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Study of Polyolefines Waste Thermo-Destruction in Large Laboratory and in Industrial Installations

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Polymer materials packagings are quickly deposited in dumps due to the short life time as a useable product. Recycling of polymer waste, mainly polyolefines, which constitute 60% of them, on the technological lines operating according to the Polish technology seems to be a long-term solution. According to this technology, the used polymers after melting flow down to the reactor, where they undergo thermal degradation in the presence of catalyst. A product which can be processed in refineries for fuel is obtained. The studies leading to the improvement of the properties of the obtained product are still conducted.

Keywords Polymer waste; polyolefines; thermo-destruction

Introduction

Polymer production has been a dynamically developing industry for years. Paradoxically, the permanence of polymer plastics, initially considered to be one of their basic advantages, is currently perceived as a disadvantage. Disposable packagings (i.e. bottles, lunch bags, product packaging and shopping bags) presents the largest problem. Due to short life time of these products, they are quickly disposed at landfills where they constitute an easily noticeable, colourful mass. Recycling processes implemented for materials of this kind should limit their impact onto the environment. However, the management of the pile of used polymer plastics is still a serious problem. Each year, over 100 million Mg of used polymer materials is landfilled or recycled in one of the available forms all over the world. Products made of polyolefines comprise up to 60% of recycled, used polymer materials [1]. Attention is drawn to the energetic potential of used polymer materials. The calorific value for polyolefines and polystyrene is \( \sim 46 \text{ MJ/kg} \), and for polyvinyl chloride and polyethylene terephthalate it is \( \sim 22 \text{ MJ/kg} \) [2]. Thus used polymer materials can be considered an excellent source of energy.

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Therefore the thermal catalytic degradation of used polymer materials in specialised installations seems to be a long-run method for its management under chemical recycling, where the products received are used for the production of fuels.

Large scale laboratory research, followed by research in industrial installations, was carried out in order to upgrade these plants in a way to receive a product that features the expected properties, simultaneously reducing plant operation related downtimes.

Research on thermal destruction of polyolefines is carried out in reactors of various types, with or without the catalysts, obtaining various products from segregated or non-segregated used polymer materials [3–8]. Intensive research on the development of technologies for processing used polymer materials into fuel components, or directly into fuels, has been carried out also in Poland for the last 15 years [9–12].

An innovative technology of thermal catalytic degradation of used polymer plastics has been developed, allowing for obtaining a product of performance characteristics close to those of commercially available diesel oil.

**Experimental**

Research of catalytic thermo-destruction of used unpurified polyolefines was conducted on the industrial vertical modular installation for thermo-destruction of polyolefines installed in the enterprise using it according to patented technology [13–15].

Research of processes of thermo-destruction in the large laboratory installation built for testing processes of uncatalytic thermo-destruction of polyolefines, industrial installation with a reactor with lead deposit [16] and installation with the integrated system of the fraction separation [17] was carried out without using a catalyst.

As a raw material for the large laboratory installation it was used wet (15% moisture) and dry polyethylene (PE) waste foil.

In the case of industrial installation located in the south-eastern part of Poland (vertical modular installation) the process of thermo-destruction of used polyolefines containing different amounts of dirty and heavily damp (containing about 30% water) and clean foil was studied. The share of PE milling in the plastic input was always comparable (mainly 6.3–6.4%).

In the case of thermo-destruction studied on installation located in the central part of Poland (installation with a reactor with lead deposit) materials was used from the same source–dirty and moist (20% moisture):

– without preliminary preparation (the first month of research),
– after preliminary preparation (the second month of research),
– after preliminary preparation (the third month of research).

In the case of research of thermo-destruction processes on installation located in the west part of Poland (installation with the integrated system of the fraction separation) communal-type foil with an average purity was processed.

On the large laboratory scale thermo-destruction process of used polyolefines materials was carried out on the installation of his own construction. To a steel cylinder with a diameter of 600 mm, laid horizontally, tin was inserted into 1/3 height. Tube with a diameter of 200 mm, which allows cleaning of the device and loading used polyolefines “cold”, was installed on the side wall. A siphon capable of delivering material during the process below the level of liquid tin and a collector receiving the gaseous products to the cooler line were made in a straight upper cylindrical wall. The device was heated by gas burners.
continuously until fully liquefied product. Each time the primary charge was the invisible dirty, dry or damp packaging polyolefines foil, cold loaded in the amount of about 1 kg and refilled three times with foil in an amount of about 0.5 kg.

Thermo-destruction of used polymer materials in industrial vertical modular installation was conducted with the use of a patented catalytic agent produced by the installation’s supplier and added to the installation together with plastic input [15].

Thermo-destruction of used polymer materials in industrial installation with a reactor with lead deposit and installation with the integrated system of the fraction separation was conducted without addition of a catalyst.

The installation’s functioning on the basis of daily recording of technological parameters was monitored and the products parameters in the final container was measured. The following data were recorded:

- average daily temperature of the reactor’s bottom (divided into three shifts of work of installation crew),
- average daily temperature on the steam collector (divided into three shifts of work of installation crew),
- monthly consumption of waste plastic input
- quantity of obtained liquid and gaseous product per a month
- quantity of industrial waste received per a month.

In accordance with the technology recommended by the manufacturer, the mean monthly operation time of a reactor in a vertical modular installation is 25 days [13, 14]. The remaining days are intended for cleaning the plant components. That time is needed for removing batch impurities, unprocessed polymer materials, carbonisation, and the catalyst from the reactor. During operation, the reactor was cleaned in accordance with the manufacturer’s recommendations every 4–6 days. The duration and the frequency of reactor cleaning depend mainly on the purity of the raw material used. Such cleaning is performed after the temperature of the bottom of the reactor has decreased by 100°C. The procedure for preparation for cleaning, the cleaning itself, and reaching the operational temperature again require approximately 8 hours. Once every 2 months, the reactor is shut down completely, and the melting crucible, the bottom of the reactor, the receiver, and the cooling system are thoroughly cleaned. The procedure of comprehensive cleaning usually takes 6 days (counting from shutting the plant down, to restarting it).

According to technology the installation with a reactor with lead deposit works in the system continuously [16]. The reactor’s running cleaning takes place every 4–8 days (depending on the purity of input). The input’s impurities, unreacted plastics, char yield and possibly the catalytic agent (if used in the process) are removed from the reactor. Such cleaning takes about eight hours.

The so-called “reactor drying” is carried out as well, i.e. maintaining constant temperature at approximately 520°C without supplying any raw material. Then the whole plant is degassed, and the impurities are removed. Once every 2–3 months, thorough cleaning of the bottom and the cooling system of the reactor takes place after the plant has shut down and cooled down to ambient temperature. A installation with the integrated system of the fraction separation according to the technology operates continuously [17], whereas every 3–4 weeks the plant undergoes periodical cleaning. At that time, the supply of raw material and energy is shut off, and the plant is cleaned after it has cooled down to ambient temperature. In normal conditions, the entire process of cleaning, from shutting the plant down to restarting it, takes 3–4 days. It is technologically impossible to clean the plant while it is in operation.
The examinations of physical and chemical properties of the products of thermo-destruction of used polymer plastics were carried out at the Department of Environment Chemistry and Technology at the University of Silesia on the basis of a long-term cooperation contract and at external laboratories on the basis of orders. At the Department of Environment Chemistry and Technology, density of liquid products were marked according to PN 90/C-04004 and the coagulation temperature according to PN-83/G 04117 and the content of olefin, aromatic and paraffin compounds in liquid products using the Reisenfeld-Bandt method.

Sulphur in the products was determined by accredited laboratory outside (ORLEN Laboratory Sp. z o.o.) in accordance with PN-EN ISO 8754:2007. Temperature of ignition for product from vertical modular installation and from installation with a reactor with lead deposit was determined by specialized laboratory for fire (Main School of Fire-Fighting in Warsaw) in accordance with PN-64/C-04006 and for product from installation with the integrated system of the fraction separation by accredited laboratory outside (Institute of Petroleum in Cracow) in accordance with PN-EN ISO 2719:07.

Research results were compared with parameters of diesel oil which properties were specified by specialized laboratory outside (Quality Control Laboratory Fuel Base N 5 in Emilianow) in accordance with norms: PN-EN ISO 12185:2002/A for density; PN-55/C-04016 for temperature of solidification; PN-86/C 04062 for fuel value; PN-EN ISO 2719:2007/A for temperature of ignition; PN-EN 12916:2006 (U) for content of aromatic substances; PN-EN ISO 20884:2006/A for content of sulphur.

The chromatographic analysis of gaseous and liquid products was conducted using Autosystem XL GC–Turbo Mass chromatograph manufactured by Perkin Elmer using PE 5MS 30 × 0,25 mm × 0,5 μm column.

Results and Discussion

At the turn of the century and in the beginning of the 21st century in Poland, processes of thermal destruction of used polyolefines were carried out in vertical modular installations, using bauxite as the catalyst. Running processes in those plants posed many difficulties resulting from using such a catalyst.

When heavily contaminated and moisture-rich used polyolefin was subjected to the process of thermal destruction, the catalyst was consumed quickly. Used-up catalyst, removed from the plant with impurities during cleaning, was a solid waste that was expensive to dispose. Moreover, this catalyst has poor thermal conductivity which hinders the initial stage of degradation of plasticised used polymer materials, causing the consumption of gas used for plant heating to rise, and increasing the operating costs.

Therefore the research on the processes of thermal destruction of used polymer materials was commenced at a laboratory and large laboratory scale, without the use of any catalyst. The research was carried out in order to provide plants with upgrades allowing, in the conditions of a non-catalytic process, for the elimination of the majority of deficiencies observed in plants utilizing bauxite as the catalyst, as well as the solidification of the product in temperatures of approximately 30°C, being the main observed disadvantage of the product obtained from non-catalytic plants. For that purpose laboratory and large-laboratory installations with an integrated fraction division system were built, which allowed examining the influence of returning of high-boiling hydrocarbon fractions to the degradation process. An additional device was installed—a separator in which hydrocarbons are divided into high-boiling and low-boiling hydrocarbons. Hydrocarbons condensed in the separator
Table 1. The yield and time of thermo-destruction process of damp and dry used polymer materials (foil) in the large laboratory installation

<table>
<thead>
<tr>
<th>No cycle</th>
<th>Type of material</th>
<th>Yield of installation* [%]</th>
<th>Time of thermo-destruction [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Damp foil</td>
<td>78.9</td>
<td>260</td>
</tr>
<tr>
<td>2</td>
<td>Damp foil</td>
<td>80.5</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>Dry foil</td>
<td>82.1</td>
<td>235</td>
</tr>
<tr>
<td>4</td>
<td>Dry foil</td>
<td>81.7</td>
<td>230</td>
</tr>
</tbody>
</table>

*Yield of installation: the quotient of quantity of received desirable liquid product to quantity of used plastic input.

were returned to the reactor. At the same time, gaseous hydrocarbons collected in the upper part of the separator were channelled through a system of coolers to the receptacle.

The previous results of examinations of boiling temperature range of thermal destruction products obtained in the laboratory and large-laboratory installation enabled to determine the critical temperature of division distilling products into low- and high-boiling fractions at 250°C. The temperature of fraction separation was used in separators in the laboratory and large-laboratory installation.

Carrying out the thermo-destruction process in large laboratory installation a slight influence of the presence of water on the thermo-destruction process has been observed. The yield of the thermo-destruction process was from 78.9% for the wet foil to 82.1% for the dry foil. A shorter time of the process by about 0.5 h was observed when the dry film was used in comparison with the damp foil. During of the thermo-destruction of damp foil the temperature dropped. It probably extended this process (Table 1).

Table 2. The type of material (used polymer materials) using during the tests for individual modules of vertical modular installation

<table>
<thead>
<tr>
<th>Module of installation</th>
<th>Dirty and moist foil [kg]</th>
<th>Dirty and moist foil [%]</th>
<th>Dry foil [kg]</th>
<th>Dry foil [%]</th>
<th>Milling [kg]</th>
<th>Milling [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5580</td>
<td>62.0</td>
<td>2845</td>
<td>31.7</td>
<td>570</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>7050</td>
<td>79.8</td>
<td>1220</td>
<td>13.8</td>
<td>570</td>
<td>6.4</td>
</tr>
<tr>
<td>3</td>
<td>6440</td>
<td>72.5</td>
<td>1870</td>
<td>21.1</td>
<td>570</td>
<td>6.4</td>
</tr>
<tr>
<td>4</td>
<td>3960</td>
<td>52.0</td>
<td>3080</td>
<td>40.5</td>
<td>570</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Studying the thermo-destruction process on 4 modules of vertical modular installation it was achieved the highest yield on the module No. 4 (73.6%), while the lowest (52.8%) on module No. 2 (Tables 2, 3). The highest yield was achieved by subjecting the thermo-destruction input of used polyolefines containing the highest amount of pure used polymer materials (over 40%), and lowest for the content of almost 80% of the dirty, damp used polymer materials (Tables 2, 3).

It was a clear dependence of the efficiency process on the purity and moisture of used polymer materials. Based on the results on large laboratory and industrial installations,
Table 3. The quantity of used polymer materials (foil) input, received product and weekly yield of thermo-destruction process on vertical modular installation

<table>
<thead>
<tr>
<th>Module of installation</th>
<th>Used plastic input [kg]</th>
<th>Intensity of power module [kg/h]</th>
<th>Quantity of received liquids [dm³]</th>
<th>Quantity of received liquids [kg]</th>
<th>Weekly yield of installation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8995</td>
<td>53.5</td>
<td>7700</td>
<td>6160</td>
<td>68.5</td>
</tr>
<tr>
<td>2</td>
<td>8840</td>
<td>52.6</td>
<td>5830</td>
<td>4664</td>
<td>52.8</td>
</tr>
<tr>
<td>3</td>
<td>8880</td>
<td>52.9</td>
<td>6810</td>
<td>5448</td>
<td>61.4</td>
</tr>
<tr>
<td>4</td>
<td>7610</td>
<td>45.3</td>
<td>7000</td>
<td>5600</td>
<td>73.6</td>
</tr>
</tbody>
</table>

*It was assumed average density of the product δ = 0.8 kg/dm³.
**Weekly yield of installation: the quotient of weekly quantity of received desirable liquid product to weekly quantity of used plastic input.

it was proposed that the contaminated used polyethylene foil was feed into the reactor alternately with foil much less contaminated in the ratio of at most 1:1 (preferable is dominance of foil less contaminated).

In industrial installation conditions, just like in laboratory conditions, water from used polyolefines was removed with the use of presses. Several hundred litres of water were discharged after pressing it out from approximately 35 Mg of polymeric materials batch on loading presses during tests that had been performed for seven days, which significantly reduced the quantity of water in the process of thermo-destruction of post-consumer polyolefin materials waste. The quantity of mineral impurities introduced to the plant and the process can be determined from the quantity of ashes obtained from burning the impurities removed during module cleaning.

From clean used polyethylene foil receives mainly clean coal in post-production wastes. The coal when burned gives about 1% ash. It was confirmed by several independent research units (Warsaw University of Technology [18], Institute of Oil and Gas in Krakow [19]). Each ash content of greater than 1% should be treated as mineral impurities introduced into the process with waste polymer materials. Research “petroleum coke”–waste after thermo-destruction carried out on the module No 2 showed an content to 46.1% of ash [20]. This ash content indicates a very large pollution plastics with mineral substances.

Numerous disturbances of process parameters were observed in an industrial plant for thermal destruction of moisture-rich post-consumer polymer materials waste (a plant with a lead bed reactor) in the course of the production process. Common fluctuations in temperature of the reactor bottom (the bottom temperature drops below of 480°C) were observed which translated into the steam temperature in the collector (Figs. 1, 2; the second day of research, III shift; the seventh day of research, II shift; the nineteenth day of research, II shift; the twentieth day of research, I shift; the twenty-third day of research, II shift; the twenty-fifth day of research, I shift). A possible cause of problems with maintaining temperatures at an appropriate level was the presence of large amounts of water in a very moist plastic material.

Moreover, it was observed that the unstable course of the thermal destruction process caused the consumption of gas used for plant heating to rise by approximately 20%. Water was condensing together with liquid hydrocarbons and accumulated in large quantities on the bottom of the storage tank (up to 10% of used polymer materials batch). Before sending the product to the consumer, this water was removed from the tanks and subjected
to expensive disposal. It was also found that if large quantities of mineral impurities such as sand, dust, small pieces of glass, etc. there are in used polymer materials input need for more frequent (every 4–5 days) and longer cleaning of reactor.

This was the reason for starting the cooperation with research departments at Silesian universities as well as construction of laboratory installations and large scale laboratory installations in order to carry out the appropriate tests and introduce changes to industrial installations. Based on the results of research works carried out in laboratory installations, it was found that it would be beneficial to remove impurities and water from used polymer materials before introducing raw material to the plant, so the assumed objective could be reached at low investments.

Figure 1. The average temperature on the bottom of the reactor of installation with a reactor with lead deposit for thermo-destruction of used polymer materials in the first month of research.

Figure 2. The average temperature on the steam collector of installation with a reactor with lead deposit for thermo-destruction of used polymer materials in the first month of research.
So the raw material were subjected to a preliminary preparation. The installed line preparing raw material consists of a shredder for used polymer materials, which mechanically shakes mineral impurities, crushes material, which facilitates their the drying in mesh/net drums by air heated exhaust gases from the furnace reactor. Thus prepared, the raw material goes through the augers to the loading press of installation for used polymer materials thermo-destruction. It was found that during the process of preparing the material removed for an average of 20% to 30% of the mineral impurities, and above 80% moisture.

The process of thermo-destruction of pre-prepared material (shredded and dried), conducted in the second month of research proceeded with a higher temperature stability of the bottom of the reactor and in steam collector (Figs. 3, 4 and Table 4).
Table 4. The results of the analysis of the composition of petroleum coke (post-production waste) from the wastes thermo-destruction on 2 modules of vertical modular installation for thermo-destruction of used polymer materials

<table>
<thead>
<tr>
<th>Moisture [%]</th>
<th>Volatiles [%]</th>
<th>Ash [%]</th>
<th>Sulphur [%]</th>
<th>Carbon [%]</th>
<th>Hydrogen [%]</th>
<th>Calorific value [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>55.6</td>
<td>27.1</td>
<td>0.24</td>
<td>63.8</td>
<td>8.16</td>
<td>15300</td>
</tr>
<tr>
<td>0.5</td>
<td>37.9</td>
<td>46.1</td>
<td>0.36</td>
<td>45.7</td>
<td>6.78</td>
<td>20671</td>
</tr>
<tr>
<td>0.2</td>
<td>46.7</td>
<td>40.6</td>
<td>0.22</td>
<td>61.2</td>
<td>7.12</td>
<td>20780</td>
</tr>
</tbody>
</table>

The temperature of the bottom of the reactor, which was about 500–510°C, gives mainly the product with the expected properties (boiling range), and increases process efficiency.

Cleaning the system during the installation work was done every 6–8 days. Simultaneously the time of this cleaning (which goes without having to clean the coolers every time) was shorted about 1/3 compared to time needed for cleaning of installation working with material without preliminary preparation (taking place every 4–6 days). The proposed preliminary preparation of material for thermo-destruction process (cleaning and drying) allowed reduce the amount of water for recycling (waste) collected at the bottom of the product storage tank by 80%, thereby reducing the costs of its utilization. It was stated that the introduction of preliminary preparation of used polymer materials for thermo-destruction process allowed to improve the efficiency from 60% in the first month of research to about 85% in the second and third month of research (Table 5).

Installation work in future months of operation shows for maintenance of the resulting effect, ie. stabilization of the temperature of the reactor bottom and in steam collector.

Table 5. The quantity of raw used polymer materials (foil), the quantity of received liquid product, monthly yield of thermo-destruction process conducted on the installation with a reactor with lead deposit, the quantity of received waste water, the quantity of received coke, the quantity of gaseous product in periods of carrying out installation work before (first month) and after introduction of preliminary preparation of material for thermo-destruction process (second and third month)

<table>
<thead>
<tr>
<th>The period of installation work [months]</th>
<th>Used plastic input [kg]</th>
<th>Quantity of received liquid product [kg]</th>
<th>The monthly installation yield [%]</th>
<th>Quantity of accompanying water (waste) [kg]</th>
<th>Quantity of coke (waste) [kg]</th>
<th>Quantity of gaseous product** [kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>88500</td>
<td>53100</td>
<td>60.00</td>
<td>24000</td>
<td>7000</td>
<td>4400</td>
</tr>
<tr>
<td>Second</td>
<td>90000</td>
<td>76450</td>
<td>84.94</td>
<td>4000</td>
<td>5000</td>
<td>4550</td>
</tr>
<tr>
<td>Third</td>
<td>89400</td>
<td>75600</td>
<td>84.56</td>
<td>4100</td>
<td>5300</td>
<td>4400</td>
</tr>
</tbody>
</table>

*The monthly installation yield: the quotient of monthly quantity of received useable liquid product to monthly quantity of used polymer materials input.
**The gaseous product is subsequently combusted in the furnace during the production process, which reduces gas consumption of external power installation.
It was also found that during operation, the plant does not need cleaning more frequently than every 6-8 days. The monthly yield of the plant was at the level of 85% (Figs. 5, 6, Table 5).

Performed analyses of hydrocarbon products obtained from the industrial vertical modular installation, installation with a reactor with lead deposit, installation with the integrated system of the fraction separation and a commercially available diesel oil allowed for comparing their physical and chemical properties, as well as the quantity of distillate obtained within the appropriate ranges of boiling temperatures (Table 6). It was found that the heating values of liquid products obtained are high and comparable with the heating values of commercial products (approximately 43 MJ/kg).
Table 6. The physical and chemical properties and the range of boiling temperature and quantity of obtained distillate for product from the large laboratory installation with a reactor with lead deposit, the large laboratory installation with the integrated system of the fraction separation and commercial diesel oil

<table>
<thead>
<tr>
<th>Properties</th>
<th>Product from vertical modular installation</th>
<th>Product from reactor with lead deposit</th>
<th>Product from installation with the integrated system of the fraction separation</th>
<th>Diesel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance (form and colour)</td>
<td>Brown gunk</td>
<td>Brown gunk</td>
<td>Light yellow liquid</td>
<td>Light yellow liquid</td>
</tr>
<tr>
<td>Density in 15°C [g/cm³]</td>
<td>0.825</td>
<td>0.805</td>
<td>0.788</td>
<td>0.824</td>
</tr>
<tr>
<td>Temperature of solidification [°C]</td>
<td>+32</td>
<td>+25</td>
<td>-12</td>
<td>-20</td>
</tr>
<tr>
<td>Fuel value [MJ/kg]</td>
<td>45.3</td>
<td>43.1</td>
<td>42.7</td>
<td>42.7</td>
</tr>
<tr>
<td>Temperature of ignition [°C]</td>
<td>13.1</td>
<td>25</td>
<td>12</td>
<td>65.5</td>
</tr>
<tr>
<td>Content of olephines [%]</td>
<td>45</td>
<td>35</td>
<td>10</td>
<td>6.2</td>
</tr>
<tr>
<td>Content of aromatic compounds [%]</td>
<td>30</td>
<td>25</td>
<td>10</td>
<td>2.8</td>
</tr>
<tr>
<td>Content of paraffines [%]</td>
<td>60</td>
<td>40</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Content of sulphur [%]</td>
<td>0.32</td>
<td>0.12</td>
<td>0.08</td>
<td>0.0007</td>
</tr>
<tr>
<td>Quantity of distillate [%] for hydrocarbon product</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiling temperature up to 100°C</td>
<td>—</td>
<td>10</td>
<td>11</td>
<td>—</td>
</tr>
<tr>
<td>Boiling temperature up to 150°C</td>
<td>3</td>
<td>23</td>
<td>24</td>
<td>—</td>
</tr>
<tr>
<td>Boiling temperature up to 200°C</td>
<td>11</td>
<td>34</td>
<td>35</td>
<td>7</td>
</tr>
<tr>
<td>Boiling temperature up to 250°C</td>
<td>25</td>
<td>45</td>
<td>56</td>
<td>41</td>
</tr>
<tr>
<td>Boiling temperature up to 300°C</td>
<td>37</td>
<td>65</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Boiling temperature up to 350°C</td>
<td>48</td>
<td>78</td>
<td>95</td>
<td>97</td>
</tr>
</tbody>
</table>
These products can be used in applications similar to those of commercially available products of such calorific values. It was observed that calorific values of products obtained from the process of thermal destruction of polyolefines were often higher and amounted to 45–46 MJ/kg. Most probably, this phenomenon was related to the chemical composition of post-consumer polymer materials and the conditions in the course of the process, with maintained reactor heating conditions. However, the cause of the increase of calorific value has been not explicitly determined to date, because such increase was observed for the thermo-destruction processes of not treated used polyolefines.

It was found that the product originating from the installation with the integrated system of the fraction separation and diesel oil have freezing point significantly below 0°C (−12°C for the product obtained from a installation with the integrated system of the fraction separation and −20°C for diesel oil). This makes the costs of storage and transport significantly lower, as compared to the costs of storage and transport of the product obtained from a lead bed plant, that solidifies in temperatures as high as 25°C, as well as the product from a vertical modular installation featuring freezing point of 32°C stored in heated storage tanks.

It was stated the density of products obtained from thermal destruction of polyolefines is lower than that of the diesel oil. The ignition temperature of products of thermo-destruction of polyolefines is so low (less than 25°C) that vapour of the substances, similarly as vapour of petrol, has explosive properties (Table 6). It was found that the product originating from a vertical modular installation contains 3–6 times more olefins, aromatic hydrocarbons and paraffins than product from installation with the integrated system of the fraction. A small amount of paraffins in a product from installation with the integrated system of the fraction separation results, probably, from the fact that heavy paraffin fractions are returned to the degradation process again. Long-chain paraffin hydrocarbon particles may undergo the cycle several times until they obtain the desired size of particles directed to the receptacle. The product from the installation with the integrated system of the fraction separation complies with the requirements imposed by applicable standards for diesel oils in respect of content of olefins, aromatic compounds and paraffins.

The highest level of sulphur content was found in the products originating from thermal destruction of used polyolefines (Table 6), which most probably is related to the fact that this result is for the process of thermal destruction of used polyolefines that was not subjected to initial cleaning, and the sulphur found in the products came from impurities.

There is no sulphur in polyolefines and therefore, it should not be found in products contained from their thermo-destruction. Thus, the level of preparation (purification) of the raw material, input to the installation, has a direct influence on the content of sulphur in those products. If used polymer materials is subjected to careful segregation, and then initial cleaning and drying, there should be no sulphur in the products of thermal destruction of such waste. Sulphur may occur only as a result of polluted input and additives of e.g. rubber.

The ranges of boiling temperatures of the hydrocarbon products analyzed correspond to fraction contents. Amount of distillate with a boiling point up to 350°C for the product from the installation with the integrated system of the fraction separation and for diesel oil is comparable.

In the case of the product obtained from a lead bed plant, the quantity of distillate is lower by approximately 20%, whereas for the product obtained from a vertical modular installation, the quantity of distillate with boiling point up to 350°C is lower by approximately 50% (Table 6).
Table 7. The quantity of raw used polymer materials (foil), the quantity of received liquid product and monthly yield of thermo-destruction process on installation with the integrated system of the fraction separation (two months)

<table>
<thead>
<tr>
<th>The period of installation work [months]</th>
<th>Used plastic input [kg]</th>
<th>Quantity of received liquid product [dm$^3$]</th>
<th>Quantity of received liquid product* [kg]</th>
<th>The monthly installation yield** [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>110500</td>
<td>92970</td>
<td>73450</td>
<td>66.47</td>
</tr>
<tr>
<td>Second</td>
<td>119200</td>
<td>100530</td>
<td>79420</td>
<td>66.63</td>
</tr>
</tbody>
</table>

*It was assumed average density of the product $\delta = 0.79$ kg/dm$^3$.

**The monthly installation yield: the quotient of monthly quantity of received useable liquid product to monthly quantity of used polymer materials input.

In addition, it was noticed that the returning of hydrocarbons with a higher boiling point to the reactor and repeated degradation has no visible influence on the efficiency of the process (Table 7).

Any significant extension of the duration of the thermal destruction process was not ascertained in this case. Further degradation of already degraded used polymer products is, probably, simpler and quicker. However, the way of conducting the thermal destruction process of used polymer materials in the reactor influences the duration of the thermo-destruction process.

Figure 7. Chromatograms: a) “oil fraction” from the vertical modular installation, b) “oil fraction” from the installation with a reactor with lead deposit, c) product from the installation with the integrated system of the fraction separation, d) diesel oil.
A comparison of chromatograms of products obtained from a vertical modular installation, the installation with the integrated system of the fraction separation and a commercially available diesel oil shows a similarity of chromatograms of the product obtained from the installation with the integrated system of the fraction separation and a commercially available diesel oil. Similar intensity and retention times of peaks can be found (Fig. 7, chromatograms a–d).

On the basis of the results obtained new solutions in the industrial installation of a new generation were proposed.

Conclusions

Based on the results of the research carried out, it can be ascertained that initial drying of used polyolefines does not have any significant influence onto the yield of the thermo-destruction process on a large laboratory scale. However, it was found that the process of thermo-destruction of dried raw material went faster by 0.5 h (11.5%), as compared to thermal destruction of moisture-rich raw material.

Based on the results of research on the processes of thermo-destruction of used polyolefines waste carried out in industrial installations, it can be ascertained that there is a stronger relation between the quantity of water in raw material and the yield of the thermo-destruction process.

In the case of used polyolefines thermo-destruction in vertical modular installation, the increase of process efficiency by over 20% by reacting the raw material at a higher (i.e. 40.5%) content of dry used polymer materials (foil) it was obtained.

Based on test results of selected parameters of industrial installations for thermo-destruction of used polymer plastics (polyolefin) after the introduction of their preliminary preparation pre-process it was found that the process efficiency increases of about 25%.

During the process of pre-prepared used polymer materials thermo-destruction it was observed greater stability of the reactor’s bottom and the steam’s collector temperature. The stability caused a reduction in gas consumption in burners supplying the installation by 15–20%.

Carrying out the thermo-destruction process of pre-prepared used polymer materials significantly reduced the need for cleaning installation during its work, also reduced the formation necessary to treat the waste, resulting in additional savings.

The products of the process of thermo-destruction of used unpurified polymer materials from the installation with the integrated system of the fraction have properties similar to the properties of liquid fuels produced from petroleum. The obtained mixture of hydrocarbons is a liquid not solidifying at temperature above $-10^\circ$C, therefore it does not need be stored in heated tanks.

Based on the results of research carried out, it can be ascertained that the properties of products obtained from the installation with the integrated system of the fraction separation (low freezing point, high calorific value, low olefin and sulphur content) are appropriate and sufficient for using these products as fuel directly.

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References