Theoretical framework of the polymer waste thermal degradation

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Abstract. The article provides a theoretical analysis of the pyrolysis of polymer waste. The main products of pyrolysis are considered. The thermal degradation of polymers was studied depending on the composition of the materials. The main factors affecting the product distribution of pyrolysis of waste plastics are determined. Gaseous medium in the pyrolysis chamber plays a significant role in the process. The operating conditions of the pyrolyser are considered. The use of pyrolysis makes it possible to significantly reduce the amount of solid waste and increase energy savings without harming the environment and human health.

1. Introduction

Pyrolysis is one of the most promising areas of MSW processing in terms of both environmental safety and the production of useful commercial products. Globally, MSW recycling is a profitable business. This is due to the fact that more developed countries have learned how to recycle household waste, to make it a valuable resource for receiving heat and different substances. However, in Russia, new waste management technologies are practically not used, and household garbage, in the best case, is simply incinerated, and in the worst, it is accumulated in landfills [1-7].

Conversion of plastic waste from municipal solid waste (MSW) into fuel by pyrolysis of long-chain hydrocarbon fragments into short-chain has several advantages. Firstly, it activates a new cycle of consumption of non-renewable energy sources. Secondly, it also provides a significant source of petrochemicals, which reduces the consumption of non-renewable energy resources. Thirdly, it offers an effective, innovative and alternative solution to eliminate waste, therefore, preventing environmental pollution by burning it or filling landfills and waterways.

The thermal degradation products of plastics are:

- pyrolytic gas (is the fuel for the operation of the plants);
- coke residue of 4-5 hazard class (included in mixtures used in construction and reclamation);
- synthetic oil (on its basis it is possible to obtain diesel fuel and a gasoline component);
- heat generated during the pyrolysis process (supplied to space heating).

The main components of pyrolytic gas are hydrogen, carbon monoxide, methane, which are used as raw materials for the synthesis of methanol, ammonia, oxoalcohols or other chemicals, as well as fuel [8]. To reduce the energy consumption for the operation of the pyrolysis installation, part of the energy from the gas obtained in the process goes to the heating of the air with its subsequent supply to the...
combustion chamber. The remaining energy is transferred to the consumer in the form of gaseous fuel or in the form of heat carriers.

The indisputable advantage of pyrolytic gas is the absence of sulfur and nitrogen in it. Since the process proceeds in the absence of oxygen, the pyrolytic gas does not contain hazardous dioxins formed during the combustion of hydrocarbons [9]. The disadvantage is the low calorific value and the difficulty of storing pyrolytic gas, the main of which is the inability to transport it over considerable distances. This implies that the gas consumption after its receipt should occur at a distance of not 3 km.

The disadvantages of pyrolysis include the complexity of the design of furnaces; high cost of equipment; the need for a large number of staff. Like any promising technology, improving pyrolysis is in demand and relevant. Mainly the modernization of pyrolysis consists in modifications to the design of plants in order to increase the energy efficiency of the process and reduce the proportion of harmful residues. Also, these goals can be achieved by changing the conditions of the process and the introduction or removal of certain chemical components.

2. Materials and methods

For the manufacture of packaging polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), polyamide (PA) etc. are used. Disposable dishes are made from PE, PP (Kaplen 01030), PS (PSM 151, PSM 115), and ABS plastics. In connection with the constant modernization of the properties of plastics with respect to physicochemical and biological factors, the number of types of polymers is constantly increasing. The development and addition of polymeric materials with various compounds adversely affects the process of MSW processing.

Depending on the decomposition temperature of inorganic compounds, low-temperature and high-temperature pyrolysis are distinguished. As a result of low-temperature pyrolysis, carried out at a temperature of 450–900 °C, the resulting pyrolytic gas is minimized, but the maximum yield of residues as well as liquid products. While maintaining the pyrolysis temperature of more than 900 °C, which is a high-temperature pyrolysis, the maximum gas yield is in contrast to the minimum yield of fixed residues and liquid product.

3. Thermal degradation of polymers

During thermal degradation, the destruction of the least strong bonds of the polymer substrate occurs first of all. Next, almost complete decomposition of the remaining bonds occurs while maintaining a higher temperature. A decrease in the mass of polymer raw materials is also observed in connection with depolymerization reactions, as well as static rupture of macromolecules and elimination of side groups [10].

The pyrolysis reaction rate increased, and thus the reaction time decreased with increasing temperature. High temperature easily breaks the bonds and, thus, accelerates the reaction and reduces the reaction time. The reaction kinetics for various plastics followed the trend of PVP> PNP> PP over the entire temperature range. This can be explained on the basis of the C – C bond strength and polymer chain orientation in various plastics. PVP with a long linear polymer chain with a low branching and a high degree of crystallinity has high strength and at the same time requires more time for decomposition. Therefore, it is necessary to carry out the process at higher temperatures, as well as the creation of more stringent conditions.

Taking into account that PNP with high branching and low crystallinity has weak bonds, which are easily destroyed compared to PVP. In PP, the presence of the side chain of the group (–CH₃) and low crystallinity reduces the overall strength, leading to a decrease in reaction time.

Based on experimental data, the dependence of the heating rate on the pyrolysis product yields is revealed. The higher the heating rate of the reactor of the pyrolyser, the greater the yield of gaseous products and the lower the mass of coke. The dependence is presented in table 1.
The process is also affected by the particle size of the raw materials used. The increase in the size of the used particles of raw materials contributes to an increase in the amount of solid residue, a decrease in the proportion of pyrolytic gas and liquid products by reducing the heating rate of raw materials [11].

An important role in the process is played by the gaseous medium in the pyrolysis chamber. It can be inert, with partial access of air, the atmosphere of hydrogen, methane, carbon dioxide, water vapor. If oxygen is present in the medium, the fraction of gaseous products contains CO and CO$_2$, and oxygen-containing compounds, which adversely affect the quality of gaseous fuels and oils, will be another pyrolysis product.

The pressure maintained in the pyrolysis reactor is also of great importance to the products obtained. So, when using low pressure, primary products are formed to a greater extent. If the installation operates at high pressure, the result of the process is the yield of mainly liquid products.

Table 2 presents the main factors affecting the pyrolysis process and the quality of the process products.

Table 1. The pyrolysis product yields depending on the heating rate of raw materials at various temperatures.

| Products       | Slow (500 °C) | Fast (500 °C) | Slow (700 °C) | Fast (700 °C) |
|----------------|---------------|---------------|---------------|---------------|
| Gas (% wt.)    | 10            | 11            | 15            | 50            |
| Liquid (% wt.) | 85            | 89            | 85            | 50            |
| Fixed residue (% wt.) | 5           | 0             | 0             | 0             |

Table 2. The main factors affecting the distribution of products of polymer waste pyrolysis.

| Influence factor                              | Effect                                                                 |
|-----------------------------------------------|------------------------------------------------------------------------|
| The chemical composition of polymers          | The primary pyrolysis products are directly related to the chemical structure of the polymers, as well as to the mechanism their thermal degradation (thermal or catalytic) |
| Pyrolysis temperature and heating rate        | High process temperatures and heating rates contribute to bond breaking and predominant formation of low molecular weight products |
| Pyrolysis time                                | A long residence time contributes to the secondary conversion of primary products, an increase in the yield of coke, tar, as well as temperature-resistant products, thus gradually hiding the effect of the original polymer structures |
| Type of reactor                               | It mainly determines the quality of heat transfer (heat transfer), mixing, retention time of liquid and gaseous phases, the formation of primary products |
| Operating pressure                            | Low pressure reduces the condensation of active fragments forming coke and high molecular weight products |
| The presence of active gases such as oxygen or hydrogen | The formation of heat, the dilution of products. Effect on balance, kinetics and mechanism |
| The use of catalysts                          | It affects the kinetics and mechanism and, therefore, the distribution of pyrolysis products |
| Additives                                     | Usually evaporate or collapse. Some may affect kinetics or mechanism. |
| Liquid or gaseous phase                       | The liquid phase of pyrolysis delays the output of developing products, thereby increasing the internal interaction |
The presence of a catalyst significantly affects the reaction rate, as well as the quality of the condensed fraction. The use of a catalyst improves the ability to decompose the polymer, thereby increasing the yield of condensed gas and leading to an increase in the yield of the liquid product. The use of a catalyst eliminates pressure fluctuations and reduces the time of processing by pyrolysis of plastic waste [12].

4. The fundamentals of pyrolysis in the processing of polymer waste

Any pyrolysis process can be divided into four stages: drying of raw materials in the drying chamber; dry distillation or the pyrolysis process itself; combustion of solid residues; obtaining pyrolysis products such as pyrolytic gas, oil and carbon residue. The schematic diagram of pyrolysis is shown in figure 1.

![Figure 1. Schematic diagram of pyrolysis.](image)

In the process of pyrolysis, the heat released as a product of the process is partially used to heat some stages, which can be observed when considering figure 1.

The reactor is a major part of the pyrolyser. The principle of operation of the installation is as follows: the raw materials entering through the upper part of the reactor are dried in the upper layers of the reactor. At the same time, the temperature of 100–300 °C is maintained in this area. Then it goes down through the superimposed pre-distillation retort. Next, the raw product moves to the middle of the reactor. There the pyrolysis process takes place, in which the raw material is thermally decomposed and its coking occurs. The temperature in this area is at around 500 °C.

The resulting ash is cooled to 100 °C and removed from the chamber with subsequent reuse. The resulting gas products are collected through a water-cooled condenser. The oil yield was determined based on the initial mass of plastic waste.

Compared to other methods of handling MSW, pyrolysis is the most preferable from an environmental point of view, since it reduces the carbon footprint of the products. The pyrolysis process also reduces emissions of carbon monoxide and carbon dioxide, effectively using an inert atmosphere free of oxygen to avoid the formation of dioxins as a result of the reaction of the product with oxygen. Pyrolysis is recognized as the cleanest technology that meets the objectives of energy security, and a measure to combat the depletion of fossil fuels [13].

The data studied in [14–15] show that, in mixtures with air, somewhat enriched in fuel, while maintaining normal pressure and an increased initial temperature, which is in the range of 60–90 °C,
the output pyrolysis products of PP have detonation ability. Based on this, studies are conducting to create a combustion chamber with detonation, rather than deflagration, combustion of chemical fuel.

Low hazardous slag formed during burning, similar to rock, can be safely disposed. For example, it can be used as a substitute for road gravel as well as in construction for soundproofing walls, which is relevant for Germany, Holland and other European countries [16].

5. Conclusion
The study of pyrolysis plants leads to better modeling of process parameters at the enterprise level. Such results are vital to realizing the potential of such technology to solve the problem of plastic waste worldwide. The development of such technologies should be included in the national policies of developing countries and those countries that currently do not have the necessary infrastructure for the collection, separation and processing of plastic waste. The widespread use of pyrolysis technology could be a viable solution to the growing problem of plastic waste worldwide and in a cost-effective way. Using waste such as plastic to generate energy can also, to some extent, satisfy the growing need for liquid fuels.

Based on the foregoing, it follows that the pyrolytic decomposition of MSW is a developing and requiring attention method due to its effectiveness and the use of recycled materials. The process itself is virtually waste-free, and thermal decomposition products can serve as raw materials for subsequent production or processing.

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