



# **Pyrolysis and Combustion Kinetics of Refuse Derived Fuel and Ash Characterization**

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**Energy Engineering and Management**

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## List of abbreviations

EU - European Union

GRG - Generalized reduced gradient

RDF - Refuse derived fuel

GHG - Greenhouse gases

MSW - Municipal solid waste

CHP - Combined heat and power

APC - Air pollution control

PCDD - Polychlorinated dibenzo-p-dioxins

PCDF - Polychlorinated dibenzofurans

PVC - Polyvinyl chloride

BAT - Best available technique

W-t-E - Waste-to-Energy

PTFE - Polytetrafluoroethylene

CEWEP - Confederation of European Waste-to-Energy Plants

MBT - Mechanical biological treatment

CBR - California Bearing Ratio

MSWI - Municipal solid waste incineration plant

CEC - Cation-exchange capacity

BA - Bottom ash

FA - Fly ash

TGA - Thermogravimetric analysis

DSC - Differential scanning calorimetry

SEM - Scanning electron microscope

EDS - Energy-dispersive X-ray spectroscopy

LDPE - Low-density polyethylene

HDPE - High-density polyethylene

XRD - X-ray powder diffraction



## Abstract

Municipal solid waste is an inevitable product of human activity. Whatever a person does he or she produces waste. Trend analysis indicates 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 and, as a matter of fact, just postpones dealing with the issue. 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. By now, an impressive progress was already achieved in the waste management sector in the developed countries, especially the EU members. However, the issue is far from being resolved and more efforts are being taken nowadays to tackle the waste issue.

Energy recovery from waste is one of the important steps in the waste hierarchy ladder. Waste-to-energy facilities do not only deal with the waste management issue but, also, contribute in saving fossil fuels and other natural resources. Taking into account the rise of greenhouse gases (GHG) emissions levels in the atmosphere due to the extensive use of fossil fuels, it must be conceded, that the energy recovery from waste is an integral measure to decrease concentration GHG and hence, prevent the global warming.

The present work studies the 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 obtained results showed differences in the morphology and chemical composition of the samples. The discussion on the potential practical use of the ash was also addressed and possible applications were suggested.

Key words: MSW, RDF, kinetic model, pyrolysis, fly ash

## Resumo

Os resíduos sólidos urbanos são um produto inevitável resultante da atividade humana. Todas as atividades dos seres humanos geram resíduos. Uma análise de tendências indica que será de esperar um crescimento constante da quantidade de resíduos produzidos a uma escala global. Até há poucas décadas atrás os resíduos urbanos eram enviados e armazenados em aterros. No entanto, esta forma de tratamento produz um grande número de problemas ambientais e, na realidade, corresponde somente a um adiamento do problema. A gestão de resíduos começou a mudar mais rapidamente em meados dos anos 70, quando o conceito de hierarquia de gestão de resíduos foi introduzido pela primeira vez na Diretiva-Quadro sobre Resíduos da União Europeia. Neste momento já foi conseguido um progresso muito significativo no setor de gestão de resíduos nos países desenvolvidos, em particular nos países membros da União Europeia. No entanto este assunto está longe de estar resolvido e estão a ser envidados mais esforços para lidar com o problema dos resíduos.

A recuperação energética a partir de resíduos é um dos degraus mais importantes na escada da hierarquia de resíduos. As unidades de valorização energética de resíduos não só asseguram uma parte da gestão de resíduos como também contribui, para a poupança de combustíveis fósseis e outros recursos naturais. Tendo em conta o crescimento contínuo dos níveis de emissões de gases com efeito de estufa para a atmosfera devido à utilização extensa de combustíveis fósseis deve reconhecer-se que a recuperação de energia a partir de resíduos constitui uma medida integral para a diminuição da concentração de gases com efeito de estufa e, conseqüentemente evitar o aquecimento global.

Este trabalho pretende estudar os processos de recuperação energética a partir de resíduos sólidos urbanos na forma de combustíveis derivados de resíduos (CDR). Esta Tese pretende compreender e modelar os processos de combustão e pirólise de CDR. Foram realizadas estudos por análise termogravimétrica e Calorimetria Diferencial de Varrimento simultâneos para obter um modelo cinético. Foram realizadas experiências sob ar no que respeita à combustão e sob atmosfera de azoto para a pirólise. Para cada uma destas atmosferas foi analisado o comportamento de amostras de CDR com três velocidades de aquecimento diferentes. É ainda discutida a influência da velocidade de aquecimento nos parâmetros cinéticos aparentes obtidos para o modelo.

Foram caracterizadas e comparadas amostras de cinzas volantes de uma unidade real de valorização energética de resíduos e das cinzas obtidas pela combustão do CDR no laboratório. Foi estudada a morfologia do material em estudo através da microscopia eletrónica, enquanto a composição em termos elementares e de fase presentes foi feita por espectrofotometria de Raios-X por dispersão de energia e por difração de raios-X respetivamente. Os resultados obtidos mostraram diferenças na morfologia e composição química destas amostras. Foi ainda discutida a potencial aplicação prática destas cinzas, sugerindo-se possíveis aplicações.

Palavras-chave: Resíduos Sólidos Urbanos, CDR, modelação cinética, pirólise, fly ash

# 1. Introduction

## 1.1. Motivation

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. In such a way the negative value of waste will be minimized to zero. 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].

The waste management includes economic, social and environmental aspect. Smart waste utilization results in resource, energy and fossil fuels saving and decreases the costs of newly manufactured products.

Energy recovery from the MSW is an integral part of the modern waste management. It helps to recover useful power and heat from waste and decrease its negative value. It plays an important role in saving fossil fuel resources, thus, contributing to the decrease of GHG in the atmosphere. Energy recovery from waste includes a set of different technologies to thermally treat waste.

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.

## 1.2. Objectives

The objective of this Master's Thesis is to study the kinetics of RDF in two thermal processes – combustion and pyrolysis. As a result, a kinetic model of RDF combustion and pyrolysis will be developed and the kinetic parameters determined. The Thesis also deals with the issues connected to the utilization of the fly ash. Concerning these issues, the chemical and morphological analysis of the ash obtained after the thermal treatment of RDF will be done. The RDF derived ash will be compared to the fly ash from the real Waste-to-Energy incineration plant. The recommendations on the future use of the fly ash will be given.

### **1.3. Organization of the thesis**

The work consists of 5 chapters. The first chapter 'Introduction' includes an overview of general issues related to MSW and the objective of the work as well as the motivation and the present sub-chapter - organization of the Thesis. The second chapter includes the literature review of the waste combustion and pyrolysis technologies, RDF potential as a source of energy as well as the review of the utilization methods of fly ash. In the third chapter, the materials and methods of RDF pyrolysis and combustion kinetics are presented including the description of the proposed kinetic model. In the same chapter the methods and materials description connected to the ash characterization are also reviewed. The third chapter is followed by the fourth chapter, in which the results of the study are presented. This chapter includes the thermogravimetric analysis results, kinetic modeling results and the results of the analysis of the fly ash and the comparison of different types of characterized ash. Finally, in the chapter 7, the conclusions on the whole work done in the Thesis are presented.

## 2. Literature review

### 2.1. Waste incineration technology

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. In Europe, the waste incineration sector started to develop rapidly in the mid 90-s. Up to current date, more than 400 facilities were built or updated. This 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].

The most recent waste incineration technology enables material and energy recovery, which gave the modern incineration plants its new name – waste-to-energy plant [1].

From the physical point of view incineration of waste is a process of thermal oxidation of any combustible materials, in particular, carbonaceous material contained in the municipal waste. Municipal solid waste (MSW) is a heterogeneous material which includes organics, metals, paper, plastics, wood, textiles and other materials. The amount of water in MSW is considerable and can reach up to 50% in the North and 60% in the South of Europe. In the South, this figure is higher because of more humid climate. During incineration, the chemical energy contained in the combustible part of the waste is turned into heat [2].

There are several factors that affect fuel properties of municipal waste, namely, composition, water content and extent of homogeneity. Waste with a high content of wet organic fraction will require more energy since a process of intense drying will be involved. A high concentration of metals will also decrease the combustibility of the material. Mixing, separation and some other pre-treatment techniques can make the material more combustible [2].

Mass burn, is the most widespread technology for incineration and consist of burning unsorted mixed MSW on the grate of the furnace. The temperatures of the process range from 850 to 1200 °C, being the optimum around 1100°C. The limit of the lower temperature enables to destroy hazardous compounds such as dioxins and furans that might be formed during the process. The furnace has several burners distributed along its height in order to guarantee complete combustion. On average, the waste spends 45 to 70 minutes in the furnace. After the combustible material is burnt, the residues, bottom ashes, are discarded to the bunker. These ashes can be used after required treatment. In order to guarantee the legislated levels of NOx emissions, ammonia is pulverized in the furnace when needed [3].

The temperature of the flue gases is maintained within limits of 250 – 300 °C to ensure necessary emission reduction. The gas is cooled in water-gas heat exchangers, where the energy heat of the flue gases is transferred to the water that will be supplied to local residential areas, as in conventional thermal power plants. The steam obtained in the boiler is used in a turbine to produce electricity. The vast majority of modern incineration plants enable combined heat and power generation (CHP). This has the highest value

when the plant is located close or in residential areas or industrial parks. In this case, the plant can be easily connected to the water network on the early stages of construction. Often production of heat can generate more money for a certain waste-to-energy plant than the production of electricity [2]. Thus in Bydgoszcz (Poland), the local waste-to-energy plant generates 14 MW of heat and 3 MW of power.

Air pollution control system is an integral part of waste incineration process. The costs of this stage account for two-thirds of the overall capital investment of the project. Modern gas cleaning systems underwent a long process of development encouraged by frequent changes in EU regulations. Nowadays such systems consist of several stages that fulfill different functions – reduction of particulate matter, of gaseous pollutants and of heavy metals [4]. Typical stages of flue gas cleaning are a dry or semi-dry scrubber, baghouse filter, activated carbon reactor. In some cases, electric precipitators and quenchers are applied.

## 2.2. Air pollution control on waste-to-energy plants

Air pollution control (APC) is a set of integral measures to neutralize the harmful influence of the flue gases. APC systems can be responsible for 2/3 of the investment capital of a waste-to-energy plant. They have an impact on the composition of fly ash and emissions released into the atmosphere. The choice of a proper APC system is a complex task involving an advance decision making [5].

Table 1 and 2 reveals the composition of untreated flue gas and of the pollutants present in the gas. High concentrations of HCl and the presence of compounds as dioxins and furans makes the process of gas treatment in waste-to-energy plant more complicated and expensive in comparison with similar processes in traditional fossil fuel power plants. As result, the limits for gaseous emissions for these plants are much stricter and are regulated by the DIRECTIVE 2000/76/EC on the incineration of waste [6].

*Table 1 Composition of flue gas prior to cleaning [4]*

Component	% (vol.) wet
CO <sub>2</sub>	10.8
H <sub>2</sub> O	16.2
N <sub>2</sub>	67.0
O <sub>2</sub>	6.0
Total	100

*Table 2 Pollutants in flue gas prior to treatment [4]*

Component	mg(Nm <sup>3</sup> ) <sup>-1</sup>
Dust	2500
HCl	1000
HF	10

SO <sub>2</sub>	300
Hg	0.8
NO <sub>x</sub>	350
CO	50
PCDD, PCDF	5.0

### 2.2.1. Nitrogen oxides

Oxides of nitrogen also known as NO<sub>x</sub> can occur in flue gas by two different ways. The first one is a result of the oxidation of the N contained in the raw waste (NO<sub>x</sub> fuel) and the second is the fixation of nitrogen inside a combustion chamber under the effect of high temperature. The factors that affect the formation of first category NO<sub>x</sub> are the content of nitrogen in fuel e.g., in the organic fraction, the excess of air and the primary/secondary air ratio. For the second category factors like temperature, pressure and gas residence time are crucial in the formation of NO<sub>x</sub>. Since the control of N in waste is not possible, measures need to be taken in order to create favorable air mixing conditions. Another important measure is the recirculation of the flue gas, which enable the prolongation of the combustion at lower peak temperatures and under a limited excess of oxygen. The first measure will lower the amount of thermal NO<sub>x</sub> while the second will restrict the reaction between N and O, which will not be available for such reaction. Another uniformly applied measure is the introduction of pulverized ammonia to the boiler. This can help to reduce roughly 20% of NO<sub>x</sub> [4].

### 2.2.2. Dioxins and furans

Dioxins and furans are the largest environmental concern when speaking about waste-to-energy incineration plants. They result from the burning of plastics and some other chlorine contained in the wastes. In order to prevent the formation of these substances a set of measures can be applied both during and after combustion. The incineration process itself is optimized to ensure complete combustion. Thus, current European regulations strictly prescribe that the gases formed in the combustion chamber must be exposed to a "temperature of 850 °C, as measured near the inner wall or at another representative point of the combustion chamber as authorized by the competent authority, for two seconds".

Removal of trace amounts of polychlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) is usually done with the help of scrubbing with the addition of activated carbon into the stream. A typical reactor is a conical or cylindrical vessel equipped with injectors. A mixture of lime and activated carbon is injected into the vessel forming a dense mist through which the flue gas passes. The result is the removal of acid gases due to reaction with lime and absorption of dioxins and furans in activated carbon. Additionally, activated carbon also serves as an absorbent of heavy metals - Cd, Hg, Pb as particularly volatile substances that tend to pass along the gas duct [4, 7].

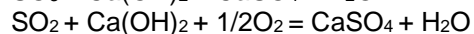
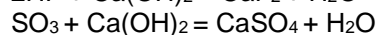
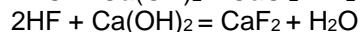
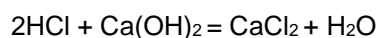
On the other hand, the use of lime and activated carbon increases the content of particulate matter in the flue gas, making necessary the use of baghouse filters immediately after the reactor to capture the particles that have not sedimented on the previous stage. Modern baghouse filters can ensure a particle capture efficiency of 98.8% [4].

### 2.2.3. Acid gases

Acidic gases are another important issue for air pollution control process. In a waste incineration process the most relevant are hydrochloric acid, hydrofluoric acid and sulfuric acid. Regarding HCl formation, 60% is from the combustion of PVC, 36% from paper materials and 4% derived from leaves and grass. In order to remove the acid gases some equipments are commonly used: packed, dry and semi-dry scrubbers, spray towers etc. It is verified that the efficiency of the process are higher for wet methods and lower for the dry ones. Concerning SO<sub>2</sub> removal, the efficiency decreases from 80 – 90% for packed bed scrubbers and spray tower to 60 - 80% for semi-dry scrubbers and to 50 – 60% for dry scrubbers. Regardless the high efficiency, wet methods have been losing popularity because they produce liquid effluent that needs to be treated afterwards. The EU has sent a clear message that the methods involving the use of liquid effluent will not be considered BAT [4]. Semi-dry techniques are the most preferable ones for the time being.

The understanding of semi-dry technique principles bears crucial importance for the present work since the reaction products in majority end up in the baghouse filter and, hence, can be found in fly ash later on.

The stream of flue gas at 230°C enters the spray absorber. Passing through profile baffle plates it mixes with lime hydrate suspension that plays a role of a scrubbing agent. The following reactions occur in the semi-dry scrubber [4]:



### 2.2.4. Particulate

The decision-making process regarding the removal of the particulate matter depends strongly on the required efficiency and the particle size distribution. The shape and size of generated particles is the major concern when selecting the technology and correspondent equipment. Systems on the wet basis generate effluent and sludge that must be further treated and dewatered respectively. The baghouse filter is one of the most spread solutions for W-t-E plants. It ensures 99% overall efficiency and up to 95% efficiency for the particles of the size of 0.2 microns and smaller. The efficiency depends on the gas temperature, incoming dust load, condensation point of metals. In order to remove particles from the fabric such methods as pulse-jet cleaning, shaking and reverse air flow are used. The filter can withstand temperature up to 220°C as well as moisture and chemical erosion. Special materials such as PTFE, glass fiber and Ryton



enable to do so. The melting point for most metals in the flue gas is above 300°C. The filter operating temperature is 220°C suffices to keep metals and chlorides in the solid state. An important advantage of fabric filter is that they operate passively without requiring power from the grid [4].

### **2.3. Type of waste and methods of treatment**

Waste incineration sector is, usually, divided into the following groups:

1. Mixed municipal waste incineration which is applied mostly to untreated domestic waste from households. These wastes can also have an insignificant amounts of non-hazardous industrial waste [7].
2. Pretreated waste incineration – applied to specific collected, sorted and treated municipal or industrial wastes. The characteristics of such fuel are different from the mixed waste. One of the most popular forms of pretreated waste is the refused-derived fuel (RDF) which will be discussed further in this work. [7].
3. Hazardous waste incineration - is incineration of industrial hazardous waste that can have a negative impact on the environment. Usually these facilities are located near the waste collection [7].
4. Sewage sludge incineration is used to utilize dried sludge obtained at wastewater treatment facilities. Sometimes this waste is incinerated along with the first category, yet nevertheless, the tendency of recent years heads toward sludge incineration on site largely due to additional costs connected to the transportation [7].
5. Clinical waste incineration – is dedicated to the thermal treatment of waste from hospitals and other healthcare institutions. This waste requires special treatment because of the possible threat that it might pose to the environment and human health. Infectious and hazardous microorganisms present in the waste should be neutralized under special conditions such as high temperature in isolated chambers [7].

In Europe, 25% of municipal solid waste is treated in incineration facilities reaching 62% in some European states making it the second waste management technique after recycling [7]. According to CEWEP (Confederation of European Waste-to-Energy Plants) waste incineration does not confront with recycling, supplementing it instead. The current market for waste-to-energy technology is based on 88 million tons of household waste remained after applying reduce, reuse and recycling techniques. In 2014 38 billion kWh of power and 88 billion kWh of heat were generated providing 17 million and 15 million inhabitants with respective energy resources. The estimated effect of saving fossil fuels equals 9 – 48 million tonnes depending on the type of fuel which corresponds to 24 – 48 million tonnes of CO<sub>2</sub> [8].

The term waste-to-energy, however, refers not only to incineration plants but also to facilities working on technologies like gasification and pyrolysis. Pyrolysis is the process of thermal decomposition of waste at temperatures 400 – 800 °C in an oxygen-free atmosphere. The chemical bonds are being broken under the

influence of heat which gives release to gases that are then directed to a combustion chamber. The resulting product of pyrolysis is the liquid oil-like fuel that can be further refined, combustible gases and char [2].

Gasification in its turn is the process of thermal treatment in low oxidant atmosphere to produce Syngas which can be used directly as fuel to produce heat and power or in chemical processes such as Fischer-Tropsch synthesis to produce liquid fuels and/or chemicals. .

In order to increase the value of waste-based fuel, raw MSW can be pre-treated and shaped into a material with improved physical characteristics. One of the widest spread forms of pre-treated MSW is refuse derived fuel or simply RDF. RDF is, as a matter of fact, ground, crushed and compressed combustible fractions of MSW. It is normally used in a form of pellets. RDF has enhanced calorific value and energy density in comparison with the original waste [1].

#### **2.4. RDF use in thermal processes**

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  $\text{NO}_x$ ,  $\text{SO}_x$ , 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. This is connected to the fact that these technologies will require air pollution control (APC) equipment of smaller size because of lowered flue gas flow and decreased temperature of the process. The APC equipment is the most expensive part of an incineration plant and amounts for up to 65% of the total capital investment [9].

Pretreatment of MSW is an important measure to increase fuel properties of the material before a thermal process. It can contribute to the improvement of the combustion stability and normalization of the water content. One of the most popular ways of MSW pre-treatment 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. The most widely used is  $\text{Ca}(\text{OH})_2$  [9].

Chlorine in MSW represents the potential source for the formation of HCl and, most important, chlorine-based toxic organic compounds such as polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). HCl is a hazardous substance responsible for the corrosion at local level, and for the formation of smog and acid rains that will have a negative impact on the environment. On the incineration plants, the corrosion caused by HCl is a major issue, there is the need to remove gaseous HCl from the flue gases before it reaches heat exchanger surface. This can be done by the use of lime as an

additive before the baghouse filters. The process of HCl removal is an important measure that helps to increase the overall efficiency of a power plant [10].

The major source of chlorine-containing compounds in the flue gas of a MSW thermal treatment processes is polyvinyl chloride (PVC). Thermal decomposition of these plastics releases chlorine that afterwards forms noxious compounds with other elements. HCl starts to be released at the temperature of 300°C. Another potential source for HCl formation is NaCl, which is presented in significant concentrations in food residues as kitchen salt. Several authors studied the formation of chloride acid gas and observed that both paper and some inorganic oxides such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> have an impact on the formation of HCl [11, 9].

An interesting observation made by Halonen et al. [12] was that more toxic chlorinated hydrocarbons were formed when the chlorine in the flue gas was from organic chlorine in comparison to inorganic one. Apart from that, the operation conditions of the incinerator are also responsible for the difference in the content of organic chlorine derived and inorganic chlorine derived compounds [12].

Spouting, a hybrid fluid-solid contacting bed, was studied as an operation mode for the incineration of RDF. It is believed that spout-fluid beds can be extremely efficient for handling sticky solids or agglomerates. The idea is to use a spouting moving bed to perform, at low temperature, the pyrolysis of RDF with the partial combustion followed by the combustion of pyrolysis gas at high temperatures using secondary air [19].

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. Table 3 reveals the fraction of Pb and Cd in different MSW steams. Looking to the values presented in the table, 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 fly ash. 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. There is a certain trade-off between the revenue obtained from the energy generation and the cost of the treatment and use of the fly ash [9].

*Table 3 Source, annual tonnage, and percent lead and cadmium in combustible MSW fraction [8]*

Source	Lead		Cadmium	
	tons	%	tons	%
Plastics	3488	71.0	567	88.0
Pigments	1169	23.8	70	10.9
Rubber and used oil	256	5.2	7	1.1
Totals	4913	100.0	644	100.0

## 2.5. RDF classification

In some EU countries (e.g. Italy) special standards are used for the classification of RDF. The main parameters defined by the standard in order to classify RDF as fuel are [14, 7]:

- Mean net calorific value - used as an economic parameter, dividing RDF into five classes.
- Chlorine content - technological parameter that has an important role in the definition of measures needed for the residue treatment
- The mercury content average value - represents an environmental parameter.

For each of the mentioned above parameters, 5 classes with specific limits were created. Using all possible combinations RDF can be divided in 125 classes. Apart from the main three parameters mentioned, a number of other important parameters can be determined. Among them, the most relevant are ash content, moisture, particle size distribution and heavy metal content. These parameters, however, are not regulated by the common EU standard UNI EN 15359 (2011) and needs to be defined by each member state individually [15].

It should be noted, that the properties and composition of RDF are site-specific, which means that the parameters of fuel are highly dependent on the place where MSW was collected and the collection method itself. Different waste management strategies, applied in the same region, can change RDF category. For instance, efficient collection of medical thermometers can decrease the content of mercury in the waste, placing the RDF produced from this waste into a different category. Another example can be garbage collection in the places where the consumption of kitchen salt is low, which can result in a lower content of Cl in RDF. The composition and hence classification of RDF is also dependent on mechanical biological treatment (MBT) facilities. Consequently, RDF classification is an input-driven which the dependence on the input waste streams is implied. Alternative classifications were suggested by several authors, which proposed to produce RDF according to the need of the consumer instead of produce fuel with pre-established parameters that later has to find its market. Another suggested change is relate to a wider range of calorific values within the classes to make fuel from different classes more universal [14].

The main potential end-users of RDF are power plants, cement kilns, and dedicated incineration plants predominantly with the grate combustion technology used. The use of RDF for co-combustion with other fossil fuels in cement production plants seems to be the most appealing option. The reason for this is the absence of strict fuel parameters for the cement production process. On the other hand, the use of RDF in the power plants, apart from the fact that is often not feasible, is also limited by very strict requirements regarding the fuel parameters. Generally, only 1 or 2 class of RDF within each criteria category is suitable for the process. The use of RDF on the designated waste-to-energy plants can be a promising solution, especially for the low-quality feedstock. This option, however, is the most vulnerable in terms of public acceptance. Decision makers have to keep in mind that the choice of a treatment option is highly dependent

on the market policies and local waste management strategies as well as the efficiency of their implementation [14].

## 2.6. Combustion of RDF

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 [16, 15].

In order to improve RDF combustion, MSW needs to be pre-treated. RDF is produced at mechanical-biological treatment facilities (MBT) by grinding and mixing selected fractions of MSW such as paper, cardboard, textiles, rubber, plastics, woody biomass etc. The RDF production diagram is represented on the Figure 1. In order to comfortably transport RDF and increase its energy content per unit of mass, it is usually shaped in pellets in automatic pellet presses. The pellets can have various sizes and shapes depending on the technological parameters required [17].

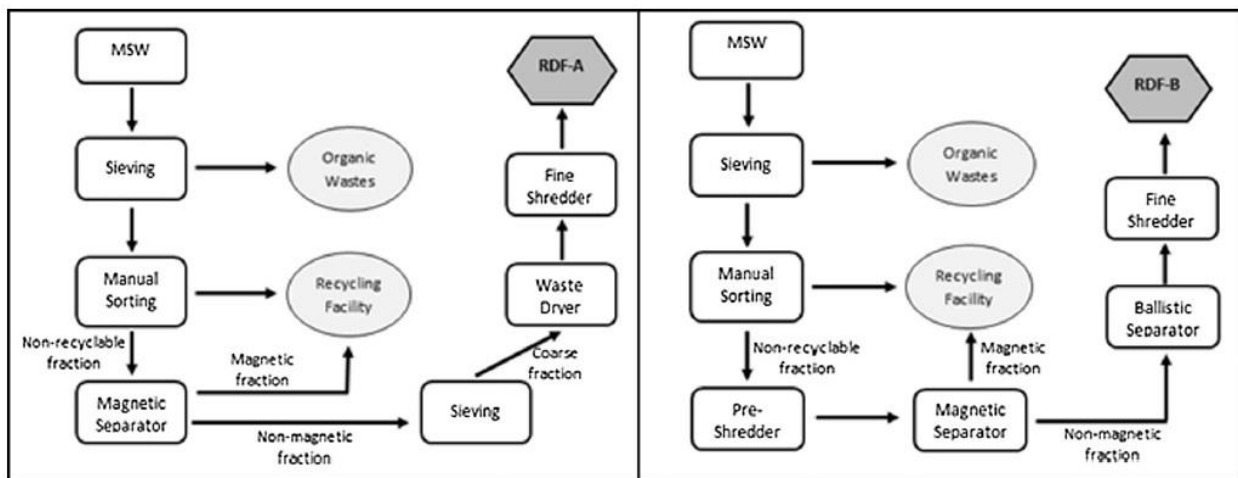


Figure 1 An example of two different schemes of RDF preparation [17]

When co-combusted with other fuels, RDF can affect the process considerably since its volatile matter content and ash content is usually different from the ones of coal or petroleum coke. Usually, RDF has higher volatile content than coal and petroleum coke and consequently lower amount of fixed carbon. This can have an influence on the co-combustion process kinetics [17].

Additionally, due to the high content of volatile inorganic compounds such as  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in RDF ash, the tendency to have slagging and fouling is high, which will undoubtedly cause problems on the boiler maintenance [17].

Because of the high content of volatiles in RDF, the co-combustion of RDF with coal can increase CO formation. This can also be explained by the fact that pellets, before being placed to the combustion chamber, have low temperature in comparison with the reactor. Incomplete combustion continues until the temperature of the pellets reaches the mean temperature in a chamber. Pre-heating of pellets before their disposal to the combustion chamber can solve this problem. It was also observed that smaller pellets tend to release more volatiles, hence the control of pellets size is also important. Carbon monoxide emissions are one of the major problems in RDF combustion. The combustion efficiency of solely burnt RDF process is usually up to 5% lower than for the blends with other fossil fuels [17].

The kinetic characteristics of the combustion process were studied by several authors. They indicated that the oxygen make the process of RDF combustion very complex in comparison with pyrolysis. The main concern is the gas-phase reactions between oxygen and volatiles produced by the decomposition of cellulose at lower temperatures. This phenomena promotes the char combustion on the early stages of the solid decomposition. The later degradation of char, according to the research, occurred only when the oxygen is present [11].

## **2.7. RDF pyrolysis**

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.

In spite of currently the main process of thermal treatment of RDF is the combustion in grate-fired incineration plants, this fuel can be successfully used for pyrolysis and gasification. The positive aspects of these alternative options are higher electric conversion efficiency and less contaminated residues in both liquid and solid state. The characteristics of the bottom and fly ash depend on the type of the process. Bottom ash obtained from RDF pyrolysis and gasification plants have different properties and composition than the one from the conventional incineration plants and, hence, can find much broader further applicability in industry. Nowadays, EU countries' legislation does not distinguish fly ash from different technologies, prescribing land filling and cement production as possible ways to the ash utilization. However this can change since numerous studies has already proved the suitability to use RDF pyrolysis ash in other applications, due, mainly to its different composition and leaching behavior [18, 9].

The efficiency of pyrolytic thermal treatment of RDF rests upon the design of complex, expensive large-scale units. The main, and one of the most expensive, part of such units is pyrolysis reactor. That is why

the understanding of pyrolysis of RDF has an utter importance. The improperly built reactor can cause significant issues for the feasibility of the process and, hence, might cause its owner financial losses. The understanding of the pyrolysis behavior of RDF is important not only for the construction of pyrolyzers but also for the modelling and design of the equipment for combustion and gasification, since pyrolysis is an integral sub-process in these thermal processes [11].

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 [19].

RDF also do not have the negative features of biomass fuel and, consequently, can be considered to be a primary fuel for pyrolysis and gasification processes. Two main disadvantages of biomass use are its expensive price and low concentration in places where it is collected. As MSW has a negative value, RDF producer can get its feedstock at prices close to zero. Additionally, MSW as a resource for RDF production is very well concentrated in collection and sorting centers. There is one more specific feature for the use of RDF in gasification/pyrolysis application. Since the composition of the fuel is highly heterogeneous, it can narrow the circle of potential users. Cement and steelworks prefer more selective input streams. In such a way pyrolyzers and gasification can be niche customers for refuse derived fuel [20, 11].

The importance of RDF pyrolysis is also explained with the fact that multiple plastics presented in RDF can be thermally cracked in order to produce liquid fuels, such as synthetic oil or different petrochemicals. Thus, RDF pyrolysis can play an important role in substituting fossil fuels and consequently contribute to a fight against global warming [21].

It would be fair to notice that the presence of chlorine-containing compounds in RDF can result in high content of HCl in flue gases, making necessary the installation of additional gas cleaning equipment, which can be a decisive factor for the plant's viability [9].

Different reactors have been studied for RDF pyrolysis. Among them fluidized and fixed bed reactors, rotary kilns as well as stationary and moving bed reactors. In a fluidized reactor, the recovery of hydrocarbons was investigated by numerous scientists. In many cases, promising results were demonstrated. The main issue of this research, though, is that they primarily are focused on the technological characteristic of the reactors and lack fundamental basics analysis which is important for understanding the role of particular species and reactions on the overall process. This Thesis is aimed to fill in the gaps in fundamental basics, particularly the ones connected to the determining the kinetic parameters for the RDF pyrolysis at low heating rates [18, 17].

In some works it was observed that the kinetic parameters of the RDF pyrolysis depend on several factors including temperature, heating rate, structure of the material, inert gas used etc. Apart from that the catalytic role of inorganic compounds should not be neglected. The composition of RDF can also have an influence on the process kinetics. Thus, the high concentration of plastics can strongly affect the activation energy [18].

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 [21].

## **2.8. Properties of ash**

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. Depending on a source and physical properties, one can distinguish several types of ashes. Differences between the types often determine their further applicability [3].

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 [3].

### **2.8.1. Bottom ash**

Bottom ash is a post-combustion residue of the combustion process that can be found bottom of the boiler. This ash contains non-combustibles, which, during treatment at high temperatures, are softened and melted to some extent. This type of ash is usually present as larger agglomerates. Bottom ash handling is usually done by inserting it into water, in order to cool it down, reduce dust and make it suitable for the further transportation [22].

As it can be seen in Table 4 and Table 5, in terms of chemical composition, the main constituents of bottom ash are silicon and calcium oxides. Obviously, all of the values differ depending on time and specific Waste-to-Energy facility, because of the nature of input material. All of the mentioned compounds are easy to predict – all of them are non-combustible, present in significant amounts in solid wastes collected [22].



Table 4 Typical oxides composition of MSWI bottom ash [22]

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
wt%	27,8	9,9	25,9	4	3,3	1,8	3,3	0,5	6,9	2

Table 5 Typical heavy metals composition of MSWI bottom ash [22]

Element	Ag	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn	Sn	Sr	V
mg/kg	4,1-14	19-80	900-2700	1,4-40	10-40	230-600	900-4800	0,01-3	0,7-1,7	60-190	1300-5400	0,6-8	800-6200	100-1300	170-350	36-90

Bottom ash is essentially composed by fused coarser ash particles. Frequently, these particles are quite porous and look like volcanic lava. If the bottom ash is competent, it can be used as lightweight aggregate, an important component to produce concrete blocks. Since the density of some bottom ash is less than half of conventional aggregate, the concrete blocks will be much lighter and just as strong. On the other hand, due to the relatively high presence of trace metals, namely lead and cadmium, as well as salt content, it is a significant concern, if bottom ash derived materials should be used as an aggregate substitute material [3].

One of the most common uses for bottom ash is as structural fill. At many construction sites, large quantities of fill are frequently required to level low places for construction and drainage purposes, build embankments, fill trenches, backfill foundations, etc. The fill is typically local aggregate or crushed stone, but bottom ash is also used when available and when its transport is economically viable. Because of calcium and other salts presence, bottom ashes are susceptible to the cementitious reaction, especially when it is a part of combined ash, which contains unreacted lime. The presence of high salt content can be problematic in terms of corrosiveness if in contact with metallic structures and, it can originate a decrease of binding properties when biomass ash are used as an additive in Portland cement concrete [23, 3].

Regarding the physical properties of bottom ash, Alhassan and Tanko [24] developed geotechnical properties of MSWI bottom ashes in order to determine its usability as construction materials. Their results indicated, that bottom ash has very similar properties in terms of specific gravity, permeability and stability than sand and gravel. California Bearing Ratio (CBR) is showing, that bottom ash can be used as a strong road sub-base material. All of the parameters checked in Alhassan's and Tanko's work shown, that according to American Association of State Highway and Transportation Officials (AASHTO) regulations, MSWI bottom ash can be used as a low-cost construction material.

Table 6 Selected geotechnical properties of bottom ash [24]

Property	Mean value
Specific gravity	2,2
Maximum dry density	1,65
% fine fraction	87,25
% silt fraction	1,5
Permeability (m/s)	$6,23 \cdot 10^{-4}$
CBR for unsoaked (soaked) 0,1 penetration	53,50 (27)

### 2.8.2. Fly ash

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 combustion gases (flue gas) requires specialized equipment such as electrostatic precipitators or fabric filters [23].

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 [22].

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 [22, 3].

Tables 7 and 8 reveal the typical composition of fly ash. Because of its nature, fly ash has similar properties as coal fly ash, what allows to use it as Supplementary Cementitious Material, however, salts presence blocks off the possibility of direct usage [23].

Table 7 Typical oxides content in the MSWI fly ash [22]

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
wt%	18,8	12,7	24,3	4	1,6	4,3	5,8	6,4	2,7	1,5

Table 8 Typical content of heavy metals in MSWI fly ash [22]

Element	Ag	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn	Sn	Sr	V
mg/kg	31-95	31-95	920-1800	250-450	29-69	140-530	860-1400	0,8-7	0,8-1,7	95-240	7400-19000	6,1-31	19000-41000	1400-1900	80-250	32-150

## 2.9. Treatment of MSWI residues

In general, there are three main methods to deal with the residues left from the MSW mass burning process:

- Separation methods
- Solidification and stabilization
- Thermal methods

The treatment strategies can be different depending on the specific goals to be reached and in practice can overlap each other. Thus, for example, separation, methods in many cases are applied as the first treatment stage followed by solidification. In all cases however the reduction of the environmental impact is the primary objective that can comprise of different sub-objectives such as decreasing the concentration of the contaminants, influencing leaching properties of the treated material or reducing the toxicity of certain substances [26].

## 2.10. Industrial applications of MSWI ash

### 2.10.1 Use as fertilizers

In theory, both bottom and fly ash has with main plants nutrients, namely, N, P and K. The high content of potassium and phosphorus in bottom ash makes it potentially suitable as a replacement to commercial fertilizers. The usage of fly ash as a liming agent is also possible due to the considerable amount of lime. Despite evident benefits that ash can provide to soils, there is a set of restriction regarding commercial usage of MSWI residues in agriculture. The main obstacle is related to the presence of heavy metals in ash that, if getting to the food chain, might cause severe environmental issues including health problems for plants, animals and humans. Toxic heavy metals might get to aquifers through soil by the process of leaching causing considerable environmental damage. Apart from the heavy metals, the high content of NaCl and other salts can be responsible for salt stress in numerous agricultural species. For the time being, more studies are required to prove the applicability of the idea [26].

In the research paper written by Rosen, Bierman and Olson the influence of the use of MSWI ash on the growth of Swiss chard and alfalfa was studied. The researchers attested that a number of favourable nutrients in the incineration ash was enough to provide substantial growth of the studied plants, comparable to the one caused by conventional fertilizers. Some problems raised concerns of the scientists, especially, the high content of molybdenum present in plant tissue as well as absorption of cadmium by plants. These heavy metals will pose a threat to the health of cattle and poultry if getting inside a digestion system of an animal. Apart from that, the study refers that the high concentration of soluble salts in the residues can negatively affect sensible plants [30].

### 2.10.2. Cement and concrete production

Oxides of Ca, Fe, Si and Al are the main composition blocks of the bottom and fly ash from incineration plants amounting for up to 65 % of the material composition. These chemical compounds are also the main ingredients in concrete and cement production. Therefore, the ash are considered to be a perspective replacement of feedstock in the production of Portland cement – the most widely spread type of cement worldwide [26].

The cement industry is one of the major contributors to global warming due to the high levels of CO<sub>2</sub> emissions. The use of fly ash in cement production can have a positive effect on the reduction of carbon dioxide release into the atmosphere. The main reaction involving CO<sub>2</sub> emission is the decomposition of calcium carbonate CaCO<sub>3</sub> to lime CaO and carbon dioxide. Since the same process is engaged in ash formation at waste incineration plant, the fly ash are already enriched with lime and hence can substitute a part of lime used in cement production. However, there are several issues that prevent a full-scale use of MSWI plants ash in cement industry. One of the most evident is the high concentration of chloride which will decrease the quality of the final product. Besides, the content of heavy metals that is usually above norm will surely cause environmental problems as with other industrial applications of the fly ash [25].

Ash pre-treatment techniques as washing and electrochemical process can help to overcome these problems, reducing chloride and heavy metals amount. But, even after such measures the amount of ash in the process should be carefully controlled [26].

There are several studies that analyse the hydration of cement clinkers. The content of alkali metals and the content of heavy metals are two parameters that have opposite influence on the hydration process. The hydration rate of clinkers that includes ash that was initially washed will be lower than the one without this ash, since in washed ash the alkali metal content is low. The presence of chloride and sulfates in the ash induces the ettringite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O) formation during hydration, which slowing down the hydration reaction [31].

The material obtained as result of solidification/stabilization processes can also be used as a replacement for cement. The concentration of residues up to 50% doesn't have a negative effect on the hardness and

strength of the material. The problem of leaching is still here but the leaching rate is in compliance with the requirements for road construction [26].

The bottom ash, in its turn, can be used in the production of concrete. Researchers indicate that the amount of gravel to be replaced by bottom ash can harmlessly for durability reach as much as 50 %. However, for this purpose, the residues must be treated with sodium hydroxide for 15 days. Without this kind of treatment, the cracks and swelling can occur due to the reaction between Al in ash and cement. Fly ash from waste incineration process can also be used as light-weight concrete aggregate in the form of pellets. The resulting product can be successfully used for the construction of isolation walls as it is being done in some Austrian landfills. Another proved safety usage of waste incineration plant residues is the use of solidified fly ash in Portland cement mortars. With low leaching rates and high compressive properties, it is a cheap and effective candidate to replace aggregate in mortars. Some researchers mentioned the possibility of enhancing the reuse of ash in the concrete industry by using water washing under the specific condition of pressure equal to 28 N/mm<sup>3</sup>, the sintering temperature of 1140 ° C for 60 minutes [32].

The leaching is still of the most important concern for the application of residues in cement and concrete industries. In spite of the fact that numerous researchers proved heavy metals leaching to be insignificant, yet sudden local leaching may occur in the case of construction damage or heavy weather conditions [27].

In Japan, some successful experiments on using the high quantities of ash in cement clinker were conducted with the resulting product gaining a name of Ecocement. In this process, the energy from MSWI plant is used to turn limestone into lime with the follow-up use of the latter in Portland cement production and later use of bottom and fly ash as feedstock in clinkers production [26].

### 2.10.3. Road pavement

On Figure 5, the typical layers of road pavement layers are presented. The upper layer consists of bituminous coating and asphalt and provides contact between car wheels and the road itself and that is why it should be even and durable. The next layer is called base course and its purpose is to distribute load evenly. Traditional materials for these layers are cement concrete, granular gravel, ground rock, materials stabilized with lime. The third layer is a sub-base and is constructed from gravel or materials stabilized with cement. The last layer called subgrade is normally just evened soil and serves as the foundation for the road [26].

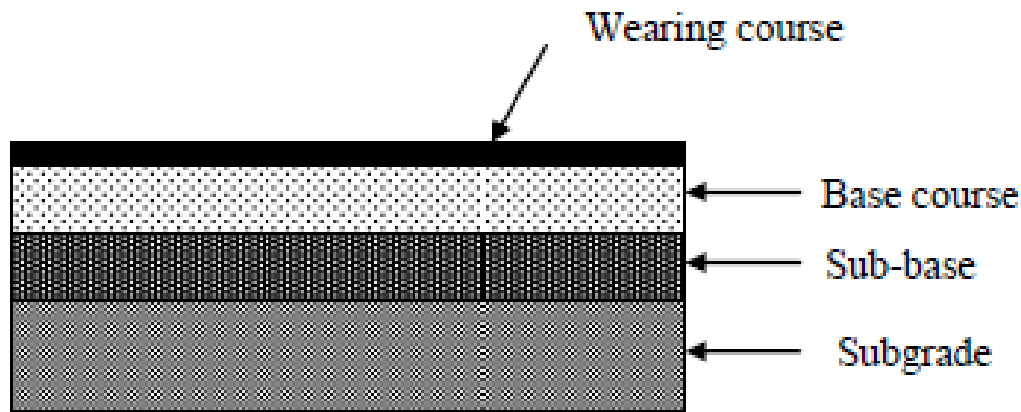


Figure 2 Traditional road pavement structure [26]

The waste incineration plant bottom ash can be, possibly, used as a substitution for the materials used in base and sub-base layers. In Sweden, an experimental road was built to test the properties of incineration ash as road construction material. The experiment proved that residues can safely replace granular gravel in the road's sub-base layer without releasing into the environment such harmful substances as Co, Fe, Ni, Mn, Pb as well as nitrate-nitrogen. A similar test was conducted on a specially created road in France where during 3 years the measurements of leaching were made. The results showed that the content of heavy metals in the leachate (the contaminated liquid released when the ash is contacted by water) is within the limits for drinkable water. The conclusion was that the use of MSWI plant residues is totally acceptable in road construction [4]. In Japan, the ash from local waste-to-energy plants was delivered to a stone producing factory to use it as material for the production of payment blocs. The study results indicated that those blocks posed no harm to either environment or human health, which consequently led to their usage as construction materials for the pavements in Chiba Prefecture park [33].

In some cases, however, leaching of contaminants did evoke environmental concern. The possible solution in such cases can be the pre-treatment of ash with washing methods to reduce heavy metals concentration. Mulder in his works reported that in most of the cases, fly ash without pre-treatment did not meet environmental regulations, whereas ash pretreated before stabilization procedure by washing meets the strictest European norms [26].

#### 2.10.4. Zeolite production

Zeolites are materials primarily consisted of silica-alumina that have extremely porous structure and are used as catalysts in numerous chemical processes such as oil cracking or biofuel production as well as adsorbents and ion-exchangers. Coal-fired power plants fly ash that consists mainly of  $\text{SiO}_3$  and  $\text{Al}_2\text{O}_3$  have been used as raw material for the production of artificial zeolites for decades. Despite the lower content of silica and alumina oxides in waste-to-energy incineration plant ashes (up to 24%), some zeolites were

successfully produced out of it by the processes of fusion and hydrothermal treatment [26]. Such parameters as surface area and CEC increased significantly for zeolites made of incineration fly ash in comparison with the initial material. Regardless the fact that the parameters appeared to be lower than the ones of commercial zeolites, however, the feasibility of using MSWI residues as raw material for the production of zeolites was proven. The main drawback was the liquid produced as a sub-product. High concentration of heavy metals in it indicates a need to further treatment [14].

To increase the quality of zeolites obtained from MSWI plant ash there is the possibility to mix it with ash from coal-fired power plants, which has a higher percentage of alumina and silica oxides. The property of synthesized zeolites is highly dependent on the temperature, crystallization time as well as on the concentration of NaOH. Different zeolites can be synthesized under different conditions. Thus, the production of Zeolite X requires lower NaOH/ash ratio and reaction temperature whereas synthesis of Zeolite HS favors higher NaOH/ash ratio and temperature [34].

Chinese authors Fang, Zhang and Feng demonstrated an artificial zeolite made from the mixture of fly ashes from MSWI plant and coal-fired power plant that showed better absorption capacity, equal 121.97 mg/g, than traditional artificial zeolite made of exclusively coal fly ash. Other studies showed that the zeolites modified with iron (II) atoms and based on the fly ash demonstrated adsorption properties no worse than for many commercial adsorbents. In spite of the fact that bottom ash is much more rarely used for the production of zeolites, still, some successful experiments were performed on the synthesis of zeolites from that material using alkaline hydrothermal treatment [35].

#### 2.10.5. Glass and ceramics production

The commercial production of glass, glass-ceramics, and ceramic materials draws attention of material scientists working with MSWI plant residue substances. As fly and bottom ash contain oxides of calcium, alumina, and silica in high quantities, its use, as a replacement of the clay for the production of ceramics, is possible even without additional treatment. Some researchers showed that the introduction of 20% of bottom ash into a body of a ceramic tile has no negative impact on its mineralogical and thermal characteristics. However, high content of chloride and potentially organic compounds can cause noticeable problems to tiles if fly ash instead of bottom one is applied. In the same research, the addition of 20% of fly ash to the tile body resulted in high compressive strength and minor water absorption after sintering at 960 °C. Additionally, a number of heavy metals leaching were diminished to 10% of that in initial material. In terms of durability of tiles though, even 50% amount of ash added during production displays values within acceptable limits [26].

During vitrification highly toxic substances got encapsulated into glass and, simultaneously dioxins and furans got entirely decomposed under the influence of temperatures higher than 1300 °C. The vitrified ash can have several applications such as road base feedstock, blasting grit, embankments, and pedestrian sidewalks, in the ceramic tiles production, water permeable blocks etc [23].

Glass-ceramics are fine polycrystalline substance obtained in the process of special heat treatment of glasses with a specific composition. They go through a controlled crystallization process to the low-energy crystalline state. Such materials can find versatile applications due to the fact that their mechanical and thermal characteristics are superior in comparison to the ones of parental glass. There were several studies conducted to determine the compliance of vitrified incinerator fly ash to the production of glass-ceramics. The appropriateness of using fly ash as raw material for glass-ceramics was proved due to its mechanical and thermal properties. The reuse of fly ash in the glass-ceramics industry at relatively lower temperatures was demonstrated with the help of additives. Thus, the process was successfully undergoing at a temperature of 1200 ° C instead of 1500 ° C which made the technique much less energy consuming and increased its viability. The obtained glass has less content of heavy metals than the raw material but when exposed to water, some leaching might occur. This phenomenon undoubtedly shrinks the possible application field of the products. Park and Heo tested the glass with inclusions of MSWI fly ash and concluded that a number of heavy metal ions have concentrations in the leachate is below the current environmental norms [26].

#### 2.10.6. Stabilizing agent

The fly ash have been tested as possible internal coverage layers in landfills. Some results showed that, the use of ashes in landfills with methane collection can have a positive effect on methane yield, intensifying bacterial activity and digestion rate. The toxic compounds that are present in ashes do not have significant adverse impact on anaerobic bacteria.

Additionally, incineration plant residues' potential as a binder for solidification/ stabilization of sludge was investigated. Research showed that the mixture in a proportion of 50 % sludge, 45 % fly ash, and 5 % cement can provide sufficient stabilization effect. The advantages of such co-disposal include considerable saving of space in landfills and minimization of cement consumption for sludge stabilization [36].

#### 2.10.7. Adsorbents

The need to remove chemicals and heavy metals from waste water require the wide use of materials called adsorbents. MSWI residues posses adsorption properties and, hence, can be used for waste water cleaning. However, there is a major problem of such application since with the contact with water the ashes themselves can generate heavy metals in so-called leachate. These metals can easily get to water poisoning it and making it unsuitable for follow-up usage. The bottom ash, however, tends to contain much less heavy metals and consequently can be used as adsorbent [37].

Cation exchange capacity (CEC) is an important parameter to estimate the adsorption potential of material. CEC is dependent on the particles size of bottom ash. The lower are the particles the higher is CEC and specific surface of the adsorbent. If the particle size is decreased from 120 to 100 mesh, the CEC will go up from 8.0 to 24.6 meq/100g [38].



Another application of bottom ash adsorbent studied is the removal of dyes from wastewater. The removal rate reached 98% and can be comparable to the conventional adsorbents. The quality of removal though is in a close relation to the chemical structure of a certain dye [26].

Bottom ash adsorbents were also investigated in the process of gas purification. The technology was tested for the purification of landfill gas from hydrogen sulfide, methyl mercaptan, dimethyl sulfide without negative impact on the methane yield, The sequestration rates of 1 kg of bottom ash for hydrogen sulfide, methyl mercaptan, dimethyl sulfide are 3.0 g, 44 mg and 86 mg respectively. The likely reason for the first two gases adsorption is acid-basic reactions involving sulfur mineralization under low solubility metal sulfides [26].

Fly ash have also been examined as an adsorbing agent for dyes and metallic ions. The main positive aspect is the material's neutralizing ability because of a significant amount of lime used in desulfurization of flue gasses process. Hence this kind of residue can be used to treat contaminated water with enhanced acidity. It should be noted, that the final pH of the treated water is in the strong dependence on the liquid to solid ratio [37].

In the table below the most economically viable applications of waste incineration plant residues are listed. Regardless the application and the technology in almost all cases, the waste material required several stage pre-treatment to decrease possible harmful effects of the ready-to-use products [26].

*Table 9 Applications of MSWI ashes [26].*

Type	Application	Composition%	Country
BA	Aggregate in concrete	up to 50%  replace up to 15% of	France
BA	Aggregate in concrete		Slovenia
BA	Road base		Spain
BA	Adsorbent for dyes		India
BA	Concrete		Italy
Mixed	Cement clinker	up to 50%	Portugal
Mixed	Cement clinker	44%	Japan
Mixed	Cement clinker	15%	Taiwan
Mixed	Cement clinker	1.75% FA 3.5% BA	Taiwan

Mixed	Concrete		Spain
FA	Concrete	50%	France
FA	Eco cement	50%	Japan
FA	Ceramic tile Binder for stabilizing		China
FA	Sludge	45%	China
FA	Glass ceramic	75% FA, 20% SiO <sub>2</sub> , 5% MgO, 2% TiO <sub>2</sub>	Korea
FA	Glass ceramic (low melting temperature)		China
FA	Cement clinker	replace up to 30% of raw material	China
FA	Blended cement	up to 45%	UK

### 3. Materials and methods

#### 3.1. TGA/DSC

Thermogravimetric analysis (TGA) 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 [40].

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 softwhere installed. This software enables to store the experiment data. The image of the Simultaneous Thermal Analyzer (STA) 6000 is presented on the figure below.



*Figure 3 Simultaneous Thermal Analyzer (STA) 6000*

#### 3.2. Fuel analysis

The RDF for this study was obtained from a waste management company in Lisbon, Portugal. It has a 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 6.



Figure 4 Studied RDF. 1 – original RDF, 2 – ground sample

Table 11 shows the composition and properties of RDF used for the current study. RDF has a high volatiles content of 80 wt%. Won Seo et al. discussed the influence of the volatile matter on the devolatilization for different alternative fuels [20]. An interesting feature of RDF combustion is the formation of agglomerated particles. The possible explanation for such formation might be the presence of plastics in RDF that when melting can originate agglomerates. The properties of RDF are presented in the table below:

Table 10 RDF composition and properties [39]

Parameter	Fuel: RDF
Proximate analysis (wt%, as received)	
Volatiles	80.2
Fixed carbon	2.8
Moisture	2.6
Ash	14.4
Ultimate analysis (wt%, as received)	
Carbon	44
Hydrogen	6.8
Nitrogen	1
Sulfur	0.06
Oxygen	31.14
Heating value	
High heating value (MJ/kg)	26.9

Low heating value (MJ/kg)	25.1
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The proximate analysis of the fuel was estimated using TGA curves, obtained from TGA experiments, which consist, firstly, in carry out test of RDF pyrolysis to determine the volatile content and moisture content. After the pyrolysis, what remained in the crucible was the combination of fixed carbon and ash - char.

The amount of water can be found from the following expression [2]:

$$M = \frac{m_{sp}^{in} - m_{sp}^{200}}{m_{sp}^{in}} \cdot 100, [\%] \quad (1)$$

Where  $m_s^{in}$  is the initial mass of the sample before the pyrolysis experiment and  $m_{sp}^{200}$  is the mass of the sample subjected to pyrolysis at 200 °C.

Knowing the moisture content in the sample, the amount of volatile matter can be easily found from the following expression [2]:

$$VM = \frac{m_{sp}^{in} - m_{sp}^{200} - m_{sp}^{fin}}{m_{sp}^{in}} \cdot 100, [\%] \quad (2)$$

In this expression  $m_{sp}^{fin}$  corresponds to the final mass of the sample after pyrolysis.

Finally, to estimate the content of fixed carbon and ash, the char was subjected to combustion tests in the same TGA. The amount of fixed carbon was found as the difference between total weight of the sample before combustion and the weight of the ash left after combustion.

An expression for fixed carbon can be written in the following form [2]:

$$FC = \frac{m_{sc}^{in} - m_{sc}^{fin}}{m_{sp}^{in}} \cdot 100, [\%] \quad (3)$$

Here  $m_{sc}^{in}$  and  $m_{sc}^{fin}$  are, respectively, initial and final mass of the sample during the combustion experiment.

Ash content can be determined as:

$$Ash = 100 - M - VM - FC, [\%] \quad (4)$$

### 3.3. Pyrolysis

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 in order to observe the behaviour in the isothermal stage.

### 3.4. Combustion

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 Table 12, the parameters of each program are illustrated.

*Table 11 Program parameters for TGA experiments*

Sample name	Weight	Gas/Type of reaction	Heating rate, °C/min	Maximum temperature, °C	Isothermal part longevity, min	Cooling rate, °C/min
RDFcomb1	24.52	Air	5	800	10	50
RDFcomb2	14.11	Air	10	800	10	50
RDFcomb3	29.98	Air	20	800	60	50
RDFpyro1	22.40	Nitrogen	5	800	10	50
RDFpyro2	18.75	Nitrogen	10	800	10	50
RDFpyro3	22.19	Nitrogen	20	800	60	50

### 3.5. Kinetic model

The model applied in the current work assumes that the sample consists of a number of pseudocomponents with initial masses  $w_1, w_2, w_3, w_4$ . One pseudocomponent represents a set of species that can be described by the equation with common parameters of activation energy  $E_a$  and reaction rate constant  $k$ . In reality a number of species in such complex material as RDF is higher than the one used in the applied model. The differences in reactivity for every pseudocomponent are described by different values of activation energy. There is an assumption that all the species go through a first order decay. Choosing of an appropriate number of species plays an important role in the model precision.

According to the numerous research the kinetic parameters depends on a number of factors including temperature, pressure, heating rate, ambient gas, mineral part composition etc [11].

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 according to the differential rate law for the 1-storder reaction [42]:

$$\frac{dW}{dt} = -k(T)W \quad (5)$$

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:

$$W_{i+1} = W_i + \frac{dW}{dt} \cdot (t_{i+1} - t_i) \quad (6)$$

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 time of the current and following moment.

Index  $i$  is responsible for a number of pseudocomponents and index  $j$  for time steps. In the initial moment of time  $j=0$ ,  $W_{i,0}$  equals to the assigned to each pseudocomponent value. For water, cellulose, hemicellulose and lignin the assigned values are 0.1, 0.3, 0.3 and 0.2 respectively based on the visual analysis of the TGA curves. The additional fifth component corresponds to fixed ash. The value assigned to this component is 0.1. The values were chosen based on the literature review of RDF kinetic models [40, 42, 43]. Since the relative weight is used in the model, the sum of  $W_{i,0}$  values must equal 1. Time step is a standard for the TGA analyzer used in the experiments and equals 0.003 second.

According to the Arrhenius relationship [40]:

$$k = k_0 e^{-E_a/RT} \quad (7)$$

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 [44]. An alternative parametrization of Arrhenius equation was proposed by several authors in order to minimize correlation between the equation's parameters [43, 44]:

$$k = k_{T_{ref}} \cdot e^{-\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)} \quad (8)$$

Here  $k_{T_{ref}}$  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. [44].

The reference temperature  $T_{ref}$  is widely defined as the mean temperature within the experiment temperature range. In some studies it is highlighted that the choice of reference temperature can have tangible influence on the kinetic parameters estimation [44]. This work, however, the decision was made to choose  $T_{ref}=573^\circ\text{C}$ .

The kinetics of RDF fuels were studied using TGA technique at three different heating rates of 5, 10, 20 °C. A simple kinetic model was applied to simulate both combustion and pyrolysis process, hence the experiments were performed in two different atmospheres – air and nitrogen consequently. The total reaction rate is expressed as the summed up rate of four individual components water, cellulose, hemicellulose and lignin. The addition of the fifth component is needed to describe the residual matter which in the case of combustion is fixed ash and in the case of pyrolysis is fixed carbon plus fixed ash.

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.

$$\text{Min OF} = \sum_i^n \sum_j^5 (w_{total\ i}^e - w_{i,j}^c)^2 \quad (9)$$

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 equaled 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:



$$w_5^c = w_{ash}^c = 1 - \sum_j^4 w_j^c \quad (10)$$

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:

$$w_{total}^c = w_1^c + w_2^c + w_3^c + w_4^c + w_{ash}^c \quad (11)$$

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.

For the optimization problem the parameters  $k_0, E_a$  and  $w_{i,0}^c$  are the variable parameters to which the initial values were assigned. The fitting of the curve representing the heating rate of 20°C/min is turned out to be the most problematic one. Consequently, the optimization problem was solve, in the first place, individually for this heating rates and the results obtained were used as initial values afterwards for the overall optimization. The weight fraction  $w_{i,4}^c$  seems to play a key role in the shape of the slope at higher temperatures. In this regard, the parameter was optimized individually keeping  $k_0$  and  $E_a$  unchanged. The results obtained for both combustion and pyrolysis model are represented and discussed below.

The comparison of the experimental and modelled curve is done with a help of the following expression [45]:

$$F = \left( 1 - \frac{\sqrt{\frac{OF}{n}}}{W_{max}^e} \right) \cdot 100\%, [\%] \quad (12)$$

Where  $W_{max}^e$  is the maximum value of the relative weight obtained from the experimental data.

### 3.6. Ash samples studied

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 course 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.

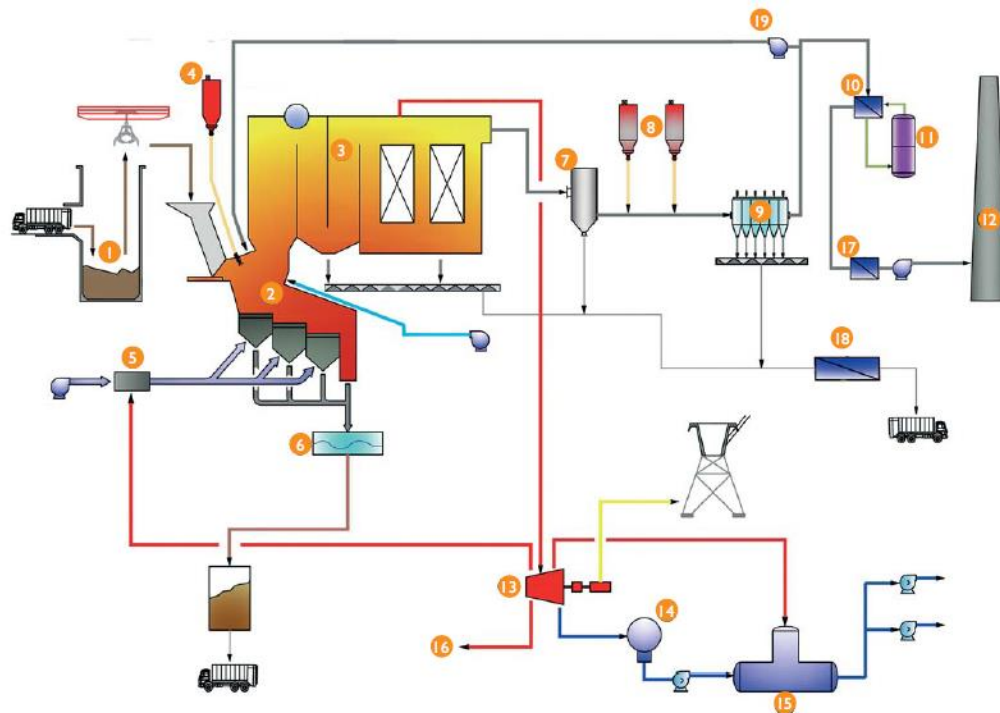


Figure 5 Technological diagram of the Waste-to-energy plant in Bydgoszcz (Poland) [49]

The fly ash samples were collected from the waste-to-energy plant in Bydgoszcz. The principle diagram of the plant's operation is presented above. Municipal solid waste is delivered to the facility by 10-ton garbage trucks that dump trash down to the waste pit (1) or the bunker. From the pit, wastes are placed in the furnace (2) by two moving cranes. Operators can control the process from the control room located above the bunker. The furnace is equipped with a moving grate that transfers trash across its bottom part. The furnace is connected to the boiler (3). In the furnace, the actual combustion of the waste materials occurs. Each of two furnaces has 18 ammonia pulverizers at the side walls. Their task is to spray ammonia solution coming from the ammonia silo (4) into the furnace to prevent the formation of NO<sub>x</sub>. Primary air comes from the bunker through the air preheater (5) and is supplied to the furnace by numerous air nozzles divided into 5 zones. Burnt down trash falls down to the slag extractor where it is mixed with water and afterward is transported as slag to the valorization house where the material is dried and subjected to the separation of fractions. In the meantime, hot flue gasses formed in the furnace go to the boiler where they take part in the heat exchange with water. The flue gas passage at the end of the boiler should be long enough to decrease dioxins and furans formation. The gasses then are directed to the conditioning tower or quencher (7) where they are cooled down before entering the reactor in which the main reaction on the neutralization heavy metals, dioxins, furans and SO<sub>x</sub> occurs. The reactants are supplied here from the activated carbon and lime silos (8). Afterwards, the gasses pass through the massive baghouse filters (9) to get rid of the

fine particles. After the filters flue gasses go through the gas/gas exchanger (10) and flow to the scrubber (11) in which the final cleaning happens. The interesting detail of the plant that scrubber does not carry much importance in the whole cleaning chain, however its presence was the obligatory condition for companies to win the initial tender. In the end the cleaned up gasses are let out to the atmosphere through the 40-meter high stack (12). As far as the water-steam cycle is concerned, steam formed in the boiler goes to the turbine (13) which has the potential to produce 13 MW of energy. The low potential worked out steam is directed to the water-cooled condenser (14) which serves as one of the heat exchangers. From the condenser, it needs to be subjected to the removal of the dissolved gasses. This process occurs in the deaerator (15). Part of the steam can also be used to heat up the water circulating in the district heating system (16). Apart from that, the steam/gas heat exchanger (17) is located at the very end of the flue gasses pass in order to give away the steam as much heat as possible. The most dangerous residues of the process – fly ash collected at the baghouse filters are treated in the FGT residues system (18) where the particles are mixed with water and cement and then carried away to a landfill. Another interesting feature of the technology is the application of the flue gasses recirculation system that is a powerful means to control the temperature of the combustion process.

### **3.7. SEM and EDS**

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 determination of the elemental composition of the studied material is based in the EDS technique. The essence of this method is to check particular areas on the images taken by the microscope.

The principle of a scanning electronic microscope operation is as follows: electron gun releases a bunch of electrons that go through the electron lens, so-called 1-th condenser, and scan coils. After the magnification control is done the beam gets to the specimen's surface. The reflected from the surface beam reaches a detector that sends the signal further to the amplifier to increase its intensity. On the final step, the amplifier sends the enhanced signal to the computer which in its turn transforms it and displays on the screen.

The interaction between the electron beam and the surface encourages the release of the secondary and backscattered electrons. Some signals coming from the surface can be linked to characteristic x-rays when energy dispersive x-ray analysis is applied. During these methods, the collisions of incident electrons with the electrons in discrete shells of sample atoms occur. EDS method is used to determine an elemental chemical composition and is usually coupled with the SEM technique.

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  $\times 10 - \times 1000000$ . The precision of EDS analysis that was used for the research in this paper is around 0.5 % on an atomic weight basis.

For the SEM/EDS characterization of fly ash, two samples of each fraction were analysed. LFA 1 and LFA 2 are two samples of the ash collected after baghouse filters. The abbreviation LFA stands for 'Light Fraction Ash' since ash at baghouse filters is usually lighter than the one collected upstream from baghouse filters. LFA 1 is an original material taken from the waste-to-energy plant and LFA 2 is an additionally thermally treated sample. Respectively, HFA 1 and HFA 2 stands for 'Heavy Fly Ash' following the same logic: fly ash collected on the economizer is the heaviest fraction of fly ash. Once again index 2 indicates thermally treated sample.

## 4. Results and discussion

### 4.1. TGA/DSC results

On the Figure 8 and 9 three mass loss curves for pyrolysis and three curves for combustion are demonstrated respectively. It is easy to notice three main zones of mass loss on every graph.

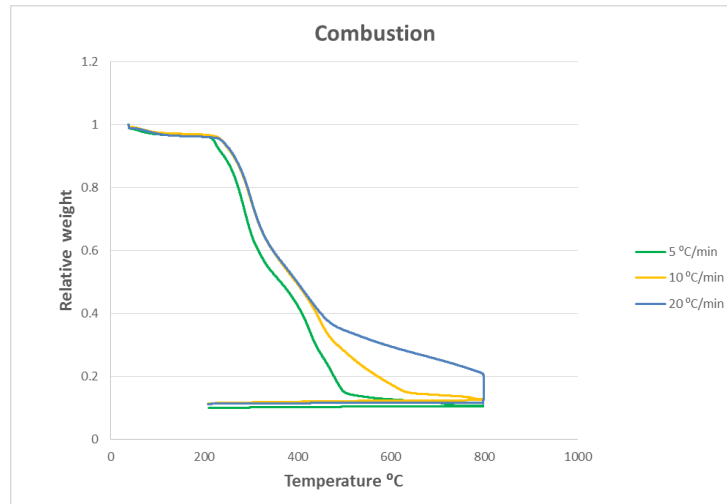


Figure 6 TGA curves obtained for RDF combustion at different heating rates

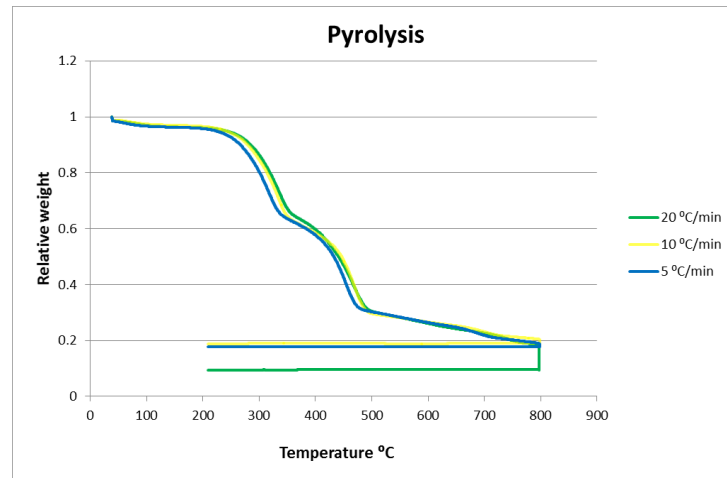


Figure 7 TGA curves obtained for RDF pyrolysis at different heating rates

The first zone occurs from the initial temperature to the sample temperature of 200°C. It should be noted, as well, that sample temperature differs from the program temperature, thus, when a sample reaches 200°C the program temperature is already about 213°C. The second zone is characterized by a very sharp mass loss and temperature range 200 – 360°C. The mass loss in this zone can be explained by the decomposition

of cellulose – the main component of paper and cardboard and hemicellulose that contains in woody biomass. The next zone temperature range is 360 - 490°C. In this zone decomposition of cellulose keeps going coupled with the vast lignin decomposition. In the final zone that starts approximately at 490°C and undergoes up to the maximum temperature of 800°C the lignin decomposition still occurs accompanied by massive devolatilization of charcoal [9].

## 4.2. Kinetic model results

The results obtained by the model demonstrated sufficient agreement with the mass loss curves based upon the experimental data. Consequently, the practical applicability of the model is proved for low heating rates. As far as higher heating rates are concerned, the additional research should be done for RDF material. The advantage of the proposed model is that it does not require the knowledge of the exact chemical composition of studied material.

In the Table 13 and 14 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 12 The amount of pseudocomponents obtained by the model*

Process	Hemicellulose %	Cellulose %	Lignin %	Fixed ash %	Moisture %	Volatile matter %
Pyrolysis	34.08	32.02	10.35	19.04*	4.51	76.45
Combustion	34.38	22.77	25.39	10.93	2.53	-

\*(including fixed carbon)

The activation energies and reaction rate constants are displayed in the table below

*Table 13 Reaction rate constant and activation energies obtained by the model*

	Water	Hemicellulose	Cellulose	Lignin	Fifth element
	Pyrolysis				
$E_a$ , cal/mol·K	2526.25	23753.18	41241.17	28880.10	7327.18
$k_0$ , min <sup>-1</sup>	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 <sup>-1</sup>	1884.51	0.3791	0.0014	0.0138	-

The following table reveals the fitting value calculated for every heating rate. Generally fitting for combustion looks better than for pyrolysis. Reaching its maximum at 5 °C/min heating rate.

*Table 14 Fitting value for different experiments*

Heating rate, °C/min	Type of experiment	Fitting, %
5	pyrolysis	95.37
10	pyrolysis	93.91
20	pyrolysis	94.23
5	combustion	97.62
10	combustion	96.87
20	combustion	97.04

In Figure 9, 10 and 11 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.

In order to guarantee satisfactory fitting for the highest rate, the optimization of the parameters for this rate was carried out individually. Then the results obtained for the highest rate were used as initial values for the overall optimization. Additional decision, that improved results for pyrolysis, was the introduction of the 5-th reaction. This reaction can be explained with a fact that some part of lignin does not decompose directly but instead is carbonized.

The plastic fraction can also influence on the shape of the curve in the high temperatures range. Even though the exact MSW fractions contribution in the studied material is not known, it is reasonable to assume that some plastics are present. The amount of plastics for industrially produced RDF according to Won Seo can reach 30.8%. The temperature range for the decomposition of stable plastics are 450 – 500 °C/min [20].

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% [20]. Numerous studies confirmed that high devolatilization yield and, consequently, decreased char yield is observed at higher pyrolysis heating rates [46, 47]. Apart from that devolatilization yield is virtually always higher if it comes to isothermal conditions in comparison to non-isothermal [20].

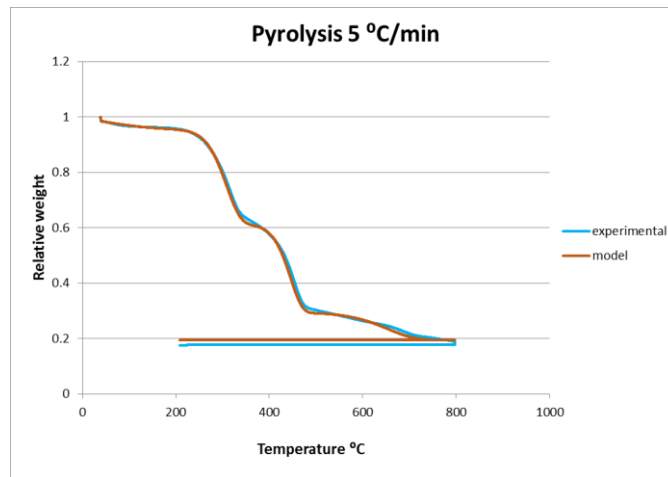


Figure 8 TGA curves from modeling and experimental data for RDF pyrolysis at 5 °C/min heating rate

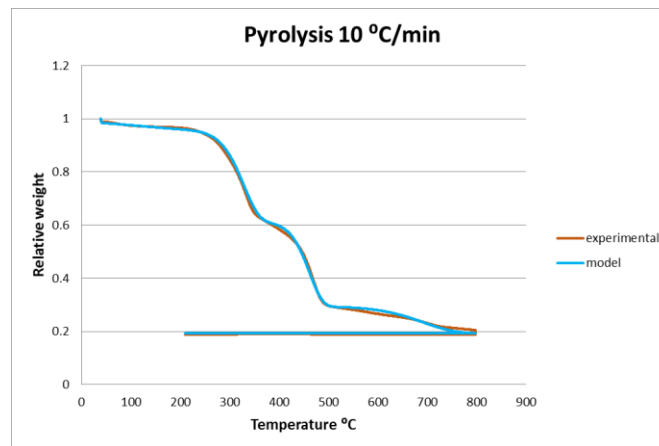


Figure 9 TGA curves from the model and real data for RDF pyrolysis at 10 °C/min heating rate



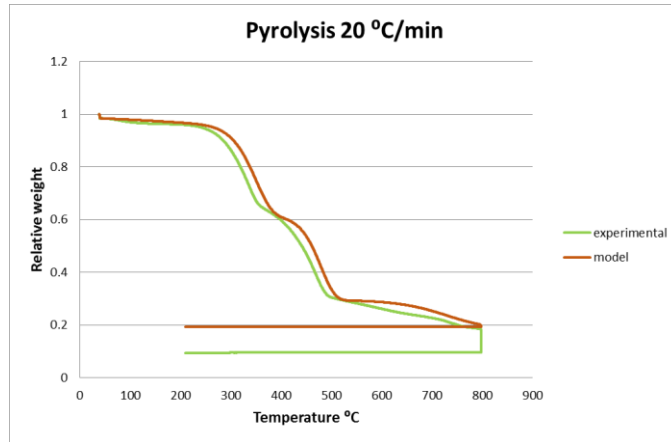


Figure 10 TGA curves from modeling and experimental data for RDF pyrolysis at 20 °C/min heating rate

The results for the combustion process at the heating rates of 5, 10 and 20 °C/min are represented on the figures 12, 13 and 14 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. However, the presence of plastics is not confirmed experimentally, since no distinctive endothermic reaction in the plastic melting temperature range was observed. 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.

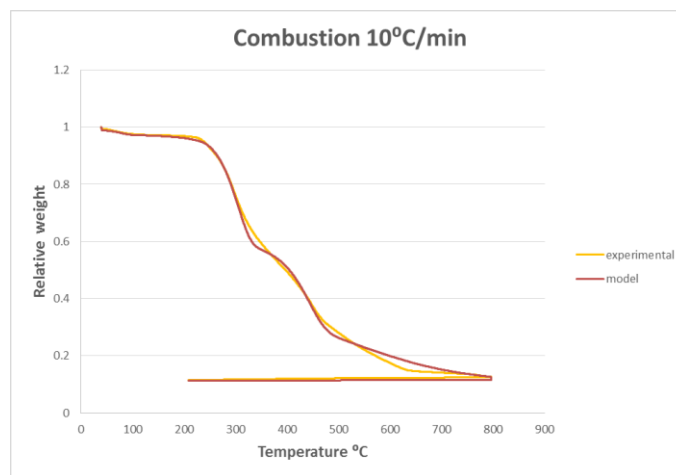


Figure 11 TGA curves from modeling and experimental data for RDF combustion at 10 °C/min rate

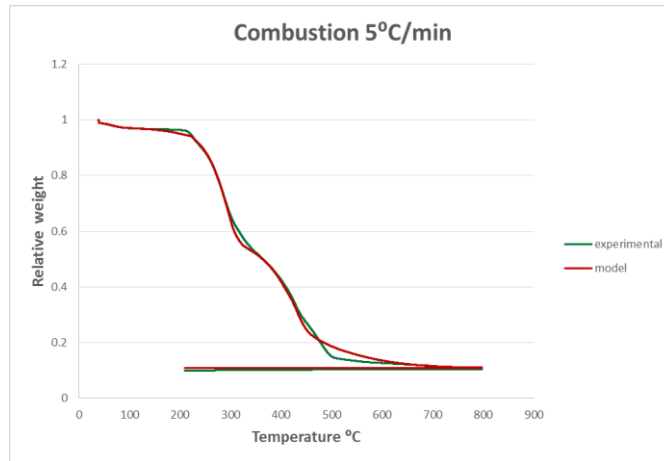


Figure 12 TGA curves from modeling and experimental data for RDF combustion at 5 °C/min heating rate

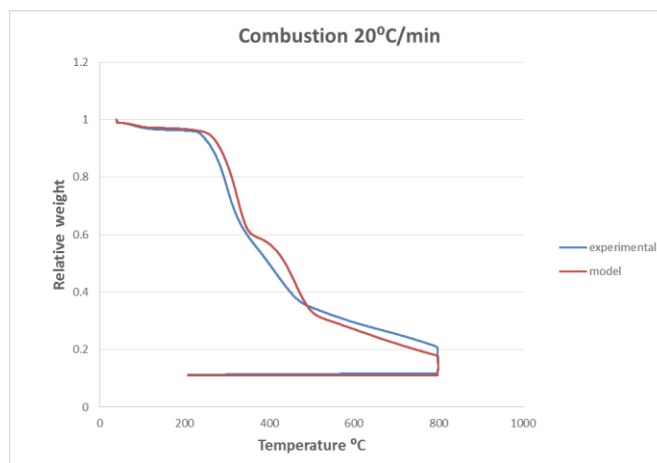


Figure 13 TGA curves from modeling and experimental data for RDF combustion at 20°C/min heating rate

In Figure 15 the mass loss rate at the heating rate 5 °C/min is illustrated. It can be observed that water vaporization in the model occurs only until 120 °C which is not totally correct, since in reality according to Senneca this process continues even at 200 °C [48]. The second peak responsible for the decomposition of cellulosic materials occurs in the range of 174 – 340 °C. This value corresponds to the ones referred in the literature [48, 20]. The third peak is in the range of 290 – 470 °C and it is assumed that represents the decomposition of cellulose as well as some plastics. Sorum at al. indicates in his work temperatures for decomposition of some plastics, namely PVC at 470 °C, LDPE at 472 °C and HDPE at 479 °C. Since the cellulose decomposition stops at around 400 °C, it is reasonable to assume that plastic were present in the RDF. Purple curve on the graph is responsible for lignin decomposition. Here one can observe typical range for some lignin-contained materials. Thus for agricultural residues, for example, thermal degradation lasts until 600 °C and even higher [44].

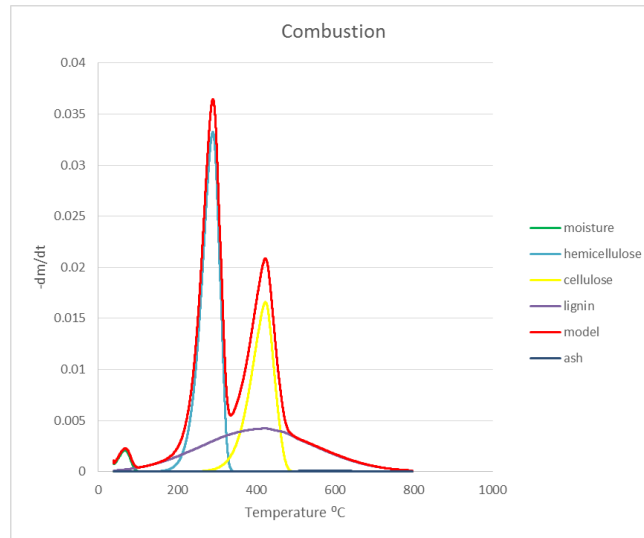


Figure 14 Mass loss rating curves for combustion at the heating rate 5 °C/min

### 4.3. Light fraction fly ash

For each sample, five regions (spectrums) were examined. The regions were chosen on the basis of morphological differences. The images below show the regions chosen for each sample. The elemental composition for each spectrum is presented in the tables below an image. The main elements detected for all samples are O, Na, Mg, Al, Si, P, S, Cl, K and Ca with Ti, Fe and Zn being trace elements. The morphology of particles appeared to be versatile: from fine amorphous powder to large spherical and cubic particles often partially covered with 'hairy' deposits.

On figure 20 magnified image of 'LFA 1' sample is presented with five spectrums from which elemental composition was checked. Oxygen is the most widely represented component reaching up to 65.42 % of atomic weight for the spectrum 2. In fly ash oxygen is an integral part of oxides formed during the fly ash formation such as  $Al_2O_3$ ,  $MgO$ ,  $SiO_2$ ,  $CaO$ ,  $P_2O_5$ ,  $K_2O$ ,  $N_2O$ ,  $Fe_2O_3$ ,  $TiO_2$ ,  $SO_2$  and some other [26]. Na and Cl are present in considerable amounts often appearing as cubic particles of sodium chloride. This compound is formed due to the treatment of exhaust gases with caustic soda which reacts with the Cl present in the gases and fly ash as a result of plastics thermal decomposition. Al and Si content ranges from 1.07 to 1.42 and 1.93 to 2.82 respectively and are much lower than in bottom ash. A considerable amount of sulfur was detected as a result of desulfurization stage of air pollution control system located upstream. Sulfur is mostly present as part of certain minerals and usually poses a limited threat. The average content of potassium is 5.14 % reaching 9.43 % in the spectrum 3. Another highly represented element is Ca, which occurs in such minerals as gehlenite, calcite, hydrogrossular and hydrated calcium phosphate [50, 3]. The average concentration of calcium in 'LFA 1' sample is 8.69 %. The EDS analysis did not show any trace heavy metals which in this particular case means that their content is lower than 0.1 – 1 %. It can be observed that particle size for this sample is versatile. Some particles are as large as 30

microns with the largest ones being silica calcium minerals with a significant amount of sulfur up to 13.66 %.

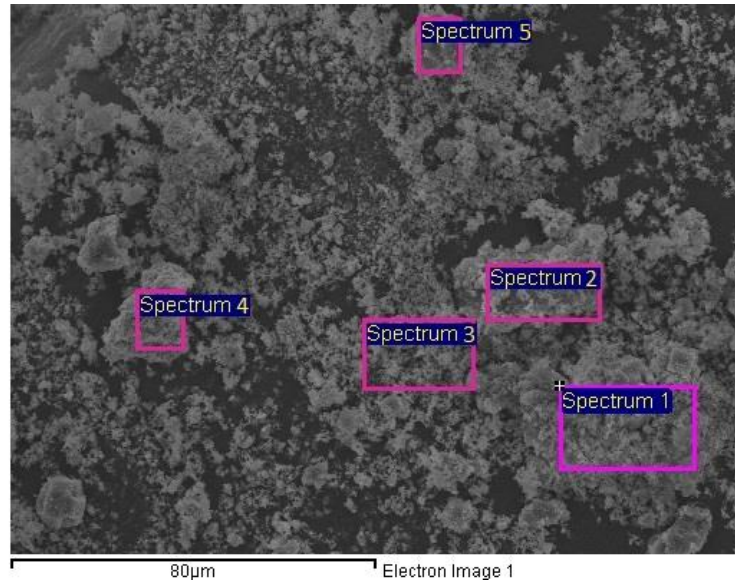


Figure 15 Light fly ash fraction 'LFA 1' with five spectrums chosen for the elemental analysis

Table 15 The elemental composition of light fraction of fly ash - spectrum 1

LFA1' / Spectrum 1	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	40.37	14.9		1.42	2.52		5.28	24.86	8.46	2.19			73.76	105.6	-17.752

Table 16 The elemental composition of light fraction of fly ash - spectrum 2

LFA1' / Spectrum 2	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	65.43	3.1						8.83	2.84	19.8			45.56	139.69	-50.812

Table 17 The elemental composition of light fraction of fly ash - spectrum 3

LFA1' / Spectrum 3	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	43.98	12.3		1.37	2.82		3.43	23.06	9.43	3.63			64.94	111.02	-26.188

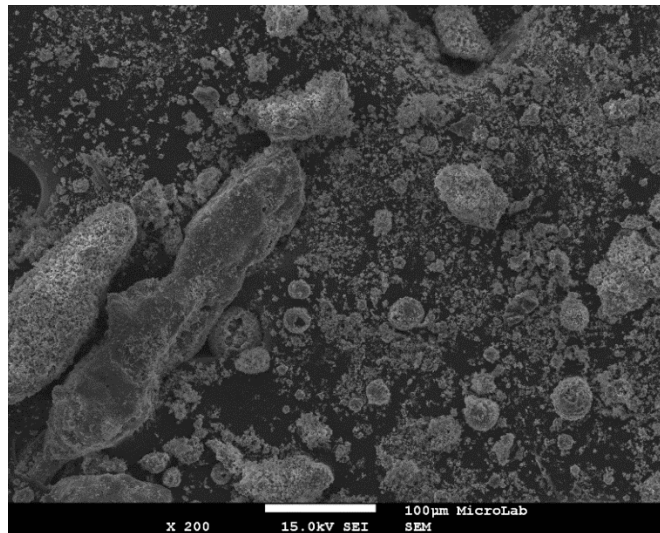
Table 18 The elemental composition of light fraction of fly ash - spectrum 4

LFA1' / Spectrum 4	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	52.11	3.86		1.07	1.93		13.7	7.74	2.68	16.9			133.31	111.96	8.7047

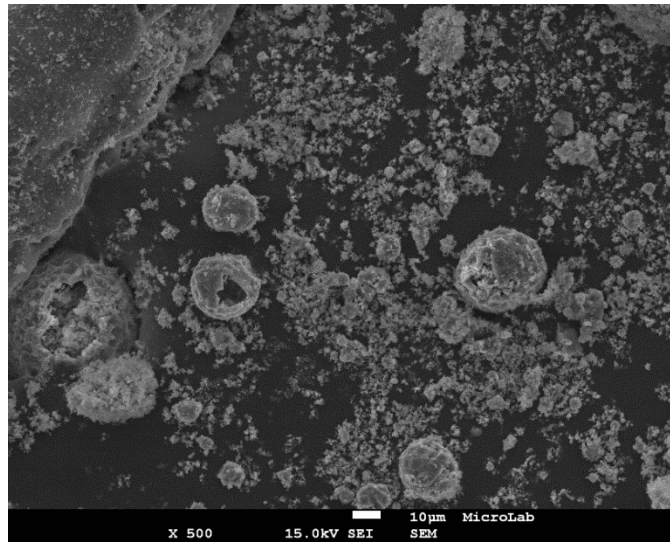
Table 19 The elemental composition of light fraction of fly ash - spectrum 5

LFA1' / Spectrum 5	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	40.39	23.3					4.8	28.38	2.3	0.87			56.11	109.16	-32.099

The morphology of the particles in the light fly ash fraction sample was studied by the images obtained in the electronic microscope. Pictures 21, 22, 23 and 24 displays 'LFA1' sample under different magnifications – x200, x500, x1000 and x3000 respectively. On the image 4, versatile particles can be seen. On the left-hand side, there are two prolonged particles reaching 400 microns of length. The surface of particles is different – the one that is located closer to the left edge is covered with numerous small particles forming 'fur-like' surface layer, the other one, located on the right hand side from the first one, has almost smooth surface. A number of particles have similar spherical shape and size of 10 – 30 microns. A closer look at them (image 21) reveals hollow inner structure with sharp edges of the holes on the surface. The same can be clearly detected under magnification of x1000. The last image of the sample exposes some spherical and cubic particles as small as 5 microns. However, the vast majority of particles here have irregular shapes and even under such magnification, it is hard to distinguish separate particles since they are mostly glued to each other.

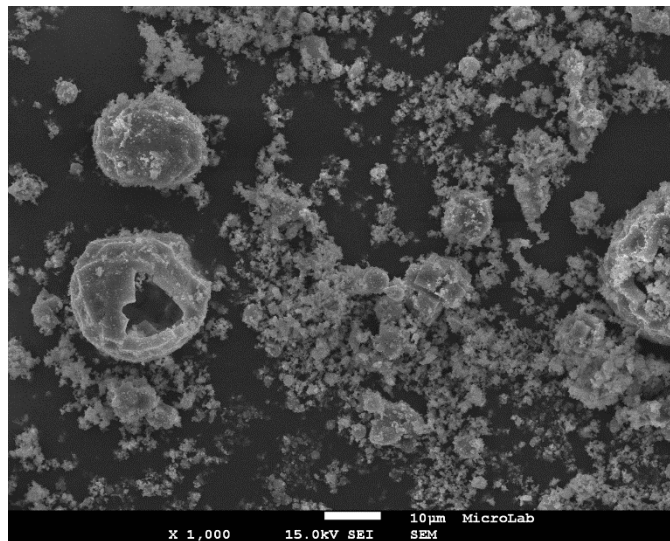


*Figure 16 Light fraction fly ash. Magnification x200*



*Figure 17 Light fraction fly ash. Magnification x500*

The EDS analysis showed the high content of sodium and chlorine in cubic particles which indicates that they are in fact micro crystals of NaCl. The largest particles are proved to be minerals with the considerable content of Ca. The two possible options might be gehlenite and hydrogrossular [50].



*Figure 18 Light fraction fly ash. Magnification x1000*

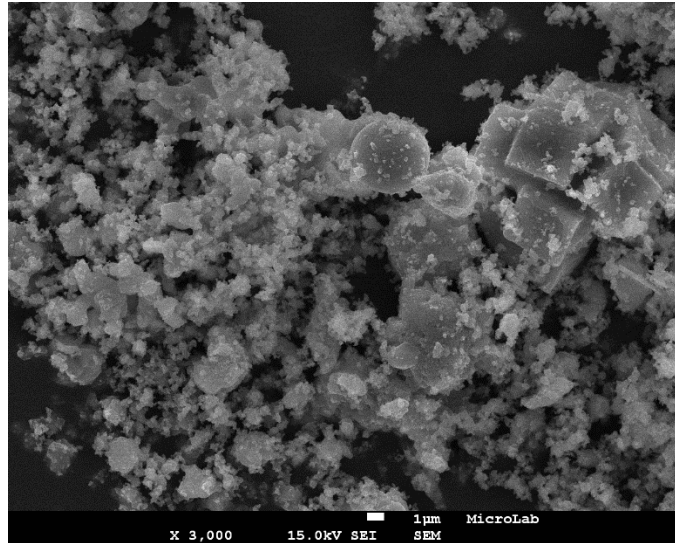


Figure 19 Light fraction fly ash. Magnification x3000

#### 4.4. Heavy fraction fly ash

The image 25 and tables 26 – 30 relates to the 'HFA 1'. The composition of this sample has a number of differences from the baghouse filter ash discussed above. First of all, more elements are present. Mg, P, Ti and Fe are present in quantities that allow their easy detection. Generally, the composition matrix of this fraction is between classical fly ash and bottom ash with elements like aluminum and silicon representing up to 35 % of the material (for spectrum 1). Silicon is mainly represented by quartz giving this fraction its sandy color. Aluminum can occur in the form of gehlenite and hydrogrossular [50].

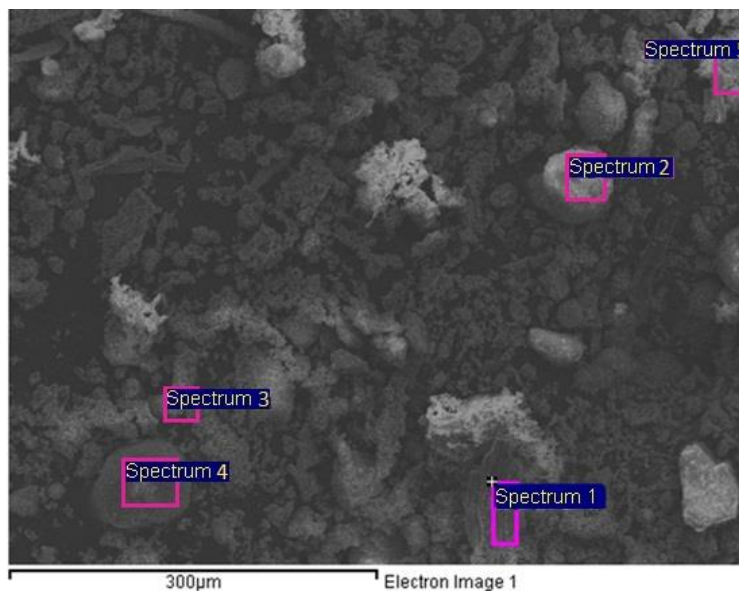


Figure 20 Heavy fly ash fraction 'HFA 1' with five spectrums chosen for the elemental analysis

Table 20 The elemental composition of light fraction of fly ash - spectrum 1

HFA1' / Spectrum 1	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	62.17			31.5	3.5					2.8			114.19	124.34	-4.2552

Table 21 The elemental composition of light fraction of fly ash - spectrum 2

HFA1' / Spectrum 2	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	59.03	1.05	1.47	3.6	5.43	1.63	3.09	3.8	1.09	19.8			103.91	121.86	-7.9506

Table 22 The elemental composition of light fraction of fly ash - spectrum 3

HFA1' / Spectrum 3	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	60.5	1.36	5.92	1.46	1.72		7.8	4.02	1.4	15.2	0.59		105.48	125.02	-8.4772

Table 23 The elemental composition of light fraction of fly ash - spectrum 4

HFA1' / Spectrum 4	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	49.47	9.15		3.39	7.45	1.54		6.8	1.48	10	6.89	3.84	117.38	105.74	5.2169

Table 24 The elemental composition of light fraction of fly ash - spectrum 5

HFA1' / Spectrum 5	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Cations	Anions	Error
Atomic weight, %	65.31		1.02	0.65	1.3		11.2	1.16		19.4			115.17	131.78	-6.7261

The sizes, shapes and structures of the particles in the studied material vary significantly. The morphology of the heavy fraction particles is depicted on the images 26 – 29.

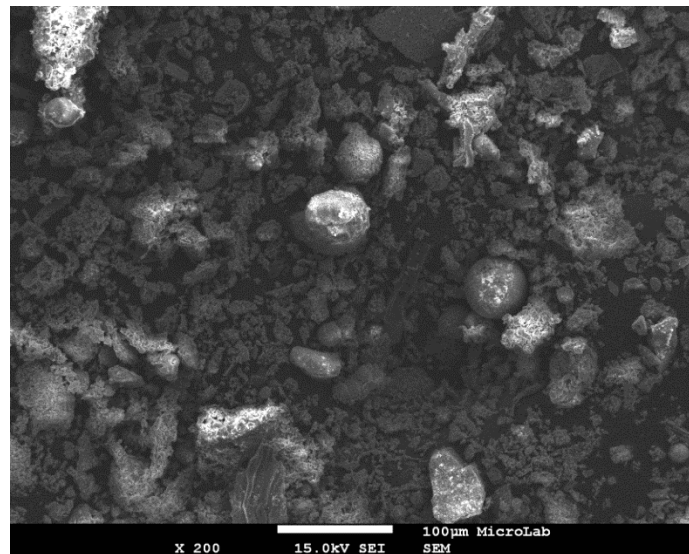
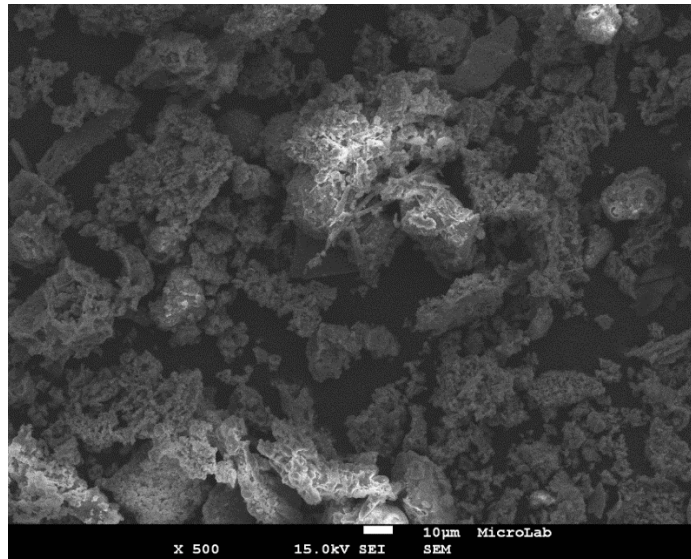


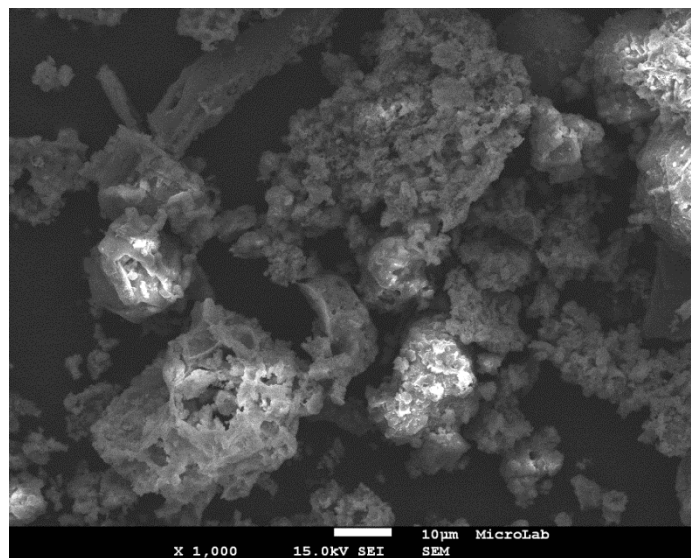
Figure 21 Heavy fraction fly ash. Magnification x200



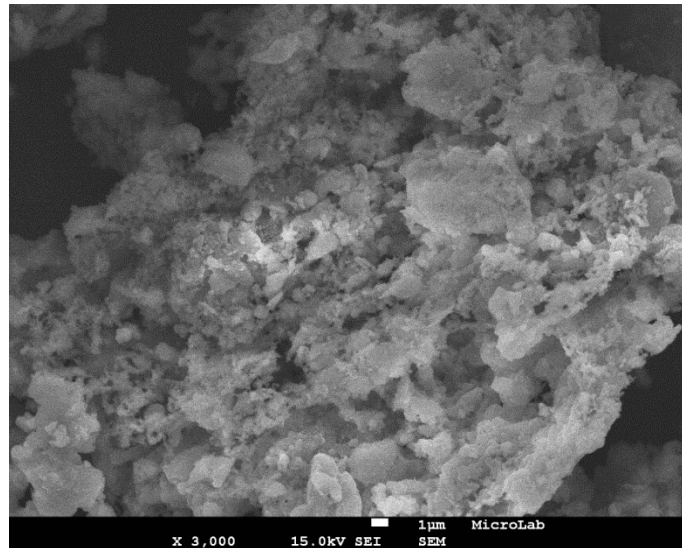


*Figure 22 Heavy fraction fly ash. Magnification x500*

The particles of this fraction are larger than in the case of light fly ash with a significantly smaller concentration of fine particles less than 1 microns. Some spherical particles are also present. These are so-called cenospheres that are widely presented in coal-derived fly ash. The vast majority of particles here forms agglomerates consisting of calcium, aluminum and silicon oxides. On the image 24, the branchy structures on the surface are clearly recognizable.



*Figure 23 Heavy fraction fly ash. Magnification x1000*



*Figure 24 Heavy fraction fly ash. Magnification x3000*

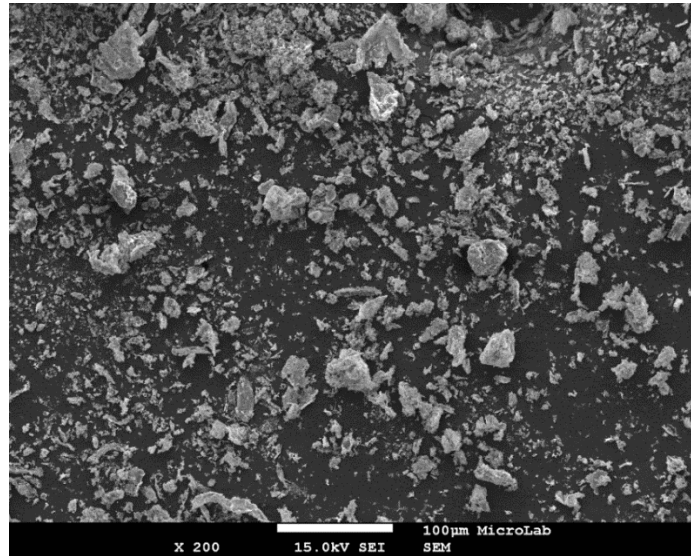
When scaling up (images 25 and 26) the 'branches' turn out to be irregular agglomerates of very fine particles, the size of which ranges from 1 micron to 5 and even 10 microns. Large particles predominantly consist of Ca, Si and Al containing minerals whereas fine ones are more diverse in chemical composition and often include metals such as Mg, Fe, Zn, P or even Ti. The source of the latter in municipal solid wastes might be titanium-containing pigments that are widely used in the cosmetics industry [51].

#### **4.5. RDF ash analysis**

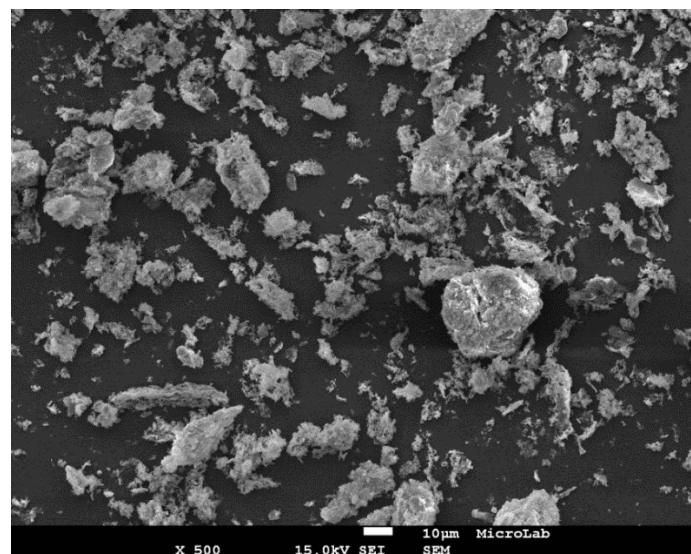
The RDF ash analysis was done in order to compare the elemental composition of the fly ash derived from the actual waste-to-energy plant with the ones originated from the thermal treatment of RDF at laboratory conditions. The sample was obtained by the combustion of RDF in the laboratory Lenton furnace with the maximum power of 1520 Watts and the maximum process temperature 1100 °C. An. The RDF sample with an initial mass of 1.229 grams was heated with a heating rate of 20 °C/min and afterwards kept at 800 °C for 10 minutes. The mass of the material after the treatment went down to 0.18 grams with corresponds to 85.64 % of the mass loss. It was assumed that all ash formed are fly ash. This assumption later was proved to be viable when the results on the particle size were obtained.

The elemental analysis was performed in the same electronic microscopy laboratory as in the case of waste-to-energy plant ashes. The same technique was used during the analysis except for the fact that gold-palladium (Au/Pd) coating was used to increase the contrast and detailization of the images. The coating with conducting metal on the top of a non-conducting specimen prevents charging of the latter that would occur otherwise due to static electric fields. The consequence of the procedure is that gold can be spotted during elemental analysis and, hence, should be subtracted afterwards.

On the images 27 – 30 one can observe the morphological structure of the RDF derived ash. Generally, the average size of the 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 25 RDF derived ash. Magnification x200*



*Figure 26 RDF derived ash. Magnification x500*

The magnified images of one of such particles is showed below. An interesting detail is a crack that passes through a half of the particle. On the last image, it is visible that the main particle's surface is covered with multiple fine particles with a diameter ranging from 0.5 to 5 microns. The surroundings of the main particle consist of irregular shaped and sized particles, which elemental composition of which include such components as P, Mg, S, Fe.

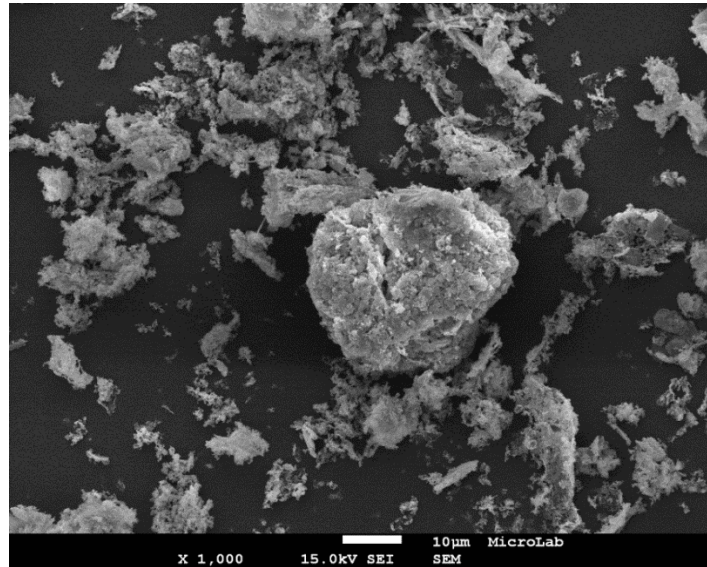


Figure 27 RDF derived ash. Magnification x1000

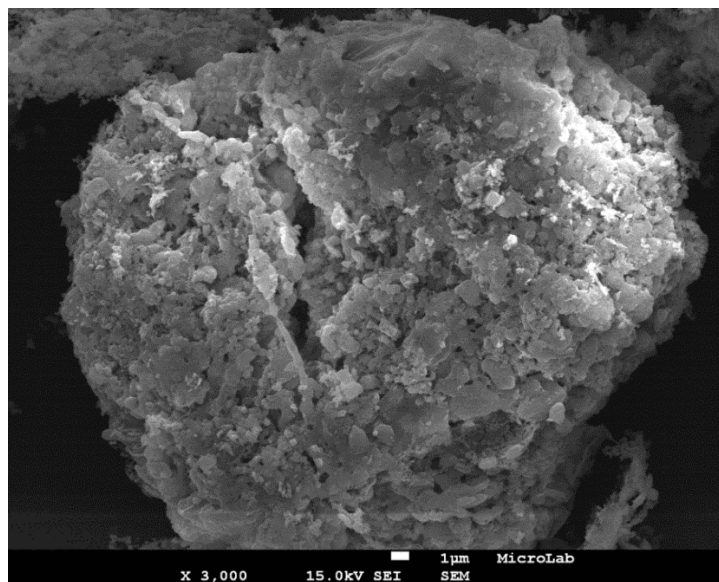


Figure 28 RDF derived ash. Magnification x3000

In the following tables, the elemental composition of five spectra chosen for elemental analysis is presented. The most widely represented elements are O, Si, Al, Ca (presented in every spectrum) as well as Na, Mg

and K (presented in 4 out of 5 spectra). The presence of chlorine in 3 out of 5 spectra confirms the presence of plastics in the original material which can have an impact on the kinetics of the combustion and pyrolysis process of the RDF studied in this work. In the fifth spectrum, the percentage of chlorine exceeded 6% clearly indicating that some PVC fraction of MSW was used for the RDF. Spectrum 1 demonstrated a large amount of carbon – 49.76%, which can be a result of the incomplete combustion of RDF that occurred in the laboratory furnace. Further research is needed, though, to find out if such situation will occur under combustion in industrial furnaces. Most of the elements presented in the material form oxides with oxygen. The following oxides were detected in the RDF derived ash: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O, Na<sub>2</sub>O, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>. The ion balance analysis exposed that in every spectrum there is a certain disproportion of cations and anions. The reasons for this phenomena are possibly undetected species or systematic laboratory measurements errors. In its turn, the main reason for undetected species is their lower concentration in the studied material that might be beyond the precision limit of the microscope.

*Table 25 The elemental composition of RDF derived ash - spectrum 1*

RDFA' / Spectrum 1	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	C	Cations	Anions	Error
Atomic weight, %	32.39	1.8	0.49	4.53	5.15				0.94	4.52			49.76	96.07	64.78	19.45291

*Table 26 The elemental composition of RDF derived ash - spectrum 2*

RDFA' / Spectrum 2	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	C	Cations	Anions	Error
Atomic weight, %	63.97	3.81		8.72	11.2			0.55	1.12	10.2				91.41	128.49	-16.8622

*Table 27 The elemental composition of RDF derived ash - spectrum 3*

RDFA' / Spectrum 3	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	C	Cations	Anions	Error
Atomic weight, %	67.68		6.5	1.05	11.9		0.78			11.5				121.5	135.36	-5.39594

*Table 28 The elemental composition of RDF derived ash - spectrum 4*

RDFA' / Spectrum 4	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	C	Cations	Anions	Error
Atomic weight, %	56.9	1.46	0.59	2.35	18.1			0.69	0.5	17		1.59		88.7	114.49	-12.6926

*Table 29 The elemental composition of RDF derived ash - spectrum 5*

RDFA' / Spectrum 5	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	C	Cations	Anions	Error
Atomic weight, %	58.16	4.6	1.87	3.98	7.28	0.88	1.01	6.36	1.04	13.9				88.926	122.68	-15.9513

## 4.6. XRD analysis

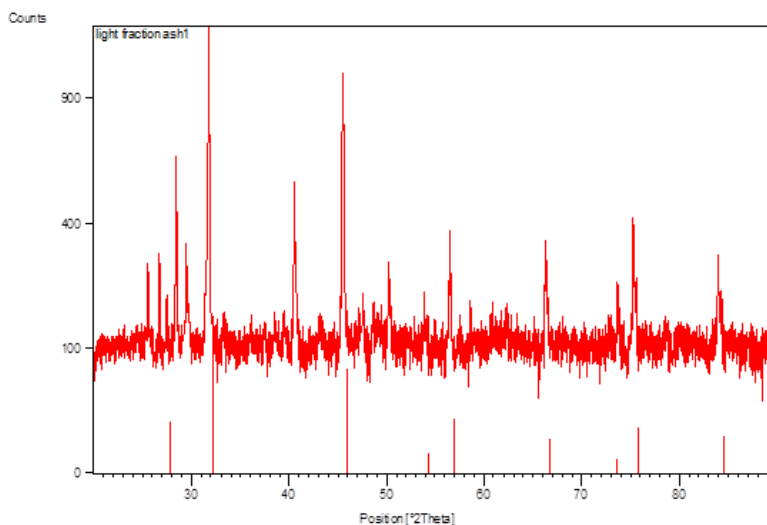
The samples of heavy and light fly ash were additionally subjected to the x-ray diffraction (XRD) analysis. The experiments were performed in the Philips PW3020 XRD analyzer. The principle of x-ray diffraction based on the registering of spherical waves produced when an x-ray strikes an electron. In 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:

$$2d \cdot \sin \theta = n \cdot \lambda$$

Where  $d$  is distance between two diffracting planes,  $\theta$  is an angle between the diffraction plane and a beam,  $n$  is any integer and  $\lambda$  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.

The diffraction patterns obtained for the studied samples revealed a rather complex composition of the material. Due to a large number of compounds of versatile chemical composition and structure, the pattern has multiple peaks frequently badly distinguished from one another. Yet the presence of certain minerals resulted in a set of highly distinctive peaks. These peaks were chosen for the closer analysis. On the picture below, the comparison of a diffraction pattern of the light fly ash with the data library pattern for halite is represented. As one can see the peaks of the material fit very well with the once for halite with a chemical formula NaCl. The SEM/EDS analysis described above proved the significant presence of Na (average value 11.48 %) and Cl (average value 18.57 %). The presence of large quantity of halite in the light fly ash can be explained by the treatment of flue gas with sodium bicarbonate ( $\text{NaHCO}_3$ ). This technique has been gaining popularity during recent years as an alternative to lime-based treatment (e.g. with  $\text{Ca(OH)}_2$ ) as means to for the removal of acidic components. The technique is particularly feasible at waste-to-energy plants due to their limited size [52]. The technique can also have a set of advantages, including economic ones, when it comes to the flue gasses from RDF combustion or pyrolysis, since the concentration of chlorine-containing plastics might be even higher than for raw MSW.



*Figure 29 Comparison of the light fly ash diffraction pattern with the halite pattern*

On the following picture the diffraction pattern of the same ash sample is compared to the pattern for sylvite mineral (chemical formula KCl). The mineral's pattern taken from the X'Pert HighScore software library fits very well with the distinctive peaks in the studied material's pattern, thus, proving the presence of potassium chloride in the light fly ash fraction. The EDS analysis carried out earlier demonstrated the presence of potassium and chloride in the concentrations of 5.14% and 18.57% respectively. The presence of K in MSW has an important effect on the capture of Cl in the flue gas. KCl is an integral agricultural product, used for the production of potassium based fertilizers [3, 26]. Being a part of the fly ash, KCl adds to the ash's potential as a fertilizer. This potential, however, is limited by factors described in the chapter 'Industrial applications of MSWI ash'.

Following analysis of XRD patterns of light fly ash as well as heavy fly ash fraction was carried out in order to detect the presence of some minerals mentioned in a number of scientific works [50, 27, 3]. However, the technique showed poor results. The conclusion was made that for such a versatile substance as waste-to-energy process fly ash XRD analysis has limited abilities, thus, other techniques should be used for more precise detection of chemical compounds present in the material. One of the potential candidates can be X-ray fluorescence analytical technique.

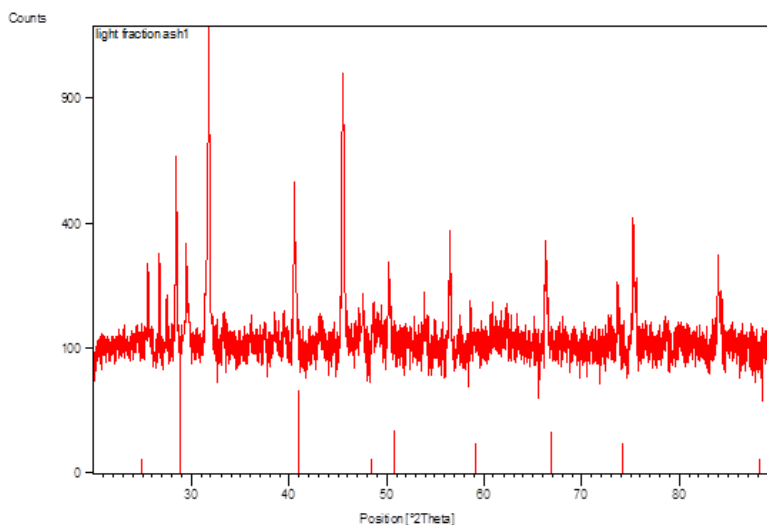


Figure 30 Comparison of the light fly ash diffraction pattern with the sylvite pattern

#### 4.7. Waste-to-Energy plant fly ash and RDF ash comparison

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.

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 [51]. 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 the fly ash might increase due to a specific flue gas treatment, such as  $\text{Na}(\text{CO})_2$  use.

*Table 30 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 advantage of using RDF instead of traditional unsorted MSW in waste-to-energy processes is that the amount of chlorine in the fuel can be, to some extent, controlled and monitored by portioning, during the sorting process, amounts of PVC and other plastics that contain this element. One of the interesting directions for the future research would be the determination of the thermal processes that are the most suitable for the treatment RDF with high chlorine content, from an economical and environmental point of view. Due to the decreased content of chlorides and heavy metals – the main environmental contaminants when it comes to waste incineration fly ash – the ash from RDF can be widely applied in a number of industrial processes without extensive pre-treatment. This can have highly positive economic value. Potential use of RDF derived ash in the industry are road construction, cement production as well as the production of zeolites, adsorbents and ceramics [3, 26].

## 5. Conclusions

### 5.1. Thermal analysis

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.

### 5.2. Kinetic modeling

The kinetic modeling for the combustion and pyrolysis of the RDF was carried out based on the results obtained from the thermal analysis. The reaction 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 introduction allowed for a slight improvement of the model.

In the table 32, the results obtained for the rate constant and activation energy are presented. 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.

*Table 31 Reaction rate constant and activation energies obtained by the model*

Parameter	Water	Hemicellulose	Cellulose	Lignin	Additional reaction
	Pyrolysis				
$E_a$ , cal/mol·K	2526.25	23753.18	41241.17	28880.10	7327.18
$k_0$ , min <sup>-1</sup>	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 <sup>-1</sup>	1884.51	0.3791	0.0014	0.0138	-

The fitting error analysis reveals the best result for both processes the model at the lowest heating rates. The results however were satisfactory with the lowest fitting rate being as high as 93.91% for the pyrolysis and 96.87% for the combustion.

### 5.3. Fly ash analysis

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.

*Table 32 Final comparison of different fly ash' composition*

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 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. These compounds represent the main environmental concern for the waste-to-energy technology. In combination with heavy metals, usually present in this type of ash, dioxins and furans make the ash inappropriate for the future use. At the moment, fly ash from waste-to-energy plants is considered to be hazardous product and, hence must be disposed of on a landfill. Amid the potential ways of treatment vitrification seems to be the most promising since the dioxins will be destroyed by the high temperature and other hazardous substances will be encapsulated without a possibility to leach out in the future. The pre-treatment techniques might include water washing. This technology shows good

efficiencies for the ashes with high content of soluble salts. 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 makes the material potentially suitable for the production of synthetic zeolites and adsorbents and also used in cement industry. The leaching of heavy metals will be, although, the major issue. Therefore, the material should be pre-treated first. In the case of heavy fly ash, the most interesting pre-treatment technology seemingly is electrodialytic recovery of heavy metals. If used in the production of cement, the product obtained should be carefully monitored with regards to leaching properties.

Finally, RDF originated ash has 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.

#### **5.4. Future proposal**

The present work can be elaborated in different directions. As the kinetic modeling is a basis for a reactor design, it would be interesting to build a reactor based on the model and study the combustion process characteristics in such a reactor. Another promising direction is to study co-combustion of the studied RDF with different fossil and non-fossil fuels. An environmental direction can be, first of all, connected to the studying of hazardous substances such as HCl in the flue gas. As far as the fly ash is concerned, the research connected to the studying the behavior of the ash in the industrial application (e.g. cement clinkers) can be done in the future.

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