



The gas evolution of a modified cellulose mixture used for gating systems in the no-bake mould process

Zbigniew Zawieja¹ · Jacek Sawicki¹

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Abstract

This paper shows the results of a study of gas evolution from a patented modified cellulose mix used in the production of no-bake casting moulds. The modified cellulose mixture was used for investigation with additives such as expanded perlite, expanded vermiculite and microspheres. The binder was an inorganic resin based on commercial technology, called Geopol. Samples were tested in different compositions in order to show the influence of all the additives mentioned. Two different methods were used—one was based on TG–TDG–MS investigation and the other was based on pyrolysis combined with a gas composition analyser. Investigations of both methods were carried out at temperatures up to 900 °C. The results showed that the gas emissions during thermal degradation of all the modified mixtures did not constitute substances that are hazardous or dangerous to health. Therefore, the material proposed can be used as a solution that is more environmentally friendly when compared to formulas which exist on the market and are abundant in harmful compounds.

Keywords Cellulose mix · Gas emissivity · Gating system · TG–DTG · Pyrolysis

Introduction

The worldwide tendency to reduce gas or exhaust gas emissions in high-temperature processes also applies to the materials employed in metal and metal alloy cast production processes [1, 2]. The gases and chemical compounds released from moulding compounds, coremaking compounds, gating systems and other auxiliary materials may lead to the appearance of problematic surface defects in casting [3–5]. They are also very often very hazardous to human life and health [1, 2]. The tendency to reduce the emission of gaseous compounds during the casting process is therefore an obvious phenomenon and leads to seeking innovative moulding materials [6].

So far, pipe fittings and circular section fittings have been used in gating systems in foundry made from ceramic- or cellulose-based mixture with microspheres called also aluminosilicates with urea–melamine–formaldehyde organic binder. Ceramic moulds are the most common choice when

it comes to the creation of gating systems for large and medium castings. In spite of having certain advantages, they unfortunately pollute the moulding compound and are very difficult to machine. The alternative solution available on the commercial market is a material based on cellulose [7] that solves the mechanical processing problem while providing similar thermal insulation. Unfortunately, it contains organic binders that are a source of very strong gas-forming effects taking place during high-temperature thermal treatment [8–11].

The paper presents the challenge of developing an innovative mixture, patented by the authors [6], that would meet the requirements for mouldings and profiles used for gating systems in the technology of no-bake sand moulds with a resin binder. This novel cellulose-based mixture was modified with natural additives, such as expanded vermiculite [12–17], expanded perlite [18–20] and microspheres [21–23]; inorganic resins were used as a binder [1, 24]. Expanded perlite and vermiculite have very interesting physicochemical properties, such as: large absorption capacity for liquids, low bulk density, high thermal resistance of a neutral chemical nature and negligible chemical reactivity. The addition of microspheres whose thermal insulating power is similar to that of previous additives, enhances the thermal insulating power of the mixture to certain

✉ Jacek Sawicki
jacek.sawicki@p.lodz.pl

¹ Institute of Materials Science and Engineering, Lodz University of Technology, Stefanowskiego 1/15 Street, 90-924 Lodz, Poland

temperature levels, when the microspheres decompose, which generates a strong exothermic effect [10, 23]. The samples under analysis contained an organic geopolymer binder, whose interesting properties have made the authors use the material as an alternative to other organic binders used in hazardous cellulose-based mixtures [25].

This article presents studies on a qualitative analysis of the gases produced per mass unit at a temperature of up to 900 °C from the materials used for gating systems in single-use sand moulds. Various materials were tested—all characterised by an original patented composition [6], made of paper pulp originating from waste paper and mineral additions which could be used for producing moulds for gating systems [10, 11]. In the original samples, expanded vermiculite, microspheres and expanded perlite were employed as composition modifiers in view of their interesting chemical and physical properties such as thermal resistance, specific gravity, water absorbency and resistance to fire. The author's composition of materials was compared to the currently used commercial material based on cellulose in gating systems [7]. The characteristics of the mix modified in such a manner allow considering such a novel material as a short-term, single-use thermal barrier for contact with liquid metal.

Experimental materials and methods

Eight varieties of cellulose mix with various compositions [6] and one reference mix referred to as “commercial”, which comes from a ready-made mould—available in the industry [7]—were used for gas emission studies. The mix compositions consisted of EP-150 expanded perlite with a granulation of 40–90 kg m⁻³, type FINE expanded vermiculite with a granulation of 100–130 kg m⁻³, F150 microspheres with a grain size of 50–150 µm, and paper pulp made of EKOFIBER waste paper. The base paper pulp was made by mixing 250 g of water at 80 °C with 20 g of paper pulp. The paper pulp obtained in this manner was modified by adding expanded perlite, expanded vermiculite and microspheres. The amount of binder in the form of aluminium silicate resin constituted 32.4% of the sample mass. After thorough mixing, reference samples were produced and were then dried in order to evaporate the water in a lab-dryer at a temperature of 130 °C for 90 min. Table 1 presents the composition of the samples produced. The logic behind choosing samples shown in Table 1 was to have examination of samples having the highest content of ingredient materials used for basic cellulose modification. In this case, it was predicted to have most visible effects on curves while making thermal degradation of samples. Due to very low density of expanded vermiculite and expanded perlite, it has been decided to have maximum 4% mass addition of each ingredient, also microspheres to be equal. It was practically

Table 1 Composition of own samples (mass%)

Sample number	Paper pulp	Exp. perlite	Exp. vermiculite	Microspheres	Binder
3	56	4	0	15	25
12	71	4	0	0	25
15	60	0	0	15	25
56	67	4	4	0	25
59	52	4	4	15	25
60	71	0	4	0	25
63	56	0	4	15	25
Pulp + resin	75	0	0	0	25

not possible to prepare samples with more than 4% mass addition of each ingredient.

TG–DTG tests

Thermogravimetric tests were carried out in the Coal Chemical Processing Institute from Zabrze using a Luxx 409 PG analyser from a company called *Netzsch*, coupled with a QMS 403D Aëolos mass spectrometer, also from *Netzsch*. Because of the low mass of the sample tested (about 10 mg), the samples provided were crushed and then mixed in a mortar in order to average their composition. The tests were carried out at a temperature range of 40–900 °C with a constant heating rate of 10 °C min⁻¹ in an atmosphere of flowing inert gas (argon, 25 cm³ min⁻¹). Mass spectrometer range test was from 1 to 80 amu with scan speed of 160 amu s⁻¹.

Testing by means of fixed bed pyrolysis

Within the framework of this paper, a pyrolysis process was carried out for samples (25–35 g) in a laboratory setup intended for examining fixed-bed pyrolysis processes, installed in the Coal Chemical Treatment Institute in Zabrze. A simplified diagram of that setup is presented in Fig. 1.

The setup includes a retort (1) that can hold, at a single time, a batch with a mass of 150 g or with volume of about 600 cm³ and operating under atmospheric pressure. The maximum temperature of processes carried out in the retort is 1100 °C. The retort is placed in a two-zone furnace (2), which enables conducting processes at a maximum heating rate of up to 20 °C min⁻¹. Volatile products pass through the cooling and condensation system of the liquid product (3).

All products pass through a mobile SICK ‘on-line’ process gas composition analyser, enabling the measurement of CO₂, CO, CH₄, H₂ and O₂ levels (4).

The process of pyrolysis of the samples examined was carried out in the presence of a flowing inert gas—nitrogen. According to the experiment plan assumed, all of the

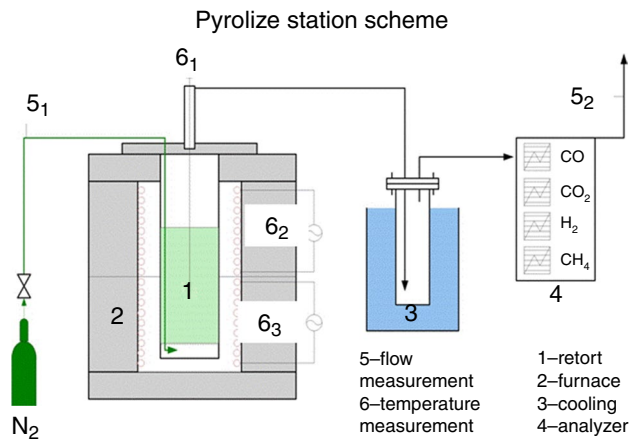


Fig. 1 Pyrolysis station scheme developed by Coal Chemical Treatment Institute in Zabrze

samples tested were heated in an atmosphere of flowing nitrogen at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to a temperature of $900\text{ }^{\circ}\text{C}$ and were then kept in this temperature for 30 min. The process gas leaving the retort was cooled in a scrubber immersed in an ice bath in order to condense water and heavy hydrocarbons, and it was then directed through a tube filled with quartz wool to a SICK MAIHAK S710 gas composition analyser (4). After the gas composition analyser, the post-process gas was directed to the flue through a flow analyser. Carried pyrolysis process due its idea is simultaneously done with gas volume emission measurements.

The crushed and weighted sample of the material examined was placed in a retort (1) and connected to the process line gas and a nitrogen cylinder. After flushing the retort

with nitrogen, its flow was set to a value of about $100\text{ cm}^3\text{ min}^{-1}$. After the gas analyser indications stabilised, the furnace heating and process parameter recording were activated. After the process finished and the retort cooled down, the solid remains (after pyrolysis) were weighed and the mass of the condensed (liquefied) ingredients was determined.

Results

Results of TG–DTG tests

Figures 2–4 present example TG–DTG curves together with ion current curves of gas products emitted during analyses, for the sample with the composition no. 59. On the curves, the final mass values for samples, expressed in mass percentage (mass%), are specified. Table 2 provides a summary of defect sizes and the mass of sample remains in a temperature of up to $900\text{ }^{\circ}\text{C}$. Table 3 provides a summary of the temperature values of the minimum points (peaks) observed on the DTG curves (corresponding to the local maximum rate of mass loss) for all the samples examined.

Results of testing by means of fixed bed pyrolysis

The mass of output samples—solid remains after pyrolysis—and condensation are presented in Table 4. Figures 5–7 show the results of post-process gas composition analyses recorded, during processes of pyrolysis of the

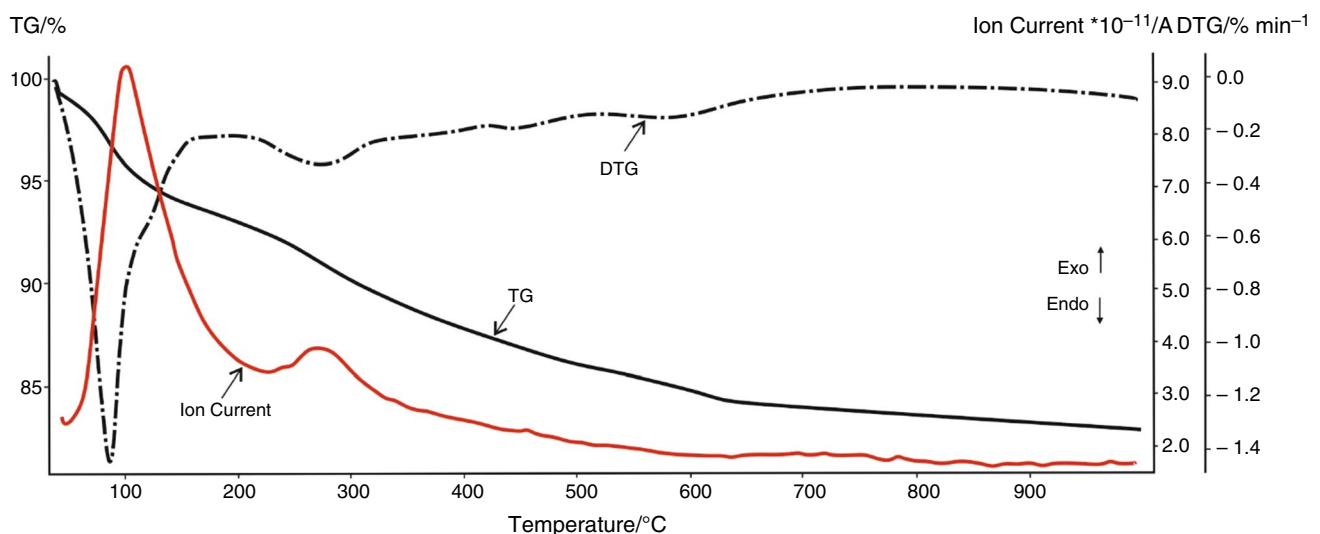


Fig. 2 TG and DTG curves and the water/ H_2O ion current curve recorded during analysis of the sample no. 59

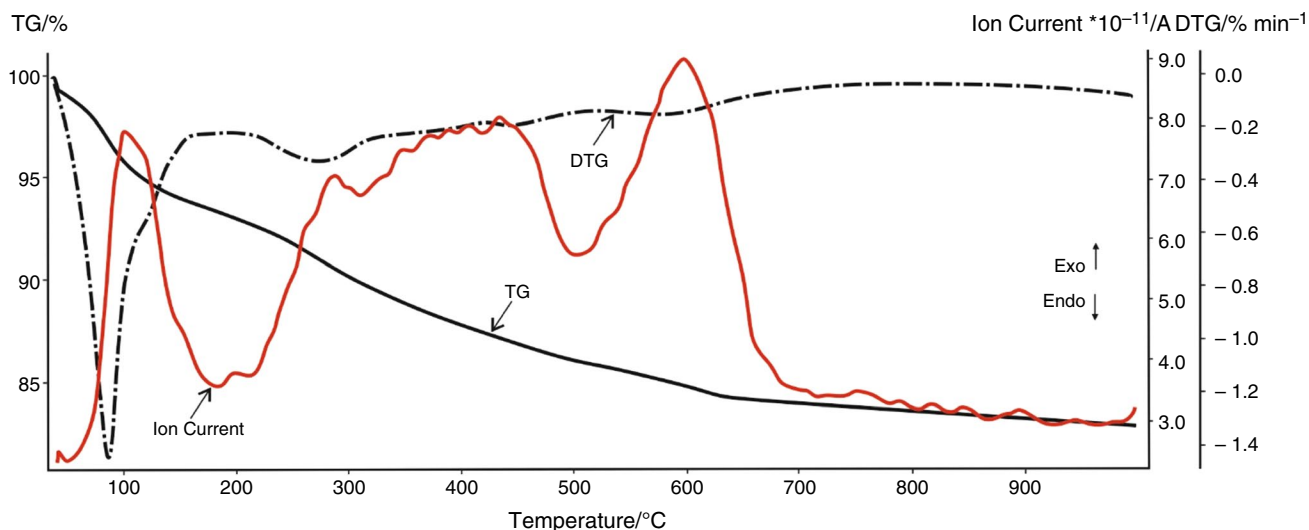


Fig. 3 TG and DTG curves and the carbon dioxide/CO₂ ion current curve recorded during analysis of the sample no. 59

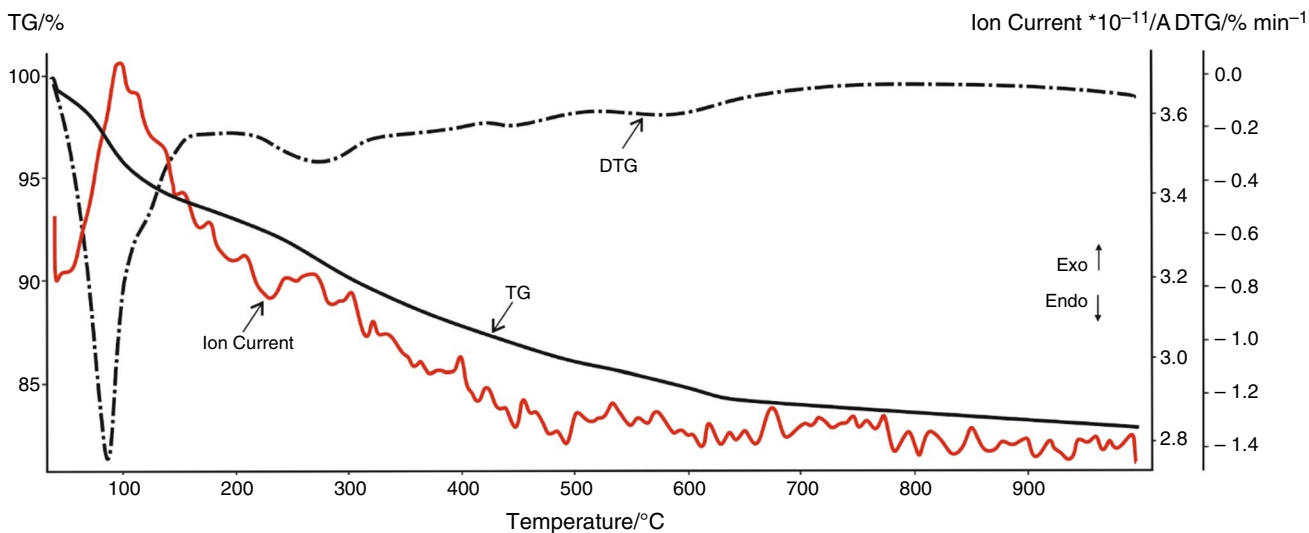


Fig. 4 TG and DTG curves and the carbon monoxide/CO ion current curve recorded during analysis of the sample no. 59

Table 2 Mass lost and dry mass left after 900 °C TG process

	Sample								Pulp + resin
	3	12	15	56	59	60	63	Commer- cial sample	
Mass lost %	19.07	35.12	17.37	24.4	16.86	24.62	23.73	31.6	32.09
Dry mass left %	80.93	64.88	82.63	75.60	83.14	75.38	76.27	68.40	67.91

Table 3 Peak temperatures on DTG curves for the samples examined

Peak temperature DTG °C	Sample									
	3	12	15	56	59	60	63	Commercial sample	Pulp + resin	
83–87	X	X	X	X	X	X	X	–	–	
104–113	–	–	X	X	–	X	–	–	–	
258–270	X	X	X	X	X	X	X	X	X	
328	–	–	–	–	–	–	–	X	–	
424	–	–	–	–	–	–	–	–	X	
444–461	X	X	X	X	X	X	X	X	–	
605–611	X	–	–	–	X	–	–	–	–	

Table 4 Samples mass after the pyrolysis process

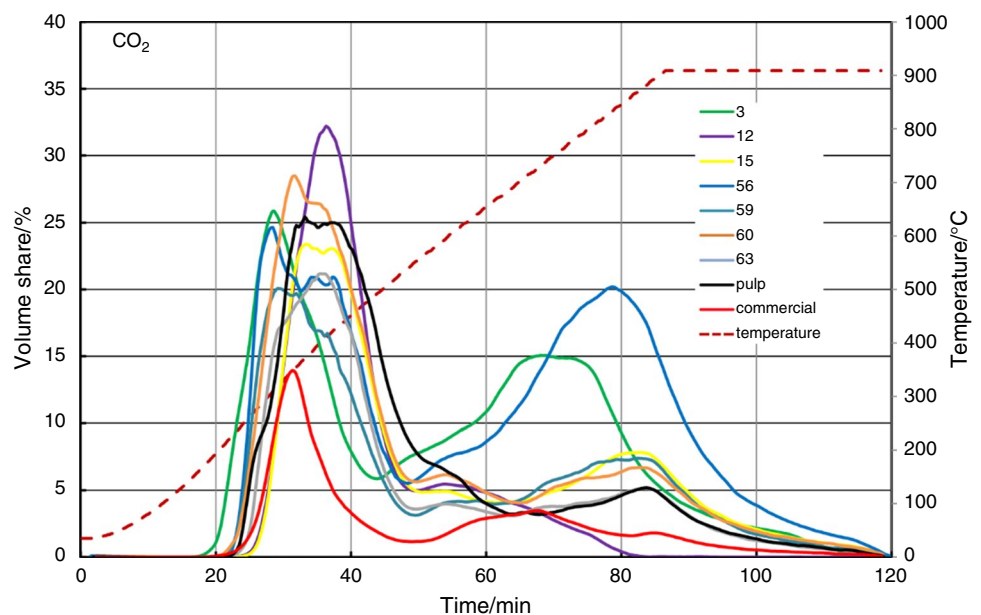
Sample	Sample mass/g		Mass loss		Condensate products mass/g
	Initial m_i	Final m_f	g	%	
3	35.26	25.00	10.26	29	4.53
12	34.30	19.75	14.55	42	10.02
56	27.68	20.77	6.91	25	3.84
15	32.57	23.31	9.26	28	5.32
59	33.94	27.18	6.76	20	2.61
60	26.93	17.72	9.21	34	3.45
63	32.17	22.73	9.44	29	4.47
Pulp + resin	24.72	16.34	8.38	34	3.23
Commercial sample	15.06	10.52	4.54	30	2.15

samples examined, in the laboratory setup intended for testing the fixed-bed pyrolysis process.

Discussion

On the basis of an analysis of the ion currents registered (Figs. 2–4), it was found that the main gas products emitted during a thermal analysis of the samples examined were water (H₂O), carbon dioxide (CO₂) and carbon monoxide (CO). Such summaries show which temperatures and sample mass losses correspond to the gas products which appear. The analysis of samples using the TG–DTG method detected no CH₄,—one of the decomposition products of cellulose included in all of the products [8, 23, 26–30]—which should be explained by the difference in absolute mass in the test method. In addition, the samples for the TG–DTG analysis were subjected to grinding, which could facilitate the reduction of CH₄ to carbon dioxide or carbon monoxide in this scale and at relatively high gas flows. The diagrams of the TG and DTG curves for all the samples examined showed a multi-signal course (Table 3). For samples 3, 12, 15, 56, 59, 60 and 63 a peak

Fig. 5 Volume share of CO₂ emitted from the samples examined



takes place at a temperature of about 80–115 °C that is related to the exothermic process of water (humidity) evaporation. It can take place in a single stage (83–87 °C) or in two stages (104–113 °C). Another signal takes place in a temperature range of 258–270 °C (for samples 3, 12, 15, 56, 60 and 63, commercial, and pulp + resin) and is related to an exothermic process related to the evaporation of structural (intercrystalline) water. For the commercial sample, this process takes place in two stages. A minor signal at a temperature of 424 °C occurs in the ‘pulp + resin’ sample, which may be related to the destruction of the geopolymer binder (an ingredient of the mix).

Further signals within a temperature range of 440–460 °C can be observed most clearly for samples no. 15 and 60 although they are present in all samples that contain inorganic resin in characteristics of CO₂ emission, which may testify to the residual degradation of cellulose fibres that were soaked the most with inorganic resin. Within a temperature range of 605–610 °C, additional samples occur for samples no. 3 and 59, resulting from the microsphere combustion process. Similar signals—although with much less defined peaks and at slightly lower temperature range of 580–600 °C—occur for samples 15 and 63, which also contain microspheres. In all the samples examined, no

Fig. 6 Volume share of CO emitted from the samples examined

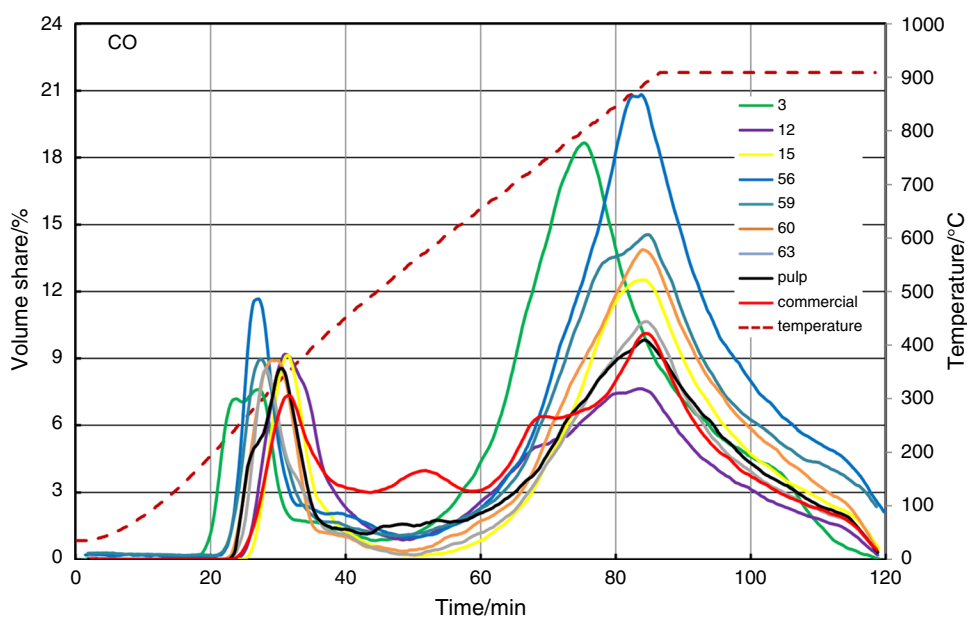
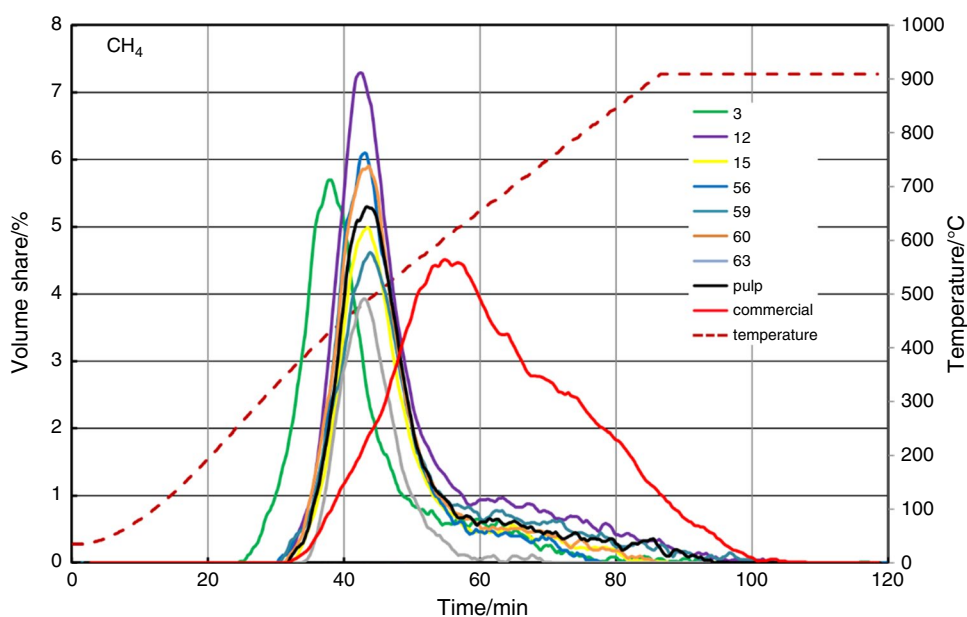


Fig. 7 Volume share of CH₄ emitted from the samples examined



signals originating from endothermic processes were registered. The mass loss for the materials examined reaches a value of about 17–35%.

For sample no. 59 (mix with expanded vermiculite and perlite, and microspheres), the above-mentioned relationships achieve the lowest level of sensitivity as a result of various influences of ingredients on one another. In the case of the signal origination from the ion current of water/H₂O (Fig. 2), the diagram translates to the DTG curves, where two signals are visible within a range of up to 300 °C, corresponding to the evaporation of humidity and the destruction of intercrystalline water. In the case of ion current of carbon dioxide/CO₂ (Fig. 3) and carbon monoxide/CO (Fig. 4), multiple signals within a temperature range of up to 700 °C occur (products of combustion of individual ingredients of the mixes). There is no correlation between the TG and DTG results (signal multiplication factor) and the composition of the samples. All the courses of ion currents (for the own samples) examined have a similar diagram type with similar sensitivity.

In the case of analysis of fixed bed pyrolysis (Figs. 5, 6, 7), it is possible to notice CO, CO₂ and CH₄ compounds—the products of cellulose decomposition. In the case of the commercial sample, it is possible to see that the emission of CH₄ has a peak with characteristics different to those of own samples, which results from the decomposition of the organic resin [9, 10, 27–29]. In addition, in the fixed-bed pyrolysis test method, it is possible that CH₄ was identified as part of another organic compound with higher molecular weight. This results from the specificity of the examination method. In the case of the ‘commercial’ sample (Fig. 7), the effect of the emission of methane is more extended in time, taking place for up to 98 min whereas for own sample the methane emission time is within a limit of 40–58 min.

In the own samples examined, the dominant emissions are those of carbon dioxide and carbon monoxide (Figs. 5, 6). The carbon dioxide and monoxide emissions take place in two stages—the first maximum was observed after 20–30 min, and the second one after 70–80 min of the process. Methane emissions (Fig. 7) mainly take place at the 40th minute of the process and their volume achieves values of below 8%. Together with an increase in the temperature of pyrolysis, the yield of individual ingredients decreases. No differences in terms of gases emitted, depending on sample composition type, were found in the qualitative examination of gases emitted from own samples.

Conclusions

The application of expended perlite expanded vermiculite and microspheres as additives that improve the thermal resistance of a cellulose mix proved to be the right choice.

These materials exhibit some very interesting physico-chemical properties that may be useful for creating moulds which come into contact with liquid metal intended for formation of gating systems in traditional single-use sand moulds. Because of their specification, these materials may contain organic or inorganic contaminants which may be a source of trace contamination appearing during thermal degradation.

The application of aluminium silicate binder did not result in significant deviations from the course of temperature changes during measurements. This enables the usage of this resin in the application of this type, which is significant given that this material is much friendlier in terms of human life and health in comparison to the materials applied in the commercial cellulose mould.

Described in this paper mixtures composition has been used to manufacture experimental laboratory gating fittings for pour liquid grey iron into sand mould in small scale. Analysis did not show any negative effect to grey iron metal casting microstructures by using described in this paper material mixtures for gating system to run liquid metal from a ladle into the mould [10, 27]. That gives some positive perspective to run very first industrial tests once the correct commercial partner will be found.

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