

POLYETHYLENE PACKAGES AND POLYETHYLENE TEREPHTHALATE BOTTLES - A SOURCE OF PRECURSORS FOR CHEMICAL SYNTHESSES

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Abstract – The aim of our work was to investigate the possibility of obtaining precursors for chemical synthesis from polyethylene bags and polyethylene terephthalate bottles by two-stage thermolysis at 750 and 1000 °C. It was established that the main products are gases. During the thermolysis of polyethylene bags, the main combustible gases are C₁-C₃ and hydrogen, and the polyethylene terephthalate bottles are carbon oxides.

Keywords – thermolysis, polyethylene bags, polyethylene terephthalate bottles, combustible gases, hydrogen, carbon oxides, thermolysis mechanisms of polymer packaging.

Introduction

The last year forced a review of priorities regarding the sources of raw materials for the chemical industry. Refusal to purchase Russian oil, gas and chemicals poses challenges in finding alternative markets and raw materials. At the same time, from June 1, 2021, the law of Ukraine "On limiting the circulation of plastic bags in the territory of Ukraine" was signed, which limits the use of low-density polyethylene bags (PE) to improve the ecological situation in the country [1]. This is primarily because more than 13 million tons of municipal solid waste (MSW) are generated in Ukraine [2]. The share of polymer waste is 9-13% (wt.). As if a small amount. However, in Ukraine, no more than 10% of MSW can be recycled [2]. At the same time, in recent decades, the number of works on the secondary processing of MSW into valuable substances and materials has been steadily growing. Therefore, our work aimed to investigate the possibility of obtaining precursors for chemical synthesis from polyethylene bags (PE) and polyethylene terephthalate (PET) bottles.

Materials and methods

Polyethylene bags and polyethylene terephthalate bottles were chosen as polymer packaging. The last one was not chosen by chance because during its destruction, condensed "resinous" substances are formed, which are difficult to remove. It is with their help that we will control the effectiveness of the proposed laboratory installation. A laboratory installation for the thermolysis of waste was created, which allows for bypassing the stage of obtaining liquid products [7]. The process is two-stage. In the first stage, polymer waste gasification was performed at a temperature of 750 °C for 90 seconds. The installation was blown with inert gas. The formed gases were passed through a layer of charcoal to trap tar. The second stage of the process consisted of the regeneration of the above-mentioned sorbent by heat treatment at 1000 °C under atmospheric pressure conditions. The gases formed at each stage were separately sent to gas chromatographic analysis. The composition of gases, the amount and change in the mass of raw materials and sorbent before and after each stage of the process were determined.

The qualitative and quantitative composition of the formed gases and liquid products was determined by the gas chromatography method. Gas chromatographic analysis of inorganic gases (H₂, CO, CO₂) and methane was carried out on a chromatograph Chrom-5 (Czech Republic) with

a detector for measuring the thermal conductivity of gases. For the analysis of light gases, stainless steel 1.5 m long and 3 mm internal diameter, filled with a sorbent: activated charcoal of the SKT brand with a fraction of 0.25–0.50 mm, impregnated with a 10% NiSO₄ solution. The carrier gas is argon, the flow rate of which was 20 ml/min. The temperature of the columns thermostat and the detector is 100 °C, the evaporator temperature – 120 °C, and the detector current – 40 mA. Hydrogen analysis was carried out on a glass chromatographic column with a length of 1.5 m and an internal diameter of 3 mm, filled with pre-fired CaA zeolite with a fraction of 0.25–0.50 mm. The carrier gas is argon, the flow rate of which was 30 ml/min. Analysis temperature – 60 °C, evaporator temperature – 120 °C, detector current – 80 mA. The gas sample was introduced into the chromatographic column through a calibrated loop using a dosing tap. The sample volume was 0.37 ml. Analysis of organic reaction products was carried out on a chromatograph “Agilent Technologies 7890A” (Agilent, USA) which was equipped with a flame ionization detector and using a DB-624 UI quartz capillary column with a length of 60 m and an internal diameter of 0.32 mm in a combined temperature regime (isothermal - 10 minutes at 40 °C, then programming the temperature from 40 to 250 °C at a speed of 5 degrees/min. Samples were introduced into the column with a microsyringe with a capacity of 1.0 µl. Processing of the analysis results was carried out according to the areas of chromatographic peaks by the method of internal normalization using calibration coefficients.

Results

In Fig. 1 presents the distribution of products depending on the original polymer packaging. As can be seen from the diagrams shown in Fig. 1, these product ratios depend on the starting polymer. However, gases are the main component (more than 60% (wt.)) during its thermolysis.

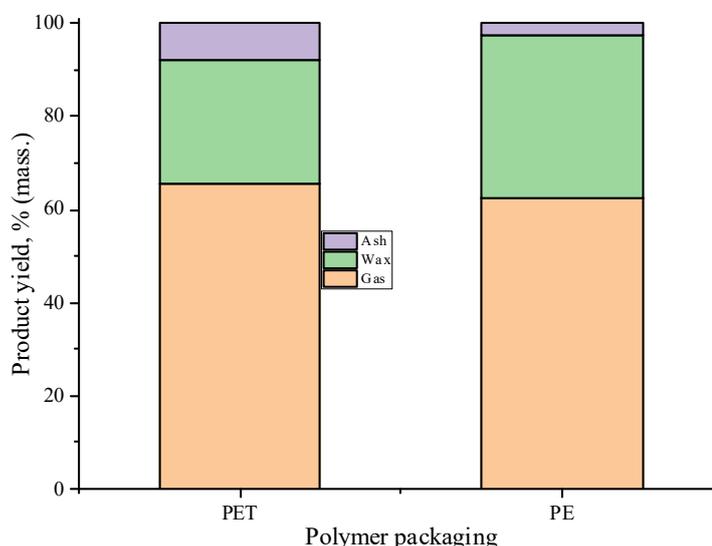


Fig. 1. Comparison of thermolysis products of different packaging containers.

The analysis of the gas phase showed that during the thermolysis of PE the main combustible gases C₁-C₃ and hydrogen are present, which indicates the perspective of such raw materials in the direction of obtaining substances that can be used as raw materials for the chemical industry, as well as as high-energy fuel (Fig. 2). At the same time, different gases are predominant at each stage. Thus, during the thermolysis of PE, a little more than 40% (wt.) of C₂ hydrocarbons and ~15% (wt.) C₁ and C₃ are formed at the first stage. This composition of the gas fraction can be explained by the nature of the polymer and the mechanism of its destruction (Fig.

3), which is in good agreement with known literature data [8-10]. Resinous substances formed after the depolymerization of polyethylene are adsorbed on the carbon material and in the second stage during thermolysis lead to an increase in the concentration of H₂. A sharp increase of the latter in the second stage can be explained according to the works [11] by the course of the following processes:

thermal and catalytic cracking: $C_nH_m \rightleftharpoons C + C_xH_y + H_2$;

dry reforming: $C_nH_m + nCO_2 \rightleftharpoons 2nCO + (m/2)H_2$,

where the C_nH_m are the tar molecules or coke on active carbon and C_xH_y – represents hydrocarbons with lower carbon numbers than those of C_nH_m. In favour of the proposed mechanisms of thermolysis, the presence of CO in the amount of ~15% (wt.) against ~1% (wt.) at the first stage testifies. At the same time, in the second stage, but in much smaller quantities, further thermal destruction of hydrocarbons is observed according to the mechanism shown in Fig. 3.

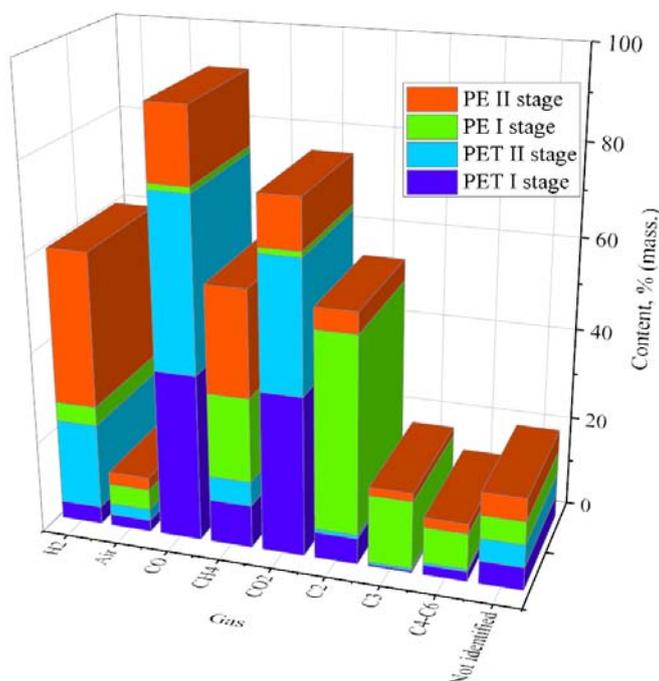


Fig. 2. Gases composition after polymer packaging's thermolysis.

At the same time, during the thermolysis of PET, the predominant gases in both stages are carbon oxides (Fig. 2), which is primarily due to the nature of the studied polymer packaging. For a better understanding of the process of thermolysis of PET waste, in Fig. 4 presents the mechanism of its depolymerization known from the literature [12], which is not desirable under the conditions of a low-carbon economy. The formation of resinous substances (Fig. 1) may have been facilitated by the structural characteristics of PET, which has an aromatic ring in the repeating unit and is very difficult to decompose during gasification due to its high thermal stability. The main products of PET decomposition are aromatic compounds such as benzoic acid, terephthalic acid and monomethyl terephthalate [12]. Such aromatic compounds can further decompose with the formation of benzene and toluene, which later condense to coke-like compounds on a carbon sorbent (Fig. 4). The methylene group of PET ethylene glycol can produce aliphatic hydrocarbons in the source gas, which explains their presence in the reaction products in the gas phase at both stages of thermolysis (Fig. 2).

The fact that at the second stage of gasification, the content of carbon monoxide is somewhat higher compared to dioxide in the gas phase (Fig. 2) attracts attention. According to

known literature data [12], this is caused not only by the cracking and reforming of resinous and coke-like compounds sorbed on a carbon sorbent but also by the interaction between CO₂ and C of these substances according to the following reaction:

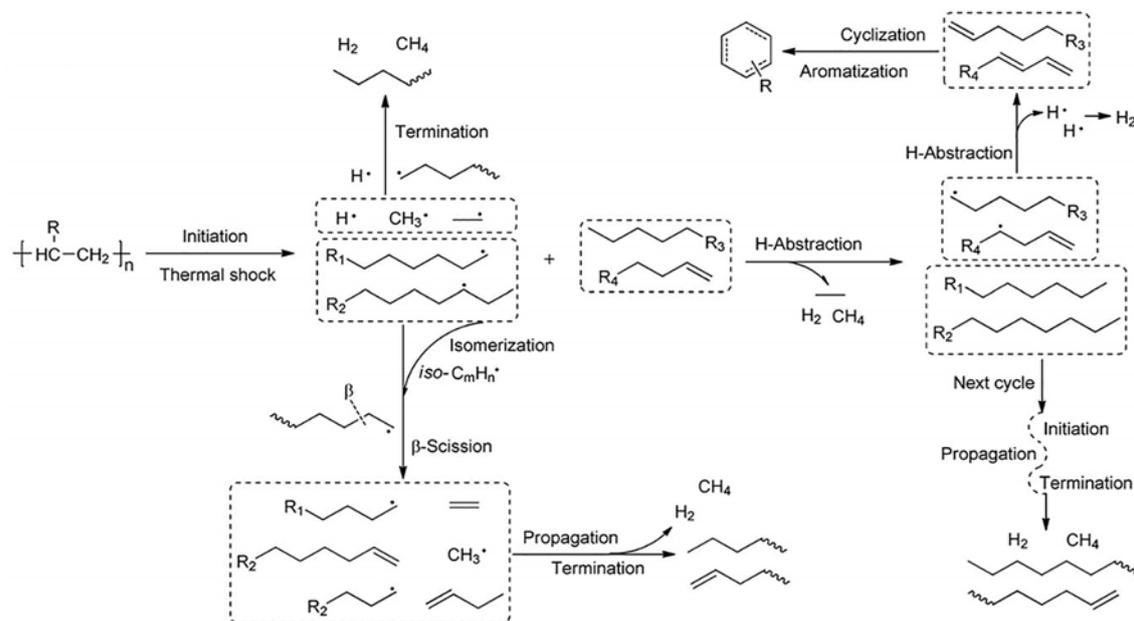


Fig. 3. A possible mechanism of PE depolymerization [10].

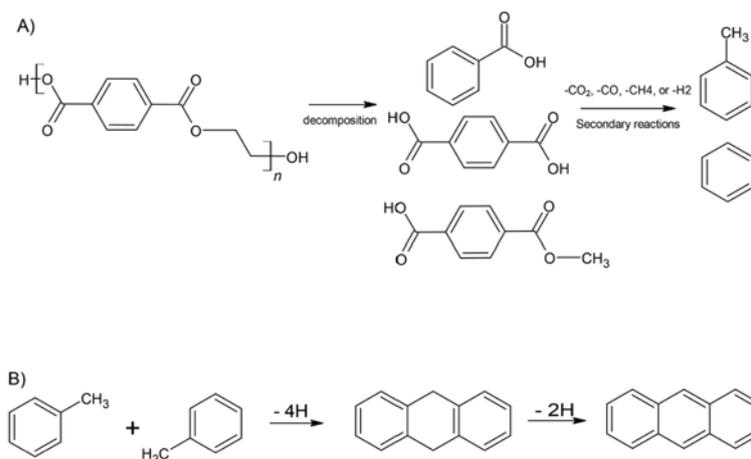


Fig. 4. A possible mechanism of PET depolymerization [12].

As can be seen from the figures shown in Fig. 3 data, the mixture of gases during the thermolysis of PE is optimal for the carbon oxides hydrogenation processes into hydrocarbons, alcohols, and ethers [13]. At the same time, during the thermolysis of PET, carbon oxides are the main ones. The ratio of hydrogen to carbon oxides is not optimal for use in the carbon oxides hydrogenation processes. It's necessary to additionally find a hydrogen source. Carbon oxides can later be used for the hydrogenation reaction, as well as for PE when hydrogen is added to them.

Conclusions

Thus, we have proposed a two-stage disposal method of polyethylene bags and PET bottles. The the formed products composition of polymer packaging thermolysis was analyzed.

The influence of the raw materials chemical composition on the reaction products was clarified, and the chemistry of the processes occurring during their thermolysis was also considered.

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