very important information from the point of view of the environment protection. It was pointed out, that slow heating of the PF binder sample in oxidizing atmosphere (combustion) is the most favorable for the environment, since under such condition the smallest amounts of harmful volatile substances are formed [8]. Among these substances dominate: CO_2, CO, carboxylic esters, esters [8].

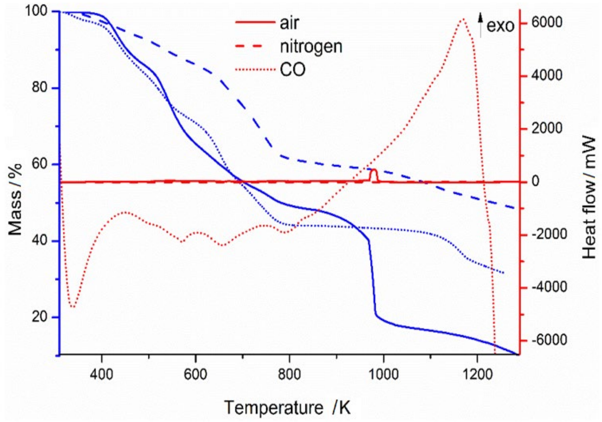


Fig. 5. TG/DSC curves of the PF binder under different atmospheres: nitrogen, air and CO [8]. *Figure reproduced from Journal of Thermal Analysis and Calorimetry, 140, A. Kmita et al. "Evaluation of pyrolysis and combustion products from foundry binders: potential hazards in metal casting." 2347–2356, 2020, with permission from Springer Nature.*

3.4. Study of thermal decomposition kinetics of phenolic binders

A study of the kinetics of the thermal decomposition process of resole resin-based casting binders is presented in reference [24]. The authors of [24] estimated the activation energy (Ea) and the value of the pre-exponential factor (A) of a given process using the so-called "free kinetics" method, thus avoiding the necessity of adopting the Friedmann and Kissinger - Akahira - Sunose (KAS) model [4, 11, 24, 26, 107, 108]. The 'model-based' method was also employed in the calculations, which entailed fitting a model to the experimental TG and DTG data using multiple non-linear regression techniques. This method is based on NETZSCH's 'Thermokinetics 3' software package [24]. As demonstrated in the authors' study [24], the activation energy (Ea) values derived using both the Kissinger-Akahira-Sunose (KAS) and Friedmann methods [24] exhibited mutual agreement (Table 7 and Table 8) [24]. The activation energy (Ea) of the thermal decomposition process of a resin-based resin binder exhibited a correlation with the degree of conversion, with an average value of approximately 124 kJ/mol [24].

As reported by the authors, the results demonstrated a high degree of correlation with the DTG experimental data within the temperature range of up to 620°C, indicating that the adopted model was an appropriate representation of the observed phenomena. The analysis revealed that the decomposition process entailed five distinct steps, each characterised by an n^{th}-order reaction [24].

Table 7.
Activation energy (Ea) calculated via KAS method [24]. *Table reprinted from Applied Thermal Engineering, 156, A. Kmita et al. "The decomposition process and kinetic analysis of commercial binder based on phenol-formaldehyde resin, using in metal casting., 263-275, 2019, with permission from Elsevier.*

Fract. Mass Loss	Activation Energy /(kJ/mol)	Std. Deviation /(kJ/mol)	Log (A/s^{-1})
0.020	74.44	2.31	9.32
0.050	49.71	0.76	6.11
0.100	43.07	0.51	4.75
0.200	68.69	0.62	6.70
0.300	71.56	0.62	6.32
0.400	88.74	1.51	7.46
0.50	100.80	2.48	7.94
0.600	95.06	2.89	6.29
0.700	166.78	2.83	10.94
0.800	232.12	7.29	14.94
0.900	366.33	13.92	22.81

Table 8.
Activation energy (Ea) calculated via Friedmann method [24]. *Table reprinted from Applied Thermal Engineering, 156, A. Kmita et al. “The decomposition process and kinetic analysis of commercial binder based on phenol-formaldehyde resin, using in metal casting., 263-275, 2019, with permission from Elsevier.*

Fract. Mass Loss	Activation Energy/(kJ/mol)	Std. Deviation /(kJ/mol)	Log (A/s^{-1})
0.020	51.66	1.56	4.98
0.050	45.40	0.63	3.78
0.100	43.92	0.58	3.12
0.200	74.72	0.64	6.09
0.300	81.29	0.61	6.23
0.400	101.77	1.99	7.86
0.500	103.63	3.77	7.28
0.600	109.28	1.79	6.46
0.700	204.41	3.45	13.58
0.800	264.69	8.61	17.47
0.900	393.88	12.28	25.48

4. Summary of studies concerning the thermal decomposition of PF binders

As has been shown in numerous studies, with particular reference to [3, 4, 7, 8, 24, 31], the thermal decomposition of commercial resin-based binders exhibited characterized multi-step process involving a series of successive reactions. The quantity and composition of the released gases were found to be dependent on kind of resin and both temperature and the heating rate of the sample, with flash pyrolysis and slow pyrolysis exhibiting distinct behaviours [4, 7, 8, 11, 24, 31]. Interestingly, the results show the presence of nitrogen compounds in the release products (both fast and slow heating) of commercial resin-based binders [4, 7, 8, 11, 24, 31].

Qualitative analysis of the gases released during flash pyrolysis [4, 7, 8, 11, 24, 31] revealed a change in composition with increasing pyrolysis temperature [8]. Prior systematic analyses have demonstrated that the high temperature range (700 to 1100°C) is associated with the highest generation of harmful substances [7, 8, 31] e.g. from BTEX groups [8, 31].

As indicated by slow pyrolysis studies [3, 4, 7, 8, 11, 24, 31], physical and chemical changes take place in PF binders during this process, in the initial stage (up to about 200 °C) mainly related to the removal of water (chemically and physically bound). As the temperature increases (above 200 °C to approx. 600 °C), decomposition of the resin takes place, involving the emission of e.g. phenol, ammonia, carbon monoxide, carbon dioxide, BTEX compounds, nitrogen compounds, etc. In the higher temperature range (above 600 °C), further release of carbon monoxide and carbon dioxide associated with carbonisation was observed.

The results presented herein may prove useful in foundry practice, as they enable the identification and modification of the most harmful stages of industrial-scale metal casting. This can lead to an improvement in working conditions and the quality of the environment.

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References

[1] Berdnikova, P.V., Zhizhina, E.G. & Pai, Z.P. (2021). Phenol-formaldehyde resins: properties, fields of application, and methods of synthesis. *Catalysis in Industry*. 13, 119-124. https://doi.org/10.1134/S2070050421020033.

[2] Alieva, A.P. (2021). Prospects for obtaining phenol-formaldehyde oligomers. *Plasticheskie massy*, (9-10), 22-26.

[3] Roczniak, A. (2019). *Research of the influence of temperature and type of atmosphere on the release of chemical compounds from mold sand Alphaset technology. (in Polish).* Kraków: AGH University of Science and Technology.

[4] Holtzer, M. & Kmita, A. (2020). Mold and core sands in metalcasting: chemistry and ecology. *Sustainable Development*.219-241.

[5] Ghosh, D.K. (2019). Comparison of molding sand technology between alphaset (APNB) and furan (FNB). *Archives of Foundry Engineering*. 19(4), 11-20. DOI: 10.24425/afe.2019.129623.

[6] Kmita, A., Roczniak, A. & Holtzer, M. (2016). The identification of pyrolysis products of the Alphaset binder with gas chromatography / mass spectrometry. *Metalurgija*. 56(1-2), 21-24.

[7] Kmita, A., Benko, A., Roczniak, A., Fraczek-Szczypta, A. & Holtzer, M. (2018). Pyrolysis of organic ester cured alkaline phenolic resin: Identification of products. *Journal of Analytical and Applied Pyrolysis*. 129, 6-12. https://doi.org/10.1016/j.jaap.2017.12.014.

[8] Kmita, A., Benko, A., Roczniak, A., & Holtzer, M. (2020). Evaluation of pyrolysis and combustion products from foundry binders: potential hazards in metal casting. *Journal of Thermal Analysis and Calorimetry*. 140, 2347-2356. https://doi.org/10.1007/s10973-019-09031-9.

[9] Scarbel, P., Bats, C.E. & Griffin, J. (2006). Effect of mold and binder formulation on gas evolution when pouring

aluminum casting. *AFS Transactions*. 114, 435-445.

[10] Lytle, C.A., Bertsch, W. & Mc Kinley, M.D. (1998). Determination of thermal decomposition product from phenolic urethane resin by pyrolysis – gas chromatography – mass spectrometry. *Journal of High Resolution Chromatography*. 21(2), 128-132. ISSN: 0935-6304.

[11] Kmita, A. (2021). *Thermal decomposition of nanocomposite foundry binder based on phenol-formaldehyde resin with zinc ferrite.* Kraków: Wydawnictwa AGH. (in Polish).

[12] Laramee, R. & Canfield, A. (1972). Carbon/Carbon Composites—Solid Rocket Nozzle Material Processing, Design, and Testing. In H.T. Corten (Eds.), *Composite Materials: Testing and Design (Second Conference)*. West Conshohocken, PA 19428-2959: ASTM International. https://doi.org/10.1520/STP27772S.

[13] Zhao, Yong, Yan, N. & Feng, M.W. (2013). Thermal degradation characteristics of phenol–formaldehyde resins derived from beetle infested pine barks. *Thermochimica Acta*. 555(10), 46-52. https://doi.org/10.1016/j.tca.2012.12.002.

[14] Gardziella, A., Pilato, L.A., Knop, A. (2000). *Phenolic resins. Chemistry, applications, standarizations, safety and ecology.* Springer, Verlag.

[15] Wang, S., Xing, X., Li, J. & Jing, X. (2018). Synthesis and characterization of poly (dihydroxybiphenyl borate) with high char yield for high-performance thermosetting resins. *Applied Surface Science*. 428, 912-923. https://doi.org/10.1016/j.apsusc.2017.09.213.

[16] Chiantore, O., Lazzari, M. & Fontana, M. (1995). Thermal decomposition of phenol-formaldehyde foundry resins. *International Journal of Polymer Analysis and Characterization*. 1(2), 119-130. https://doi.org/10.1080/10236669508233867.

[17] Johnston, P. K., Doyle, E. & Orzel, R. A. (1988). Phenolics: a literature review of thermal decomposition products and toxicity. *Journal of the American College of Toxicology*. 7(2), 201-220.

[18] He, G.B. & Riedl, B. (2003). Phenol –urea-formaldehyde cocondensed resol resins. Their synthesis, curing kinetics, and network properties. *Journal of Polymer Science, Part B*. 41(16), 1929-1938. https://doi.org/10.1002/polb.10558.

[19] Fyfe, C.A., McKinnon, M.S., Rudin, A. & Tchir, W.J. (1983). Investigation of the mechanism of the thermal decomposition of cured phenolic resins by high-resolution carbon-13 CP/MAS solid-state NMR spectroscopy. *Macromolecules*. 16(7), 1216-1219.

[20] Wang, J., Jiang, N. & Jiang, H. (2009). Effect of the evolution of phenol-formaldehyde resin on the high-temperature bonding. *International Journal of Adhesion and Adhesives*. 29(7), 718-723. https://doi.org/10.1016/j.ijadhadh.2009.03.001.

[21] Mustata, F., Tudorachi, N. & Bicu, I. (2015). The kinetic study and thermal characterization of epoxy resins crosslinked with amino carboxylic acids. *Journal of Analytical and Applied Pyrolysis*. 112, 180-191. https://doi.org/10.1016/j.jaap.2015.01.030.

[22] Visakh, P.M., Arao, Y. (2015). *Thermal degradation of polymer blends, composites and nanocomposites.* Springer.

[23] Rao, M.P.R., Rao, B.C. & Rajan, R.S.G. (1998). Thermal degradation kinetics of phenol—crotonaldehyde resins. *Polymer Degradation and Stability*. 61(2), 283-288. https://doi.org/10.1016/S0141-3910(97)00210-3.

[24] Kmita, A., Knauer, W., Holtzer, M., Hodor, K., Piwowarski, G., Roczniak, A. & Górecki, K. (2019). The decomposition process and kinetic analysis of commercial binder based on phenol-formaldehyde resin, using in metal casting. *Applied Thermal Engineering*. 156, 263-275. https://doi.org/10.1016/j.applthermaleng.2019.03.093.

[25] Poljanšek, I. & Krajnc, M. (2005). Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy. *Acta Chimica Slovenica*. 52(3), 238-244.

[26] Friedman, H. (1969). New methods for evaluating kinetic parameters from thermal analysis data. *Journal of Polymer Science Part B: Polymers Letters.* 7, 41-46. https://doi.org/10.1002/pol.1969.110070109.

[27] Levchik, S.V. & Weil, E.D. (2004). Thermal decomposition, combustion and flame-retardancy of epoxy resins - A review of the recent literature. *Polymer International*. 53(12), 1901-1929. https://doi.org/10.1002/pi.1473.

[28] Holtzer, M., Dańko, R., Dańko, J., Kubecki, M., Żymankowska-Kumon, S., Bobrowski, A., Spiewok, W. (2013). The assesment of harmfulness of binding materials used for a new generation of core and molding sands. *AKAPIT, Kraków (in Polish)*.

[29] Holtzer, M, Kmita, A. & Dańko, R, (2015). The gases generation during thermal decomposition of moulding sands - comparison of inorganic and organic binders. *Slévárenství*. 63(7-8), 246-247.

[30] Trinowski, D.M. (2016). Comparing moulding and core trends in the US and EU casting industries. *Huttenes-Albertus Chemische Werke GmbH*, 1-13.

[31] Kmita, A., Fischer, C., Hodor, K., Holtzer, M. & Roczniak, A. (2018). Thermal decomposition of foundry resins: A determination of organic products by thermogravimetry-gas chromatography-mass spectrometry (TG-GC-MS). *Arabian Journal of Chemistry*. 11(3), 380-387. https://doi.org/10.1016/j.arabjc.2016.11.003.

[32] Holtzer, M., Dańko, R. & Kmita, A. (2016). Influence of a reclaimed sand addition to moulding sand with furan resin on its impact on the environment. *Water, Air and Soil Pollution.* 227(1), 1-12. https://doi.org/10.1007/s11270-015-2707-9.

[33] Holtzer, M., Dańko, R., Górny, M., Kmita, A. (2015). *The mold/casting interface phenomena and their influence on the surface quality of casting*. Cracow University of Technology Publisher.

[34] Holtzer, M., Dańko, R., Kmita, A., Drożyński, D., Kubecki, M., Skrzyński, M. & Roczniak, A. (2020). Environmental impact of the reclaimed sand addition to molding sand with furan and phenol-formaldehyde resin—a comparison. *Materials*. 13(19). 4395, 1-12. https://doi.org/10.3390/ma13194395.

[35] Holtzer, M., Dańko, R., Piasny, S., Kubecki, M., Drożyński, D., Roczniak, A., Skrzyński, M. & Kmita, A. (2021). Research on the release of dangerous compounds from the BTEX and PAHs groups in industrial casting conditions. *Materials*. 14(10), 2581. https://doi.org/10.3390/ma14102581.

[36] Report (2021). *Phenolic Resin Market.* Retrieved October

18, 2024, from https://www.researchandmarkets.com/reports/4053239/phenolic-resin-market-by-typeresol-novolac.

[37] EPA United States Environmental Protection Agency. (2018). *What are hazardous air pollutants?* Retrieved October 17, 2024, from https://www.epa.gov/haps/what-are-hazardous-air-pollutants.

[38] Giese, S.R, Shepard, A. (2014). Understanding emissions characteristics of a foundry sand binder. In 71st World Foundry Congress, 19-21 May 2014 (pp. 934-942). Bilbao, Spain.

[39] Lefebvre, J., Mamleev, V., Le Bras, M. & Bourbigot, S. (2005). Kinetic analysis of pyrolysis of cross-linked polymers. *Polymer Degradation and Stability*. 88(1), 85-91. https://doi.org/10.1016/j.polymdegradstab.2004.02.020.

[40] Bouajila, J., Raffin, G., Alamercery, S., Waton, H., Sanglar, C. & Grenier-Loustalot, M.F. (2003). Phenolic resins (IV). Thermal degradation of crosslinked resins in controlled atmospheres. *Polymers and Polymer Composites*. 11(5), 345-357. https://doi.org/10.1177/096739110301100501.

[41] Giese, S.R., Roorda, S.C. & Patersson, M.A. (2009). Thermal analysis of phenolic urethane binder and correlated properties. *AFS Transactions*. 117, 355-366.

[42] Gao Z, Lang X, Chen S, Zhao C (2021). Mini-review on the synthesis of lignin-based phenolic resin. *Energy & Fuels.* 35, 22, 18385-18395.

[43] Wan, P., Zhou, J., Li, Y., Yin, Y., Huang, D., Ji, X. & Shen, X. (2019). Experimental study on gas evolution process of binders in foundry industry based on TG-MS. *Procedia Manufacturing*. 37, 311-318. https://doi.org/10.1016/j.promfg.2019.12.053.

[44] Qian, X., Wan, P., Yin, Y., Qi, Y., Ji, X., Shen, X., Li, Y. & Zhou, J. (2022). Gas evolution characteristics of three kinds of no-bake resin-bonded sands for foundry in production. *China Foundry*. 19(2), 140-148. https://doi.org/10.1007/s41230-022-1031-4.

[45] Lewandowski, J.L. (1997). *Materials for foundry moulds.* AKAPIT. (in Polish)

[46] Pielichowski, K. (2013). *Application of thermal analysis methods in the study of organic materials.* Retrieved October 20, 2024, from https://Pg.Gda.Pl/Info/Polimery/Files/2013/10/Im-Swp-l-002h.pdf. (in Polish).

[47] Pielichowski, K., Njuguna, J., Majka, T.M. (2022). *Thermal degradation of polymeric materials.* Elsevier.

[48] Schnabel, W. (1981). *Polymer degradation: principles and practical applications*. Walter de Gruyter GmbH & Co KG.

[49] Fink, J. K. (2017). *Reactive polymers: fundamentals and applications: a concise guide to industrial polymers*. William Andrew.

[50] Rabek, J.F. (2017). *Modern knowledge about polymers.* Wydawnictwo Naukowe PWN. (in Polish).

[51] Bortel, E. (1994). *Introduction to Polymer Chemistry.* UJ, Kraków (in Polish).

[52] Pielichowski, J., Sobczak, J., Żółkiewicz, Z., Hebda, E. & Karwiński, A. (2011). The thermal analysis of polystyrene foundry model. *Transaction of the Foundry Research Institute*. 1, 15-21. (in Polish).

[53] Florjańczyk, Z., Penczek, S. (2002). *Polymer Chemistry. Volume II Basic Synthetic Polymers and Their Applications*. Oficyna Wydawnicza Politechniki Warszawskiej. (in Polish).

[54] Shuklaa, S.K., Srivastavaa, D. (2001). Epoxy/Resole blends-A study of its degradation kinetics. *Indian Journal of Chemical Technology*. 8, 357-361.

[55] Yangfei, C., Zhiqin, C., Shaoyi, X. & Hongbo, L. (2008). A novel thermal degradation mechanism of phenol-formaldehyde type resine. *Thermochimi Acta.* 476(1-2), 39-43. https://doi.org/10.1016/j.tca.2008.04.013.

[56] Chaussoy, N., Brandt, D. & Gérard, J.F. (2023). Formaldehyde-free and phenol-free non-toxic phenolic resins with high thermostability. *ACS Applied Polymer Materials.* 5(7), 5630-5640.

[57] Wang, C., Wu, Y., Liu, Q. & Wang, F. (2011). Analysis of the behaviour of pollutant gas emissions during wheat straw/coal cofiring by TG-FTIR. *Fuell Process Technology*. 92(5), 1037-1041. https://doi.org/10.1016/j.fuproc.2010.12.029.

[58] Chai, Y., Liu, J., Zhao, Y. & Yan, N. (2016). Characterization of modified phenol formaldehyde resole resins synthesized in situ with various boron compounds. *Industrial & Engineering Chemistry Research.* 55(37), 9840-9850.

[59] McKinley, M.D., Jefcoat, I.A., Herz, W.J. & Frederick, C. (1993). Air emissions from foundries: a current survey of literature, supplies and foundrymen. *American Foundry Society Transactions*. 101, 979-990.

[60] Liu, Y., Xie, Q., Li, X., Tian, F., Qiao, X., Chen, J. & Ding, W. (2019). Profile and source apportionment of volatile organic compounds from a complex industrial park. *Environmental Science: Processes & Impacts*. 21, 9-18. DOI: 10.1039/C8EM00363G.

[61] Major-Gabryś, K. (2016). *Environmentally friendly foundry moulding and core sands.* Archives of Foundry Engineering. Habilitation dissertation.(in Polish).

[62] Jiang, H., Wang, J., Wu, S., Wang, B. & Wang, Z. (2010). Pyrolysis kinetics of phenol-formaldehyde resin by non-isothermal thermogravimetry. *Carbon*. 48(2), 352-358. https://doi.org/10.1016/j.carbon.2009.09.036.

[63] Wang, J., Jiang, H. & Jiang, N. (2009). Study on the pyrolysis of phenol-formaldehyde (PF) resin and modified PF resin. *Thermochimica Acta*. 496(1-2), 136-142. https://doi.org/10.1016/j.tca.2009.07.012.

[64] Grochowalski, A., Lassen, C., Holtzer, M., Sadowski, M. & Hudyma, T. (2007). Determination of PCDDs, PCDFs, PCBs and HCB emissions from the metallurgical sector in Poland. *Environmental Science and Pollution Research-International.* 14, 326-332. https://doi.org/10.1065/espr2006.05.303.

[65] Holtzer, M, Kmita, A. & Roczniak, A. (2014). New more friendly furfuryl resins. *Archives of Foundry Engineering*, 14(4SI), 47-50.

[66] Alonso, M.V., Oliet, M., Domínguez, J.C., Rojo, E. & Rodríguez, F. (2011). Thermal degradation of lignin-phenol-formaldehyde and phenol-formaldehyde resol resins: Structural changes, thermal stability, and kinetics. *Journal of Thermal Analysis and Calorimetry*. 105(1), 349-356. https://doi.org/10.1007/s10973-011-1405-0.

[67] Holtzer, M. (2015). *Influence of the addition of the reclaimed*

sand on the quality of castings and harmfulness of the new generation core and moulding sands. AKAPIT. (in Polish).

[68] Kubecki, M. (2016). *Determination of selected dangerous air pollutants, generated in the process of thermal decomposition of molding sands with furan resins.* AGH University of Science and Technology in Krakow. (in Polish).

[69] Major-Gabryś, K., Grabarczyk, A. & Dobosz, S.M. (2018). Modification of foundry binders by biodegradable material. *Archives of Foundry Engineering*. 18, 31-34. DOI: 10.24425/122498.

[70] Kmita, A. & Hutera, B. (2012). Effect of water glass modification on its viscosity and wettability of quartz grains. *Archives of Foundry Engineering*. 12(3). DOI: 10.2478/v10266-012-0082-1.

[71] Kmita, A. & Roczniak, A. (2017). Nanocomposites based on water glass matrix as a foundry binder: chosen physicochemical properties. *Archives of Foundry Engineering*. 17(1), 93-98. DOI: 10.1515/afe-2017-0017.

[72] Kmita, A., Drożyński, D., Roczniak, A., Gajewska, M., Marciszko, M., Górecki, K. & Baczmański, A. (2018). Adhesive hybrid nanocomposites for potential applications in moulding sands technology. *Composites. Part B, Engineering*. 146, 124-131. https://doi.org/10.1016/j.compositesb.2018.03.046.

[73] Kmita, A. & Hutera, B. (2013). Water glass modification and its impact on the mechanical properties of moulding sands. *Archives of Foundry Engineering*. 13(2), 81-84.

[74] Kusch, P., Knupp, G., Fink, W., Schroeder-Obst, D., Obst, V. & Steinhaus, J. (2014). Application of pyrolysis–gas chromatography–mass spectrometry for the identification of polymeric materials. *LCGC North America*. 32(3), 20-217.

[75] Chuang, W., Lei, P., Zhen-hai, S., Bing-liang, L & Ke-Zhi, L. (2019). Preparation, thermal stability and deflection of a density gradient thermally-conductive carbon foam material derived from phenolic resin. *Results in Physics.* 14, 102448, 1-12. https://doi.org/10.1016/j.rinp.2019.102448.

[76] Li, X.H., Meng, Y.Z., Zhu, Q. & Tjong, S.C. (2003). Thermal decomposition characteristics of poly(propylene carbonate) using TG/IR and Py-GC/MS techniques. *Polymer Degradation and Stability*. 81(1), 157-165. https://doi.org/10.1016/S0141-3910(03)00085-5.

[77] Sobera, M. & Hetper, J. (2003). Pyrolysis – gas chromatography – mass spectrometry of cured phenolic resins. *Journal of Chromatography A.* 993(1-2), 131-133. https://doi.org/10.1016/S0021-9673(03)00388-1.

[78] Chen, Y., Chen, Z., Xiao, S. & Liu, H. (2008). A novel thermal degradation mechanism of phenol-formaldehyde type resins. *Thermochimica Acta*. 476(1-2), 39-43. https://doi.org/10.1016/j.tca.2008.04.013.

[79] Testoni, F. & Frisina, G. (1990). Qualitative analysis of a commercially available phenol—formaldehyde resin, by static and dynamic headspace analysis using a mass-selective detector. *Journal of Chromatography A.* 509(1), 101-109. https://doi.org/10.1016/S0021-9673(01)93242-X.

[80] Phillips, O., Schwartz, J.M. & Kohl, P.A. (2016). Thermal decomposition of poly(propylene carbonate): end-capping, additives, and solvent effects. *Polymer Degradation and Stability.* 125, 129-139. https://doi.org/10.1016/j.polymdegradstab.2016.01.004.

[81] Lu, X.L., Zhu, Q. & Meng, Y.Z. (2005). Kinetic analysis of thermal decomposition of poly(propylene carbonate). *Polymer Degradation and Stability*. 89(2), 282-288. https://doi.org/10.1016/j.polymdegradstab.2004.12.025.

[82] Laino, T., Tuma, C., Moor, P., Martin, E., Stolz, S. & Curioni, A. (2012). Mechanisms of propylene glycol and triacetin pyrolysis. *The Journal of Physical Chemistry A*. 116(18), 4602-4609.

[83] Zhao, Y., Yan, N. & Feng, M.W. (2013). Thermal degradation characteristic of phenol – formaldehyde resins derived from betele infested pine barks. *Thermochimica Acta*. 555, 46-52. https://doi.org/10.1016/j.tca.2012.12.002.

[84] Wang, Yujue, Cannon, F.S., Salama, M., Goudzwaard, J. & Furness, J.C. (2007). Characterization of hydrocarbon emissions from green sand foundry core binders by analytical pyrolysis. *Environmental Science and Technology*, 41(22), 7922-7927.

[85] Wang, Y., Zhang, Y., Su, L., Li, X., Duan, L., Wang, C. & Huang, T. (2011). Hazardous air pollutant formation from pyrolysis of typical chinese casting materials. *Environmental Science & Technology.* 45(15), 6539-6544.

[86] Tiedje, N., Crepaz, R., Eggert, T. & Bey, N. (2010). Emission of organic compounds from mould and core binders used for casting iron, aluminium and bronze in sand moulds. *Journal of Environmental Science and Health Part A.* 45(14), 1866-1876. https://doi.org/10.1080/10934529.2010.520595.

[87] Strzemiecka, B., Zięba-Palus, J., Voelkel, T., Lachowicz, T. & Socha, E. (2016). Examination of the chemical changes in cured phenol-formaldehyde resines during storage. *Journal of Chromatography A.* 1441, 106-115. https://doi.org/10.1016/j.chroma.2016.02.051.

[88] Dungan, R.S. & Reeves, J.B. (2005). Pyrolysis of foundry sand resins: a determination of organic products by MS. *Journal of Environmental Science and Health.* 40, 1557-1567. https://doi.org/10.1081/ESE-200060630.

[89] Hunter, B. (2001). *Reference document on best available techniques in the ferrous metals processing industry.* Integrated Pollution Prevention and Control (IPPC).

[90] Bats, C. E. & Scott, W.D. (1977). Decomposition of resin binders and the relationship between the gases formed and the casting surface quality. *AFS Transactions*. 85(3), 209–226.

[91] Matsushita, T., Sundaram, D., Belov, I. & Dioszegi, A. (2024). Kinetic model for the decomposition rate of the binder in a foundry sand application. *Archives of Foundry Engineering*. 24(3), 43-49. https://doi.org/10.24425/afe.2024.151289.

[92] European Commission. (2015). *Best Available Techniques (BAT) Reference Document for the Propuction of pulp, paper and board. Industrial Emission Directive 2010/75/EU (Intergated Pollution Prevention and Control).* https://doi.org/10.2791/370629.

[93] Huang, R., Zhang, B. & Tang, Y. (2016). Application conditions for ester cured alkaline phenolic resin sand. *China Foundry.* 13(4), 231-237. https://doi.org/10.1007/s41230-016-6022-x.

[94] Kmita, A., Drozyński, D., Mocek, J., Roczniak, A., Zych, J.

& Holtzer, M. (2016). Gas evolution rates of graphite protective coatings in dependence on the applied solvent and kind of atmosphere. *Archives of Metallurgy and Materials*. 61(4), 2129-2134. DOI: 10.1515/amm-2016-0284.

[95] Sobczak, J. (2013). *Founder's Guide.* Wydawnictwo Stowarzyszenia Technicznego Odlewników Polskich. (in Polish).

[96] Dańko, J., Dańko, R., Łucarz, M. (2007). *Processes and devices for reclamation of used moulding sands.* Akapit.

[97] Roczniak, A., Kmita, A. (2017). Thermosetting polymers used in foundry to bond the mineral matrix and their impact on the environment. In Z. Czyż & K. Maciąg (Eds.), *Current technologies of material technology.* Wydawnictwo Naukowe TYGIEL. (in Polish).

[98] Roczniak, A., Holtzer, M. & Kmita, A. (2018). Research of emission of commercial binders used in ALPHASET technology - Estimated quantitative analysis. *Archives of Foundry Engineering*. 18(1), 109-114. DOI: 10.24425/118821.

[99] Chen, Z.Q., Chen, Y.F. & Liu, H.B. (2013). Pyrolysis of phenolic resin by TG-MS and FTIR analysis. *Advanced Materials Research*. 631-632, 104-109. https://doi.org/10.4028/www.scientific.net/AMR.631-632.104.

[100] Yu, Z.L, Gao, Y.C., Qin, B, Ma, Z.Y. & Yu, S.H (2024). Revitalizing traditional phenolic resin toward a versatile platform for advanced materials. *Accounts of Materials Research.* 5(2), 146-159.

[101] Liang, B., Wang, J., Hu, J., Li, C., Li, R., Liu, Y., Zeng, K., & Yang, G. (2019). TG-MS-FTIR study on pyrolysis behavior of phthalonitrile resin. *Polymer Degradation and Stability*. 169, 108954, 1-8. https://doi.org/10.1016/j.polymdegradstab.2019.108954.

[102] Giese, S.R, Roorda, S.C. & Patersson, M.A. (2009). Thermal analysis of phenolic urethane binder and correlation properties. *American Foundry Society Transactions*. 117, 355-366.

[103] Otero, M., Díez, C., Calvo, L.F., García, A.I. & Morán, A. (2002). Analysis of the co-combustion of sewage sludge and coal by TG-MS. *Biomass and Bioenergy*. 22(4), 319-329. https://doi.org/10.1016/S0961-9534(02)00012-0.

[104] Wang, Y.X., Wang, C.G., Wu, J.W. & Jing, M. (2007). High-temperature DSC study of polyacrylonitrile precursors during their conversion to carbon fibers. *Journal of Applied Polymer Science*. 106(3), 1787-1792. https://doi.org/10.1002/app.26862.

[105] Wang, S., Xing, X., Wang, Y., Wang, W. & Jing, X. (2017). Influence of poly (dihydroxybiphenyl borate) on the curing behaviour and thermal pyrolysis mechanism of phenolic resin. *Polymer Degradation and Stability*. 144, 378-391. https://doi.org/10.1016/j.polymdegradstab.2017.08.034.

[106] Shuttleworth, P.S., Budarin, V., White, R.J., V.M., G., Luque, R. & Clark, J.H. (2013). Molecural- level understanding of the carbonization of polysaccharides. *Chemistry – A European Journal*. 19, 9351-9357. https://doi.org/10.1002/chem.201300825.

[107] Kissinger, H.E. (1957). Reaction kinetics in differential thermal analysis. *Analytical Chemistry*. 29(11), 1702-1706. https://doi.org/10.1021/ac60131a045.

[108] Akahira, T. & Sunose, T. (1971). Joint Convention of Four Electtical Institutes. Research *Reports of Chiba Institute of Technology.* 16, 22-31.