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Waste management of half-finished products and thermosetting wastes

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Plastics are the widely used materials and their application increases every year considerably. Therefore, appropriate waste management policy should be used in relation to the utilization or recycling of scrap plastic components. Although most of these materials refer to thermoplastics, a huge widening demand is observed in the field of thermosets. They find a wide range of applications as the dielectric or insulating materials, high-current breaker switches, sensors and other electrical and electronic devices, as well as high-resistant sleeves in mechanical devices. The substantial part of the thermohardening products is used in a car, heavy, light, chemical industry and agriculture as well. The thermohardening wastes contain a large amount of combustible fraction as thermosetting resins, and various materials as a different kind of metals group like ferromagnetic and copper. Therefore, they are potential sources of energy and secondary materials. Application of thermal methods for the utilization of these wastes in the pyrolysis process was investigated. The development of the utilization of these wastes with the possibility of gas and liquid substance recovery as a potential source of energy on a commercial scale is the main aim of this paper.

Keywords: plastic waste, thermosetting waste, pyrolysis utilization.

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INTRODUCTION

The problems connected with waste management and waste utilization belong to the most serious problems of the present industrial civilization. Stable growth of the quantity of waste material from plastics (thermoplastic and thermosetting) causes large hazard for the natural environment because most of these wastes are warehoused on municipal landfills where they take up about 40% volumes[1]. Therefore, is necessary to research the methods for their effective utilization.

Recycling of plastics has become an important topic during the last two decades, when a huge increase in the usage of such materials was observed. Various thermoplastics (polyethylene, polypropylene, polystyrene) may be re-melted and re-used in new products, so recycling of thermoplastic components is quite well recognized. A much more complicated situation regards thermosets (e.g. polyurethanes, phenolic, epoxy, furan and furfurol resins), which cannot be re-melted and reformed into new products. During the processing of such material (curing process) a chemical reaction that results in infusible and insoluble network, proceeds. Therefore, currently there is no explicit utilization option for cured resins and recycling was not a popular option for the minimization of these wastes either, although UE places enormous emphasis on the recycling and utilization of plastic wastes (94/62/EU European Union directive on waste packaging and recycling regulation).

However, bearing in mind all the environmental regulations it would be highly valuable to propose any utilization option for thermosetting refuse. In this paper the investigations on the thermosetting wastes utilization through the pyrolysis process with a simultaneous recovering of gas and liquid products as fuels has been presented.

CHARACTERISTIC OF PLASTIC MATERIALS

Plastic is made from the fractions of natural gas or crude oil changed chemically into a solid form. There are two basic types of plastic: thermoplastics and thermosetting. Thermoplastic polymers can be heated and repeatedly formed. The shapes of the polymer molecules are generally linear or slightly branched. This means that the molecules can flow under the pressure when heated above their melting point. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET) belong to the thermoplastics. Thermosetting polymers undergo a chemical change when heated, creating a three-dimensional network. After they are heated and formed, these molecules cannot be re-heated and re-formed. The cross-linking processes can take place under the influence of chemical agents introduced to the resin - then such materials are called chemically hardenable (epoxy resins, non-saturated polyester resins). This process takes place at ambient temperature or above. If these processes are performed under the influence of warm or physical factors then these materials are called as thermohardening (phenol-aldehyde resins). When comparing these types, thermoplastics are much easier to adapt to recycling.

Today the world economy produces over 150 million tones of plastics per year, and in Poland the production of polymers is above 0.7 million tones. Below, Figure 1 introduces the main polymer products in Poland in the year 2000[2].

METHODS OF THERMOSET WASTES UTILIZATION

At present there are three well-known main directions of the utilization of plastic waste material (especially the thermoplastics), including the high-molecular matter. Depending on the kind of the plastic waste material a suitable method of the utilization which would minimize

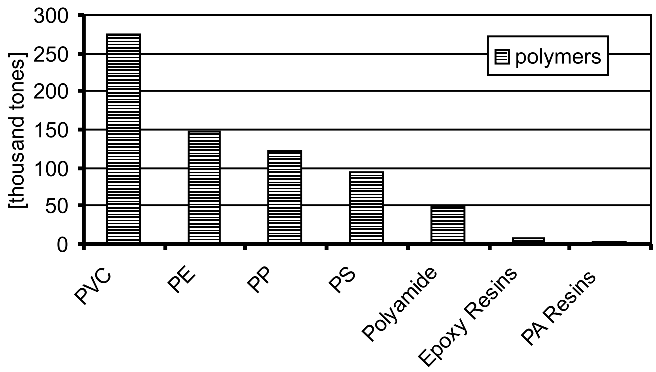

Figure 1. Polymer products in Poland in the year 2000

the noxious influence on the environment should be applied. Plastic wastes can be neutralized by:

– material recycling – obtaining the granulated product with the properties close to those of the original raw material,

– chemical recycling (raw material) – receiving the standard value products gas- or liquid fulfilling the function of autonomous matter or of the substrates for the synthesis of the following products,

– thermal utilization (combustion, gasification, degassing) – using the generated thermal energy (in the case of combustion) or converting into gases and liquids or the char rest as the fuel after the process.

In the case of the thermosets, the most widely used method of utilization is the landfill, and currently above 90% of such wastes is landfilled[3]. Instead of landfilling, the following options are currently being considered for the utilization of thermosetting wastes:

– application as a construction material,

– energy recovery,

– degradation.

The use of cured epoxy based scrap in the concrete or asphalt construction material has been considered many times, and that method seems to be a simple way of utilization. However, bearing in mind that the amount of such material is relatively low and waste streams are distributed, there is a very low economic impact of such a solution. It should also be emphasized that epoxy scrap is widely used in electrical equipment, thus various internal parts (cores, windings) made of metals are embedded in epoxy which introduces a necessity to apply the pre?treatment process of the scrap (removal of metallic parts and crushing).

Considering the energy content of thermosets (lower heating value – LCV from 10 to 20 MJ/kg, depending on the filler content), energy recovery by combustion can be a valuable option[4]. Of course, in such treatment a large amount of inorganic matter in the form of filler is generated and it must be handled in the economic way. From the air pollution point of view combustion of thermosets is relatively safe in a properly defined process and no hazardous emissions are obtained[5, 6].

The next utilization option, namely degradation, refers to the reduction of plastics to the lower molecular weight materials through the application of such processes as photodegradation or chemical degradation. One of the interesting methods of the utilization of thermosets can be pyrolysis process, as a result of which gas, liquid and char (coal) are made.

CHARACTERISTIC OF THERMOSET WASTES

A profitable price and continuously improved properties of plastic products are the main cause that this material found a very wide application in our everyday life. Figure 2 presents the share in the plastic wastes market.

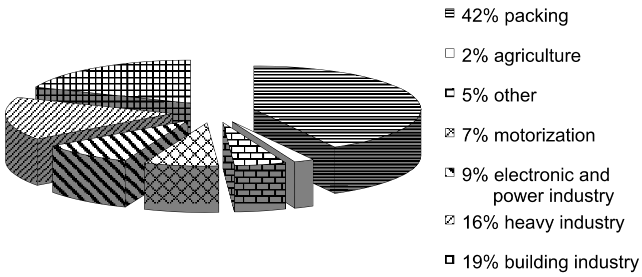

Figure 2. Share in the plastic wastes market in Poland[7]

Various kinds of mechanical, electronic, electrical and other devices contain thermosetting mixtures, as a composition containing epoxy resin, hardener, filler, colorant as well as other components as flexibilizers and accelerators (Table 1). These resins are used as an insulating casing with high dielectric properties and plastics for constructional and special aims. Mostly, silica is used as a filler and iron oxide as dies. Additionally, the electronic and electrical devices consist of metal (ferromagnetic), copper (coil winding) and also organic matter (Table 2). For this substance, physicochemical and thermal properties are illustrated in Table 3.

The above data refer to the epoxy wastes being generated in the manufacturing process of voltage and current transformers and were based on the mixture of silica-filled, flexibilized bisphenol-A epoxy resin with phthalic anhydride as the hardener.

Table 1. The composition of the resin mixture

No.	Kind of substance	Mass fraction, (wt %)
1.	Resin	17 – 35
2.	Hardener	12 – 20
3.	Filler	40 – 65
4.	Dye	0.2 – 0.6

Table 2. Average composition of the metal components for the electronic and electrical devices

No.	Kind of substance	Mass fraction, (wt %)
1.	Metal (ferromagnetic)	17 – 62
2.	Copper (coil winding)	0 – 14
3.	Resin	24 – 88

Table 3. The parameters of resin wastes

No.	Chemical, physical and thermal parameters of resin wastes	Value
1.	Ash, (wt %)	58.90
2.	VM (volatiles), (wt %)	37.87
3.	Weight loss, (wt %)	41.10
4.	Moisture, (wt %)	0.04
5.	Carbon, (wt %)	27.11
6.	Hydrogen, (wt %)	3.30
7.	Combustible sulphur, (wt %)	–
8.	HCV, (kJ/kg)	11326
9.	LCV, (kJ/kg)	10587
10.	Density, (kg/m^3)	1875
11.	Bulk density, (kg/m^3)	837

PYROLYTICAL DEGRADATION

Pyrolysis is one of the methods of thermal utilization of wastes; it is a distillation process affected by the application of heat in the insufficiency of air[8]. Pyrolysis gases, untreated oils, and the solid matter in a form of char are the main products of the process (Figure 3). These products may be utilized as the ecological fuel during the next step of the waste neutralization. The pyrolytical technologies are especially useful for the utilization of plastic wastes. In the way of thermal treatment under the neutral conditions of different plastics, it is possible to obtain highly valuable substances for petrochemical and refinery industries[6]. The low-temperature pyrolysis runs at the temperatures between 350 – 400°C, and above 600°C the high-temperature pyrolysis takes place, where the technical solutions of the reactors are especially important, playing a decisive role in selectivity of the processes and the degree of batch transformations. These in turn depend mostly on the conditions of heat exchange and determine the parameters of an estimation of each technology.

Pyrolytical utilization can be favorably used not only for gas and oil recovery from scrap thermosetting but also for recycling metallic parts (like copper, aluminum, brass) from such material.

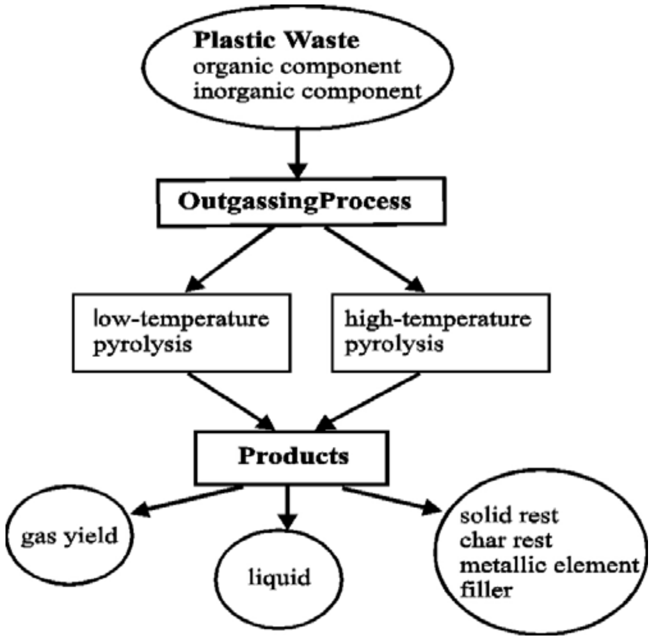

Figure 3. A schematic flow for the pyrolysis utilization of thermosets

EXPERIMENTAL ARRANGEMENT

The pyrolysis process was carried out using an experimental arrangement showed in Figure 4.

The pyrolytical reactor, preheater with electric heaters and the thermocouple were the main parts of the system. The design of the reactor allowed controlling the temperature inside the reactor in a wide range to 1000°C. This was achieved by the use of the type K thermocouple connected to the temperature control system.

The cyclone and the demister were the main components of the purification system for the pyrolysis gas and then burnout in the combustion chamber, equipped with a Bunsen burner. Liquid products were separated by the condensation and they were collected in the cyclone and the demister.

EXPERIMENTAL PROCEDURE

The experiments were conducted in the pyrolyser designed for that purpose, with a possibility of collecting the pyrolysis products. The minimal time of the proper pyrolysis was about three hours for one feed of the processed material and the maximal time was approximately 5 hours.

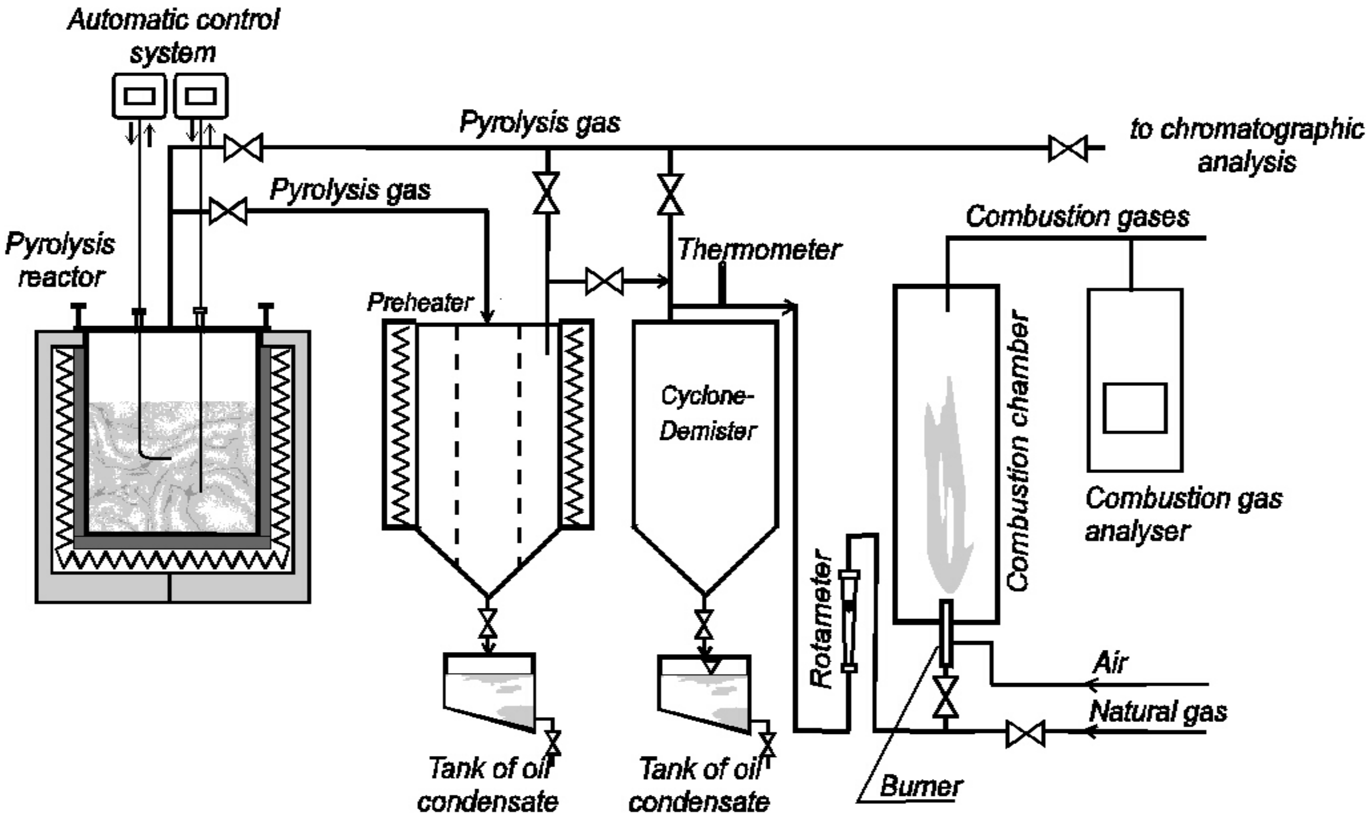

Figure 4. A schematic diagram of the experimental apparatus

The low-temperature pyrolysis was conducted at 450°C, whereas the high-temperature process was performed at 850°C.

Totally, a few different sets of low- and high-temperature pyrolysis experiments were performed with the view to finding the optimal process parameters, assuring a high decomposition of the organic material (the low content of carbon in solid residues), as well as a good quality of the pyrolytical gas, liquid recovery and the recycled metallic parts.

Control measurements of the temperature distribution inside the reactor, the quantity of pyrolytical gases, the amount of the solid residues, and the amount of the process liquids were conducted during all the experiments. The gas HP 5890II chromatographs were used for the chemical analysis of the pyrolytical gas. The delivered sample was analysed on two HP gas chromatographs, one of which one equipped with the TCD detector serving for the analysis of permanent gases and the other one with the FID detector was used for the analysis of hydrocarbons. The samples of the pyrolytical gas were taken at different stages of the process, and the presented results are the average values.

The laboratory experiments were continued until the evolution of gases was completed.

The liquid products of the pyrolysis process undergo the distillation and rectification, of which the main products are fractions: the light and average oily distillates. The remainder after distillation is sometimes turned back to the pyrolytical reactor to the plastic wastes and their pyrolysis again.

RESULTS AND DISCUSSION

The final results of the pyrolysis experiments are presented in two series. The data of the low-temperature pyrolysis are presented in Tables no. 4, 5, and 6. The data of high- temperature pyrolysis are shown in Tables no.7, 8 and 9.

On the basis of the obtained data it can be noticed that the high content of carbon (almost 15%) was decided upon to perform the high-temperature pyrolysis. Such a high content of the carbonaceous matter would disqualify the potential re-use of the filler.

On the basis of these data and the experiments it was proved that in this type of installation, the mixtures of the thermosetting waste can be utilized at the temperatures from 450°C to 850°C. The gaseous products of the pyrolysis (C1 to C4 hydrocarbons) after the cyclone-demister are devoid of solids, because the combustion process of pyrolytical gases on the burner was stable and smooth. The liquid products after the pyrolysis could be received as a light and average oil fractions (the density below 990kg/m^3). For the high-temperature pyrolysis after the process, the amount of carbon in the solid residue was low and the silica filler can be recycled.

CONCLUSIONS

According to the experiments carried out, it was found that the pyrolysis could be used for the thermal utilization of thermosetting wastes with a simultaneous recovery of the pyrolytical gas, the liquid fuel and with recycling of metallic components.

Based on all the runs, the optimal conditions for the investigated epoxy mixture are achieved at 850°C for the high-temperature pyrolysis.

The presented pyrolysis is a very good process for thermosetting waste liquidation with absolutely slight pollution of atmospheric air and the necessity to secure the remaining solid residues.

All the solid residues after the pyrolysis, for example: metal (ferromagnetic), copper (coil winding) and silica flour can be recycled.

Table 4. The parameters of the gaseous pyrolysis product (temp. 450°C)

No.	Chemical, physical and thermal parameters of pyrolytical gas	Value
1.	H_2, (%)	74.93
2.	O_2, (%)	0.20
3.	N_2, (%)	0.41
4.	CO, (%)	7.30
5.	CO_2, (%)	–
6.	Hydrocarbons to C_4, (%)	17.06
7.	Hydrocarbons above C_4, (%)	0.10
8.	HCV, (kJ/kg)	17001
9.	LCV, (kJ/kg)	14804
10.	Ratio of quantity, (dm^3/kg resin wastes)	97

Table 5. The parameters of the liquid pyrolysis product (temp. 450°C)

No.	Chemical, physical and thermal parameters of liquid product	Value
1.	Ash, (wt %)	0.28
2.	VM (volatiles), (wt %)	99.41
3.	Weight loss, (wt %)	99.72
4.	Moisture, (wt %)	3.87
5.	Carbon, (wt %)	73.94
6.	Hydrogen, (wt %)	12.03
7.	Combustible sulphur, (wt %)	–
8.	HCV, (kJ/kg)	27131
9.	LCV, (kJ/kg)	24980
10.	Density, (kg/m^3)	986
11.	Ratio of quantity, (g/kg resin wastes)	83.6

Table 6. The parameters of the solid pyrolysis product (temp. 450°C)

No.	Chemical and thermal parameters of solid product	Value
1.	Ash, (wt %)	80.54
2.	VM (volatiles), (wt %)	1.46
3.	Weight loss, (wt %)	19.46
4.	Moisture, (wt %)	–
5.	Carbon, (wt %)	14.54
6.	Hydrogen, (wt %)	–
7.	Combustible sulphur, (wt %)	–
8.	HCV, (kJ/kg)	4681
9.	LCV, (kJ/kg)	4623

Table 7. The parameters of the gaseous pyrolysis product (temp. 850°C)

No.	Chemical and thermal parameters of pyrolytical gas	Value
1.	H_2, (%)	67.07
2.	O_2, (%)	1.19
3.	N_2, (%)	2.96
4.	CO, (%)	8.73
5.	CO_2, (%)	–
6.	Hydrocarbons to C_4, (%)	19.93
7.	Hydrocarbons above C_4, (%)	0.12
8.	HCV, (kJ/kg)	17232
9.	LCV, (kJ/kg)	15204
10.	Ratio of quantity, (dm^3/kg resin wastes)	103

Table 8. The parameters of the liquid product after the pyrolysis (temp. 850°C)

No.	Chemical and thermal parameters of liquid product	Value
1.	Ash, (wt %)	0.31
2.	VM (volatiles), (wt %)	99.40
3.	Weight loss, (wt %)	99.69
4.	Moisture, (wt %)	4.13
5.	Carbon, (wt %)	75.26
6.	Hydrogen, (wt %)	9.42
7.	Combustible sulphur, (wt %)	–
8.	HCV, (kJ/kg)	26498
9.	LCV, (kJ/kg)	24290
10.	Density, (kg/m^3)	1073
11.	Ratio of quantity, (g/kg resin wastes)	261.3

Table 9. The parameters of the solid product after the pyrolysis (temp. 850°C)

No.	Chemical and thermal parameters of solid product	Sample
1.	Ash, (wt %)	91.86
2.	VM (volatiles), (wt %)	0.90
3.	Weight loss, (wt %)	8.14
4.	Moisture, (wt %)	–
5.	Carbon, (wt %)	5.63
6.	Hydrogen, (wt %)	–
7.	Combustible sulphur, (wt %)	–
8.	HCV, (kJ/kg)	1680
9.	LCV, (kJ/kg)	1670

The pyrolysis products such as gas and oils can be utilized as an ecological fuel in the next step of this technology of the waste neutralization with the possibility of their recovery as a potential source of energy[9, 10, 11].

The gases generated during the pyrolysis can be burned in situ and can be utilized after cleaning as an additional energy source. Emission of toxic pollutants into the atmosphere: CO, SO_2 and NO_x from the combustion process of pyrolytical gases was not large.

The ratio of the volume waste reduction after the pyrolysis was up to 55 – 70%.

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