



ARCHIVES of FOUNDRY ENGINEERING

 ISSN (2299-2944)
 Volume 2020
 Issue 1/2020

31 – 36

10.24425/afe.2020.131279

6/1



Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Influence of the Atmosphere on the Type of Evolved Gases from Phenolic Binders

S. Żymankowska-Kumon *, K. Kaczmarek, B. Grabowska, A. Bobrowski, S. Cukrowicz

 AGH University of Science and Technology, Faculty of Foundry Engineering,
 Reymonta 23, 30-059 Kraków, Poland

* Corresponding author. E-mail address: szk@agh.edu.pl

Received 28.06.2019; accepted in revised form 10.09.2019

Abstract

The problem of harmful casting resins has been present in foundries for many years. Manufacturers are introducing new products that contain in their composition environmentally and eco-friendly ingredients. Unfortunately, not all types of technology can be used, sometimes environmental benefits are disproportionate to the quality of castings and their price. In the foundry industry, the most popular binders are based on organic compounds (often carcinogenic) and other harmful substances. Due to strict legal regulations regarding environmental protection, as well as care for the foundry's workers' comfort - their occurrence should be reduced to a minimum. These compounds often behave also depending on the conditions of use (temperature, atmosphere). The application of various methods of thermal analysis and spectroscopic methods allows to verify the mechanism of resin decomposition process in relation to conditions in the form in both inert and oxidizing atmosphere. For analysis the resins from cold-box technology, were used TG-DTG-DSC, Py-GC/MS methods and specified the course of changes occurring in combination of different atmosphere.

Keywords: Environment protection, Resin, Emission, Atmosphere, Thermal analysis

1. Introduction

The atmosphere of the furnace is a gas environment in the furnace working space. It describes the chemical composition, temperature and pressure. The atmosphere of the furnace may be inert or technological (active atmosphere), causing changes in the charge predicted by the technological process - usually gas carburizing, cyanating, reducing [1, 2]:

- a reducing atmosphere is said to contain reducers (e.g. H₂, CO), usually for the purpose of reducing oxides to pure metals;
- oxidizing atmosphere is one in which oxidants (e.g. O₂, CO₂) are contained;
- diffusion atmosphere - used to obtain changes in the heated material by diffusion;

- protective atmosphere - protecting the batch from undesirable changes [3-8].

In some cases, the furnace gas environment is inadvisable, e.g. a vacuum furnace. Controlled atmosphere is an artificially created gas environment with self-regulated chemical composition.

The temperature at which the decomposition of compounds begins is a measure of the thermal stability of chemical compounds. The temperature of the beginning of the decomposition depends on the assumed property, which changes at the moment the distribution begins and the measurement conditions - in particular the heating rate of the sample. Sometimes thermal stability tests are conducted under isothermal conditions and then the measure of thermal stability is the time after which the beginning of the sample distribution is observed. Thermal stability tests are carried out in the atmosphere [6, 9-14]:

- inert: N₂, Ar, He;
- oxidizing: O₂, O₂ + 4N₂ (air);

- other gases, e.g. CO₂.

The atmosphere often has a significant impact on the distribution of the substances tested. The oxygen-containing atmosphere often facilitates the decomposition of organic compounds, since it can act as an initiator of free radical reactions. Decomposition can take place with the participation of oxygen contained in the atmosphere of the furnace – with the participation of oxidation reactions [15, 16].

The aim of this work was the influence of atmosphere on the emission of harmful substances from phenolic resin used in cold-box technology (older generations (III) and new (IV) - with silicate modifier). For many years, the assessment of the harmfulness of foundry resins has been the subject of research in Faculty of Foundry Engineering in AGH University of Science and Technology in Cracow [2, 14, 15].

2. Tested materials

The research were conducted phenolic resins used in cold-box technology, mainly to cores production. Resin R1 (reduction of the level of free phenol) is synthetic phenolic resin dissolved in plant solvents and resin R2 is the same synthetic phenolic resin but dissolved in an anhydride based on alkyl orthosilicate (use of silicate-based solvents with the goal of reducing odour emissions, smoking and condensate deposits after pour off). Table 1 presented short characteristic of the tested materials.

Table 1.

Characteristic of the tested resins

Parameters	Resin R1	Resin R2
Density (20°C)	1.111 g/cm ³	1.115 g/cm ³
Viscosity (20°C)	0.60-0.70 Pa·s	0.13-0.16 Pa·s
Harmful substances	Phenol Aromatic hydrocarbons	Phenol Aromatic hydrocarbons Ethyl silicate

3. Research methodology

The aim of research was to check how atmosphere (inert or oxidizing) influence on the emission of harmful substances (especial hydrocarbons) from phenolic binders used in cold-box technology. The article obtained three type of research (adequate to determination the kind of evolved gases, especial Py-GC/MS method, and parameters of decomposition process of samples - TG/DTG/DSC analysis):

- kinetics of evolved gases (Czylok tube furnace with peristaltic pump) – to check gas volume and gas evolution rate in different atmospheres (oxidizing-air and inert-argon), from 25 to 1150°C, gas flow of 3 dm³/h for 3 minutes. The results were recorded using a peristaltic pump at a rate of every 2 seconds for a period of 5 minutes (possibly if the time was longer - until a constant gas volume was established). Additionally, a capsule with an adsorbent in the form of activated carbon was connected to the system to absorb gases (mainly hydrocarbons). The sample size is 1 g.

The amount of activated carbon used for the study: 350 mg (main layer); 100 mg (control / safety layer);

- SDT Q600 (TA Instruments) differential scanning calorimeter was used for simultaneous evaluation of the mass change and transformation energetics in the function of increasing temperature. The measurement was started at a temperature range of 25 to 1150°C, at a rate of 20°C/min in the neutral (argon) and oxidizing atmosphere with a flow of 100 ml/min. The measurements were made in sintered Al₂O₃ sample pans with a capacity of 70 microliters. The control and tested sample was heated at the same rate, ensuring that the temperatures of both samples were identical throughout the entire measurement cycle;
- ISQ single quadrupole GC-MS (Thermo Scientific) chromatographic analysis by pyrolysis (CDS Analytical) gas chromatography mass spectrometry (Py-GC/MS) method – to check the impact of different atmosphere to quality of emission of evolved gases (mainly aromatic hydrocarbons and phenol), identification of gases products from extracts (samples absorbed on active carbon from kinetics research). A temperature program of gas chromatograph was applied: an initial temperature of 40°C was held for 3 min; ramped 3°C/min up to 100°C and held for 3 min, and then 250°C with heating rate 20°C/min was maintained for 3 min. Helium carrier gas at 1 ml/min, sample split ratio 1:20. The separated compounds are analysed in a mass spectrometer “MS” in the full range m/z. Electron ionisation (70 eV) at a temperature of 250°C was applied. The gas products were identified based on the own pattern and mass spectral library NIST MS Search 2.0 Libera (Chem. SW, Version 2.0, Fairfield, CA, USA) [14, 15].

4. Results and discussion

Kinetics of evolved gases

The curves of kinetics of evolved gases are presented on Fig. 1 and 2. Additional data is shown in Table 2. Curves were recorded in the temperature range of 25-1150°C, in the air and argon atmosphere. Gases were absorbed on active carbon capsules.

Table 2.

Results of gases emission

Sample	Gases emission from the tested resins					
	Gas volume, ml/g		Maximum gas evolution rate (dV/dt), ml/g·s		Time of maximum gas evolution rate, s	
	Air	Ar	Air	Ar	Air	Ar
R1	174	378	1,4	2,2	40	15
R2	248	418	2,2	2,4	45	10

Depending on atmosphere of process the kinetics curves are different. The smallest volume (approx. 174 ml) were recorded for resin R1 in air atmosphere (Fig. 1). Gas evolution rate was the

most intense for resin R2 in argon atmosphere (the maximum attained in the first ten seconds the process, Fig. 2, table 2).

The biggest volume of gases (approx. 418 ml) was recorded for resin R2 (Fig. 1) in argon atmosphere (the process was also the most intense). Generally, the inert (argon) atmosphere has influence on intensity of process (acceleration) and gases volume (growth). In oxidizing (air) atmosphere the process was slower (about 4 times). Two or more maxima of emission rates were seen in the curves describing the kinetics of gases emissions (area between 0-150 s, Fig. 2).

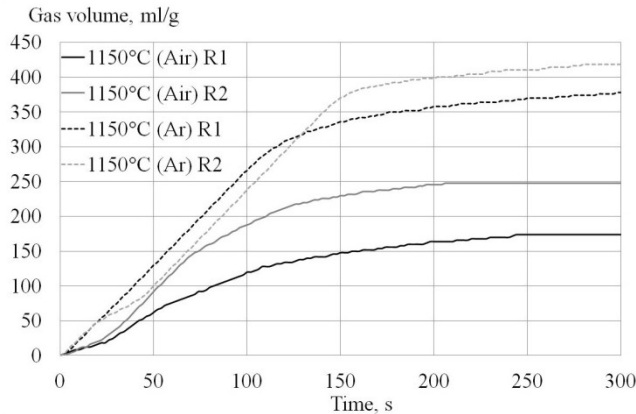


Fig. 1. Emissivity of gases in dependence on time and atmosphere from the tested samples of resins

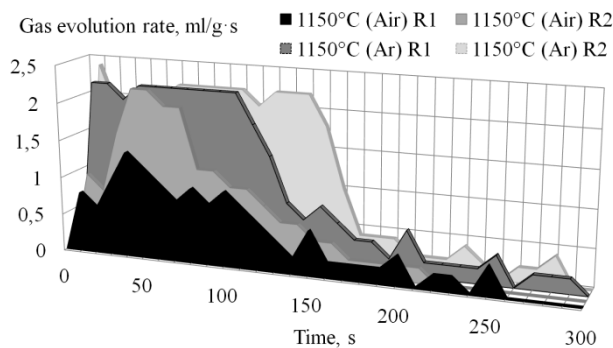


Fig. 2. Gas evolution rate from the tested samples of resins

Thermal analysis

On the basis of TG-DTG and DSC curves the following parameters characterizing the decomposition process were determined: weight losses (Δm), temperature of the maximum of weight loss rate (T_{peak}), temperature corresponding to 10% (T_{10}) and 50% (T_{50}) weight loss, temperature of exo- or endothermic effects occurring. On the course of thermal curves it is possible to determine the subsequent stages of degradation of the resins. The changes in the material due to the rising temperature and influence of the atmosphere for tested samples are presented on Fig. 3-6 and tables 3, 4.

In an inert atmosphere the resin R1 is decomposed with two-stage weight loss. The first weight loss within the temperature range 25-224°C is 47.27% with maximum rate of change in

temperature 115 and 156°C (Fig. 3). In this temperature range two endothermic and one exothermic effects were recorded at 58, 120 and 218°C. The second loss of 16.73% was attributed to irreversible degradation of the resin. In the range of temperature 224-1100°C were observed: two exothermic effects at 352°C and 811°C (Tab. 3). Sample of resin in an inert atmosphere was not completely decomposed and its residual mass determined at 1100°C was 36%. At 1100°C, the residual mass of sample probably contained carbonized carbon or heavy plasticizers (decomposed in temperature higher than 1200°C).

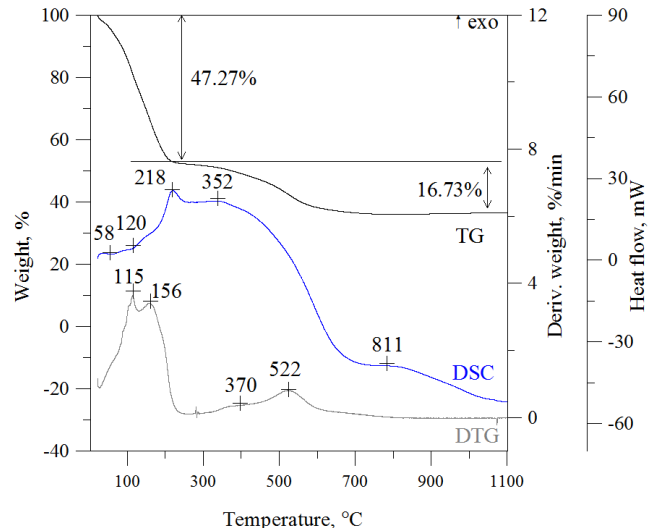


Fig. 3. TG-DTG-DSC curves of resin R1 under an inert atmosphere

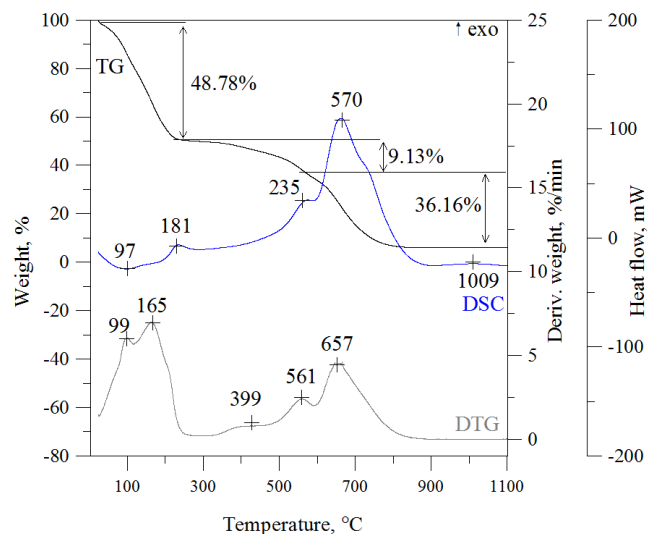


Fig. 4. TG-DTG-DSC curves of resin R1 under an oxidizing atmosphere

Under the presence of the oxygen (synthetic air atmosphere), the decomposition of the resin R1 takes place with a three-stage weight loss (Fig. 4): 48.78% in the range 25-223°C ($T_{peak} = 99$ and 165°C), 9.13% in the range 223-519°C ($T_{peak} = 399$ °C) and

36.16% in the range 519-1100°C ($T_{peak} = 561$ and 657°C). At 1100°C the sample is not completely degraded and the sample residue was 7.30%. The residual mass of the sample is probably still formed by small amount of carbonized carbon and plasticizers.

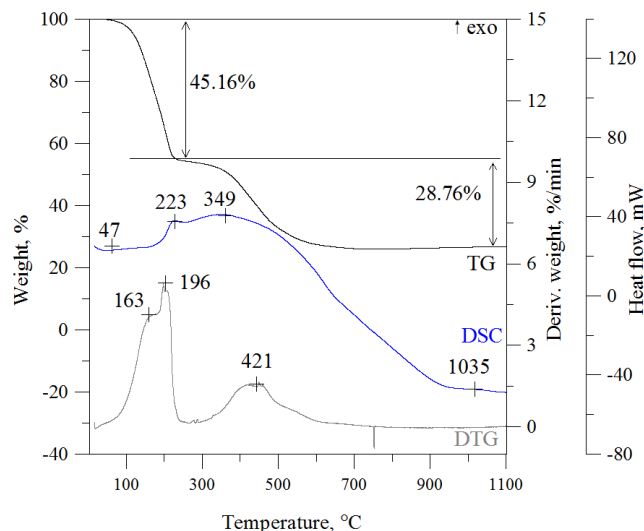


Fig. 5. TG-DTG-DSC curves of resin R2 under an inert atmosphere

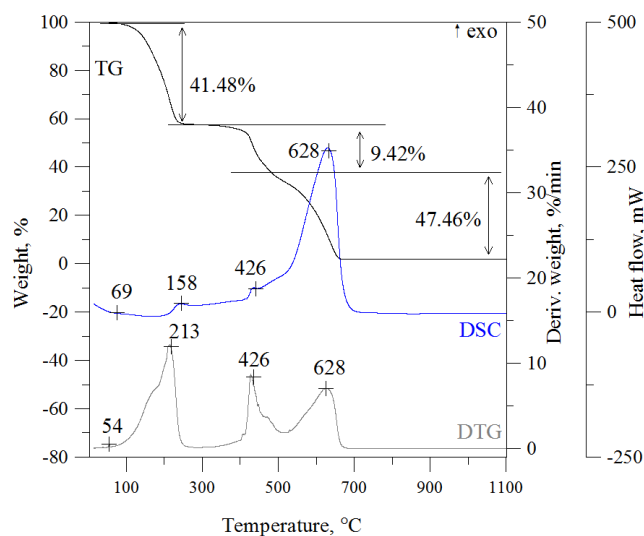


Fig. 6. TG-DTG-DSC curves of resin R2 under an oxidizing atmosphere

In an inert atmosphere the resin R2 is decomposed with two-stage weight loss (similar like resin R1). The first weight loss within the temperature range 25-231°C is 45.16% with maximum rate of change in temperature 163 and 196°C (Fig. 5). In this temperature range one endothermic and one exothermic effects were recorded at 47 and 223°C. The second loss of 28.76% was attributed to irreversible degradation of the resin. In the range of temperature 231-1100°C were observed: two exothermic effects at 349°C and 1035°C (Tab. 4). Sample of resin in an inert

atmosphere was not completely decomposed and its residual mass determined at 1100°C was 26.08%. At 1100°C, the residual mass of sample probably contained carbonized carbon or silicate modifier.

Table 3.

Thermal data selected from the TG-DTG-DSC analysis for resin R1

Atm. Stage	Range of temp., °C	Δm , %	T_{peak} , °C	Thermal effect peak, °C	T_{10} , °C	T_{50} , °C
inert	I	25-224	47,27	115 156	58/endo 120/endo 218/exo	84 361
	II	224-1100	16,73	370 522	352/exo 811/exo	
Residual mass: 36.00% (at 1100°C)						
oxidizing	I	25-223	48,78	99 165	97/endo 181/endo	85 265
	II	223-519	9,13	399	235/exo	
	III	519-1100	36,16	561 657	570/exo 1009/exo	
Residual mass: 7.30% (at 1100°C)						

Under the presence of the oxygen, the decomposition of the resin R2 takes place with, also like resin R1, a three-stage weight loss (Fig. 6): 41.48% in the range 25-237°C ($T_{peak} = 54$ °C), 9.42% in the range 237-434°C ($T_{peak} = 213$ and 426°C) and 47.46% in the range 434-1100°C ($T_{peak} = 628$ °C). At 1100°C the sample is completely degraded and the sample residue was 1.64%. The residual mass of the sample is probably formed by small amount of silicate modifier.

Table 4.

Thermal data selected from the TG-DTG-DSC analysis for resin R2

Atm. Stage	Range of temp., °C	Δm , %	T_{peak} , °C	Thermal effect peak, °C	T_{10} , °C	T_{50} , °C
inert	I	25-231	45.16	163 196	47/endo 223/exo	139 369
	II	231-1100	28.76	421	349/exo 1035/exo	
Residual mass: 26.08% (at 1100°C)						
oxidizing	I	25-237	41.48	54	69/endo 158/endo	157 430
	II	237-434	9.42	213 426	241/exo 426/exo	
	III	434-1100	47.46	628	628/exo	
Residual mass: 1.64% (at 1100°C)						

To evaluate and compare the thermal behavior of tested resins in different condition, the parameters T_{10} and T_{50} were considered. Analyzing these characteristic temperature of weight losses by

thermal decomposition, it can be affirmed that the resin R2 has higher thermal stability in both types of atmosphere to the ~370-430°C.

Identification of gases by gas chromatograph-mass spectrometry method

The chromatograms for resins R1 and R2 are given in Fig. 7. Attention was focused to the emission of gases in two different atmospheres (especial aromatic hydrocarbons and phenol). The list of obtained compounds was shown in Tables 5.

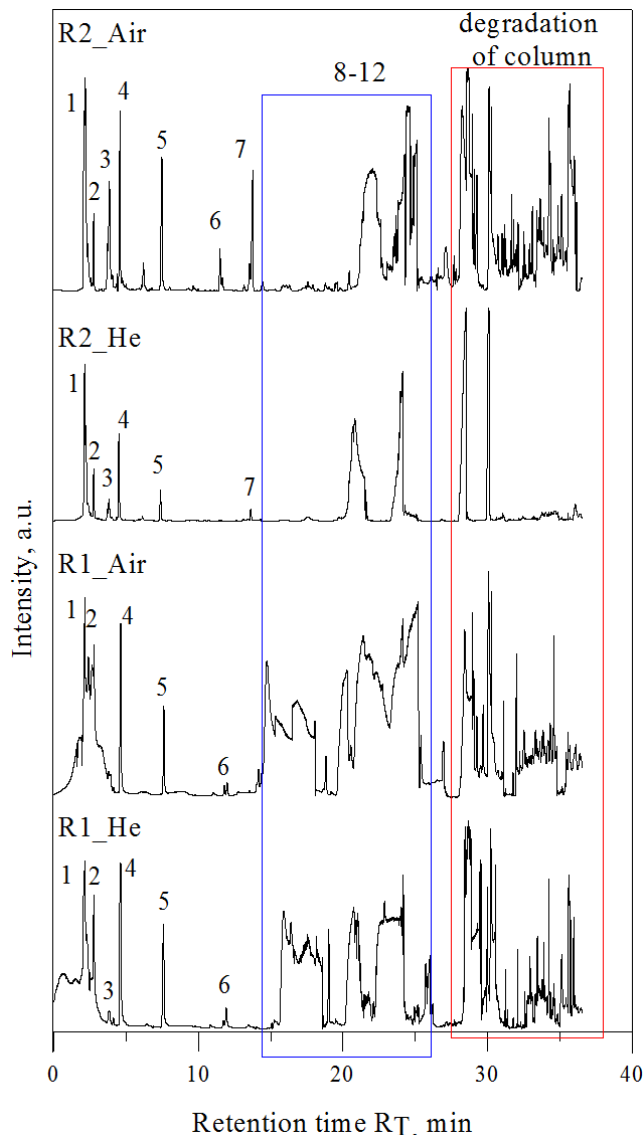


Fig. 7. Chromatograms for resins R1 and R2 depending on the atmosphere (temperature 1150°C)

Carbon dioxide, thermal degradation products of plant solvents (resin R1) and phenol (both resins) were found. For resin R2 (Fig. 7, table 5) in oxidize atmosphere recorded more products of thermal degradation (a lot of signals). Benzene, toluene and

simple hydrocarbons were found in the products of both resins. In inert atmosphere the signals were less intense (both resins).

For the resin R1 the chromatograms have much more signals than for resin R2. The characteristic area for resin R1 within a retention time (R_T) range of about 15-27 min includes a number of signals that derived from the decomposition of plant solvents and phenol. As the changing atmosphere (from inert to oxidize), these compounds will be more pronounced and intense in the chromatograms. The number of signals from simple hydrocarbons is also increasing. Chromatogram for the resin R2 has much less signals than for R1 (Fig. 7, table 5). In the products of thermal degradation were identified some hydrocarbons (benzene, toluene, ethylbenzene), phenol and its derivatives (e.g. m-cresol) [15].

Table 5.

Results of the qualitative analysis of Py-GC/MS research

	No.	Compound	Retention time R_T , min	
			Air	He
R1	1	Carbon dioxide	2,25	2,28
	2	1,3-Cyclopentadiene	2,83 ^a	2,85
	3	1,4-Pentadiene	n.a.	4,24
	4	Benzene	4,58	4,62
	5	Toluene	7,24	7,29
	6	Ethylbenzene	12,34	12,38
	7	Benzene, 1-etyl-2-metyl	n.a.	n.a.
	8	Phenol	15,02	15,21
	9	m-Cresol	16,22	16,25
	10	p-Cresol	17,18	17,29
	11	thermal degradation products of plant solvents and phenol	15-27	
	12	2,3-Xylenol	24,81	n.a.
R2	No.	Compound	Retention time R_T , min	
			Air	He
	1	Carbon dioxide	2,21	2,24
	2	1,3-Cyclopentadiene	2,83	2,81
	3	1,4-Pentadiene	4,12	4,14
	4	Benzene	4,57	4,59
	5	Toluene	7,21	7,25
	6	Ethylbenzene	12,14	n.a.
	7	Benzene, 1-etyl-2-metyl	14,12	14,18
	8	Phenol	15,12	15,15
	9-12	thermal degradation products of phenol	15-27 ^b	

^a more products in the close area

^b less products in the close area

5. Conclusions

Based on the obtained results, the following conclusions can be drawn:

- the emission of gases is dependent on the atmosphere, it grows in an inert atmosphere, as well as the intensity of the process;
- the thermal analysis of tested resins allows the indicate of characteristic temperature points accompanied by a loss of weight. It was probably related to the loss of solvent (main component of resin), the next one to the decomposition of C-H bonds and phenol, in addition, the change in the atmosphere (from neutral to oxidising) increases the multistage character of the degradation process; the degradation of the tested samples, regardless of the applied decomposition conditions, is complex and multistage;
- the Py-GC/MS analysis showed that there are less compounds in an inert atmosphere than in an oxidizing one, also silicate modifier (R2) reduces emission of some hydrocarbons and products of phenol.

The research allowed to determine the type of gases emitted from the tested samples, mainly due to the use of gas chromatography. Knowledge about the thermal stability of both resins obtained from the studies and influence on the atmosphere has allowed to identify the course of resin degradation in the context of its safe to the environment and work condition in foundries.

Acknowledgements

The work was supported by the subsidy for research No. 16.16.170.654 (Ministry of Science and Higher Education).

References

- [1] Li, C. et al.(2016). Silicone-modified phenolic resin: Relationships between molecular structure and curing behavior. *Thermochimica Acta*. 639, 53-65. DOI: 10.1016/j.tca.2016.07.011.
- [2] Żymankowska-Kumon, S. & Kolczyk, J. (2016). Chromatographic analysis of selected products of thermal decomposition of core sands made in cold-box technology. *Transactions of the Foundry Research Institute*. 16(4), 369-378. DOI: 10.7356/ioid.2016.25.
- [3] Reduction of foundry odor emissions by use of new generations of organic binders, materials from Hüttenes-Albertus.
- [4] Fabbri, D. & Vassura, I. (2006). Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials by analytical pyrolysis. *Journal of Analysis and Applied Pyrolysis*. 75, 150-158. DOI: 10.1016/j.jaap.2005.05.003.
- [5] Fox, J.R., Adamovits, M. & Henry, C. (2002). Strategies for Reducing Foundry Emissions. *AFS Transactions*. 110, 1299-1309.
- [6] Fang, S. et al. (2015). Preparation and curing behavior of silicone-modified phenolic resin. *Applied Mechanics and Materials*. 713-715, 2798-2803. DOI: 10.4028/www.scientific.net/AMM.713-715.2798.
- [7] Nason, H.K. (1939). Silicon modified phenolic resins and process for producing same. Patent US 2182208 A.
- [8] Ahamad, T. & Alshehri, S.M. (2014). Thermal degradation and evolved gas analysis: A polymeric blend of urea formaldehyde (UF) and epoxy (DGEBA) resin. *Arabian Journal of Chemistry*. 7, 1140-1147. DOI: 10.1016/j.arabjc.2013.04.013.
- [9] Jiang, H. & Wang, J. et al. (2012). The pyrolysis mechanism of phenol formaldehyde resin. *Polymer Degradation and Stability*. 97(8), 1527-1533. DOI: 10.1016/j.polyimdegradstab.2012.04.016.
- [10] Poljanšek, I., Šebenik, U. & Krajnc, M. (2006). Characterization of phenol-urea-formaldehyde resin by inline FTIR Spectroscopy. *Journal of Applied Polymer Science*. 99, 2016-2028. DOI: 10.1002/app.22161.
- [11] Zhao, Y., Yan, N. & Feng, M.W. (2013). Thermal degradation characteristic of phenol-formaldehyde resins derived from beetle infested pine barks. *Thermochimica Acta*. 555, 46-52. DOI: 10.1016/j.tca.2012.12.002.
- [12] Jiang, D. et al. (2009). Simulating the initial stage of phenolic resin carbonization via the reaxff reactive force field. *J. Phys. Chem. A* 113(25), 6891-6894. DOI: 10.1021/jp902986u.
- [13] Alonso, M.V. et al. (2011). Thermal degradation of lignin-phenol-formaldehyde and phenol-formaldehyde resol resins. *Journal of Thermal Analysis and Calorimetry*. 105(1), 349-356. DOI: 10.1007/s10973-011-1405-0.
- [14] Grabowska, B., Kaczmarska, K., Bobrowski, A., Żymankowska-Kumon, S. & Kurleto-Kozioł, Ż. (2017). TG-DTG-DSC, FTIR, DRIFT, and Py-GC-MS Studies of Thermal Decomposition for Poly(sodium acrylate)/Dextrin (PAANa/D) – New Binder BioCo3. *Journal of Casting & Materials Engineering*. 1(1), 27-32. DOI: 10.7494/jcme.2017.1.1.27.
- [15] Żymankowska-Kumon, S., Bobrowski, A., Drożyński, D., Grabowska, B. & Kaczmarska, K. (2018). Effect of Silicate Modifier on the Emission of Harmful Compounds from Phenolic Resin used in Cold-Box Technology. *Archives of Foundry Engineering*. 18(1), 151-156.
- [16] Dungan, R., Reeves III, J. (2005). Pyrolysis of Foundry Sand Resins: A Determination of Organic Products by Mass Spectrometry. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*. 40, 1557-1567. DOI: 10.1081/ESE-200060630.