



Analysis of thermal conversion of non-homogeneous solid recovered fuels

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Abstract

Solid Recovered Fuel (SRF) is produced from households and industrial solid waste. Due to European Union regulation, which prohibits the disposal of waste with calorific value higher than 6 MJ / kg by storage on landfills, there is a need of utilizing it in different way. SRF's in times of increasing demand of energy could be used as an alternative fuel due to its energy attractiveness. The aim of this work is to verify the suitability of waste as a fuel. For this purpose, samples of waste were collected from three waste treatment plants located in Poland. Detailed physicochemical properties have been obtained by the proximate, ultimate and ash analysis. To evaluate the combustion behavior, thermogravimetric analysis was used. Using the results of the TGA, the kinetic model for the process of combustion and gasification of SRF had been created. In this thesis, energy usefulness of tested samples was confirmed and compared with other studies of the literature. Thermogravimetric analysis allowed to observe a similar behavior between the samples. Additionally, the activation energy, based on designed kinetic models, was obtained.

Keywords: SRF, solid recovered fuel, waste, combustion, TGA, kinetic model.

Resumo

Os combustíveis sólidos recuperados (SRF) são produzidos a partir de resíduos domésticos e resíduos sólidos industriais. Devido à regulamentação da União Europeia, que proíbe a eliminação de resíduos com poder calorífico superior a 6 MJ / kg para um armazenamento em aterro, existe a necessidade de utilizá-lo de maneira diferente. Desta forma, é necessário tornar este tipo de combustível energeticamente viável. O objetivo deste trabalho foca-se na avaliação dos resíduos como combustível. Para isso foram recolhidas amostras, em estações de tratamento, de três resíduos localizados na Polónia. As propriedades físico-químicas foram obtidas através de análise elementar, aproximada e análise de cinzas finais. Esta avaliação do comportamento foi feita através de análise termogravimétrica. Utilizando os resultados obtidos no TGA, foi criado um modelo cinético para o processo de combustão e gaseificação de SRF. Nesta tese, a utilidade de energia das amostras testadas foi confirmada e comparada com outros estudos da literatura. A análise termogravimétrica permitiu verificar o comportamento semelhante entre as amostras estudadas. Adicionalmente, foram obtidas energias de activação com base em modelos de cinética.

Palavras-chave: SRF, combustível sólido recuperado, resíduos, combustão, TGA, modelo cinético.

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Nomenclature

CEWEP – Confederation of European Waste-to-Energy Plants

HHV – Higher Heating Value

LHV – Lower Heating Value

MBT – Mechanical Biological Treatment

RDF – Refused Derived Fuels

SRF – Solid Recovered Fuels

1. Introduction

At the beginning it is worth to mention what are Solid Recovered Fuels (SRF) and Refused Derived Fuels (RDF). SRF and RDF terms are often used alternatively. Refused Derived Fuels RDF is produced from Municipal Solid Waste (MSW) which according to Directive 2010/75/EU [1] means waste from households as well as commercial, industrial and institutional waste which, because of its nature and composition, are similar to waste from households. SRF can be produced only from non-hazardous waste namely those which are not a threat to life and health of humans and the environment.

1.1. History of waste

Waste were, are and will be exist, because the current products are packed in various types of packaging from paper, cartons through metal cans, until the plastic bottles. Garbage, because that is the common name for waste, accompanied mankind since the dawn of history. You can find the first mention in a mythology and the Bible, in which they say that "in the beginning there was chaos." People with the development of their civilization and the beginning of sedentary life began to plan the development of the area in which they live in order to ensure comfort and safety. Not to accept was settling physiological needs and living in a place someone has to live. In this way, the zone set: hygiene, sleeping and eating. In the next stage of social development problem began to be accumulated leftovers in the form of bones, which enticed the predators that are a threat to humans. Another reason for storing leftover food away from home was the smell of rotting waste and insects associated with this process. [2]

Beginning of antiquity associated with the establishment of the first civilizations in the Middle East, North Africa and Europe. They began to consciously plan for the functioning of the environment in which mind everything is unsuitable for use. There was the beginning of what today we would call cleaning settlements and cities. Waste transported to destinations outside settlements, previously collected in homes, in clay pots or dug pits, which were later evacuated. In Jerusalem many years before our era there was a place located in the Valley of Hinnom, called Gehenna, for the storage of waste and unnecessary things, which is a huge garbage dump. Tribes living in the desert, the remnants of his burned and crumbled ashes outside dwellings. In Europe, collected and dried manure in summer, heating in winter served dugouts, being very caloric fuel. [2]

The first purity requirements were issued in Athens in 320 BC the collected garbage and faeces was exported out of the city at a distance of not less than one mile. However, not Athens but Thebes was the cleanest city of ancient Greece, thanks to Epaminondas who built the sewers; the city organized the cleaning and removal of garbage. Soon came the ancestors of today's businesses, paid for the waste. They were the coprologists featuring the right equipment and knowing their stuff. Then, the first organized landfill. Not yet known relationship between health and infectious diseases, but the ancients intuitively sensed that the dirt and grime is no laughing matter. [2]

After more cares about the purity of antiquity came the dirty medieval times. Excrement and sewage poured through the door homes. Waste, which increased, thrown out on the unpaved streets, piling mounds, which were feeding the herd of rats, lugging previously unknown disease. Infections spread rapidly, consuming hundreds of thousands of victims in a very short time. Plague and cholera decimated the city. For example, in Strasbourg in 1349 died as a result of the epidemic 16,000 people. [2]

In 1373, in Krakow was released called "City Danzig" law or act of the current needs of the city, on the rules of cleanliness in the city, and disposal of solid and liquid. Homeowners in Krakow were required to collect dirt from their property, and from the middle of the street. For non-compliance was applied fine. Krakow sanitary provision was one of the first in Europe at the time the regulation in the field of maintenance of cleanliness and order. Overtook similar provisions in Paris (1539) and in Vienna (1560). [2]

Over the years, increased the amount of garbage and changed their composition. The wastes have always been a characteristic of the era kinds of garbage, are today an invaluable resource for archaeologists. Well, at the beginning of the fourteenth century in many European cities, street boxes were introduced animal droppings. Later it was extended also to the obligation to receive household waste, requiring residents to set up similar platforms in their homes. [2]

During the Renaissance, spreading plague and still unresolved sanitation slowly become one of the major topics of debate many of the great rulers, European cities. To prevent further outbreaks of the epidemic was introduced troops responsible for the sanitary disposal of waste. [2]

Today may seem to us that selective waste collection an invention of the modern world. Nothing could be further from the truth. Problem of waste worried peoples of the Far East. Japanese were the first in the history that took care of - today we would say - recycling, because in the tenth century they collected waste paper and reused it. [2]

In the nineteenth and early twentieth century was a period of industrial revolution. Along with it there was a rapid development of cities. For small areas began to dwell more and more people. The amount of waste generated also began to grow in diametrically pace. Environmental hygienisation began to be a big problem. [2]

In 1865 was founded acting today paramilitary charity "The Salvation Army", which at the beginning of its existence took care of the collection and processing of waste.

Shortly after the invention of the steam engine, thermally dispose of waste was begun. Production of steam as an energy source for the machines installed in large manufacturing plants requires the design and implementation of the boiler, which needed fuel. The most commonly used fuel was coal. However with the growing number of urban waste it had to be done something. There was the belief that the fire shall devour every plague. It was therefore an attempt to replace coal with garbage. The beginning was not promising. Wastes were too wet to burn well. Trials, however, were not interrupted. The first in the world, a well-designed incinerator was launched in 1876 in Manchester, England. In Germany the first incinerator was established in 1895 in Hamburg, see Figure 1. At the turn of the century there were 210 such installations, including the incinerator in Warsaw opened in 1912. [2]



Figure 1. Incineration plant in Hamburg [2].

In the early 1950s incineration plants were considered too expensive in comparison with the alternative, more or less organized, landfills. There was a decline in the construction of new thermal waste disposal plants, which lasted until the 1970s. [2]

The turn of the nineteenth and twentieth century is not only the energy use of waste. This is also the time of the first selective collection of household waste. The first manual sorting was built in New York in 1898; recovering 37% recycled materials by weight of the transported. Sorting was part of the first separate collection system whose creator was George E. Waring. His idea was adopted in other countries and few years later manual sorting plants appeared in Berlin and Hamburg. A mechanical sorting plant equipped with sorting conveyors and rotary screens operated in Munich. At the beginning of the 20th century composting of municipal waste was introduced. Since that time a steady progression in this method was observed. We have already observed numerous variations of this method, like composting in piles or in boxes in the open air, in closed receptacles of various kinds, or in airtight drums. [2]

Collecting waste and transporting it to landfills turned out to be unsuitable in terms of environmental protection. Therefore, something had to be done to promote the use of processed waste, for example in agriculture. Following a temporary withdrawal from the construction of waste incineration plants, after 1970 there was a return to this discontinued technology. A new generation of incinerators appeared. They used less electricity, generated less heat and thus the emissions of pollutants entering the atmosphere were reduced. Currently, Japan has the largest number of incinerators – 1280. They are, however, unlike the incinerators built in Europe and the United States, small objects of local relevance. In the European Union (with Norway and Switzerland) there are 470 functioning incinerators. In general, they serve large urban agglomerations or have a regional character. The use of waste as alternative fuel in, for example, cement plants is another issue. Co-incineration is now one of the world's top trends.[2]

In Europe the beginning of modernization of waste management reaches to the 1960s. The first act on waste appeared in Germany in 1972. Replaced in 2001 to meet the demands of the European Union. It was then that the hierarchy of waste treatment was established. This acts on waste management defined the course of action that should be taken in this field. Until this time personnel dealing with waste did not have any specializations in this field. Meanwhile, it turned out that the complexity of the

issue required new, previously unfamiliar knowledge from personnel dealing with organizational matters and problem solving. This was not only technical and technological knowledge but also legal and economic. Today it has expanded to the fields of education, psychology and sociology. [2]

As is known from the history, the waste is with human since the beginning of civilization. One of the main problems of the world is its influence on the environment as well as their storage, recovery or disposal. Every year the number of waste production increases which leads to a deeper reflection on the use of waste as fuel for energy purposes.

1.2 Problem scale

The amount of waste comparison was created according to Confederation of European Waste-to-Energy Plants (CEWEP) country report for Poland [3] and Portugal [4].

Table 1 shows total amount of waste in Poland and Portugal in 2010.

Table 1. Comparison of amount of waste between Poland and Portugal 2010 [3, 4].

Country	Total amount of waste per inhabitant	Total amount of waste in million tones
Poland	315/kg/inh	12.038
Portugal	511/kg/inh	5.467

In Poland, in 2010, the production of waste was 315 kilograms per inhabitant and in Portugal was 511 kilogram per inhabitant. Therefore, the total amount of waste, in the respectively country, was 12.04 and 5.47 million tones.

These large quantities of garbage are treated in different ways. Table 2 shows the different treatment data for waste in Poland and Portugal in 2010.

Table 2. Comparison of treatment of waste in Poland and Portugal 2010 [3, 4].

Country	Treatment of waste	%	In million tones
Poland	Recycling (including composting)	18	2.167
	Composting	8	0.963
	Incineration	1	0.120
	Landfilling	73	8.788
Portugal	Recycling (including composting)	12	0.656
	Composting	7	0.383
	Incineration	19	1.039
	Landfilling	62	3.389

In Poland treatment of waste by landfilling in 2010 was 73% and was much higher than in Portugal where was 62%. Portugal dispose 19% of produced waste using incineration where Poland disposed in this way only 1% of waste. Recycling and composting respectively for Poland were 18 and 8%, for

Portugal 12 and 7%. This data show situation in both countries and show how big the problem is. It also shows that waste is reused less in compare to their storage. Besides Poland and Portugal, the waste issues occur in the whole Europe. Table 3 presents data about the generation, landfill and incineration in the countries of the European Union for 2011.

Table 3. Data from Central Statistical Office about generation, landfill and incineration of waste in UE countries [5].

Countries	Per capita in kilograms		
	Generated	Landfilled	Incinerated
UE-27	500	180	111
Belgium	464	6	193
Bulgaria	375	349	0
Czech Rep.	320	206	58
Denmark	719	25	387
Germany	597	3	220
Estonia	298	178	0
Greece	623	408	0
Spain	496	314	41
France	498	146	184
Ireland	527	306	27
Italy	535	248	88
Cyprus	658	528	0
Latvia	350	258	0
Lithuania	442	341	2
Luxemburg	687	106	264
Hungary	382	257	41
Malta	583	491	6
Netherlands	596	4	193
Austria	552	18	183
POLAND	315	181	3
PORTUGAL	487	286	103
Romania	365	289	0
Slovenia	411	204	6
Slovakia	327	245	34
Finland	505	203	126
Sweden	460	4	237
Great Britain	578	253	60
Croatia	373	340	0
Turkey	395	331	0
Iceland	571	386	60
Norway	483	11	269
Switzerland	689	0	344

Generation of waste and landfilling in Poland shows one of the lowest values in comparison of Portugal and others European countries. Incineration of waste in Poland was amounted to 3 kg/per capita while in Portugal shows the higher value of 103 kg/per capita, which is close to average of European countries.

Figure 2 shows the data of generation, landfill and incineration for the countries of European Union, in order to illustrate the differences between them.

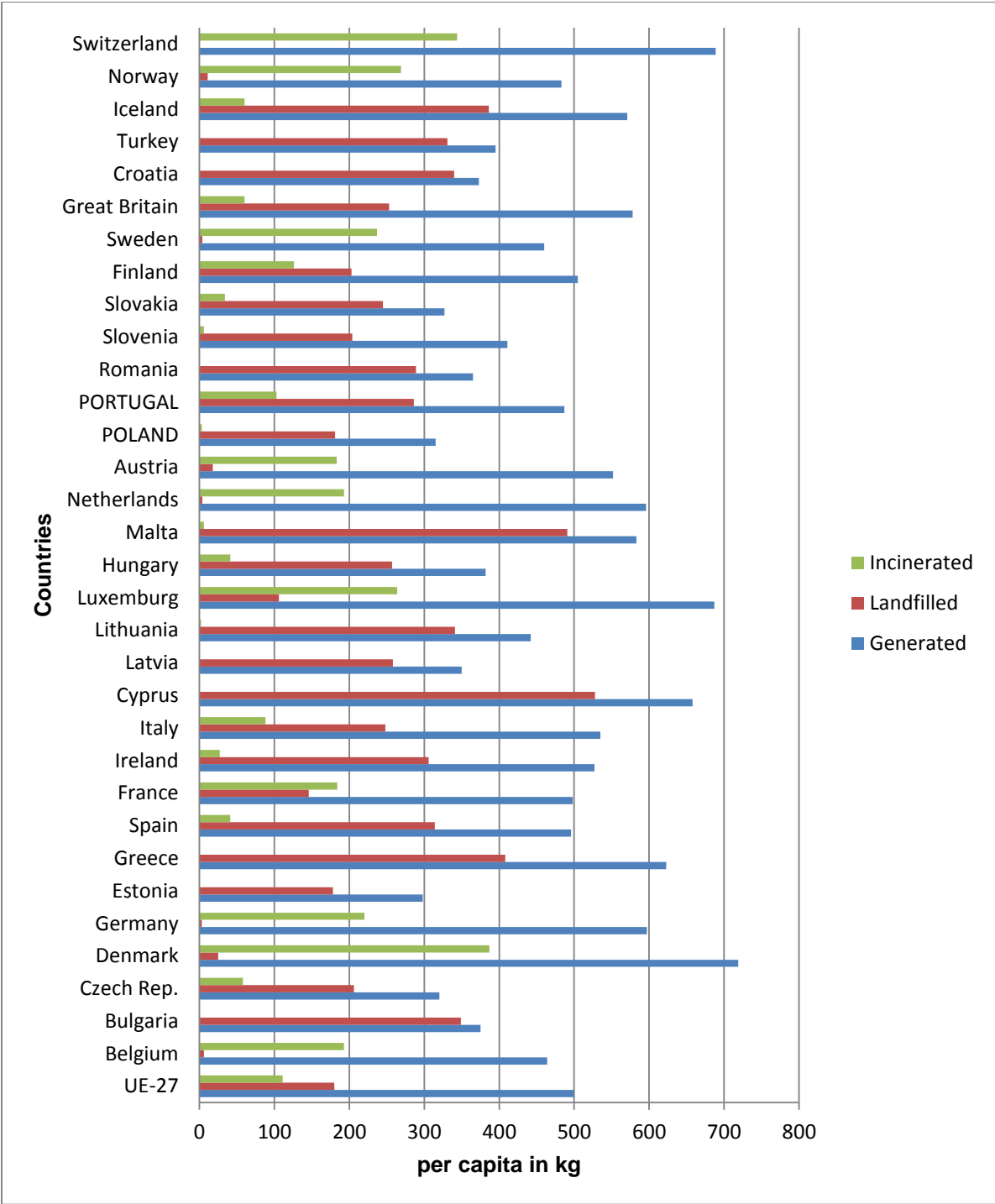


Figure 2. Generated, landfilled, incinerated municipal waste in European Union in 2011.

In all countries, except Estonia, production of waste per capita is higher than 300 kilograms. For Poland, from 2010 to 2011, this value is the same. However, for Portugal the values decrease from 511 to 487 kg/inh. There is a visible correlation between landfill and incineration. The higher number of waste is incinerated and the lower values correspond to landfill. It can be seen that the incineration performed very well in Denmark and Switzerland, because of their small territorial areas on which they can not afford to landfill large amounts of waste.

1.3 Treatment methods

As previously mentioned, there are many different ways to manage the waste utilization. Two main groups of methods can be distinguished: mechanical-biological and thermal treatment. Mechanical - Biological Treatment (MBT) is a method that combines the mechanical and biological treatment. Mechanical processes have two main roles. One of them is reduction of volume of waste using shredding and crushing of material for further treatment. Second is to separate remaining recyclable waste such as glass, metals, and plastics from the waste stream and recycle them [6]. Biological processes involve the decomposition of biodegradable waste by microbes (microorganisms: bacteria and fungi) which produce special enzymes to digest complicated organic substances present in waste into simpler forms. Biological processes can be divided in two types of conditions in which such microbes live: aerobic – in the presence of oxygen, and anaerobic – in the absence of oxygen [6].

An example of aerobic condition is composting process where biodegradable material is decomposed into carbon dioxide (CO_2), water (H_2O), and heat through microbial respiration in the presence of oxygen leaving a stabilized residual solid material, compost [6].

Composting takes place in two stages [7]:

- Phase I called thermophilic composting named intense composting or high-temperature phase
- Phase II mesophilic composting (low temperature process) also known as maturation

Anaerobic digestion is an example of anaerobic conditions where organic material is converted into a residual solid, slurry, methane (CH_4), carbon dioxide (CO_2) and water (H_2O) through microbial fermentation in the absence of oxygen. Anaerobic digestion is the consequence of a series of metabolic interactions among various groups of microorganisms. It occurs in three stages [8].

In the first stage of hydrolysis or liquefaction fermentative bacteria convert insoluble complex organic matter into simpler soluble molecules. The complex polymeric matter is hydrolyzed to monomer. In the second stage, acetogenic bacteria (also known as acid formers), convert products from first phase to simple organic acids, carbon dioxide and hydrogen. Finally, in the last stage methanogens (known also as methane formers) produce methane [8].

Thermal Treatment is a group of waste treatment methods which include all processes converting the waste into gas, liquid and solid products with release of thermal energy. Main processes used in thermal treatment are pyrolysis, gasification and combustion [9].

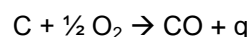
The first process is pyrolysis. It is a thermal transformation of carbon-rich organic substances, which takes place at increased temperatures with absence of air. Whole process is endothermic and extends at temperatures up to 1000 °C but at the rise of fuel temperature exothermic effects may also appear. The composition and quantity of the pyrolysis products depends on the type of waste, their physico-chemical properties, heating rate, pressure, type of inert atmosphere and the temperature of the process. During the process of pyrolysis mass of waste is converted to [10]:

- pyrolysis gas mainly comprising hydrogen, methane, ethane, and their homologues oxide and carbon dioxide and other compounds such as hydrogen sulfide, ammonia, hydrogen chloride and hydrogen fluoride;
- pyrolysis coke - a solid phase comprising carbon and metals and a number of rare elements;
- a liquid phase comprising a mixture of oils, tars and water, and dissolved it simple aldehydes, alcohols and organic acids.

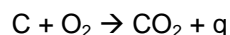
The second process, which may be applied to thermal conversion of waste, is gasification. It occurs at a temperature close to 1000 °C in the presence of oxidizing agent, which may be air, oxygen, CO₂ and water vapor. Products of gasification are typically hydrogen and carbon monoxide, as well as small amounts of methane, carbon, nitrogen and steam [10].

The gasification process of solid hydrocarbons can be described by the following simplified chemical equations [10]:

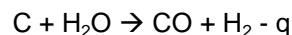
Gasification with oxygen:



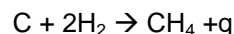
Combustion with oxygen:



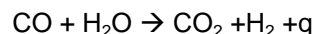
Gasification with steam:



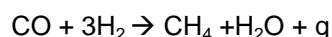
Gasification with hydrogen:



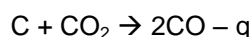
Water-gas shift:



Methanation:



Gasification with carbon dioxide:



Some of the above-mentioned chemical reactions are exothermic reactions ((+q) - extending from separating heat), the endothermic part ((-q) - require bringing heat from outside).

Concept of "burning" is usually understood as a reaction of oxidation of organic fuel components, related with the release of significant amounts of heat. Depending on the type of material to be burned, and the purpose of carrying out this process, we have to deal with the combustion in the conventional sense of the word, and the incineration. The purpose of the combustion process is to obtain energy (heat) for industrial energy processes or heating. On the other hand the incineration process is to eliminate or only reduce the volume of harmful waste for the environment. It is also possible to combine these two objectives by the use of waste energy [11].

An important benefit of thermal waste treatment processes is the ability to generate significant amounts of heat, thus saving non-renewable fuel and reduces emissions to the environment of the combustion products [11].

2. Characterization of waste treatment plant

Waste treatment plant is the facility where waste suitable for recycling is selectively collected from mixture of garbage. These are:

- Paper and cardboards,
- Glass,
- Ferrous and non-ferrous metals,
- Plastics,
- Foils,
- Aluminum,
- Textiles.

Waste that cannot be segregated goes to the landfill.

Recycling by the law [12] means any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations;

Recovery operations according to Annex II [12] are:

R 1 Use principally as a fuel or other means to generate energy

R 2 Solvent reclamation/regeneration

R 3 Recycling/reclamation of organic substances which are not used as solvents (including composting and other biological transformation processes)

R 4 Recycling/reclamation of metals and metal compounds

R 5 Recycling/reclamation of other inorganic materials

R 6 Regeneration of acids or bases

R 7 Recovery of components used for pollution abatement

R 8 Recovery of components from catalysts

R 9 Oil re-refining or other reuses of oil

R 10 Land treatment resulting in benefit to agriculture or ecological improvement

R 11 Use of waste obtained from any of the operations numbered R 1 to R 10

R 12 Exchange of waste for submission to any of the operations numbered R 1 to R 11

R 13 Storage of waste pending any of the operations numbered R 1 to R 12 (excluding temporary storage, pending collection, on the site where the waste is produced)

Figure 3 shows exemplary scheme of waste treatment plant with selected sampling place.

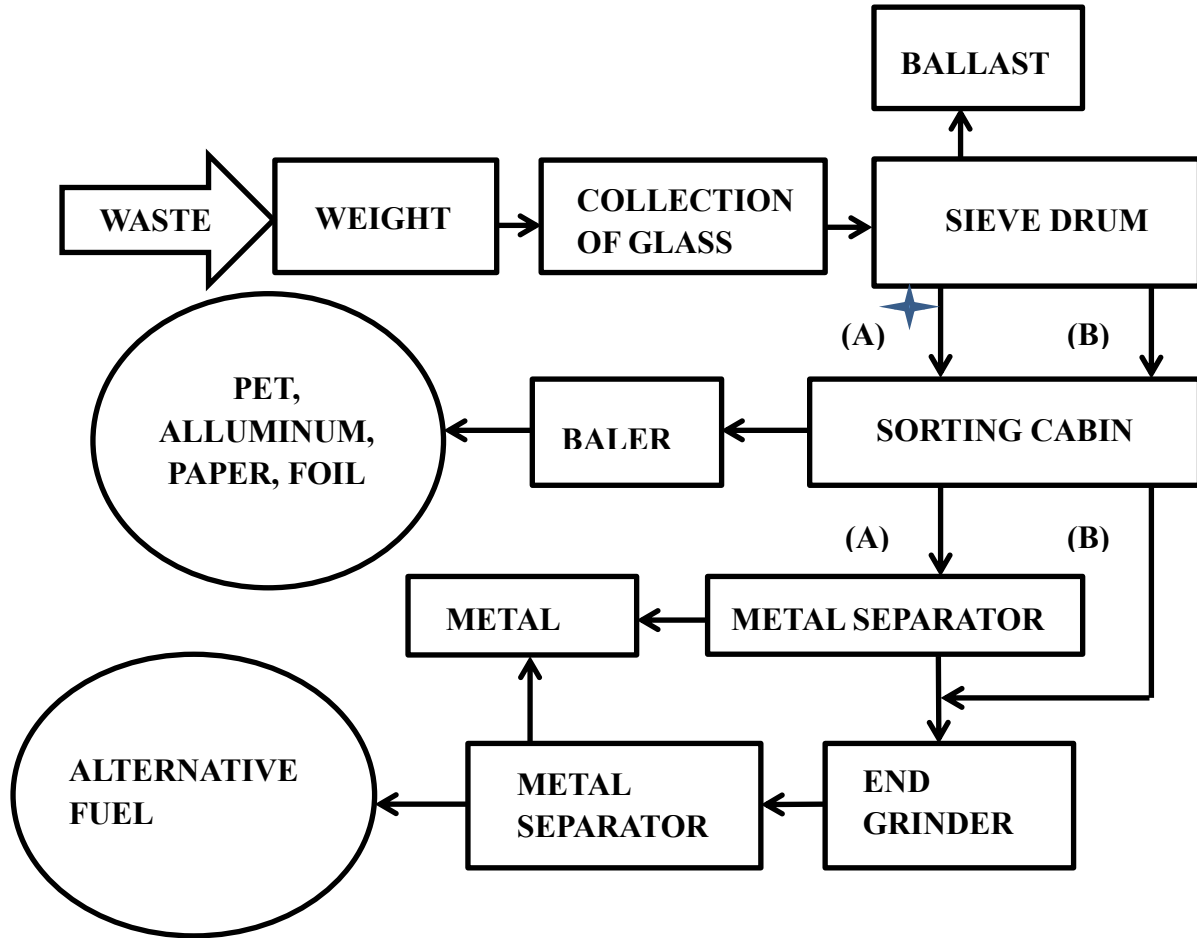


Figure 3. Example scheme of waste treatment plant.

Sorting process begins at the moment of delivery of the waste through a special car called a “garbage truck”. At the beginning garbage are weighed and then thrown on the sorting tape. In the first stage glass is selected. The second stage takes place in the sieve drum shown in Figure 4, which is divided into two parts in which mesh have diameter of 80 mm and 200 mm. The fraction that falls through the sieve with mesh having the smaller diameter is called ballast it is mineral matter.



Figure 4. Sieve drum.

Garbage, which falls on the second drum part get on the tape which goes to the sorting cabin can be seen on Figure 5 where from the waste are main stream are hand-selected: plastics, aluminum, paper, remains of glass and textiles.



Figure 5. Sorting cabin.

Selectively sorted materials are going to the press visible on Figure 6 in order to reduce their volume and facilitate transport to recycling.



Figure 6. Baler.

From remaining garbage on tape with help of electro magnet metals are separated. The waste that do not sieve well are going into the sorting cabin. Most frequently these are cardboards and foils. At the end of sorting process both lines are connecting in one, waste that are on line are transported to the end grinder. After grinding again are subjected to metal separation and are already stored as an alternative fuel.

3. Aim of the work

In the past, garbage was collected and transported to the sorting place. During the sorting process good quality: plastics, foils, glasses and metals were selected and subjected to the process of recycling. The remaining part of waste as organic matter, mineral components and residues after sorting were stored in landfills.

Nowadays with the entry into force of the new Act of 14 December 2012 [13] the storage of waste of calorific value greater than 6 MJ/kg will be prohibited. With the growing demand for energy, and plans to increase production of energy from renewable sources till 2030 [14] we need to consider other and more effective methods of waste disposal.

The main objective of this work was to determine the physicochemical properties of a sieve fraction of municipal waste of Poland. The proximate and ultimate analysis was performed. The thermochemical behavior of waste was assessed by thermogravimetry simulating combustion and gasification conditions. Kinetics studies of waste were performed using thermogravimetry data obtained for different heating rates. The kinetic models were based on three separate fitting methods.

The environmental issues were also studied. The mercury, chlorine and fluorine as well as heavy elements were analysis in order to prevent danger coming from their toxicity.

4. Sampling and pre-treatment of laboratory samples

The samples were collected at two waste treatment plants located in the Silesia province and one waste treatment plant in the Łódź province. From each of them was taken one sample weighing about 50 kg from fraction above sieve mesh 80 mm sieve (on example scheme sampling place is marked by star). Prepared samples of waste are shown in Figure 7.



Figure 7. Samples of waste from three waste treatment plants.

Samples were collected using standard EN 15442 from March 2011 [15] and prepared with help of procedure shown in Figure 8.

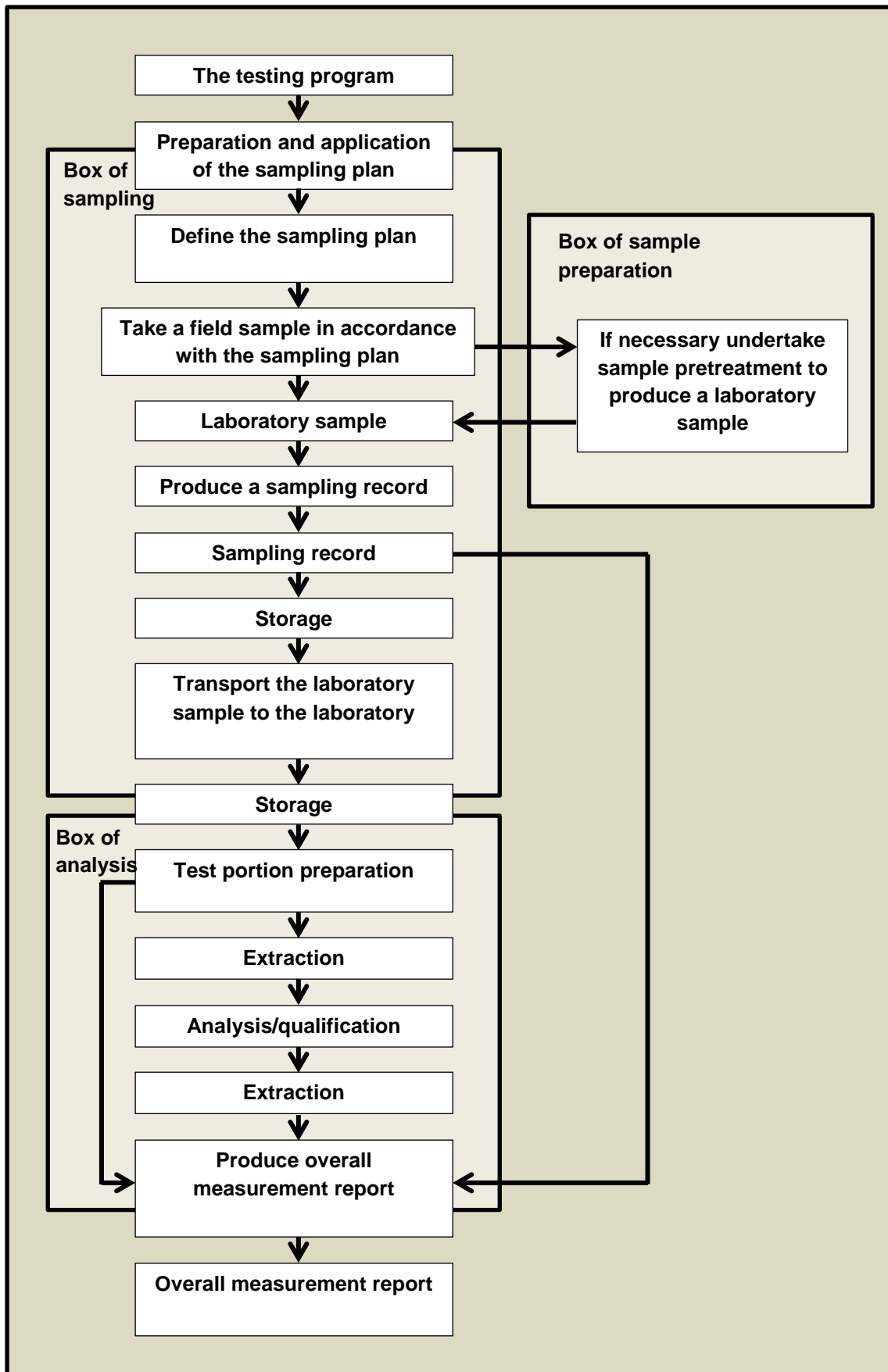


Figure 8. Links between the essential elements of a testing program [15].

The samples were pre-treated due to the fact that the material is not unitary. Three grinders were used to prepare of the material.

First grinder produced by company MERCODOR type ZM-1 shown on Figure 9 was used to preliminary grinding of waste from bigger to smaller parts.



Figure 9. Grinder from company MERCODOR type ZM-1.

Second grinder manufactured by TRYMET type T-2 shown on Figure 10 was grinding smaller parts of waste to below 2.0 mm.



Figure 10. Grinder from company TRYMET type T-2.

Third grinder created by RETSCH type SM-100 shown on Figure 11 was grinding material from 2.0 mm to laboratory sample.



Figure 11. Grinder from company RETSCH type SM-100.

Optional fourth grinder constructed by SPEX shown on Figure 12 was used to cryogenic pulverizing of waste from 2.0 mm to 0.1 mm needed to thermogravimetric analysis.

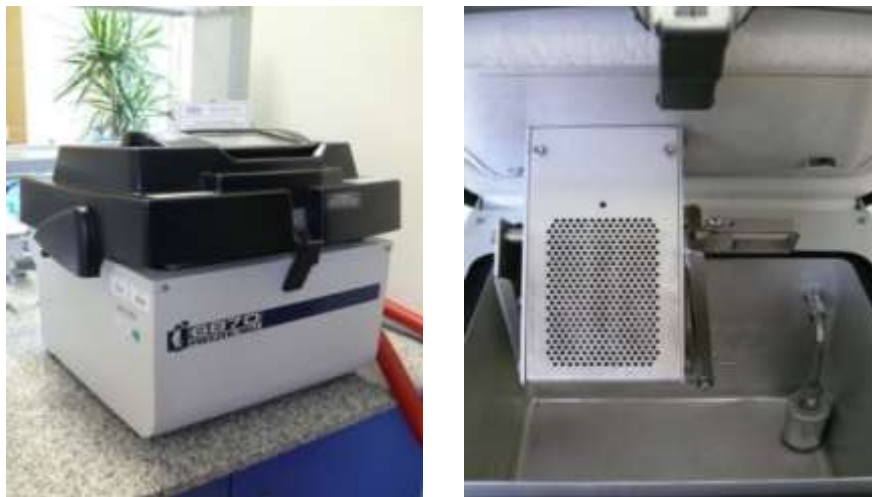


Figure 12. Cryogenic grinder from company SPEX type 6870.

Laboratory samples are visible on Figure 13 and are ready for use in the analysis described in the following chapters.



Figure 13. Laboratory samples of waste from three waste treatment plants in sequence SRF 1, SRF 2, SRF 3.

5. Morphology of waste composition

There are many methods to classify waste. They illustrate how many different points of view on dividing the waste exist. According to the Directive of 27 April 2001 [16] which is still used: 'waste' shall mean any substance or object in the categories set out in Annex I:

- Q01** - Production or consumption residues not otherwise specified below
- Q02** - Off-specification products
- Q03** - Products whose date for appropriate use has expired
- Q04** - Materials spilled, lost or having undergone other mishap, including any materials, equipment, etc., contaminated as a result of the mishap
- Q05** - Materials contaminated or soiled as a result of planned actions (e.g. residues from cleaning operations, packing materials, containers, etc.)
- Q06** - Unusable parts (e.g. reject batteries, exhausted catalysts, etc.)
- Q07** - Substances which no longer perform satisfactorily (e.g. contaminated acids, contaminated solvents, exhausted tempering salts, etc.)
- Q08** - Residues of industrial processes (e.g. slags, still bottoms, etc.)
- Q09** - Residues from pollution abatement processes (e.g. scrubber sludges, baghouse dusts, spent filters, etc.)
- Q10** - Machining/finishing residues (e.g. lathe turnings, mill scales, etc.)
- Q11** - Residues from raw materials extraction and processing (e.g. mining residues, oil field slops, etc.)
- Q12** - Adulterated materials (e.g. oils contaminated with PCBs*, etc.)
- Q13** - Any materials, substances or products whose use has been banned by law
- Q14** - Products for which the holder has no further use (e.g. agricultural, household, office, commercial and shop discards, etc.)
- Q15** - Contaminated materials, substances or products resulting from remedial action with respect to land
- Q16** - Any materials, substances or products which are not contained in the above categories.

*) PCB – polychlorinated biphenyl

Overall method is placed in Directive 2000/532/EC [17] and based on it in catalogue of waste. In this document waste are divided according to the source of their creation in the following 20 groups:

1. Wastes resulting from exploration, mining, dressing, and further treatment of minerals and quarry
2. Wastes from agriculture, horticulture, hunting, fishing and aquacultural primary production, food preparation and processing
3. Wastes from wood processing and the production of panels, cardboard, pulp, panels and furniture
4. Wastes from the leather, fur and textile industries
5. Wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal
6. Wastes from inorganic chemical processes
7. Wastes from organic chemical processes
8. Wastes from the manufacture, formulation, supply and use (MFSU) of coatings (paints, varnishes and vitreous enamels), adhesives, sealants and printing inks
9. Wastes from photographic industry
10. Inorganic wastes from thermal processes
11. Inorganic metal-containing wastes from metal treatment and the coating of metal, and non-ferrous hydrometallurgy
12. Wastes from shaping and surface treatment of metals and plastics
13. Oil wastes (except edible oils, 05 and 12)
14. Waste from organic substances used as solvents (except 07 and 08)
15. Waste packaging; absorbents, wiping cloths, filter materials and protective clothing not otherwise specified
16. Wastes not otherwise specified in the list
17. Construction and demolition wastes (including road construction)
18. Wastes from human or animal health care and/or related research (except kitchen and restaurant wastes not arising from immediate health care)
19. Wastes from waste treatment facilities, off-site waste water treatment plants and the water industry
20. Municipal wastes and similar commercial, industrial and institutional wastes including separately collected fractions

According to National Waste Management Plan 2014 [18] the quantity and morphological composition of municipal waste are very large rank dependent on where the waste was generated, and mainly on the wealth of the local community. The amount of municipal waste collected per capita depends on the economic condition of the different regions of the country. Over the last few years, there have been stable quantities of collected waste. This can be caused by many factors. On the one hand, this may be related to massive emigration, financial and economic crisis and inadequate management practices for municipal waste management. On the other hand, it may be the effect of deliberate actions aimed at prevention of waste. These actions included increased charges for waste disposal, which resulted in raising the charges for collecting municipal waste from real estate owners, and consequently greener consumer behaviours, reinforced by environmental education [18].

Table 4 presents a balance of municipal waste generated in Poland between 2004 and 2008. Figures 14-16 show the morphological composition of municipal waste according to where it was generated.

Table 4. Municipal waste generated in Poland in 2008 [18].

No.	Type of waste	Mass of generated waste in Mg thousand			
		2008			
		Total	Including		
in large cities (>50 k)	in small towns		in rural areas		
1	Paper and paperboard	1,520.5	1,045.0	302.5	173.0
2	Glass	1,216.3	545.9	323.4	347.0
3	Metals	279.0	146.0	48.5	84.5
4	Plastics	1,533.6	830.9	346.1	356.6
5	Composite waste	401.2	134.7	124.5	141.9
6	Kitchen and garden waste	3,888.6	1,582.3	1,156.7	1,149.7
7	Mineral waste	467.9	173	89.1	205.8
8	Fraction < 10 mm	1,030.7	229.7	215.7	585.3
9	Textiles	325.8	124.8	126.8	74.2
10	Wood	44.8	12.8	9.3	22.7
11	Hazardous waste	89.4	41.1	20	28.2
12	Other categories	485.7	173	142.4	170.3
13	Bulky waste	268.3	141.8	82	44.5
14	Waste from green areas	549.4	292.1	166.8	90.6
	Total	12,101	5,472.1	3,153.8	3,474.4

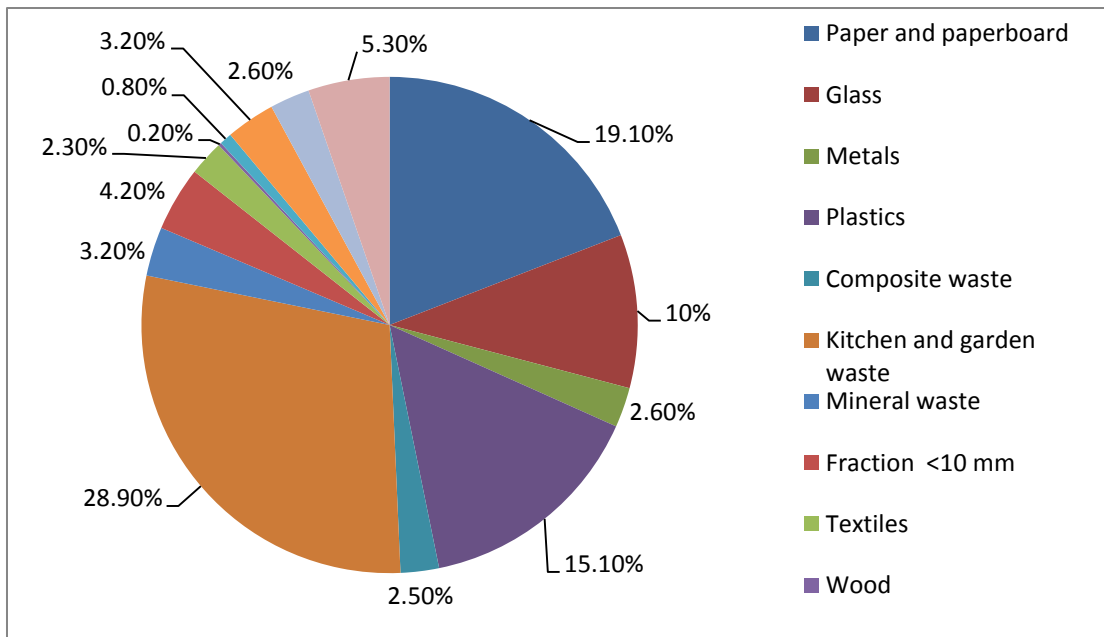


Figure 14. Morphological composition of municipal waste generated in big cities, cities of over 50 thousand residents in 2008, inhabited by 14.18 million of Poland's residents (37.18%) [18].

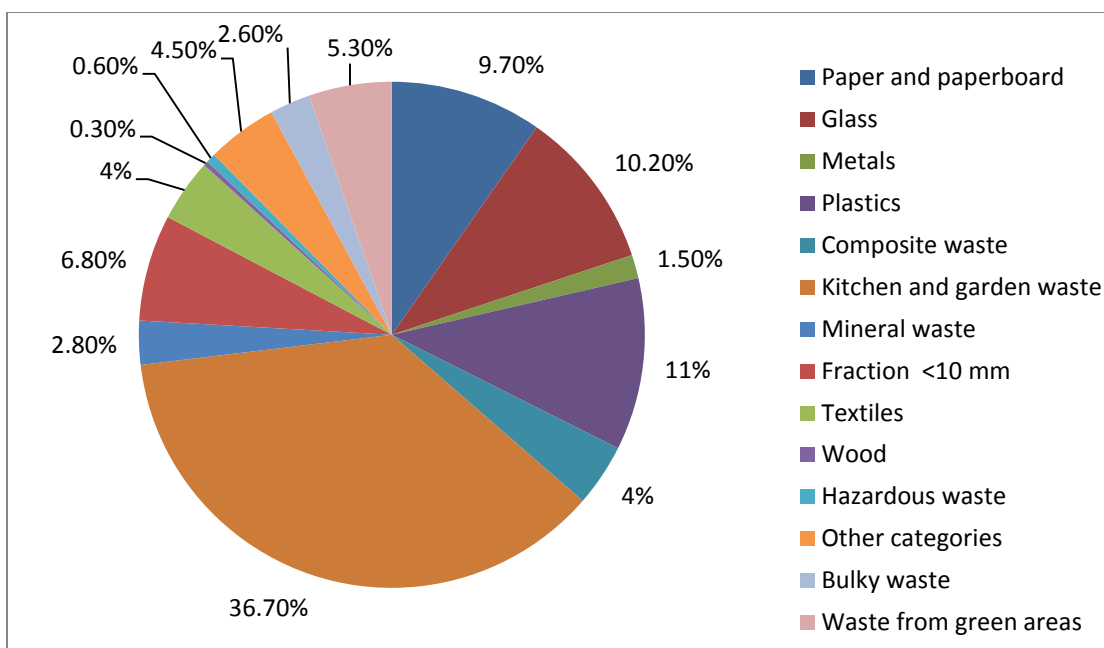


Figure 15. Morphological composition of municipal waste generated in small cities, with populations below 50 thousand and inhabitants in 2008, inhabited by 9.11 million of Poland's residents (23.89%) [18].

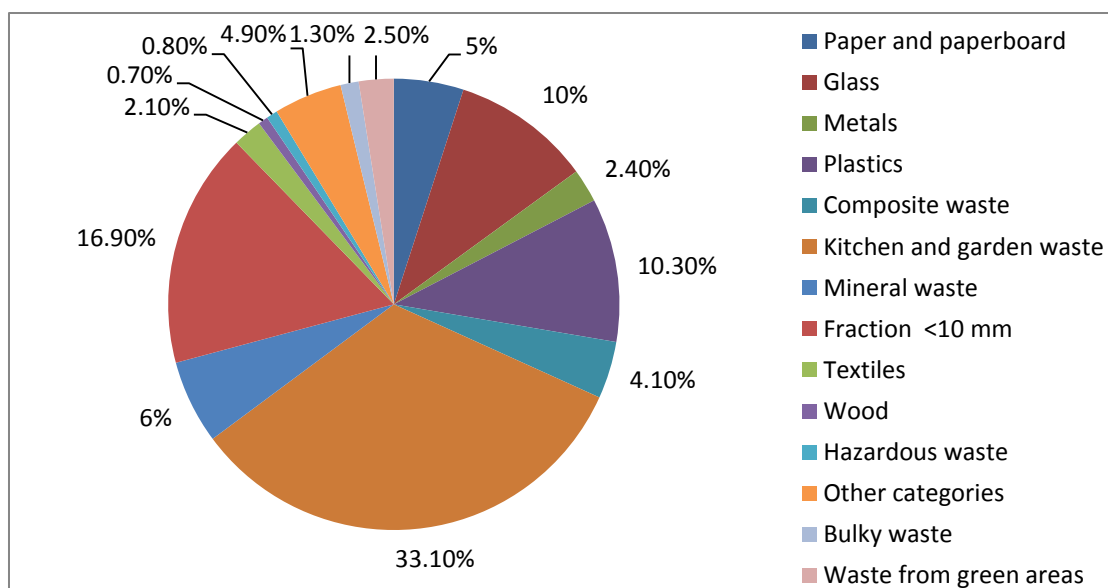


Figure 16. Morphological composition of municipal waste generated in rural areas in 2008, inhabited by 14.85 million of Poland's residents (38.93%) [18].

In big cities content of paper and paperboard in waste was the highest and amounted to 19.10%, in small cities and rural areas was respectively 9.7 and 5%. Content of plastic was the highest in big cities and reached 15.1%, in small cities it was 11% and in rural areas 10.3%. For morphological composition in big cities, small cities and rural areas content of glass was at this same level of 10%. From the Figures 14, 15 and 16 can be concluded that the morphological composition of waste depends on the location where they were sampled and thus, depending on the amount of the inhabitants of the region of their earnings as well as information on whether the region is industrialized or agricultural.

Table 5 shows collected and disposed different types of waste in 2004-2008.

Table 5. Mixed municipal waste collected and disposed of in 2004-2008 [18].

Year	Total collected waste	Waste collected without separated waste					Disposed of during the year		Separated from mixed waste	Landfilled
		Total	Per capita	Including:			thermally	biologically		
				commerce, small business, offices and institutions	municipal services	households				
k Mg		kg								
2004	9,759	9,516	249.3	2,441	473	6,602	87	234	-	9,194
2006	9,877	9,473	248.4	2,279	568	6,627	45	297	144	8,987
2008	10,036	9,354	245.4	2,405	521	6,428	63	262	336	8,693

In 2008, 10036 Mg thousands of municipal waste was collected. It is about 159 Mg thousand more than in 2006 and 277 Mg thousand more than in 2004 [18].

Between years 2004 and 2008 the mass of the fraction of municipal waste collected under separate collection grown systematically from 243 to 670 Mg thousand. The waste collected with the highest per capita rate in 2008 was glass (175 Mg thousand) and waste paper (145 Mg thousand), and the lowest rate was noticed for hazardous waste (Figure 17). [18]

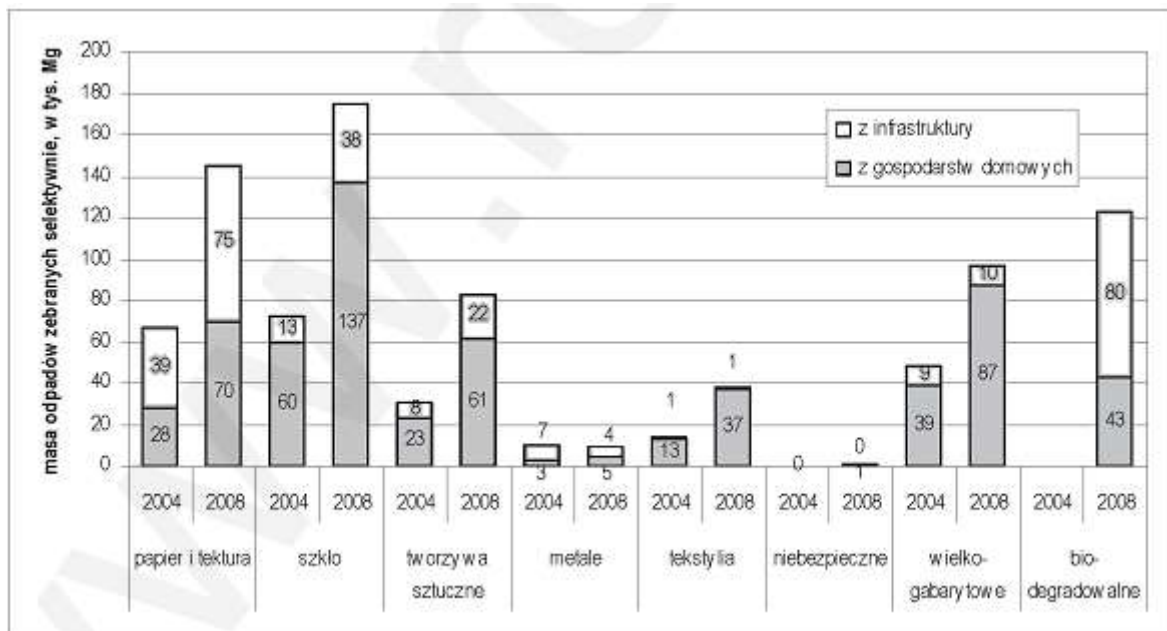


Figure 17. Mass of separately collected waste between 2004 and 2008 [18].

Important fraction of municipal waste is biodegradable waste. Biodegradable waste is waste that undergoes aerobic or anaerobic decomposition with the contribution of microorganisms. [18]

Municipal biodegradable waste includes [18]:

- paper and paperboard,
- clothing and textiles made from natural materials,
- waste from green areas,
- wood,
- kitchen and garden waste,
- composite waste,
- small fraction < 10 mm.

Despite the growing demand for testing of municipal waste at local, regional and national levels, as well as international is not introduced yet official, uniform and universal research methodology waste in the European Union. Lack of such official method prevents direct comparison of the characteristics of the waste in each country, as and between EU countries. At the end of the eighties have been developed different methods of quantitative research and qualitative waste, the use of is not always mandatory (Poland). Developed

methods apply research so daily mixed household waste and eventually from municipal waste infrastructure facilities. Most test methods of waste were created in Germany in the 80s. In other countries (Italy, Spain, Greece) does not have a standardized existing test methods or are unclear and unhelpful to the wider characteristics waste. In the twenty-first century knowledge of the quantity and composition of waste generated becomes more and more necessary, particularly for the collection of operations planning and processing of waste, as well as to identify pollutants in the waste. In the coming years it need to develop a uniform and mandatory for all the countries of the European Union complementary method for current research. In addition, must be performed a number of regular monitoring studies the morphological and fractional waste sites in different regions of the world taking into account their location and the nature of the functional and economic. This would enable the development of reliable waste management plans [19].

One of more specific method is MODECOM (*MODE de Caractérisation des Ordures Ménagères*) which was developed in France and consists of choosing random vehicles transporting waste. Table 6 shows categories of waste in MODECOM method.

Table 6. Fraction of waste in MODECOM methodology [20].

Code	Main fraction	Sub-fraction
01	Bio-degradable waste	Food waste
		Garden waste
02	Paper	Packages
		Newspapers, magazines and others
		Office paper
		Other papers
03	Cardboard	Packages
		Other cardboards
04	Multimaterial waste	Multimaterial package containing cardboards
		Other multimaterial packages
		Non-packaging multimaterial waste
05	Textile	
06	Textile from health protection	
07	Plastic waste	Foils (films) PE i PP
		Transparency bottles PET
		Bottles and container PET, PVC, PEHD
		Other packages from plastic
		Other waste from plastic
08	Classified combustible waste	Non-classified combustible packages
		Other non-classified combustible waste
09	Glass waste	Glass packages
		Other glass (non-packaging)
10	Metal waste	Packages from ferrous metals
		Aluminum packages
		Other metal waste (non-packaging)
11	Non-flammable unclassified waste	
12	Special household waste	Batteries and accumulators
		Other special waste
13	Fraction below 20 mm	

Sample preparation is to empty the entire contents of the vehicle and the random selection of the 10 trials a weight of about 50 kg each, which, after giving a basic attempt to merge with a mass approximately 500 kg designed for further sorting. In areas with a population of over 200000 people be sampled with 10 vehicles on the rest of the 5. The process involves manually sorting, according to its directory sorted waste. Then waste is weighed, sieving through a sieve with round holes of a diameter 100 mm, graded on a coarse fraction > 100 mm (for certain categories of materials). The remainder of the sample is sieved through a sieve with round holes a diameter of 20 mm to obtain a fraction of the mean (20-100 mm). This fraction is weighted, reduced by quartering to obtain a trial of mass approximately 1/8 the initial weight of the fraction, and then sorted and weighed again. Final step is weighing the fine fraction (<20 mm) [19].

In 2003, research was conducted in Krakow based on the composition and quantity of waste municipal project SWA Tool (Solid Waste Analysis Tool). Studies using this method were also carried out in Wroclaw in 2004-2005 and in parallel in the United Kingdom and Ireland. this method involves the separation of the fraction: <10 mm, 10-20 mm, 20-40 mm, 40-80 mm, 80-100 mm and >100 mm. Fractions 10-20 mm and 20-40 mm are divided into 11 main categories. Material with a larger diameter is divided into 34 sub-categories. Sorting scheme shown in Figure 18 [19].

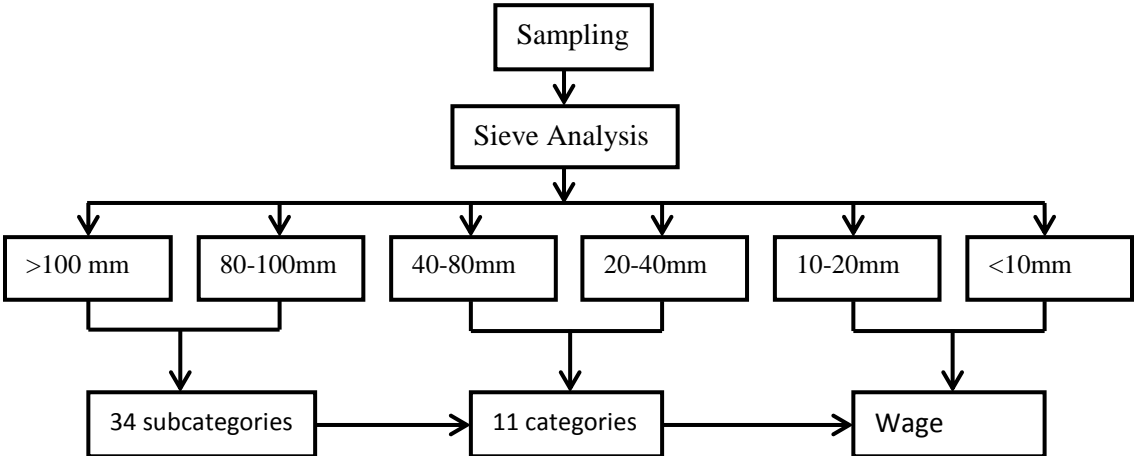


Figure 18. Pattern of investigation of morphological composition municipal waste by SWA Tool [19].

The research carried out in accordance with PN-93/Z-15006, include a breakdown of waste into 10 categories (including the fine fraction <10 mm), and then on the four fractions. Research of material composition is performed for the entire mass of waste grain size above 10 mm. This standard recommends testing waste composition consisting in collecting the sample mean of the waste in the landfill and then separation by hand into individual fractions and weighing them [19].

Figure 19 shows sorting scheme according to Polish standard PN-93/Z/15006.

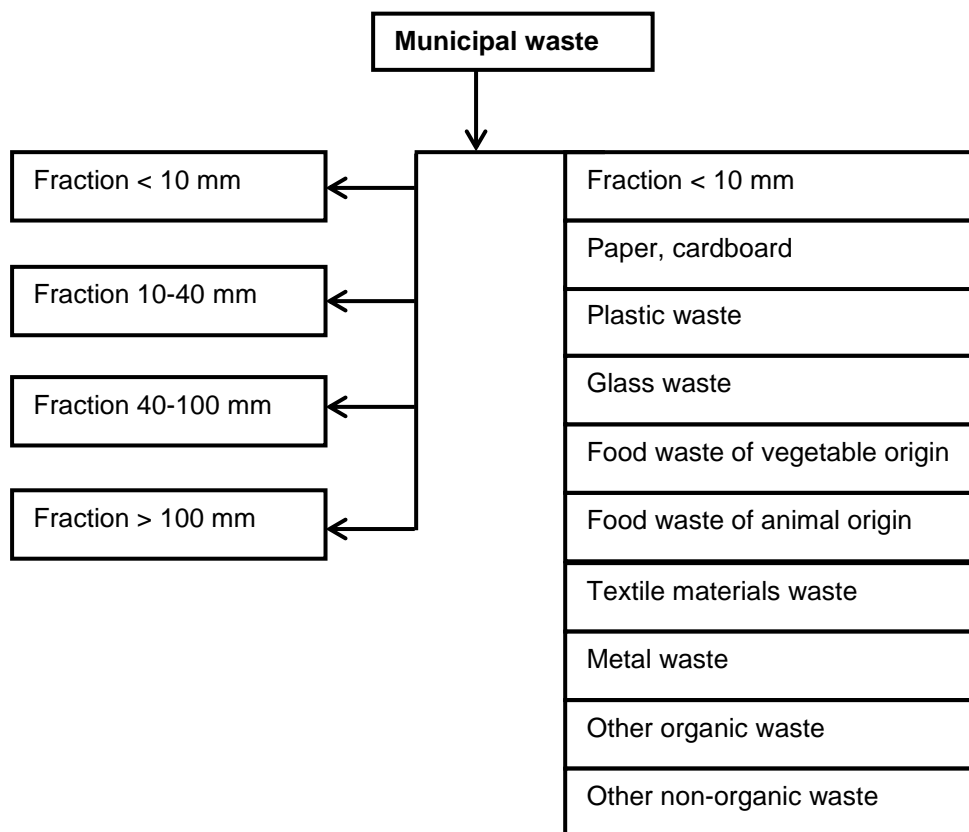


Figure 19. Scheme of granulometric composition and waste material analysis according to Polish standard PN-93/Z/15006 [20].

Morphology of samples was determined using the standard PN-93/Z15006 [21] results are placed in Table 7.

Table 7. Morphological composition of samples.

No.	Name of component	SRF 1 (%)	SRF 2 (%)	SRF 3 (%)
1	Fraction below 10 mm	0.00	0.00	0.00
1	Food waste of vegetable origin	6.48	4.93	3.00
2	Food waste of animal origin	0.49	0.73	4.29
3	Paper and cardboard waste	40.61	23.94	37.92
4	Plastic waste	36.22	45.06	28.62
5	Textile materials waste	13.64	21.40	14.17
6	Glass waste	0.62	1.26	1.70
7	Metal waste	0.53	1.92	1.60
8	Other organic waste	0.75	0.68	8.43
9	Other non-organic waste	0.66	0.08	0.27
10	SUM(%)	100.00	100.00	100.00

In Table 7 can be noticed that the biggest percentage in morphological composition of samples have paper and cardboard from 23.94 to 40.61% and plastic between 28.62 and 45.06%. Both of these components can have a big impact on the calorific value of the mixture. Therefore, it is important to analyze morphological composition of the material to know impact of the individual components on the properties of the fuel.

6. Analysis of Solid recovered fuels laboratory samples

Very important factor right next to morphology are the chemical properties of waste. To verify if the waste are suitable for energy industry as alternative fuel there are a number of standards that examine this. All of this standards have been shown to illustrate how developed is knowledge about waste. Those are listed below [22]:

CEN/TR 14980:2004 Solid recovered fuels - Report on relative difference between biodegradable and biogenic fractions of SRF

CEN/TR 15404:2010 Solid recovered fuels - Methods for the determination of ash melting behaviour by using characteristic temperatures

CEN/TR 15441:2006 Solid recovered fuels - Guidelines on occupational health aspects

CEN/TR 15508:2006 Key properties on solid recovered fuels to be used for establishing a classification system

CEN/TR 15591:2007 Solid recovered fuels - Determination of the biomass content based on the ¹⁴C method

CEN/TR 15716:2008 Solid recovered fuels - Determination of combustion behavior

CEN/TS 15401:2010 Solid recovered fuels - Determination of bulk density

CEN/TS 15405:2010 Solid recovered fuels - Determination of density of pellets and briquettes

CEN/TS 15406:2010 Solid recovered fuels - Determination of bridging properties of bulk material

CEN/TS 15412:2010 Solid recovered fuels - Methods for the determination of metallic aluminium

CEN/TS 15414-1:2010 Solid recovered fuels - Determination of moisture content using the oven dry method - *Part 1*: Determination of total moisture by a reference method

CEN/TS 15414-2:2010 Solid recovered fuels - Determination of moisture content using the oven dry method - *Part 2*: Determination of total moisture content by a simplified method

CEN/TS 15639:2010 Solid recovered fuels - Determination of mechanical durability of pellets

EN 15357:2011 Solid recovered fuels - Terminology, definitions and descriptions

EN 15358:2011 Solid recovered fuels - Quality management systems - Particular requirements for their application to the production of solid recovered fuels

EN 15359:2011 Solid recovered fuels - Specifications and classes

EN 15400:2011 Solid recovered fuels - Determination of calorific value

EN 15402:2011 Solid recovered fuels - Determination of the content of volatile matter

EN 15403:2011 Solid recovered fuels - Determination of ash content

EN 15407:2011 Solid recovered fuels - Methods for the determination of carbon (C), hydrogen (H) and nitrogen (N) content

EN 15408:2011 Solid recovered fuels - Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content

EN 15410:2011 Solid recovered fuels - Methods for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti)

EN 15411:2011 Solid recovered fuels - Methods for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Ti, V and Zn)

EN 15413:2011 Solid recovered fuels - Methods for the preparation of the test sample from the laboratory sample

EN 15414-3:2011 Solid recovered fuels - Determination of moisture content using the oven dry method - *Part 3:Moisture in general analysis sample*

EN 15415-1:2011 Solid recovered fuels - Determination of particle size distribution - *Part 1: Screen method for small dimension particles*

EN 15415-2:2012 Solid recovered fuels - Determination of particle size distribution - *Part 2:Maximum projected length method (manual) for large dimension particles*

EN 15415-3:2012 Solid recovered fuels - Determination of particle size distribution -*Part 3:Method by image analysis for large dimension particles*

EN 15440:2011 Solid recovered fuels - Methods for the determination of biomass content

EN 15440:2011/AC:2011 Solid recovered fuels - Methods for the determination of biomass content

EN 15442:2011 Solid recovered fuels - Methods for sampling

EN 15443:2011 Solid recovered fuels - Methods for the preparation of the laboratory sample

EN 15590:2011 Solid recovered fuels - Determination of the current rate of aerobic microbial activity using the real dynamic respiration index

Waste analyses were carried out according to the procedures of Institute for Chemical Processing of Coal (Zabrze-Poland) based on the European Union standards and experience of employees of the Institute. Measurement include: proximate, ultimate, higher heating value, lower heating value and ash analysis.

6.1. Proximate analysis

Proximate analysis is measurement of technical properties of fuel. Analysis includes:

- moisture content,
- volatile matter content,
- ash content,
- fixed carbon.

The total moisture content of the SRF sample was determined according to Institute for Chemical Processing of Coal procedure number Q/LP/18/A:2011 [23] which consists determination of the weight loss of the waste sample, comminuted to a grain size below 60 mm during drying to constant weight at a temperature of (105 ± 3) °C. The analysis was made using a dryer from company Venticell, model 55.

The analytical moisture content was determined according to Institute for Chemical Processing of Coal procedure number Q/LP/28/A:2011 [24]. The principle of the sample is based on thermogravimetric determination of the weight loss of the laboratory sample and drying it to constant weight at (105 ± 3) °C. The measurement was made using apparatus from company LECO type TGA-701 (Figure 20).



Figure 20. Thermogravimetric analyser from company LECO type TGA-701.

The measurement of volatile matter of the SRF sample is determined according to Institute for Chemical Processing of Coal procedure number Q/LP/20/A:2011 [25] which consists in the calcination of the sample in a closed crucible without contact with air at a temperature of $(900 \pm 10) ^\circ\text{C}$ for 7 minutes, and calculating the content of volatile as the difference between the total loss of weight of the sample and the weight loss due to water evaporation. The analysis of volatile matter was made using the muffle furnace from company Heraeus.

The ash of the SRF sample is determined according to Institute for Chemical Processing of Coal procedure number Q/LP/19/A:2011 [26] which consists in the complete combustion of the sample and the remains of calcination at $(815 \pm 15) ^\circ\text{C}$ degrees in the case of waste wood and waste type textiles, paper, plastics (ex. PET, PVC) ash content determination must be carried out at a temperature of $600 ^\circ\text{C}$. The analysis of ash was made using the muffle furnace from company Nabertherm (Figure 21).



Figure 21. Muffle furnace from company Nabertherm.

The fixed carbon is calculated as a subtraction of the moisture, volatile matter and the ash content from the total (100%).

Results of proximate analysis are presented in Table 8.

Table 8. Result of proximate analysis of waste.

Proximate analysis (wt %, as received)	SRF 1	SRF 2	SRF 3	Uncertainty (\pm)
Volatiles	63.1	73.7	67.6	0.29
Fixed Carbon	11.4	10.6	12.0	*
Moisture	3.1	4.6	3.2	0.6
Ash	22.4	11.1	17.2	0.3
SUM	100.0	100.0	100.0	

* Uncertainty was not considered. Fixed Carbon values were calculated.

High content of volatile matter may favorably influence the calorific value of the waste. While the ash content and moisture that are ballast may reduce this value. Studies of Wagland et al. (2011) [27], and Bosmans et al. (2014) [28], shows related proximate analysis results of waste. Content of volatile matter in their studies was respectively 79.6 and 69.3%, ash content was 11.1 and 22.1%, moisture content was 3.0 and 4.6%. Data from Table 8 in comparison with results from other studies show that content of volatile matter in all three samples is lower than in studies of Wagland et al. (2011). In comparison to studies of Bosmans et al. (2014) content of volatile matter is lower in SRF 1 and SRF 3 and higher in SRF 2. Ash content in SRF 1 is higher in compare to other studies. In SRF 2 is lower than in Bosmans et al. (2014) and similar to Wagland et al. (2011) studies. In SRF 3 ash content is higher than in Wagland et al. (2011) studies and lower than in Bosmans et al. (2014) studies. Moisture content in all three samples of SRF is between values from studies of Wagland et al. (2011) and Bosmans et al. (2014). It is possible to verify a small correlation between morphological composition and proximate analysis, for example amount of paper waste in sample composition can increase ash content. Content of volatiles matter is higher when in composition of SRF is a big amount of plastic waste and ash content can depend on content of paper and cardboards in waste.

6.2. Ultimate analysis

Ultimate analysis is measurement of the content of the elements such us:

- carbon content (C).
- hydrogen content (H),
- nitrogen content (N),
- sulphur content (S),
- and oxygen content (O).

Elemental analysis of the C, H, N was determined by Institute for Chemical Processing of Coal procedure number Q/LP/22/B:2011 [29], which consists in: automatic and quantity burning in the pipe exhaust gas of the analyzer, samples of waste in an oxygen stream at temperature > 950 °C, deprivation resulting gases with halogen oxides of sulfur and other impurities, analysis of the combustion product contained in the H_2O and CO_2 , a detector for infrared, reductions due interestingly, during the combustion of nitrogen oxide NO_x into N_2 and its analysis for the help of the

thermal conductivity detector. The whole cycle analysis is automatic computer controlled since the introduction of samples up to achieve results in the form of a printout. The analysis was made using the apparatus from company LECO type CHN-628 (Figure 22).



Figure 22. Analyzer from company LECO type CHN-628.

Analysis of the sulphur is determined by Institute for Chemical Processing of Coal procedure number Q/LP/21/A:2011 [30]. The principle of the method consists in the quantitative combustion in the pipe Combustion Analyzer waste sample in a stream of oxygen at 1350 °C purification of the resulting gases from dust and moisture and the determination contained in purified SO₂ gas adsorption method of infrared radiation. The analysis was made using the apparatus from company LECO type SC-632 (Figure 23).



Figure 23. Analyzer from company LECO type SC-632.

The oxygen content was calculated as subtraction of the carbon, hydrogen, nitrogen, sulphur from total (100%).

Table 9 shows the results from ultimate analysis.

Table 9. Results of ultimate analysis of waste.

Ultimate analysis (wt %, dry ash free)	SRF 1	SRF 2	SRF 3	Uncertainty (\pm)
Carbon	65.6	60.6	61.1	0.5
Hydrogen	8.3	4.8	8.1	0.15
Nitrogen	1.2	0.9	1.2	0.11
Sulphur	0.5	0.9	0.5	0.3
Oxygen	24.4	32.8	29.1	*
SUM	100.0	100.0	100.0	

* Uncertainty was not considered. Oxygen values were calculated

The high content of carbon (respectively 65.6, 60.6, 61.1%) and hydrogen (sequentially 8.3, 4.8, 8.1%) in the samples can increase calorific value. In studies of Pinto et al. (2014) [31], and Zhou et al. (2013) [32], related ultimate analysis results of waste. Content of carbon in their studies respectively was 67.9 and 63.3%. Content of hydrogen respectively 5.1 and 8.9%. The obtained results show that carbon content in all samples are lower than Pinto et al. (2014) but SFR 1 is higher than in Zhou et al. (2013) studies. Hydrogen content in SRF 1 and 3 is lower than in Zhou et al. (2013) analysis but higher than in Pinto et al. (2014). In SRF 2 content is lower in comparison to both studies. However, the obtained values are accordingly with literature.

6.3. Calorific value

Furthermore, another important aspect in assessment of the fuel behavior is the determination of calorific value, which represents the amount of heat that the fuel produce in a process of combustion.

Higher Heating Value (HHV) was measured and Lower Heating Value (LHV) was calculated according to Institute for Chemical Processing of Coal procedure number Q/LP/23/A:2011 [33]. Higher Heating Value is measured by method that involves the complete combustion of weighed waste and alternative fuels in an atmosphere of oxygen under pressure in a bomb calorimeter at constant volume to the isothermal or adiabatic system and measuring the temperature rise of water in the calorimeter vessel as well as the determination of the amendments to the heat generated during the combustion of wire, thread and heat resulting from the formation of sulfuric acid. The analysis was made using the apparatus from company LECO type AC-500 (Figure 24).



Figure 24. Calorimeter from company LECO AC-500.

Lower Heating Value (LHV) is calculated by using the following formula [33]:

$$LHV = HHV - 24.42 \times (M + 8.94 \times H)$$

Where:

LHV – Lower Heating value in [kJ/kg]

HHV – Higher heating value in [kJ/kg]

24.42 - heat of vaporization of water at 25 °C equivalent to 1% water in the waste

M – Moisture content in the waste sample [%]

8.94 – conversion ratio of hydrogen content into water

H – Hydrogen content in the waste sample [%]

Results of Higher and Lower Heating Value are placed in table below.

Table 10. Results of calorific value.

Heating value (wt MJ/kg, analytical state)	SRF 1	SRF 2	SRF 3	Uncertainty (±)
Lower	19.0	22.9	20.0	165
Higher	20.4	23.9	21.5	154

The caloric value is close to the calorific value of the biomass. These results illustrate the opportunity to use waste as a fuel to combustion or co-firing. In study of Luo et al. (2010) [34], results revealed that higher heating value of SRF was found to be 21.3 MJ/kg. Thus, the obtained values for SRF's are comparable with literature study [34].

6.4. Ash analysis

Characteristic melting temperature of ash were analyzed according to Institute for Chemical Processing of Coal procedure number Q/LP/35/A:2011 [35]. Principle of the method is to heat the fitting of ash in the form of a cylinder or a cube in an oxidizing or half reductive atmosphere and reading the characteristic melting temperature of ash on the basis of changes in the contours of the

test observed shapes on a grid measuring characteristic melting temperature of ash and atmosphere of measurement defined. The analysis was made in a heating furnace type PR-25/1750 (Figure 25)



Figure 25. Furnace from company Tele and Radio Research Institute type PR-25/1750.

In Table 11 are placed ash melting temperatures of SRF samples measured in oxidizing (air) and half-reduced (mixture of carbon oxide and carbon dioxide in mass ratio 3:2) atmosphere.

Table 11. Results of ash melting temperatures.

Oxidizing atmosphere (°C)	SRF 1	SRF 2	SRF 3	Uncertainty (±)
Temperature of sintering	1160	1140	1120	18
Temperature of softening point	1190	1190	1150	13
Temperature of melting	1200	1210	1230	7
Temperature of flow	1210	1240	1250	12
Half-reduction atmosphere (°C)	SRF 1	SRF 2	SRF 3	Uncertainty (±)
Temperature of sintering	1060	1030	1070	24
Temperature of softening point	1150	1150	1170	19
Temperature of melting	1180	1180	1180	5
Temperature of flow	1210	1190	1200	21

Analysis was also carried the content of oxides in the ash with the apparatus Thermo Scientific iCAP 6500 (Figure 26) according to Institute for Chemical Processing of Coal procedure number Q/LP/65/A:2011 [36]. The method consists of: excited inductively coupled plasma silicon atoms of iron, aluminum, calcium, magnesium, sodium, potassium, manganese, sulfur, phosphorus, titanium, strontium contained in the sample solution prepared from the ash measuring the radiation intensity is still recovering reading of the concentration of various elements were based on calibration curves reading levels of the individual elements on the basis of calibration curves calculation on the basis of the content of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, P₂O₅, SO₃, SrO, BaO, TiO₂, Mn₃O₄ in ash from waste.



Figure 26. Analyzer from company Thermo Scientific type ICAP 6500.

Table 12 shows the results from measurement content of oxides in ash of SRF samples.

Table 12. Results of content of oxides in the ash.

Ash analysis (wt %, dry basis)	SRF 1	SRF 2	SRF 3
SiO ₂	35.7	33.4	35.1
Al ₂ O ₃	16.2	12.0	17.3
Fe ₂ O ₃	14.4	7.0	8.8
CaO	20.4	22.6	24.5
MgO	2.8	2.3	2.8
P ₂ O ₅	1.0	1.9	1.1
SO ₃	3.6	11.9	4.8
Mn ₃ O ₄	0.2	0.1	0.2
TiO ₂	1.6	2.4	2.2
BaO	0.2	0.2	0.2
SrO	0.1	0.6	0.1
Na ₂ O	2.4	3.8	1.8
K ₂ O	1.4	1.8	1.1
SUM	100.0	100.0	100.0

In case of specific temperatures and content of oxides in ash, correlation can be observed. Studies show that [37] the melting temperature is also influenced by the chemical composition of ash. Larger contents ash components such as: SiO₂, Al₂O₃, K₂O caused an increase in the melting temperature ash. Components: Fe₂O₃, CaO, MgO, SO₃, Mn₃O₄ have more complex effect on the temperatures. As the content of these components increased followed first reduction and then a rise of the ash melting temperature. In the case of the remaining components there was no significant effect. There is a weak relationship between the melting temperature of ash and the ash content in material. With increasing ash content, the fusion temperature of ash slightly increases.

All these measurements are needed to be able to predict behavior of waste during combustion and to determine if the waste is suitable as fuel from which energy can be produced, and to understand the process of combustion and consequently, could design of appropriate installations for the disposal of waste as well as check the impact of incineration on the environment.

7. Environmental issues

Concern for the environment goes in pair with management and disposal of waste. Garbage contains a different kind of substances negatively influencing nature.

The problem of negative effects on the environment starts from the very beginning of waste management. Mostly these are inadequate or insufficient collection of recyclable or reusable waste, as well as the inappropriate disposal of hazardous waste, also influenced by the wrong location, design, operation and maintenance of landfills and dumps [38].

Inappropriate management of waste may cause [38]:

- Increase in the disease transmission, or otherwise danger to public health
- Contaminate ground and surface water
- Create greenhouse gas emissions and other air pollutants
- Damage ecosystem
- Injure people and property

This is the reasons to analysis harmful particles which have negative impact on environment.

7.1 Mercury, Chlorine, Fluorine

The mercury content analysis according Institute for Chemical Processing of Coal procedure number Q/LP/54/A:2011 [39]. The principle of the method consists in thermal decomposition of the sample at 850 °C absorbed atomic mercury amalgam by heating to a temperature of 600 °C assay concentrations of mercury releasing the absorption chamber atomic absorption method of cold vapor technique at 253.7 nm length of wave Carrier gas when analyzing air is drawn through the analyzer from the environment passing through the filter to trap pollutants and mercury contained in the air. The analysis was made using the apparatus from company Nippon Instruments Corporation type MA-2 (Figure 27)



Figure 27. Analyzer from company Nippon Instruments Corporation type MA-2.

The chlorine content is determined by Institute for Chemical Processing of Coal procedure number Q/LP/21/A:2011[40] which consists in the complete combustion of the sample waste in the presence of Eschka mixture in a calorimetric bomb in an oxygen atmosphere and determination of the chlorine content in a solution containing combustion products by potentiometric titration. Method should be used to determine the content of chlorine present in quantities not less than 0.005%. The potentiometric titration was made using apparatus seen on Figure 28.



Figure 28. Apparatus for potentiometric titration for determining of chlorine content.

The fluorine content is determined by Polish Norm number PN-82/G-04543 [41]. The principle of the method is based on combustion of the sample in a bomb calorimeter under an oxygen atmosphere and then determination of the fluoride ions in a solution containing combustion products by potentiometric determination using ion-selective electrode. The potentiometric titration was made using apparatus seen on Figure 29.



Figure 29. Apparatus for potentiometric titration for determining of fluorine content.

Results of analysis are presented in Table 13.

Table 13. Content of mercury, chlorine and fluorine in particular samples.

Particle	SRF 1	SRF 2	SRF 3
Hg (wt ppm, dry state)	0.21	0.33	0.22
Cl (wt %, analytical state)	1.36	0.85	1.55
F (wt %, analytical state)	0.01	<0.005	<0.005

Those elements have been examined because of their negative impact on the human and ecosystem, in which we live.

Mercury and its compounds have very strong toxicity to the human body. System most sensitive to mercury in small doses is the nervous system. Changes are also created within the cardiovascular and renal function [42].

Chlorine present in waste after the burning is a source of acid pollution such as HCl. Chlorine its crucial element in formation of organic chlorine compounds as for example dioxins or chloramine. Dioxins are 10,000 time more poisoning than potassium cyanide. Through its bioaccumulative ability accumulates in adipose tissue and migrate into the food chain. Getting into the human body causes including: carcinogenicity, teratogenicity, decrease in immunity, weakening growth processes, impairment reproductive, neurological and hormonal disorders [43].

Fluorine it is source of HF acid which causes the dissolution of aluminosilicates. In soil poisoned by fluorine the content of organic substances and microbial activity is reduced [44].

Knowing data of Lower Heating Value, content of mercury and chlorine waste can be qualify using standard EN 15359:2011 [45] which is based on three parameters: Net Calorific Value, chlorine and mercury content. These parameters are including estimation of fuel, associated with the economical, technological and emissivity use. For all three parameters assigned five quality classes with their limits. Combination of class number of each parameter give class code of the fuel. These three parameters are not fully describes the characteristics of the fuel. They are helpful in identify fuel for contacts between the manufacturer and the customer [46].

Table 14. Values of classification parameters for solid recovered fuels [47].

Criterion	Unit	1	2	3	4	5
Net Calorific Value	MJ/kg as recived	≥25	≥20	≥15	≥10	≥3
Cl content	% dry matter	≤0.2	≤0.6	≤1.0	≤1.5	≤3.0
Hg content	mg/MJ as recived	≤0.02	≤0.03	≤0.08	≤0.15	≤0.50

Class codes for samples are presented in Table 15.

Table 15. Class code for particular samples.

Criterion	Net Calorific value	Cl content	Hg content
SRF 1	3	4	1
SRF 2	2	1	1
SRF 3	2	5	1

Class code has been attributed to better identify measured samples which being a waste product from a waste treatment plants which are purchased by the cement industry.

7.2 Heavy elements

The content of heavy metals is determined by Institute for Chemical Processing of Coal procedure number Q/LP/66A:2013 [47]. The method consists of excited inductively coupled plasma atoms As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, and Zn contained in the sample solution prepared from the ash of waste, then the resulting measurement of the intensity of radiation, reading of the concentration of various elements on calibration curves and calculation on that basis the contents of these elements in the samples.

Thermo Scientific iCAP 6500 seen on Figure 26 from Chapter 6.

Table 16. Content of heavy elements in particular samples.

Other Particles (wt mg/kg, dry state)	SRF 1	SRF 2	SRF 3
As	5.39	2.82	3.46
Cd	0.21	2.17	0.21
Co	5.57	1.84	5.06
Cr	106.00	32.60	178.00
Cu	91.10	55.00	78.30
Mn	180.00	72.40	208.00
Mo	4.67	136	5.92
Ni	37.80	34,30	37.70
Pb	11.30	34.00	15.60
Sb	46.40	18.60	40.20
V	18.90	5.86	16.70
Zn	638.00	742.00	539.00

These elements have been investigated because of their properties that make them toxic and harmful to the environment. Particular attention should be given to cadmium and lead that its effect, regardless of the size of their concentration, is always a threat.

In case of acute poisoning by cadmium the most vulnerable organ is the liver. Cadmium has also negative effect on bones because of disruption of homeostasis of calcium and phosphorus, which

increased excretion from the organism, causes kidney damage. The consequence of chronic poisoning can damage the olfactory receptors or fibrils. It is also carcinogenic. [48].

Symptoms of lead poisoning are: lack of appetite, inhibiting the growth of young animals, kidney damage, anemia, encephalopathy, and disruption of behavior, which results disorders of the nervous system [48].

8. Thermogravimetric analysis

Thermal analysis is defined as the set of methods that measure the changes in the physical properties of the substance under the influence of temperature. Depending on the test may undergo a change in the environment surrounding the test sample (the chemical composition of the atmosphere, pressure) or physical (mechanical factors, electric fields, etc.). This means that the method of thermal analysis enables determination of changes in the test substance with a change at temperature at various conditions measurement [49].

Methods of thermal analysis are used to study chemical reactions and phase transformations occurring during the heating / cooling substance. Some of them allow to determine thermodynamic and kinetic parameters of the reaction. There are also those which are useful for the qualitative and quantitative determination of phase and chemical composition of the substance methods for analyzing the test of high-temperature reactions associated with the production of many plastics, as well as allows to evaluate the thermal stability test materials. Thermal methods depending on the method of heating the sample during the measurement can be divided into static and dynamic methods [49].

Thermal analysis of the static sample temperature is changed stepwise and maintained at that level until reaching the steady state components of the sample, as the specific temperature. The use of static methods enables the study of processes such as crystallization process and thermal dissociation of the substance by registering changes of its weight. Static methods also allow the determination of the equilibrium temperature of the investigated processes. Thermal analysis of the dynamic temperature of the sample is changed in a linear fashion. Dynamic methods are often used because it allows to quickly obtain the results of thermal analysis [49].

Thermogravimetric analysis is a technique that belongs to the group of thermal analyses. The thermal analysis (TA) is often used to describe analytical experimental techniques which examine the behavior of a sample as a function of temperature. The ability of TA to characterize, quantitatively and qualitatively, enormous variety of materials over a considerable temperature range has been crucial in its acceptance as an analytical technique. TA is widely used in basic research and other applications by many scientists and engineers from around the world [50].

For each tested material were prepared 8 samples of 20 mg each. Analyzes were done using a NETZSCH STA-409 PC/PG Luxx thermogravimetric analyzer (Figure 30).



Figure 30. Thermogravimetric analyzer from company NETZSCH type STA-409 PG Luxx [51].

First thermogravimetric analysis was performed as follows: three samples per 20 mg each were measured in two stages process; in the first, non-isothermal stage heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$ in the atmosphere of Ar with flow rate of 25 ml/min; after reaching assumed temperatures of 475, 600, 800 $^{\circ}\text{C}$ the heating was stopped and the atmosphere was changed to synthetic air (N_2/O_2) with flow rate 100 ml/min, to enable isothermal combustion process.

Second thermogravimetric analysis for three samples 20 mg each in different heating rates was performed for gasification. Analysis conditions were in an atmosphere of Ar with flow rate 25 ml/min and CO_2 with flow rate of 100 ml/min in three assumed heating rates 5, 10, 20 $^{\circ}\text{C min}^{-1}$. Process was carried out to a temperature of 1100 $^{\circ}\text{C}$.

Third thermogravimetric analysis was performed for two samples, using 20 mg each, in order for two processes, pyrolysis and combustion. Both processes were carried out from 40 $^{\circ}\text{C}$ to a temperature of 1100 $^{\circ}\text{C}$. Heating rate was 10 $^{\circ}\text{C}/\text{min}$. Pyrolysis was carried out in an atmosphere of Ar with flow rate of 25 ml/min. Combustion was carried out in an atmosphere of Ar with flow rate 25 ml/min and synthetic air (N_2/O_2) with flow rate 100 ml/min.

The degree of conversion (α) for tested material was calculated using the equation [52]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$

where m_0 mass of sample at the beginning, m_t mass of sample at time t and m_f is the final mass of the sample.

8.1 Non-isothermal pyrolysis and isothermal combustion

Results obtained from first thermogravimetric analysis were used in creation of graphs showing the dependence of weight loss and conversion on time. Figures were made to compare behavior of three samples in non-isothermal and isothermal process in assumed temperatures.

The weight loss vs. time thermogram for both stages at temperature 475 °C for SRF 1, SRF 2, and SRF 3 is presented in Figure 31.

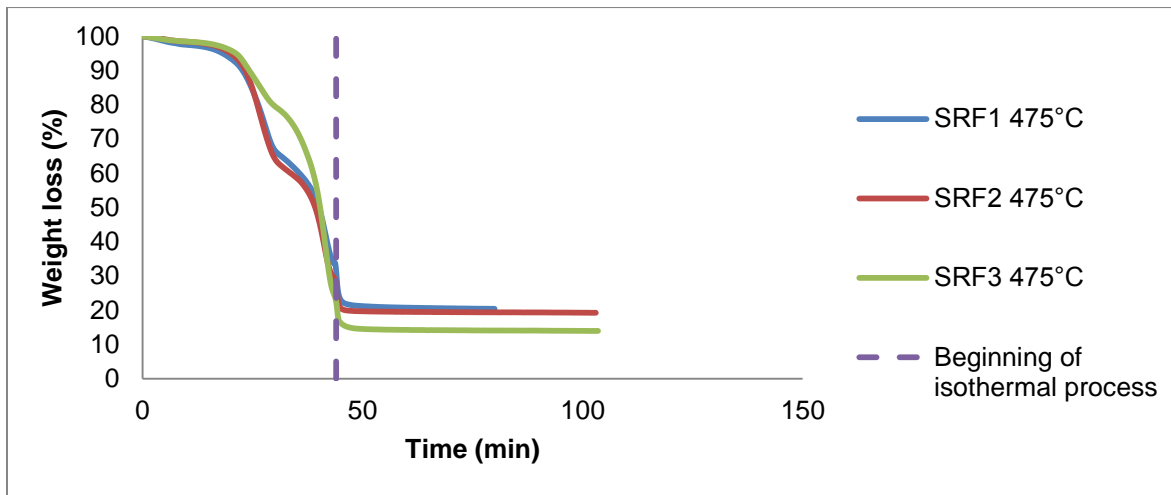


Figure 31. Comparison for non-isothermal stage and isothermal combustion at 475 °C for SRF 1, SRF 2, SRF 3.

The degree of conversion vs. time thermogram for both stages at temperature 475 °C for SRF 1, SRF 2, and SRF 3 is presented in Figure 32.

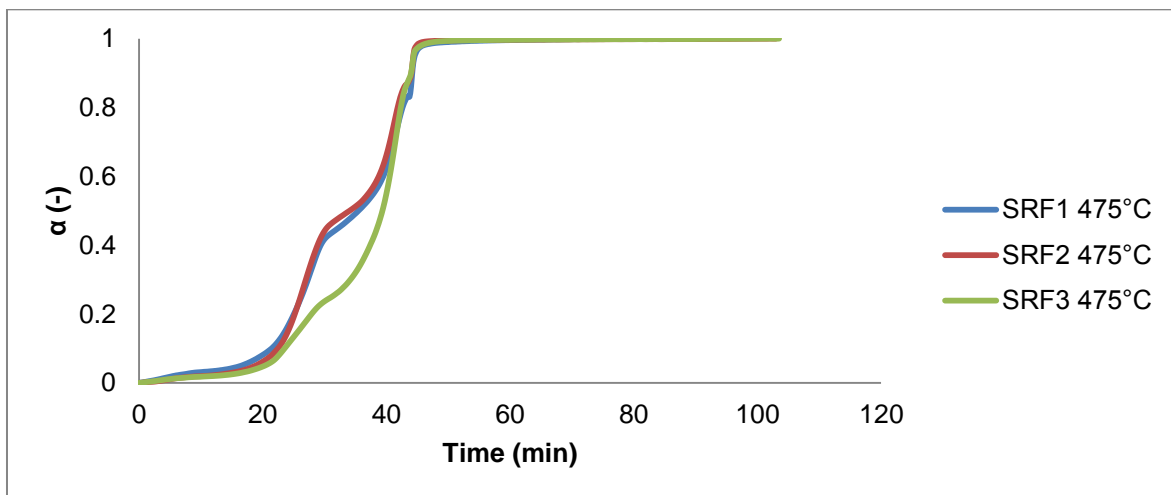


Figure 32. Comparison for the degree of conversion for non-isothermal and isothermal combustion at temperature 475 °C SRF 1, SRF 2 and SRF 3.

The weight loss vs. time thermogram for both stages at temperature 600 °C for SRF 1, SRF 2, and SRF 3 is presented in Figure 33.

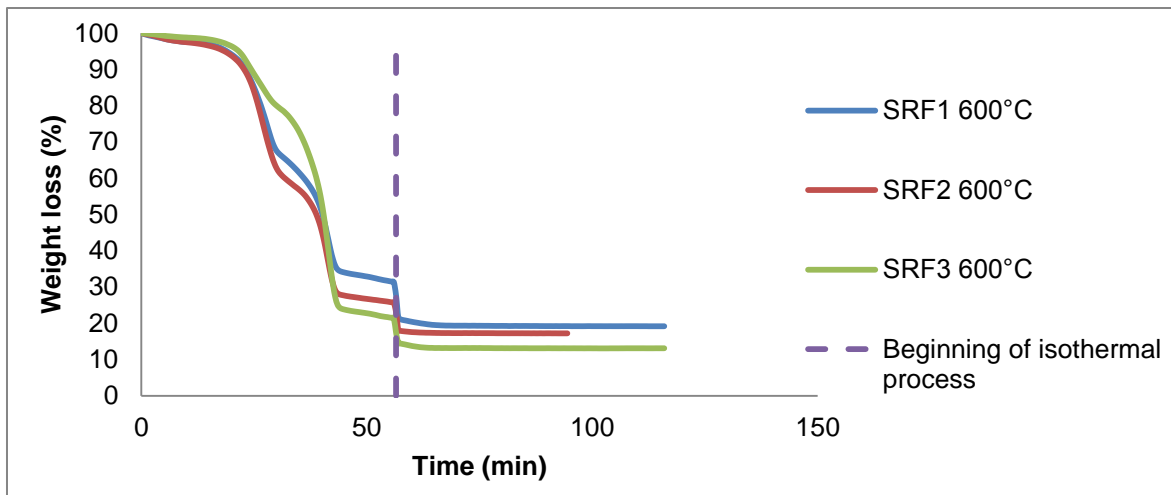


Figure 33. Comparison for non-isothermal stage and isothermal combustion at 600 °C for SRF 1, SRF 2, SRF 3.

The degree of conversion vs. time thermogram for both stages at temperature 600 °C for SRF 1, SRF 2, and SRF 3 is presented in Figure 34.

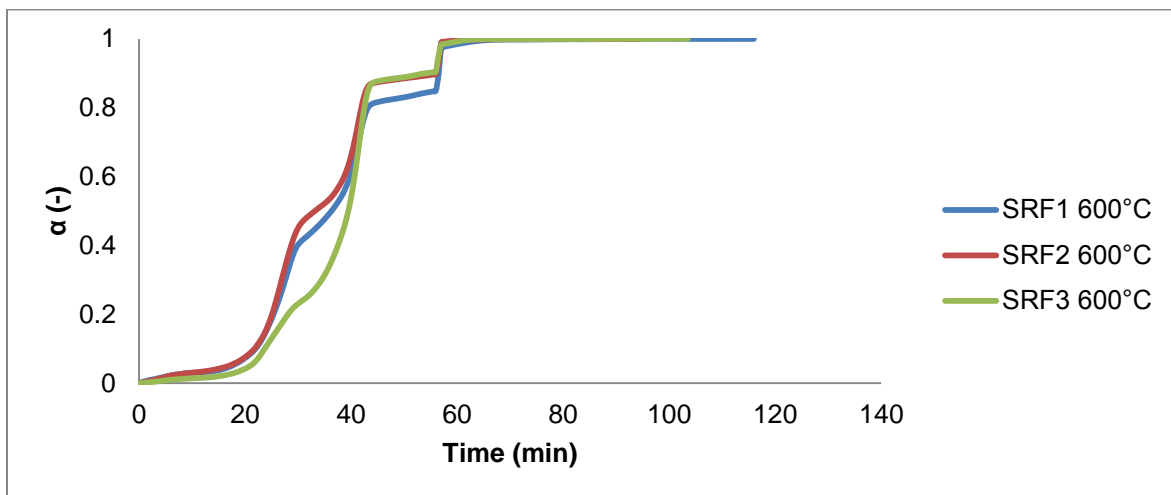


Figure 34. Comparison for the degree of conversion for non-isothermal and isothermal combustion at temperature 600 °C SRF 1, SRF 2 and SRF 3.

The weight loss vs. time thermogram for both stages at temperature 800 °C for SRF 1, SRF 2, and SRF 3 is presented in Figure 35.

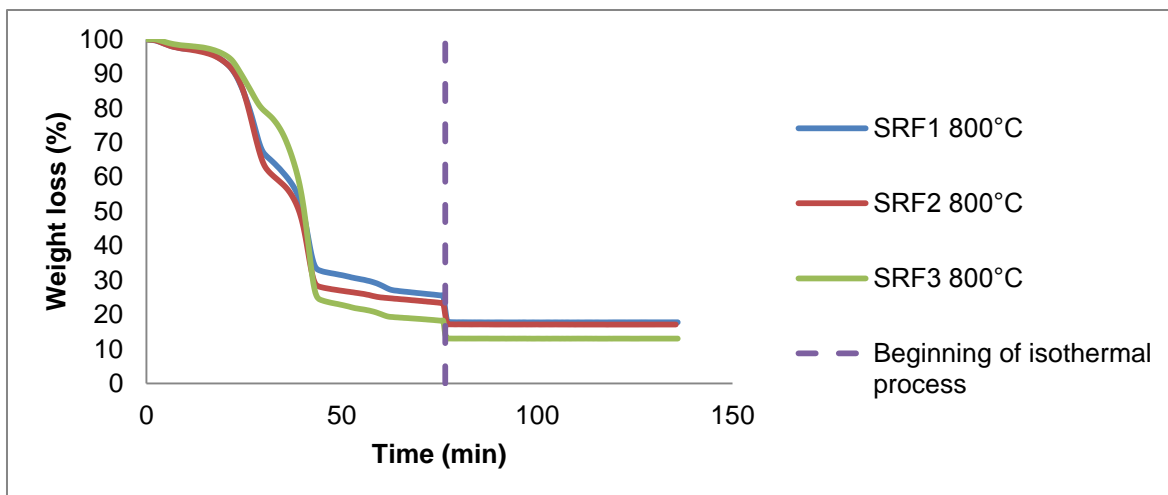


Figure 35. Comparison for non-isothermal stage and isothermal combustion at 800 °C for SRF 1, SRF 2, SRF 3.

The degree of conversion vs. time thermogram for both stages at temperature 800 °C for SRF 1, SRF 2, and SRF 3 is presented in Figure 36.

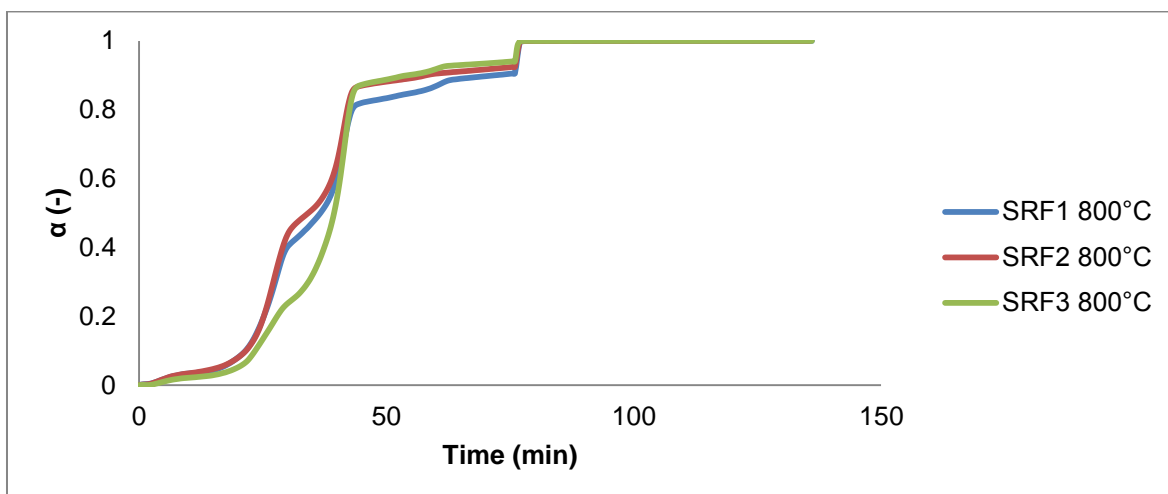


Figure 36. Comparison for the degree of conversion for non-isothermal and isothermal combustion at temperature 800 °C SRF 1, SRF 2 and SRF 3.

As it can be seen in Figure 31, 33 and 35 the thermogravimetric analysis shows both stages. In non-isothermal stage occurs the biggest weight loss (from 94 to 40%), which can be observed between 20 and 40 minute of measurement. This may be caused by moisture vaporization and release of volatile matter as well as conversion of higher hydrocarbons into simpler chains. Combustion was conducted in isothermal stage (beginning of the process was marked by dash line), which was carried out at three temperatures sequentially in 475, 600, 800 °C.

In Figure 33 between 44 and 56.5 minute and in Figure 35 between 44 and 76.5 minute can be noticed stable weight loss for all three samples, which may be related with degradation of char.

Isothermal process began, for three assumed temperatures, sequentially in 44, 56.5, 76.5 minute. Mass become constant after 46, 60, 78 minute of measurement, respectively. In first minutes swift weight loss can be observed. Below 20% of weight loss are residues, which was burn out.

Figures 32, 34 and 36 show that the degree of conversion increased with time. The largest increase can be observed between 20 and 40 minute from 0.1 up to 0.9. Curves for SRF 1 and SRF 2 are almost similar, but in case of SRF 3 increase of conversion is slower in this time. In Figure 33 between 44 and 56.5 minute and in Figure 35 between 44 and 76.5 minute can be noticed stable grown of conversion. In 44, 56.5 and 76.5 minute respectively for 475, 600 and 800 °C swift increase of conversion can be observed.

In all three figures can be noticed that curves for SRF 1 and SRF 2 in non-isothermal stage are almost similar. In case of SRF 3 which weight loss is slower between 30 and 40 minute, this may be due to higher content of other organic waste in this sample, which need more time for vaporization and devolatilization.

8.2 Gasification

Results of thermogravimetric analysis performed for gasification in three heating rates for all samples were used to create graphs of weight loss and conversion vs. temperature. All curves were compared with each other.

Figure 37 shows gasification in three different heating rates 5, 10, 20 °C min⁻¹ for SRF1, SRF2, SRF3.

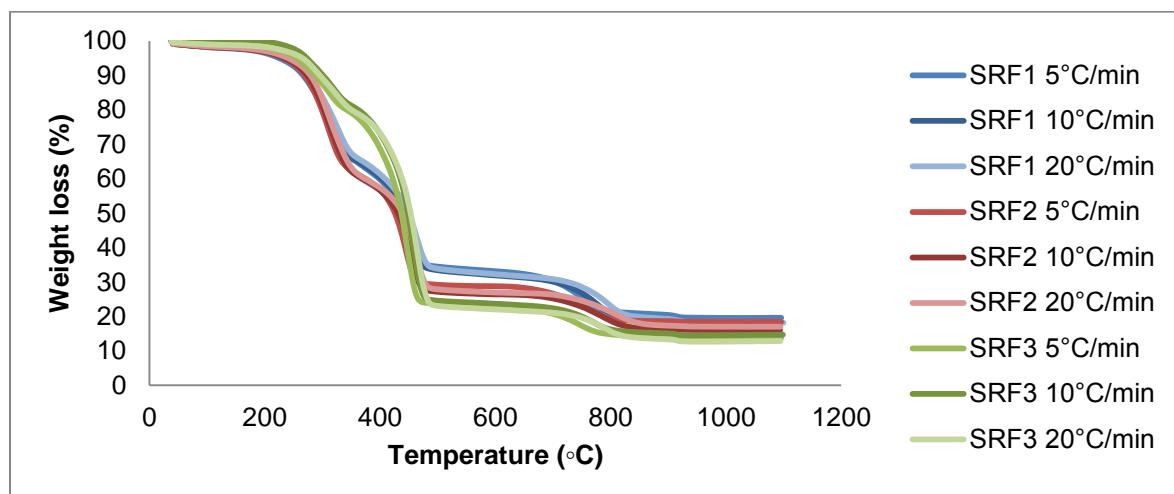


Figure 37. Thermogravimetric analysis for gasification in three heating rates 5, 10, 20 °C min⁻¹ for SRF1, SRF2 and SRF3.

Looking at all nine curves in Figure 37 approximately the same weight loss is observed. The gasification process began in 190 °C. The higher weight loss (95-70%) was observed from 190 °C to 325 °C corresponding to the moisture vaporization. Following, the second weight loss (70-35%) occurs

between 325 and 470 °C and may correspond to the devolatilization of hydrocarbons. The gasification process terminates between 470 and 1100 °C, where residues of material were degraded.

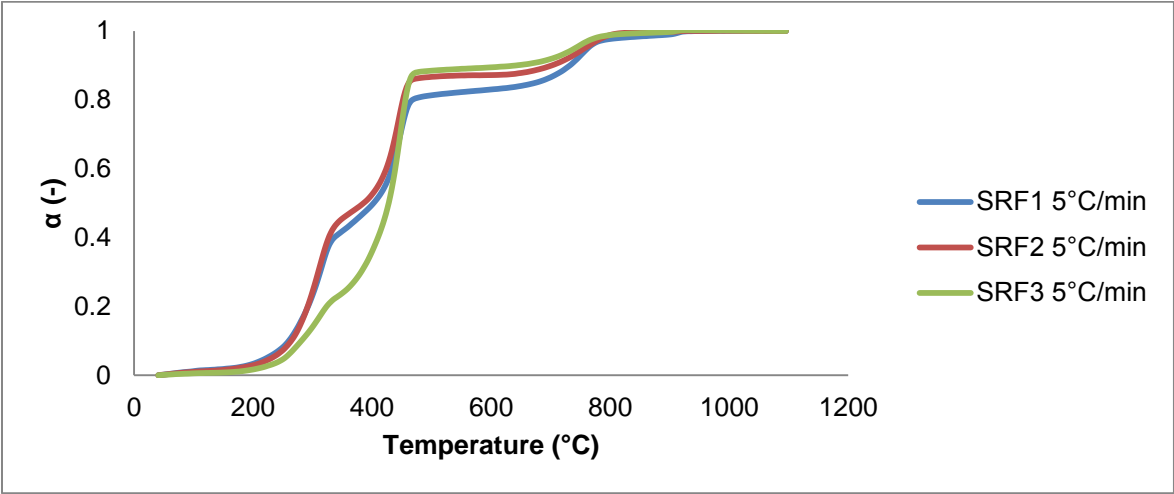


Figure 38. Degree of conversion of gasification in heating rate 5 °C min⁻¹ for SRF1, SRF2 and SRF3.

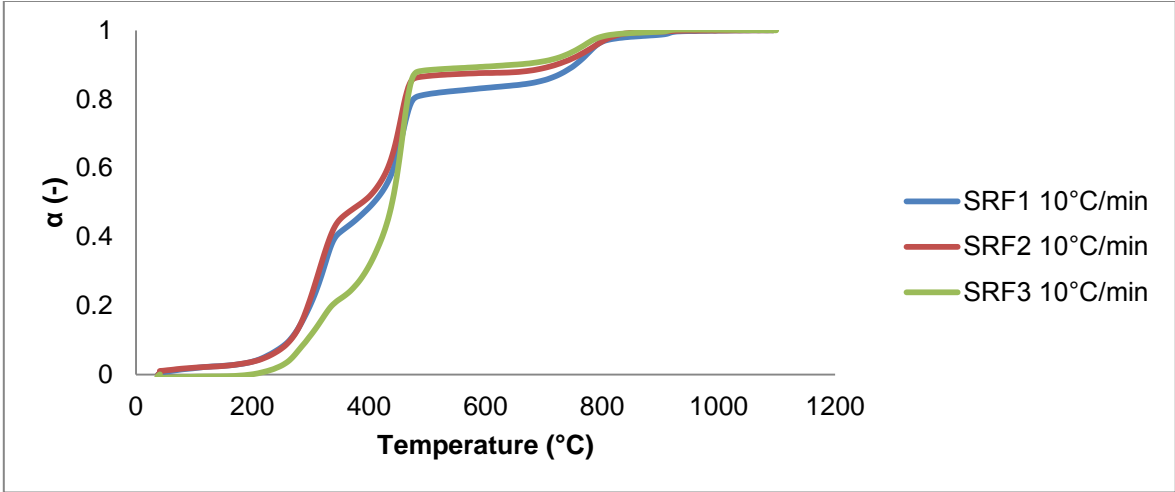


Figure 39. Degree of conversion of gasification in heating rate 10 °C min⁻¹ for SRF1, SRF2 and SRF3.

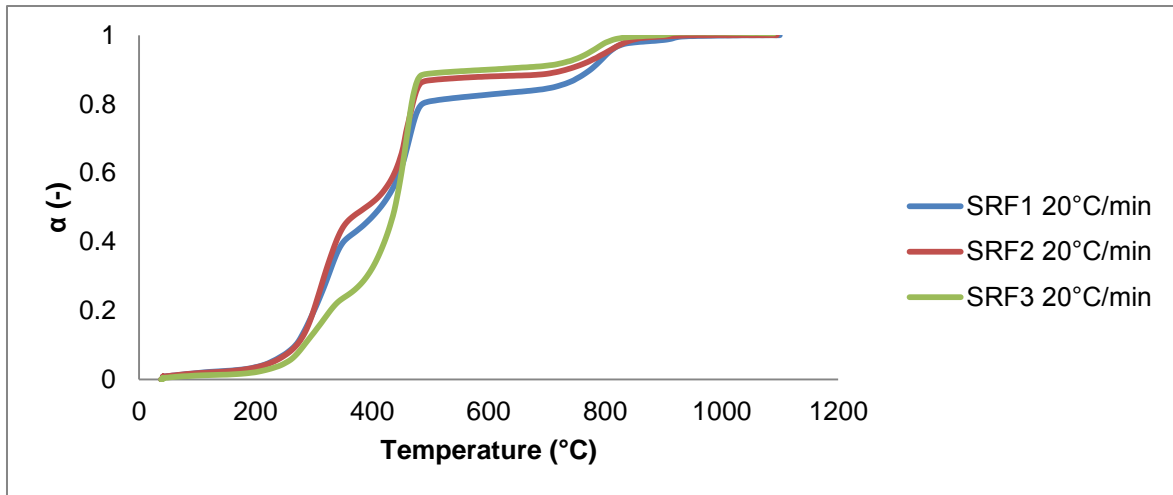


Figure 40. Degree of conversion of gasification in heating rate $20\text{ }^{\circ}\text{C min}^{-1}$ for SRF1, SRF2 and SRF3.

In Figures 38, 39 and 40 can be seen dependence of degree of conversion to temperature for three different heating rates, which had the largest increase between 190 and $470\text{ }^{\circ}\text{C}$ from 0.1 up to 0.8 for curves of SRF 1 and up to 0.9 for curves of SRF 2 and SRF 3. In this temperature zone can be noticed slower conversion of SRF 3. Between 470 and $1100\text{ }^{\circ}\text{C}$ progressively heading to 1 can be noticed.

The difference between heating rates is observed on plot weight loss vs. time presented in Figure 39. Figure 39 show dependence of weight loss to time for three samples gasified in three heating rates.

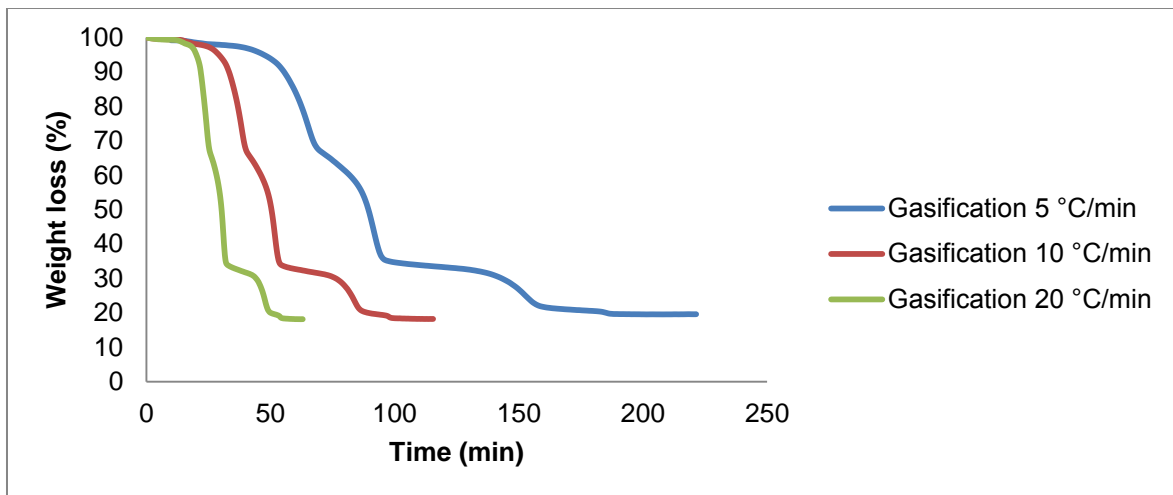


Figure 41. Thermogravimetric analysis for gasification in three heating rates $5, 10, 20\text{ }^{\circ}\text{C min}^{-1}$ for SRF 1.

The Gasification process is fastest in heating rates of $20\text{ }^{\circ}\text{C min}^{-1}$ and most slowly in $5\text{ }^{\circ}\text{C min}^{-1}$. The gasification process is faster with increasing temperature. It is similar for the three samples os SRF.

8.3 Comparison of pyrolysis and combustion

Results obtained from third thermogravimetric analysis were used to create comparison graphs of pyrolysis and combustion processes.

Figure 40 show comparison of pyrolysis for SRF 1, SRF 2 and SRF 3.

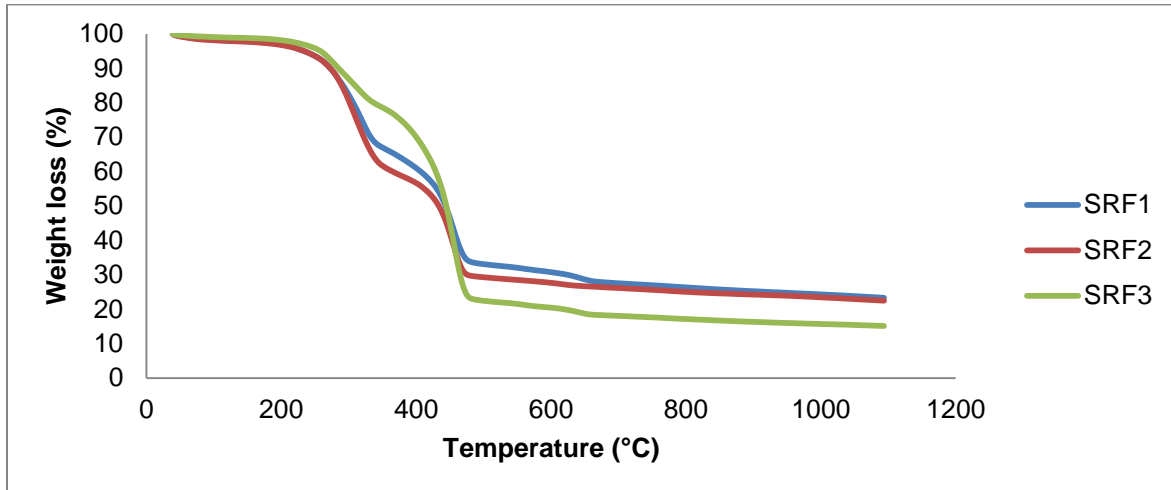


Figure 42. Comparison of pyrolysis for SRF 1, SRF 2 and SRF 3.

Figure 41 shows comparison of conversion for combustion of SRF 1, SRF 2 and SRF 3.

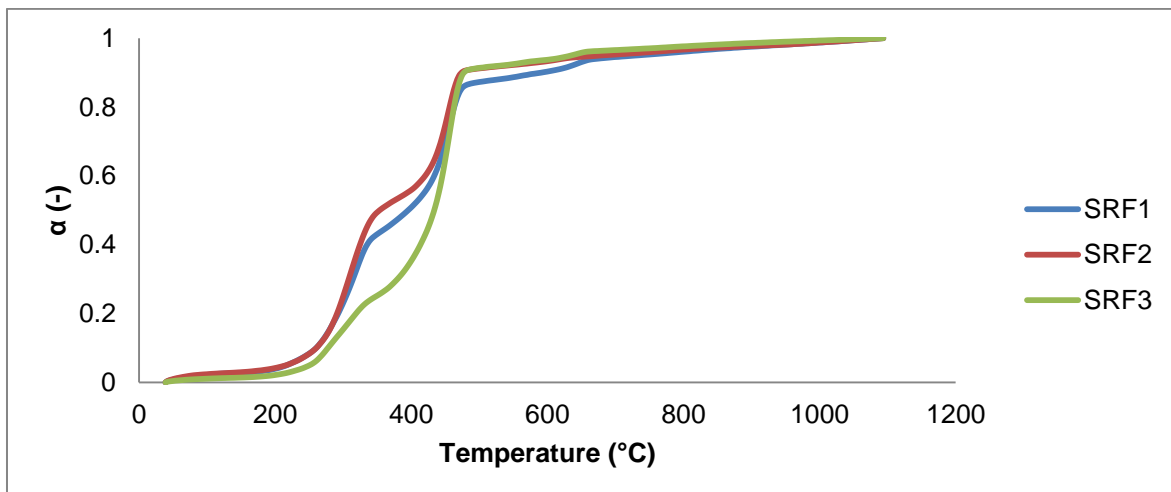


Figure 43. Comparison of degree of conversion for pyrolysis of SRF 1, SRF 2 and SRF 3.

As it can be seen in Figure 40, thermogravimetric analysis shows pyrolysis conducted from 40 to 1100 °C. The largest weight loss can be observed between 200 and 470 °C (from 90 to 50%), which is related with vaporization and devolatilization. Curves for SRF 1 and SRF 2 are almost similar. In case of SRF 3 in this temperature zone weight loss is slower it could be due to higher content of other

organic waste in this sample, which need more time for vaporization and devolatilization. Process terminates between 470 and 1100 °C.

In Figure 41 growth of conversion depending on temperature could be observed. The largest increase may be noticed between 200 and 470 °C. At temperature between 470 to 1100 °C conversion gradually was heading to 1.

Figure 42 shows comparison of combustion for SRF 1, SRF 2 and SRF 3.

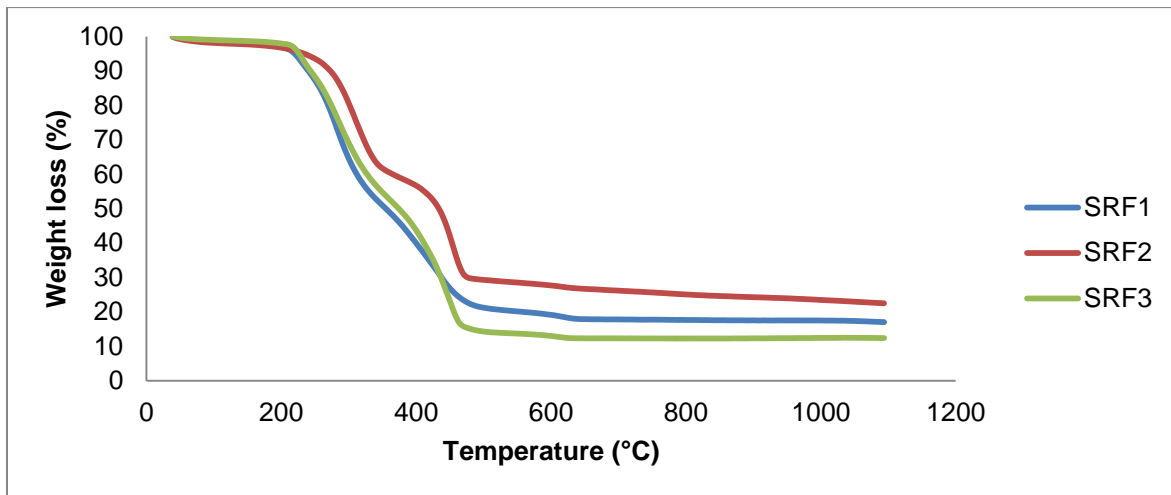


Figure 44. Comparison of combustion for SRF 1, SRF 2 and SRF 3.

Figure 43 shows comparison of conversion for combustion of SRF 1, SRF 2 and SRF 3.

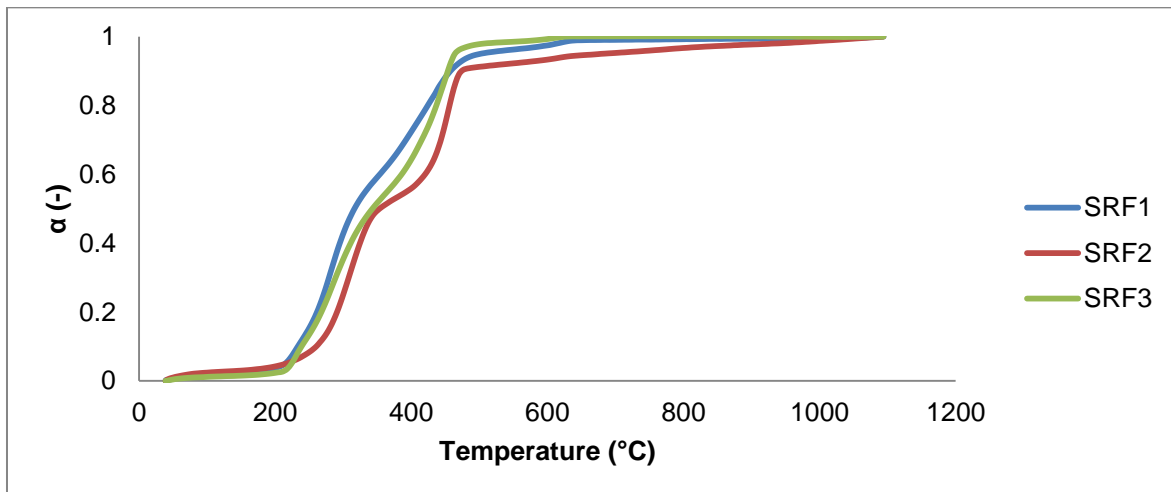


Figure 45. Comparison of degree of conversion for combustion of SRF 1, SRF 2 and SRF 3.

Figure 42 show weight loss of samples during temperature growth. Between 200 and 470 °C the biggest weight loss can be observed. Curves for SRF 1 and SRF 3 were almost similar. In case of SRF 2 weight loss in this temperature range was slower, which could be caused by high content of

plastic and textile materials in composition of this sample. Between 470 and 1100 °C difference in curves can be noticed, which could be due to various percentages content of ash and fixed carbon in the samples.

As it can be seen in Figure 43 curves for conversion for combustion of all samples were almost similar. The largest increase of conversion is between 200 and 470 °C. At temperature between 470 and 1100 °C conversion steadily was heading to 1.

Combustion process began earlier than pyrolysis process. This fact occurs because the pyrolysis was performed with absence of air or oxygen. Instead in combustion, high amount of oxygen can help and accelerate heating process. Considering the weight loss (from 70 to 35%), it is possible to verify differences between pyrolysis and combustion curves which could correspond to a faster release of volatile matter and/or a different behavior of material in combustion process.

In studies of Grammelis et al. (2009) [53], the results of thermogravimetry for combustion and pyrolysis processes are similar to results present in Figure 40 and 42. In studies of Quan et al. (2013) [54], on the electric waste material that was studied by the authors, they obtained almost identical results for the pyrolysis process shown in Figure 40.

Both processes can be divided in three steps. Step 1 is drying, step 2 is devolatilization and step 3 is burnout residues.

Thermogravimetric analyzes show the behavior of the tested material during the individual processes under assumed parameters. They show the variable behavior of the samples which could be caused by the differences seen in proximate and ultimate analysis as well as in morphological composition.

8.4 Comparison of conversion degree of all processes

In the figures below the conversion degree was compared for non-isothermal pyrolysis till assumed temperatures, gasification, pyrolysis and non-isothermal combustion in heating rate 10 °C min⁻¹ for SRF 1, SRF 2 and SRF 3.

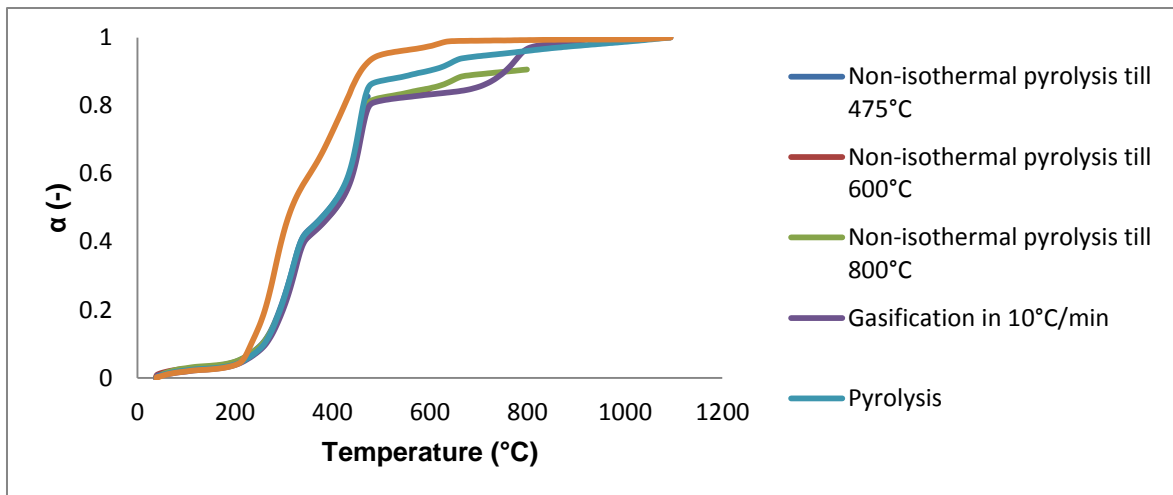


Figure 46. Comparison of conversion of all processes in heating rate 10 C min^{-1} for SRF 1.

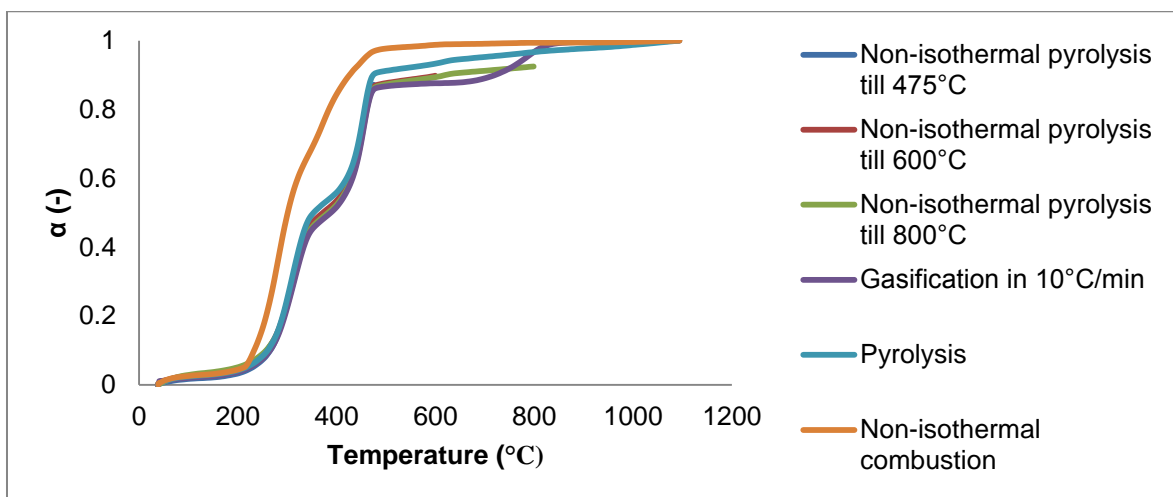


Figure 47. Comparison of conversion of all processes in heating rate 10 C min^{-1} for SRF 2.

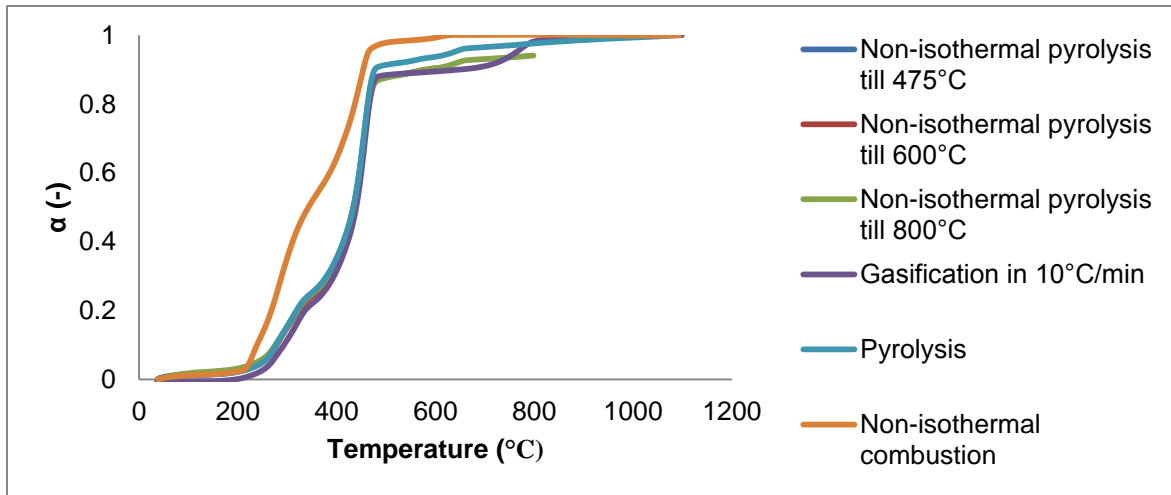


Figure 48. Comparison of conversion of all processes in heating rate 10 C min^{-1} for SRF 3.

In Figures 44, 45 and 46 it could be seen that all curves except non-isothermal combustion were overlapped until they reached 0.8 conversion degree. In case of pyrolysis after reaching this conversion point the different stages of pyrolysis can be distinguished. For gasification can be concluded that at the beginning of the process, pyrolysis occurred. For non-isothermal combustion for all three samples, conversion swiftly increased, which in comparison with other processes may be caused by an oxidizing agent.

Using the results obtained from thermogravimetric analysis in chapter 9, kinetic models were designed.

9. Kinetic model

A kinetic model is used for better knowing behavior of the material in thermal processes and to calculate activation energy of the material.

There are many methods used to study kinetics. Generally they can be grouped into two categories: experimental and computational [52].

Experimental methods are: isothermal and non-isothermal method. For isothermal methods, process is conducted at several constant temperatures while non-isothermal (dynamic) methods, process involve one or more heating rates [52].

Calculation methods to analyze isothermal or non-isothermal kinetic data are: model-fitting and model-free/isoconversional methods. For model-fitting methods, different model are fit to the data and best matching model is selected, from which the activation energy (E_a) and frequency factor (A) are calculated using the Arrhenius equation. For model-free/isoconversional methods activation energy (E_a) is calculated without assumed model. Using intercept of the linear equation with model assumption, frequency factor (A) can be calculated [52].

In model-fitting methods can be distinguished [52]:

- Isothermal model-fitting methods:
 - **Conventional method.**
- Non-isothermal model-fitting methods:
 - **Direct differential method,**
 - **Freemna-Carroll method,**
 - **Coats-Redfern method.**

In model-free methods can be distinguished [52]:

- Isothermal isoconversional methods :
 - **Standard isoconversional method,**
 - **Friedman isoconversional method,**
 - **Advanced isoconversional (AIC) method.**
- Non-isothermal isoconversional methods:
 - **Kissinger method,**
 - **Ozawa, Flynn and Wall (OFW) method,**
 - **Vyazovkin (VYZ) method,**
 - **Vyazovkin modified isoconversional method,**
 - **Vyazovkin advanced isoconversional (AIC) method.**

Kinetic modeling in this work is based on the results obtained on section 8 and it is divided in three different processes. First process is isothermal combustion in three different temperatures. Second process is gasification in three different heating rates. Third process is comparison of pyrolysis and combustion in 1100 °C.

9.1 Isothermal combustion

Standard isoconversional method [52] was chosen to calculate activation energy for isothermal combustion.

A generally used equation expressed as [52]:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

and

$$g(\alpha) = kt \quad (2)$$

Where $f(\alpha)$ is the differential reaction model and $g(\alpha)$ is the integral reaction model.

The rate constant (k) is frequently given by the Arrhenius equation:

$$k = A \exp\left(-\frac{Ea}{RT}\right) \quad (3)$$

Replacing rate constant (k) in equation 1 and 2 gives:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (4)$$

and

$$g(\alpha) = A \exp\left(-\frac{Ea}{RT}\right) t \quad (5)$$

Where α is degree of conversion, t is time, T is temperature, A is frequency factor, R is gas constant and Ea is activation energy.

This method may be obtained by taking logarithm of equation 5:

$$\ln g(\alpha) = \ln A - \frac{Ea}{RT} + \ln t \quad (6)$$

This equation can be transformed to give:

$$-\ln t = \ln\left(\frac{A}{g(\alpha)}\right) - \frac{Ea}{R} \cdot \frac{1}{T} \quad (7)$$

Plot $-\ln t$ vs. $1/T$ linear function creates a linear function with which it will be possible to calculate the activation energy and the coefficient of correlation.

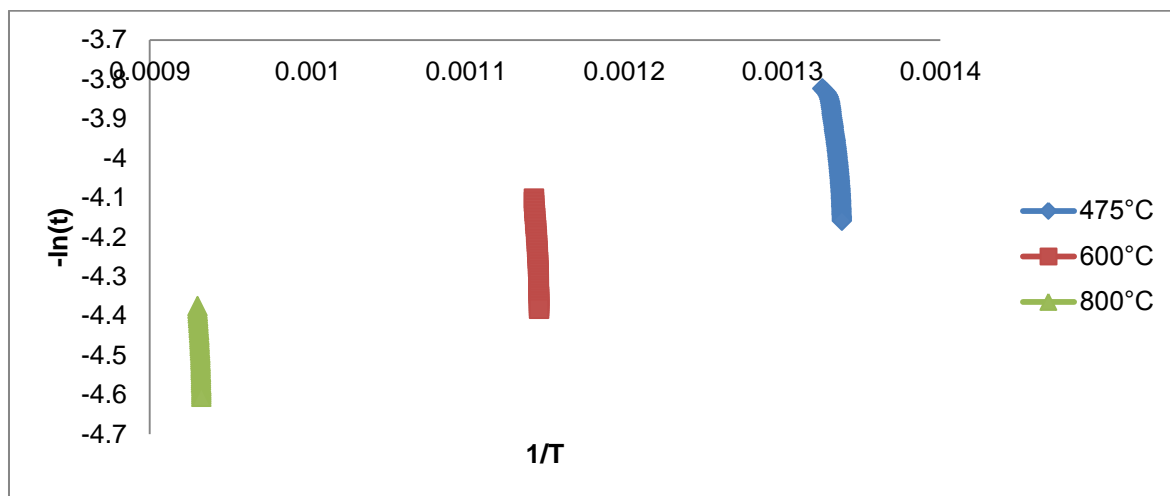


Figure 49. Graph of $(-\ln t)$ vs. $1/T$ for isothermal combustion in 475, 600, 800 °C of SRF 1.

Using linear regression function, the activation energy and correlation coefficient were calculated. Results are presented in Table 17.

Table 17. Activation energy and correlation coefficient for SRF 1, SRF 2 and SRF 3 from standard isoconversional method for isothermal combustion.

	SRF 1		SRF 2		SRF 3	
	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²	Ea (kJ/mol)	R ²
475 °C	268.49	0.9245	282.65	0.9501	258.04	0.9217
600 °C	636.41	0.9446	641.92	0.9610	628.09	0.9586
800 °C	717.71	0.9562	806.47	0.9529	883.59	0.9589

At temperature 475 °C activation energy was the highest for SRF 2 and almost similar for SRF 1 and SRF 3. At temperature 600 °C activation energy was almost similar for all three samples. The biggest difference in activation energy can be observed at temperature 800 °C where for SRF 1 was 717.71 kJ/mol, for SRF 2 was 806.47 kJ/mol and for SRF 3 was 883.56 kJ/mol. For all three samples it can be observed regularity that together with the rise of temperature, the activation energy increases.

9.2 Gasification

Ozawa-Flynn-Wall method [55] was selected to calculate activation energy for gasification process in three heating rates.

Equation which described the reaction rate for non-isothermal process is:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

Where t is time and T is the temperature. The mathematical expression of kinetic model is represented by the function $f(\alpha)$, α is the degree of conversion expressed by the equation below:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

Where m_0 and m_t represent the mass at $t=0$ and $t=t$, respectively, and m_f the final mass of the sample.

Inserting instead $k(T)$ the Arrhenius equation gives [55]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{Ea}{RT}\right) \cdot f(\alpha) \quad (3)$$

Where Ea (activation energy) and A (frequency factor) and R is the gas constant. In non-isothermal processes carried out with linear heating rates $\beta = dT/dt$, reaction rate $d\alpha/dt$ in equation 2 gives [55]:

$$\frac{d\alpha}{dt} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (4)$$

Without choosing reaction model, activation energy can be obtained from isoconversional method of Ozawa-Flynn-Wall using Doyle's linear approximation [52]:

$$\log p(x) \approx -2.315 - 0.4567x \quad (5)$$

According to the Ozawa-Flynn-Wall method, which involves measuring the temperatures adequate to fixed values of α from experiments at different heating rates β , the activation energy, E at any particular value of α is determined by equation below [55]:

$$\log \beta = \log \left[\frac{AE}{Rg(\alpha)} \right] - 2.315 - 0.4567 \left(\frac{Ea}{RT} \right) \quad (6)$$

The plot $\log \beta$ vs. $1/T$ plot obtained from thermogravimetric data performed at three heating rates, should give straight lines which slope enables the evaluation of activation energy [55]:

$$\text{slope} = \frac{d(\log \beta)}{d(1/T)} = 0.4567 \frac{Ea}{R} \quad (7)$$

This method allows to receive activation energy without using assumed kinetic model.

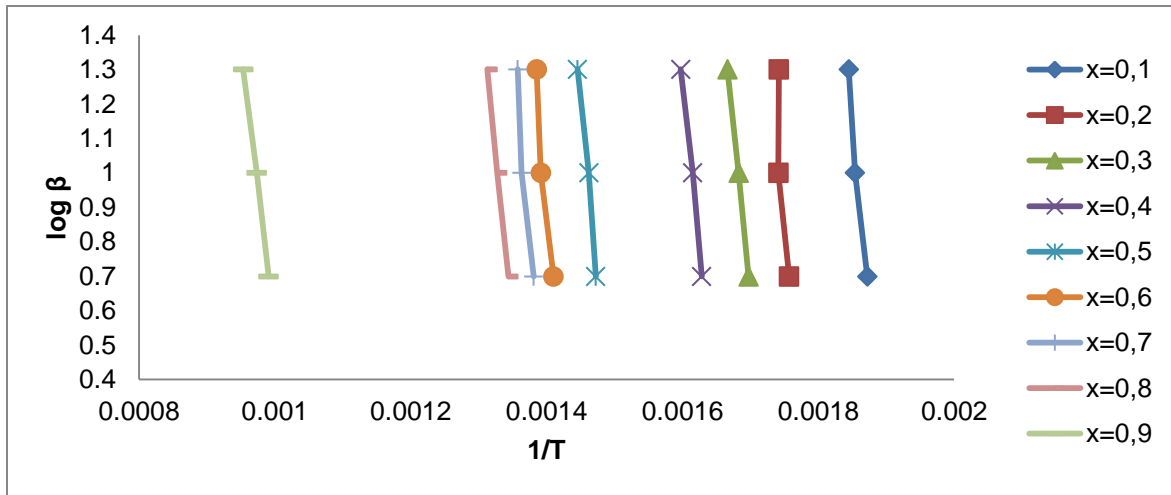


Figure 50. Graph $\ln\beta$ vs. $1/T$ for gasification of SRF 1 in three different heating rates.

Using a linear regression function, the activation energy and correlation coefficient were calculated. Results are presented in Table 18.

Table 18. Activation energy and correlation coefficient for SRF 1, SRF 2 and SRF 3 from Ozawa-Flynn-Wall method for gasification.

α (-)	SRF 1		SRF 2		SRF 3	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
0.1	80.83	0.9625	166.24	0.7772	62.91	0.0804
0.2	107.66	0.7147	73.55	0.9999	37.51	0.0103
0.3	73.13	0.9985	114.81	0.8360	235.63	0.6239
0.4	74.03	0.9936	61.57	0.8448	268.32	0.6369
0.5	83.24	0.9810	109.58	0.2620	279.93	0.6645
0.6	85.32	0.9194	87.86	0.9743	409.37	0.5606
0.7	89.72	0.9223	67.84	0.9983	465.62	0.5951
0.8	73.68	0.9981	61.92	0.8852	311.27	0.6536
0.9	60.92	0.9984	61.61	0.9595	-	-

In conversion 0.1 for SRF 2 the high activation energy 166.24 kJ/mol can be verified. The highest value of activation energy was observed for sample SRF 3, which could be due to morphological composition as well as low correlation coefficient. At conversion points 0.6, 0.7 and 0.9, it could be observed the highest activation energy of 409.37, 465.62 and 311.27 kJ/mol, respectively. Activation energy for SRF 1 and SRF 2 were almost similar.

In comparison with the results of studies of Ren et al. (2012) [56] performed on mixture of coal and plastic waste respectively 60 and 40%, activation energy of SRF 1 and SRF 2 for the specified conversion degree was twice smaller. In studies Naskar et al. (2010) [57] carried out on mixture of

bitumine/plastic blend (7% of plastic), activation energy of SRF 1 and SRF 2 was smaller. In case of SRF 3 activation energy is bigger than in Ren et al. (2012) and Naskar et al. (2010) studies.

9.3 Comparison of pyrolysis and combustion

Coats-Redfern method [58] was chosen to calculate activation energy for comparison of pyrolysis and combustion processes.

The kinetic equation of pyrolysis and combustion can be written as follows [58]:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

And

$$k = A \exp\left(-\frac{Ea}{RT}\right) \quad (2)$$

Where k is the reaction rate, $f(\alpha)$ represents the hypothetical model of the reaction mechanism, E is the activation energy (kJ/mol), A is the pre-exponential factor (min^{-1}), T is the temperature (K), t is the time (min) and α in the extent of conversion defined by [58]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (3)$$

Where m_0 and m_t represent the mass at $t=0$ and $t=t$, respectively, and m_f the final mass of the sample.

Equation 1 for constant heating rate β (K/min) during combustion and pyrolysis $\beta=dT/dt$, can be transformed into [5/]:

$$dx/f(\alpha) = K/\beta dt \quad (4)$$

By integrating equation 4 :

$$g(\alpha) = \int_0^{\alpha} \frac{dx}{f(\alpha)} - \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dt \quad (5)$$

Where $g(\alpha)$ is the integral function of conversion. Equation 5 was integrated using Coats-Redfern method [58]:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[A \cdot \frac{R}{\beta} \cdot E \cdot \left(1 - \frac{2RT}{E}\right)\right] - E/R \cdot T \quad (6)$$

Generally, the term $2RT/E$ can be not taken into account as it is lower than unity. It has been demonstrated that for both temperature of combustion range and most values of E the expression $\ln[AR/\beta E]$ in equation 6 actually constant. If, therefore, correct expression of $g(\alpha)$ is used, the plot of $\ln[g(\alpha)/T^2]$ versus $1/T$ should give a straight line with a high correlation coefficient from which activation energy and frequency factor can be calculated from the slope of the line and the intercept respectively [58].

Figure 51 shows the curves for linear fitting of pyrolysis for SRF 1.

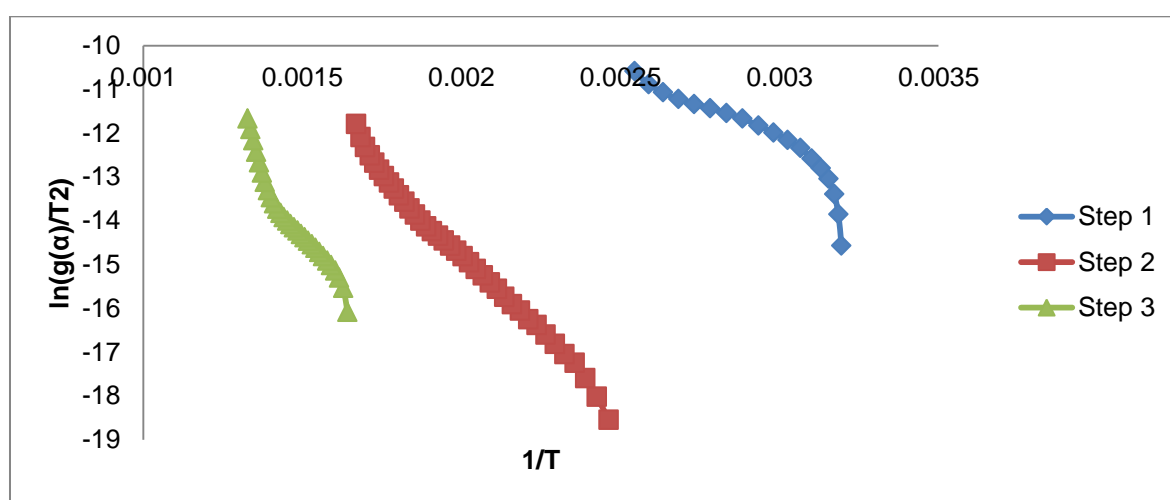


Figure 51. Graph $\ln(g(\alpha)/T^2)$ vs. $1/T$ for three steps of pyrolysis for SRF 1.

Using linear regression function, the activation energy, frequency factor and correlation coefficient were calculated. Results of this calculation are presented in Table 19.

Table 19. Activation energy, frequency factor and correlation coefficient calculated for SRF 1, SRF 2 and SRF 3 from Coats-Redfern method for pyrolysis.

	SRF 1			SRF 2			SRF 3		
	Ea (kJ/mol)	A (1/sec)	R ²	Ea (kJ/mol)	A (1/sec)	R ²	Ea (kJ/mol)	A (1/sec)	R ²
Step 1	37.34	2.04*10 ³	0.8497	34.36	8.72*10 ²	0.9065	31.10	2.36*10 ²	0.9376
Step 2	62.11	1.49*10 ³	0.9920	55.47	1.60*10 ²	0.9097	60.06	1.38*10 ³	0.9846
Step 3	92.00	1.93*10 ⁴	0.9381	65.16	1.71*10 ²	0.9065	81.68	2.67*10 ³	0.9481

In step 1, activation energy was 37.34, 34.46 and 31.10 kJ/mol, respectively. The biggest difference of activation energy could be verified in step 3, where it was 92 kJ/mol for SRF 1, 65.16 kJ/mol for SRF 2

and 81.69 kJ/mol for SRF 3. For all three samples can be observed regularity that together with the next process step, the activation energy increases.

Figure 52 shows curves for linear fitting in combustion for SRF 1.

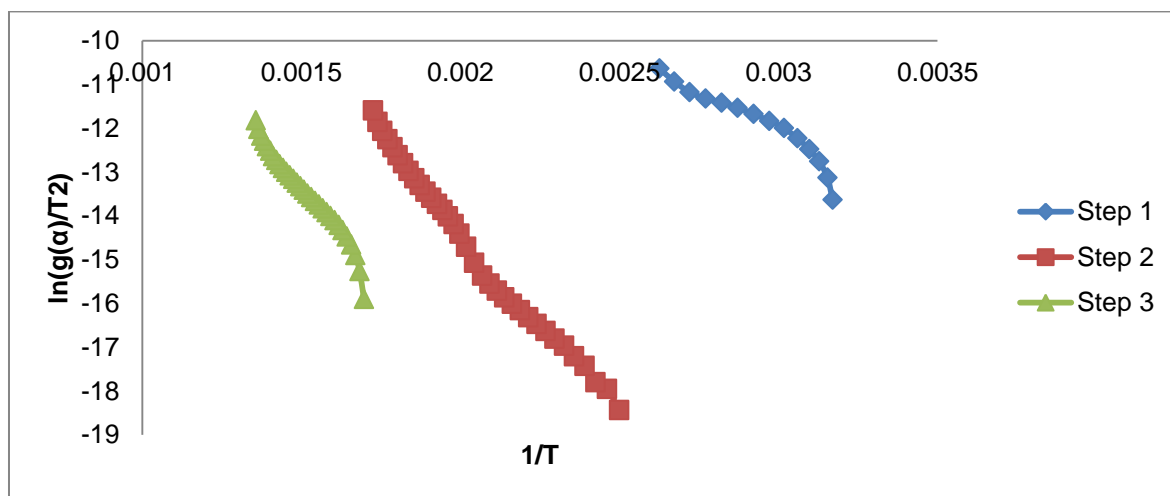


Figure 52. Figure Graph $\ln(g(\alpha)/T^2)$ vs. $1/T$ for three steps of combustion for SRF 1.

Using linear regression function, the activation energy and correlation coefficient were calculated. Results of this calculation are presented in Table 20.

Table 20. Activation energy, frequency factor and correlation coefficient calculated for SRF 1, SRF 2 and SRF 3 from Coats-Redfern method for combustion.

	SRF 1			SRF 2			SRF 3		
	Ea (kJ/mol)	A (1/sec)	R ²	Ea (kJ/mol)	A (1/sec)	R ²	Ea (kJ/mol)	A (1/sec)	R ²
Step 1	36.66	2.01*10 ³	0.9082	31.78	4.27*10 ²	0.9019	30.00	1.65*10 ²	0.9388
Step 2	70.91	2.10*10 ⁴	0.9881	70.41	1.71*10 ⁴	0.9808	73.24	3.61*10 ⁴	0.9795
Step 3	76.70	2.53*10 ⁴	0.9648	74.52	2.23*10 ³	0.9526	77.49	2.30*10 ³	0.9494

Step 1 and step 2 were characterized by the lowest activation energy, while the highest was observed in step 3. For all three samples the activation energy in each step is almost similar. For all three samples can be noticed regularity that together with the next process step, the activation energy increases.

10. Conclusions

The main aim of the study was to provide the necessary data for the modeling of the process of combustion and gasification, as well as to evaluate the usefulness of energy and influence on environment of three SRF samples taken from three waste treatment plants from Poland. Evaluation was done on the basis of the results of the following analysis:

- Morphological analysis
- Proximate analysis
- Ultimate analysis
- Ash analysis
- Mercury, Fluorine and Chlorine and heavy metal analysis
- Thermogravimetric analysis
- Kinetic models

Based on the results of this study it can be concluded:

1. Morphological analysis showed that the waste is a non-homogenous material which is hard to unify and needs to be pre-treated before use as a fuel. Also knowledge on the content of each component in the composition of the material could give information on its impact on the fuel properties.
2. Proximate analysis showed some differences in the characteristics of the tested samples, despite the fact that they were samples of a very similar nature. SRF 2 has the highest content of volatiles (73.7%) and the lowest content of ash, 11.1%. The lowest content of volatile matter (63.1%), with the highest ash content was found in the sample marked as SRF 1.
3. The high content of carbon and hydrogen identified during the elemental analysis of the tested samples makes it attractive as a fuel that can be used for energy production purposes. SRF 1 has the highest content of carbon and hydrogen respectively 65.6 and 8.3%. An important feature of the tested samples is a not very high content of sulphur in each of them (the highest in sample SRF 2 – 0.9%).
4. Calorific value for all three samples is almost similar to the calorific value of a comparable study. Sample SRF 2 has the highest calorific value, where HHV is 23.9 MJ/kg and LHV is 22.9 MJ/kg.
5. Ash analysis provide data that could be helpful to better knowing the correlation between composition and specific temperatures of ash, which may have an impact on better design of furnaces for waste combustion. The determined melting temperatures of ash (very similar for each sample) were quite high. Only in the case of high-temperature conversion processes of these fuels (>1100 °C), it can be noted the problems associated with the appearance of phenomena of fouling and slagging.

6. Analysis of harmful elements allows to verify the negative impact of waste on the environment, as well as on the basis of their content in the composition of the material to give the possibility to develop preventive methods. The content of mercury and fluorine in the tested samples is typical for waste fuels and should not cause problems during thermal conversion of fuels with these characteristics. The relatively high content of chlorine (up 1.55% for the sample SRF 3) can intensify corrosion phenomena in the treatment systems of flue gas or process gas generated during conversion such fuels.
7. Thermogravimetry analysis of tested material showed that the behavior of the pyrolysis, gasification and combustion depends on the conditions under which those analysis were conducted as well as the composition of the tested material.
8. The kinetic data reveal for isothermal combustion occurring regularity of activation energy demand was dependent on the temperature at which the isothermal process is performed. For temperature 475 °C the highest activation energy was for sample SRF 3. At temperature 600 °C the activation energy for all three samples was almost similar. At 800 °C the activation energy was the highest for sample SRF 3.
9. In the case of gasification process the activation energy was dependent on the degree of conversion. Activation energy for SRF 1 and SRF 2 in all extent of conversion was stable. In SRF 3 can be noticed high values of activation energy which may be due to low correlation coefficient.
10. In comparison of combustion and pyrolysis, the activation energy was dependent on step in which the sample currently remains at the given time. For pyrolysis process the lowest activation energy can be observed for sample SRF 2 in all three steps. In the case of combustion process in all steps for three samples the activation energy is almost the same.

According to the analysis carried out on samples SRF 1, SRF 2, SRF 3 it can be concluded a promising usefulness of waste in energy field. In future research, the analysis of exhaust gases and also the impact of waste combustion on environment should be performed to fulfill characterization of samples, which will help in the design of flue gas purification systems.

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