Migration of Sulfur and Nitrogen in the Pyrolysis Products of Waste and Contaminated Plastics

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Abstract: The most advantageous way of managing plastics, according to circular economy assumptions, is recycling, i.e., reusing them. There are three types of plastics recycling: mechanical, chemical and energy recycling. The products of the pyrolysis process can be used for both chemical and energy recycling. Possibilities of further use of pyrolysis products depend on their physicochemical parameters. Getting to know these parameters was the aim of the research, some of which are presented in this article. The paper presents the research position for conducting the pyrolysis process and discusses the results of research on pyrolysis products of waste plastics. The process was conducted to obtain the temperature of 425 °C in the pyrolytic chamber. Such a value was chosen on the basis of my own previous research and literature analysis. The focus was on the migration of sulfur and nitrogen, as in some processes these substances may pose a certain problem. Studies have shown high possibilities of migration of these elements in products of pyrolysis process. It has been shown that the migration of sulfur is similar in the case of homogeneous and mixed waste plastics—it immobilizes mainly in pyrolytic oil. Different results were obtained for nitrogen. For homogeneous plastics, nitrogen immobilizes mainly in char and oil, whereas for mixed plastics, nitrogen immobilizes in pyrolytic gas.

Keywords: pyrolysis; contaminated plastic; migration of sulfur and nitrogen; recycling

1. Introduction

Despite the growing awareness in society about the threats posed by all kinds of waste, a continuous increase in the amount of waste can be observed. This is related to the development of the economy, increasing prosperity and growing consumption [1,2]. Waste that is not subjected to recovery, reuse or safe disposal processes adversely affects the environment. It leads to pollution of air, soil, surface water and groundwater. A particularly troublesome group of waste to be managed is waste plastics [3]. This is related to the large number of types of plastics and the requirements they have to meet before recycling. The most important methods of processing waste plastics are chemical recycling and mechanical recycling. Chemical recycling is the conversion of individual plastics into different chemical compounds that can be used in various technological processes. Mechanical recycling consists of appropriate mechanical and possibly thermal treatment of the selected plastic to obtain a regranulate [4–6]. Both of the presented recycling methods are used on a large scale, but have certain limitations. Recycling requires the waste to be homogeneous (prior to the recycling process, different types of plastics cannot be mixed, e.g., PET and PP) and free of contaminants (e.g., organic substances, sand, etc.). There is one recycling method that is resistant to these limitations—pyrolysis.

Pyrolysis is a thermal process of decomposition of hydrocarbons, which occurs under anaerobic conditions at temperatures ranging from 200 °C upwards [7,8]. Under the influence of temperature increase in polymer molecules, the chemical bonds break, resulting in the formation of radicals, which form the products of the process. The main advantage of pyrolysis is the possibility of conducting it at low temperatures (in comparison with combustion), which prevents the formation of harmful substances and facilitates control...
over the process [9–11]. The lack of air supply prevents the rise of small pollutants along with the gaseous phase. The process is characterized by high tolerance for the composition of the input material. Three products are produced during pyrolysis: char, pyrolytic oil and pyrolytic gas. Unfortunately, poorly managed products of the pyrolysis process can be harmful to the environment due to substances from the input material [12,13]. Depending on the temperature at which the process is carried out, different quantities of given products with different chemical and physical properties can be obtained. The higher the temperature, the greater the weight loss of the input material and the greater the amount of pyrolytic gas produced [14,15]. By applying the pyrolysis process to contaminated or mixed plastics, the amount of waste to be incinerated or co-incinerated can be reduced [16–18]. Pyrolysis products can be transformed into other useful substances, thus contributing to the reduction of the consumption of natural resources [19]. Such an action fits perfectly in the circular economy. Apart from pyrolysis, there are many methods of economic and ecological management of waste plastics [20,21].

2. Materials and Methods

The materials used for the research were plastic waste obtained from recycling of used vehicles (ground and mixed, consisting of both hard and soft plastics, additionally contaminated with inorganic substances) and foils and plastic bags (can be treated as a homogeneous substance) contaminated with organic and inorganic substances. A common feature of the selected samples was the presence of PVC-type plastics containing significant amounts of chlorine. Migration of chlorine was described in the paper [22]. Before further testing, the waste was ground and homogenized.

Tests of the low-temperature pyrolysis process were carried out on a test stand consisting of a pyrolytic chamber with a volume of 25 dm$^3$ and a pyrolytic gas cooler made of a DN 25 pipe with a length of 1000 mm. The main chamber was electrically heated.

The pyrolysis chamber is made of cube-shaped alloy steel and its dimensions are: 400/250/250 (mm). It is shell-heated with electric heaters. The maximum operating temperature of the chamber is 500 °C. The heaters work in a fireproof coating. The chamber is closed with a special cover to prevent air inflow. In the upper right corner of the chamber there is a connection for the discharge of pyrolysis gases. A pipe-in-pipe gas cooler is connected to the stub pipe. The cooling medium is water. The cooler has the ability to regulate the water temperature in the range from 15 to 50 °C. At the cooler outlet, there is a built-in separator separating the gas fraction from the liquid fraction. The stand is shown schematically in Figure 1.

![Figure 1. Scheme of the test stand for carrying out the pyrolysis process.](image-url)
switched on. At the same time, pyrolytic oil accumulated in the separator was collected from the separator.

The total sulfur content was determined using the high-temperature combustion method. The test consisted in burning a sample of the substance in an electric furnace with a ceramic tube at a temperature of 950 °C and the absorption of SO$_2$ was generated during combustion in hydrogen peroxide, located in a flask connected to the furnace. Then the resulting solution, after boiling, was titrated with NaOH. The sulfur content in the tested sample was calculated from the formula:

$$S^a = \frac{(V_1 - V_2) \times 0.0008}{m} \times 100 \%$$  \hspace{0.5cm} (1)

where:
- $S^a$—sulfur content in the tested sample (%);
- $V_1$—amount of NaOH used to titrate the tested sample (mL);
- $V_2$—the amount of NaOH used for the titration of the blank (mL);
- 0.0008—mass of sulfur corresponding to 1 cm$^3$ of 0.05 n sodium hydroxide solution (g/cm$^3$);
- $m$—mass of the waste sample (g).

Determination of total nitrogen content was conducted (this nitrogen combines nitrate, nitrite, organic and ammonium). The determination was carried out in two phases. First, a sample of the waste had to be mineralized with the addition of sulfuric acid (VI) and a catalyst. Then, distillation of the obtained solution after mineralization containing ammonia was carried out, together with the addition of NaOH and indicator. The final stage of the determination was the titration of the distillate receiver, which was hydrochloric acid, with sodium hydroxide. The results were compiled according to the formula:

$$N_{og} = \frac{0.28 \times (b - a) \times 100}{m} \%$$  \hspace{0.5cm} (2)

where:
- $N_{og}$—the amount of total nitrogen in the tested sample (%);
- $b$—the amount of the standard solution, 0.02 n HCl (cm$^3$), metered into the receiver;
- $a$—0.02 m of NaOH standard solution used to back titrate the excess HCl (cm$^3$);
- $m$—mass of the tested waste sample (mg).

The results of the experiment are shown in Table 1, summarizing the process.

Table 1. Masses of substrates and products.

| Type of Plastic     | Input [g] | Char [g] | Clear Pyrolytic Oil [g] | Pyrolytic Oil, Turbid [g] | Pyrolytic Gas [g] |
|---------------------|-----------|----------|-------------------------|---------------------------|-------------------|
| Soft foils          | 746       | 140      | 328.9                   | 144.5                     | 132.6             |
| Mixed materials     | 748       | 160      | 116.7                   | 207.2                     | 246.1             |

3. Results

During the tests, the mass of samples used and products obtained, temperature and process duration were measured. After the test on the laboratory stand, the phenomenon of delamination was observed in the collected oil fraction. After 24 h, the difference between the clear and turbid fractions became evident. Similar phenomena have been described in [15]. The fractions were separated using a sedimentation funnel. The amount of gases was determined from the balance equations. Moreover, flammable and non-flammable parts, volatile parts, density, humidity, carbon, chlorine, sulfur and nitrogen content were
determined, combustion heat was measured and calorific value was calculated. The substrates and products of the process were analyzed in accordance with the applicable standards. In connection with the adopted topic, the publication presents and discusses results concerning sulfur and nitrogen content. In the case of these tests, the pyrolysis gas stream was not measured directly. Its composition was also not measured. The pyrolysis gas was discharged to the atmosphere via an off-gas cleaning system.

In the first stage of research, the mass balance for the substrate and process products (Table 1) was determined. The results of mass balance calculations are presented in Table 2.

Table 2. Results of mass balance calculations.

| Type of Plastic | Input [%] | Char [%] | Clear Pyrolytic Oil [%] | Pyrolytic Oil, Turbid [%] | Pyrolytic Gas [%] |
|----------------|-----------|----------|------------------------|-------------------------|------------------|
| Soft foils     | 100.0     | 18.8     | 44.1                   | 19.4                    | 17.7             |
| Mixed materials| 100.0     | 21.4     | 15.6                   | 27.7                    | 35.3             |

For contaminated foils, the weight distribution of the obtained products is as follows: pyrolytic gas constitutes 17.7% of the charge, char 18.8%, pyrolytic oil 63.5%. After separation of the oil fraction, nearly 70% of the clear substance and 30% of the turbid fraction were obtained from it (which gives 44.1% and 19.4%, respectively, of the foil charge).

For plastics obtained from the recycling process of end-of-life vehicles, the weight distribution of the obtained products is as follows: pyrolytic gas constitutes 35.3% of the charge, char 21.4%, pyrolytic oil 43.3%. After separation of the oil fraction, 36% of the clear substance and 64% of the turbid fraction were obtained from it (which gives 15.6% and 27.7%, respectively, of the plastic charge).

Analyzing the results obtained, it can be concluded that for both samples under consideration the amount of char obtained is at a similar level—about 20%. Differences occur in the case of gas and pyrolytic oil. From processing of the foil, a larger amount of oil was obtained (by 20%); additionally, a larger part of it was clear.

In the next step, a number of planned tests and markings on the products obtained were carried out. The percentage of total sulfur and nitrogen was determined in batch samples and in the obtained char and pyrolytic oil (separately for the clear and turbid fraction). In order to determine the sulfur and nitrogen content in the pyrolytic gas, appropriate balance calculations were made.

The results of testing the pyrolysis process for sulfur content are presented in Table 3. The results of the sulfur migration calculations are presented in Table 4.

Table 3. Sulfur content of substrates and products.

| Type of Plastic | Input [%] | Char [%] | Clear Pyrolytic Oil [%] | Pyrolytic Oil, Turbid [%] | Pyrolytic Gas [%] |
|----------------|-----------|----------|------------------------|-------------------------|------------------|
| Soft foils     | 0.736     | 0.510    | 0.801                  | 1.381                   | 0.111            |
| Mixed materials| 1.684     | 1.031    | 1.959                  | 3.823                   | 0.280            |
Table 4. Sulfur migration in products.

| Type of Plastic        | Input [%] | Char [%] | Clear Pyrolytic Oil [%] | Pyrolytic Oil, Turbid [%] | Pyrolytic Gas [%] |
|------------------------|-----------|----------|-------------------------|---------------------------|-------------------|
| Soft foils             | 100.0     | 13.00    | 47.98                   | 36.35                     | 2.67              |
| Mixed materials        | 100.0     | 13.10    | 18.15                   | 62.89                     | 5.87              |

For contaminated foils, the percentage distribution of sulfur in the substrate and products is as follows: input—0.736%, pyrolytic gas—0.111%, char—0.510%, in the separated oil fraction—0.801% in the clear substance and 1.381% in the turbid fraction. Taking into account these results, the migration of sulfur is as follows: 2.67% is discharged with pyrolytic gas, 13.00% with char and 84.33% with pyrolytic oil (47.98% with clear and 36.35% turbid). These results are presented in Figure 2a.

For plastics obtained from recycled end-of-life vehicles, the percentage distribution of sulfur in the substrate and products shall be as follows: input—1.684%, pyrolytic gas—0.280%, char—1.031%, in the separated oil fraction—1.959% in the clear substance and 3.823% in the turbid fraction. Taking into account these results, the migration of sulfur is as follows: 5.87% is discharged with pyrolytic gas, 13.10% with char and 81.04% with pyrolytic oil (18.15% with clear and 62.89% turbid). These results are presented in Figure 2b.

The results of the pyrolysis process tests for nitrogen content are presented in Table 5. The results of nitrogen migration calculations are presented in Table 6.

Table 5. Nitrogen content of substrates and products.

| Type of Plastic   | Input [%] | Char [%] | Clear Pyrolytic Oil [%] | Pyrolytic Oil, Turbid [%] | Pyrolytic Gas [%] |
|-------------------|-----------|----------|-------------------------|---------------------------|-------------------|
| Soft foils        | 0.390     | 0.900    | 0.202                   | 0.321                     | 0.393             |
| Mixed materials   | 1.396     | 1.908    | 0.628                   | 0.581                     | 2.065             |

Figure 2. Migration of sulfur in pyrolysis products: (a) for contaminated foils; (b) for mixed plastics.
For contaminated foils, the percentage distribution of nitrogen in the substrate and products is as follows: input—0.390%, pyrolytic gas—0.393%, char—0.900%, in the separated oil fraction—0.202% in the clear substance and 0.321% in the turbid fraction. Taking into account these results, the nitrogen migration is as follows: 17.91% is discharged with pyrolytic gas, 43.31% with char and 38.78% with pyrolytic oil (22.84% with clear oil and 15.94% with turbid oil). These results are presented in Figure 3a.

![Figure 3a](image1)

**Figure 3**: Migration of nitrogen in pyrolysis products: (a) for contaminated foils; (b) for mixed plastics.

For plastics from recycled end-of-life vehicles, the percentage distribution of nitrogen in the substrate and products is as follows: input—1.396%, pyrolytic gas—2.065%, char—1.908%, in the separated oil fraction—0.628% in the clear substance and 0.581% in the turbid fraction. Considering these results, the nitrogen migration is as follows: 52.22% is discharged with pyrolytic gas, 29.24% with char and 18.55% with pyrolytic oil (7.02% with clear oil and 11.53% with turbid oil). These results are presented in Figure 3b.

### 4. Discussion

This paper assesses the content of sulfur and nitrogen in contaminated foils and plastics obtained from the recycling process of used vehicles and in the products of their pyrolysis (with the final temperature of 425 °C). A mass balance was also carried out for these elements. The high migration potential of sulfur and nitrogen was shown for the waste subjected to the pyrolysis process.

Sulfur: for homogeneous foils and mixed plastics, most of the sulfur is immobilized in oil, while for foils it is clear oil (in proportions of 57% to 43%), and for recycled plastics mainly in turbid oil (in proportions of 22% to 78%). The sulfur content of char for both types of plastics is practically the same (about 13%). Slight differences occur for pyrolytic gases (approx. 3% for foils and approx. 6% for recycled plastics). The phenomenon of sulfur migration is described, for example, in [10]. Waste tires were tested there and the pyrolysis process was carried out at temperatures ranging from 600 °C to 800 °C. The tests were carried out for small samples and with fast heating in a flow screw reactor. The results of these studies confirm the sulfur migration possibilities presented in this article. There, the sulfur content in the oil varies from 20% to 10% when the process temperature changes from 600 °C to 800 °C, respectively (it decreases with increasing temperature), for

| Type of Plastic          | Input [%] | Char [%] | Clear Pyrolytic Oil [%] | Pyrolytic Oil, Turbid [%] | Pyrolytic Gas [%] |
|--------------------------|-----------|----------|-------------------------|---------------------------|-------------------|
| Soft foils               | 100.0     | 43.31    | 22.84                   | 15.94                     | 17.91             |
| Mixed materials          | 100.0     | 29.24    | 7.02                    | 11.53                     | 52.22             |

**Table 6. Nitrogen migration in products.**
char—the change ranges from 70% to 50% (decreases with increasing temperature), for gas—change is in the range from 11% to 30% (increases with temperature increase).

Nitrogen: for homogeneous foils and mixed plastics, nitrogen migration is different. For homogeneous foils, most nitrogen is immobilized in char (approx. 43%), then in pyrolytic oil (39%); the remainder is transferred to gas (approx. 18%). For mixed plastics, most of the nitrogen is immobilized in pyrolytic gas (over 52%), the remainder goes to char (nearly 30%) and pyrolytic oil (over 18%). The phenomenon of nitrogen migration is described, for example, in [23]. There, waste rigid polyurethane foam was tested and the pyrolysis and gasification processes were carried out. Similarly, migration of nitrogen between the pyrolysis products was observed. In addition, greater nitrogen migration to gas was observed with the increase in process temperature (and in the presence of a catalyst) and the possibility of nitrogen conversion to pure nitrogen dioxide was demonstrated.

The results of research and analysis will allow the identification of possible ways of managing the problematic waste, which consists of contaminated and mixed, non-recyclable plastics. For example, when energy recycling is chosen, sulfur and nitrogen form sulfur dioxide and fuel oxides of nitrogen, respectively—knowing the contents of these elements, the flue gas treatment process can be designed accordingly [5].

Substances obtained as a result of the pyrolysis process can be used in many ways. Pyrolysis gas can be used in the combustion process and the released energy can be directed to the pyrolysis process. Pyrolysis oil can be used to produce new plastics. The obtained char can be subjected to another thermal treatment in order to produce activated carbon. At each of these stages, the presence of sulfur and nitrogen should be kept in mind [6,15].

Both sulfur and nitrogen can form acidic substances under certain conditions and as a result of certain chemical reactions. This unfavorable effect must be taken into account by the designers of both the pyrolysis equipment on an industrial scale and the equipment for the management or further processing of pyrolysis products. In these cases, particular attention should be paid to the selection of appropriate construction materials resistant to sulfur and nitrogen compounds in a wide range of temperature changes. In recycling processes, temperatures may vary from ambient temperature to 500 °C for pyrolysis [16], 800 °C in the production of activated carbon [7], and even up to 1000 °C in the case of combustion processes [5].

It should be noted that the obtained results show a certain tendency in the migration of sulfur and nitrogen in the products of the pyrolysis process with the final temperature of 425 °C. The specific values expressed in (%) should be treated with some approximation. The extensive research carried out by the author (the results of which are currently being developed) show that for other end temperatures of the pyrolysis process, the differences in the migration of sulfur and nitrogen in the products of this process are significant (in relation to the results presented in the article and after taking into account the repetitions of the tests performed).

5. Conclusions

Mixed and contaminated waste plastics are a serious problem in both mechanical and chemical recycling. They are most often subjected to combustion processes in waste incineration plants, and if there is no such possibility, they go directly to the environment, causing soil and water pollution. In order to prevent such actions, these wastes can be subjected to a low-temperature pyrolysis process. As a result of the pyrolysis process, we obtain solid, liquid and gaseous products. Pyrolysis products can be transformed into other useful substances; this contributes to reducing the consumption of natural resources.

During the pyrolysis process, the elements contained in the waste can migrate to the individual products of the process. The conducted tests showed such possibilities for sulfur and nitrogen. The knowledge of the degree of migration of substances which, as a result of various chemical processes, may create substances hazardous to the natural environment and to the designed recycling devices, is important for designers of such devices (at the time of transition from laboratory to industrial scale). This information is also important.
for technologists who will develop methods of using or managing the products of the pyrolysis process.

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