

# PYROLYTIC RECOVERY AS A PROSPECTIVE USE OF PLASTIC WASTE MATERIALS

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Prospective use of plastic material components resulting from their pyrolytic recovery is presented in the paper. Selected plastic waste materials (PE, PP, PS) were evaluated using modern analytical method GS-MS after the low-temperature pyrolysis. The low-temperature pyrolysis shows that the sample of PS was well-suited to this application and this recovery is important in the case of all three samples as well. The presence of 26 substances with 1-Hexene (13.72%) was observed in the case of pyrolysis products, specifically PE. When investigating PP, 36 substances with the highest content of 2,4-Dimethyl-1-heptene (38.35%) were defined. 20 substances containing especially Styrene (79.97%) were determined as the major products of PS pyrolysis. Moreover, using the GC-MS analysis, it was found out that chemical compounds present in all samples could be further recovered. The possibility of using the pyrolysis to recover the plastic waste materials in order to protect the environment is necessary.

## KEYWORDS

pyrolysis, thermogravimetry, gas chromatography, plastic waste materials, chemical compounds

## 1 INTRODUCTION

Polymers are natural or synthetic substances with one basic monomer unit multiply repeating as a segment in their chain. They contain mainly the atoms of C, H and O, often also Cl, N and other elements [Mleziva 2000]. Polymers are divided into elastomers and plastics [Duchacek 2006]. Elastomers (Indian rubber) are elastic polymer substances which can be bent out easily with no disruptions under standard conditions. In most cases, they can return to its original shape. Indian rubber (caoutchouc) is an essential group of elastomers used for producing rubber. Under standard conditions, plastics are tough but often brittle polymers. They become plastic and moldable. While the changes from plastic to solid state are returnable we can speak about thermoplastics (PE, PP, PS, PET, PVC, etc.). On the contrary, when the changes are not returnable resulting in a chemical reaction between a molecule, we can speak about thermosets (polyesters, phenoplastics, aminoplastics) [Duchacek 2006].

Car manufacturing especially in the 70s was accompanied by the global fast-growing consumption of plastics. It was connected with the increasing demands for passive safety and vehicle economy. Car body metal components were replaced by polymers to a great extent resulting in greater passive safety. An ecological point of view is an important factor taken into consideration in the application of plastics in car

manufacturing. Polymer material recycling from used cars must meet greater demands in terms of ecology as well. Apart from beneficial functional properties and manufacturing properties, the design of the components made of plastics is attractive and they are pleasant to touch. Using the plastics in car manufacturing allows the progressive design solutions especially in the case of a car body. Moreover, car manufacturing is more effective, the costs are reduced and the quality is improved. Kongsak [2014] mentioned in his study that using more plastic materials in car manufacturing from 10% in the 80s to 18% at present, the average weight of a vehicle has been reduced by 200kg. It is mainly due to the lightness, durability, plasticity.

The specific difficulties in waste management are because of the nature of plastic materials. Plastics are relatively cheap used widespread in various industries. Therefore, they were developed significantly during the last century and the trend will continue to rise. Plastics are very resistant material in the environment and their lifetime is longer in comparison to the products made of them. Therefore, plastic waste generation increases [Green book 2013].

Tertiary recycling or chemical recycling, uses chemical processes to break down the polymer into value-added commodities Tertiary recovery by pyrolysis is one of the possibilities of secondary use of plastics [Hegberg 1993; Onwundili 2009]. Pyrolysis of plastic waste is a prospective method. At the higher temperature (from 250 up to 1650 °C) with no access of air (or limited access of air), pyrolysis oil, pyrolysis gas, and solid residue are obtained [Aguado 1999]. These components can be used for scrap materials to produce various chemicals, fuel for vehicles or they can be burnt in boilers distributing heat [Moldoveanu 1998]. Material recovery of industrial waste (plastics of one type – polyethylene, polypropylene, used tyres) is of great importance, because of original monomers exploiting for further petrochemical processing obtained from it. The conditions of thermal decomposition are aimed at deriving the liquid share from waste. Liquid products are further distilled to fractions similar to petrol and diesel. Detailed analyses are carried out and physical and chemical properties are determined. All limits and standards associated with fuels, petrol and diesel must be met. The composition and number of pyrolysis units are affected by lots of factors. The composition of pyrolysis products depends especially on the composition of input material, organic/inorganic ratio, and the particle size of input material. The recovery ratio of individual fractions (solids, liquids, gases) is affected by the final temperature of the pyrolysis process as well [Phan 2008] by the carrier gas used, heating temperature, time of holding the gaseous products in pyrolysis chamber, construction and pressure in the pyrolysis equipment. Properties of pyrolysis products can be significantly affected by the catalysts and their ratio (catalyst: material) [Inguanzo 2002].

Any material containing an organic element can be used for the pyrolysis. However, its efficiency depends on material properties. In order to optimise the process, material performance during pyrolysis and the effect of operational processes must be defined. Differential thermal analysis and thermogravimetric analysis (DTA/TG) should be used to determine the decomposition temperature and thermal gradient of a material [Gedde 1990].

The aim of the paper is to determine the tertiary recovery of selected plastic materials, polyethylene (PE), polypropylene (PP) and polystyrene (PS) using the low temperature pyrolysis and to describe individual products.

## 2 MATERIAL AND METHODS

### 2.1 Material

PE – disposable gloves; PP – food container; PS – expanded polystyrene (a cup)

### 2.2 Methods

#### Low temperature pyrolysis

The plastic sample (10 g) closed in the retort with no access of air was affected by heat. A gradual increase in the temperature resulted in water evaporation and decomposition of individual elements of plastic sample. The sample of plastics carbonized and released volatile substances were passing through the condenser. Condensed part of volatile substances (pyrolysis oil) got stuck as a condensate and the number of uncondensed gases was calculated due to the weight of the original sample, of the carbonized residue in the retort and the amount of the condensate. 10g of the plastic sample was inserted into the retort and closed tightly. The condenser was connected with the pipe and the beaker catching the pyrolysis oil placed to the outfall on the lab scale. The retort was heated over the flame from the propane gas bottle. The amount of pyrolysis oil with a dependence on time and the rising temperature was observed. After finishing the pyrolysis and cooling the retort, large amount of carbonized residue was discovered at the bottom of the retort.

#### Thermogravimetric analysis (TG)

Thermogravimetric analysis took place in a nitrogen atmosphere (with the nitrogen purity of 3.0 with the flow rate of 50 ml/min<sup>-1</sup>) with the same temperature in the case of all three samples. The samples were disintegrated with milling. The final size of a sieve mesh was 0.5 mm. The weight of samples ranged between 67.970 – 10.790 mg. Nitrogen with the permanent flow rate was also used as a protective gas close to lab scales. The measurement was carried out at the temperatures ranging between 30 - 800 °C in three segments. During the first three minutes and at a temperature of 30 °C – isothermal segment, the sample was stabilised. Subsequently, the thermodynamic segment continued at the speed of heating of 10 °C/min. When a temperature of 800 °C was reached, the measurement was finished – isothermal segment with a temperature of 800 °C for 3 minutes.

#### Pyrolysis and GC-MS analysis (Py-GC-MS)

The pyrolysis was performed with a Pyroprobe 5150 Series (CDS Analytical Inc.). The pyrolyser was interfaced (interface temperature 150°C). For the pyrolysis, approximately 1.87 – 3.30 mg of the sample was put in the quartz tube. The sample was closed with quartz wool on both sides. The pyrolysis temperature of the given samples was determined following the fastest material decomposition resulting from the thermogravimetric analysis. In these cases, the speed of heating was 10 °C/ms and the retention time was 10 s.

Pyrolysis products were analysed by the method GC-MS using the device: a gas chromatograph GC 7890A Agilent Technologies and a mass spectrometer with ion source Agilent Technologies model 5975C (MSD). The condition of GC: columns HP-5MS (30 m × 250 µm × 0.25 µm), carrier gas: Helium (constant flow rate 2 ml·min<sup>-1</sup>), temperature program: from 60 °C (1 min) to 280 °C (15 °C·min<sup>-1</sup>) 280 °C (2 min), the temperature of an injector - 300 °C in the split-screen mode. The software ChemStation E 02.01.1177 was used to record and evaluate the measured data. The components were identified comparing the measured mass spectra to the NIST and Wiley mass spectral libraries.

## 3 RESULTS

### 3.1 Low-temperature pyrolysis evaluation

#### Polyethylene (PE)

Low-temperature pyrolysis of PE was performed for 60 minutes after reaching the maximum temperature of 280 °C. In the device used in the case of the PE sample, the temperature was increasing in the fastest way during the first 30 minutes of the experiment. The low-temperature pyrolysis of the PE sample resulted in the carbonised residue, condensate, and gas. The composition of individual phases and individual components is shown in Table 1. If is used Low-temperature pyrolysis, the main products of additives, monomers and oligomers can be obtained. This temperature is suitable for several additives [Lippmann 2001].

From the original PE sample, 50% was degraded and changed to liquids and gases. In the case of the PE sample, despite the drops quite a large amount of tar stuck in a condenser emerged. At the same time, uncondensed gaseous components of decomposition were released. The maximum amount of condensate appeared at a temperature of 280 °C. After low-temperature pyrolysis, the percentage of pyrolysis oil in the case of the PE sample was 3% and the percentage of tar was 27%.

#### Polypropylene (PP)

The low-temperature pyrolysis of PP was performed for 60 minutes after reaching the maximum temperature of 260 °C. The temperature increased in the fastest way in the device used in the case of the PP sample after the beginning of the experiment during the first 30 minutes. Carbonized residue, condensate and gas resulted from the low-temperature pyrolysis PP. The composition of individual phases and individual components is shown in Table 1.

50% of the original PP sample was degraded and changed to liquids and gases. The first drops of the condensate started to occur at a temperature of 160 °C while uncondensed gaseous components of decomposition released. The maximum amount of condensate appeared at a temperature of 260 °C. The percentage of pyrolysis oil in the case of the PP sample was 30% and the percentage of tar was 4%.

#### Polystyrene (PS)

The low-temperature pyrolysis PS took place during 60 minutes after reaching the maximum temperature of 260 °C. The fastest increase in a temperature in the case of the PS sample occurred during the first 20 minutes after the beginning of the experiment. During the low-temperature pyrolysis, carbonized residue, condensate and gas appeared. The composition of individual phases and individual components is mentioned in Table 1.

| sample | phases | content (%) |
|--------|--------|-------------|
| PE     | solid  | 50          |
|        | liquid | 30          |
|        | gas    | 20          |
| PP     | solid  | 50          |
|        | liquid | 34          |
|        | gas    | 16          |
| PS     | solid  | 9.6         |
|        | liquid | 41          |
|        | gas    | 49.4        |

Table 1. Composition of individual phases of samples after low-temperature pyrolysis

90.4 % of the original PS sample was degraded and change to a liquid and gaseous phase. At a temperature of 180 °C, the first drops of the condensate of the PS sample started to emerge. Uncondensed gaseous components of decomposition released at the same time. The maximum amount of the condensate was at a temperature of 260 °C. The percentage of pyrolysis oil was 35% and the percentage of tar was 6%.

### 3.2 Evaluation of the thermogravimetric analysis

#### Polyethylene (PE)

Using the TG analysis, the temperature when the decomposition of the sample started as well as the percentage of the sample degraded was discovered. The initial weight of the PE sample used – disposable gloves was 7.970 mg.

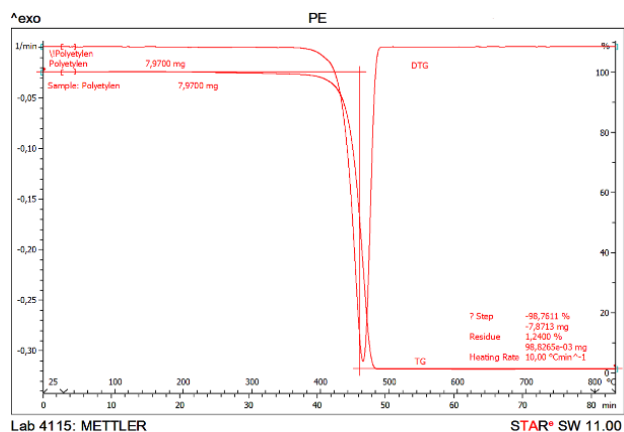


Figure 1. Final graph of the thermogravimetric analysis – PE

Following the TG analysis of the PE sample (Fig. 1), it can be seen that there was no change in the weight of the sample until the 28<sup>th</sup> minute and the temperature of approximately 278 °C. It is also called *plato*, it means the area of thermal stability. At a temperature above 278°C, the thermal degradation of PE associated with the mass loss emerged. The mass loss taking 48 minutes at a temperature of 480 °C equaled 98.7611%, i.e. 7.8713 mg. Afterward, the area of mass stability appeared. In the end, there was a residue of 1.240 % that equals 0.0988 mg.

#### Polypropylene (PP)

The initial weight of the PP sample was 10.79 mg. Following the TG analysis of the PP sample (Fig. 2), it can be seen that there was *plato* – area of thermal stability until the 32<sup>nd</sup> minute and the temperature of approximately 320 °C.

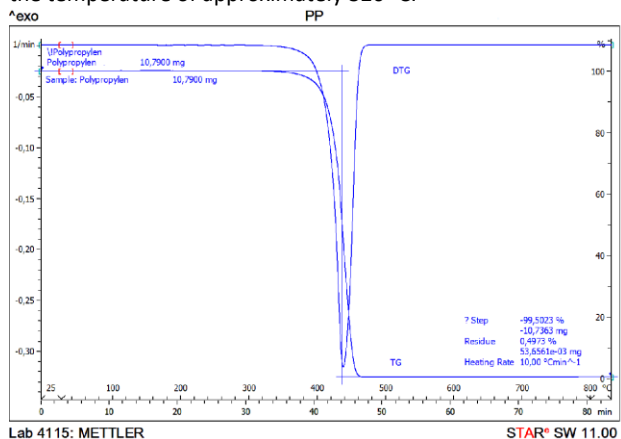


Figure 2. Final graph of the thermogravimetric analysis – PP

Above the mentioned temperature, the PP sample was thermally degraded until the 46<sup>th</sup> minute and 458 °C connected

with the mass loss of approximately 99.5023%, i.e. 10.7363 mg. Subsequently, the area of thermal stability emerged. Finally, there was observed a residue of 0.4973 % that equals 0.0536 mg.

#### Polystyrene (PS)

The initial weight of the PS sample was 8.3300 mg. It was thermally stable until the temperature of 285 °C (Fig. 3) was reached. In the case of the PS sample, the thermal degradation took place from the 29<sup>th</sup> minute and 285 °C to the 46<sup>th</sup> minute and the temperature of 460 °C. The mass loss equaled 96.9707%, i.e. 8.0777 mg. Then, the area of thermal stability came with the residue equaled 3.0328% (0.2526 mg).

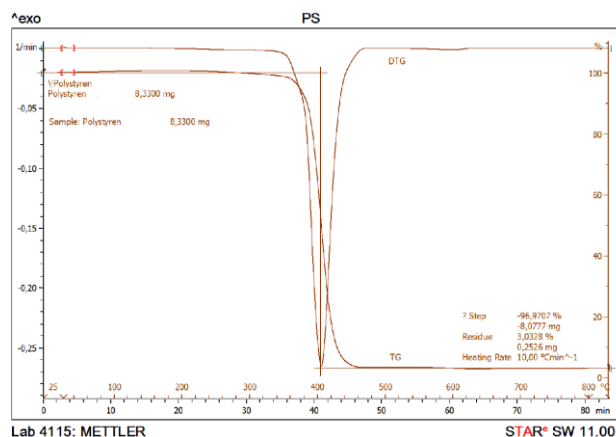


Figure 3. Final graph of the thermogravimetric analysis – PS

### 3.3 Evaluation of the Py-GC-MS analysis

#### Polyethylene (PE)

PE is an industrially used polymer. During the pyrolysis of PE, the chain is broken at a random point and small hydrocarbons with free radicals are formed. They can be stabilized by taking a hydrogen atom from them or by beta cleavage. N-alkanes, alkenes, alkadienes, etc. are created this way. Elimination of the ethylene (monomer) is not convenient in terms of energy and pyrolysis of the polyethylene does not occur as an unzipping process [Moldoveanu 2005; Kusch 2016]. The weight of the PE sample was 1.87 mg. The temperature of the pyrolysis of the given sample was determined following the material degradation using the thermogravimetric analysis. Pyrolysis products were analysed using the GC-MS method. The components were identified comparing the measured mass spectra to the mass spectral libraries. In total, 26 compounds with the quality defined following the individual peaks (Table 2) were determined in the pyrolysis products. Especially 1-alkenes (most 1-hexane), 2-alkenes, alkanes, various alkyl alkanes and, to a lesser extent, alkyl cyclopentane and others were formed. Alkadienes in the pyrolysis products were not determined, although they were identified in the PE pyrolysis products by Kusch [Kusch 2016].

| No. | RT (min) | Compound name            | Mol Weight (amu) | CAS         | Quantity (%) |
|-----|----------|--------------------------|------------------|-------------|--------------|
| 1   | 1.84     | 2-Butene, (E)-           | 56.06            | 000624-64-6 | 3.43         |
| 2   | 1.89     | 2-Pentene, (E)-          | 70.08            | 000646-04-8 | 8.46         |
| 3   | 2.03     | 1-Hexene                 | 84.09            | 000592-41-6 | 13.72        |
| 4   | 2.31     | Aziridine, 2,2-dimethyl- | 71.07            | 002658-24-4 | 10.74        |

|    |      |  |        |              |      |
|----|------|--|--------|--------------|------|
| 5  | 2.75 | Cyclopentane, 1,2,3-trimethyl-, (1.alpha., 2.alpha., 3.beta.)- | 112.13 | 015890-40-1  | 5.68 |
| 6  | 2.8  | Heptane, 2,4-dimethyl-   | 128.16 | 002213-23-2  | 4.08 |
| 7  | 3.08 | 2,4-Dimethyl-1-heptene   | 126.14 | 019549-87-2  | 3.81 |
| 8  | 3.44 | 1-Nonene   | 126.14 | 000124-11-8  | 3.86 |
| 9  | 3.5  | Nonane   | 128.16 | 000111-84-2  | 3.94 |
| 10 | 4.27 | 1-Decene   | 140.16 | 000872-05-9  | 8.92 |
| 11 | 4.35 | Decane   | 142.17 | 000124-18-5  | 2.75 |
| 12 | 4.66 | D-Limonene   | 136.13 | 005989-27-5  | 1.39 |
| 13 | 5.18 | 1-Undecene   | 154.17 | 000821-95-4  | 5.77 |
| 14 | 5.25 | Undecane   | 156.19 | 001120-21-4  | 3.69 |
| 15 | 6.08 | 1-Dodecene   | 168.19 | 000112-41-4  | 3.66 |
| 16 | 6.15 | Dodecane   | 170.20 | 000112-40-3  | 3.19 |
| 17 | 6.95 | 1-Tridecene  | 182.20 | 002437-56-1  | 2.35 |
| 18 | 7.02 | Tridecane  | 184.22 | 000629-50-5  | 2.06 |
| 19 | 7.08 | 1-Heptadecene  | 238.27 | 006765-39-5  | 0.61 |
| 20 | 7.23 | 11-Methyldodecanol   | 200.21 | 085763-57-1  | 0.45 |
| 21 | 7.78 | 3-Tetradecene, (Z)-  | 196.22 | 041446-67-7  | 2.74 |
| 22 | 7.84 | Tetradecane  | 198.24 | 000629-59-4  | 1.54 |
| 23 | 8.57 | 5-Octadecene, (E)-   | 252.28 | 007206-21-5  | 1.03 |
| 24 | 8.63 | Pentadecane  | 212.25 | 000629-62-9  | 0.98 |
| 25 | 9.32 | 3-Chloropropionic acid, heptadecyl ester                       | 346.26 | 1000283-05-1 | 0.50 |
| 26 | 9.37 | Octadecane   | 254.3  | 000593-45-3  | 0.63 |

Unk - unknown

a/ only organic components of the sample were determined (the content of inorganic components, e.g. water, was not determined),

b/ RT-retention time; Compound Name (name of the determined compound); Ref – number of the MS spectrum in the database; Quantity – quantity of the compound; CAS – Chemical Abstract Service

Table 2. GC/MS analysis of PE pyrolysis products

the main product of the PP degradation by Tsuge et al. [14] and Kusch [13]. Apart from them also C<sub>6</sub> and C<sub>9</sub> alkenes such as 2-methyl-1-pentene and 2,4-dimethyl-1-heptene that is propylene dimer and trimer were defined by them. Propylene tetramer and pentamer are generated during the PP pyrolysis at the lower temperature.

The weight of PP sample was 2.64 mg. The temperature of the PP pyrolysis was determined following the thermal degradation using the thermogravimetric analysis. According to the presence and peak areas, in total, 36 compounds were determined qualitatively. Moreover, the quantity of individual pyrolysis products was defined (Table 3).

| No. | RT (min) | Compound name                       | Mol Weight (amu) | CAS         | Quantity (%) |
|-----|----------|-------------------------------------|------------------|-------------|--------------|
| 1   | 1.91     | Diaziridine,3,3-dimethyl-           | 72.07            | 004901-76-2 | 5.67         |
| 2   | 2.03     | 1-Pentene, 2-methyl-                | 84.09            | 000763-29-1 | 9.19         |
| 3   | 2.16     | 1-Pentene, 2,4-dimethyl-            | 98.1             | 002213-32-3 | 1.01         |
| 4   | 2.61     | Heptane, 4-methyl-                  | 114.14           | 000589-53-7 | 4.15         |
| 5   | 2.72     | 1-Heptene, 2-methyl-                | 112.23           | 015870-10-7 | 1.64         |
| 6   | 3.07     | 2,4-Dimethyl-1-heptene              | 126.14           | 019549-87-2 | 38.35        |
| 7   | 3.21     | Cyclohexane, 1,2,4-trimethyl-       | 126.14           | 002234-75-5 | 0.53         |
| 8   | 3.34     | Styrene                             | 104.06           | 000100-42-5 | 1.36         |
| 9   | 3.46     | 2-Pentene, 3-methyl-, (Z)-          | 84.09            | 000922-62-3 | 2.55         |
| 10  | 4.01     | Octane, 2,5-dimethyl-               | 142.17           | 015869-89-3 | 0.45         |
| 11  | 4.31     | 1,1,4-Trimethyl-cyclohexane         | 126.14           | 007094-27-1 | 0.70         |
| 12  | 4.33     | Unk                                 | Unk              | Unk         | 0.91         |
| 13  | 4.43     | Octane, 2,3,6,7-tetramethyl-        | 170.20           | 052670-34-5 | 0.88         |
| 14  | 4.47     | Dodecane, 2,6,10-trimethyl-         | 212.3            | 003891-98-3 | 0.92         |
| 15  | 4.66     | Hexane, 1-(hexyloxy)-5-methyl-      | 200.21           | 074421-19-5 | 0.32         |
| 16  | 4.75     | Cyclohexane, 1,1-dimethyl-2-propyl- | 154.17           | 081983-71-3 | 0.40         |
| 17  | 4.87     | Decane, 4-ethyl-                    | 170.20           | 001636-44-8 | 0.44         |
| 18  | 5.08     | Cyclopentane, propyl-               | 112.12           | 002040-96-2 | 5.36         |

### Polypropylene (PP)

Propylene (monomer) often occurred in degradation products resulting from the thermal degradation of PP. It is mentioned as

|    |      |  |        |             |      |
|----|------|--|--------|-------------|------|
| 19 | 5.11 | 2-Undecene, 4-methyl-                    | 168.19 | 091695-32-8 | 3.44 |
| 20 | 5.52 | 2,3-Dimethyl-3-heptene, (Z)-             | 126.14 | 059643-73-1 | 0.85 |
| 21 | 5.57 | Cyclopentane, 1,1,3,4-tetramethyl-, cis- | 126.14 | 053907-60-1 | 0.24 |
| 22 | 6.31 | 1-Hexene, 3,3-dimethyl-                  | 112.13 | 003404-77-1 | 0.25 |
| 23 | 6.44 | Cyclopentane, 1-methyl-2-propyl-         | 126.14 | 003728-57-2 | 0.28 |
| 24 | 6.47 | 1-Hexanol, 5-methyl-2-(1-methylethyl)-   | 158.17 | 002051-33-4 | 0.54 |
| 25 | 6.54 | Decane, 3,6-dimethyl-                    | 170.20 | 017312-53-7 | 0.33 |
| 26 | 6.75 | 3-Octene, 2,2-dimethyl-                  | 140.16 | 086869-76-3 | 0.27 |
| 27 | 6.81 | Decane, 1,1'-oxybis-                     | 298.32 | 002456-28-2 | 0.24 |
| 28 | 6.86 | Decane, 2,3,7-trimethyl-                 | 184.22 | 062238-13-5 | 0.43 |
| 29 | 6.91 | Cyclononane                              | 140.12 | 003350-30-9 | 0.82 |
| 30 | 7.09 | Cyclooctane, 1-methyl-3-propyl-          | 168.19 | 255885-37-1 | 9.04 |
| 31 | 7.16 | Unk                                      | Unk    | Unk         | 2.33 |
| 32 | 7.23 | Unk                                      | Unk    | Unk         | 7.45 |
| 33 | 7.46 | 3-Decene, 2,2-dimethyl-                  | 168.19 | 055499-02-0 | 0.59 |
| 34 | 8.62 | Hexadecane                               | 226.27 | 000544-76-3 | 0.36 |
| 35 | 8.84 | Cyclohexane, 1-ethyl-2,3-dimethyl-       | 140.16 | 007058-05-1 | 0.83 |
| 36 | 8.91 | Cyclooctane, butyl-                      | 168.19 | 016538-93-5 | 0.30 |

Table 3. GC/MS analysis of PP pyrolysis products

36 analysed compounds in pyrolysis products were dominated by 1-heptene (propylene trimer), with the content of 38.35%. It was followed by propylene dimer 2-methyl-1-pentene with the content of 9.19%. In contrast to Tsuge [2011] and Kusch [2016], besides alkanes, alkyl alkanes, there was a relatively great amount of alkyl cycloalkanes, even aromatic hydrocarbon styrene present in our pyrolysis products. There were no monomers discovered in PE or in PP degradation products.

#### Polystyrene (PS)

Expanded polystyrene (EPS) is produced by polymerizing styrene monomer and adding iso-pentane as a blowing agent and is used for food packaging, protecting the products or in the structural industry for insulation of exterior walls [Kusch 2005].

The PS sample with a weight of 3.30 mg was analysed. The temperature of the pyrolysis of the given sample was determined following the material degradation in the thermogravimetric analysis. Degradation products of the PS pyrolysis are summarised in Table 4. In total, 20 compounds were determined in the pyrolysis products. Following Table 4,

styrene is the main PS pyrolysis product under given conditions (80.25%).

| No. | T (min) | Compound name                                    | Mol Weight (amu) | CAS          | Quantity (%) |
|-----|---------|--|------------------|--------------|--------------|
| 1   | 1.83    | Methylenecyclopropane                            | 54.05            | 006142-73-0  | 2.75         |
| 2   | 2.23    | 3-Vinyl-1-cyclobutene                            | 80.06            | 006555-52-8  | 0.60         |
| 3   | 2.64    | Toluene  | 92.06            | 000108-88-3  | 6.33         |
| 4   | 3.05    | Cyclohexene-ethenyl-                             | 108.09           | 000100-40-3  | 4.60         |
| 5   | 3.25    | Ethylbenzene                                     | 106.08           | 000100-41-4  | 1.48         |
| 6   | 3.49    | Styrene  | 104.06           | 000100-42-5  | 80.25        |
| 7   | 3.92    | Benzene, 2-propenyl-                             | 118.08           | 000300-57-2  | 0.29         |
| 8   | 4.23    | .alpha.-Methylstyrene                            | 118.08           | 000098-83-9  | 0.85         |
| 9   | 4.64    | Benzene, cyclopropyl-                            | 118.08           | 000873-49-4  | 0.27         |
| 10  | 5.03    | Pyrazine, ethyl-                                 | 108.07           | 013925-00-3  | 0.31         |
| 11  | 5.41    | Tricyclo[4.3.0.0(3,7)]non-8-en-4-ol              | 136.09           | 1000190-47-8 | 0.14         |
| 12  | 5.83    | Cyclohexane, 1,5-diethenyl-3-methyl-2-methylene- | 162.14           | 074742-35-1  | 0.53         |
| 13  | 5.88    | Cyclooctene, 5,6-diethenyl-, cis-                | 162.14           | 053264-72-5  | 0.13         |
| 14  | 6.05    | Cyclohexane, 1,5-diethenyl-3-methyl-2-methylene- | 162.14           | 074742-35-1  | 0.35         |
| 15  | 6.36    | Cyclooctene, 5,6-diethenyl-, cis-                | 162.14           | 053264-72-5  | 0.15         |
| 16  | 6.47    | 1,4,8-Dodecatriene                               | 162.14           | 024252-85-5  | 0.27         |
| 17  | 6.69    | Cyclooctene, 5,6-diethenyl-, cis-                | 162.14           | 053264-72-5  | 0.23         |
| 18  | 6.73    | cis-anti-cis-Tricyclo                            | 162.14           | 070702-18-0  | 0.17         |
| 19  | 7.4     | Benzene, 3-cyclohexen-1-yl-                      | 158.11           | 004994-16-5  | 0.08         |
| 20  | 10.3    | Unk  | Unk              | Unk          | 0.23         |

Table 4. GC/MS analysis of PS pyrolysis products

Kusch [2016] mentions that the number of styrene increases when the temperature of pyrolysis rises. At the same time, the amount of styrene dimers and trimers decreased. Toluene, ethylbenzene and alpha-methylstyrene are other typical products of the PS thermal degradation identified in the pyrolysis products. Apart from them, other alkyl benzene, cycloalkanes, and cycloalkenes were identified in the degradation products.

## 4 CONCLUSIONS

The paper deals with tertiary material recovery in the form of pyrolytic decomposition of plastic materials. Its efficiency depends on the quality of final sorting of materials. Material recovery remains the best option to solve the problem with plastic waste.

The pyrolysis of plastic materials results in chemicals, fuel or monomers used in further polymerisation. Therefore, this way of material recovery is considered beneficial. This waste recovery and the development of such an industry is an important step in terms of protecting the environment, developing the society as well as sustainable development.

The experiment was focused on the pyrolysis and the analysis of pyrolysis products of three types of synthetic polymers which can be found in products, it means in waste as well. It was polyethylene, polypropylene and polystyrene.

Following the results of the individual experiments, it can be stated that:

- When evaluating these types of plastics using the low-temperature pyrolysis, the most effective sample was the PS sample due to the largest amount of pyrolysis oil and pyrolysis gases, i.e. products which can be evaluated.

- The PP sample seems to be the most stable in the thermogravimetric analysis with the area of thermal stability up to 320 °C. On the contrary, the PE sample was the most unstable with the area of thermal stability below 278 °C.

- Using the Py-GC-MS analysis, it was found out that the highest number of chemical compounds (36) was identified in the PP sample (food container). The content of propylene trimer and dimer was the highest one. This fact can be used for PP recovery, other products can be used as a source of fuels and for energetic purposes.

- The highest content of the monomer resulted from the PS pyrolysis (80.25% styrene). The fact that the pyrolysis is a suitable method to obtain a monomer and subsequent PS recovery was confirmed.

- The PE pyrolysis resulted especially in 1-alkenes (most 1-hexene), 2-alkenes, alkanes and various alkyl alkenes and alkanes. The monomer did not occur in the PE pyrolysis. Pyrolysis products could be used as a source of chemicals or in the process of preparing fuels.

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