

Pyrolysis and Combustion Kinetics of Refuse Derived Fuel and Ash Characterization

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Abstract

Municipal solid waste is an inevitable product of human activity. Whatever a person does he or she produces waste. Trend analysis indicates that a constant growth of the quantity of waste at a global scale. With this, the problem of waste management becomes increasingly more important. Until recent decades municipal waste was disposed of and stored in landfills. However, this way of treatment introduces numerous environmental problems. The situation in waste management started to change rapidly in the mid 70-s when the waste hierarchy concept was introduced for the first time in The European Union's Waste Framework Directive.

The present work studies energy recovery processes from municipal solid waste in the form of refuse derived fuel (RDF). The Thesis aims at understanding and modeling the RDF combustion and pyrolysis processes. Thermal gravimetric analysis and Differential Scanning Calorimetry were carried out to obtain the data used for the creation of a kinetic model. The experiments were performed under air for combustion and nitrogen atmosphere for pyrolysis. For each atmosphere, the behavior of the RDF samples at three different heating rates were studied. The influence of the heating rate on the apparent kinetic parameters of the model was discussed.

The characterization and comparison of the fly ash samples from a real waste-to-energy plant and the ash obtained from the RDF combustion in the laboratory was made. The morphology of the studied material was analyzed by electron microscopy, whereas elemental and phase composition was studied by energy dispersive X-ray analysis and X-ray diffraction respectively. The discussion on the potential practical use of the ash was also addressed and possible applications were suggested.

Keywords: MSW, RDF, kinetic model, pyrolysis, fly ash

1. INTRODUCTION

Municipal solid waste (MSW) is a product that has lost its economic and social value. Thus, a car can become waste when it gets broken, a book – when it is read, a toy wrapping – when a toy is removed from it for the future use. Municipal solid waste has a negative value, since money should be spent to remove it from the place where it was thrown away and people do not want to have degrading waste in front of their doors.

Currently, it is considered that MSW is still a product or a resource, that can be reused. Indeed, zero-waste concept implies that waste can be used in several lifecycles and/or turned into a valuable resource or energy for the production of new goods. The zero-waste concept is the base of the circular economy – the industrial economy in which waste will be eliminated due to reduction, reuse, recycle and recovery of useful material and energy on every stage of a product's lifecycle. The circular

economy is an official goal of the European Union regarding material resource management [1].

One of the prospective technologies of the energy recovery from municipal waste is the use of refuse derived fuel (RDF). RDF is a fuel obtained from combustible fractions of MSW after pre-treatment. It is shaped as pellets or briquettes in order to increase its physical characteristics. The main environmental concerns when it comes to RDF combustion are the high concentration of chlorine-containing compounds in the flue gas and the contaminants present in the fly ash.

Incineration of municipal solid waste is an industrial process which aims to reduce waste volume neutralizing, at the same time, potential hazard of the original material and of the resulting products. The progress in the technology development was encouraged by the new strict emission limits introduced in the EU regulations.

These stricter limits led to the drastic improvement in air pollution control systems [2].

Thermal methods of MSW treatment are seen to be significantly more environmentally friendly than the conventional land filling. Being the most widely spread among them incineration, however, raises concerns about noxious pollutants such as NO_x , SO_x , HCl, dioxins, furans and some other gaseous and solid contaminants. In some studies it is referred that the use of gasification and pyrolysis, instead of traditional incineration based in combustion, results in lower hazardous emissions, enabling the reduction of investment costs [3].

Pretreatment of MSW is an important measure to increase fuel properties of the material before a thermal process. It can contribute to improvement of the combustion stability and normalization of the water content. One of the most popular ways of MSW pretreatment is the refuse derived fuel (RDF). In this treatment, municipal waste is dried, crushed and compressed. The treated material is shaped as pellets, that gives it quite homogenous composition and increase the energy density, which will reduce transportation costs, since more energy content is transported in a lower space. Another advantage is the possibility to control the chlorine and sulfur level by adding special chemical compounds during molding [3].

The use of RDF in thermal processes can have an important advantage in terms of ashes composition. Since, MSW streams can be selected prior to the fuel production, the steams with a high content of toxic substances, namely chlorine and heavy metal, can be eliminated. It can be conceded, that the removal of colored plastics from the stream coming to the RDF production, will drastically reduce or even eliminate the content of these toxic metals in the ash residues. However, the benefits from such measures should be carefully calculated. An overdone separation of certain fractions can dramatically affect the physical and chemical properties of the material, which are relevant for the combustion and, hence, make the entire process economically unfeasible.

As the prices for traditional MSW treatment shows constant growth, the alternative methods gain popularity. One of the most promising waste treatment options is the transformation of the combustible fraction of MSW into RDF with its further thermal decomposition. At the moment, the most widely spread technique applied to RDF is combustion. The combustion of RDF, as referred before, can

be done in cement production facilities, conventional thermal power plants as well as in designated waste-to-energy plants. RDF can be burnt individually or in a co-combustion process. Currently, the best option seems to be the co-combustion in the cement production units [4, 5].

The use of RDF, in pyrolysis and gasification process presents a number of advantages when compared with raw MSW. Since the fuel is produced only from the combustible fraction of waste it has much less inert substances and consequently demonstrates better performance in thermal treating processes. It also has advantages in transportation and storage due to the higher calorific density.

The RDF use in thermal processes is a relatively new topic, hence, there is the need to improve knowledge, especially as far as process modeling is concerned. However, existing research is enough to verify some similarities between RDF and biomass pyrolysis. This can be explained by the fact that cellulosic compounds and lignin are the main structural blocks for both fuels. However, RDF containing a significant amount of plastics can have some specific features that can considerably affect both the process and its modeling. The temperature range at which pyrolysis occur is similar for RDF and biomass, yet, the presence of plastics may strongly affect the yield and composition of products [6].

Regarding the analysis of the thermal decomposition of RDF, both kinetic and equilibrium models are usually used. Equilibrium models are important because they can predict thermodynamic limits, however, a lot of studies showed their poor performance in terms of matching experimental results. Kinetic models, in their turn, even though being restricted to a small number of reaction and species, show extremely good matching in different heating rates [7].

Waste-to-Energy technologies are strongly connected with the production of problematic process residues. These residues mainly come in a form of ash which have to be disposed of to minimize its environmental impact. [8].

Ash is a mixture of materials, which were not combusted during incineration process. Ash composition is affected by the type of waste used in the incineration process and by the combustion conditions. Incomplete combustion can cause the presence of char inside ash. Mostly, ashes consist of incombustible materials, mainly mineral ones, like silicates, aluminates and oxides, unoxidized metals, ceramic and glass

materials. In the next chapters a description of the type of ashes is performed

Fly ash is a material, which has fine powdery properties. It is composed mainly by non-combustible inorganic material, but also contains some carbon that is leftover from partially combusted wastes. Although fly ash particles are generally spherical, it is usual to found also irregular particle. The spherical shape of fly ash results from the formation of tiny molten droplets as the ash travels through the boiler. Since it is so fine, removal and collection of fly ash from flue gas requires specialized equipment such as fabric filters [9].

In terms of chemical composition, the main constituents remaining the same as in the bottom ash, being silicon oxide and calcium the main ones. The significantly lower concentration of iron should be noted. It is caused by a fact, that the vast majority of ferrous materials remained unburned in a form of large and heavy pieces of metal and, hence, it remained in the bottom ash [10].

Fly ash has significantly higher concentrations of heavy metals, such mercury and cadmium, than bottom ash, due to the fact that fly ash has adsorption properties facilitating the adsorption of metal atoms [10, 8].

The possible application of MSW ash include its use as fertilizers, cement and concrete production, road pavement, zeolite production, glass and ceramics production etc.

2. METHODOLOGY

Thermogravimetric analysis is a method to study the kinetics parameters of thermal processes such as combustion, gasification and pyrolysis. The TGA has proved to be a precise method especially at low heating rates. The linearization techniques of nonisothermal reactions do not match well with the complex composition of biomass-contained materials. To overcome this issue, the most popular method to estimate the biomass thermal degradation kinetic parameters from TGA data, is the nonlinear method of least squares (LSQ). This method assumes that the process is composed by several reactions [11].

The thermogravimetric tests were done in a Simultaneous Thermal Analyzer (STA) 6000 by PerkinElmer. The device is equipped with a vertical displacement balance sensor providing weight insensitivity to sample position as well as know-how sensor to measure both sample and reference temperature directly. The temperature

limit for the device is 1100°C. However, in this work the maximum temperature was 800°C. The microscales on which a crucible is placed register the mass loss of the sample. The device can also collect data on the heat flow change. The temperature is measured in two places. Program temperature is measured by a thermocouple located on the wall of the combustion chamber whereas the samples temperature is checked at the bottom of a crucible. The cooling of the sample is performed by cool ambient gas injected into the combustion chamber. The device is connected to a computer with the TA instrument software installed. This software enables to store the experiment data.

The RDF for this study was obtained from a waste management company in Lisbon, Portugal. It has a high low calorific value of 25.1 MJ/kg and consists mainly of paper, cardboard, and cloths fraction of MSW with the addition of plastics and wood. The initial fuel was subjected to crushing in the grinding machine in order to diminish initial particles to the size of 1 mm suitable for thermogravimetric analysis (TGA). The image of the treated RDF used in the experiments is displayed on figure 1.

RDF used in the present work has a high volatiles content of 80 wt%. The high volatile content might be connected to the large fraction of small particles. Won Seo et al. discussed the influence of the volatile matter on the devolatilization for different alternative fuels [12].



Figure 1 Studied RDF. 1 – original RDF, 2 – ground sample

The experiments were performed in nitrogen, with a flow of 20 ml/min, at heating rates of 5, 10 and 20 °C/min. The samples were spread evenly along the alumina crucible with the diameter of 6 mm. The mass of the samples ranging from 14.169 to 30.132 mg. For each samples a particular heating program was created with the main differences being heating rates, ambient gas and the time for which a

sample was held at the highest programmed temperature. For each experiment an initial temperature of 40 °C was chosen. The first stage of each experiment was the even heating of the sample from an initial temperature to 800°C at the previously set heating rate. When program reached the maximum temperature the isothermal stage followed. At this stage the sample was hold at 800°C for 10 minutes in the case of 5 and 10°C/min heating rates and for 1 hour in the case of 20°C/min rate.

For the combustion of RDF three TGA experiments were performed with different heating rates - 5, 10 and 20 °C/min. The same aluminum crucible as for pyrolysis was used. The program steps replicated the ones for pyrolysis. The difference was in the medium gas used for the thermal treatment. In this case it was air. The maximum temperature of the process was 800°C. For lower heating rates the isothermal stage time equalled 10 minutes whereas for the highest rate the time was increased up to 60 minutes.

In order to analyze ash obtained from the combustion of RDF an additional experiment was carried out since the amount of ash obtained from TGA was not enough for the SEM/EDS analysis. The ash sample was burnt in the laboratory furnace at 800°C. The average heating rate was 15°C/min. The sample was held at 800°C for 30 minutes. The obtained ash has light grey color and the sintered pieces can be observed. However, when touched it is fell to smaller pieces with some particles forming agglomerates around 2 mm in diameter and some being separate. In order to compare this ash with the one obtained from a waste-to-energy plant, it was assumed that all formed ash can be considered fly ash. This assumption is rested upon the particle size distribution that is close to the one of the industrial fly ash. The experiment showed the mass loss of 85.36% that corresponds well with the figure obtained from TGA experiments.

In order to obtain the expressions used in the kinetic model a set of assumptions were made: 1) the decomposition is based on the Arrhenius equation where the constant reaction rate is a function of the temperature 2) the effect of the interactions between fractions of the material on the reaction rate is neglected. In this sense, the weight loss rate of a pseudocomponent can be expressed by the following equation [13]:

$$\frac{dW}{dt} = -k(T)W \quad (1)$$

Where $k(T)$ is the reaction rate constant at temperature T and W is weight of a pseudocomponent at time t .

Solving this differential equation we obtain:

$$W_{i,j+1} = W_{i,j} + \frac{dW}{dt} \cdot (t_{j+1} - t_j) \quad (2)$$

Where $W_{i,j}$ and $W_{i,j+1}$ are the weights of the component i at the current and following moment of time, respectively. t_j and t_{j+1} are the temperatures of the sample at the current and following moment of time.

According to the Arrhenius relationship [11]:

$$k = k_0 e^{-E_a/RT} \quad (3)$$

Here k is reaction rate constant, k_0 is the exponential factor, E_a is the activation energy, R gas constant which equals 8314 J/mol·K and T temperature in Kelvins. k depends on the temperature of the process. The dependence of k_0 , E_a and R on the temperature is insignificant and can be neglected [14]. An alternative parametrization of Arrhenius equation was proposed by several authors in order to minimize correlation between the equation's parameters [15, 14]:

$$k = k_{Tref} \cdot e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{Tref} \right)} \quad (4)$$

Here k_{Tref} a specific reaction rate at the reference temperature T_{ref} , which in the present work equals to 573°C. If the reference temperature is infinite, then the equation will take the previous form. Thus, one can understand k_0 as the specific reaction rate at infinite temperature. An important role of the reparametrization procedure is that it enables to reduce the computation time for the optimization problem [14].

The model was developed in Excel solver. The method chosen for the solving was the GRG Nonlinear Solving method that uses the Generalized Reduced Gradient method. In fact, the method is a non-linear extension of the SIMPLEX method. The function to be minimized is the sum of squared errors which is represented by the difference between the relative weight of a sample during the experiment and the relative weight calculated in the model.

$$Min OF = \sum_i^n \sum_j^4 (w_i^e - w_{i,j}^c)^2 \quad (5)$$

Where n is the number of time steps in the experiment and 4 corresponds to the four pseudocomponents. The amount of fixed ash should be equalled the difference between the

total related weight of the sample and the sum of related weights of pseudocomponents. The constraint for the fixed ash content should be specified as:

$$w_{ash}^c = 1 - \sum_j^4 w_j^c \quad (6)$$

Consequently, the total calculated sample weight can be represented as the sum of the weight of the four pseudocomponents plus the weight of fixed ash:

$$w_{total}^c = w_1^c + w_2^c + w_3^c + w_4^c + w_{ash}^c \quad (7)$$

Where w_1^c, w_2^c, w_3^c and w_4^c corresponds to the relative weights of water, cellulose, hemicellulose and lignin respectively. The initial values were assigned to each of the pseudocomponents. For water, cellulose, hemicellulose and lignin the assigned values are 0.1, 0.3, 0.3 and 0.2 respectively.

The samples of fly ash studied in this work were collected at the waste-to-energy plant in Bydgoszcz, Poland. The plant has a capacity of 180 000 tons of municipal solid waste per year. The fuel is combusted in the PENSOTTI boiler on the moving grate in the process known as mass burning. The boiler is connected to the one-stage condensation turbine generating up to 13 MW of electrical power. It is possible though to use a combined heat and power mode when there is a need to supply heat to the residential district connected to the waste-to-energy plant.

There are several places along the flue gasses duct where the fly ash can be collected. For this research two fractions of fly ash were collected. The first one was the ash captured beneath the economizer. This material has white to sandy color with predominantly ranging from 1 to 400 microns coarse particles. The second fraction was ash coming from under the baghouse filter. The ash in the second fraction is gray and very fine. Visually and on touch it resembles cement.

The scanning electronic microscope (SEM) allows the analysis of the morphology and chemical composition of a given sample. In SEM a high energy beam of electrons is used to initiate numerous signals on the surface of the studied material. The signals bring back to the detector information about the surface of the material. Then the computer processes the information and transforms it into a form convenient for the user. The output data includes 2-d pictures of the surface layer as well as material composition. The magnitude of the technique ranges from x20 to x30000. In this work the magnification of x200,

x400, x500, x750, x1000, x3000, x5000, x10000 was used to analyze fly ash fractions.

The experiments in the present research were carried out in the laboratory located at the IST University in Lisbon, Portugal. During the study, the JEOL JSM-7001F analytical FEG-SEM with Oxford model INCA 250 PREMIUMEBSD (electron backscatter diffraction) and energy dispersive X-ray spectrometer (EDS) light elements detector attachments electronic microscope was used. The images were obtained with a help of PC-SPM software environment. The voltage of electron beam is equaled to 30 kV and the magnification range x10 – x1000000. The precision of EDS analysis that was used for the research in this paper is around 0.5 % on an atomic weight basis.

The samples of heavy and light fly ash were additionally subjected to the x-ray diffraction (XRD) analysis. The experiments were performed in the Philips PW3020 XRD analyzer. The principle of x-ray diffraction based on the registering of spherical waves produced when an x-ray strikes an electron. In this case, the electron is called the scatterer. When such scatterers are arranged in a regular order the waves produced are also regular. Even though in many directions such waves fade out due to mutual interference, they, nonetheless, add up in a few particular directions. These directions can be described by the Bragg's law:

$$2d \cdot \sin \theta = n \cdot \lambda \quad (8)$$

Where d is distance between two diffracting planes, θ is an angle between the diffraction plane and a beam, n is any integer and λ is the beam's wavelength. The directions in which the waves add up are represented as spots on the diffraction pattern. These spots bear the name reflections. X-rays gained popularity in the obtaining the diffraction patterns since their wavelength is similar in magnitude to the value of d between the diffracting planes of a crystal.

3. RESULTS AND DISCUSSION

In the Table 1 and 2 amount of pseudocomponents obtained by the model as well as reaction rate constant and activation energies are presented. The values of activation energy and rate constant for each component obtained for the combustion model fit pretty well when applied to the pyrolysis model. Consequently final pyrolysis parameters do not differ much. The moisture content is proved to be the same for every sample. The volatile matter however, depending on the heat rate varies

considerably for different pyrolysis experiments reaching 84.7% for 20°C/min heating rate. Consequently, the concentration of charcoal is also different for each sample. The amount of fixed ash is roughly the same for each sample and shows independence on the operation conditions.

Table 1 The amount of pseudocomponents obtained by the model

Process	Hemicell %	Cellul %	Lign in %	Fixed ash %	Moistu re %	Volatile matter %
Pyrolysis	34.08	32.02	10.3	19.04*	4.51	76.45
Combusti on	34.38	22.77	25.3	10.93	2.53	-

Table 2 Reaction rate constant and activation energies obtained by the model

	Water	Hemicell ulose	Cellul ose	Lignin	Fifth eleme nt
Pyrolysis					
E_a , cal/mol-K	2526.25	23753.18	41241.17	28880.10	7327.18
k_0 , min ⁻¹	0.25039	0.13086	0.00013	0.000005	0.000099
Combustion					
E_a , cal/mol-K	14573.23	27407.90	30974.20	5011.12	-
k_0 , min ⁻¹	1884.51	0.3791	0.0014	0.0138	-

In Figure 2, 3 and 4 represent the comparison between the mass loss experimental curves and the model curves for RDF pyrolysis at three heating rates of 5, 10 and 20 °C/min is presented. The decision was made not to apply individual optimization for each heating rate. Instead, one curve that describes the process with maximum precision for all heating rates was obtained. The importance of this decision links to the practical applicability of the model. Since the obtained results are aimed at designing of RDF incinerators and pyrolysis reactors, it is important to ensure adequate behavior in the wide range of heating rates. The model shows very good fitting for 5 and 10 °C/min, however, for the rate of 20 °C/min turned out to be problematic.

The studied material revealed curious behavior in the isothermal part. At the heating rate of 20°C/min additional mass loss amount for 11% on the initial sample mass basis was detected. This phenomena can be explained by the belated devolatilization of charcoal obtained during late stages of the process, for example, stable plastics decomposition. Works of other authors prove that the average mass loss for RDF during isothermal stage is greater than for traditional fuels. The difference between coal and RDF in isothermal zone is around 38% [12]. Numerous studies confirmed that high devolatilization yield and, consequently, decreased char yield is observed at higher pyrolysis heating rates [16, 17]. Apart from that devolatilization yield is virtually always higher if it comes to isothermal conditions in comparison to non-isothermal [12].

The results for the combustion process at the heating rates of 5, 10 and 20 °C/min are represented on the figures 5, 6 and 7 respectively. The model showed generally good fittings especially in the moisture evaporation and cellulose decomposition zone. As in the case of pyrolysis the most problematic heating rate appeared to be 20 °C/min. The problems however appeared in the 3-d zone within temperature range 380 – 500 °C. This zone is responsible for the thermal decomposition of lignin and plastic compounds. The best fitting was obtained when the initial values for the overall optimization got based on the optimized values received for the individual optimization of the highest heating rate. For the 5 °C/min the curve fitting equals 97.62 %. The model still can be subjected to additional adjusting especially in the middle temperature range.

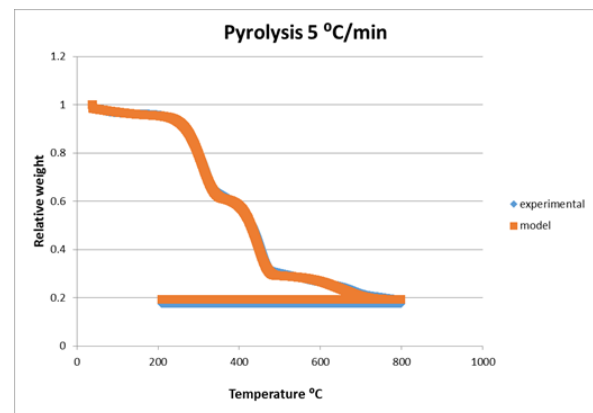


Figure 2 TGA curves from modeling and experimental data for RDF pyrolysis at 5 °C/min heating rate

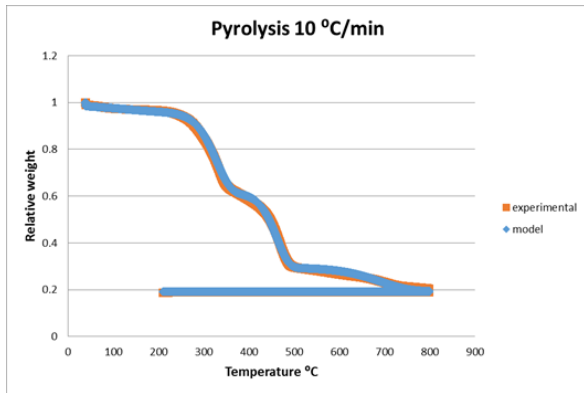


Figure 3 TGA curves from the model and real data for RDF pyrolysis at 10 °C/min heating rate

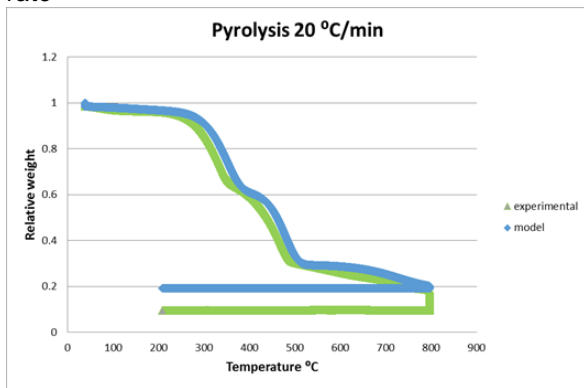


Figure 4 TGA curves from modeling and experimental data for RDF pyrolysis at 20 °C/min heating rate

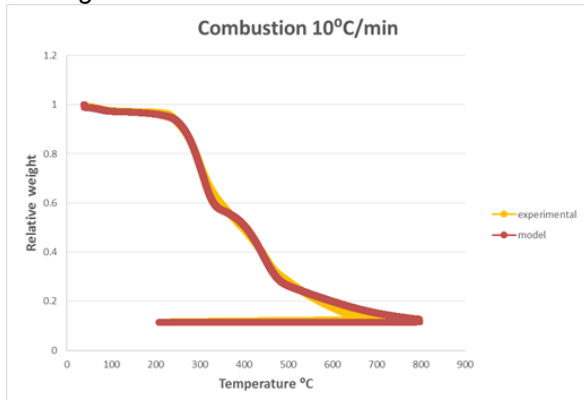


Figure 1 TGA curves from modeling and experimental data for RDF combustion at 10 °C/min rate

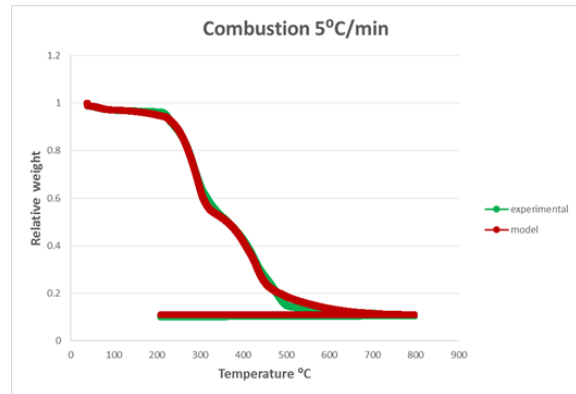


Figure 2 TGA curves from modeling and experimental data for RDF combustion at 5 °C/min heating rate

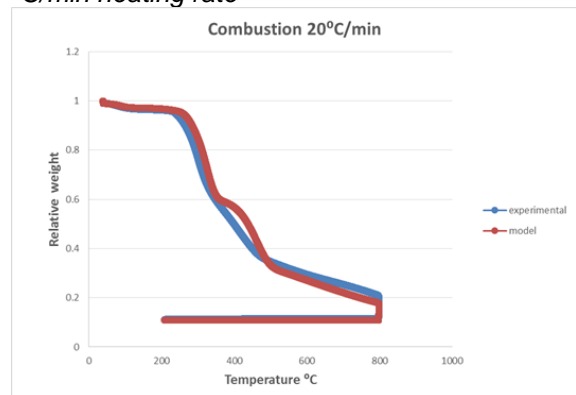


Figure 3 TGA curves from modeling and experimental data for RDF combustion at 20°C/min heating rate

The comparison table of the composition of light fly ash, heavy fly ash and RDF ash is presented below. It is noticeable that the composition of the RDF derived ash has a closer resemblance to the heavy ash fraction of the MSW incineration plant. The major differences are the lowered content of Cl, increased content of Si and almost complete absence of Ti and S. On the contrary, the concentration of carbon is much higher which can be explained by an incomplete combustion of the RDF in the laboratory. The large particles consist almost on unburnt carbon and were detected predominantly in the lower layers of ash after the experiment. This can be explained by insufficient air supply that occurred due to the fast formation of an inorganic top layer of ash in the experimental crucible. The possible solution for this problem can be the pyrolysis of RDF or multiple stage combustion. These topics have a large potential for investigation in future works. Also, the form of fuel might have a tangible effect on the efficiency of the combustion process. In the industrial application the fuel is normally used in a form of

2 – 3 cm long pellets, whereas in the present work it was utilized in form of homogeneous cotton-like material obtained after grounding the original materials down to 1 mm. An alternative technology for RDF thermal treatment can be the fluidization.

Table 3 Elemental composition comparison of the three studied ash fractions

Residue type	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Zn	C
Light fly ash	48.46	11.48	0	0.77	1.45	0	5.43	18.57	5.14	8.69	0	0	0	0
Heavy fly ash	59.296	2.31	1.68	8.13	3.88	0.63	4.42	3.16	0.79	13.44	1.50	0.77	0	0
RDF ash	55.82	2.334	1.89	4.126	10.73	0.176	0.36	1.52	0.72	11.41	0	0.32	0	9.952

The low content of sulfur in the RDF residues can be caused by its lower concentration in the original wastes from which RDF derived. The main sources of sulfur in MSW are paper, plaster board and sludge [53]. It will be reasonable to assume that the two latter fractions were not present in the RDF analysed. The insignificant content of phosphorous, in its turn, resulted from the separation of an organic waste fraction before the RDF formation process. Besides, a number of metals in the RDF ash is rather limited too, with the concentration of aluminum hardly reaching a half of the concentration of this element in the heavy fly ash fraction. Concentrations of Ti, Fe and Zn are lowered too. The reason for such phenomena is the removal of a metal fraction from the MSW streams before RDF formation. Based on the literature review, one can assume that content of heavy metals in RDF ash is also decreased. This can play an important role in a further utilization of this material and its use in commercial applications. One of the main concerns is the presence of chlorine [18]. In the RDF assessed on the present study, the concentration of this element reaches 1.52 %. This is much lower than for heavy and especially light fly ash fractions. However, if RDF is burnt or pyrolyzed on the industrial scale the amount of chlorine in ash residues might increase due to a specific flue gas treatment, such as $\text{Na}(\text{CO})_2$ use.

The morphological difference of three studied types of ash can be observed on the figures 8, 9 and 10. Generally, the average size of the RDF ash particles is smaller than for heavy and light fly ash fractions with the largest ones reaching 50 – 60 micron. The shape of the particles are closer to light fraction ash, however, some distinctions are present. Predominantly the particles are of amorphous shape sometimes with sharp edges. The biggest ones, though, represents agglomerated ‘balls’ of irregular shape. The elemental analysis of the ‘balls’ revealed considerable amounts of Ca (10.15 %), Si (11.17 %) and Al (8.72 %) which give them a

resemblance to some particles presented in heavy fly ash samples.

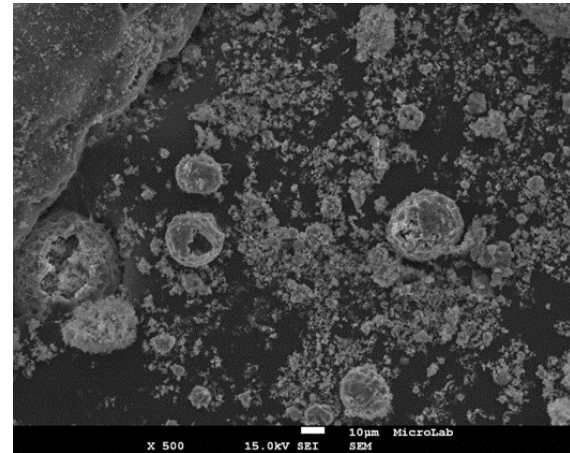


Figure 8 Light fraction fly ash. Magnification x500

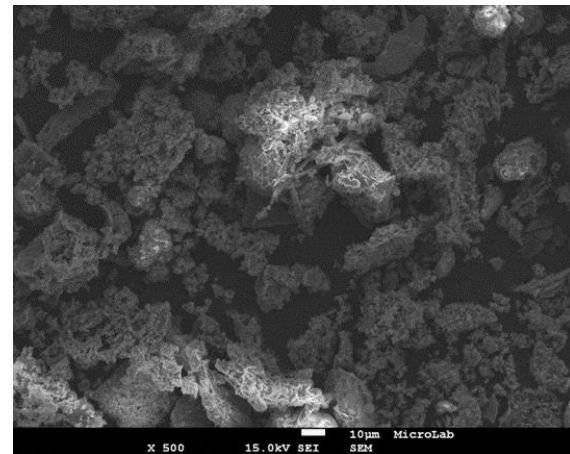


Figure 9 Heavy fraction fly ash. Magnification x500

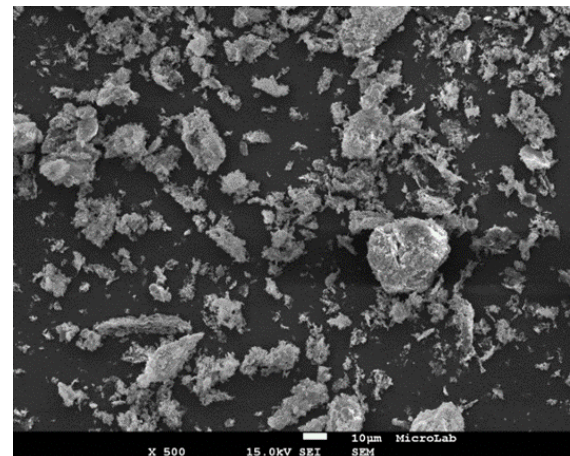


Figure 10 RDF derived ash. Magnification x500

4. CONCLUSIONS

Based in TGA experiments the thermal decomposition of RDF samples was studied. The experiments were conducted at three different heating rates and in different atmospheres. Pyrolysis was performed in nitrogen atmosphere whereas combustion in air. The mass loss curves, obtained from pyrolysis tests, showed four distinctive mass loss regions, which represent the thermal moisture evaporation and the thermal decomposition of main material's components: cellulose, hemicellulose and lignin. The temperatures range for the evaporation of water is 20 – 200°C, the decomposition of hemicellulose occurs at 200 – 360°C, cellulose decomposes at 360 - 470°C whereas lignin from 400 to 800°C. The plastics content might have influence on shape of the curves. High and low density polyethylene decomposes at higher temperatures of 400 – 500°C.

In the case of combustion, it was noticed that evaporation of moisture occurs between ambient temperature to 200°C. The second stage from 200 to 450°C is characterized by the release and combustion of volatile matter as well as the formation of char. During the final stage the thermal degradation of char occurs accompanied with a considerable mass loss. The content of the ash left after the process amounts for 11 – 13% of the initial mass of the sample.

Interesting observations were made with respect to the heating rate. In the combustion experiment the complete degradation of the material at the heating rate 5°C/min occurred at lower temperature than the one at 10°C/min and 20°C/min, whereas for the pyrolysis the difference between 5 and 10°C/min was insignificant. However, at 20°C/min, in the pyrolysis process the sample showed an intricate behaviour when the mass loss was still happening after the sample reached 800°C. This phenomena is typical for RDF, since the RDF devolatilization yield in the isothermal conditions is greater than the one for conventional fossil fuels, particularly coal.

The kinetic modeling for the combustion and pyrolysis of the RDF was carried out based on the results obtained from the thermal analysis. The rate constant k at reference temperature of 573K and activation energy for each pseudocomponent were obtained. In the case of pyrolysis an additional reaction were introduced. This reaction was responsible for the carbonization of a part of lignin. The additional

reaction allowed for a slight improvement of the model.

The lower activation energy for moisture in the case of pyrolysis is stipulated by the introduction of the fifth reaction. The solving algorithm, it seems, sacrificed the first component to reach an optimum solution of the problem. In both cases the activation energy proved to be higher than for similar models built for agricultural wastes and wooden biomass found in the literature. This can be explained by first impurities present in the RDF and second by the morphology of the material.

The SEM/EDS analysis of two samples of the fly ash taken from a waste-to-energy plant and a sample of RDF originated ash was carried out. The elemental composition of the samples is presented in the table below. The results proved that all samples have their own specific features and, hence, the different ways of further treatment and utilization can be applied to each of them.

The light fly ash fraction is characterized very high content of chlorine. Even though most of it is bounded with Na in a form of NaCl (mineral halite), some of it still can occur in a form of polychlorinated dibenzodioxins and dibenzofurans. In combination with heavy metals, usually present in this type of ash, dioxins and furans make the ash inappropriate for the future use. Amid the potential ways of treatment vitrification seems to be the most promising. The high concentration of soluble salts KCl and NaCl in the studied ash was confirmed by the XRD analysis.

The heavy fraction fly ash has much lower content of chlorine but much higher content of metals, including heavy ones. It consists primarily of aluminosilicates with high concentration of calcium-containing minerals. This make the material potentially suitable for the production of synthetic zeolites and adsorbents and also used in cement industry.

Finally, RDF originated ash the highest potential to be used in industrial application due to the low content of chlorine (1.52%) which can be further decreased if the separation of PVC and chlorine-containing paper products is done beforehand. The concentration of soluble salts is low, so washing even though being a cheap pre-treatment option might not prove to be appropriate. The ash can be a potential candidate for zeolites and cement clinkers production as the content of Si is the highest in comparison with other ashes studied. Another perspective application is the ash using as a material for a

base and subgrade layer in the road construction. The leaching of heavy metals must be controlled. Decreasing the content of such toxic heavy metals as Pb and Cd can be realized during the fuel making stage by removing colored plastics from the MSW streams used for the production of RDF.

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