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Original Research Article

ALUMINUM RECOVERY FROM MULTIMATERIAL TETRA-PAK WASTE PYROLYSIS

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A b s t r a c t

A constant growth of the multimaterial waste production can be observed in the recent years. The multimaterial waste that contain aluminum are especially hard to process due to the fact that multiple layers of various materials are bonded permanently. Tetra-Pak waste contain high amounts of paper (approx. 70%) and are usually processed in papermills in order to recover cellulose. The overview on the methods used to process waste as well as the characteristics of the produced waste are presented in the paper. The application of pyrolysis has many advantages: the products are characterized by a high calorific value and can be used as fuels, and the process itself is much more environmentally friendly than the chemical methods used currently. The tests were performed with a special focus on the minimization of the aluminum oxidation level, so that in can be further processed. In order to determine the decomposition temperature of the individual components of the examined materials, the tests started with a thermogravimetric analysis of the pyrolysis process performed with the application of argon. The next step were the pyrolysis tests on a laboratory scale installation aimed in the verification of the results obtained during the thermogravimetry.

Keywords: pyrolysis, Tetra-Pak, aluminum recovery

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1. INTRODUCTION

The amount of waste generated in Europe has been constantly increasing within the last several years. This includes both industrial waste and the waste generated by households. Due to the legal requirements, the level of waste recycling is also increasing. Poland is required to recycle at least 60% of waste by 2020 and at least 70% by 2030 [1].

Unfortunately, there still are some groups of materials which are hard to recycle and process or reuse. One of them are the multimaterial waste. They are composed of at least two different materials which are permanently connected and therefore impossible to separate mechanically. Usually, the multimaterial waste are treated like the material that is present in the waste in the highest amount, what makes it challenging to recover other valuable materials from the waste stream, since the majority of the multimaterial waste is usually composed of paper and/or plastic, while other valuable materials are neglected.

This study was focused on the specific group of multimaterial waste – Tetra-Pak packagings.

1.1. Municipal waste in Poland and EU

In 2014, the majority of municipal waste produced in Poland – 32% – wre the biodegradable waste, glass 23%, plastics 17%, paper and cardboard 13%, bulky waste 12%, fabrics 2%, metal 1% and the hazardous waste was less than 1%. Only 10% of the total amount of municipal waste was recycled in 2014. The fractions that are most commonly recycled are paper and cardboard, glass and plastics [1]. The diagram representing the composition of the municipal waste in Poland in 2014 is presented in fig. 1.

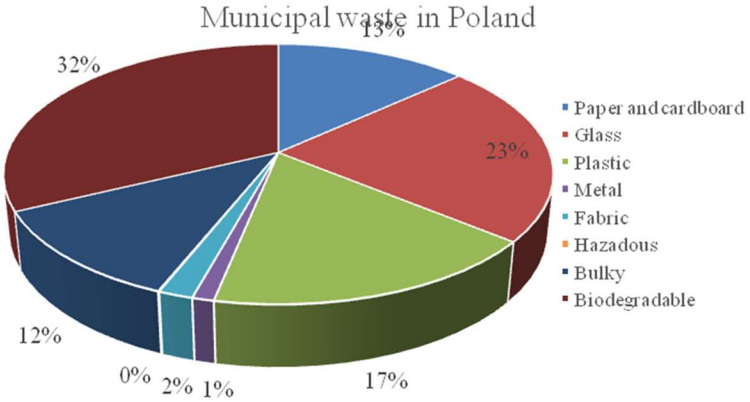

Fig. 1. Municipal waste in Poland in 2014 [1]

According to [2], approximately 85% of the selectively collected municipal was produced by the households in 2014. In 2014, 31% of the districts collected paper (separate containter), glass (separate container) and plastics, multimaterial waste and metals (separate container), 19% districts collected glass (separate container) and paper, plastics, multimaterial waste and metals (separate container), and 7% districts provided the separate containers for paper, glass and plastics. 1 300 751 Mg recycleable waste was collected in 2014, while the amount of the biodegradable waste in the whole municipal waste stream was 756 465 Mg. In 2014, approx. 1 mln Mg (9.4% of the total mass of the collected waste) of waste was recycled and/or reused.

According to the European Environment Agency [11], the municipal waste production in Poland in 2014 was almost the lowest in EU – 272kg per capita. Only Romania produced less waste (249kg per capita). The countries which generate the largest amounts of municipal waste are Denmark (758kg per capita), Switzerland (730kg per capita) and Germany (618kg per capita). The average municipal waste production in European Union per capita in 2016 was 483kg, while only 141kg was recycled [12]. The waste composition in EU is presented in fig. 2.

The most important short-term (by 2020) goal described in the National Waste Management Plan 2030 is to increase the amount of waste to be reused and/or recycled to at least 50%. The long-term goals (by 2030) is to increase this number to at least 65% and decrease the amount of stored waste to 10% of the total amount of the generated municipal waste [2].

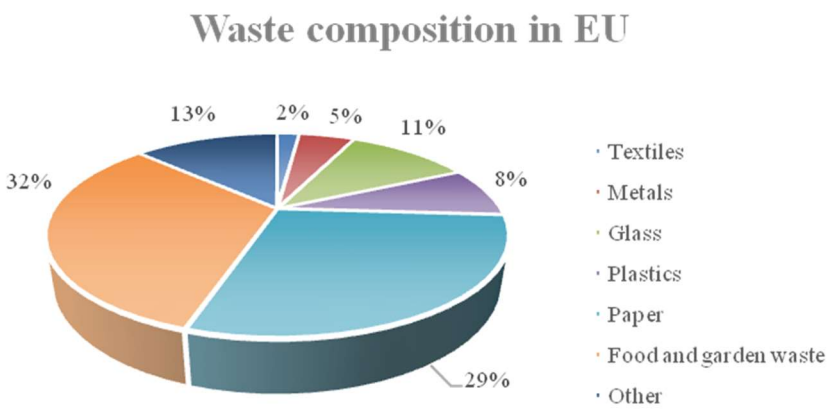

Fig. 2. Municipal waste composition in EU [13]

1.2. Utilization of the multimaterial waste packagings

Multimaterial waste packagings are still a large group of products that is not handled properly. Multimaterial waste are type of waste that contain at least two different materials which are permanently connected and therefore impossible to separate with mechanical methods. Usually, the multimaterial waste are collected with a group of the material which is present in the waste in the highest amount – they are treated like paper or plastic. Still, they may contain significant amounts of other materials, especially metals, i.e. Tetra-Pak packaging contain approx. 5% Al, while the empty pharmaceutical waste packagings contain as much as 20% metal alloy (approx. 85% Al, 11,5% Mg, 0,8 %Ti and 2,7% other metals).
The presented research was focused on the specified group of multimaterial waste packagings – Tetra-Pak. They are most commonly used to store liquids, like juices, mils or tomato pulp. The packaging is composed of six layers:

- Outer layer made of polyethylene, which protects the product from bacteria and moisture,
- Cellulose – structural layer, helps maintain the desired shape of the packaging,
- Polyethylene – adhesive layer,
- Aluminum – one of the most important layers. Protects the product from oxygen and sunlight in order to extend the lifetime of the product while allowing it to be stored outside the fridge,
- Polyethylene – adhesive layer,
- Polyethylene – sealant layer.

After the product is disposed, the layers are still strongly connected, therefore it is almost impossible to separate them without any material losses. The multimaterial waste packagings are recycled in a limited amount, usually with the application of the following techniques:

- The cellulose can be recovered in the paper mill, in a process that starts with the initial comminution of the packagings in the hydropulper in order to separate cellulose from other materials, and then the cellulose mass is transported to the paper-making machine,
- Application of the organic solvents to solute the polyethylene and then granulate the aluminum foil,
- Thermal processes: combustion (oxygen present in the atmosphere) or pyrolysis (oxygen-free atmosphere) [1].

2. PYROLYSIS OF THE MULTIMATERIAL TETRA-PAK WASTE

The main goal of the study was to analyze the pyrolysis process of the multimaterial Tetra-Pak waste in order to determine the process conditions that

prevent the aluminum oxidation – metal recovery process is much easier and cheaper when the metal is not oxidized [10]. First, the material needed to be sufficiently examined. The calorific value of the waste was measured on a laboratory scale calorimeter. The average calorific value obtained during the measurements performed on a PRECYZJA-BIT KL-12Mn2 calorimeter was 22,3MJ/kg. The average moisture content in the sample of the Tetra-Pak waste comminuted on a 2cm sieve was 5.59%.

Pyrolysis can be described as the endothermic process of thermal decomposition of the organic substances characterized with a high carbon content, that occurs at the elevated temperatures in the oxygen-free atmosphere. Pyrolysis usually takes place in the temperature range between 300°C-1000°C. The products are gas, oil, and solid fraction (char). The composition of the products depends on a number of parameters, mostly the composition of the batch material, temperature, heating speed, residence time in the reactor, particle size and the reactor type [4].

2.1. Thermogravimetric study

In order to determine the optimal process parameters, a sample of the material was analyzed on a Mettler TA1 analyzer with the application of the thermal differential method (DTA). The scheme of the analyzer is presented in fig. 3.

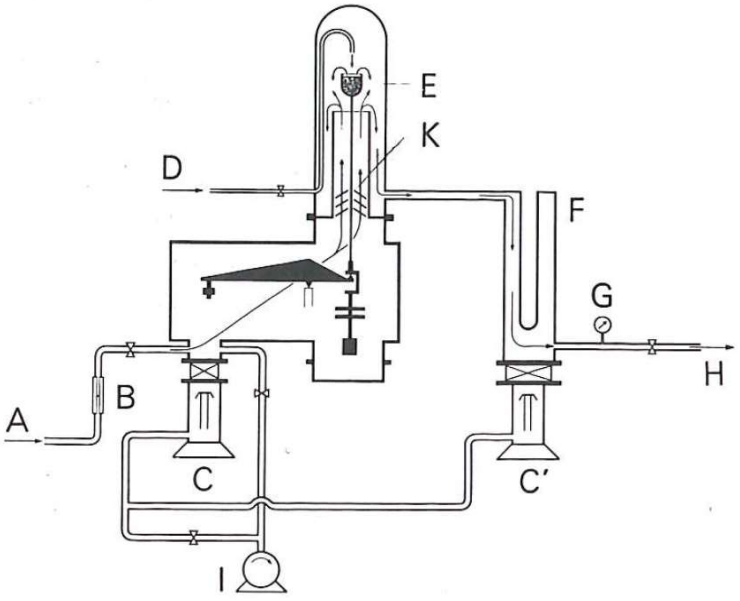

Fig. 3. Scheme of the thermoanalyzer. A – needle valve gas inlet, B – flowmeter, C, C' – oil diffusion pumps, D – auxiliary gas inlet/outlet, E – sample, F – cold trap, G – manometer, H – gas outlet, I – rotary pump, J – baffle

The aim of this analysis was to determine and identify the thermal effects that occur during the process. During the analysis, two materials – the analyzed sample and the reference material – were simultaneously heated in the same conditions. The thermoelements are located in both samples in order to determine the temperature difference ΔT of the substances. The temperatures are equal at the beginning of the process. If the endothermic reaction occurs in the analyzed sample, its temperature will be lower than the reference material, and if the exothermic reaction occurs, the temperature is higher than the reference sample. The registered measurements are used to determine the $\Delta T=f(t)$ curve. The thermogravimetric studies were performed with the specified parameters:

- The crucible made of Al_2O_3,
- Reference material: Al_2O_3, crucible made of Al_2O_3 – total mass 2,20817 g,
- The oxygen-free atmosphere was provided by the application of 5N argon,
- Heating rate: 10 K/min. (up to 90 °C); 6 K/min. (above 90 °C),
- DTA range: 50 μV,
- TG range: 1000 mg,
- $T_{max} = 550^{\circ}C$.

The mass balance of the process is presented in table 1.

Table 1. The mass balance for thermogravimetric study of the Tetra-Pak pyrolysis

Input mass		
Crucible mass	2,04478	[g]
Sample mass	0,11906	[g]
TOTAL	2,16384	[g]
Output mass		
Crucible mass	2,04478	[g]
Sample mass	0,02868	[g]
TOTAL	2,07346	[g]
MASS DECREMENT	90,38	[mg]

The DTA, DTG and TG curves for the Tetra-Pak multimaterial waste pyrolysis are presented in fig. 4.

The most important effects can be observed for the temperature range between 250°C – 500°C. A significant mass loss can be observed in the temperature range between 290°C - 382°C. The increment of the mass drop speed can be observed at the temperature approx. 300°C. The rate of the mass decrement is the highest at 360°C. The process slows down up to approx. 443°C, where the mass dropped rapidly. The final mass was obtained at approx. 503°C.

Based on [4,5] it can be estimated, that the first, the most rapid mass loss observed during the thermogravimetric studies, is associated with the decomposition of cellulose, while the second peak is a result of the polyethylene decomposition.

Cellulose pyrolysis is a complex process that involves multiple multiphase chemical reactions. Regardless of the fact, that this process has been analyzed for over 60 years, its final kinetic model still has not been developed. The most recent model developed by Liao suggests, that during the initial phase of the process, the "active cellulose" is produced. If the process temperature is low, the water is removed and the active cellulose transforms into char, and if the temperature increases, it is decomposed in two simultaneous reactions: cracking of the glycosidic bonds, that leads to the formation of the levoglucosan and its isomeric anhydrosugar (requires lower activation energy), and the pyranoid ring transformation, that forms hydroxyl-acetaldehyde (HAA), acetol, furfural, carbon oxide and other compounds (higher activation energy). For the long gas residence times, the anhydrosuger will further decompose to produce gas and secondary char and bio oil [6]. The decomposition of polyethylene occurs at higher temperatures than cellulose, as confirmed during the thermogravimetric studies. The decomposition starts with the random, homolytic scission, where the hydrocarbons are consumed to produce the primary radicals. The main reaction that can be observed during the whole pyrolysis process is the β-scission, which involves cracking of the radical that leads to the formation of a primary radical and a hydrocarbon. Ethylene is generated during the β-scission of the primary radical. Other primary radicals (alkenes or dialkenes) are also generated during the β-scission. The hydrogen transfer take place at the lower temperatures, and higher temperatures favor the β-scission [8].

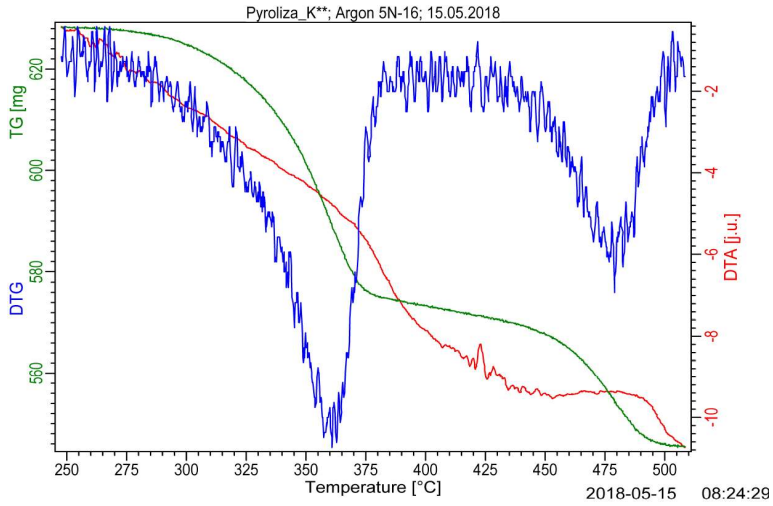

Fig. 4. DTA, DTG and TG curves for the multimaterial waste pyrolysis

2.2. Measurement equipment

The process was performed in a small (150x200x550cm) fixed bed reactor equipped with two IZOHEAT heating modules (2x1,9kW) insulated with ceramic fiber panels (max. temperature 1430°C). The scheme of the reactor with marked locations of the thermocouples is presented in fig.4. The reactor was sealed with 10 M5 screws and a high-temperature silicone and filled with argon. The oxygen meter was used to monitor the oxygen level during the whole process in order to provide the oxygen-free atmosphere (O_2 concentration not higher than 1%). Metronic MPI-CL analyzed the temperature inside the furnace, within the sample and the temperature of the process gases leaving the reactor. The scheme of the reactor with the locations of the thermocouples is presented in fig. 5.

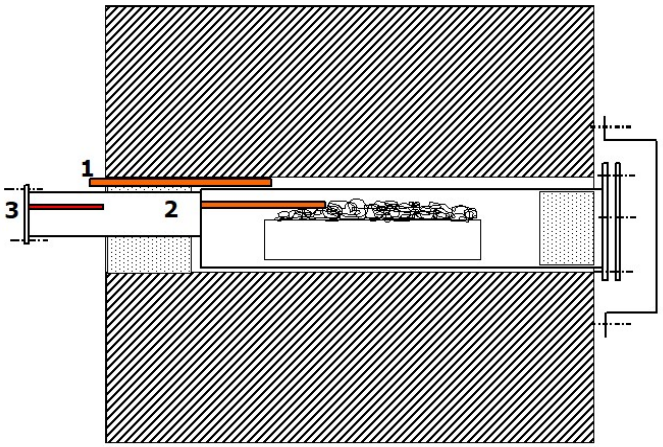

Fig. 5. Schematic cross-section of the reactor. 1 – control thermocouple, 2 – material temperature, 3 – gas temperature

The process gases and the oil fraction can be cooled with water. A special flask was used to collect the pyrolytic oil. The gases were pumped into a gas separator. The gas was constantly measured for CO, CO_2, SO_2 (Hartmann-Braun analyzer) and O_2 (Servomex analyzer). The remaining part of the gas was absorbed in wet scrubbers for Cl, Br and F analysis and in absorption tubes for chromatography. The scheme of the measurement equipment is presented in the fig. 1. The solid phase generated during the process was analyzed for the content of carbon, total Al and metallic Al in order to determine the oxidation level of the metal. The measurement equipment is presented in fig. 6. The process temperature was 550°C. The assumed process time was 2 hours – after that, the process gases were no longer generated. The sample size was approx. 100g for each test. The maximum temperature was 550°C.

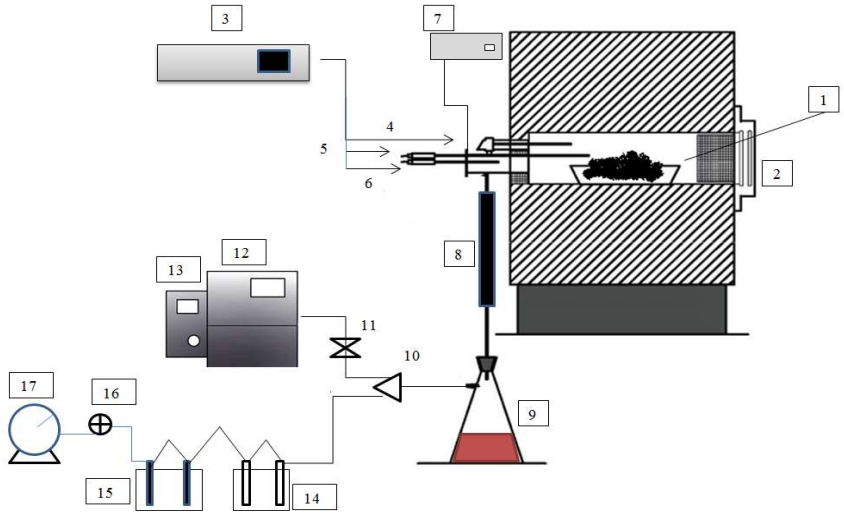

Fig. 6. Scheme of the equipment used for the pyrolysis measurements. 1 – reaction chamber, 2 – reaction chamber sealed with 10 M5 screws and the high-temperature silicone, 3 – Metronic MPI-CL analyzer, 4, 5, 6 – thermocouples, 7 – excess pressure measured with CMR-10 differential micromanometer or U-tube, 8 – water cooler, 9 – flask with pyrolytic oil, 10 – gas separator, 11 – filtration scrubbers, 12 – Hartmann-Braun gas analyzer, 13 – Servomex gas analyzer, 14 – wet scrubbers for Cl, Br and F analysis, 15 – absorption tubes for chromatography, 16 – pump, 17 – wet gas flowmeter

3. RESULTS AND DISCUSSION

The collected samples were measured for the content of carbon, total aluminum and metallic aluminum in order to determine the level of aluminum oxidation. The results of the chemical analysis are presented in table 2. TP0 represents the sample of the material before pyrolysis.

Table 2**.** Results of the chemical analysis of the pyrolysis products

Sample ID	Total aluminum (Al), %	Metallic aluminum (Al met.), %	Carbon (C), %	Al oxidation level, %
TP0	5,50	5,20	48,9	5,45
PTp1	14,20	11,95	62,3	15,85
PTp2	20,30	20,20	50,9	0,49
PTp3	22,30	19,40	52,6	13,00

PTp4	30,30	29,05	42,5	4,13
PTp5	23,30	21,6	51,18	7,30

The first test (sample PTp1) was performed in order to determine if the system was hermetic. The air was removed from the reactor to the oxygen level 0.5%. After that, the argon was no longer supplied to the system. The gas analysis indicated, that during the process, the oxygen concentration increased, and by the end of the process the O_2 content was 16.5%. Starting from the second test (sample PTp2), argon was supplied to the system during the whole process with a flowrate 200l/h. The oxygen concentration at the beginning of the process was 0.1%. During the third test (sample PTp3) the oxygen level at the beginning of the process was 0.0% (after 40 minutes argon flowrate was reduced to 100l/h). After two hours of the process, due to the high pressure in the system, the vessel used to collect the process oil exploded, and ended the process. The high level of Al oxidation is caused by the untimely event that caused the oxygen penetration inside the system before the process was ended. The oxygen content at the beginning of test 4 was 0.26%. Argon flowrate during tests 4 and 5 was 200l/h for the whole process duration. The oxygen content at the beginning of test 5 was 0.15%. The results of the gas analysis collected during test 5 are presented in fig. 7.

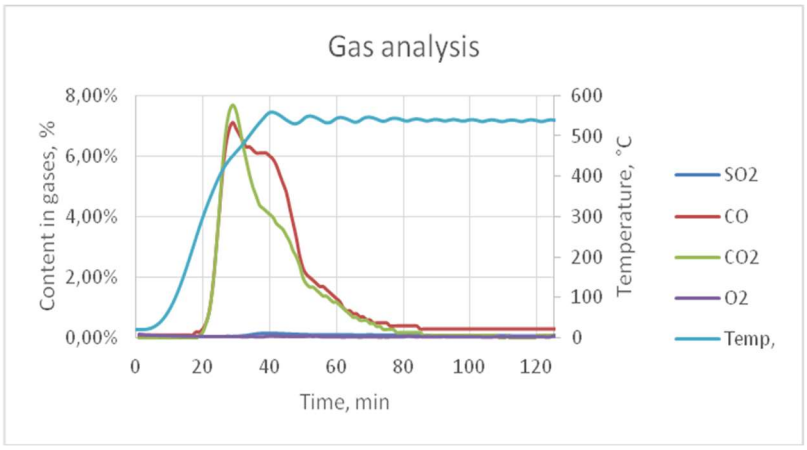

Fig. 7. Gas analysis during test 5

The pyrolysis process started when the concentrations of CO and CO_2 increased significantly at 348.7°C. The decomposition of cellulose can be observed between 20-35 minute of the process, followed by the decomposition of polyethylene. The gases are generated for approx. 1 hour. The measurements ended after approx. 2 hours. The picture of the material before and after pyrolysis is presented in fig. 8 and fig. 9.

Fig. 8. The material before pyrolysis

Fig. 9. The material after pyrolysis (PTp5)

According to [9], polypropylene and polyethylene do not produce any char during the pyrolysis – the only products are oil and gas. The gas produced during PE decomposition contains mostly methane and ethylene, ethane, propylene, propane, butene, butane, pentane and other hydrocarbons.

After the process, the solid fraction was analyzed in order to determine the amount of produced metal and organic residue. The organic material is bound with a certain portion of aluminum and is hard to separate. Therefore, the material was leached with hydrochloric acid. The organic residue has been dried at 55°C for 24 hours. The metal fraction in the measured sample was 51.4%, and the organic residue was 48.6%. Further investigations will be performed in order to determine the most efficient method of metal separation from organic residue and aluminum recovery.

4. CONCLUSIONS

The multimaterial waste are a significant group of waste which are not properly handled. A part of them is used to recycle paper and/or plastic fraction, however the metal present in the waste is not recovered. The recovery of aluminum is complicated due to the fact that Al is often present in the oxidized form, which is hard and expensive to process. The study was focused on the thermal decomposition of the multimaterial waste with a special focus of Al oxidation level in order to provide the metal resource that will be easy to reuse in metallurgical recovery processes.

The thermogravimetric study was performed in order to determine the optimal process conditions and the temperatures of the decomposition of different components of the multimaterial waste. The analysis indicates that two decomposition reactions occur at different temperatures – cellulose decomposition starts at 290°C, and polyethylene decomposes at 443°C.
The results obtained during the measurements performed on a laboratory scale equipment confirm the results obtained during the thermogravimetric studies. The changes in the gas composition in time are related to two identified processes: decomposition of cellulose (between minutes 20 and 35) and decomposition of polyethylene (between 35 and 55).
Aluminum content in the Tetra-Pak waste is approx. 5%. After the process, metal content in the solid fraction is 51.4%. The initial oxidation level in the sample before pyrolysis was 5.45%. The oxidation level after pyrolysis is satisfactory. The experiments were performed in the conditions designed to limit the level of aluminum oxidation. The highest oxidation level was obtained during test 1 and 3. During test 1, the oxygen was removed from the system with argon before the process started, and no additional inert gas was inserted to the system during the process – the oxygen level raised and caused oxidation of the part of the material. During test 3, the vessel used to collect process oil exploded due to the high pressure, what caused air penetration inside the reactor and the oxidation of the examined material.
The Al oxidation level in the samples produced during the adequate conditions (argon constantly supplied to the system, low average oxygen level – 0.17% at the beginning of the process), a parameter of high importance for the further recovery processes, was low. The average level of aluminum oxidation for those samples was 3.97%. After pyrolysis, the metal fraction can be separated from the organic residues and processed in order to produce the commercial quality aluminum alloy or pure aluminum. Further tests are planned to determine the most efficient methods for the separation of metal and char and aluminum recovery with the application on pyrometallurgical methods.

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ODZYSK ALUMINIUM Z PRODUKTÓW PIROLIZY ODPADÓW OPAKOWAŃ TETRA-PAK

Streszczenie

Postępujący rozwój gospodarczy wiąże się z wytwarzaniem coraz większej ilości odpadów, w tym znacznej grupy odpadów wielomateriałowych. Odpady te składają się z co najmniej dwóch różnych materiałów, połączonych ze sobą w sposób trwały, co uniemożliwia ich rozdział za pomocą prostych metod mechanicznych. Opakowania Tetra-Pak składają się z siedmiu warstw celulozy (ok. 70%), polietylenu (ok. 25%) i aluminium

(ok. 5%). W artykule zaprezentowano krótki przegląd metod stosowanych obecnie do przetwarzania tego typu odpadów. W ramach przeprowadzonych badań wykonano analizę termograwimetryczną w atmosferze argonu w celu określenia zakresów temperatur w których występuje ubytek masy oraz towarzyszących mu efektów termicznych. Następnie wykonano testy pirolizy w skali laboratoryjnej i określono zawartość glinu w produktach stałych oraz stopień jego utlenienia w materiale przed oraz po procesie pirolizy.

Słowa kluczowe: piroliza, Tetra-Pak, odzysk aluminium

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